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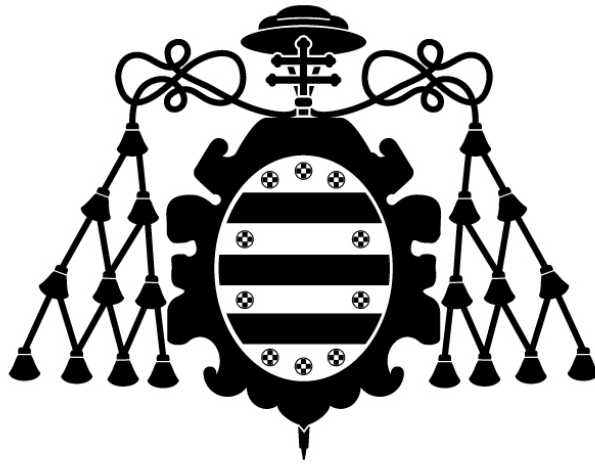
Programa de Doctorado de Materiales

MODELIZACIÓN DE LA DESCOMPOSICIÓN TÉRMICA DE
FOSFATOS METÁLICOS

TESIS DOCTORAL

Isabel Iglesias Santamarina

Junio 2019



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FOSFATOS METÁLICOS

TESIS DOCTORAL

María Belén Fernández Alfonso
María del Camino Trobajo Fernández



RESUMEN DEL CONTENIDO DE TESIS DOCTORAL

1.- Título de la Tesis	
Español: Modelización de la descomposición térmica de fosfatos metálicos.	Inglés: Metal phosphates: modeling thermal decomposition processes.
2.- Autora	
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RESUMEN (en español)

En este trabajo se propone una modificación del método isoconvensional de Friedman para disminuir la influencia del ruido y obtener valores más aproximados de la energía de activación (E). Esta modificación se basa en la idea de considerar, para un grado de conversión dado α , no solo la información correspondiente a α , sino también la de su entorno. Para validar el método se aplica a procesos teóricos. Además, el método modificado se utiliza para determinar los parámetros cinéticos de la degradación térmica del compuesto γ - $\text{Ti}(\text{PO}_4)(\text{NH}_4\text{HPO}_4)$. También se presenta un procedimiento para determinar parámetros cinéticos y obtener un modelo matemático discreto que posibilita chequear los parámetros cinéticos calculados y realizar predicciones para velocidades de calentamiento diferentes a las utilizadas experimentalmente. Este procedimiento se aplica a modelos teóricos y se utiliza para chequear los valores de E en la transformación térmica del $(\text{NH}_4)_2\text{Th}(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ desde temperatura ambiente hasta 1000 °C. La parte final de este trabajo se dedica al estudio de un nuevo fosfato de amonio-cromo(III)-hierro(III). Se sintetiza hidrotérmicamente y se caracteriza física y químicamente el $\text{Cr}_{0.34}\text{Fe}_{0.66}\text{NH}_4(\text{HPO}_4)_2$. A partir de datos de difracción de rayos X se determina que cristaliza en el sistema triclinico, grupo espacial $P-1$. Presenta túneles infinitos en las direcciones $[0\ 1\ 0]$ y $[1\ 0\ 0]$ donde se sitúan los cationes amonio. Es estable hasta aproximadamente 600 K que pierde agua. A 900 K pierde agua y amoníaco. Aplicando métodos isoconvensionales se realiza el estudio cinético. Se analiza el comportamiento magnético a partir de la dependencia de la susceptibilidad magnética con la temperatura y de las medidas de la imanación con el campo magnético aplicado. Es compatible con la siguiente secuencia de estados magnéticos: paramagnético desde temperatura ambiente hasta $T_C = 17.9$ K, ferrimagnético por



debajo de esta temperatura hasta la temperatura de transición, $T_i = 3.1$ K y antiferromagnético hasta 2 K.

RESUMEN (en Inglés)

A modification of Friedman's isoconversional method is proposed in order to reduce the influence of noise and obtain more accurate values of activation energy (E). This improvement is based on the idea of considering, for a given extent of conversion α , not only the information corresponding to α but also that of its neighborhood. To validate the method, it is applied to theoretical processes. Moreover, the modified method is used to determine the kinetic parameters on the thermal degradation of the γ -Ti(PO₄)(NH₄HPO₄). In addition, a procedure to determine kinetic parameters and to obtain a discrete model describing the process is introduced. The implementation of this model allows checking the kinetic parameters and make predictions for different heating rates to those used experimentally. The procedure was tested by considering to theoretical simulations and it was applied to analyze the values of E in the thermal transformation of (NH₄)₂Th(PO₄)₂·H₂O from room temperature to 1000 °C. The final part of this work is devoted to study of a new ammonium-chromium(III)-iron(III) phosphate. It has been hydrothermally synthesized and characterized physically and chemically the Cr_{0.34}Fe_{0.66}NH₄(HPO₄)₂. Powder X-ray pattern was used to determine that it crystallizes in the triclinic system, space group $P-1$, and displays infinite tunnels in the directions [0 1 0] and [1 0 0] where the ammonium cations are located. Thermal analysis shows that it is stable up to approximately 600 K, where it loses water. The compound loses water and ammonia at 900 K. Isoconversional methods were used to study the kinetic behavior. The magnetic behavior was studied from measurements of the dependence of magnetic susceptibility with the temperature and of the magnetization with the applied magnetic field. It is compatible with the following sequence of magnetic states: paramagnetic from room temperature to $T_c = 17.9$ K, ferrimagnetic below this temperature to the transition temperature, $T_i = 3.1$ K and antiferromagnetic to 2 K.



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	SI	NO
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Introducción justificativa de la unidad temática y objetivos	X	
Copia completa de los trabajos *	X	
Resultados/discusión y conclusiones	X	
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Se acompaña aceptación de todos y cada uno de los coautores a presentar el trabajo como tesis por compendio	X	
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Artículos, Capítulos, Trabajos

Trabajo, Artículo 1

Título (o título abreviado)
Fecha de publicación
Fecha de aceptación
Inclusión en Science Citation Index o bases relacionadas por la CNEAI (indíquese)
Factor de impacto

Reducing the effects of noise in the calculation of activation energy by the Friedman method
2016
2015
Chemometrics and Intelligent Laboratory Systems
2.303

Coautor2	<input checked="" type="checkbox"/> Doctor	<input type="checkbox"/> No doctor .	Indique nombre y apellidos
Coautor3	<input checked="" type="checkbox"/> Doctor	<input type="checkbox"/> No doctor .	Indique nombre y apellidos
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María Belén Fernández Alfonso
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Trabajo, Artículo 2



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Thorium(IV) phosphate-triphosphate: A valuable ceramic material obtained by thermal treatment of a layered ammonium-thorium(IV) phosphate. Kinetic analysis of the transformation
2017
2017
Ceramics International
3.057

María Belén Fernández Alfonso
Zakariae Amghouz
María del Camino Trobajo Fernández
José Rubén García Menéndez
José Ángel Huidobro Rojo

Trabajo, Artículo 3

Hydrothermal synthesis, crystal structure, thermal behaviour and magnetic properties of a new ammonium-chromium-iron(III)bis(hydrogenphosphate)
2019
2018
Journal of Solid State Chemistry
2.179

María Belén Fernández Alfonso
María del Camino Trobajo Fernández
José Ángel Huidobro Rojo
Zakariae Amghouz
David Martínez Blanco
Jesús Ángel Blanco Rodríguez
José Rubén García Menéndez

En caso de compendio de un número de artículos superior a seis, se incorporarán hojas suplementarias conforme a este modelo

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De acuerdo con el Reglamento de los Estudios de Doctorado aprobado por el Consejo de Gobierno de la Universidad de Oviedo el 17 de Junio de 2013 (Boletín Oficial del Principado de Asturias Nº 146, de 25-06-2013), para presentar la Tesis Doctoral como Compendio de Publicaciones es necesario incluir en la presente Memoria un informe con el factor de impacto de las publicaciones presentadas, junto con un detalle informativo sobre la calidad de las mismas, basado en el índice de impacto y en la posición que ocupa la revista científica dentro de una determinada categoría. De este modo, el informe correspondiente a los índices de impacto de las revistas en las que se han publicado, o están en trámite de publicación y los artículos que forman parte de la presente Memoria de Tesis Doctoral se resumen en la siguiente Tabla.

Título	Revista	Año	Índice de Impacto	Área	n° de orden/ n° total	Cuartil
Reducing the effects of noise in the calculation of activation energy by the Friedman method	Chemometrics and Intelligent Laboratory System	2016	2.303	Instruments & Instrumentation	12/61	Q1
				Mathematics, Interdisciplinary Applications	14/103	Q1
				Statistics & Probability	7/123	Q1
				Automation & Control Systems	19/61	Q2
				Chemistry, Analytical	25/81	Q2
				Computer science, Artificial Intelligence	34/132	Q2
Thorium(IV) phosphate-triphosphate: A valuable ceramic material obtained by thermal treatment of a layered ammonium-thorium(IV) phosphate. Kinetic analysis of the transformation	Ceramics International	2017	3.057	Materials Science, Ceramics	2/27	Q1
Hydrothermal synthesis, crystal structure, thermal behaviour and magnetic properties of a new ammonium-chromium-iron(III) bis(hydrogenphosphate)	Journal of Solid State Chemistry	2019	2.179	Chemistry, Inorganic & Nuclear	17/45	Q2
				Chemistry, Physical	83/147	Q3
Thermal behavior of layered α -titanium phosphates: from the titanium(IV) bis(hydrogenphosphate) monohydrate to an europium(III)-phase via propylamine intercalation	Journal of Thermal Analysis and Calorimetry	2018	2.209	Chemistry, Analytical	37/81	Q2
				Thermodynamics	18/59	Q2
				Chemistry, Physical	79/147	Q3
Modeling Chemical Kinetics in Solid State Reactions	Computational Mathematics, Numerical Analysis and Applications	2017				
Kinetic analysis of the thermal decomposition of iron(III) phosphates: $\text{Fe}(\text{NH}_3)_2\text{PO}_4$ and $\text{Fe}(\text{ND}_3)_2\text{PO}_4$	Journal of Thermal Analysis and	2019	2.209	Chemistry, Analytical	37/81	Q2
				Thermodynamics	18/59	Q2
				Chemistry, Physical	79/147	Q3

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Resumen

La obtención de modelos que describan los procesos de descomposición térmica es fundamental para conocer la cinética de las reacciones con el objetivo de optimizar las condiciones del proceso y de sus posibles aplicaciones.

Para conseguir este propósito es necesaria la determinación de los parámetros cinéticos; con el fin de calcularlos se han propuesto múltiples métodos. El método isoconversional de Friedman es uno de los más populares y ha sido ampliamente utilizado debido, por una parte, a que no necesita realizar ninguna aproximación matemática para determinar la energía de activación (E) y por otra, a que es relativamente sencilla su implementación. Sin embargo, su alta sensibilidad al ruido, especialmente cuando se aplica a datos integrales, puede introducir desviaciones importantes en los valores de la energía de activación, por lo que su empleo puede amplificar el ruido experimental.

En este trabajo se propone una modificación del método de Friedman para disminuir la influencia del ruido y obtener valores más aproximados de E . Esta modificación se basa en la idea de considerar, para un grado de conversión dado α , no solo la información correspondiente a esta conversión sino también la de su entorno. Para validar el método propuesto se aplica a procesos simulados teóricamente. Además, se utiliza para determinar los parámetros cinéticos de la degradación térmica del compuesto $\gamma\text{-Ti}(\text{PO}_4)(\text{NH}_4\text{HPO}_4)$, proporcionando buenos resultados.

La obtención de los parámetros cinéticos utilizando métodos diferenciales es relativamente sencilla, pero su determinación cuando se usan otros métodos puede ser compleja, por lo que suele calcularse únicamente la energía de activación. En este trabajo se presenta un procedimiento para determinar el resto de parámetros cinéticos, lo que permite obtener un modelo discreto para describir el proceso. La determinación de este modelo posibilita, por un lado, chequear los parámetros cinéticos calculados: se reconstruyen los datos originales y se comparan con los experimentales. Por otro lado, se pueden realizar predicciones para velocidades de calentamiento diferentes a las utilizadas experimentalmente. Este procedimiento resulta satisfactorio en su aplicación a dos simulaciones teóricas. También se utiliza para chequear los valores de la energía de activación obtenidos en la

transformación térmica del compuesto $(\text{NH}_4)_2\text{Th}(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$, desde temperatura ambiente hasta 1000 °C, proporcionando buenos resultados.

La parte final de este trabajo se dedica al estudio de un nuevo fosfato de amonio-cromo(III)-hierro(III). Se sintetiza hidrotermalmente y se caracteriza física y químicamente el compuesto $\text{Cr}_{0.34}\text{Fe}_{0.66}\text{NH}_4(\text{HPO}_4)_2$. Su estructura cristalina se determina a partir de datos de difracción de rayos X. Cristaliza en el sistema triclinico, grupo espacial $P-1$, presenta túneles infinitos en las direcciones $[0\ 1\ 0]$ y $[1\ 0\ 0]$ donde se sitúan los cationes amonio. Los análisis térmicos muestran que es estable hasta aproximadamente 600 K donde pierde agua. A 900 K pierde agua y amoniaco. Aplicando métodos isoconversionales se realiza el estudio cinético. El análisis del comportamiento magnético del compuesto se hace a partir del estudio de la dependencia de la susceptibilidad magnética con la temperatura y de las medidas de la imanación con el campo magnético aplicado. El comportamiento magnético del material es compatible con la siguiente secuencia de estados magnéticos: paramagnético desde temperatura ambiente hasta $T_C = 17.9\text{ K}$, ferrimagnético por debajo de esta temperatura hasta la temperatura de transición, $T_t = 3.1\text{ K}$ y antiferromagnético hasta 2 K.

Abstract

Modelling thermal decomposition of processes is a fundamental question in order to describe the kinetics of a chemical reaction and to be capable of optimizing the conditions for the process and their possible applications.

To achieve this purpose, the calculation of the kinetic parameters is a key point and several methods have been proposed for computing these parameters. The isoconversional method proposed by Friedman is one of the most popular and has been widely applied because no mathematical approximations are necessary for computing the activation energy (E). Moreover, the method can be easily implemented. However, it is very sensitive to experimental noise, particularly when it is applied to data of the integral type, and this can introduce significant deviations in the values of the activation energy. Thus, when it is applied the effects of experimental noise can be amplified.

In this work, a modification of Friedman's method is proposed with the aim of reducing the influence of noise and obtaining more accurate values of E . The improvement is based on the idea of considering, for a given extent of conversion α , not only the information corresponding to conversion, but also that of its neighbourhood. To validate the procedure, it is applied to two theoretical processes. Moreover, the proposed method is used to determine the kinetic parameters on the thermal degradation of the compound $\gamma\text{-Ti}(\text{PO}_4)(\text{NH}_4\text{HPO}_4)$, and provided successful results.

Obtaining other kinetic parameters is not really difficult as differential methods are used, but their determination is not so straightforward when other isoconversional methods are applied and frequently only the activation energy is calculated. In this work, a procedure to determine other kinetic parameters and to obtain a discrete model describing the process is introduced. The implementation of this model allows, on the one hand, checking the kinetic parameters by reconstructing the original data and comparing with the experimental ones. On the other hand, predictions can be made for different heating rates to those used experimentally. The procedure was tested by considering two theoretical simulations and it was also applied to analyze the values of the activation energy

in the thermal transformation of the compound $(\text{NH}_4)_2\text{Th}(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$, from room temperature up to 1000 °C, and provided good results.

The final part of this work is devoted to study of a new ammonium-chromium(III)-iron(III) phosphate compound. $\text{Cr}_{0.34}\text{Fe}_{0.66}\text{NH}_4(\text{HPO}_4)_2$ has been hydrothermally synthesized and characterized both physically and chemically. The powder X-ray pattern was used to determine the crystal structure. It crystallizes in the triclinic system, space group $P-1$, and displays infinite tunnels in the directions $[0\ 1\ 0]$ and $[1\ 0\ 0]$ where the ammonium cations are located. Thermal analysis shows that it is stable up to approximately 600 K, where it loses water. The compound loses additional water and ammonia at 900 K. Isoconversional methods were used to study the kinetic behavior. Magnetic properties of the compound were investigated from the study of the dependence of magnetic susceptibility with the temperature and of measurements of magnetization with the applied magnetic field. The magnetic behavior is compatible with the following sequence of magnetic states: paramagnetic from room temperature to $T_c = 17.9\text{ K}$, ferrimagnetic below this temperature to the transition temperature, $T_i = 3.1\text{ K}$ and antiferromagnetic to 2 K.

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CrFeNP	Bis(hidrogenofosfato) de amonio-cromo(III)-hierro(III), $\text{Cr}_{0.34}\text{Fe}_{0.66}\text{NH}_4(\text{HPO}_4)_2$
DSC	Calorimetría diferencial de barrido
DTA	Análisis térmico diferencial
DTG	Termogravimetría diferencial
FC	(Field Cooling) Medidas de la susceptibilidad magnética al disminuir la temperatura con campo magnético aplicado
FeNP	Bis(hidrogenofosfato) de amonio-hierro(III), $\text{FeNH}_4(\text{HPO}_4)_2$
FR	Método isoconversional diferencial de Friedman
KAS	Método isoconversional integral Kissinger-Akahira-Sunose
MFR	Método modificado de Friedman
MFR3	Método modificado de Friedman (tres puntos)
MFR5	Método modificado de Friedman (cinco puntos)
SEM	Microscopía electrónica de barrido
TGA	Análisis termogravimétrico
Vyaz	Método isoconversional integral de Vyazovkin
ZFC	(Zero Field Cooling) Medidas de la susceptibilidad magnética enfriando a campo magnético cero y midiendo después al aumentar la temperatura con campo aplicado.

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1. INTRODUCCIÓN

1. Introducción

La Ciencia de Materiales es una de las áreas de conocimiento más importante y activa en la sociedad contemporánea. En la Encyclopedia Britannica Concise se describe la Ciencia de Materiales como: *El estudio de las propiedades de los materiales sólidos y cómo esas propiedades están determinadas por la composición y estructura de un material. Creció a partir de una amalgama de física de estado sólido, metalurgia y química, ya que la rica variedad de propiedades de los materiales no se puede entender dentro del contexto de una sola disciplina clásica. Con una comprensión básica de los orígenes de las propiedades, los materiales se pueden seleccionar o diseñar para una enorme variedad de aplicaciones, que van desde aceros estructurales hasta microchips de computadora. La ciencia de los materiales es, por lo tanto, importante para las actividades de ingeniería tales como electrónica, aeroespacial, telecomunicaciones, procesamiento de información, energía nuclear y conversión de energía.*

Durante muchos siglos, la relación entre las propiedades de los materiales y su estructura no se conocía, de manera que frecuentemente, la ciencia avanzaba mediante el procedimiento de prueba y error. En la actualidad, este conocimiento facilita el desarrollo de nuevos materiales de forma más rápida y económica, lo que ha permitido avanzar en campos tan versátiles y novedosos como la nanotecnología, que desde principios de este siglo, incrementó notablemente su presencia en los ámbitos científicos y comerciales, siendo especialmente interesantes sus aplicaciones en medicina [1, 2]. Otro ejemplo notable de materiales actuales y con gran potencial de futuro, lo constituyen los materiales moleculares multifuncionales [3] por su capacidad de unir propiedades magnéticas, ópticas, térmicas, estructurales, etc., mediante estímulos externos como variación de la energía térmica, presión o luz. Estos materiales pueden, entre otras utilidades, funcionar desde adsorbentes de CO₂ [4, 5], a ser usados en aplicaciones electrónicas, sensores, etc. [6]. Siguiendo esta línea, una parte de este trabajo consiste en la síntesis y caracterización de un nuevo compuesto inorgánico de estructura abierta.

El origen de los materiales microporosos o de estructura abierta data del siglo XVIII. A. F. Crönsted (1722-1756) acuñó el término zeolita al calentar el mineral estilbita y observar vapor de agua, en griego, zeo significa "hervir" y lithos "piedra". Las zeolitas son aluminosilicatos de elementos de los grupos 1 y 2, metales alcalinos y alcalinotérreos, tales como sodio, potasio, magnesio y calcio [7, 8]. Químicamente, se representan por la fórmula empírica $M_{2/n}O \cdot Al_2O_3 \cdot ySiO_2 \cdot wH_2O$ donde y puede tomar valores entre 2 y 10, n es la valencia del catión y w representa el agua contenida en los huecos de la zeolita. Estructuralmente, son polímeros inorgánicos cristalinos basados en tetraedros $[SiO_4]$ y $[AlO_4]$ unidos unos a otros a través de iones oxígeno. Cada tetraedro $[AlO_4]$ porta una carga neta negativa que está compensada con la carga del catión. Esta estructura contiene canales o huecos interconectados que son ocupados por los cationes y las moléculas de agua. El agua puede ser fácilmente extraída al calentar, quedando una estructura cristalina microporosa que puede llegar al 50 % del volumen del cristal, facilitando posibles aplicaciones industriales. La familia de las zeolitas se extendió a todos los compuestos naturales o sintéticos de fórmula $\{M_{x/n}^{n+} [(AlO_2)_x (SiO_2)_y]^{x-} \cdot wH_2O\}$ donde x e y son los números de tetraedros por celda unidad [9].

En 1982, Flanigen y colaboradores [10] realizaron la síntesis hidrotérmica de una veintena de aluminofosfatos cristalinos porosos, tamices moleculares, $AlPO_4-n$ (n se refiere al tipo de estructura), basándose en la relación $2Si(IV) \rightarrow P(V)+Al(III)$. Sus estructuras están formadas por tetraedros $[AlO_4]$ y $[PO_4]$ que se alternan. Su fórmula puede expresarse como $[(AlO_2)_x (PO_2)_x] \cdot wH_2O$, se diferencian de las zeolitas en que la relación Al/P es siempre la unidad. Algunas de estas estructuras tridimensionales presentan analogías con la familia de las zeolitas, como el $AlPO_4-20$ relacionado con la sodalita, cuya estructura se muestra en la figura 1.1. Entre las estructuras determinadas se encuentra la del $AlPO_4-5$ (figura 1.2) de simetría hexagonal, que se caracteriza por poseer anillos de doce miembros formando canales en la dirección $[0 0 1]$ [11, 12].

Independientemente de las similitudes estructurales, la química de los tamices moleculares cristalinos $AlPO_4$ y las zeolitas difiere considerablemente.

Por un lado, la red de los aluminofosfatos es neutra en contraste con la carga negativa de los aluminosilicatos. Por otro lado, la coordinación de los átomos de aluminio en los aluminosilicatos siempre es tetraédrica mientras que en los aluminofosfatos puede ser tetraédrica, trigonal bipyramidal u octaédrica [13]. Flanigen y colaboradores, ya anticiparon el posible uso industrial de los nuevos compuestos como adsorbentes moleculares y catalizadores. Desde ese momento, el aumento en el interés de compuestos inorgánicos que presentan una estructura abierta no ha dejado de crecer.

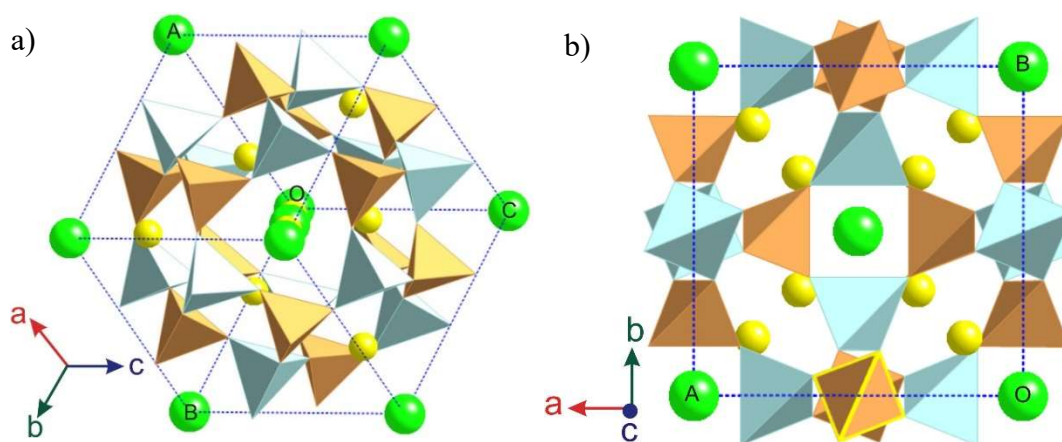


Figura 1.1. Sodalita, $\text{Na}_8[\text{Al}_6\text{Si}_6\text{O}_{24}]\text{Cl}_2$. a) Anillos de seis miembros formando túneles en la dirección $[1\ 1\ 1]$. b) Anillos de cuatro miembros formando túneles en la dirección $[0\ 0\ 1]$. Tetraedros SiO_4 : marrón, tetraedros AlO_4 : azul, Cl^- : verde y Na^+ : amarillo.

Las estructuras porosas de los aluminofosfatos pueden ser modificadas por otros elementos. La incorporación de silicio en su síntesis hidrotérmal dio como resultado tamices moleculares silicoaluminofosfatos, SAPO- n , de propiedades muy interesantes en aplicaciones de adsorción, catálisis e intercambio iónico [14]. La adición de cationes metálicos ($\text{M} = \text{Fe}^{2+}$, Fe^{3+} , Mg^{2+} , Mn^{2+} , Co^{2+} , Zn^{2+}) conduce a metaloaluminofosfatos o MAPO- n o metalosilicoaluminofosfatos MSAPO- n [15].

También a mediados de la década de los ochenta, la investigación se extendió a fosfatos microporosos en los que el aluminio se reemplazaba completamente por otros elementos. Parise [16] describió la síntesis de varios galiofosfatos relacionados con la familia AlPO_4 . El galio, al igual que el aluminio

en los aluminofosfatos, puede coordinarse de forma tetraédrica, trigonal bipyramidal u octaédrica. Otros iones diferentes que se utilizan en la síntesis de este tipo de fosfatos de estructura abierta, además del galio [17], son: estaño [18], hierro [19], cobalto [20], vanadio [21, 22], molibdeno [23, 24], etc. La incorporación en la síntesis de metales de transición resulta especialmente importante en catálisis [25] debido a sus propiedades redox. Los fosfatos de cobalto presentan un interés particular debido a las interacciones magnéticas $\text{Co}^{2+}\text{-Co}^{2+}$ [26], y a la propiedad del Co^{2+} de coordinarse en un entorno tetraédrico, bipyramidal trigonal u octaédrico [27]. Asimismo, el dopaje con Co^{2+} potencia el rendimiento catalítico de ciertas zeolitas y compuestos relacionados [28].

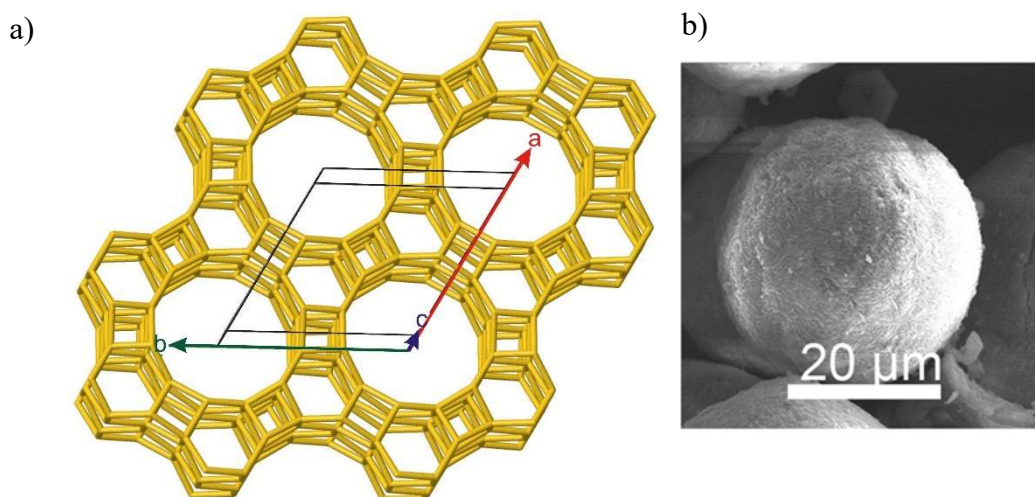


Figura 1.2. a) Estructura cristalina del $\text{AlPO}_4\text{-5}$. b) Imagen SEM de una partícula esférica $\text{AlPO}_4\text{-5}$ [11].

Además de fosfatos, se obtuvieron una gran cantidad de otros compuestos porosos: fosfitos [29], sulfatos [30], seleniatos [31], etc. y también compuestos mixtos como fosfatonitratos [32]. Aunque la mayoría contiene oxígeno, se han sintetizado materiales de características similares sin oxígeno como es el caso de ciertos nitruros mesoporosos de cobalto o cromo [33].

Un avance importante en el logro de estos compuestos se debió a Guth y Kessler [34, 35] quienes introdujeron los iones fluoruro en la síntesis hidrotermal de un galiofosfato similar a la cloverita. El flúor, como agente director de la estructura, contribuye a la formación de fases cristalinas homogéneas. Además,

los iones fluoruro también pueden incorporarse a la red como se aprecia en la estructura del aluminosilicato microporoso ZSM-5 [36], mostrado en la figura 1.3. En este caso, el flúor interacciona preferentemente con los átomos de silicio, modificando la coordinación tetraédrica del $[\text{SiO}_4]$ a trigonal bipyramidal $[\text{SiO}_4\text{F}]$. Francis y colaboradores [37] sintetizaron hidrotérmicamente un tipo de fluoruros de uranio (IV), $[\text{H}_3\text{N}(\text{CH}_2)_n\text{NH}_3]\text{U}_2\text{F}_{10}\cdot x\text{H}_2\text{O}$ siendo $n = 3, 4$ o 6 y $x = 2$ o 3 , híbridos orgánicos/inorgánicos y publicaron el intercambio de cationes orgánicos interlaminares de estos materiales con una gran variedad de cationes alcalinos, alcalinotérreos y metales de transición.

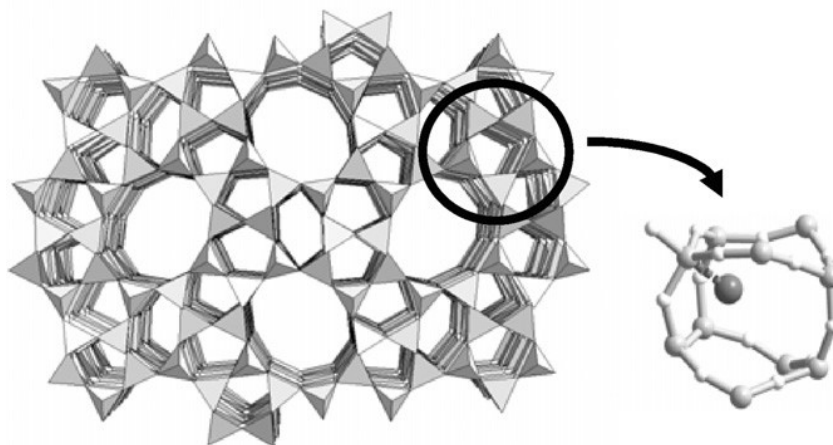


Figura 1.3. Anión fluoruro atrapado en la cavidad de una zeolita silicalita-1, ZSM-5, delimitado por un anillo de cinco miembros $[\text{TO}_4]$ con $\text{T} = \text{Si}, \text{Al}$. [36].

Los fosfatos de hierro forman parte de las familias de compuestos más conocidas del reino mineral [38]. El ejemplo más sorprendente de un fosfato de hierro poroso lo constituye la cacoxenita, $[\text{AlFe}_{24}(\text{OH})_{12}(\text{PO}_4)_{17}(\text{H}_2\text{O})_{24}]\cdot 51\text{H}_2\text{O}$ (figura 1.4), que tiene una estructura de túneles cilíndricos de gran tamaño, formados por anillos de 24 miembros ocupados por moléculas de agua, esta estructura colapsa al deshidratarse [39, 40]. Los primeros fosfatos de hierro sintéticos fueron análogos a los minerales hureaulita y alluaudita [41]. Desde entonces, una gran cantidad de fosfatos de hierro porosos han sido obtenidos en laboratorio, muchos de ellos sintetizados hidrotérmicamente [42, 43]. Dependiendo de las condiciones de la reacción se han preparado compuestos formados por octaedros centrados en el hierro unidos a átomos de flúor ($\text{Fe}-\text{F}-\text{Fe}$), a átomos de oxígeno ($\text{Fe}-\text{O}-\text{Fe}$) o a grupos fosfato ($\text{Fe}-\text{O}-\text{P}-\text{O}-\text{Fe}$) [44].

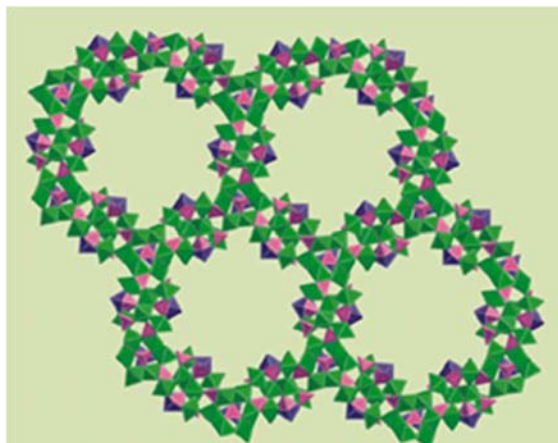


Figura 1.4. Estructura de la cacoenita, mostrando canales en la dirección $[0\ 0\ 1]$ [40].

La naturaleza de estas uniones determina, no solo, la estructura del compuesto, sino también las interacciones magnéticas. Las interacciones de intercambio magnético dependen, entre otros factores, de los átomos a través de los que se unen los cationes, del ángulo de estos enlaces y del estado de oxidación. Generalmente, las interacciones entre orbitales d de dos iones de hierro acoplados a través de grupos fosfato son antiferromagnéticas débiles [45]. En 1996 se publicó la síntesis hidrotermal de un fosfato férrico magnético de estructura cristalina tridimensional abierta, $[\text{Fe}_4(\text{PO}_4)_4\text{F}_2(\text{H}_2\text{O})_3] \cdot [\text{C}_6\text{H}_{14}\text{N}_2]$ (figura 1.5), se observó la presencia de cuatro Fe^{3+} no equivalentes en su estructura y orden antiferromagnético a una temperatura de 10.7 K [42].

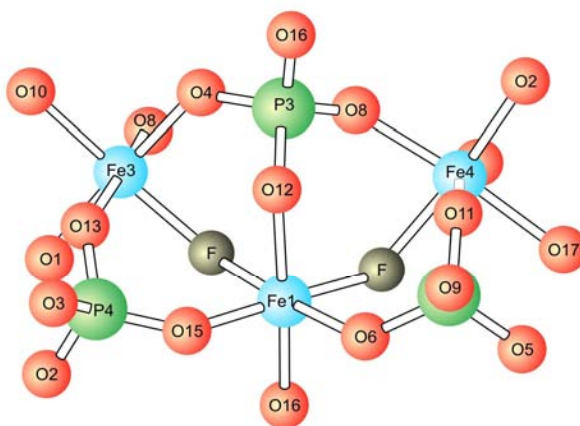


Figura 1.5. Imagen de $[\text{Fe}_4(\text{PO}_4)_4\text{F}_2(\text{H}_2\text{O})_3] \cdot [\text{C}_6\text{H}_{14}\text{N}_2]$ con los iones Fe^{3+} en coordinación octaédrica [42].

1.1. Síntesis hidrotermal

La mayoría de los compuestos citados en el apartado anterior han sido sintetizados hidrotermalmente. El término "hidrotermal" tiene un origen puramente geológico. Fue utilizado por primera vez por el geólogo británico Sir Roderick Murchison (1792-1871) [46] para describir la acción que el agua produce en la corteza terrestre, a temperatura y presión elevadas, formando distintas rocas y minerales. La definición de proceso hidrotermal, basado en el significado de las palabras griegas "hidro" y "termo", se ha ampliado desde su origen. Aunque dependiendo de los autores pueden existir pequeñas diferencias, Byrappa y Yoshimura [47] consideran el proceso hidrotermal como una reacción química heterogénea, en presencia de un solvente (acuoso o no acuoso), por encima de la temperatura ambiente y a una presión mayor de una atmósfera en un sistema cerrado.

La investigación hidrotermal comienza en el siglo XIX con el estudio sobre la génesis de rocas y minerales, en el que un grupo de geólogos simularon en el laboratorio las condiciones naturales existentes bajo la corteza terrestre. Desde ese inicio hasta nuestros días, pueden destacarse algunas fechas relevantes en el avance de esta técnica. El primer trabajo relacionado con la síntesis hidrotermal de materiales se atribuye a R. W. Bunsen que sintetizó, en 1839, un carbonato de bario y estroncio a temperatura superior a 200 °C y presión mayor de 100 bares [47]. Posteriormente, en 1845, E. Schafhautl obtuvo hidrotermalmente pequeños cristales de cuarzo a partir de un precipitado de ácido silícico, utilizando un equipamiento precursor del autoclave. En la mayoría de los experimentos hidrotermales llevados a cabo entre finales del siglo XIX y principios del XX se obtenían productos nanocristalinos que eran desechados debido a que las técnicas microscópicas no permitían su estudio [48], aunque posteriormente se observó que muchos presentaban propiedades interesantes. A mediados del siglo pasado se sintetizaron, mediante procesos hidrotermales, un gran número de minerales arcillosos y de compuestos de la familia de las zeolitas en un rango muy amplio de composiciones [49], poniendo de manifiesto que la síntesis hidrotermal ofrece muchas ventajas sobre los métodos sintéticos cerámicos convencionales. Permite preparar todas las formas de compuestos: cerámicos, polvos, fibras, monocristales, etc., con la diferencia de que el gasto en material, energía y

precursores es mucho menor para los hidrotermales. Desde la perspectiva ambiental, son menos perjudiciales que muchos otros métodos de síntesis. Esto se puede atribuir a las relativamente bajas temperaturas del proceso y a la capacidad de reciclar los desechos o eliminar de forma segura los que no pueden reciclarse. Las bajas temperaturas de reacción pueden evitar problemas que ocurren cuando los compuestos cerámicos se enfrían a temperatura ambiente, tales como un bajo control estequiométrico debido a la volatilidad de los componentes, defectos inducidos por estrés causados por transformaciones de fase, etc. [50].

En las últimas décadas, los productos cristalinos micrométricos y nanométricos han supuesto la gran revolución en ciencia y tecnología, la “nanotecnología”. Estos compuestos presentan mejoras en las propiedades físicas al compararlos con materiales de mayor tamaño, tales como mayor resistencia mecánica, mejor difusividad térmica, calor específico más alto, etc. [51-53]. Cabe destacar el aumento de la utilización de agua y fluidos supercríticos en la producción de nanopartículas y también en la transformación y reciclado de residuos, ya que presentan ventajas en rendimiento y velocidad [54]. Además, existe un creciente interés en mejorar la cinética de la reacción hidrotermal mediante microondas, ultrasonidos, etc., lo que lleva a la tecnología hidrotermal a enlazar varias ramas interdisciplinarias de la ciencia [55]. En la figura 1.6 se presenta un esquema con algunas de estas relaciones.

El objetivo de la síntesis hidrotermal consiste en obtener materiales a partir de la reacción de sustancias que en condiciones normales de presión y temperatura son poco solubles, pero que en el interior del recipiente cerrado donde la presión es más elevada que la ambiental, permite a los solventes superar la temperatura del punto de ebullición formándose fluidos en estado crítico.

En el caso del agua, el producto iónico alcanza el valor máximo en el rango de temperaturas habitual en este tipo de síntesis, experimentando una disociación (H_3O^+ , OH^-) mucho mayor que a presión normal. En estas condiciones, el agua puede reaccionar como ácido o como base. Los valores de temperatura y presión críticos para el agua son 374 °C y 22.1 MPa respectivamente. La densidad y constante dieléctrica del agua varían con la temperatura y presión como se muestra en la figura 1.7. La constante dieléctrica relativa del agua a temperatura ambiente es 78, donde compuestos iónicos como las sales inorgánicas pueden ser

solubles, esta constante disminuye al aumentar la temperatura y al disminuir la presión. El agua en condiciones supercríticas reduce la solubilidad de compuestos inorgánicos y favorece la solubilidad de compuestos orgánicos. Al disminuir la polaridad del agua aumenta la velocidad de reacción. La densidad del agua disminuye con la temperatura y aumenta con la presión [47, 57].

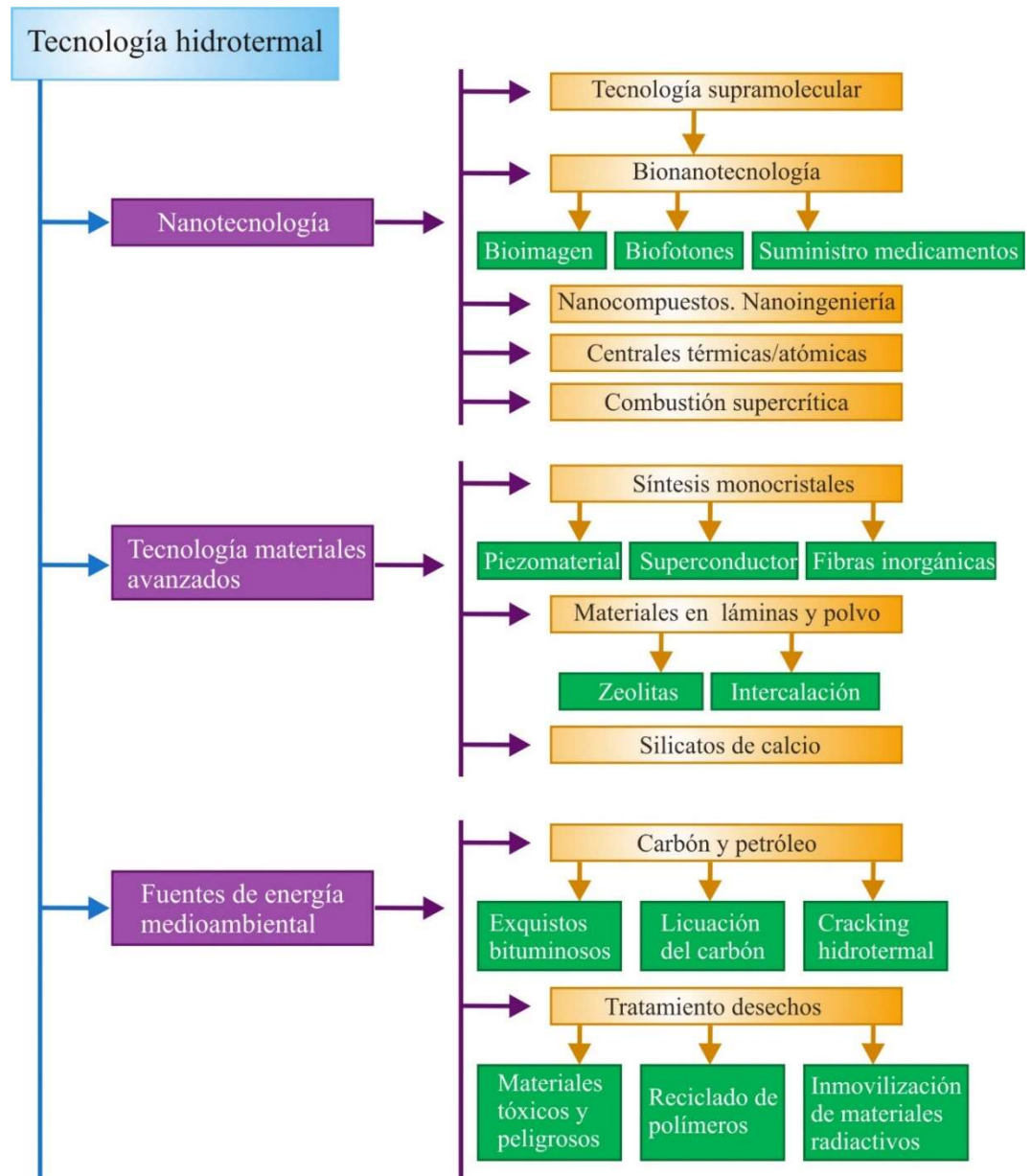


Figura 1.6. Distintas ramas de ciencia y tecnología relacionadas con la síntesis hidrotermal [56].

Un ejemplo de la influencia de la densidad del agua fue presentado por Noguchi y colaboradores [58] que sintetizaron hidrotermalmente nanopartículas

de $\gamma\text{-Al}_2\text{O}_3$ partiendo de $\text{Al}(\text{NO}_3)_3$ y utilizando agua como solvente en condiciones supercríticas. Variaron la temperatura desde 400 a 500 °C y la presión desde 25 a 35 MPa, obtuvieron $\gamma\text{-AlOOH}$ por debajo de 410 °C y por encima de esta temperatura sintetizaron $\gamma\text{-Al}_2\text{O}_3$. Consideraron que este resultado era debido a la disminución de la densidad del agua en tan solo 10 °C, desde 0.357 a 0.251 g/cm³.

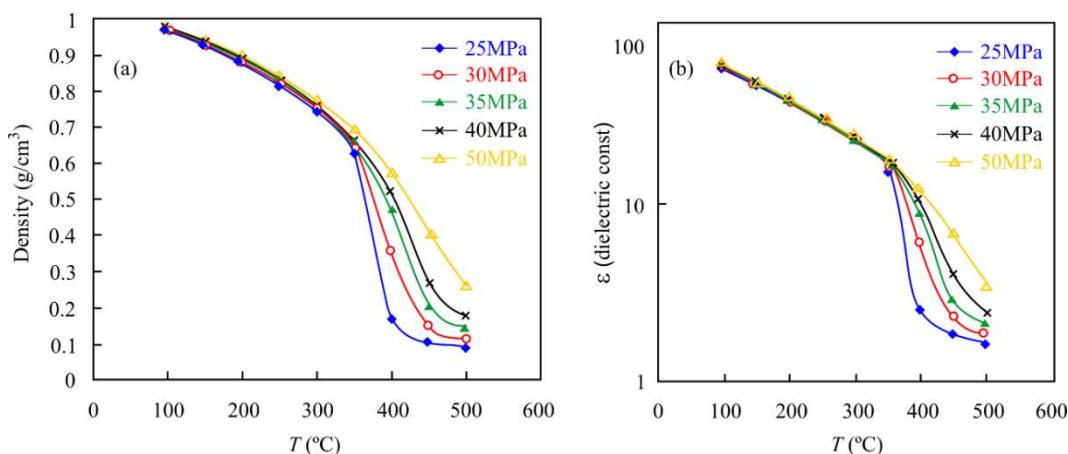


Figura 1.7. (a) Densidad. (b) Constante dieléctrica relativa del agua en función de la temperatura a diferentes presiones [57].

Además de la naturaleza de los reactivos, de sus propiedades fisicoquímicas como solubilidad, estabilidad térmica, etc., de la elección y concentración del solvente, los parámetros que determinan el proceso hidrotermal son presión, temperatura, tiempo de reacción, valores de pH, presencia de aditivos y geometría del autoclave. De la optimización de estos factores depende el resultado de la síntesis [59-61]. La incorporación de aditivos, inorgánicos u orgánicos, ácidos, básicos, oxidantes, reductores, se utiliza habitualmente para controlar el pH de la reacción, la solubilidad de los reactivos, la morfología del cristal, etc. [56, 62].

Diseñar un recipiente para realizar síntesis hidrotermales es difícil ya que cada proyecto presenta diferentes objetivos y tolerancias. El primer autoclave conocido lo utilizó Sénarmont en 1851, fue fabricado con cañones de armas donde introducía ampollas de vidrio selladas para sintetizar óxidos, carbonatos, fluoruros, sulfatos, etc. [63]. Las características que debe cumplir un autoclave ideal pueden resumirse en: ser inerte a ácidos, bases o agentes oxidantes; fácil de montar y desmontar; longitud suficiente para obtener el gradiente de temperatura

deseado; totalmente hermético a la temperatura y presión que sean necesarias alcanzar; capaz de soportar altas temperaturas y presiones durante periodos largos de tiempo. Teniendo en cuenta estos requisitos, los autoclaves consisten en cilindros de espesor considerable que pueden ser de vidrio, cuarzo, acero inoxidable, aleaciones de cobalto o titanio, etc. En algunos experimentos los reactores no necesitan contener ningún revestimiento interno, como puede ser el crecimiento de cuarzo en reactores de acero con bajo contenido en carbono. Sin embargo, cuando los materiales se obtienen a partir de ácido fosfórico u otros medios altamente corrosivos, un revestimiento de teflón, oro, plata o platino es necesario para proteger el reactor [64]. En la figura 1.8 se muestra el tipo de autoclaves utilizado en este trabajo.



Figura 1.8. Autoclaves de uso general para tratamiento hidrotermal.

La síntesis y cristalización hidrotermal se puede dividir en dos etapas. Inicialmente una disolución-supersaturación y posteriormente una cristalización. En la primera etapa, la temperatura y la presión favorecen la disolución de los precursores, dando lugar a la formación de especies en solución que muestran mayor tendencia a reaccionar para formar el producto deseado. Esta es una fase estable bajo condiciones hidrotermales, obtenida a partir de la nucleación. Por ejemplo, la síntesis de un óxido metálico en condiciones hidrotermales se puede entender de la siguiente manera: al comienzo del proceso, según aumenta la temperatura, se produce la hidrólisis del precursor, una sal metálica, formándose hidróxidos metálicos. A continuación, cuando el sistema alcanza la temperatura adecuada, los hidróxidos se deshidratan obteniéndose el óxido del metal. Esta reacción se ve favorecida por la disminución de la constante dieléctrica del agua y el aumento de la solubilidad del oxígeno en el agua [65].

Durante la etapa de cristalización tiene lugar un crecimiento de partículas a

partir de la redisolución y una nueva precipitación de las fases ya formadas. Se observa un crecimiento de cristales más grandes a partir de aquellos de menor tamaño que presentan una mayor solubilidad. Este fenómeno se conoce como la regla de Oswald y ocurre durante la segunda etapa del proceso [66, 67].

Para mejorar el rendimiento del proceso hidrotermal convencional se puede combinar con diferentes técnicas. En general, los métodos de síntesis híbridas resultantes de la asociación con ultrasonidos, electroquímica, microondas etc., ofrecen ventajas adicionales sobre el método convencional, incluyendo reducción del tiempo de reacción y ahorro de energía. Estos métodos pueden modificar las características de los productos como pureza, tamaño y morfología de las partículas.

La síntesis ultrasónica-hidrotermal es una técnica que puede aplicarse de dos formas, como un pretratamiento con ultrasonido a la solución precursora y su posterior cristalización hidrotermal o con el uso simultáneo de ultrasonido en condiciones hidrotermales [68]. En ambos casos, se aumenta la velocidad de la reacción y se obtienen partículas de pequeño tamaño [69]. La figura 1.9 recoge un ejemplo de autoclave con emisor de ultrasonido. El tratamiento sonoquímico hidrotermal fue introducido por Aymonier y colaboradores [70]. Demostraron que la utilización de ultrasonidos en las soluciones hidrotermales conduce a un aumento considerable de la velocidad de descomposición de residuos orgánicos. A este tipo de síntesis se le atribuyen otras ventajas como la posibilidad de obtener morfologías diferentes tales como nanotubos [71], así como la viabilidad de preparar materiales dopados, como en el caso del TiO_2 mesoporoso dopado con Fe [72].

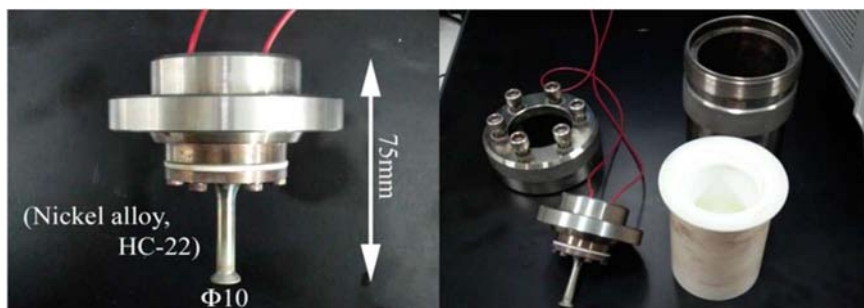


Figura 1.9. Transductor (emisor) de ultrasonido y autoclave [73].

Esta metodología se basa en que la presión que ejercen las ondas sonoras en un medio líquido puede dar lugar a la formación de burbujas de vapor, fenómeno conocido como cavitación. Cuando las burbujas colapsan aparecen pequeñas zonas de presión y temperatura elevadas [74].

La cristalización electroquímica-hidrotermal es una técnica utilizada para obtener películas cerámicas cristalinas. Las principales ventajas atribuidas a esta técnica son mayor pureza de los productos, menor temperatura de reacción y mayor rendimiento de crecimiento de la película [50, 75]. La microestructura de las películas puede controlarse variando parámetros como la composición del electrodo, el tiempo de carga o la densidad de corriente [76]. La figura 1.10 muestra un esquema del autoclave utilizado por Yoshimura y colaboradores para sintetizar películas delgadas de ATiO_3 y AZrO_3 ($\text{A} = \text{Ba}, \text{Sr}$) [77].

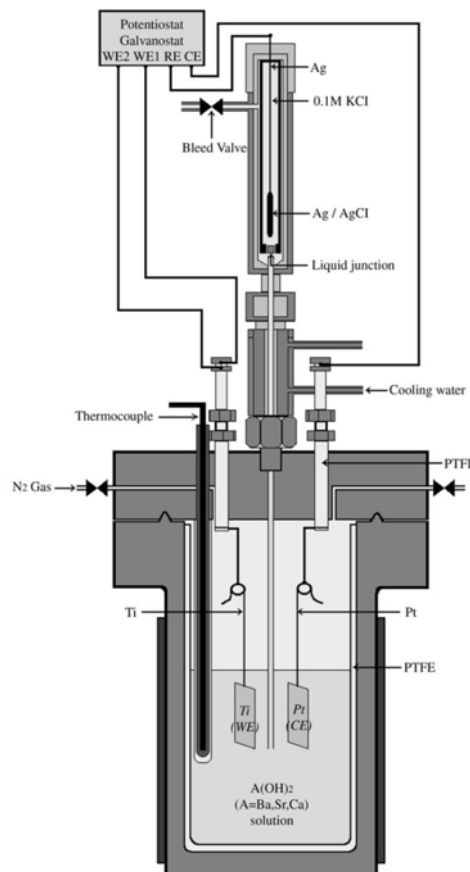


Figura 1.10. Celda electroquímica, ensamblada en un autoclave, con dos electrodos, uno de Ti y otro de Pt y un electrodo externo de referencia de Ag/AgCl [77].

Los primeros estudios sobre la cristalización hidrotérmal con microondas fueron realizados por Komarmani y colaboradores [78] que en 1992 publicaron la síntesis en polvo de los compuestos TiO_2 , ZrO_2 , Fe_2O_3 , KNbO_3 y BaTiO_3 utilizando una frecuencia de 2.45 GHz. Observaron ciertas ventajas sobre la técnica convencional como la reducción del tiempo de reacción y la formación, en algunos casos, de fases cristalinas diferentes a las obtenidas por síntesis hidrotérmal convencional. La mejora de la síntesis con esta técnica se basa principalmente en el calentamiento por irradiación de las microondas que favorece la nucleación homogénea y el proceso de crecimiento durante la reacción mejorando la pureza del producto [79].

En la figura 1.11 se muestran imágenes SEM de nanoestructuras de óxidos de Fe, Co, Mn y Cr sintetizados combinando el método hidrotérmal más microondas. Los óxidos metálicos presentan espectaculares morfologías octaédricas, esféricas, varillas, etc. [80].



Figura 1.11. Imágenes SEM de nanoestructuras de varios óxidos metálicos obtenidos por síntesis hidrotérmal con microondas [80].

1.2. Propiedades magnéticas

El conocimiento de las propiedades magnéticas de un compuesto es primordial, no solo para entender el comportamiento magnético de la materia condensada, sino también para el desarrollo de nuevos materiales y dispositivos electrónicos. Los momentos magnéticos de los átomos que constituyen los sólidos pueden actuar conjuntamente y comportarse de forma diferente a como lo harían si estuviesen aislados unos de otros. Este comportamiento cooperativo, junto a la diversidad de tipos de interacciones magnéticas que se pueden encontrar, conduce a interesantes propiedades magnéticas. Algunas de sus aplicaciones pueden ser, entre otras muchas, funcionar como parámetros que contribuyen a determinar la pureza de electrodos en baterías recargables de ion litio [81], utilidades biomédicas como las imágenes de resonancia magnética [82], o su uso para eliminar basura tóxica [83].

Parámetros tales como susceptibilidad magnética o momento magnético caracterizan el magnetismo de los sólidos. Cuando una sustancia está situada en un campo magnético H , la imanación o momento magnético por unidad de volumen M , está relacionada con H a través de la susceptibilidad magnética χ de la sustancia [84, 85]

$$\chi = \frac{\partial M}{\partial H} \quad (1.1)$$

En general, χ se expresa como susceptibilidad magnética molar χ_M , donde $\chi_M = \chi V_M$, y V_M es el volumen ocupado por un mol de sustancia.

El momento magnético de un átomo o un ion es $\vec{\mu} = \gamma \hbar \vec{J} = -g \mu_B \vec{J}$ siendo $\hbar \vec{J}$ el momento angular total (\hbar es la constante reducida de Planck), igual a la suma del momento angular orbital $\hbar \vec{L}$, más el momento angular de espín $\hbar \vec{S}$. γ es la relación giromagnética entre el momento magnético y el momento angular, $g \cong 2$ para un espín electrónico. μ_B es el magnetón de Bohr, unidad acorde con los valores de los momentos magnéticos, definido por

$$\mu_B = \frac{e \hbar}{2 m_e} = 9.2734 \cdot 10^{-24} \text{ J/T} \quad (1.2)$$

donde m_e es la masa del electrón.

Los diferentes tipos de magnetismo (figura 1.12) de los materiales pueden describirse a partir de su comportamiento en presencia de un campo magnético.

Una propiedad intrínseca de todas las sustancias es el diamagnetismo, que se debe a un efecto de inducción electromagnética en el sistema electrónico de los átomos. Un campo magnético se debilita en un material diamagnético. Estos materiales presentan susceptibilidad magnética molar pequeña, negativa ($\approx -10^{-6}$ cm³/mol) e independiente de la temperatura [85].

Los materiales paramagnéticos contienen electrones no emparejados que están orientados aleatoriamente. Cada átomo, ion o molécula de una sustancia paramagnética puede considerarse como un pequeño imán con su momento magnético asociado. Un campo magnético externo produce una orientación de estos imanes paralela al campo, siendo este reforzado en el material paramagnético. Presentan χ_M positiva, pequeña (< 0.01 cm³/mol) y dependiente de la temperatura, su conducta puede expresarse con la ley de Curie:

$$\chi_M = \mu_0 \frac{N_A \mu_{eff}^2 \mu_B^2}{3k_B T} = \frac{C}{T} \quad (1.3)$$

donde μ_0 es la permeabilidad magnética del vacío, N_A el número de Avogadro, k_B es la constante de Boltzman y C la constante de Curie. μ_{eff} es el momento magnético efectivo, surge del resultado de las interacciones entre el momento angular de espín del electrón y el momento angular orbital del electrón.

Se define:

$$\mu_{eff}^{teor} = g\sqrt{J(J+1)} \quad (1.4)$$

donde $J = L + S$ En algunos casos, el momento angular aparece bloqueado $L = 0$, sustituyéndose la ecuación anterior por $\mu_{eff}^{teor} = g\sqrt{S(S+1)}$ [85]. Experimentalmente, el momento magnético efectivo de un material puede ser obtenido a partir de las medidas de la susceptibilidad magnética molar. La ecuación 1.3 puede expresarse:

$$\mu_{eff}^{exp} = 797.8\sqrt{\chi_M^{SI} T} = 2.827\sqrt{\chi_M^{cgs} T} \quad (1.5)$$

μ_{eff} está medido en magnetones de Bohr por fórmula unidad [86].

Por ejemplo, en el caso del ion Fe^{3+} de alto espín, con cinco electrones d desapareados, el momento magnético calculado teóricamente y el obtenido experimentalmente coinciden, siendo su valor $5.9 \mu_B$, debido a que el momento magnético orbital es cero; mientras el momento magnético experimental para el Fe^{2+} va de 5.1 a $5.5 \mu_B$, es un poco más alto que el obtenido teóricamente, suponiendo $L = 0$, lo que indica una contribución del momento orbital del ion [87].

La dependencia de la susceptibilidad con la temperatura es el resultado de dos tendencias opuestas. Al aumentar la temperatura, el alineamiento de los momentos magnéticos en el material va disminuyendo debido a las fuertes vibraciones térmicas, produciéndose una reducción del valor de la susceptibilidad. Esta relación se expresa con la ley de Curie-Weiss

$$\chi_M = \frac{C}{T - \theta_p} \quad (1.6)$$

Por debajo de una cierta temperatura que depende del tipo de sustancia, esta experimenta una transición desde una situación paramagnética a un estado ordenado magnéticamente: ferromagnético, ferrimagnético o antiferromagnético. Para materiales ferro y ferrimagnéticos se llama temperatura de Curie (T_C) y para los antiferro es la temperatura de Néel (T_N). En la figura 1.12 se muestran los tipos de magnetismo más generales de los materiales.

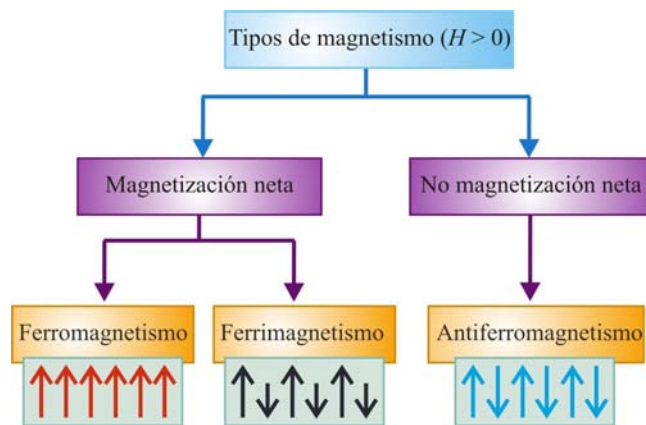


Figura 1.12. Ordenamientos magnéticos ($H > 0$).

Los materiales ferro y ferrimagnéticos tienen electrones desapareados cuyos momentos se deben a las interacciones entre espines vecinos que permanecen, al

menos parcialmente, alineados incluso cuando no están en presencia de ningún campo magnético. La energía de acoplamiento de los espines es positiva. En las sustancias ferromagnéticas los espines electrónicos se alinean paralelamente, por lo que tienen un momento magnético neto y una χ_M positiva grande ($0.01 - 10^6 \text{ cm}^3/\text{mol}$). Cuando la temperatura se eleva, el alineamiento ordenado de los espines se reduce con respecto a las fluctuaciones térmicas de los momentos magnéticos individuales y la χ_M desciende bruscamente. La dependencia de la susceptibilidad con la temperatura no obedece la ley de Curie-Weiss para temperaturas inferiores a T_C .

En un material antiferromagnético los espines electrónicos tienen igual momento magnético y están ordenados en posición antiparalela. Estos materiales muestran un momento magnético igual a cero y una χ_M positiva y pequeña ($0 - 0.1 \text{ cm}^3/\text{mol}$). El aumento de la temperatura generalmente conlleva un aumento en la susceptibilidad, debido a la distorsión del orden magnético, hasta alcanzar un valor máximo a la temperatura de Néel. La figura 1.13 muestra el comportamiento de la susceptibilidad con la temperatura en materiales para, ferro y antiferromagnéticos. Los materiales ferri y antiferromagnéticos pueden considerarse formados por dos subredes magnéticas con alineamiento de espines antiparalelos alternas. En los ferrimagnéticos las redes no son iguales, de lo que resulta un momento magnético neto.

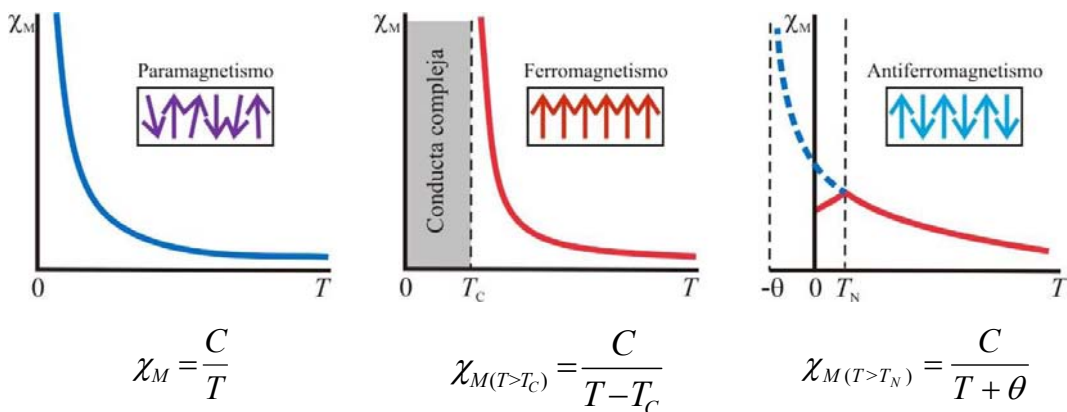


Figura 1.13. Influencia de la temperatura sobre la susceptibilidad magnética en materiales para, ferro y antiferromagnéticos [81].

Las sustancias ferro, ferri y antiferromagnéticas presentan estructura de dominios, solo las partículas con un tamaño entre 50 y 500 nm pueden ser un único dominio. Los espines dentro de un dominio están alineados, paralela o antiparalelamente, pero diferentes dominios pueden alinearse en diferentes direcciones. Los dominios se eliminan utilizando un campo magnético adecuado, a medida que este aumenta, la alineación de los espines en los dominios crece y cuando es lo suficientemente grande se tiene la imanación de saturación, todos los espines están paralelos. En la figura 1.14 se esquematiza esta situación.

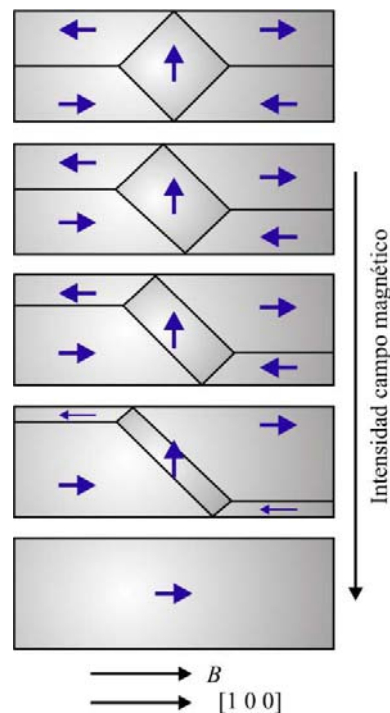


Figura 1.14. Efecto del desplazamiento de las paredes de los dominios de un monocristal de hierro al aplicar un campo magnético que aumenta desde cero hasta un valor máximo [86].

Un ciclo de histéresis consiste en la representación de la imanación frente al campo magnético, presenta dos ramas, una representa la imanación y la otra la desimanación del proceso. La magnitud del campo necesario para desimanar un material ferro o ferrimagnético se define como coercitividad. Se distingue entre materiales con baja o alta coercitividad. Los primeros son fáciles de imanar, son materiales blandos como el permaloy, aleación comercial de Ni/Fe, que presenta un campo coercitivo de unos $2 \cdot 10^{-7}$ T. Los segundos son difíciles de imanar, son

magnéticamente duros y frecuentemente involucran tierras raras como el $\text{Nd}_2\text{Fe}_{14}\text{B}$ con un campo coercitivo de 1.2 T [86].

El comportamiento magnético de un sólido depende de muchos factores, entre ellos, la simetría local del ion magnético. En sales inorgánicas, raramente se presentan enlaces metal-metal, la mayoría de las interacciones entre metales de transición son de superintercambio a través de ligandos de conexión. El intercambio electrostático es la base de las interacciones magnéticas más importantes en materiales sólidos que contienen iones hierro [87]. En el caso de los fosfatos de hierro, las interacciones de superintercambio que se producen entre dos iones hierro enlazados a través de grupos fosfato son débiles, mientras que las que suceden a través de puentes de oxígeno o flúor son fuertes. Estas últimas son anti- o ferromagnéticas dependiendo del estado de oxidación del hierro y del ángulo entre los tres átomos que interactúan [45]. En general, las interacciones entre iones Fe^{3+} , d^5-d^5 , son antiferromagnéticas para ángulos entre 90° y 180° . Sin embargo, cuando la interacción implica sistemas de valencia mixta $\text{Fe}^{3+}/\text{Fe}^{2+}$, el superintercambio d^5-d^6 es básicamente antiferromagnético para ángulos cercanos a los 180° , mientras que es ferromagnético para ángulos próximos a 90° . Una conducta similar la muestran los iones Fe^{2+} , superintercambio d^6-d^6 antiferromagnético y ferromagnético débil para ángulos cercanos a 180° y 90° respectivamente. Por otro lado, el superintercambio entre orbitales d de dos iones Fe acoplados a través de grupos fosfato (Fe-O-P-O-Fe), en general, es débil y antiferromagnético [88].

1.3. Cinética de los procesos de estado sólido

La cinética de reacciones en estado sólido ha sido ampliamente analizada durante los últimos años resultando de gran utilidad en la caracterización de procesos físicos y químicos en sistemas orgánicos, inorgánicos y metálicos, que implican efectos térmicos. Proporciona valiosa información cualitativa y cuantitativa sobre las propiedades térmicas y, más importante aún, información cinética sobre transformaciones de fase [89], cristalización de vidrios metálicos [90], precipitación en estado sólido [91], cambios estructurales asociados con nanomateriales [92], etc.

Un cambio en la temperatura afecta directamente a todos los tipos de movimiento molecular en el sistema y provoca procesos físicos y químicos dentro de él. La energía del movimiento molecular aumenta al hacerlo la temperatura. Cuando esta energía se aproxima a la energía de las interacciones intermoleculares, las fuerzas de cohesión ya no pueden mantener a las moléculas en la fase condensada de modo que esta última se transforma en la fase gaseosa. Como resultado, un líquido se vaporiza y un sólido se sublima. Estos son ejemplos de un proceso físico, es decir, un proceso que no rompe los enlaces dentro de las moléculas. Sin embargo, cuando la temperatura se eleva lo suficiente, la energía del movimiento molecular comienza a acercarse a la energía de los enlaces químicos rompiéndolos, de manera que el sistema experimenta transformaciones químicas. La descomposición térmica de una sustancia sólida es un ejemplo de un proceso químico [93].

La cinética y la termodinámica son dos aspectos importantes para la comprensión de los procesos en estado sólido. La termodinámica estudia los estados iniciales y finales del proceso mientras que la cinética se ocupa del mecanismo seguido por la reacción y del tiempo requerido, es decir, de la velocidad de reacción. No todas las partículas en un sistema reaccionan a la vez. Al aumentar la temperatura, el número de partículas que alcanzan el estado activado va creciendo. En este proceso, la energía de estos átomos o moléculas aumenta hasta un máximo para disminuir, posteriormente, hasta un valor final. La energía de activación está relacionada con la barrera energética que los reactivos deben superar para transformarse en productos [94, 95]. La figura 1.15 representa la barrera energética en la teoría del complejo activado.

Una de las técnicas experimentales más común empleada para estudiar la cinética de reacciones activadas térmicamente es el análisis termogravimétrico (TGA) que mide el peso de una muestra en función del tiempo o de la temperatura mientras se somete a un proceso de calentamiento. El proceso puede ser isoterma, no isoterma o una combinación de ambos. Lo habitual es que se produzca una pérdida de peso, aunque no está totalmente descartada una posible ganancia. La atmósfera puede ser estática o dinámica con un caudal determinado, siendo los gases más habituales N_2 , aire, Ar o CO_2 . El TGA sólo permite detectar variaciones de peso en procesos tales como descomposiciones, sublimaciones, etc.

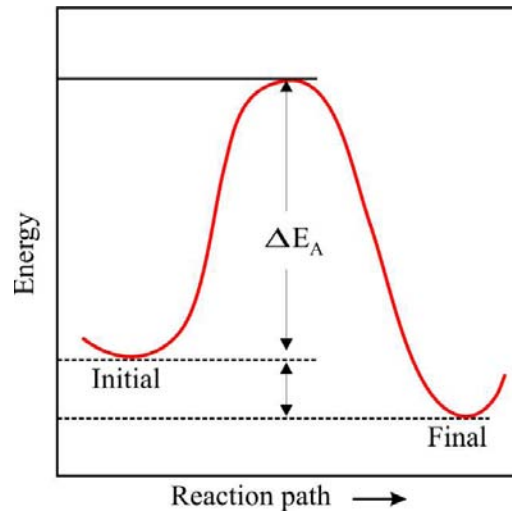


Figura 1.15. Barrera energética en la teoría del complejo activado [94].

Los métodos térmicos a menudo requieren análisis complementarios mediante otras técnicas para una completa comprensión de los procesos que están ocurriendo, incluso en los más sencillos. Suelen combinarse diferentes métodos térmicos entre sí debido a su similitud en los programas de temperatura y control de atmósfera, de forma que la información obtenida se complementa. Los métodos térmicos más utilizados de manera simultánea con el TGA son análisis térmico diferencial (DTA) y calorimetría diferencial de barrido (DSC) dando lugar a las técnicas TG-DTA y TG-DSC [96, 97]. La figura 1.16 muestra un ejemplo de curvas TGA y DSC.

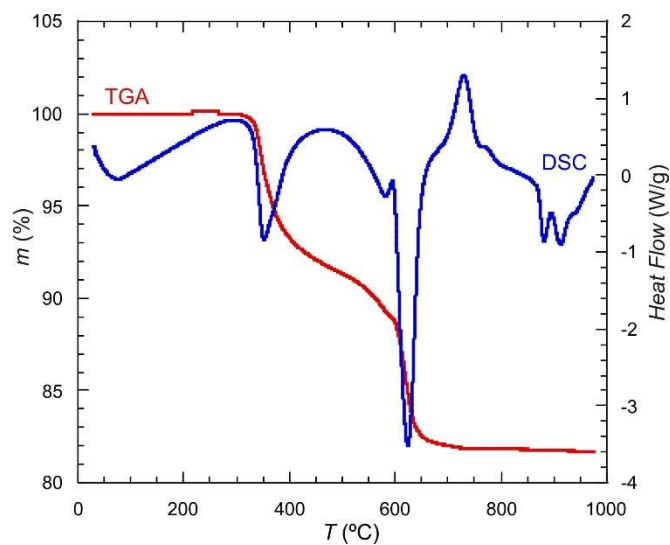


Figura 1.16. Curvas DSC y TGA de una muestra $\text{Cr}_{0.34}\text{Fe}_{0.66}\text{NH}_4(\text{HPO}_4)_2$ obtenidas con una velocidad de calentamiento $\beta = 20 \text{ }^\circ\text{Cmin}^{-1}$.

El grado de conversión, α , refleja el progreso de la reacción desde el estado inicial, antes de que comience la reacción ($\alpha = 0$), hasta el estado final, cuando se completa la reacción ($\alpha = 1$).

En el análisis termogravimétrico, el grado de conversión es la relación entre la variación de la masa en un instante determinado y la variación de masa total

$$\alpha = \frac{m(t_i) - m(t)}{m(t_i) - m(t_f)} \quad (1.7)$$

donde $m(t)$ es la masa en el instante t , t_i y t_f corresponden a los tiempos inicial y final respectivamente. En general, el grado de conversión, se determina experimentalmente como una fracción del cambio total de una propiedad física que acompaña al proceso. Si en una reacción se produce una pérdida de masa, el grado de conversión se evalúa como la fracción de la masa total perdida en el proceso. Si en el proceso se produce absorción o desprendimiento de calor, el grado de conversión se evalúa como una fracción del calor total absorbido o desprendido [93].

La velocidad de reacción puede expresarse en función de tres variables: la temperatura, el grado de conversión y la presión, según la ecuación [98]

$$\frac{d\alpha(t)}{dt} = k(T)f(\alpha)h(P) \quad (1.8)$$

La dependencia con la presión, $h(P)$, se ignora en la mayoría de los estudios cinéticos utilizados en análisis térmico. Es debido a que la presión tiene una contribución importante en los procesos cinéticos en los que reactivos o productos son gases, pero en el caso de cinéticas de estado sólido la velocidad de la reacción se considera función solo de T y α

$$\frac{d\alpha(t)}{dt} = k(T)f(\alpha) \quad (1.9)$$

$k(T)$ es conocida como la constante de velocidad, dependiente de T y $f(\alpha)$ la función llamada modelo de reacción que describe la dependencia de la velocidad de reacción con el grado de conversión. En medios fluidos $f(\alpha)$ expresa la relación entre la concentración de reactivos y productos. Sin embargo, en sólidos, donde el movimiento molecular está más restringido y las reacciones dependen de la estructura local, el concepto de concentración resulta menos útil porque el

grado de conversión depende del tipo de experimento, aquí $f(\alpha)$ juega el papel de una función empírica [97].

La ecuación 1.9 describe la reacción de un proceso simple. En general, la reacción total puede involucrar más de una reacción simple, es decir, múltiples reacciones, cada una de las cuales tiene su grado de conversión específico. Por ejemplo, una reacción en la cual el proceso total implica dos reacciones paralelas se podría describir con la siguiente ecuación:

$$\frac{d\alpha(t)}{dt} = k_1(T)f_1(\alpha_1) + k_2(T)f_2(\alpha_2) \quad (1.10)$$

siendo α_1 y α_2 los grados de conversión específicos asociados con las dos reacciones individuales y su suma es el grado de conversión total, $\alpha_1 + \alpha_2 = \alpha$. Sin embargo, esto no significa que la ecuación 1.9 no sea válida. En estos casos, los métodos isoconversionales describen el proceso mediante el uso de múltiples ecuaciones cinéticas 1.9 utilizadas en rangos de conversión y temperatura lo suficientemente pequeños de forma que en cada intervalo la reacción puede considerarse un proceso simple [93].

En las reacciones de estado sólido, la ecuación de Arrhenius es una buena aproximación de la dependencia de la constante cinética con la temperatura

$$k(T) = Ae^{-E/RT} \quad (1.11)$$

donde los parámetros cinéticos están asociados con conceptos fundamentales de la teoría del complejo activado: A con la frecuencia de vibración y E con la energía de activación, R es la constante universal de los gases [99, 100]. La velocidad de reacción se expresa

$$\frac{d\alpha}{dt} = Ae^{-E/RT} f(\alpha) \quad (1.12)$$

$f(\alpha)$ está relacionado con el mecanismo de reacción [98].

Los modelos de reacción se pueden clasificar básicamente en tres tipos: acelerado, decelerado y sigmoideal o autocatalítico. Cada uno de estos tipos tiene un perfil de reacción característico (figura 1.17). Los perfiles se reconocen fácilmente en reacciones isotérmicas, ya que la forma de la curva de conversión solo depende del modelo de reacción. En condiciones no isotérmicas $k(T)$ y

$f(\alpha)$ varían simultáneamente, lo que hace difícil reconocer el tipo de modelo de reacción.

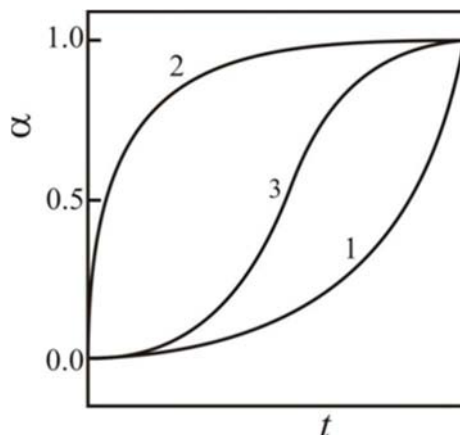


Figura 1.17. Modelos de conversión: 1-acelerado, 2-decelerado, 3-sigmoidal [98]

Los modelos acelerados representan procesos cuya velocidad aumenta continuamente con el grado de conversión y alcanza su valor máximo al final del proceso. Un ejemplo de modelo acelerado es el Power law de la tabla 1

$$f(\alpha) = n\alpha^{(n-1)/n} \quad (1.13)$$

donde n es el orden de reacción.

El tipo de modelo decelerado representa reacciones cuya velocidad tiene un máximo al principio del proceso y después decrece continuamente hasta completar la reacción. El ejemplo más común es

$$f(\alpha) = (1-\alpha)^n \quad (1.14)$$

Los modelos Difusión de la tabla 1 son decelerados.

Los modelos sigmoidales representan procesos con estado inicial correspondiente a un modelo acelerado y el final a uno decelerado por lo que la velocidad máxima de la reacción tendrá lugar para un grado de conversión intermedio, es el caso de los modelos Avrami-Erofeev

$$f(\alpha) = n(1-\alpha)[- \ln(1-\alpha)]^{(n-1)/n} \quad (1.15)$$

Sestak y Berggren [98] introdujeron un modelo empírico

$$f(\alpha) = \alpha^m (1 - \alpha)^n [-\ln(1 - \alpha)]^p \quad (1.16)$$

que dependiendo de los valores que tomen m , n , y p puede representar distintos modelos de reacción y engloba la mayoría de los tipos más utilizados de los modelos anteriores.

Tabla 1. Algunos de los modelos cinéticos usados en las cinéticas del estado sólido [98].

Modelo reacción	$f(\alpha)$ (forma diferencial)	$g(\alpha)$ (forma integral)
Power law Pn ($n = 2/3, 2, 3, 4$)	$n\alpha^{(n-1)/n}$	$\alpha^{1/n}$
1D Diffusion D1	$1/2\alpha^{-1}$	α^2
Mampel (First-Order) F1	$1 - \alpha$	$-\ln(1 - \alpha)$
Avrami-Erofeev An ($n = 2, 3, 4$)	$n(1 - \alpha)[- \ln(1 - \alpha)]^{(n-1)/n}$	$[- \ln(1 - \alpha)]^{1/n}$
3D Diffusion D3	$3/2(1 - \alpha)^{2/3} [1 - (1 - \alpha)^{1/3}]^{-1}$	$[1 - (1 - \alpha)^{1/3}]^2$
Contracting sphere R3	$3(1 - \alpha)^{2/3}$	$1 - (1 - \alpha)^{1/3}$
Contracting cylinder R2	$2(1 - \alpha)^{1/2}$	$1 - (1 - \alpha)^{1/2}$
2D Diffusion D2	$[- \ln(1 - \alpha)]^{-1}$	$(1 - \alpha) \ln(1 - \alpha) + \alpha$

El propósito del análisis cinético es parametrizar la velocidad del proceso en términos de variables tales como la temperatura y el grado de conversión. Se puede conseguir evaluando la tripleta cinética, A , E y $f(\alpha)$, lo que permite describir el proceso y utilizarlo para realizar predicciones. Entre sus aplicaciones cabe destacar el conocimiento de la estabilidad térmica de un material, la determinación de su vida útil o la cuantificación cinética del proceso fuera del rango de temperatura en la que se obtuvieron los datos experimentales.

La interpretación de los parámetros cinéticos debe realizarse cuidadosamente, sus valores se obtienen escogiendo una ecuación de la velocidad de reacción y ajustándola a los datos experimentales, podría suceder que el ajuste

fuese muy bueno desde el punto de vista estadístico pero la ecuación de la velocidad de reacción no tuviese sentido físico [101].

Los datos experimentales siempre presentan cierta incertidumbre. Dependiendo de la técnica utilizada, los datos pueden ser integrales, como los provenientes de TGA, o diferenciales como los obtenidos de DSC. A su vez, los métodos de análisis cinético pueden ser integrales o diferenciales. La diferenciación de datos numéricos tiende a magnificar el ruido. Los datos diferenciales proporcionan más información sobre la reacción que los integrales, pero su análisis cinético implica establecer una referencia, también llamada línea de base, apropiada. En el caso de condiciones no isotérmicas es un problema más difícil de resolver [102, 103].

Los programas de temperatura más utilizados son los isotérmicos y los de velocidad de calentamiento constante. Ambos tienen ventajas y desventajas. En realidad, los experimentos estrictamente isotérmicos no son posibles, siempre existe un tiempo de calentamiento no isotérmico. La mayor desventaja de los programas isotérmicos es debida a que tienen un rango de temperaturas limitado. Para las temperaturas más bajas puede ser difícil alcanzar una conversión completa en un tiempo razonable. Para las temperaturas más altas puede ocurrir que el tiempo de calentamiento sea comparable con el tiempo de reacción, se alcanzará parte de la conversión antes de llegar al régimen isotérmico. Esta situación puede darse, en particular, para los modelos decelerados de la figura 1.17, en los que la velocidad de reacción es más rápida para valores de α próximos a cero. En estas situaciones debe considerarse el grado de conversión alcanzado en la etapa no isotérmica. Este problema puede evitarse utilizando programas de velocidad de calentamiento constante, en cuyo caso, se recomienda comenzar el calentamiento a una temperatura lo suficientemente baja para garantizar que sea inferior a la de inicio del proceso [104]. Una desventaja que presentan estos programas respecto a los isotérmicos es que los cálculos asociados al análisis cinético son más complejos [98].

El estudio cinético de las reacciones de descomposición térmica puede realizarse utilizando métodos isoconversionales. Todos derivan del mismo principio: “La velocidad de reacción para un grado de conversión dado es solo

función de la temperatura”. Este principio permite omitir el modelo de reacción de los cálculos cinéticos. Derivando la ecuación 1.12

$$\left[\frac{\partial \ln(d\alpha/dt)}{\partial T^{-1}} \right]_{\alpha} = \left[\frac{\partial \ln(Ae^{-E/RT})}{\partial T^{-1}} \right]_{\alpha} + \left[\frac{\partial \ln(f(\alpha))}{\partial T^{-1}} \right]_{\alpha} \quad (1.17)$$

donde el subíndice α indica valores isoconversionales, es decir, los valores relacionados con el grado de conversión dado. Teniendo en cuenta, que para un α dado, $f(\alpha)$ es constante

$$\left[\frac{\partial \ln(d\alpha/dt)}{\partial T^{-1}} \right]_{\alpha} = -\frac{E_{\alpha}}{R} \quad (1.18)$$

De la ecuación anterior se deduce que el conocimiento de la dependencia de la velocidad de reacción con la temperatura puede utilizarse para calcular la energía de activación, E_{α} , sin necesidad de conocer el modelo de reacción (figura 1.18). Por esta razón, los métodos isoconversionales se llaman frecuentemente “model-free”. Sin embargo, aunque el método no necesita el modelo de reacción, asume que la velocidad de reacción es función del grado de conversión mediante alguna función $f(\alpha)$.

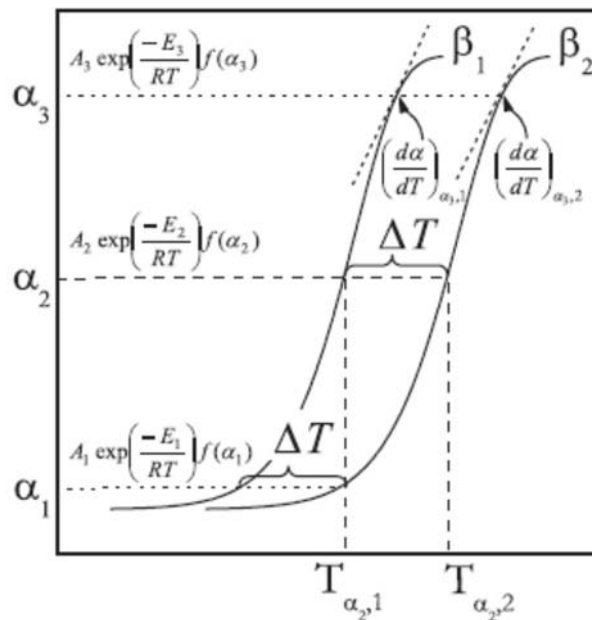


Figura 1.18. La velocidad de reacción para un grado de conversión determinado solo depende de la temperatura [105].

Para obtener experimentalmente la dependencia de la velocidad de reacción con la temperatura se mide, para el mismo grado de conversión, la temperatura a varias velocidades de calentamiento. Es recomendable determinar la energía de activación en el rango $0.05 \leq \alpha \leq 0.95$ en incrementos no más grandes de 0.05 y, posteriormente, representar la dependencia de la E_α frente a α . Una variación significativa de la energía de activación con el grado de conversión indica que el proceso es cinéticamente complejo. Algunos autores utilizan el término energía de activación aparente para indicar que es una combinación de energías de activación de reacciones simples [97, 98, 101].

El principio isoconversional es el fundamento de un gran número de métodos. El método diferencial más común es el de Friedman [FR] [106], basado en la siguiente ecuación

$$\ln\left(\frac{d\alpha}{dt}\right)_{\alpha,i} = \ln[f(\alpha)A_\alpha] - \frac{E_\alpha}{RT_{\alpha,i}} \quad (1.19)$$

que deriva de la aplicación del principio isoconversional a la ecuación fundamental de la cinética. Para un α dado, el valor de E_α se determina a partir de la pendiente de la recta obtenida al representar gráficamente $\ln(d\alpha/dt)_{\alpha,i}$ frente a $1/T_{\alpha,i}$. El índice i indica distintos programas de temperatura. $T_{\alpha,i}$ es la temperatura a la que se alcanza el grado de conversión con los distintos programas de calentamiento. Si el programa de temperatura es isotérmico, i corresponde a una temperatura única.

Para programas de temperatura lineales no isotérmicos se introduce la variable velocidad de calentamiento, $\beta = dT/dt$

$$\frac{d\alpha}{dt} = \beta \frac{d\alpha}{dT} \quad (1.20)$$

y denotando por β_i la velocidad del programa de calentamiento $T = T_0 + \beta_i t$, la ecuación 1.19 conduce a

$$\ln\left[\beta_i\left(\frac{d\alpha}{dt}\right)_{\alpha,i}\right] = \ln[f(\alpha)A_\alpha] - \frac{E_\alpha}{RT_{\alpha,i}} \quad (1.21)$$

E_α se determina a partir de la pendiente de la recta obtenida al representar gráficamente $\ln[\beta_i(d\alpha/dT)_{\alpha,i}]$ frente a $1/T_{\alpha,i}$. La principal ventaja de los

métodos diferenciales es que no utilizan ninguna aproximación por lo que son potencialmente más exactos que los integrales. Sin embargo, en la práctica, los métodos diferenciales llevan asociada cierta inexactitud e imprecisión. Por una parte, la aplicación de métodos diferenciales a datos integrales, como son los de análisis TGA, requiere utilizar diferenciaciones numéricas que introducen imprecisión [98]. Por otra parte, son muy sensibles al ruido experimental, introduciendo desviaciones en la E_α [107]. Estos métodos no permiten evaluar de forma directa el factor pre-exponencial ni el modelo de reacción. Actualmente cobra fuerza la idea de que muchos efectos cinéticos no solo están vinculados a un cambio de la energía de activación, pueden estar relacionados con variaciones del factor pre-exponencial o del modelo de reacción [108].

Con la idea de evitar los inconvenientes de los métodos diferenciales surgieron los isoconversionales integrales que expresan la ecuación de la velocidad de reacción en la forma

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \int_0^t A e^{-E/RT} dt \quad (1.22)$$

esta integral tiene solución analítica para programas de temperatura isotérmicos

$$g(\alpha) = A e^{-E/RT} t \rightarrow t = \frac{g(\alpha)}{A} e^{E/RT} \rightarrow \ln t_{\alpha,i} = \ln \left[\frac{g(\alpha)}{A_\alpha} \right] + \frac{E_\alpha}{RT_{\alpha,i}} \quad (1.23)$$

donde $t_{\alpha,i}$ es el tiempo para alcanzar un grado de conversión determinado con diferentes temperaturas T_i .

En los métodos no isotérmicos, en los que los programas utilizados habitualmente son de velocidad de calentamiento constante,

$$g(\alpha) = \frac{A}{\beta} \int_0^T e^{-E/RT} dT \quad (1.24)$$

donde se ha aproximado $T_0 = 0$ ya que, en general, la velocidad de reacción es muy lenta a temperaturas bajas [104, 109]. Esta integral de temperatura no tiene solución analítica por lo que se han propuesto soluciones aproximadas para su resolución. Muchas de estas aproximaciones conducen a ecuaciones lineales de expresión general [107, 109]

$$\ln \left(\frac{\beta_i}{T_{\alpha,i}^B} \right) = Cte - C \left(\frac{E_\alpha}{RT_{\alpha,i}} \right) \quad (1.25)$$

donde B y C son parámetros deducidos a partir de la aproximación utilizada [98]. El método Kissinger-Akahira-Sunose [KAS] [110] utiliza la aproximación de Coats-Redfern [111, 112] obteniendo la ecuación

$$\ln\left(\frac{\beta_i}{T_{\alpha,i}^2}\right) = Cte_{(KAS)} - \frac{E_\alpha}{RT_{\alpha,i}} \quad (1.26)$$

siendo

$$\ln\left(\frac{AR}{E_\alpha g(\alpha)}\right) = Cte_{(KAS)} \quad (1.27)$$

Representando en una gráfica $\ln \beta_i$ frente a $1/T_{\alpha,i}$ obtenemos puntos que se pueden ajustar a una recta mediante una regresión lineal, de cuya pendiente se obtiene E_α .

El método isoconversional integral no lineal desarrollado por Vyazovkin [Vyaz] [113-115], basado en integración numérica, consigue aumentar la precisión frente a los métodos lineales. Para un α dado, $g(\alpha)$ permanece constante para n velocidades de calentamiento

$$g(\alpha) = \frac{A_\alpha}{\beta_1} I(E_\alpha, T_{\alpha,1}) = \frac{A_\alpha}{\beta_2} I(E_\alpha, T_{\alpha,2}) = \dots = \frac{A_\alpha}{\beta_n} I(E_\alpha, T_{\alpha,n}) \quad (1.28)$$

siendo la integral de temperatura

$$I(E_\alpha, T_\alpha) = \int_0^{T_\alpha} e^{-E_\alpha/RT} dT \quad (1.29)$$

La E_α se obtiene minimizando la siguiente función [113]:

$$\Phi(E_\alpha) = \sum_{i=1}^n \sum_{j \neq i}^n \frac{I(E_\alpha, T_{\alpha,i}) \beta_j}{I(E_\alpha, T_{\alpha,j}) \beta_i} \quad (1.30)$$

Realizando este proceso para cada grado de conversión se obtiene la dependencia de E_α con α .

En la figura 1.19 se comparan los errores relativos en las energías de activación estimadas con el método lineal de KAS y el no lineal de Vyazovkin en función de $x = E/RT$. La energía de activación fue calculada a partir de un modelo teórico que simuló una reacción de primer orden. El método no lineal presenta un error extremadamente bajo en la obtención de la energía de activación y es prácticamente independiente del valor de E/RT [93, 113].

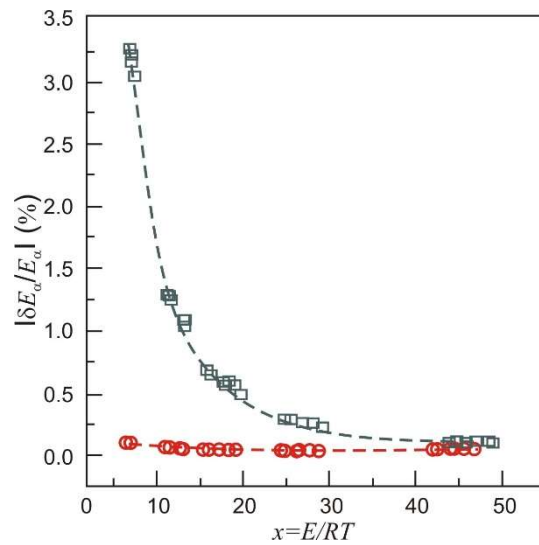


Figura 1.19. Error relativo en la E_α , como una función de $x = E/RT$. Circunferencias rojas corresponden al método no lineal (Vyaz), cuadrados grises al método lineal (KAS) [93].

Los métodos integrales considerados hasta aquí han sido propuestos para programas de temperatura determinados, bien sean isotérmicos o de velocidad de calentamiento constante. Pero, los métodos isoconversionales integrales no lineales pueden utilizarse con cualquier programa de temperatura, al igual que sucede con el método diferencial de Friedman. En el método de Vyazovkin, si los datos se obtienen de diferentes programas de temperatura $T_i(t)$, el valor de E_α se obtiene de minimizar la función [114]

$$\Phi(E_\alpha) = \sum_{i=1}^n \sum_{j \neq i}^n \frac{J[E_\alpha, T_i(t_\alpha)]}{J[E_\alpha, T_j(t_\alpha)]} \quad (1.31)$$

siendo

$$J[E_\alpha, T_i(t_\alpha)] = \int_0^{t_\alpha} e^{-E_\alpha/RT(t)} dt \quad (1.32)$$

$\Phi(E_\alpha)$ se minimiza para cada valor de α obteniéndose la dependencia de E_α con α . Realizando la integración con respecto al tiempo se amplía el rango de aplicación de los métodos isoconversionales integrales, ya que permite tener en cuenta procesos de enfriamiento [98, 116].

Además de las aproximaciones mencionadas anteriormente, los métodos isoconversionales integrales presentan otra importante limitación, ya que asumen que para un α dado la E_α es constante en el rango completo de conversión, de tal forma que los valores de la energía de activación solo son precisos cuando E_α no varía con α [93]. En las reacciones experimentales, la energía de activación varía frecuentemente con α [105]. Si esto sucede, la suposición de E_α constante introduce un error sistemático en su valor que puede alcanzar el 20-30 % cuando dicha variación es considerable [115]. Este error, que no aparece en el método diferencial de Friedman, puede eliminarse en los métodos integrales al realizar la integración en pequeños segmentos de temperatura o tiempo. De esta forma se puede resolver la integral de temperatura de la ecuación 1.29

$$I(E_\alpha, T_i) = \int_{T_{\alpha-\Delta\alpha}}^{T_\alpha} e^{-E_\alpha/RT} dT \quad (1.33)$$

o la integral de tiempo de la ecuación 1.32

$$J[E_\alpha, T(t_\alpha)] = \int_{t_{\alpha-\Delta\alpha}}^{t_\alpha} e^{-E_\alpha/RT} dt \quad (1.34)$$

en ambos casos la hipótesis de que E_α es constante se supone solo para pequeños intervalos de conversión $\Delta\alpha$ [103, 115, 117].

En la figura 1.20 se representa la energía de activación de una calcita natural en función del grado de conversión calculada, por los tres métodos anteriores: diferencial FR, integral lineal KAS e integral no lineal Vyaz.

La capacidad de los métodos isoconversionales para estimar la energía de activación sin conocer el modelo de reacción se considera una de sus ventajas. Sin embargo, se puede pensar que estos métodos no son capaces de evaluar el modelo de reacción ni el factor pre-exponencial, y no es así. Friedman [106] describe su método diferencial para obtener la energía de activación y, también propone una forma de determinar el factor pre-exponencial y el modelo de reacción.

Otro método utilizado para obtener la tripleta cinética [105] consiste en sustituir algún modelo de reacción (p.ej. de la tabla 1) en la ecuación

$$\ln\left(\frac{1}{f(\alpha)} \frac{d\alpha}{dt}\right) = \ln A - \frac{E}{RT}$$

y ajustar su dependencia de la temperatura a una línea recta. Del ajuste lineal se obtienen los valores del factor pre-exponencial y la

energía de activación. Se tendrán tantas tripletas cinéticas como modelos de reacción se utilicen. De este conjunto, se elige la tripleta cuyo valor de la energía de activación coincida con el valor obtenido por un método isoconversional. Este método puede resultar poco exacto: por un lado, los valores de la energía de activación que se están comparando pueden no coincidir con la suficiente precisión; por otro lado, varios modelos de reacción pueden conducir a similares valores de la energía de activación [105, 118]. Esto supone una cierta ambigüedad a la hora de determinar parámetros cinéticos fiables.

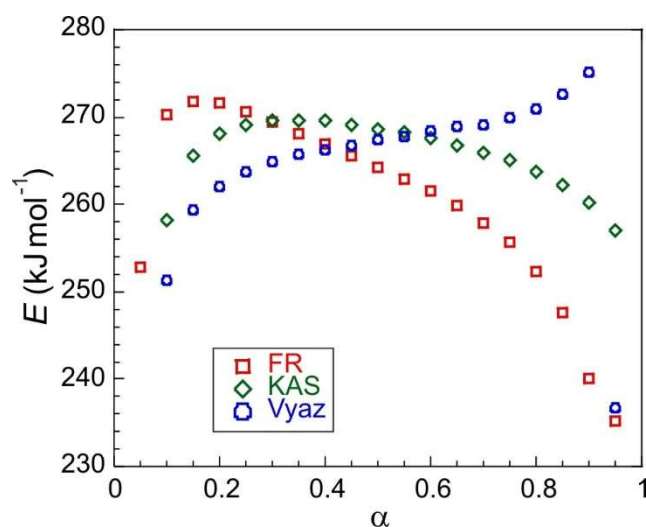


Figura 1.20. Energía de activación en función de la conversión de una calcita natural de pureza 99 % obtenida por los tres métodos isoconversionales FR, KAS y Vyaz.

Con la idea de superar estos inconvenientes, algunos autores [119, 120] utilizan el concepto de *pre-factor efectivo* definido como el producto del factor pre-exponencial por el modelo de reacción $c_\alpha = Af(\alpha)$. Al igual que la E_α el pre-factor tiene un valor determinado para una conversión dada. La determinación de la tripleta cinética proporciona una descripción matemática del proceso. Su conocimiento se utiliza, no solo para predecir la cinética del proceso a temperaturas distintas de las experimentales, sino también para reproducir los datos cinéticos originales y compararlos con las medidas experimentales [101, 116]. Esto último puede utilizarse para verificar los valores obtenidos de los parámetros cinéticos.

2. OBJETIVOS

2. Objetivos

El estudio de la cinética de reacciones de descomposición de fosfatos metálicos mediante estimulación térmica constituye el marco general en el que se desarrolla este trabajo.

1. De los múltiples métodos recogidos en la literatura que se pueden utilizar para determinar los parámetros cinéticos, a partir de datos termogravimétricos, los métodos isoconversionales son los más empleados en la actualidad.
 - El primer objetivo de esta memoria es analizar los métodos isoconversionales diferenciales e integrales de uso frecuente e implementarlos para determinar la cinética de la descomposición térmica de fosfatos metálicos.
 - Partiendo del estudio anterior, seleccionar los métodos más adecuados y proponer posibles mejoras de estos métodos. Evaluar los métodos nuevos, analizando su respuesta, con simulaciones teóricas y aplicaciones a casos experimentales. Además, analizar la fiabilidad de los parámetros cinéticos obtenidos en las reacciones de descomposición térmica de fosfatos metálicos.
2. Uno de los aspectos más importantes del estudio de la descomposición térmica de un compuesto es conocer la evolución de la reacción con el tiempo o la temperatura. Para ello se propone:
 - Obtener un modelo cinético que describa la reacción. Se pretende que el modelo sirva para chequear los parámetros cinéticos calculados y predecir las cinéticas de descomposición térmica de procesos de calentamiento diferentes a los utilizados en el laboratorio.
 - Comprobar la validez del modelo aplicándolo a simulaciones teóricas y a descomposiciones térmicas de fosfatos metálicos.
3. Con la finalidad de obtener nuevos fosfatos de metales de transición se consideró la posibilidad de sintetizar soluciones sólidas con más de un átomo magnético, se propone:
 - Sintetizar hidrotermalmente nuevos fosfatos de amonio-cromo-hierro, y caracterizarlos química y estructuralmente.

Objetivos

- Describir la cinética de la reacción de su descomposición térmica y, obtener y validar los parámetros cinéticos
- Caracterizar magnéticamente los nuevos fosfatos obtenidos y analizar cómo afecta al comportamiento magnético la introducción de cromo (III) en un fosfato de amonio-hierro (III).

3. RESULTADOS Y DISCUSIÓN

3. Resultados y discusión

3.1. Cinética de estado sólido

En este capítulo se presentan dos artículos (I y II) relativos a la obtención de los parámetros cinéticos. En el primero (I), se introduce una mejora al método de Friedman para la obtención de la energía de activación. En el segundo artículo (II), se muestra un procedimiento para obtener un modelo numérico que permite describir el progreso de la reacción.

ARTÍCULO I:

En cinéticas de estado sólido, la velocidad de reacción se expresa generalmente mediante la ecuación 1.12. Como se ha mencionado anteriormente, los métodos isoconversionales permiten evaluar la energía de activación en función del grado de conversión sin conocer el modelo de reacción [101]. De entre ellos, el método diferencial de Friedman [106] presenta ciertas ventajas frente a los integrales, pero también algunos inconvenientes. Entre sus ventajas cabe destacar que no precisa utilizar ninguna aproximación en la obtención de la energía de activación; además, puede ser empleado con datos obtenidos a partir de cualquier programa de calentamiento y su implementación es relativamente sencilla. Sin embargo, uno de los mayores inconvenientes que presenta es su alta sensibilidad al ruido experimental, que se acrecienta al diferenciar datos integrales, tal como se ha dicho previamente [98].

El propósito de este trabajo (artículo I), surge de la idea de disminuir la influencia del ruido en el método FR debido a que, en general, los datos que utilizamos para determinar los parámetros cinéticos de la descomposición térmica son integrales. Con la modificación propuesta se busca mantener las ventajas de este método y reducir su mayor inconveniente. En el artículo se propone una modificación al método de Friedman para reducir la incertidumbre en los valores de la energía de activación. Este procedimiento está basado en la idea de considerar, para un valor dado del grado de conversión α , no solo la información correspondiente a α , sino también los datos correspondientes a sus vecinos más próximos, asumiendo que la energía de activación E_α es constante en el intervalo considerado. Para este propósito, dado $\Delta\alpha > 0$, se consideran los valores

$\alpha_1 = \alpha - \Delta\alpha$, $\alpha_2 = \alpha$, $\alpha_3 = \alpha + \Delta\alpha$. Utilizando n programas de velocidad de calentamiento constante β_i y aplicando la ecuación 1.21 se obtiene, para cada $j = 1, 2, 3$, los siguientes puntos

$$\left(\frac{1}{T_{\alpha_{j,i}}}, \ln \left[\beta_i \left(\frac{d\alpha}{dT} \right)_{\alpha_{j,i}} \right] \right) \quad i=1, \dots, n \quad (3.1)$$

que describen una recta r_j , de pendiente $-\frac{E_\alpha}{R}$. Las tres rectas r_1, r_2 , y r_3 tienen la misma pendiente y, entonces, la energía de activación se obtiene mediante un ajuste lineal por mínimos cuadrados de los puntos de las tres rectas simultáneamente, minimizando la siguiente función

$$h(m, n_1, n_2, n_3) = \sum_{j=1}^3 \sum_{i=1}^n (y_{j,i} - mx_{j,i} - n_j)^2 \quad (3.2)$$

Los valores n_j corresponden a los valores de las ordenadas en el origen de cada recta que vienen dados por $n_j = \ln(Af(\alpha_j))$. El conocimiento del producto $Af(\alpha_j)$ junto con la E permitirá chequear los datos cinéticos obtenidos y predecir los que se obtendrían a temperaturas diferentes a las utilizadas. En el trabajo de Friedman [106] ya se consideró un procedimiento para determinar A y, en su caso, se obtuvo la tripleta cinética suponiendo que se cumpliría un modelo de reacción determinado. Sin embargo, la determinación del modelo de reacción cuando los datos experimentales se obtienen de reacciones de calentamiento no isotérmicas es complicada, ya que cualquier imprecisión en la selección de $f(\alpha)$ se compensa con otra imprecisión equivalente en la constante de temperatura y se pueden encontrar múltiples pares de funciones $k(T)$, $f(\alpha)$ que se ajusten estadísticamente bien a los datos experimentales [93, 98].

En la aplicación de nuestro modelo modificado de Friedman [MFR] se pueden encontrar más rectas r_j , añadiendo más valores, $\alpha - 2\Delta\alpha$, $\alpha + 2\Delta\alpha$, etc. En este trabajo hemos utilizado tres y cinco puntos, observando que el método con cinco puntos mejora sensiblemente los resultados respecto al de tres puntos. Se realizaron algunas pruebas utilizando siete puntos y no se advirtieron mejoras significativas con respecto al de cinco puntos.

La energía de activación obtenida utilizando el método MFR con tres [MFR3] y cinco [MFR5] puntos se compara con el método original FR en tres

casos: dos procesos teóricos, el primero representa una reacción simple y el segundo corresponde a dos reacciones paralelas de primer orden; y un proceso experimental, la descomposición de la sal $\gamma\text{-Ti}(\text{PO}_4)(\text{NH}_4\text{HPO}_4)$.

Para evaluar el efecto del ruido en el cálculo de E , en los dos modelos teóricos se simula el ruido modificando la temperatura. Se emplea la expresión $T = T_0 + \beta t + cN(t)$, donde $N(t)$ es un número pseudoaleatorio generado por una distribución normal de probabilidad $N(0,1)$ y c es una constante que toma diferentes valores según el nivel de ruido que se desea generar. Este proceso se realiza para cuatro velocidades de calentamiento, β_i .

Se generan pares de valores (α, T) que simulan una reacción simple utilizando $f(\alpha) = 1 - \alpha$, $E = 100 \text{ kJmol}^{-1}$ y $A = 10^9 \text{ min}^{-1}$ [121] y se añaden varios niveles de ruido diferentes perturbando los valores de la temperatura. Se aplican los métodos FR, MFR3 y MFR5 a estos valores, con $\Delta\alpha = 0.05$, para obtener la energía de activación y el producto $Af(\alpha)$. Con estos resultados, de E y $Af(\alpha)$, se reconstruyen las curvas $\alpha - T$ correspondientes a los tres métodos que, finalmente, se comparan con las obtenidas con los datos dados. Se observa que los valores de α calculados con el método MFR están más próximos a los originales que los encontrados con el método FR. También se obtienen los valores del factor de correlación R^2 , para todas las velocidades de calentamiento y para todos los niveles de ruido considerados, resultando siempre más próximos a la unidad los calculados con el método MFR.

De forma similar se procede en el segundo caso, utilizando un modelo teórico que simula dos reacciones paralelas de primer orden cuya velocidad de reacción se describe de la siguiente forma [122]:

$$\frac{d\alpha}{dt} = A_1 \exp\left(\frac{-E_1}{RT}\right)(1-\alpha) + A_2 \exp\left(\frac{-E_2}{RT}\right)(1-\alpha) \quad (3.3)$$

donde $E_1 = 167 \text{ kJmol}^{-1}$, $A_1 = 10^{12} \text{ min}^{-1}$, $E_2 = 351 \text{ kJmol}^{-1}$ y $A_2 = 10^{26} \text{ min}^{-1}$.

Se generan los pares de valores (α, T) y se simulan los diferentes niveles de ruido experimental modificando la temperatura de la misma forma que en el caso anterior. Se aplican los métodos FR y MFR para obtener la energía de activación aparente y el producto $Af(\alpha)$ que se utilizan para reconstruir las curvas $\alpha - T$ y

posteriormente compararlas con las originales, verificándose que en todos los casos los valores obtenidos por el método MFR están más cercanos a los originales que los obtenidos por el método FR.

Para evaluar el método MFR en un caso experimental se considera la descomposición térmica de la sal $\gamma\text{-Ti}(\text{PO}_4)(\text{NH}_4\text{HPO}_4)$ cuya síntesis y caracterización había sido realizada anteriormente por nuestro grupo de trabajo [123]. Para el análisis cinético de la descomposición térmica se calienta el sólido utilizando cuatro velocidades de calentamiento 6, 10, 15 y 20 Kmin^{-1} . La dependencia de E con α se obtuvo por los métodos FR, MFR3, MFR5 y KAS. Se observó que la descomposición térmica de este compuesto es un proceso complejo en el que se distinguen tres zonas de energía de activación diferentes. Se compararon los valores experimentales de α con los calculados de forma similar a los modelos teóricos para las cuatro velocidades de calentamiento. En todos los casos los resultados obtenidos por el método MFR están más próximos a los valores experimentales que los obtenidos por el método FR.

De la aplicación del método MFR a los tres modelos anteriores y la comparación con el FR se deduce que el método propuesto proporciona valores más uniformes de los parámetros cinéticos. Esta no es la única ventaja, el método MFR, al igual que el FR, no presenta la inconsistencia de los métodos integrales que consideran que E es constante con α aunque la reacción no sea simple [93]. Además, frente a los métodos integrales no lineales, que no presentan la inconsistencia anterior [103, 115, 117] pero su programación numérica es mucho más compleja, tiene la ventaja de la sencillez de su aplicación ya que se utiliza un ajuste lineal cuadrático casi tan sencillo como en el método FR.

Artículo I

Reducing the effects of noise in the calculation of activation
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Reducing the effects of noise in the calculation of activation energy by the Friedman method

Jose A. Huidobro^{a,*}, Isabel Iglesias^b, Belen F. Alfonso^b, Aranzazu Espina^c, Camino Trobajo^d, Jose R. Garcia^d^a Departamento de Matemáticas, Escuela Politécnica de Ingeniería, Universidad de Oviedo, 33204-Gijón, Spain^b Departamento de Física, Escuela Politécnica de Ingeniería, Universidad de Oviedo, 33204-Gijón, Spain^c Servicios Científico-Técnicos, Universidad de Oviedo-CINN, 33006 Oviedo, Spain^d Departamento de Química Orgánica e Inorgánica, Facultad de Química, Universidad de Oviedo-CINN, 33006 Oviedo, Spain

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ABSTRACT

The Friedman method for analysis of kinetic parameters of solid-state reactions has been widely used. One of the drawbacks of this method is its sensitivity to noise which can be caused by both experimental error and the intrinsic inaccuracy of the differential methods, particularly for non-isothermal kinetic data obtained by means of thermogravimetric analysis (TGA). This paper proposes a modified version of the Friedman method in order to decrease the effect of noise and consequently obtain more accurate activation energy values. The new method is based on the idea of considering, for a given value of the extent of conversion α , not only information corresponding to α but also data in its neighbourhood. To check the procedure, it is applied to simulated data and the activation energy obtained is compared with the preset value and that given by the Friedman method. Moreover, the proposed method is used to determine the activation energy on the thermal degradation of γ -Ti(PO₄)(NH₄HPO₄) compound as a function of the extent of conversion.

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1. Introduction

Thermal analysis techniques have been used since the 20th century to study solid-state reactions and they have been revealed as a useful tool in obtaining the kinetic parameters of reactions involving weight or enthalpy change by using a small amount of sample. Weight loss data are converted to a normalized form called extent of conversion α , which ranges from 0 to 1 and it is a measure of the reaction progress as a function of time or temperature.

For non-isothermal thermogravimetric analysis, the extent of conversion at any temperature is

$$\alpha = \frac{m_0 - m_T}{m_0 - m_\infty} \quad (1)$$

where m_T represents the sample mass at temperature T , and m_0 and m_∞ are the sample mass at the beginning and at the end of the process, respectively.

The theory concerning kinetic analysis is based on the differential equation [1]

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (2)$$

where $k(T)$ is the temperature-dependent rate and $f(\alpha)$ is the reaction model function, which is related to the mechanism of the process.

The temperature dependence of the reaction rate solid-state function is usually given by the Arrhenius equation [2]

$$k(T) = A \exp\left(\frac{-E}{RT}\right) \quad (3)$$

where A is the pre-exponential factor (frequency), E is the activation energy and R is the gas constant. Then, Eq. (2) turns into

$$\frac{d\alpha(t)}{dt} = A \exp\left(\frac{-E}{RT}\right) f(\alpha(t)) \quad (4)$$

The experimental data for studying the kinetic behavior of thermally stimulated solid reactions obtained at several constant temperatures are considered in isothermal methods, and those involving heating samples at one or more heating rates are included in non-isothermal

* Corresponding author.

E-mail address: jahuidobro@uniovi.es (J.A. Huidobro).

(dynamic) methods. Usually, non-isothermal methods employ a constant heating rate β , in which the temperature changes linearly with the time:

$$T = T_0 + \beta t \tag{5}$$

Replacing temporal derivative with a temperature derivative, Eq. (4) turns into

$$\frac{d\alpha(T)}{dT} = \frac{A}{\beta} \exp\left(\frac{-E}{RT}\right) f(\alpha(T)) \tag{6}$$

The determination of A , E and $f(\alpha)$, the so-called kinetic triplet, is an interlinked problem. An important number of mathematical methods have been developed to evaluate solid-state kinetics and to get the kinetic parameters from thermal experiment data. They generally fall into two categories: model-fitting and isoconversional methods. Model-fitting methods consider a particular reaction model function which is assumed to represent the conversion dependence on the reaction rate. This assumption is not necessary in isoconversional methods and, for this reason, they are also named model-free methods.

Isoconversional methods require several kinetic curves at different temperature programs to perform the analysis and they have therefore been called multi-curve methods [3]. For a fixed value of extent of conversion α , thus the name isoconversional, calculation from several curves at different heating rates are performed obtaining a plot of the activation energy versus the extent of conversion.

Isoconversional methods can be divided into integral and differential methods [4,5]. The first ones may lead to significant mistakes in the activation energy values due to the fact that some approximations are necessary for estimation of the temperature integral [6]. The most popular isoconversional integral methods are the Ozawa-Flynn-Wall (OFW) [7,8], Kissinger-Akahira-Sunose (KAS) [9–11] and Ortega [12] methods, which are based on approximations of the temperature integral and they are limited to the use of a linear variation of the temperature. Over the years, advances in computational software have made it easier for different kind of methods to avoid the temperature integral approximation, although a more computational effort is required. For instance, the non-linear method proposed by Vyazovkin [13,14] or the iterative procedure introduced by Cai [15].

One of the main sources of inaccuracy in the differential methods is its sensitivity to noise [4,12]. It is due to the fact that the value of the activation energy is obtained from Eq. (6), where only data corresponding to a fixed value of the extent of conversion α for the different heating rate programs are involved. Consequently, imprecision in the determination of temperatures or process rates may introduce significant differences between the right and the calculated values, in particular when a small number of runs is considered. This imprecision may be caused both by experimental noise or/and by intrinsic inaccuracy of the differential methods. On the one hand, significant inaccuracy can be introduced when differential experimental data, such as DTA and DSC, are considered because of the difficulty in determining the baseline. On the other hand, when integral experimental data are considered, such as TGA, numerical differentiation is necessary to obtain the extent of conversion rate.

Friedman proposed a method [16] that is included in the family of differential isoconversional methods. It has been widely used and is one of the simplest procedures to obtain the activation energy. Taking logarithms in Eq. (4), we get

$$\ln\left(\frac{d\alpha(t)}{dt}\right) = \ln(A f(\alpha(t))) - \frac{E}{RT} \tag{7}$$

Considering several runs for different constant heating rates β_i and for a given value of α , Eq. (7) leads to

$$\ln\left(\frac{d\alpha(T)}{dT} \beta_i\right) = \ln(A f(\alpha(T))) - \frac{E}{RT} \tag{8}$$

and thus, since $\ln(A f(\alpha(T)))$ is independent of β_i , the points

$$\left(\frac{1}{T_{\alpha,i}}, \ln\left(\frac{d\alpha(T)}{dT} \beta_i\right)\right) \tag{9}$$

are in the same straight line. Hence, by fitting the experimental data, the activation energy E can be obtained. Although constant heating rates have been considered, this relation also holds for any temperature heating program changing β by the temperature derivative.

The aim of the present research is to propose an improvement on the isoconversional differential Friedman (FR) method. More specifically, we introduce a procedure to reduce the uncertainty in the values of the activation energy by the FR method. This procedure is applied to two simulated models and the results by both the FR and the modified Friedman (MFR) methods are compared. In addition, the kinetic study of a practical case is performed.

2. Methods

The influence of noise in the Friedman method could be reduced if information corresponding to a value of α is the only data considered. For this purpose, given a fixed value of α , set $\alpha_j = \alpha, \alpha_{j-1} = \alpha - \Delta\alpha, \alpha_{j+1} = \alpha + \Delta\alpha$. For each $k = j - 1, j, j + 1$ and for n constant heating programs of temperature β_k , Eq. (8) leads to

$$\ln\left(\frac{d\alpha(T_{k,i})}{dT} \beta_i\right) = \ln(A f(\alpha_k)) - \frac{E}{RT_{k,i}} \tag{10}$$

Assuming the activation energy E is constant or, if it were not the case, variations of E over the interval $[\alpha_{j-1}, \alpha_{j+1}]$ can be neglected, this means the points

$$\left(\frac{1}{T_{k,i}}, \ln\left(\frac{d\alpha(T_{k,i})}{dT} \beta_i\right)\right) \tag{11}$$

belong to three different straight lines r_k but note they are parallel and their slopes are exactly the same, $-E/R$. Thus, we can try to find this slope by fitting the data for all these points simultaneously. So we are looking for four numbers m, n_1, n_2, n_3 minimizing the function

$$h(m, n_1, n_2, n_3) = \sum_{k=j-1}^{j+1} \sum_{i=1}^n (y_{k,i} - mx_{k,i} - n_k)^2 \tag{12}$$

where $y_{k,i} = \ln\left(\frac{d\alpha(T_{k,i})}{dT} \beta_i\right)$, $x_{k,i} = \frac{1}{T_{k,i}}$ and $n_k = \ln(A f(\alpha_k))$.

This algorithm, as all computations in this study, has been implemented in MatLab and the built-in function `fminsearch` has been used to find the minimum. Naturally, in the hopes of getting better results, more points can be considered, for instance, $\alpha_{j-2}, \alpha_{j-1}, \alpha_j, \alpha_{j+1}, \alpha_{j+2}$. The implementation in this case is similar to the previous one.

3. Results and discussion

To validate the modification of the FR method that has been proposed for calculation of activation energy, it was applied to both simulated and experimental data.

3.1. Simulation data

Firstly, a theoretical model corresponding to a single-step reaction given by $f(\alpha) = 1 - \alpha$, $E = 100 \text{ kJmol}^{-1}$ and $A = 10^9 \text{ min}^{-1}$ was

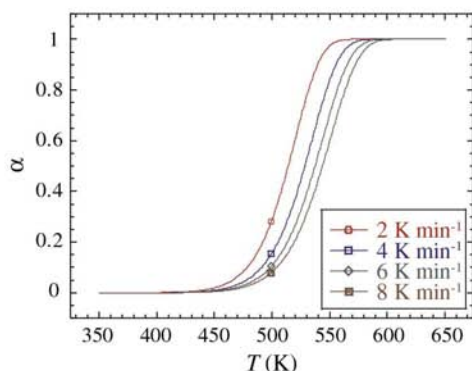


Fig. 1. Simulated α -temperature plots corresponding to a single-step reaction with $f(\alpha) = 1 - \alpha$, $E = 100 \text{ kJmol}^{-1}$ and $A = 10^9 \text{ min}^{-1}$ for heating rates 2, 4, 6 and 8 Kmin^{-1} .

considered [17]. The modified method of Friedman for both three (MFR3) and five points (MFR5) was applied to obtain the activation energy and the results were compared to the ones obtained from the original FR method. Fig. 1 shows the extent of conversion as a function of temperature corresponding to 2, 4, 6, 8 Kmin^{-1} heating rates. To evaluate the effect of noise in the computation of the activation energy, the temperature was modified by the formula

$$T = T_0 + \beta t + cN(t) \quad (13)$$

where $N(t)$ is a pseudorandom number generated by a normal distribution of probability $N(0,1)$, and c is a constant characterising the level of noise.

Fig. 2 shows the preset value of the activation energy and the values computed by the FR, MFR3 and MFR5 methods, with $\Delta\alpha = 0.01$ and $c = 0$ (no noise) (a), and $c = 0.40$ (b). Similar analyses were carried out for $c = 0.05$, $c = 0.15$ and $c = 0.80$. In Fig. 2(a) two zones can be

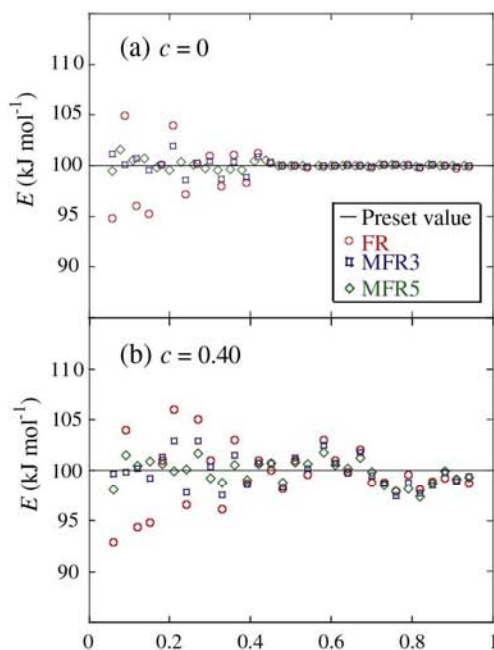


Fig. 2. Dependencies of E on α calculated by (red circles) FR, (blue squares) MFR3 and (green diamonds) MFR5 methods corresponding to $c = 0$ (a) and $c = 0.40$ (b).

distinguished: $0.05 \leq \alpha < 0.45$ and $0.45 \leq \alpha < 0.95$. In the second zone, both methods provide good values for E , whereas in the first zone, the deviations between the obtained and the preset values are greater. This is probably due to the fact that numerical differentiation is necessary to get the rate of α . Whereas in the second zone, the slope of α versus T has slight changes; in the other zone, the changes are more significant and therefore greater inaccuracy is introduced when the differentiation of α is computed. The activation energy deviations of the preset value increase as the noise grows (see Fig. 2(b)). The relative error of E , with and without noise, is shown in Fig. 3. As can be observed, when the level of noise rises, more inaccuracy appears and in all cases the MFR method provides better results than the FR method.

After computing the activation energy and the product $Af(\alpha)$, the differential Eq. (4) can be solved [18]. Then, the extent of conversion can be obtained using the solver ode45 in MatLab and compared with the original ones. In Fig. 4 the results for $\beta = 4 \text{ Kmin}^{-1}$ are pictured, finding that the values for the MFR method are nearer the diagonal than those obtained by the FR method. For all heating rates, $\beta = 2, 4, 6, 8 \text{ Kmin}^{-1}$ and the levels of noise $c = 0, 0.05, 0.10, 0.15, 0.40, 0.80$, Table 1 summarises the values of the correlation factor R^2 obtained from the FR, MFR3 and MFR5 methods.

Following the framework above, a second theoretical model, with and without noise, was also studied. This model was analysed by Ortega [12] and simulates two parallel first-order reactions where the rate of the process is given by

$$\frac{d\alpha}{dT} = A_1 \exp\left(\frac{-E_1}{RT}\right)(1-\alpha) + A_2 \exp\left(\frac{-E_2}{RT}\right)(1-\alpha) \quad (14)$$

where $E_1 = 167 \text{ kJmin}^{-1}$, $A_1 = 10^{12} \text{ min}^{-1}$, $E_2 = 351 \text{ kJmin}^{-1}$, $A_2 = 10^{26} \text{ min}^{-1}$.

The results obtained using the FR method for the case without noise are similar to those shown in reference [12] where it is observed that the apparent activation energy E_a changes almost linearly with α . When noise is introduced, small jumps appear which are stronger as the noise level increases. As can be seen in Fig. 5 for $c = 0.40$ and $c = 0.80$, the jumps are slightly smoother when the MFR methods are applied.

Solving the differential Eq. (14), the obtained values of α by the MFR methods are slightly nearer to the original data than those given by the FR method (Fig. 6).

3.2. Experimental example

In order to assess the MFR method, a practical case was considered, the layered monoammonium salt of γ -titanium phosphate ($\gamma\text{-Ti}(\text{PO}_4)(\text{NH}_4\text{HPO}_4)$), whose synthesis, characterization and thermal decomposition have been previously reported by our group [19]. As can be read in the above reference, combining thermogravimetric techniques, mass spectrometric analysis and powder X-ray thermogravimetric analysis it was deduced that thermal decomposition of the compound occurs in three stages; in the interval 300–570 K, the compound is stable; then, the first evacuation process appears in the range of 570–690 K with the loss of ca. half of NH_3 and H_2O ; later, in the interval 720–820 K, the evacuation of the rest of the NH_3 takes place, and finally, the remaining H_2O leaves the compound at very high temperature (ca. 1.030–1.070 K). The activation energy of thermal decomposition was calculated as a function of the extent of conversion applying the Kissinger–Akahira–Sunose (KAS) isoconversional method to the thermogravimetric data.

A Mettler–Toledo TGA/SDTA851^e was used for the thermal analyses in nitrogen dynamic atmosphere (50 mL min^{-1}) at four different heating rates, 6, 10, 15 and 20 Kmin^{-1} . Fig. 7(a) shows the experimental conversion curves as a function of temperature for the thermal decomposition of $\gamma\text{-Ti}(\text{PO}_4)(\text{NH}_4\text{HPO}_4)$. The heating rate does not affect the total mass loss, although it has an effect on the shape of the conversion

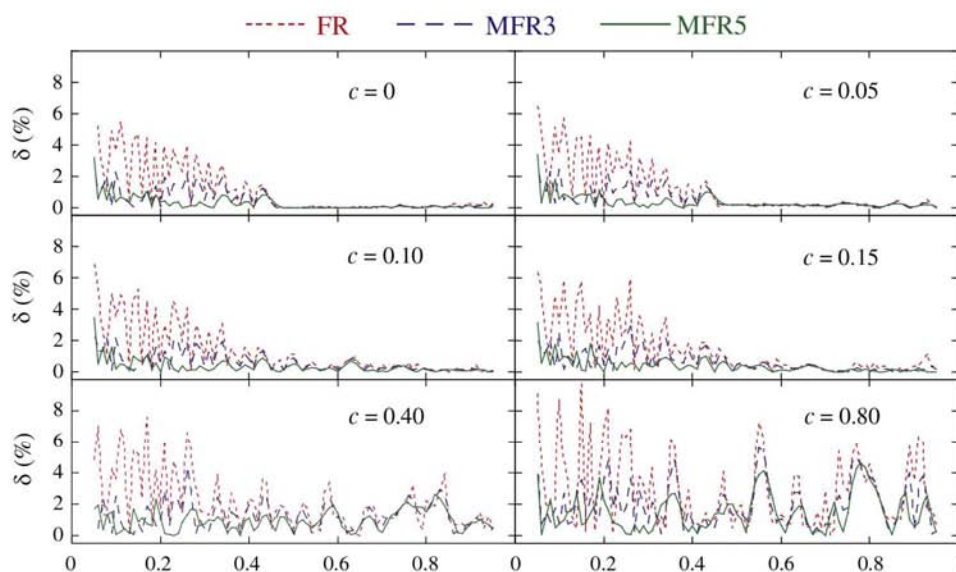


Fig. 3. The relative error δ of E values obtained by FR, MFR3, MFR5 methods, without noise ($c=0$) and with noise ($c=0.05, 0.10, 0.15, 0.40$ and 0.80).

curves, which move to higher temperatures when the heating rate increases and consequently slightly modifies the temperature ranges in which the evacuation of gases occurs. The dependence of E_a on α obtained by FR, MFR3, MFR5 and KAS methods is shown in Fig. 7(b); as can be observed, thermal decomposition of this compound is a complex process. The activation energy increases slightly (from ca. 140 to 175 kJ mol^{-1}) until the conversion is ca. 0.45. Later, it diminishes from ca. 175 to 135 kJ mol^{-1} (0.6 of conversion). However, when α increases slightly to ca. 0.8, an abrupt increase takes place. The values of E_a obtained by the

four methods have many similarities in the zones where activation energy is quite uniform, whereas most significant differences arise in the presence of peaks which correspond to the three stages of decomposition.

In Fig. 8 the experimental values of α and those calculated by FR, MFR3, MFR5 and KAS methods for the four heating rates are compared. The highest differences are linked with the values of α corresponding to the peaks of E_a . In all cases, the results provided by the MFR method are nearer to the experimental values than those obtained by the FR method.

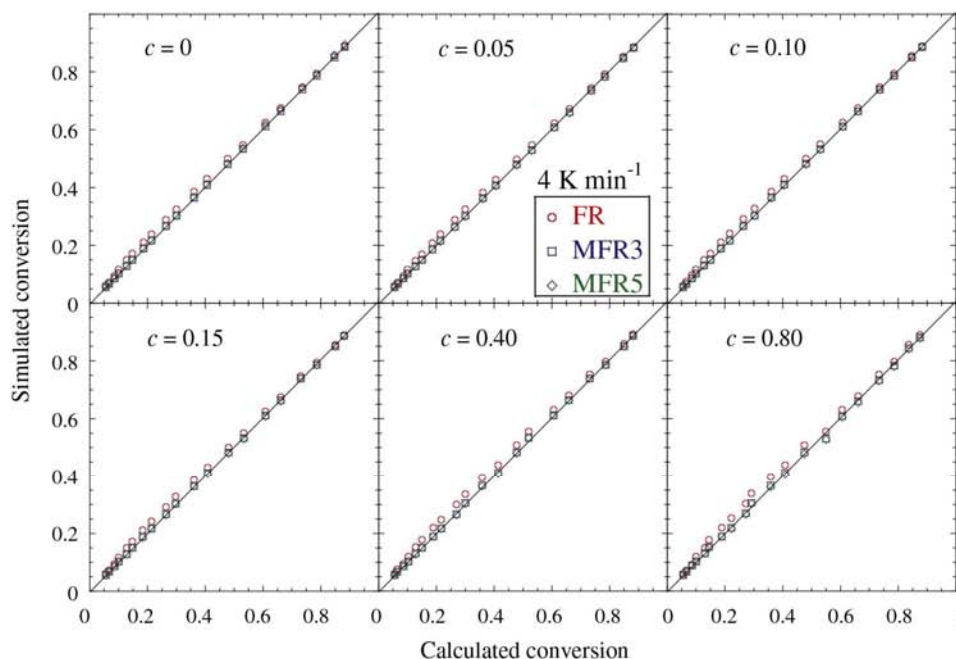


Fig. 4. Comparison between the calculated (FR, MFR3 and MFR5 methods) and the simulated α values at 4 K min^{-1} corresponding to $c=0, 0.05, 0.10, 0.15, 0.40, 0.80$.

Table 1
Correlation factor in the fitting of the conversion obtained for FR, MFR3, MFR5 and for different levels of noise.

Method	$c = 0$	$c = 0.05$	$c = 0.10$	$c = 0.15$	$c = 0.40$	$c = 0.80$	
2/Kmin ⁻¹	FR	0.99927	0.99924	0.99925	0.99913	0.99823	0.99781
	MFR3	0.99999	0.99998	0.99995	0.99997	0.99975	0.99934
	MFR5	1.00000	1.00000	0.99999	0.99997	0.99977	0.99937
4/Kmin ⁻¹	FR	0.99926	0.99933	0.99923	0.99917	0.99840	0.99809
	MFR3	0.99999	0.99999	0.99998	0.99996	0.99976	0.99950
	MFR5	1.00000	1.00000	0.99999	0.99996	0.99977	0.99953
6/Kmin ⁻¹	FR	0.99921	0.99919	0.99921	0.99910	0.99876	0.99800
	MFR3	0.99999	0.99998	0.99997	0.99995	0.99987	0.99942
	MFR5	1.00000	0.99999	0.99999	0.99997	0.99985	0.99943
8/Kmin ⁻¹	FR	0.99923	0.99923	0.99921	0.99912	0.99839	0.99750
	MFR3	0.99999	0.99999	0.99998	0.99996	0.99985	0.99918
	MFR5	1.00000	1.00000	0.99998	0.99997	0.99986	0.99923

4. Conclusions

The Friedman method is a simple and very used procedure to obtain values of the activation energy but, as is well known, it is very sensitive to noise. In this study, a modification of the Friedman method is developed which is based on the idea of considering not only data for a specific value of α but also information in its neighborhood.

To assess the new method, it was applied to both simulated and experimental data. In this research, one can observe that for a theoretical model where the results can be checked, the modified method provides more accurate values of the activation energy than those given by the Friedman method and so the influence of noise is reduced. More consistent activation energy values are obtained when the level of noise increases. Consequently, the same effect can be expected for experimental data. As can be observed in this study, the values obtained by the proposed method are more uniform than those given by the Friedman method, particularly when jumps or peaks appear in the graph of the

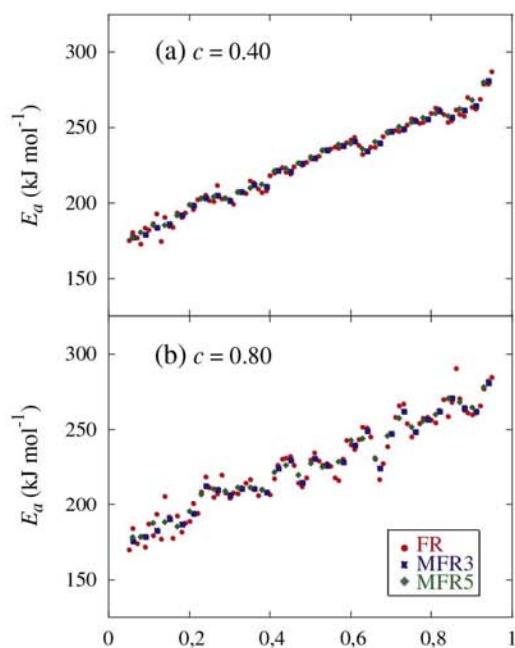


Fig. 5. Dependencies of E_a on α calculated by (solid red circles) FR, (solid blue squares) MFR3 and (solid green diamond) MFR5 methods corresponding to $c = 0.40$ (a) and $c = 0.80$ (b) for the model with two parallel first-order reactions.

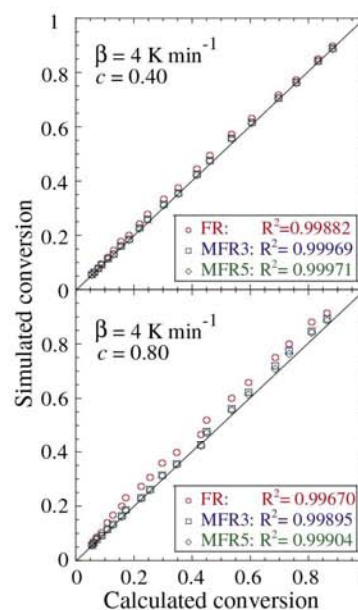


Fig. 6. Comparison between the calculated (FR, MFR3 and MFR5 methods) and the simulated α values for the level of noise $c = 0.40$ and $c = 0.80$, and the correlation factor R^2 .

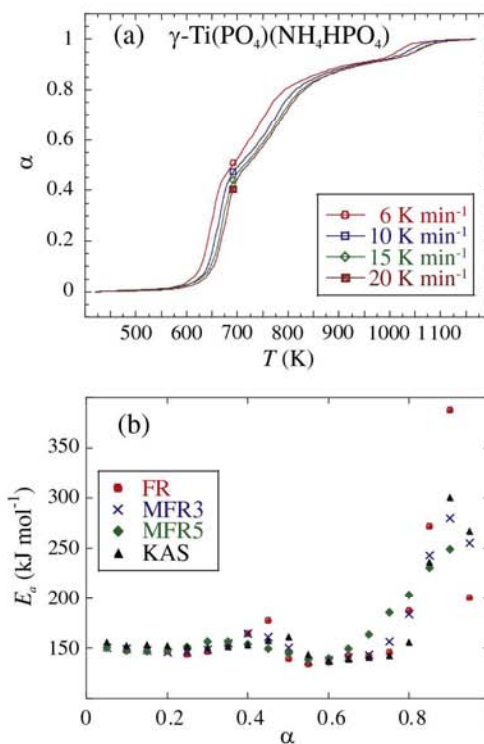


Fig. 7. Dependencies of α on T (a) and E_a calculated by (solid red circles) FR, (blue \times) MFR3, (solid green diamonds) MFR5 and (solid black triangle) KAS methods on α (b) for γ -Ti(PO₄)(NH₄HPO₄).

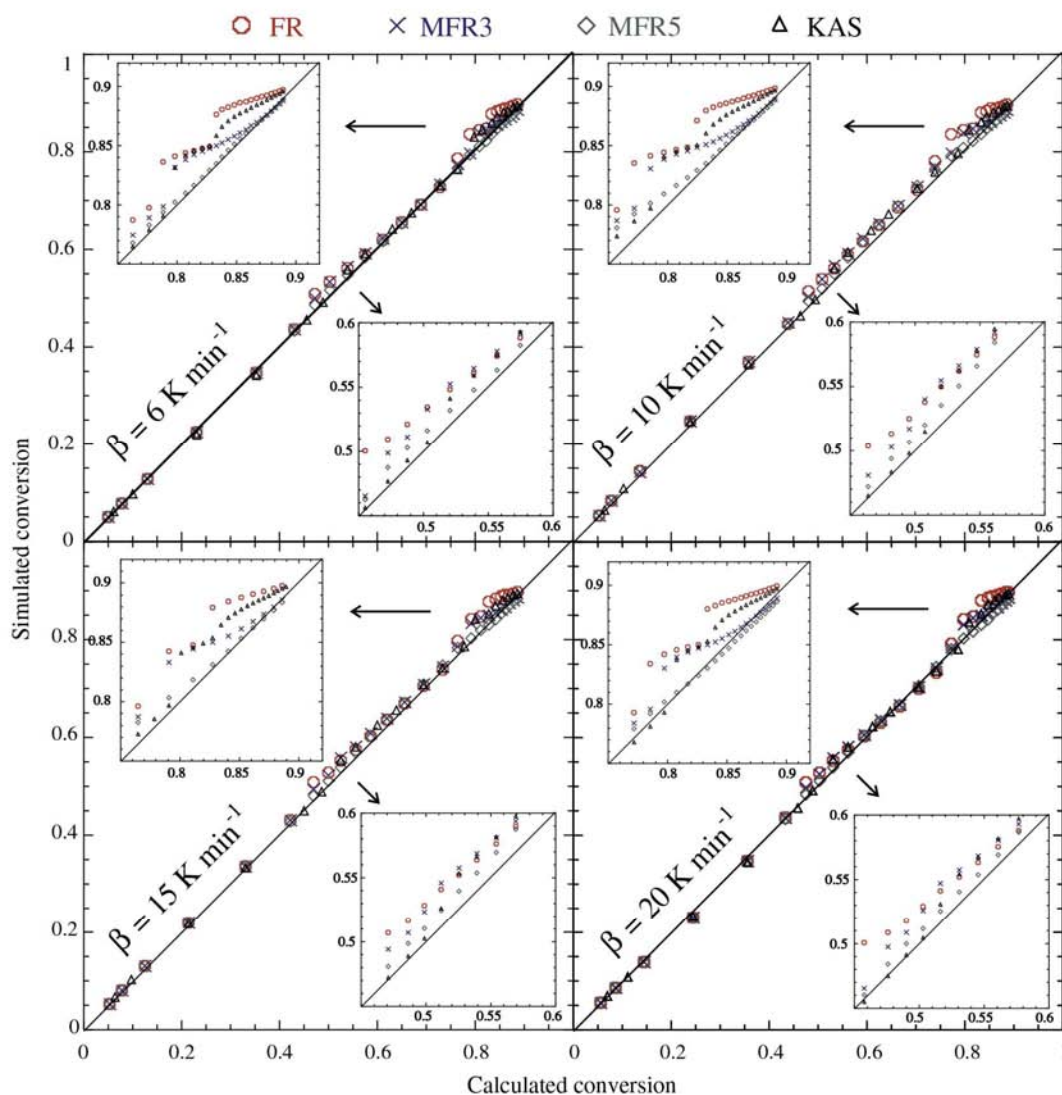


Fig. 8. Comparison between the calculated (red circles) FR, (blue squares) MFR3, (green diamonds) MFR5 and (black triangles) KAS methods, and the experimental values at 6, 10, 15 and 20 Kmin^{-1} .

dependence of the activation energy with respect to the extent of conversion.

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ARTÍCULO II

El propósito del análisis cinético es describir la velocidad del proceso en términos de variables tales como la temperatura y el grado de conversión. Sin embargo, es conocida la ambigüedad en la determinación de la tripleta cinética cuando se utilizan procesos no isotérmicos y, aunque la utilización de métodos isoconversionales permite obtener la energía de activación en función del grado de conversión, sin necesidad de determinar el modelo de reacción ni el factor pre-exponencial, el conocimiento únicamente de E puede no resultar suficiente para interpretar físicamente la reacción [124]. Por ello, parece necesario encontrar algún procedimiento fiable que permita determinar los parámetros cinéticos y utilizar algún método para comprobar la validez de los valores obtenidos.

En este trabajo (artículo II) se presenta un procedimiento para obtener un modelo discreto que describe la velocidad de reacción del proceso en función de la temperatura y del grado de conversión.

La obtención de este modelo se basa en la idea de algunos autores [119, 120, 125] que han considerado el producto $Af(\alpha)$ como un factor único, al que denominan *pre-factor efectivo*, c_α . Sin embargo, en todos los trabajos anteriores, el cálculo de $c_\alpha = Af(\alpha)$ dependía de cómo se había obtenido la energía de activación. En la figura 3.1 se muestra un esquema del proceso del análisis cinético completo en la descomposición térmica de un compuesto.

En este estudio se propone un método nuevo para determinar c_α directamente de la ecuación 1.12 e independiente del procedimiento utilizado para evaluar la energía de activación. Asumiendo que E_α ya ha sido calculada, c_α debe verificar

$$\beta_i \frac{d\alpha(T_{\alpha,i})}{dT} = c_\alpha \exp\left(-\frac{E_{\alpha,i}}{RT_{\alpha,i}}\right) \quad i = 1, \dots, n \quad (3.4)$$

Así, c_α se puede obtener a partir de un ajuste lineal cuadrático. Este método no introduce ninguna transformación matemática ni utiliza aproximaciones que puedan ser inconsistentes. A diferencia de lo que sucede, por ejemplo, en el modelo propuesto por Samuelsson y colaboradores [119] que obtuvieron E_α utilizando el método Vyazovkin, la integral de tiempo se ha

definido $J[E_\alpha, T(t_\alpha)] = \int_{t_{\alpha-\Delta\alpha}}^{t_\alpha} \exp(-E/RT) dt$ y asumieron que c_α era constante en el intervalo de integración, de manera que se cumple

$$\Delta\alpha = c_\alpha J_i(E_\alpha) \quad (3.5)$$

y obtuvieron c_α

$$c_\alpha = \frac{\Delta\alpha}{\langle J_i(E_\alpha) \rangle} \quad (3.6)$$

donde $\langle J_i(E_\alpha) \rangle$ es la media de $J_i(E_\alpha)$. La consideración de que c_α es constante en el intervalo $[\alpha - \Delta\alpha, \alpha]$ no es irrelevante, ya que si no es constante, debería incluirse en la integral de la ecuación 3.5. Esta situación no es improbable, debido a que el factor pre-exponencial suele tener valores altos [116, 120] y aunque se multiplique por el modelo de reacción que probablemente será pequeño en el intervalo considerado, las variaciones del producto $Af(\alpha)$ podrán ser notables en dicho intervalo. En el modelo propuesto en este trabajo no es necesario asumir que c_α sea constante en el intervalo $[\alpha - \Delta\alpha, \alpha]$.

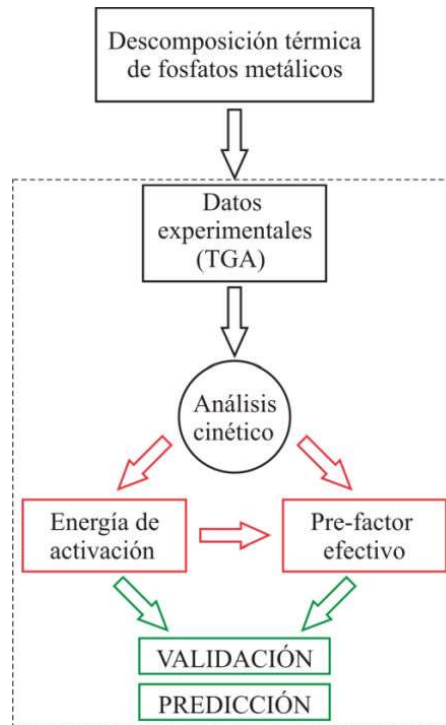


Figura 3.1. Esquema del análisis cinético de la descomposición térmica de un compuesto.

También, se podría pensar en obtener información sobre el factor pre-exponencial o el modelo de reacción a partir de métodos isoconversionales integrales, como el KAS, pero, aunque estos métodos permiten calcular $A/g(\alpha)$ de la ecuación 1.27, el resultado no parece facilitar la descripción de la velocidad de reacción.

Debido a que en la resolución de la ecuación 3.4 es necesario utilizar diferenciaciones numéricas, siendo esta una posible causa de imprecisión, se propone sustituir el cociente incremental simple que converge a la derivada con orden h por el siguiente [126]

$$f'(x) \approx \frac{-f(x+2h) + f(x-2h)}{12h} + \frac{2f(x+h) - 2f(x-h)}{3h} \quad (3.7)$$

que converge a la derivada con orden h^4 , con lo que se disminuye la imprecisión.

Para evaluar el procedimiento propuesto se aplica a los dos modelos simulados teóricamente descritos anteriormente, utilizando cuatro velocidades de calentamiento diferentes y constantes. La dependencia de E con α se calcula empleando los métodos isoconversionales: FR, MFR, KAS y Vyaz.

Los valores que se obtienen de la energía de activación en el proceso teórico que simula una reacción simple ($f(\alpha) = 1 - \alpha$, $E = 100 \text{ kJmol}^{-1}$ y $A = 10^9 \text{ min}^{-1}$) son muy similares para los cuatro métodos utilizados y, además, muy cercanos al valor teórico. Con estos valores de E se determinan los valores de c_α empleando la ecuación 3.4, verificándose que también son próximos a los teóricos. Utilizando ambos, E_α y c_α , se resuelve la ecuación

$$\beta \frac{d\alpha}{dT} = A e^{-E/RT} f(\alpha) \text{ para las cuatro velocidades de calentamiento distintas. Las}$$

gráficas $\alpha - T$ que se obtienen se comparan con las generadas directamente a partir del modelo teórico. Se observa una alta coincidencia entre las dos curvas para los cuatro métodos isoconversionales utilizados. Esta coincidencia también se manifiesta en los valores obtenidos para el coeficiente de determinación R^2 . Esto indica que el modelo propuesto reproduce bien los datos originales. Asimismo, para evaluar el comportamiento del modelo es interesante conocer su respuesta cuando los valores de la energía de activación no son los correctos. Para ello se modifica E añadiéndole ruido de la siguiente forma

$$E = 100 + \gamma N(\alpha) \quad (3.8)$$

$N(\alpha)$ es un número pseudoaleatorio generado por una distribución normal de probabilidad $N(0,1)$ y γ es una constante característica del nivel de ruido. Se modifica la E con cuatro niveles de ruido distintos. En los resultados se observa que al aumentar el nivel de ruido los valores de las curvas $\alpha - T$ reconstruidas se alejan más de los simulados. Este resultado permite utilizar el modelo para chequear los valores de E .

El modelo discreto propuesto también puede ser utilizado para predecir comportamientos cinéticos, siendo esta una de las aplicaciones más interesantes del análisis cinético [101, 116]. Se considera una velocidad de calentamiento distinta a las β_i con las que se han obtenido los valores $\alpha - T$ experimentales (de acuerdo a lo que hemos observado, se recomienda hacer las predicciones a velocidades de calentamiento β cercanas a las experimentales). Se utilizan los valores de E_α y c_α obtenidos anteriormente y la nueva velocidad de calentamiento para resolver la ecuación $\beta d\alpha/dT = c_\alpha e^{-E/RT}$. De esta forma se pueden predecir cinéticas de reacciones térmicas de estado sólido en condiciones diferentes a las medidas experimentalmente.

Este procedimiento se aplica al modelo teórico anterior para predecir los parámetros cinéticos de dos velocidades de calentamiento diferentes a las utilizadas para generar el modelo discreto. Se comparan las curvas $\alpha - T$ obtenidas con las verdaderas mostrando una alta coincidencia.

El mismo método se utiliza con el segundo modelo teórico $E_1 = 167 \text{ kJmol}^{-1}$, $A_1 = 10^{12} \text{ min}^{-1}$, $E_2 = 351 \text{ kJmol}^{-1}$, $A_2 = 10^{26} \text{ min}^{-1}$ y los modelos de reacción $f_1(\alpha) = (1 - \alpha)$ y $f_2(\alpha) = (1 - \alpha)$ que simula dos reacciones paralelas. Se obtiene la energía de activación aparente utilizando los métodos FR, MFR, KAS y Vyaz, con estos valores de E_α se determina el *pre-factor*. Se reconstruyen las curvas $\alpha - T$ y se comparan con las obtenidas a partir de los datos teóricos. Se observan algunas diferencias en los valores de E_α según el método isoconversional utilizado. Al igual que en la simulación anterior, se estudia el comportamiento del modelo cuando se añade ruido, observándose que

las curvas reconstruidas se alejan más de las simuladas cuanto mayor es el ruido añadido. Esta conducta se repite en el valor de R^2 . También se realizan predicciones para dos β diferentes encontrándose una buena concordancia entre las curvas $\alpha-T$ obtenidas y las simuladas.

El modelo discreto propuesto también se aplica para chequear los valores de la energía de activación obtenidos en la transformación térmica del compuesto $(\text{NH}_4)_2\text{Th}(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ a la fase $\text{Th}_2(\text{PO}_4)(\text{P}_3\text{O}_{10})$ por calentamiento desde temperatura ambiente hasta 1000 °C. El bisfosfato de amonio-torio(IV) monohidratado fue sintetizado hidrotermalmente a partir de nitrato de torio hidratado, urea y ácido fosforoso [127]. Su transformación térmica es un proceso complejo, la deshidratación tiene lugar en dos etapas, con la formación de una fase intermedia $(\text{NH}_4)_2\text{Th}(\text{PO}_4)_2 \cdot n\text{H}_2\text{O}$ ($n < 1$), previa a la fase anhidra. El posterior proceso de condensación y pérdida de amoníaco da lugar a un material amorfo que cristaliza a $\alpha\text{-ThP}_2\text{O}_7$ cuando la temperatura aumenta y posteriormente se transforma en $\text{Th}_2(\text{PO}_4)(\text{P}_3\text{O}_{10})$ a $T=1000$ °C [128].

En este trabajo se utilizaron los datos experimentales publicados por García-Glez y colaboradores para obtener los valores de la energía de activación en función del grado de conversión mediante los métodos isoconversionales FR, MFR, KAS y Vyaz, encontrándose valores muy similares para los cuatro métodos. Puede considerarse que hay dos valores prácticamente constantes de E correspondientes a dos intervalos de conversión, en el primero $E = 63 \pm 3 \text{ kJ mol}^{-1}$ desde el inicio de la reacción hasta aproximadamente $\alpha = 0.20$, en el segundo intervalo $E = 105 \pm 5 \text{ kJ mol}^{-1}$ cuando $0.30 < \alpha < 0.80$. Este resultado concuerda con la transformación en dos etapas mencionada anteriormente [128]. Con los valores de E se reconstruyen las curvas de conversión y se comparan con las experimentales mostrando una alta coincidencia en el rango completo de temperaturas. Se realizan predicciones de la dependencia de la conversión con la temperatura para $\beta = 1.25 \text{ }^\circ\text{C min}^{-1}$ y $\beta = 20 \text{ }^\circ\text{C min}^{-1}$, se comparan con las medidas experimentales para esas velocidades de calentamiento encontrándose un buen acuerdo entre ambas para los cuatro métodos isoconversionales utilizados.

En el Artículo S1 se aplica el procedimiento para obtener el modelo cinético a una simulación teórica y a un caso experimental. En el caso teórico se utiliza la función de Avrami-Erofeev A4 de la tabla 1 con $A=10^2 \text{ min}^{-1}$ y $E=20.9 \text{ kJmol}^{-1}$. La figura 3.2 muestra las curvas $\alpha-T$ simuladas y reconstruidas utilizando los cuatro métodos isoconversionales anteriores [129].

En el caso experimental el modelo cinético propuesto se utiliza para describir la degradación térmica del compuesto $\text{FeNH}_4(\text{HPO}_4)_2$, con cuatro velocidades de calentamiento constante. Las curvas TG y DTG indican que el proceso sucede en dos etapas consecutivas [130]. El análisis por espectrometría de masas muestra que el material pierde agua aproximadamente a 600 K y posteriormente agua y amoníaco sobre los 900 K.

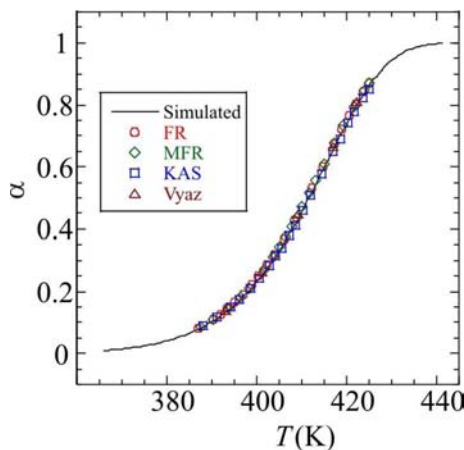


Figura 3.2. Comparación de las curvas $\alpha-T$ simuladas y reconstruidas para $\beta = 8 \text{ K min}^{-1}$.

En la figura 3.3a se muestran las curvas de la energía de activación frente al grado de conversión obtenidas por los métodos FR, MFR, KAS y Vyaz. La figura 3.3b indica que los datos experimentales son satisfactoriamente reconstruidos.

Se puede concluir que, independientemente del método usado para determinar la energía de activación, el modelo discreto propuesto describe adecuadamente la cinética del proceso, tanto en las simulaciones teóricas como en los casos experimentales.

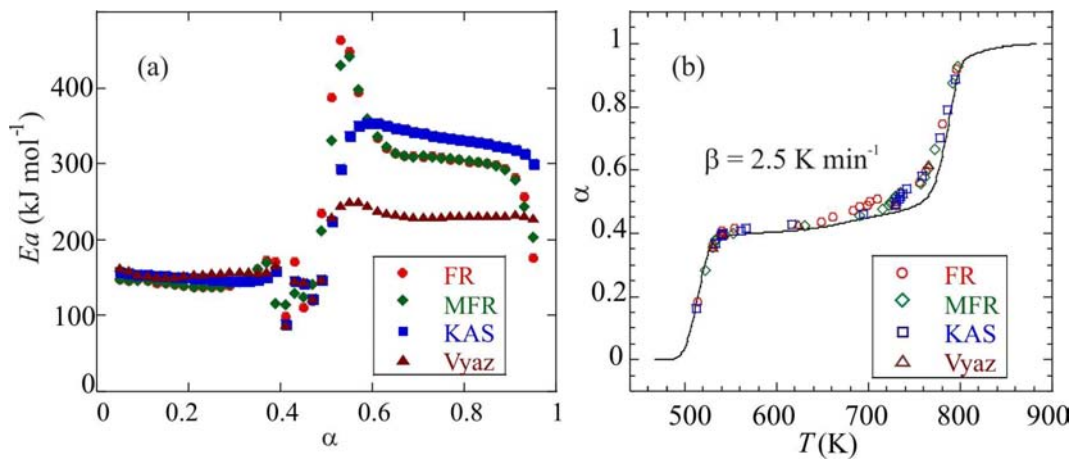


Figura 3.3. (a) Energía de activación en función del grado de conversión. (b) Curvas $\alpha-T$, experimental (línea) y reconstruidas (puntos) para $\beta = 2.5 \text{ Kmin}^{-1}$.

Artículo II

Thorium(IV) phosphate-triphosphate: A valuable ceramic material obtained by thermal treatment of a layered ammonium-thorium(IV) phosphate. Kinetic analysis of the transformation

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Thorium(IV) phosphate-triphosphate: A valuable ceramic material obtained by thermal treatment of a layered ammonium-thorium(IV) phosphate. Kinetic analysis of the transformation



Isabel Iglesias^a, Belén F. Alfonso^{a,*}, Zakariae Amghouz^b, Camino Trobajo^c, José R. García^c, José A. Huidobro^d

^a Dpto. de Física, Escuela Politécnica de Ingeniería, Universidad de Oviedo, 33204 Gijón, Spain

^b Dpto. de Ciencia de los Materiales e Ingeniería Metalúrgica, Escuela Politécnica de Ingeniería, Universidad de Oviedo, 33204 Gijón, Spain

^c Dpto. de Química Orgánica e Inorgánica, Universidad de Oviedo-CINN, 33006 Oviedo, Spain

^d Dpto. de Matemáticas, Escuela Politécnica de Ingeniería, Universidad de Oviedo, 33204 Gijón, Spain

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ABSTRACT

Morphological and structural characterization of both $(\text{NH}_4)_2\text{Th}(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ (**1**) and $\text{Th}_2(\text{PO}_4)(\text{P}_3\text{O}_{10})$ (**2**) have been performed by using electron microscopy techniques (SEM, HR-TEM, DF-STEM and SAED), which reveal a morphological transformation from star-shaped particles to irregularly rhombohedral-like aggregates after thermal treatment at 1000 °C. The **1** → **2** thermal conversion is monitored by thermogravimetric analysis and the activation energy has been obtained by using isoconversional methods. A discrete model describing the kinetic process is obtained and so the original data set can be reconstructed and compared with the experimental measures. By using heating rates different from those involved for getting the model, predictions can be also made. The procedure has worked efficiently in recovering the original kinetic parameters in two theoretical simulations.

1. Introduction

Ceramics, especially phosphate based ones, were clearly identified as good candidates for the immobilization of long half-life radionuclides [1–3]. Among them, thorium phosphate diphosphate (β -TPD), β - $\text{Th}_4(\text{PO}_4)_4\text{P}_2\text{O}_7$, has been proposed as an actinide-bearing phase of immobilization in the field of the nuclear waste management [4,5]. This material, which can be loaded *in situ* with large amounts of tetravalent actinides, appears to be highly resistant to aqueous corrosion and exhibits a high thermal stability [6–8].

A decade ago, our research group reported both the synthesis and structural characterization of the first inner-transition metal monohydrogenphosphate, $\text{Th}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ [9]. The experimental procedure (hydrothermal synthesis with H_3PO_3 as the source of phosphorus) was similar to that we used previously in the well crystallized $\text{Th}_2(\text{PO}_4)_2(\text{HPO}_4) \cdot \text{H}_2\text{O}$ preparation [10], which is the precursor (by thermal treatment) of β -TPD. In addition, the ammonium-thorium phosphates, $(\text{NH}_4)_2\text{Th}(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ and $\text{NH}_4\text{Th}_2(\text{PO}_4)_3$, were synthesized by using a simple experimental strategy, and their structure was solved by powder X-ray diffraction [11]. The structure of $\text{NH}_4\text{Th}_2(\text{PO}_4)_3$ is similar to their alkaline analogues

$\text{M}^{\text{IV}}\text{M}^{\text{V}}_2(\text{PO}_4)_3$ ($\text{M}^{\text{I}}=\text{Li, Na, K, Rb, Cs}$; $\text{M}^{\text{IV}}=\text{Th, U, Np, Pu}$) [12,13]. It is built with PO_4 monophosphate groups and ThO_9 polyhedra sharing their apices and their edges, thereby forming a three dimensional framework. This is a different structure from the one adopted by the $\text{Th}_{1/4}\text{Zr}_2(\text{PO}_4)_3$ (NZP-structural family, NASICON-type) in which the extra-framework thorium(IV) is hexa-coordinated [14]. More recently, we reported a structural model for the $\text{Th}_2(\text{PO}_4)(\text{P}_3\text{O}_{10})$, a novel thorium(IV) phosphate-triphosphate obtained by thermal treatment of $(\text{NH}_4)_2\text{Th}(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ [15].

In the kinetic analysis of thermally activated solid-state reactions, it is well known that the ambiguity in the computation of the kinetic triplet ($E, A, f(\alpha)$) creates difficulties for determining reliable kinetic parameters, particularly in model-fitting methods. This ambiguity can be, in part, overcome by using isoconversional methods which allow estimating the activation energy E as a function of the extent of conversion α , without the need to specify the reaction model $f(\alpha)$ or the pre-exponential factor A . In any case, some procedure to test the values of the kinetic parameters should be applied. The basic assumption of isoconversional methods is that the reaction rate for a constant extent of conversion, α , depends only on temperature [16–18]. A character-

* Corresponding author.

E-mail address: mbernaldez@uniovi.es (B.F. Alfonso).

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istic of these methods is that they do not need to determine $f(\alpha)$ to perform the analysis and, very often, they have been focused on obtaining E , although the knowledge of only this parameter may be not enough to reach physical interpretations [17,19]. Some authors have faced this question by considering the product $Af(\alpha)$ as a unique factor. Friedman [20], by taking logarithms in the general equation of kinetics, computed E and $Af(\alpha)$. Then, assuming a particular form of $f(\alpha)$, he obtained the kinetic triplet. Two factors may cause inaccuracy in this method. On the one hand, numerical differentiation applied to integral data. On the other hand, taking logarithms tends to overestimate errors involved in the process, particularly for small values of the reaction rate. The assumption about the form of $f(\alpha)$ can be included in the family of model-fitting methods. More recently, other researchers [17,21,22] have provided methods to reconstruct the experimental $\alpha - T$ curves without any assumption about $f(\alpha)$ but depending on how the activation energy had been obtained.

In this paper, we are moving in the knowledge of both structural and morphological features of the ammonium-thorium(IV) bis(phosphate) monohydrate and thorium(IV) phosphate-triphosphate. In addition, a model describing the kinetic process is provided. It is obtained from the general equation of kinetics, without any transformation, and it is based on computing the product $Af(\alpha)$ independently of the model function and the method applied to obtain the values of E .

2. Sample preparation and analytical procedures

(NH₄)₂Th(PO₄)₂·H₂O was hydrothermally synthesized from thorium nitrate hydrate (Fluka), urea (VWR) and phosphorous acid (Panreac) at 180 °C (7 days) as previously reported [11]. The phosphorus and thorium contents of the solids were determined by inductively coupled plasma mass spectrometry (ICP-MS) analysis (Finnigan, Element model) after dissolving a weighed amount in HF(aq). A Mettler-Toledo TGA/SDTA851^e was used for the thermal analyses in nitrogen dynamic atmosphere (50 mL min⁻¹). In all cases, ca. 15 mg of powder sample was thermally treated, and blank runs were performed. Powder X-ray diffraction patterns were collected on an X'Pert PRO MPD X-ray diffractometer with PIXcel detector, operating in the Bragg-Brentano ($\theta/2\theta$) geometry, using CuK α radiation ($\lambda=1.5418$ Å). SEM micrographs were recorded with a JEOL JSM-6100 electron microscope operating at 20 kV. Transmission electron microscopy (TEM) studies were performed on a JEOL JEM-2100F microscope operated at an accelerating voltage of 200 kV, equipped with a field emission gun (FEG) and an ultra-high resolution pole-piece that provided a point-resolution better than 0.19 nm. The samples for TEM were dispersed in ethanol, sonicated and sprayed on a carbon-coated copper grid and then allowed to air-dry.

3. Theory

Isoconversional methods in solid state reactions typically start from the equation

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E}{RT}\right) f(\alpha) \tag{1}$$

where t is the time, T the temperature and R the universal gas constant. Although mechanisms in solid state processes are normally very complexes and tend to involve several steps, Eq. (1) represents a simple kinetic model which can be used to describe an approximation of the kinetics of the process [23–25] and E represents the apparent activation energy.

In the case of a constant heating rate programme of temperature $T = T_0 + \beta t$, T_0 is the initial temperature, Eq. (1) can be written in the form

$$\beta \frac{d\alpha}{dT} = Af(\alpha) \exp\left(-\frac{E}{RT}\right) \tag{2}$$

There is a variety of isoconversional methods in order to obtain the kinetic parameters and not all of them lead to the same values [26,27]. So, the question is how to choose the right ones. The answer is not an easy matter and probably other kind of complementary analysis should be carried out [15,28].

Inaccuracies in the values of the activation energy can be caused by several reasons as the limitations assumed in some isoconversional methods, which are not frequently analysed [29], or the numerical errors involved in numerical computations. It seems clear that values of the activation energy obtained by a computational method should not be accepted without an elementary check. Focusing only on kinetic analysis, a way of checking the values of the kinetic parameters is to use them to build a model which is capable of reproducing the experimental data used to carry out the analysis. With this end in view, an idea is to solve the differential Eq. (2) for the heating rates used in the experiments and compare the values of the extent of conversion obtained by this way with the experimental values measured in the laboratory. If there are significant differences, these values of the kinetic parameters should be refused.

The Friedman method [20] is one of the most simple and popular in kinetic analysis. For several runs with different heating rates β_i , $i = 1, \dots, n$ and for a given value of the extent of conversion, Eq. (2) turns into

$$\ln\left(\beta_i \left(\frac{d\alpha}{dT}\right)_{\alpha,i}\right) = \ln(Af(\alpha)) - \frac{E_a}{RT_{\alpha,i}} \tag{3}$$

and E_a and $\ln(Af(\alpha))$ are computed by fitting to the experimental data.

As is well known, one of the main drawbacks of the Friedman method is its sensitivity to noise. Recently, with the aim of improving the sensitivity of experimental noise in the Friedman method, a modified procedure (MFR) was proposed by Huidobro et al. [30].

The Kissinger-Akahira-Sunose (KAS) method [31–33], included in the family of integral isoconversional methods leads to the equation

$$\ln\left(\frac{\beta_i}{T_{\alpha,i}^2}\right) = \ln\left(\frac{AR}{E_a g(\alpha)}\right) - \frac{E_a}{RT_{\alpha,i}} \tag{4}$$

where $g(\alpha) = \int_0^\alpha [1/f(\alpha)]d\alpha$.

Thus, by fitting to the experimental data, E_a can be calculated. Integral methods are widely used in kinetic analysis in spite of the mathematical inconsistency, particularly when the activation energy varies with the extent of conversion [23,34,35].

In the method proposed by Vyazovkin (Vyaz) [36,37] A and E_a are assumed to be constant over the interval $[\alpha - \Delta\alpha, \alpha]$ and E_a is obtained by minimization of the function

$$\Phi(E_a) = \sum_{i=1}^n \sum_{j \neq i}^n \frac{J_i(E_a)}{J_j(E_a)} \tag{5}$$

where $J(E_a) = \int_{\alpha-\Delta\alpha}^\alpha \exp(-E_a/RT)dt$.

The knowledge of the kinetic triplet allows describing the thermal decomposition of the process but, as has been mentioned, the determination of the model function is usually connected to certain level of ambiguity [23]. Some authors have proposed different methods in order to describe the kinetic process without specifying the form of $f(\alpha)$. Cai et al. [17] proposed an iterative method to obtain the values of the activation energy and the pre-factor $Af(\alpha)$ as a function of conversion. Wu et al. [21] used the Friedman method not only to obtain the activation energy but also $Af(\alpha)$ without assuming a particular form of $f(\alpha)$. Samuelsson et al. [22] computed E_a by Vyazovkin's method and wrote Eq. (1) as

$$\frac{d\alpha}{dt} = c_a \exp\left(-\frac{E_a}{RT}\right) \tag{6}$$

where the coefficient $c_a = Af(\alpha)$ is named the effective pre-factor. Assuming that c_a is constant over the interval, integration of Eq. (6)

gives

$$\Delta\alpha = c_a J_f(E_a) \tag{7}$$

and the pre-factor c_a can be computed by the formula

$$c_a = \frac{\Delta\alpha}{\langle J_f(E_a) \rangle} \tag{8}$$

where $\langle J_f(E_a) \rangle$ is the average of $J_f(E_a)$.

The method proposed for computing c_a [22] is essentially based on the ideas mentioned above although they introduced a modified Arrhenius equation in order to get a better estimation of the effective pre-factor. This assumes that both the activation energy and the effective pre-factor are constant over the interval where the integration is performed. The assumption about c_a is relevant for the mathematical consistency of the method because in case of large variations of the product $Af(\alpha)$ over the interval $[\alpha - \Delta\alpha, \alpha]$, this factor cannot be written outside the integral in Eq. (7). This happens frequently because in many processes the pre-exponential factor A is large [21,29] and despite the fact that variations of $f(\alpha)$ could be small, changes in $Af(\alpha)$ are significant and this factor cannot be considered as constant. For instance, considering a single step process with $A = 10^9 \text{ min}^{-1}$, $f(\alpha) = 1 - \alpha$, when $\Delta\alpha = 0.01$, $\Delta(Af(\alpha)) = 10^7 \text{ min}^{-1}$.

Concerning the integral isoconversional methods as KAS, Eq. (4) allows obtaining the value of $A/g(\alpha)$ but any interesting information about the pre-exponential factor or the product $Af(\alpha)$ cannot be extracted.

In the methods mentioned above, the effective pre-factor $Af(\alpha)$ is obtained depending on how the activation energy has been computed. In the following, a discrete model describing the kinetic process is provided. The procedure is based on the computation of $c_a = Af(\alpha)$ directly from Eq. (2) and independently of the procedure used to calculate the activation energy.

Assuming E_a has already been computed, c_a has to verify

$$\beta_i \frac{d\alpha(T_{a,i})}{dT} = c_a \exp\left(-\frac{E_a}{RT_{a,i}}\right), i = 1, \dots, n \tag{9}$$

Then, c_a can be obtained by the least-squares method. In this method no mathematical transformations are introduced, they may cause less accuracy [22,24], and the assumption of assuming that c_a is constant over the interval $[\alpha - \Delta\alpha, \alpha]$ is not necessary.

A possible weak point of this method is that numerical differentiation is necessary to achieve the conversion rate. So we have not used a simple incremental quotient [38] that converges to the derivative with order h but we have considered the formula

$$f'(x) \approx \frac{-f(x+2h) + f(x-2h)}{12h} + \frac{2f(x+h)2f(x-h)}{3h} \tag{10}$$

that converges with order h^4 .

4. Results and discussion

The morphologies of the $(\text{NH}_4)_2\text{Th}(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ compound and its thermal transformation to $\text{Th}_2(\text{PO}_4)(\text{P}_3\text{O}_{10})$ phase, obtained by heating $(\text{NH}_4)_2\text{Th}(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ from room temperature to 1000 °C, were analysed by scanning electron microscopy (SEM) and transmission electron microscopy (HR-TEM, DF-STEM, and SAED). SEM micrographs of $(\text{NH}_4)_2\text{Th}(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ presented in Fig. 1a,d,e reveal star-shaped morphologies for the large particles, whereas the small particles (Fig. 1b,c) with a size below 2 μm have a nearly square plate-like shape. It seems that the crystal growth can promote morphological transformation from the square plate-like to star-shaped morphologies as illustrated in Fig. 1b-d, and this takes place by favouring the growth of corners rather than the growth of edges when these square-plate particles reach a certain particle size. The inset of Fig. 1e shows a magnification of a single star-shaped particle with a 4-fold axis. This one has a base resembling a square-planar, where the peaks of the star

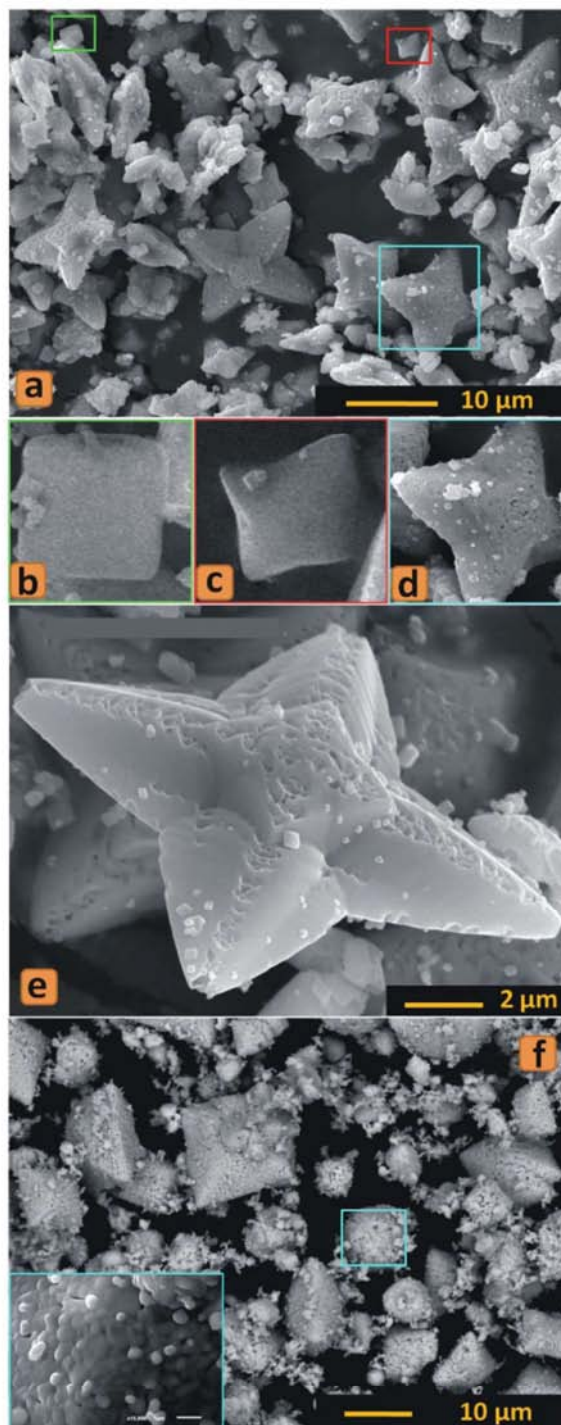


Fig. 1. SEM images of $(\text{NH}_4)_2\text{Th}(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ (a-e) and $\text{Th}_2(\text{PO}_4)(\text{P}_3\text{O}_{10})$ (f), where (b-d)-images correspond to the insets marked on (a)-image.

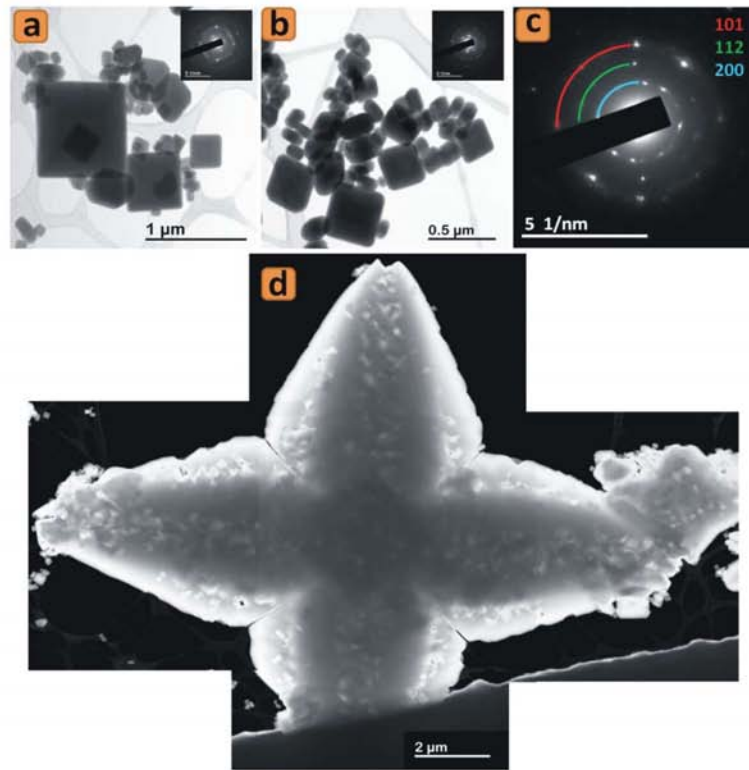


Fig. 2. (a,b) TEM images, (c) SAED pattern, and (d) DF-STEM image of $(\text{NH}_4)_2\text{Th}(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$. The image (d) has been constructed by combining partly overlapping image frames because of the large size of the particle.

have a tetrahedron shape where the lengths range from ca. 2–6 μm . Moreover, some void defects (due to the crystal growth) on the edges of these tetrahedron peaks are also observed. After thermal treatment at 1000 $^\circ\text{C}$, the morphology of the material changed completely (Fig. 1f), where the peaks of the star-shaped particles disappeared and the morphology transformed to rhombohedral-like shape of different sizes. The inset of Fig. 1f shows that these rhombohedral-like particles are made up of densely packed spherical and elongated particles.

For $(\text{NH}_4)_2\text{Th}(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$, TEM and SEM micrographs are in agreement and both show square plate-like morphologies with variable size in the range of ca. 0.1–1 μm (Fig. 2a,b). SAED pattern (for instance, Fig. 2c) shows the crystalline nature of these square plate-like particles and all the observed diffraction rings have been unambiguously assigned to the $(\text{NH}_4)_2\text{Th}(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ phase (tetragonal, space group $I4_1/amd$, $a=7.0192(4)$ \AA , $c=17.9403(8)$ \AA , ICSD# 246070), being some Miller indices depicted. Moreover, star-shaped particles are also observed as illustrated by the reconstructed DF-STEM image (Fig. 2d) of a single particle, which fulfils 4-fold rotational symmetry with peaks length of ca. 6 μm . Due to the thickness of the particles the SAED studies on their core and peaks could not be performed to analyse the possible twinning. TEM data for $\text{Th}_2(\text{PO}_4)(\text{P}_3\text{O}_{10})$ phase are shown in Fig. 3a–e. The square plate-like particles transformed to sintered grains composed of nearly spherical particles which tend to form sticks (Fig. 3a,b), whereas the star-shaped particles changed to irregularly rhombohedral-like aggregates (Fig. 3e). SAED pattern and HR-TEM image of an individual spherical particle shown in Fig. 3c,d, respectively, reveal the single-crystalline nature of these particles with preferential exposed {001} facet. All the observed diffraction spots in the SAED pattern and the calculated d -spacing in HR-TEM image (for instance, $d_{200}=5.8$ \AA and $d_{010}=7.2$ \AA) are assigned

to the $\text{Th}_2(\text{PO}_4)(\text{P}_3\text{O}_{10})$ phase (orthorhombic space group $Pn2_1a$, $a=11.6846(2)$ \AA , $b=7.1746(1)$ \AA , $c=12.9320(3)$ \AA) [15].

The transformation of $(\text{NH}_4)_2\text{Th}(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ to $\text{Th}_2(\text{PO}_4)(\text{P}_3\text{O}_{10})$ is a complex process. Dehydration of the starting material takes place in two steps, with a layered intermediate phase, $(\text{NH}_4)_2\text{Th}(\text{PO}_4)_2 \cdot n\text{H}_2\text{O}$ ($n < 1$), previous to the formation of the anhydrous compound [15]. The later condensation process produces an amorphous material that crystallizes to $\alpha\text{-ThP}_2\text{O}_7$ when the temperature increases, that slowly transforms to $\text{Th}_2(\text{PO}_4)(\text{P}_3\text{O}_{10})$ when $T=1000$ $^\circ\text{C}$. Surprisingly, there is no parallel drawn with the uranium counterpart, $\text{U}_2(\text{PO}_4)(\text{P}_3\text{O}_{10})$. The uranium compound transforms to $\alpha\text{-UP}_2\text{O}_7$ at $T=870$ $^\circ\text{C}$ [39], while that $\alpha\text{-ThP}_2\text{O}_7$ yields to $\text{Th}_2(\text{PO}_4)(\text{P}_3\text{O}_{10})$ after heating.

The kinetic analysis of thermal transformation of $(\text{NH}_4)_2\text{Th}(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ to $\text{Th}_2(\text{PO}_4)(\text{P}_3\text{O}_{10})$ was performed by the isoconversional methods described in the theoretical section. Previously we assess the procedure to obtain the discrete model applying it to two theoretical simulations. The simulated data set are generated and the capacity of the discrete model to recover the original data and make predictions is analysed.

In the first simulation, a process describing a single step reaction given by $A=10^9$ min^{-1} , $E=100$ kJ mol^{-1} and $f(\alpha) = 1 - \alpha$ was considered [40] and simulated data for the heating rates of 2, 4, 6 and 8 $^\circ\text{C min}^{-1}$ were generated. Values of the activation energy were computed by using the four methods seen above and the obtained dependence of the activation energy as a function of the extent of conversion is displayed in Fig. 4. As shown, all methods gave similar results, the activation energy values are very close to the pre-set value of 100 kJ mol^{-1} . Using these values, the effective pre-factor $c_a = Af(\alpha)$ was obtained by fitting in Eq. (9). Fig. 5 shows the effective pre-factor as a function of conversion. Notice that the values of c_a obtained are

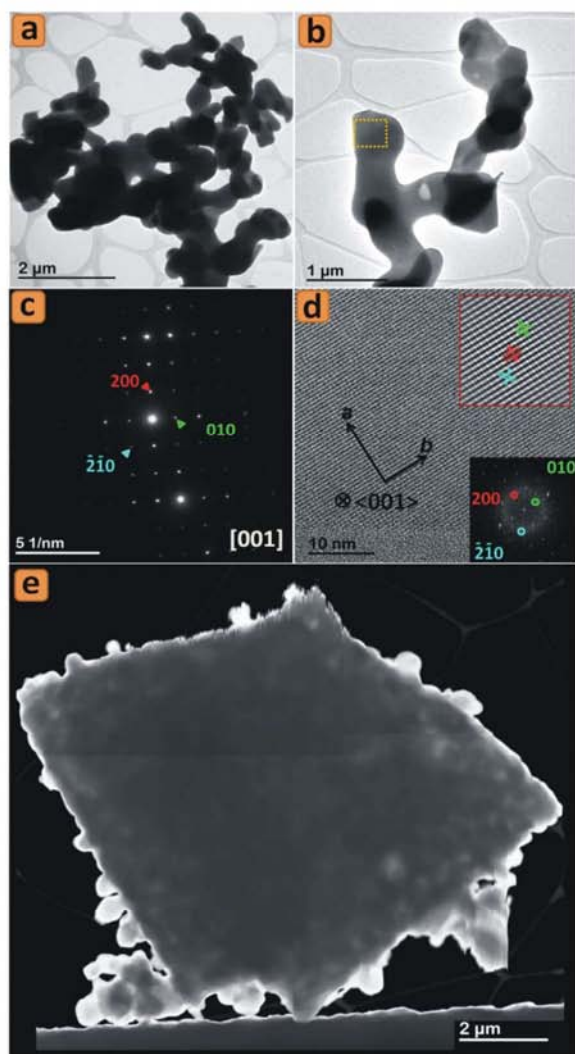


Fig. 3. (a,b) TEM images, (c) SAED pattern, and (d) HR-TEM image of $\text{Th}_2(\text{PO}_4)$ (P_3O_{10}). The image (d) corresponds to magnification of the zone highlighted by the yellow square in (b) and the insets of (d) show its FFT pattern and the processed HR-TEM image. The image (e) has been constructed by combining partly overlapping image frames because of the large size of the particle. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

practically identical to the pre-set value. The largest values of the error were obtained in the interval $0 < \alpha < 0.30$ when the activation energy was computed by the Friedman method. For $\alpha > 0.4$ the effective pre-factor corresponding to the activation energy calculated by the four methods shows a good agreement with the pre-set value. Using these values of E_α and c_α , Eq. (2) was solved for the heating rates of 2, 4, 6 and $8\text{ }^\circ\text{C min}^{-1}$ and the curves obtained were compared with the simulated ones used as input data. The graphics are shown in Supplementary Material (see Fig. S1). The agreement is generally good for the four isoconversional methods. The largest differences are at the beginning of the curves, in the zone where the values of E_α and c_α are further from the pre-set values.

Evaluating how well a curve $y = f(x)$ matches a set of points (x_i, y_i) is not an easy matter. Perhaps the best way of obtaining an idea about the goodness of this fit is to compare the plots of the function and the

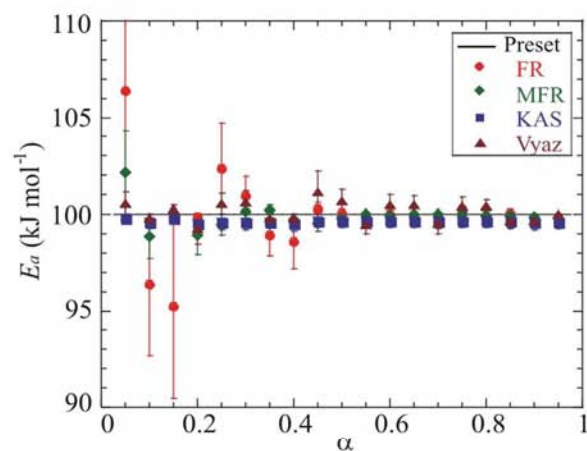


Fig. 4. Comparison of the pre-set and computed activation energy for a single step process (simulation 1: $A=10^9\text{ min}^{-1}$, $E=100\text{ kJ mol}^{-1}$ and $f(\alpha) = 1 - \alpha$). Absolute errors are included.

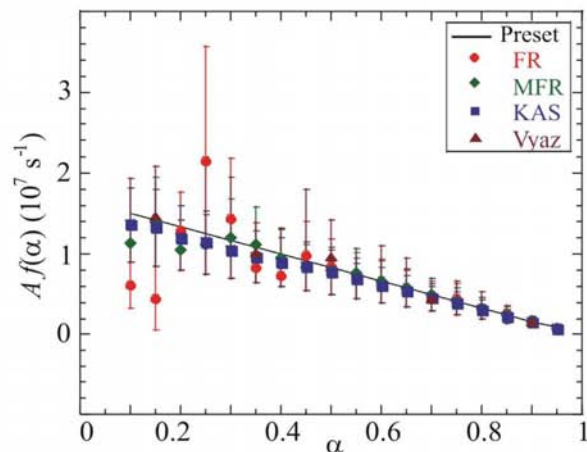


Fig. 5. Comparison of the pre-set and computed effective pre-factor $c(\alpha) = Af(\alpha)$ for simulation 1 ($A=10^9\text{ min}^{-1}$, $E=100\text{ kJ mol}^{-1}$ and $f(\alpha) = 1 - \alpha$). Absolute errors are included.

points. Numerical measures can also be carried out but their meaning may be not very clear because they try to compress the information into a single number. In this study both options have been considered. A numerical measure of the error of the fit is given by the sum of the square errors

$$SSE = \frac{1}{n} \sum_{i=1}^n (y_i^* - y_i)^2 \quad (10)$$

that can be normalized to

$$R^2 = 1 - \frac{SSE}{SST} \quad (11)$$

where

$$SST = \frac{1}{n} \sum_{i=1}^n (y_i - \bar{y})^2 \quad (12)$$

with $y_i^* = f(x_i)$ and $\bar{y} = \sum_{i=1}^n y_i/n$, the average. When $R^2 = 1$, all points lie on the curve with no scatter. The R^2 coefficients for the curves in Fig. S1 are shown in Table S1 (see Supplementary Material).

The results allow us to say that the model satisfactorily reproduces

the original data, but to evaluate the approach it is also interesting to study the behaviour of the discrete model when it has been obtained from wrong values of the activation energy. In this case, one should expect that the reconstructions and the original data set not to match so well as in Fig. S1. To this end, the activation energy was modified by introducing artificial noise in the form

$$E = 100 + \gamma N(\alpha) \tag{13}$$

where $N(\alpha)$ is a pseudorandom number generated by a normal distribution of probability $N(0,1)$, and γ is a constant characterising the level of noise. Four values of γ corresponding to maximum relative errors of 0.5%, 1%, 2%, and 4% were considered. The results showed that when the level of noise increases, the reconstructed curves move away from the data set. Fig. 6 shows the reconstructed curves and the simulated data for $\beta = 6 \text{ }^\circ\text{C min}^{-1}$ and for the four levels of noise. As can be seen, the fit is worse as the level of noise grows and the Friedman method is the least stable. Similar results were obtained for the rest of the heating rates (see the R^2 coefficients in Table S2 in the Supplementary Material).

Apart from recovering the original data, the capacity of the discrete model to make predictions was analysed. Making kinetic predictions is one of the most interesting practical applications of kinetic analysis [23,34]. In this sense, a reliable model is important and so predictions about the behaviour of the material for different heating rates that those considered in the laboratory can be achieved. So, considering the true values of E , A , $f(\alpha)$ and $\beta = 1 \text{ }^\circ\text{C min}^{-1}$ and $\beta = 10 \text{ }^\circ\text{C min}^{-1}$, $\alpha - T$ curves were generated. These heating rates are slight lower and higher than those used to generate the discrete model. Then, considering the values of E and $Af(\alpha)$ obtained by applying the proposed method, the differential equation was solved and similar results to those coming from the true values of the kinetic triplet were achieved. The plots are shown in Fig. S2 and the R^2 coefficients were: 0.997133, 0.999962, 0.999994 and 0.999987 for $\beta = 1 \text{ }^\circ\text{C min}^{-1}$, and 0.998563, 0.999992, 0.999966 and 0.999992 for $\beta = 10 \text{ }^\circ\text{C min}^{-1}$, for FR, MFR, KAS and Vyaz methods, respectively.

A theoretical parallel two-step process [41] given by $A_1 = 10^{12} \text{ min}^{-1}$, $E_1 = 167 \text{ kJ mol}^{-1}$, $f_1(\alpha) = 1 - \alpha$, $A_2 = 10^{26} \text{ min}^{-1}$, $E_2 = 352 \text{ kJ mol}^{-1}$ and $f_2(\alpha) = 1 - \alpha$, was also studied. The apparent activation energy, see Fig. 7, and the effective pre-factor $Af(\alpha)$ were obtained from the simulated data for the constant heating rates of 2, 4, 6 and $8 \text{ }^\circ\text{C min}^{-1}$. Although the shape of the activation energy dependence is quite similar, the values obtained depend on the method

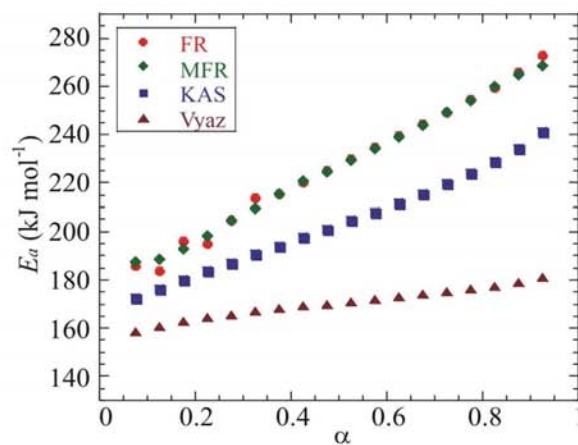


Fig. 7. Apparent activation energy for a two parallel step process (simulation 2: $A_1 = 10^{12} \text{ min}^{-1}$, $E_1 = 167 \text{ kJ mol}^{-1}$, $f_1 = 1 - \alpha$, $A_2 = 10^{26} \text{ min}^{-1}$, $E_2 = 352 \text{ kJ mol}^{-1}$ and $f_2 = 1 - \alpha$).

used. In spite of this (see Fig. S3), the reconstructed conversion curves are quasi-identical, and coincide with the simulated ones (the R^2 coefficients are shown in Table S3).

As in the previous simulation, the behaviour of the model was also studied in the presence of noise. In this case, since a parallel two-step process was simulated, the true value of activation energy does not make sense and so, the apparent activation energy considered was $E_a + \gamma N(\alpha)$, where E_a denotes the apparent activation energy obtained without noise. Likewise the first simulation, the results showed that when the level of noise increases, the reconstructed curves move away from the original data. Fig. 8 displays the reconstructed curves and the simulated data for $\beta = 6 \text{ }^\circ\text{C min}^{-1}$. Similar results were obtained for the rest of the heating rates (see the R^2 coefficients in Table S4).

Predictions were also carried out for two heating rates. The obtained $\alpha - T$ curves were compared with those obtained using the right values. A good fit was achieved as can be seen in Fig. S4 for $\beta = 1$ and $10 \text{ }^\circ\text{C min}^{-1}$. The R^2 coefficients were: 0.998834, 0.998298, 0.990128 and 0.886163 for $\beta = 1 \text{ }^\circ\text{C min}^{-1}$, and 0.995157, 0.999073, 0.998439 and 0.983983 for $\beta = 10 \text{ }^\circ\text{C min}^{-1}$, for FR, MFR, KAS and

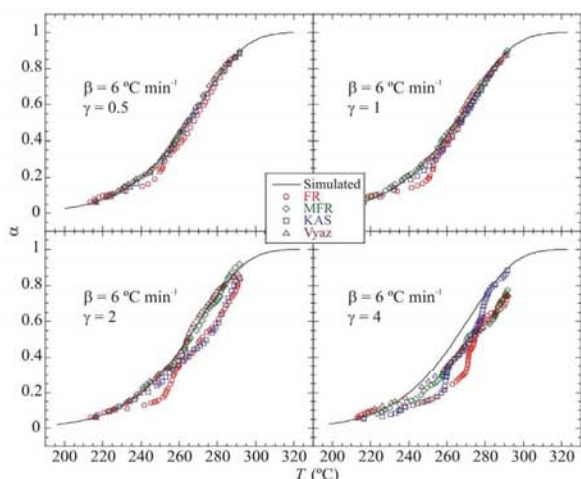


Fig. 6. Comparison of the simulated (solid lines) and reconstructed (points) $\alpha - T$ curves for simulation 1 ($A = 10^9 \text{ min}^{-1}$, $E = 100 \text{ kJ mol}^{-1}$ and $f(\alpha) = 1 - \alpha$) for several levels of noise (0.5%, 1%, 2% and 4%).

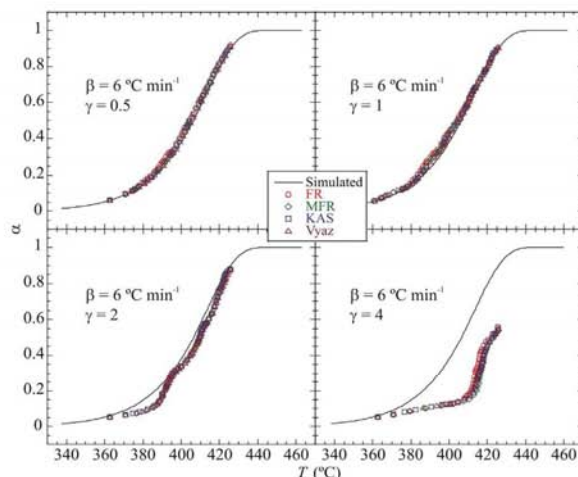


Fig. 8. Comparison of the simulated (solid lines) and reconstructed (points) $\alpha - T$ curves for simulation 2 ($A_1 = 10^{12} \text{ min}^{-1}$, $E_1 = 167 \text{ kJ mol}^{-1}$, $f_1 = 1 - \alpha$, $A_2 = 10^{26} \text{ min}^{-1}$, $E_2 = 352 \text{ kJ mol}^{-1}$ and $f_2 = 1 - \alpha$) for several levels of noise (0.5%, 1%, 2% and 4%).

Vyaz methods, respectively.

So we can say that for the theoretical simulations considered, the approach above provides a reliable discrete model that works efficiently in recovering the original kinetic parameters, reconstructing the original data set and making predictions for heating rates different from those used for getting the model.

In ref. [15], for thermal transformation of $(\text{NH}_4)_2\text{Th}(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ to $\text{Th}_2(\text{PO}_4)_3(\text{P}_3\text{O}_{10})$, and using thermogravimetric data obtained at four different heating rates ($\beta = 2.5, 5, 10, 15 \text{ }^\circ\text{C min}^{-1}$), the activation energy as a function of the extent of conversion was calculated by the KAS method obtaining two approximately constant values, $E \approx 62 \text{ kJ mol}^{-1}$ in the conversion range of 0.05–0.20, and $E \approx 105 \text{ kJ mol}^{-1}$ for α between 0.50 and 0.80. In this work, by using the experimental data previously reported, the dependence of the apparent activation energy on the extent of conversion is computed by the isoconversional methods described in the theoretical section, see Fig. 9. The agreement of the values of the E obtained by the applied methods can be observed. The activation energy initially starts at nearly a constant value of $E = 63 \pm 3 \text{ kJ mol}^{-1}$ until $\alpha = 0.20$, an increase follows and a plateau appears in the $0.30 < \alpha < 0.80$ range, in which $E = 105 \pm 5 \text{ kJ mol}^{-1}$. Again, these results denote two decomposition mechanisms. In general, constant E -values can be expected in the case of a single reaction. However, in our experiment, the E curve profile indicates that the decomposition mechanism depends on the extent of conversion. This fact should be related to the difference in both water and ammonia desorption steps. The dehydration process takes place in two steps, with the formation of an intermediate phase that, in our experimental conditions, is not possible to isolate. The interlayer distance decreases from 6.53 Å (monohydrated phase) to 6.31 Å (anhydrous phase), with intermediate values for the partially hydrated phase (6.42 Å). After dehydration, the condensation process provokes the formation of an amorphous material that crystallizes to thorium(IV) diphosphate when the temperature increases. At higher temperatures, the α -ThP2O7 slowly transforms to the $\text{Th}_2(\text{PO}_4)_3(\text{P}_3\text{O}_{10})$ [15]. Fig. S5 shows the reconstructed conversion curves and the experimental ones obtained in the laboratory, they show an excellent agreement in the whole temperature range (the R^2 coefficients can be seen in Table S5).

Predictions about the conversion dependence for $\beta = 1.25$ and $20 \text{ }^\circ\text{C min}^{-1}$ heating rates were obtained using the discrete model and they were compared with the measurements registered in the Lab for the same heating rates. As Fig. S6 shows, a good agreement in the four isoconversional methods was achieved (R^2 coefficients were 0.980642, 0.981619, 0.982029, 0.979758 for

$\beta = 1.25 \text{ }^\circ\text{C min}^{-1}$, and 0.978207, 0.979723, 0.979833, 0.977351 for $\beta = 20 \text{ }^\circ\text{C min}^{-1}$, for FR, MFR, KAS and Vyaz methods, respectively) supporting that, independent of the method used to compute the activation energy, the model based on the kinetic parameters obtained describes the kinetics of the process properly.

5. Conclusions

The thermal transformation of $(\text{NH}_4)_2\text{Th}(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ to $\text{Th}_2(\text{PO}_4)_3(\text{P}_3\text{O}_{10})$ has been analysed by using electron microscopy techniques (SEM, HR-TEM, DF-STEM and SAED). The study reveals a morphological transformation from star-shaped particles to irregularly rhombohedral-like aggregates after thermal treatment at $1000 \text{ }^\circ\text{C}$. The activation energy was computed by four isoconversional methods (FR, MFR, KAS and Vyaz) denoting two decomposition mechanisms: $E = 63 \pm 3 \text{ kJ mol}^{-1}$ until $\alpha = 0.20$ and $E = 105 \pm 5 \text{ kJ mol}^{-1}$ in the $0.30 < \alpha < 0.80$ range. Similar results were achieved for the four methods. In order to test the values of E a discrete model was built. The model is obtained directly from the general kinetic rate equation, without any mathematical transformation that could cause overestimation of experimental errors, and it is independent of how the activation energy has been calculated. Although constant heating rate programmes have been considered, other cases can be easily implemented. The procedure was checked by using two theoretical simulations. For both the theoretical simulations and the experimental case, the results showed an excellent agreement in the whole temperature range.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.ceramint.2017.05.091.

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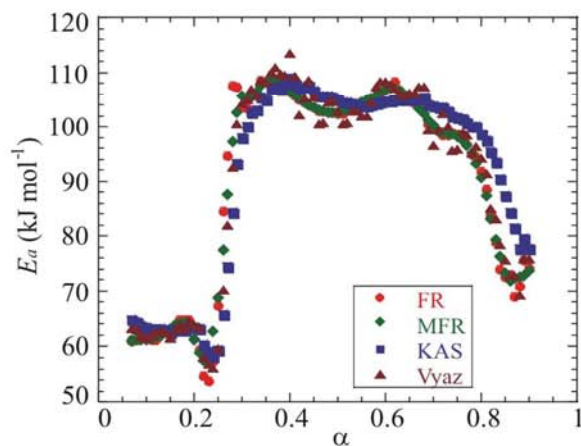


Fig. 9. Dependence of the apparent activation energy on the extent of conversion obtained by four isoconversional methods for the $(\text{NH}_4)_2\text{Th}(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ thermal decomposition.

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Thorium(IV) phosphate-triphosphate: A valuable ceramic material obtained by thermal treatment of a layered ammonium-thorium(IV) phosphate. Kinetic analysis of the transformation

Isabel Iglesias^a, Belén F. Alfonso^{a,*}, Zakariae Amghouz^b, Camino Trobajo^c, José R. García^c, José A. Huidobro^d

^a *Dpto. de Física, Escuela Politécnica de Ingeniería, Universidad de Oviedo, 33204 Gijón, Spain*

^b *Dpto. de Ciencia de los Materiales e Ingeniería Metalúrgica, Escuela Politécnica de Ingeniería, Universidad de Oviedo, 33204 Gijón, Spain*

^c *Dpto. de Química Orgánica e Inorgánica, Universidad de Oviedo-CINN, 33006 Oviedo, Spain*

^d *Dpto. de Matemáticas, Escuela Politécnica de Ingeniería, Universidad de Oviedo, 33204 Gijón, Spain*

*Corresponding author Belén F. Alfonso, mbafernandez@uniovi.es

Supplementary Material

TABLES

Table S1 Coefficient R² in the 2, 4, 6 and 8 °C min⁻¹ reconstructed curves for one step process by applying the FR, MFR, KAS and Vyaz methods.

Method	2/°Cmin ⁻¹	4/°Cmin ⁻¹	6/°Cmin ⁻¹	8/°Cmin ⁻¹
FR	0.996713	0.996845	0.997149	0.997141
MFR	0.999943	0.999940	0.999961	0.999949
KAS	0.999997	0.999995	0.999987	0.999986
Vyaz	0.999995	0.999997	0.999997	0.999996

Table S2 Coefficient R^2 in the 2, 4, 6 and 8 °C min⁻¹ reconstructed curves for one step process with perturbation of 0.5, 1, 2 and 4 in the activation energy. The FR, MFR, KAS and Vyaz methods were applied.

	Method	$\gamma = 0.5$	$\gamma = 1$	$\gamma = 2$	$\gamma = 4$
2/°Cmin ⁻¹	FR	0.951410	0.994048	0.820818	0.817124
	MFR	0.995677	0.997240	0.951963	0.868347
	KAS	0.992731	0.997320	0.927708	0.771202
	Vyaz	0.998108	0.990147	0.968711	0.858497
4/°Cmin ⁻¹	FR	0.951066	0.993658	0.824984	0.823692
	MFR	0.995722	0.997391	0.954320	0.880044
	KAS	0.992841	0.997374	0.931174	0.791481
	Vyaz	0.998102	0.990229	0.971021	0.873792
6/°Cmin ⁻¹	FR	0.951661	0.993537	0.829496	0.826925
	MFR	0.995782	0.997502	0.955741	0.879766
	KAS	0.992727	0.997439	0.932711	0.787484
	Vyaz	0.998131	0.990490	0.972145	0.871243
8/°Cmin ⁻¹	FR	0.952339	0.993526	0.833667	0.831034
	MFR	0.995911	0.997482	0.957578	0.883437
	KAS	0.992926	0.997480	0.934790	0.792563
	Vyaz	0.998144	0.990553	0.973473	0.875133

Table S3 Coefficient R^2 in the 2, 4, 6 and 8 °C min⁻¹ reconstructed curves for parallel two steps process by applying the FR, MFR, KAS and Vyaz methods.

Method	2/°Cmin ⁻¹	4/°Cmin ⁻¹	6/°Cmin ⁻¹	8/°Cmin ⁻¹
FR	0.996249	0.992273	0.992507	0.994389
MFR	0.998990	0.996583	0.997035	0.998438
KAS	0.986910	0.993234	0.998080	0.999924
Vyaz	0.935737	0.985374	0.999290	0.996273

Table S4 Coefficient R^2 in the 2, 4, 6 and 8 °C min⁻¹ reconstructed curves for a parallel two steps process with perturbation of 0.5, 1, 2 and 4 in the activation energy. The FR, MFR, KAS and Vyaz methods were applied.

	Method	$\gamma = 0.5$	$\gamma = 1$	$\gamma = 2$	$\gamma = 4$
2 ^o Cmin ⁻¹	FR	0.989525	0.974076	0.978690	0.375130
	MFR	0.994501	0.982441	0.971126	0.337773
	KAS	0.984504	0.955292	0.984350	0.391102
	Vyaz	0.937448	0.877521	0.980768	0.449758
4 ^o Cmin ⁻¹	FR	0.985776	0.964953	0.980851	0.274783
	MFR	0.992165	0.974800	0.974781	0.250200
	KAS	0.989858	0.966029	0.981392	0.281423
	Vyaz	0.982658	0.949423	0.986906	0.322972
6 ^o Cmin ⁻¹	FR	0.985531	0.964672	0.980671	0.348567
	MFR	0.992026	0.974908	0.974586	0.320856
	KAS	0.993776	0.976907	0.976499	0.341998
	Vyaz	0.995777	0.980618	0.975993	0.365474
8 ^o Cmin ⁻¹	FR	0.986794	0.966998	0.979093	0.360812
	MFR	0.993096	0.977429	0.971757	0.327920
	KAS	0.995681	0.985507	0.967119	0.345519
	Vyaz	0.994686	0.993591	0.952385	0.355314

Table S5 Coefficient R^2 in the 2.5, 5, 10 and 15 °C min⁻¹ reconstructed curves for thermal decomposition of the (NH₄)₂Th(PO₄)₂·H₂O by applying the FR, MFR, KAS and Vyaz methods.

Method	2.5 ^o Cmin ⁻¹	5 ^o Cmin ⁻¹	10 ^o Cmin ⁻¹	15 ^o Cmin ⁻¹
FR	0.999576	0.999890	0.999788	0.999748
MFR	0.999713	0.999841	0.999911	0.999898
KAS	0.999395	0.999676	0.999857	0.999889
Vyaz	0.999428	0.999861	0.999778	0.999719

FIGURES

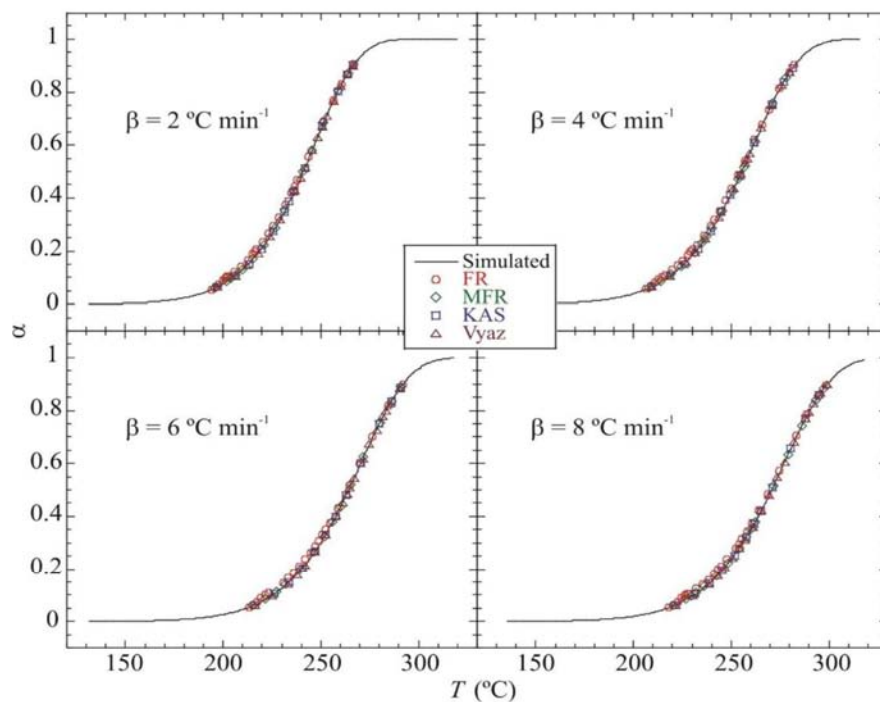


Fig. S1 Comparison of the simulated (solid lines) and reconstructed (points) $\alpha - T$ curves for simulation 1 ($A = 10^9 \text{ min}^{-1}$, $E = 100 \text{ kJ mol}^{-1}$ and $f(\alpha) = 1 - \alpha$).

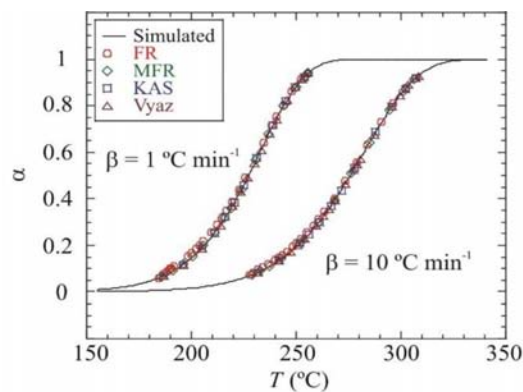


Fig. S2 Predicted (points) and simulated (solid lines) $\alpha - T$ curves for simulation 1 ($A = 10^9 \text{ min}^{-1}$, $E = 100 \text{ kJ mol}^{-1}$ and $f(\alpha) = 1 - \alpha$).

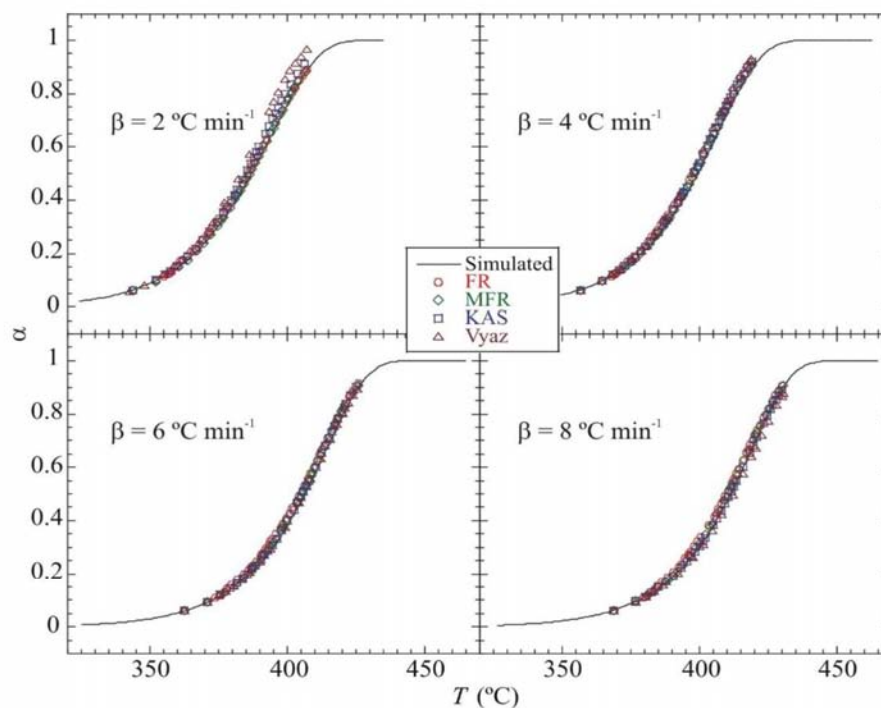


Fig. S3 Comparison of the simulated (solid lines) and reconstructed (points) $\alpha - T$ curves for simulation 2 ($A_1 = 10^{12} \text{ min}^{-1}$, $E_1 = 167 \text{ kJ mol}^{-1}$, $f_1 = 1 - \alpha$, $A_2 = 10^{26} \text{ min}^{-1}$, $E_2 = 352 \text{ kJ mol}^{-1}$ and $f_2 = 1 - \alpha$).

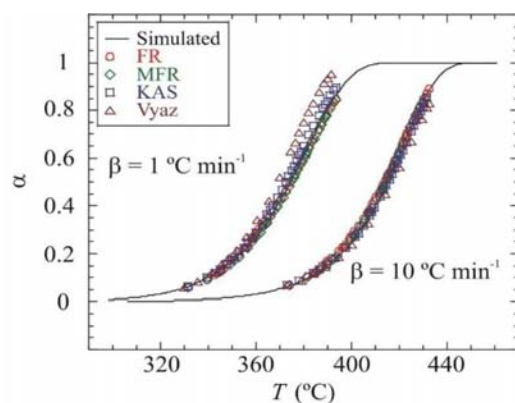


Fig. S4 Predicted (points) and simulated (solid lines) $\alpha - T$ curves for simulation 2 ($A_1 = 10^{12} \text{ min}^{-1}$, $E_1 = 167 \text{ kJ mol}^{-1}$, $f_1 = 1 - \alpha$, $A_2 = 10^{26} \text{ min}^{-1}$, $E_2 = 352 \text{ kJ mol}^{-1}$ and $f_2 = 1 - \alpha$).

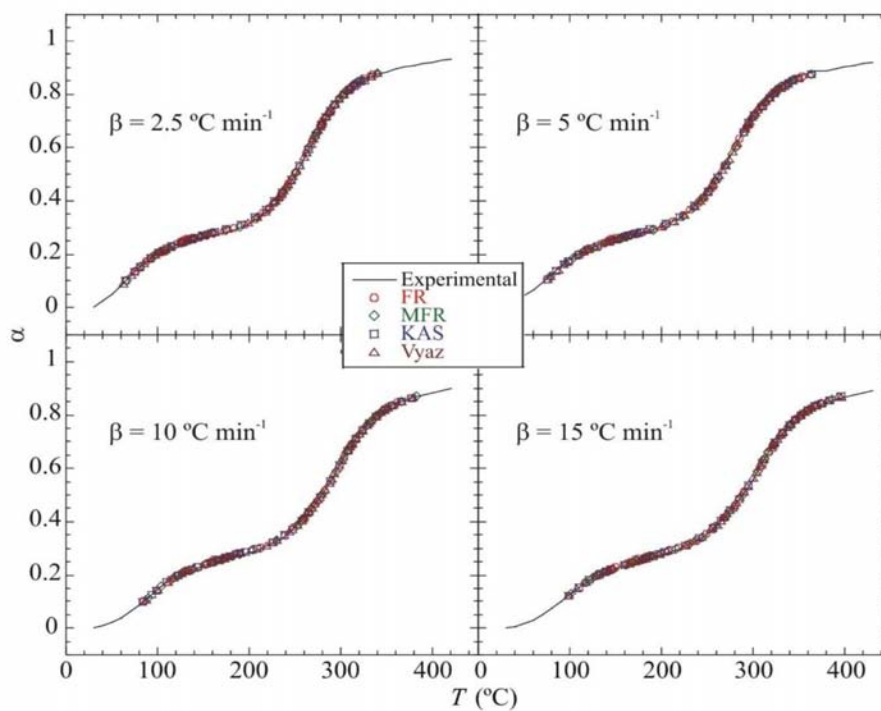


Fig. S5 The experimental (solid lines) and reconstructed (points) $\alpha - T$ curves for $(\text{NH}_4)_2\text{Th}(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ thermal decomposition.

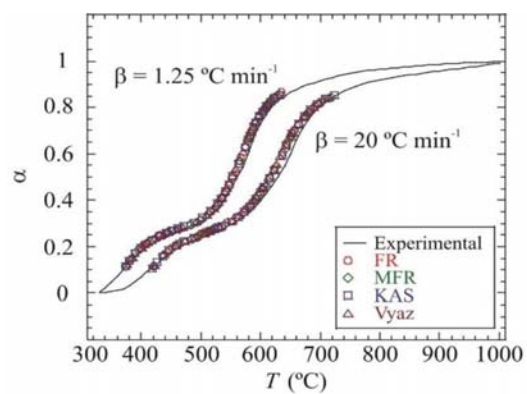


Fig. S6 Predicted (points) and simulated (solid lines) $\alpha - T$ curves for the $(\text{NH}_4)_2\text{Th}(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ thermal decomposition.

3.2. Síntesis y caracterización de $\text{Cr}_{0.34}\text{Fe}_{0.66}\text{NH}_4(\text{HPO}_4)_2$

Dentro de la amplia familia de fosfatos de hierro, tanto naturales como sintéticos, que contienen nitrógeno y, en particular, de los preparados por vía hidrotermal, se han descrito multitud de materiales con propiedades químicas y físicas interesantes [10]. En este artículo se presenta la síntesis hidrotermal y la caracterización físico-química de una nueva fase cristalina de un hidrógeno fosfato de amonio-cromo-hierro.

En trabajos previos de nuestro grupo de investigación se han publicado síntesis hidrotermales de varios fosfatos de hierro(III) a partir de la reacción de FeCl_3 (acuoso) y H_3PO_4 (acuoso) en presencia de urea a 180 °C [131]. Los compuestos finales dependían, por un lado, de la acidez de la solución y por otro, de la relación molar entre el hierro y el fósforo. Entre los compuestos sintetizados se obtuvo el bis(hidrogenofosfato) de amonio-hierro(III), $\text{FeNH}_4(\text{HPO}_4)_2$ [FeNP].

La estructura cristalina de este compuesto fue resuelta por Yakubovich [132] a partir de datos de difracción de rayos X de monocristal, descrita con un grupo espacial no convencional triclinico *I*-1. Nuestro grupo de trabajo realizó un análisis más profundo del FeNP, confirmó la estructura cristalina triclinica y la transformó a una celda primitiva reducida, grupo espacial *P*-1. A partir de los datos obtenidos mediante difracción de neutrones, medidas de imanación y calor específico se estudió la estructura cristalina y magnética del compuesto FeNP. En la resolución de su estructura magnética se observó una doble transformación de fase magnética [133-137].

Continuando esta línea de investigación, se propuso la síntesis de compuestos similares en los cuales parte de los átomos de hierro sean sustituidos por otros metales de transición con el objetivo de conocer cómo se verá afectada la estructura y se modificaran las propiedades térmicas y magnéticas respecto a las del FeNP.

Se sintetizaron sólidos $\text{Cr}_x\text{Fe}_{1-x}\text{NH}_4(\text{HPO}_4)_2$ ($0 \leq x \leq 1$) por vía hidrotermal a partir de una mezcla de $\text{MCl}_3 \cdot 6\text{H}_2\text{O}$ ($\text{M}=\text{Cr}, \text{Fe}$), H_3PO_4 y $(\text{NH}_2)_2\text{CO}$ calentándola a 453 K durante periodos de tiempo que variaron entre 1 y 20 días. Las relaciones molares utilizadas fueron $\text{C}/\text{P}=0.25$, $\text{P}/\text{M}=15$ y la relación

Cr:Fe entre los metales: 1:9, 2:8, 3:7, 4:6, 5:5, 9:1. Cuando la relación Cr:Fe fue 10:0 no se obtuvo precipitado.

En este trabajo se recoge la síntesis, caracterización estructural y térmica, y las propiedades magnéticas del bis(hidrogenofosfato) de amonio-cromo(III)-hierro(III) $\text{Cr}_{0.34}\text{Fe}_{0.66}\text{NH}_4(\text{HPO}_4)_2$ [CrFeNP], compuesto cristalino de color verde brillante obtenido con la relación Cr:Fe de 1:9. En la figura 3.4 muestra una fotografía de este compuesto.



Figura 3.4. Cristales del compuesto $\text{Cr}_{0.34}\text{Fe}_{0.66}\text{NH}_4(\text{HPO}_4)_2$.

La morfología del CrFeNP, muy similar a la del FeNP, está originada por placas delgadas que se agrupan en formas parecidas a la “rosa del desierto”.

El CrFeNP cristaliza en el grupo espacial $P-1$ del sistema triclinico. A partir de datos obtenidos por difracción de rayos X se determina la ocupación de los iones M^{3+} . Debido a que los dos iones tienen un número atómico muy próximo no se puede conocer, mediante esta técnica, si existe un orden de ocupación preferencial de uno de los iones, Cr^{3+} o Fe^{3+} , o si la ocupación es aleatoria, aunque las medidas magnéticas sugieren una ocupación preferencial. La estructura cristalina del CrFeNP consiste en octaedros $(\text{Fe}/\text{Cr})\text{O}_6$ que comparten vértices con tetraedros PO_4 , de forma que cada octaedro está rodeado de seis tetraedros y, a su vez, cada tetraedro está unido a tres octaedros a través de átomos de oxígeno y a un hidrógeno mediante el oxígeno restante. La celda primitiva contiene tres iones M^{3+} situados en dos sitios cristalográficos con distinta simetría local. Uno de ellos está localizado en un centro de inversión espacial y los otros dos únicamente

tienen la identidad como elemento de simetría. La red aniónica contiene dos tipos de túneles infinitos perpendiculares entre sí a lo largo de las direcciones $[0\ 1\ 0]$ y $[1\ 0\ 0]$ donde están localizados los cationes amonio que compensan la carga negativa de la red. Ambos túneles están formados por cuatro octaedros $(\text{Fe}/\text{Cr})\text{O}_6$ y por cuatro tetraedros PO_4 . Los compuestos FeNP y CrFeNP son isoestructurales.

A partir de análisis termogravimétricos y de espectrometría de masas se observa que el compuesto es estable hasta aproximadamente 600 K. A esta temperatura sufre la primera pérdida de masa y, posteriormente, a unos 900 K tiene lugar la segunda (figura 3.5). La primera corresponde a una evacuación de agua y la segunda está asociada a una pérdida de agua y amoniaco.

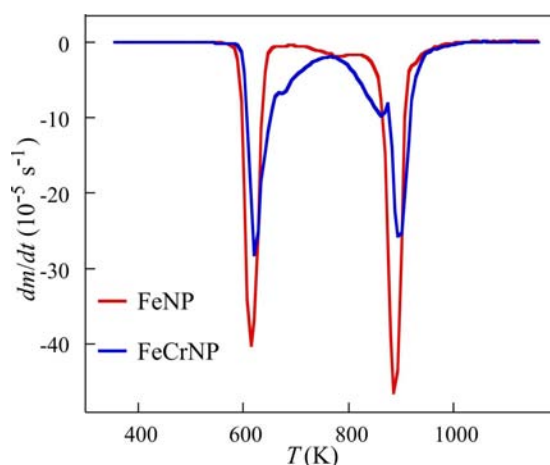


Figura 3.5. Curvas DTG de CrFeNP y FeNP obtenidas a una velocidad de calentamiento $\beta = 10\ \text{Kmin}^{-1}$.

Los parámetros cinéticos de la descomposición térmica del CrFeNP se determinan, utilizando cuatro velocidades de calentamiento constante, aplicando los métodos isoconversionales MFR y Vyaz. La dependencia de la energía de activación con el grado de conversión muestra dos zonas bien diferenciadas. En el rango $0.05 \leq \alpha \leq 0.30$ el valor de E es aproximadamente $150\ \text{kJ mol}^{-1}$, que corresponde a la primera pérdida de agua. En el rango $0.70 \leq \alpha \leq 0.90$ se obtiene $E \approx 300\ \text{kJ mol}^{-1}$ que coincide con la desorción de agua y amoniaco. Si comparamos las curvas $E - \alpha$ del CrFeNP con las del FeNP se observa que los valores obtenidos de la energía de activación son más altos para el primer compuesto.

La descomposición térmica del FeNP es menos irregular que la del CrFeNP, como se puede observar al comparar las curvas DTG de ambos compuestos obtenidas a una velocidad de calentamiento de 10 K min^{-1} (figura 3.5). Este hecho también se aprecia en la forma de las curvas $E-\alpha$ (artículo: figura 6) y, con mayor claridad en el método MFR debido a que los métodos isoconversionales diferenciales son más sensibles a los cambios experimentales que los integrales.

Utilizando los métodos MFR y Vyaz se calcula el factor efectivo c_α y se resuelve la ecuación cinética 3.1. Se comparan las curvas $\alpha-T$ reconstruidas por los dos métodos con las experimentales encontrándose una alta coincidencia entre ellas. En la figura 3.6 se muestran las curvas $\alpha-T$ reconstruidas y experimentales del compuesto CrFeNP a $\beta = 15 \text{ Kmin}^{-1}$.

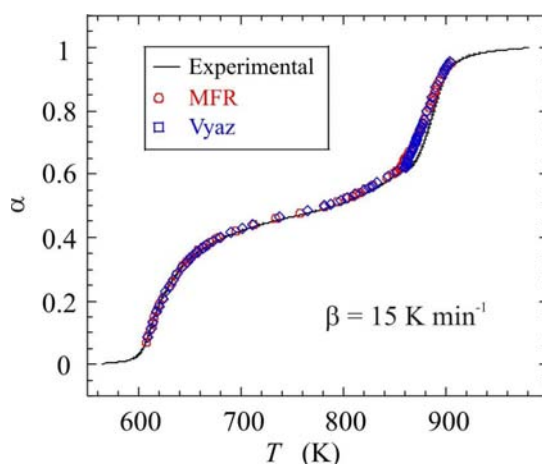


Figura 3.6. Comparación de las curvas $\alpha-T$ simuladas y reconstruidas del CrFeNP a $\beta = 15 \text{ Kmin}^{-1}$.

El análisis del comportamiento magnético del compuesto CrFeNP se realiza a partir del estudio de la dependencia de la susceptibilidad magnética con la temperatura $\chi_M(T)$, y de las medidas de la imanación con el campo magnético aplicado $M(H)$ a temperatura constante. La conducta es compatible con la siguiente secuencia de estados magnéticos: paramagnético desde temperatura ambiente hasta $T_C = 17.9 \text{ K}$, ferrimagnético por debajo de esta temperatura hasta la temperatura de transición, $T_i = 3.1 \text{ K}$ y antiferromagnético hasta 2 K . Entre las temperaturas T_C y T_i se observan diferencias en las medidas ZFC y FC de la

susceptibilidad cuando el campo magnético aplicado es de 10 Oe, sugiriendo que la fase ferrimagnética es termomagnéticamente irreversible.

La susceptibilidad magnética sigue la ley de Curie-Weiss en el rango de temperaturas entre 300 y 50 K, pero al acercarse a T_C se desvía de esta ley. La relación $\chi_M^{-1}(T)$ corresponde a una función hiperbólica, por esta razón se ajusta la dependencia de la inversa de la susceptibilidad magnética con la temperatura a la expresión de la teoría de Néel para un material ferrimagnético [138]

$$\frac{1}{\chi_M} = \frac{T - \Theta_p}{C} - \frac{\gamma}{T - \Theta} \quad (3.9)$$

Se obtienen los siguientes valores de los parámetros: $\Theta_p = -58.63$ K, $C = 3.63$ emu K (mol Oe)⁻¹, $\gamma = 37.03$ mol Oe (emu K)⁻¹ y $\Theta = 16.43$ K. El valor negativo de Θ_p indica interacciones antiferromagnéticas entre los momentos magnéticos de las dos subredes que corresponden a las dos posiciones cristalográficas diferentes de iones M^{3+} . El valor positivo de Θ implica interacciones ferromagnéticas entre iones de la misma subred. Para evaluar numéricamente la bondad del ajuste se utiliza el coeficiente de determinación R^2 obteniéndose el valor de 0.9999.

También se han realizado medidas de la variación de la imanación con la temperatura en los compuestos obtenidos con las diferentes relaciones molares indicadas anteriormente. En la figura 3.7 se muestra la dependencia de la imanación con la temperatura en un compuesto $\text{Cr}_x\text{Fe}_{1-x}\text{NH}_4(\text{HPO}_4)_2$ obtenido con las relaciones molares $C/P = 0.25$, $P/M = 15$ y la relación Cr:Fe entre los metales de 3:7 cuando se aplica un campo magnético de 1 kOe.

Utilizando la ecuación 1.5 se calcula el momento magnético efectivo del CrFeNP , $\mu_{eff} = 5.4 \mu_B$, cuyo valor está muy próximo al calculado teóricamente $\mu_{eff}^{calc} = 5.3 \mu_B$, obtenido aplicando la expresión

$$\mu_{eff}^{calc} = \sqrt{x\mu_{Cr}^2 + (1-x)\mu_{Fe}^2} \quad (3.10)$$

considerando los valores experimentales de los momentos magnéticos de los iones $\mu_{Fe} = 5.9 \mu_B$ y $\mu_{Cr} = 3.7 \mu_B$ [139].

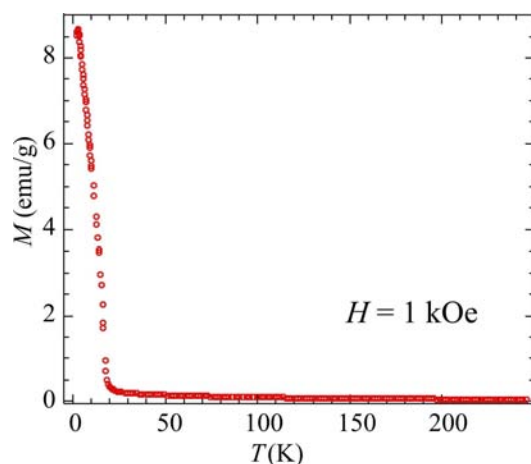


Figura 3.7. Dependencia de la imanación con la temperatura en un compuesto $\text{Cr}_{0.34}\text{Fe}_{0.66}\text{NH}_4(\text{HPO}_4)_2$ de composición inicial $x = 0.3$.

Se realizan medidas de imanación en el compuesto CrFeNP cuando se aplica un campo magnético externo hasta un valor máximo de 140 kOe, obteniéndose las isothermas de imanación a $T = 2, 3, 10, 19, 30$ y 50 K. Se observa que la imanación no alcanza la saturación ni con los valores máximos del campo magnético aplicado. Además, se encuentra que el valor del momento magnético a campo máximo aplicado en el CrFeNP ($1.2 \mu_B/\text{fu}$ a 2 K) es más pequeño que el correspondiente al FeNP ($1.5 \mu_B/\text{fu}$ a 2 K). Una explicación de este hecho, asumiendo que la estructura magnética del CrFeNP a 2 K está totalmente compensada igual que sucede con el FeNP, es suponer que en la fase intermedia la celda unidad magnética está formada por tres iones M^{3+} situados en dos posiciones cristalográficas distintas, formando dos subredes magnéticas. La disposición de los momentos magnéticos en cada subred presenta ordenación ferromagnética, mientras que las subredes se colocan antiparalelamente dando lugar a un momento magnético neto. El motivo magnético estará formado por tres momentos magnéticos paralelos, dos en un sentido y el tercero en sentido contrario, $\uparrow\downarrow\uparrow$. Si uno de los dos momentos, de los que llevan el mismo sentido, corresponde al del ion Cr^{3+} , el momento magnético por fórmula unidad de este compuesto será distinto que el del FeNP, indicando que la ocupación del cromo no es totalmente aleatoria. Serán necesarios análisis con difracción de neutrones para verificar esta hipótesis.

Se ha detectado histéresis magnética en las curvas de imanación a temperaturas bajas, cuando se modifica la magnitud del campo magnético en uno u otro sentido, relacionada con la transición de una fase magnética totalmente compensada a una fase ferrimagnética. Los valores críticos del campo magnético aplicado disminuyen al aumentar la temperatura desde valores de algo más de 1 kOe a 2 K a menos de 0.5 kOe para temperaturas entre 3 y 10 K.

En resumen, se ha sintetizado hidrotérmicamente un nuevo compuesto, el $\text{Cr}_{0.34}\text{Fe}_{0.66}\text{NH}_4(\text{HPO}_4)_2$ isoestructural con el compuesto $\text{FeNH}_4(\text{HPO}_4)_2$. Las curvas TG-DTG indican que presenta una buena estabilidad térmica. Se ha obtenido la energía de activación de la descomposición térmica del CrFeNP en función del grado de conversión, por los métodos isoconversionales MFR y Vyaz, mostrando dos zonas bien diferenciadas que coinciden con las dos pérdidas de masa que experimenta el compuesto. Del análisis del comportamiento magnético se observa que sufre dos transiciones magnéticas: de paramagnético a ferromagnético a $T_C = 17.9$ K y de ferromagnético a antiferromagnético a $T_i = 3.1$ K.

Artículo III

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Hydrothermal synthesis, crystal structure, thermal behaviour and magnetic properties of a new ammonium-chromium-iron(III) bis(hydrogenphosphate)



Isabel Iglesias^a, Belén F. Alfonso^{a,*}, Camino Trobajo^b, José A. Huidobro^c, Zakariae Amghouz^d, David Martínez-Blanco^e, Jesús A. Blanco^a, José R. García^b

^a Dpto. de Física, Universidad de Oviedo, 33007 Oviedo, Spain

^b Dpto. de Química Orgánica e Inorgánica, Universidad de Oviedo-CINN, 33006 Oviedo, Spain

^c Dpto. de Matemáticas, EPI Gijón, Universidad de Oviedo, 33204 Gijón, Spain

^d Dpto. de Ciencia de los Materiales e Ingeniería Metalúrgica, EPI, Universidad de Oviedo, 33204 Gijón, Spain

^e Servicios Científico-Técnicos, Universidad de Oviedo, 33006 Oviedo, Spain

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ABSTRACT

The hydrothermal synthesis and the chemical-physical characterization of an ammonium-chromium(III)-iron(III) bis(hydrogenphosphate), $\text{Cr}_{0.34}\text{Fe}_{0.66}\text{NH}_4(\text{HPO}_4)_2$ [CrFeNP] is reported. It was obtained in aqueous media by reaction between chromium(III) chloride, iron(III) chloride, urea, and orthophosphoric acid. The crystal structure of CrFeNP was determined from single-crystal X-ray diffraction data. It crystallizes in the triclinic system, space group *P*-1, and exhibits two types of different infinite tunnels along [0 1 0] and [1 0 0] directions, where the ammonium cations are located. Thermal analysis shows that the solid is stable up to ca. 600 K. The activation energy of the thermal decomposition up to 1273 K was computed by isoconversional methods. In addition, the magnetic behaviour of the material was investigated from magnetic susceptibility and magnetization measurements. CrFeNP undergoes two successive magnetic transitions at temperatures $T_C = 17.9$ K and $T_I = 3.1$ K, which could be related to a ferri- and an antiferromagnetic magnetic phase transitions, respectively.

1. Introduction

In previous works, we have investigated on the crystal and magnetic structures, and the structural and magnetic phase transitions of some iron phosphates such as $\text{Fe}(\text{NH}_3)_2\text{PO}_4$ [1,2] and $\text{NH}_4\text{Fe}(\text{HPO}_4)_2$ [3–7] finding that both phosphates show unusual magnetic behaviour. On the other hand, the sequential formation of $\text{NH}_4\text{Fe}_2(\text{OH})(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$, $\text{NH}_4\text{Fe}_2(\text{PO}_4)_2$ and, finally, $\text{NH}_4\text{FePO}_4 \cdot \text{H}_2\text{O}$ were achieved in solvothermal conditions starting from $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$, $(\text{NH}_2)_2\text{CO}$ and $(\text{CH}_3)_2\text{CO}$. In the dissolution-precipitation process, a certain structural memory is conserved in iron(III) cation environments, that disappears in the reduction to iron(II) [8]. We have carried out research on the crystal and magnetic structures of polycrystalline ammonium-iron(III) bis(hydrogenphosphate) [FeNP] from neutron powder diffraction, as well as its thermal decomposition and physical properties [3,4]. The body-centred unit cell (described with no conventional space group with a triclinic crystal structure *I*-1 reported by Yakubovich from single crystal X-ray diffraction data [9]) was transformed into a reduced

primitive cell (*P*-1 space group). Combining powder neutron diffraction, magnetization measurements, and specific-heat data, we have studied in detail both the crystal and magnetic structures of $\text{FeND}_4(\text{DPO}_4)_2$ and $\text{FeNH}_4(\text{HPO}_4)_2$ compounds [5–7]. The low symmetry of this structure gives rise to a complex pattern of competing super-exchange interactions between the magnetic moments of two types of Fe^{3+} sites that are responsible for the existence of two magnetic phase transitions. The magnetic moments of the Fe^{3+} ions are arranged ferrimagnetically below $T_C = 17.82 \pm 0.05$ K with magnetic moments $\mu_{\text{FI}} = 4.19 \pm 0.02 \mu_B$ at 4 K. They undergo a magnetic phase transition below $T_I = 3.52 \pm 0.05$ K in order to adopt an antiferromagnetic arrangement with equal moment antiphase structure. This is characterized by a long-period propagation vector close to $k_{\text{AF}} \approx (1/16, 0, 1/16)$ rlu and a magnetic moment for the Fe^{3+} ions of $\mu_{\text{AF}} = 4.41 \pm 0.03 \mu_B$ at 1.5 K, as was clearly evidenced from the temperature dependence of the magnetization under a low applied magnetic field.

This paper reports the hydrothermal synthesis, structural charac-

* Corresponding author.

E-mail address: mabfernandez@uniovi.es (B.F. Alfonso).

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terization and magnetic properties of a new ammonium-chromium(III)-iron(III) bis(hydrogenphosphate). The activation energy of thermal decomposition was obtained using isoconversional methods. Magnetic susceptibility measurements revealed that the sample has ferrimagnetic properties.

2. Materials and methods

2.1. Sample preparation and analytical procedures

$\text{NH}_4\text{Cr}_x\text{Fe}_{1-x}(\text{HPO}_4)_2$ ($0 \leq x \leq 1$) solids were hydrothermally synthesized in a stainless steel Teflon-lined vessel under autogenous pressure from a mixture of $\text{MCl}_3 \cdot 6\text{H}_2\text{O}$ ($\text{M} = \text{Cr}, \text{Fe}$) (1 M, 99%, Merck), H_3PO_4 (85%, Merck), and $(\text{NH}_2)_2\text{CO}$ (solid, 99%, Merck). The total volume of the reaction mixture was 40 mL, and the autoclave was sealed and heated at 453 K during 10 days. The reaction product was filtered off, thoroughly washed with an excess of ionized water until neutral pH, and dried in air at room temperature. When the molar ratio was $\text{C/P} = 0.25$ and $\text{P/M} = 15$ ($\text{M} = \text{Cr}, \text{Fe}$) for metal ratio Cr:Fe of 0:10 light violet crystals of $\text{NH}_4\text{Fe}(\text{HPO}_4)_2$ [FeNP] were obtained, for Cr:Fe of 1:9 brilliant green crystals of $\text{NH}_4\text{Cr}_{0.34}\text{Fe}_{0.66}(\text{HPO}_4)_2$ [CrFeNP] were achieved and for Cr:Fe of 10:0 no precipitated was obtained. The phosphorus, chromium and iron contents of the solids were determined by inductively coupled plasma mass spectrometry (ICP-MS) analysis (Finnigan, Element model) after dissolving a weighed amount in HF (aq). Microanalytical data for nitrogen was obtained with a Perkin Elmer 2400B elemental analyzer.

2.2. Scanning and transmission electron microscopy

SEM micrographs and X-ray microanalysis (SEM/EDX) were recorded using a JEOL-6610LV scanning electron microscope operating at 30 kV and coupled with an Oxford X-Max microanalysis system (EDX). STEM(DF)-EDX and EFTEM studies were performed on a JEOL JEM-2100F field emission transmission electron microscope operated at an accelerating voltage of 200 kV using Gatan 636 Liquid N₂ Cooling holder. Fine powder of the sample was dispersed in ethanol, sonified and sprayed on a carbon-coated copper grid, and then allowed to air-dry. Finally, SOLARUS 950 Advanced Plasma Cleaning System was used to clean samples before observation.

2.3. X-ray diffraction studies

Powder X-ray diffraction (PXRD) patterns were recorded on a Panalytical X'pert PRO MPD X-ray diffractometer with PIXcel detector, operating in the Bragg-Brentano ($\theta/2\theta$) geometry, using $\text{CuK}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). Data were collected at room temperature between 5° and 80° in 2θ with a step size of 0.02° and count time of 10 s per step. The samples were gently ground in an agate mortar in order to minimize the preferred orientation.

Single-crystal X-ray diffraction studies were performed on an Oxford Diffraction Xcalibur Gemini R CCD single crystal diffractometer. The measurements were collected at 293 K, using also $\text{CuK}\alpha$ radiation. The intensities were measured using the ω scan method. The crystal structures were solved by direct methods. A refined absorption correction was applied. Structures were refined by using full-matrix least squares on F₂. Crystallographic calculations were made by using data collection, cell refinement, and data reduction: CrysAlisPRO [10]; program used to solve structure: SUPERFLIP [11] program used to refine structure: SHELXL97 [12], molecular graphics: Mercury [13], software used to prepare material for publication: WinGX publication routines [14].

2.4. Thermal analysis and kinetic data

For the thermal analysis, approximately 15 mg of powder sample was used in a Mettler-Toledo TGA/SDTA851e, in a dynamic nitrogen atmo-

sphere (50 mL min^{-1}) at a heating rate of 10 K min^{-1} . Blank runs were performed previously. The evacuated vaporous were also determined with a Pfeiffer Vacuum Thermo Estar TM GSD301T mass spectrometer. The masses 15 (NH_3) and 18 (H_2O) were tested by using a detector C-SEM, operating at 1200 V, with a time constant of 1 s.

The kinetics of a solid-state reaction, in conditions far from equilibrium and assuming the temperature dependence is given by the Arrhenius equation [15,16], can be described by the general equation

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E}{RT}\right) f(\alpha) \quad (1)$$

where $f(\alpha)$ is the reaction model, α the extent of conversion, that is determined experimentally as a fraction of the total mass loss in the process, T (K) the temperature, t (s) the time, A (s^{-1}) the pre-exponential factor, E (J mol^{-1}) the activation energy, and R ($\text{J mol}^{-1} \text{ K}^{-1}$) the gas constant. For a non-isothermal process with a constant heating rate β , $T = T_0 + \beta t$, the Eq. (1) can be written as

$$\beta \frac{d\alpha}{dT} = A f(\alpha) \exp\left(-\frac{E}{RT}\right) \quad (2)$$

Isoconversional methods were used to carry out the kinetic analysis because they allow estimating the activation energy as a function of the extent of conversion without the need to know either the reaction model or the pre-exponential factor. The basic assumption of these methods is that the reaction rate, for a constant extent of conversion, depends only on temperature [17,18]. A large number of mathematical methods, differential and integral, have been developed to evaluate solid-state kinetics and to get the kinetic parameters from thermal experiment data. The differential methods are very sensitive to the experimental noise and tend to be numerically unstable, especially when the reaction rate is estimated by numerical differentiation of experimental data [19]. The popular differential Friedman method [20] is derived by taking logarithms on the general kinetic Eq. (2)

$$\beta \ln \frac{d\alpha}{dT} = \ln A + \ln f(\alpha) - \frac{E}{RT} \quad (3)$$

For different constant heating rates, by linear fitting Eq. (3) to the experimental data, the activation energy is determined. A modified version of the Friedman method has been proposed by Huidobro et al. [21] in order to reduce noise effects.

Integral methods are widely used in the kinetic analysis in spite of the fact they may lead to important errors in the activation energy values. On the one hand, some approximations are used for estimation of the temperature integral and, on the other hand, their intrinsic inconsistency when the activation energy changes with α [16,22]. In order to avoid these drawbacks, incremental integral methods were developed assuming that activation energy is constant in a small interval. Vyazovkin proposed an advanced non-linear method [23,24] where the activation energy is obtained by minimization of the function

$$\Phi(E_\alpha) = \sum_{i=1}^n \sum_{j \neq i}^n \frac{J_i(E_\alpha)}{J_j(E_\alpha)} \quad (4)$$

where

$$J_i(E_\alpha) = \int_{t_{\alpha-\Delta\alpha}}^{t_{\alpha_i}} \exp\left(-\frac{E_\alpha}{RT_{\alpha,i}}\right) dt \quad (5)$$

In this study, the modified Friedman (MFR) and the Vyazovkin (Vyaz) procedures were applied. In any case, the physical meaning of the obtained results should be treated with care [25].

In order to check the values obtained for the apparent activation energy, the factor $c_\alpha = Af(\alpha)$ has been computed directly from Eq. (1). After computing the activation energy by each method mentioned above, for a fixed value of α , the product $Af(\alpha)$ can be obtained by fitting Eq. (6) to the experimental data

$$\beta_i \frac{d\alpha(T_{\alpha,i})}{dT} = c_\alpha \exp\left(-\frac{E_\alpha}{RT_{\alpha,i}}\right) \quad (6)$$

for $i = 1, \dots, n$. This means the points $\left(\exp\left(-\frac{E_\alpha}{RT_{\alpha,i}}\right), \beta_i \frac{d\alpha(T_{\alpha,i})}{dT}\right)$ are on a straight line passing through the origin and whose slope $Af(\alpha)$ can be obtained by the least-squares method. Then $Af(\alpha)$ corresponds to the minimum of the function

$$k(c) = \sum_{i=1}^n \left[\beta_i \left(\frac{d\alpha}{dT} \right)_{\alpha,i} - Af(\alpha) \exp\left(-\frac{E_\alpha}{RT_{\alpha,i}}\right) \right]^2 \quad (7)$$

that can be obtained by differentiation and equalling zero. Then, by solving the differential Eq. (2) the experimental $\alpha - T$ curves were reconstructed and compared with those obtained in the laboratory [26,27]. This algorithm, as all computations in this study, has been implemented in MatLab.

2.5. Magnetic measurements

DC magnetic susceptibility measurements were performed using a Quantum Design PPMS-14T magnetometer in the temperature range $2 \leq T$ (K) ≤ 300 under an applied magnetic field of 1 kOe. The temperature dependence of DC magnetization of CrFeNP was measured under zero field cooled ZFC and field cooled FC conditions. In ZFC mode, the sample was cooled from 300 K to 2 K in the absence of magnetic field, followed by the application of 10 Oe and 1 kOe magnetic field values at 2 K and magnetization data were recorded while increasing the temperature up to 300 K. In FC mode, the sample was cooled from 300 K in the presence of the magnetic field of 1 kOe. Magnetization curves as a function of the magnetic field were measured using the same magnetometer under magnetic fields up to 140 kOe at 2, 3, 10, 19, 30 and 50 K. No changes have been observed in the sample after the magnetic measurements.

3. Results and discussion

3.1. Morphological and structural results

SEM images of CrFeNP and FeNP are shown in Fig. 1a and b respectively. Both materials present a similar morphology, and they crystallize quite well with a plates-habit whose thickness varies between 0.1 and 7.5 μm . A large number of the thin plates are agglomerated in a structure similar to the 'desert rose'.

TEM image corresponding to CrFeNP is displayed in Fig. 2. The 2a BF-STEM and 2b DF-STEM images with EDX line profiles of Cr (green), and Fe (red) referred to the yellow line, measured in STEM mode along one plate of the solid revealed the presence of a chromium-iron mixed phosphate. An electron diffraction (SAED) pattern along $[-1\ 1\ 0]$ direction was performed in a selected zone, see Fig. 2c. The 3D electron diffraction tomography (Fig. 2d) of a nanocrystal reveals a triclinic cell with $a = 7.61$ \AA , $b = 8.45$ \AA , $c = 9.91$ \AA , $\alpha = 65.3^\circ$, $\beta = 70.8^\circ$, $\gamma = 71.1^\circ$.

The powder X-ray pattern of this compound, collected at room temperature, shows that it is isostructural with the monoclinic FeNP. Cell parameters reported from single-crystal X-ray experiments on FeNP by Yakubovich [9] were used as starting point. Indexing for the CrFeNP was performed with TREOR90 and Dicvol04 on the basis of the first 30 observed lines. They crystallize in the triclinic system and the space group $P-1$. Suitable single crystals were selected for the data collection and structure determination of FeCrNP and FeNP. The $\text{Cr}^{3+}/\text{Fe}^{3+}$ mixed occupation of the two inequivalent metal sites in FeCrNP was refined. The detailed crystallographic data and the structure refinement parameters for single-crystal studies are summarized in Table 1. Concerning to the occupation of the transition metal ions within the crystallographic unit cell, it is worth noting that the fact that

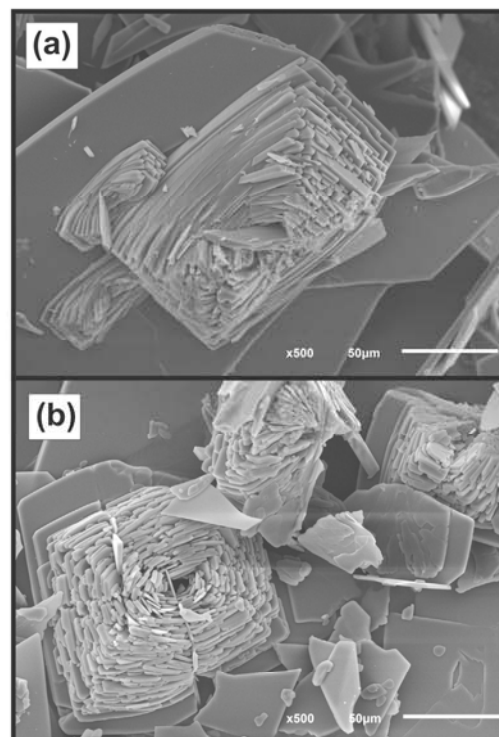


Fig. 1. SEM images showing the morphology of (a) CrFeNP and (b) FeNP samples.

the X-ray form factors of Cr^{3+} ($Z = 24$) and Fe^{3+} ($Z = 26$) are not very different from each other makes very difficult to ascertain any trend about preferential or random occupation using X-ray diffraction data. However, the magnetic data seems to suggest the existence of a certain preferential occupation, as will be discussed below.

The crystal structure of CrFeNP consists of octahedral $(\text{Fe}/\text{Cr})\text{O}_6$ which are sharing corners with tetrahedrons PO_4 so that each octahedron is surrounded by six tetrahedrons while each tetrahedron is bonded to three octahedrons through one oxygen and one hydrogen through the fourth oxygen. The primitive unit cell contains three M^{3+} ($\text{M} = \text{Cr}, \text{Fe}$) ions in two different crystallographic sites with dissimilar local symmetry: one M1 ion located at the spatial inversion center and two M2 ions located on a site with only the identity symmetry. The asymmetric unit, shown in Fig. 3, comprises one and a half independent M^{3+} ions, three PO_4 groups and one and a half independent ammonium cations (N1 and N2). The bond distances metal-oxygen in the octahedron are in the range of 1.940(2)–2.039(2) \AA [1.942(3)–2.063(3) \AA for FeNP], and the *cis* and *trans* bond angles are in the range 84.28(9)–94.31(10) $^\circ$ [84.82(13)–94.27(14) $^\circ$ for FeNP] and 172.00(9)–180 $^\circ$ [171.88(14)–180 $^\circ$ for FeNP] respectively. The bond distances P-O in the tetrahedron are in the range of 1.496(2)–1.592(2) \AA [1.504(3)–1.594(3) \AA for FeNP], and the O-P-O angles vary from 104.28(13) $^\circ$ to 112.77(13) $^\circ$ [102.47(18) $^\circ$ to 113.47(19) $^\circ$ for FeNP]. The anionic framework contains two types of different infinite tunnels along $[0\ 1\ 0]$ and $[1\ 0\ 0]$ directions, where the ammonium cations are located and the negative charge is balanced by NH_4^+ . Fig. 4a and b show that both different tunnels are constructed by four $(\text{Cr}/\text{Fe})\text{O}_6$ octahedrons and four PO_4 tetrahedrons. In this compound, hydrogen-bonded network (Table 2) exists between ammonium cations and coordinating and non-coordinating oxygen atoms of the HPO_4 groups. The non-coordinating oxygen atoms (O3, O7 and O11) and coordinating oxygen atoms (O8, O1 and O6) of the HPO_4 groups also participate

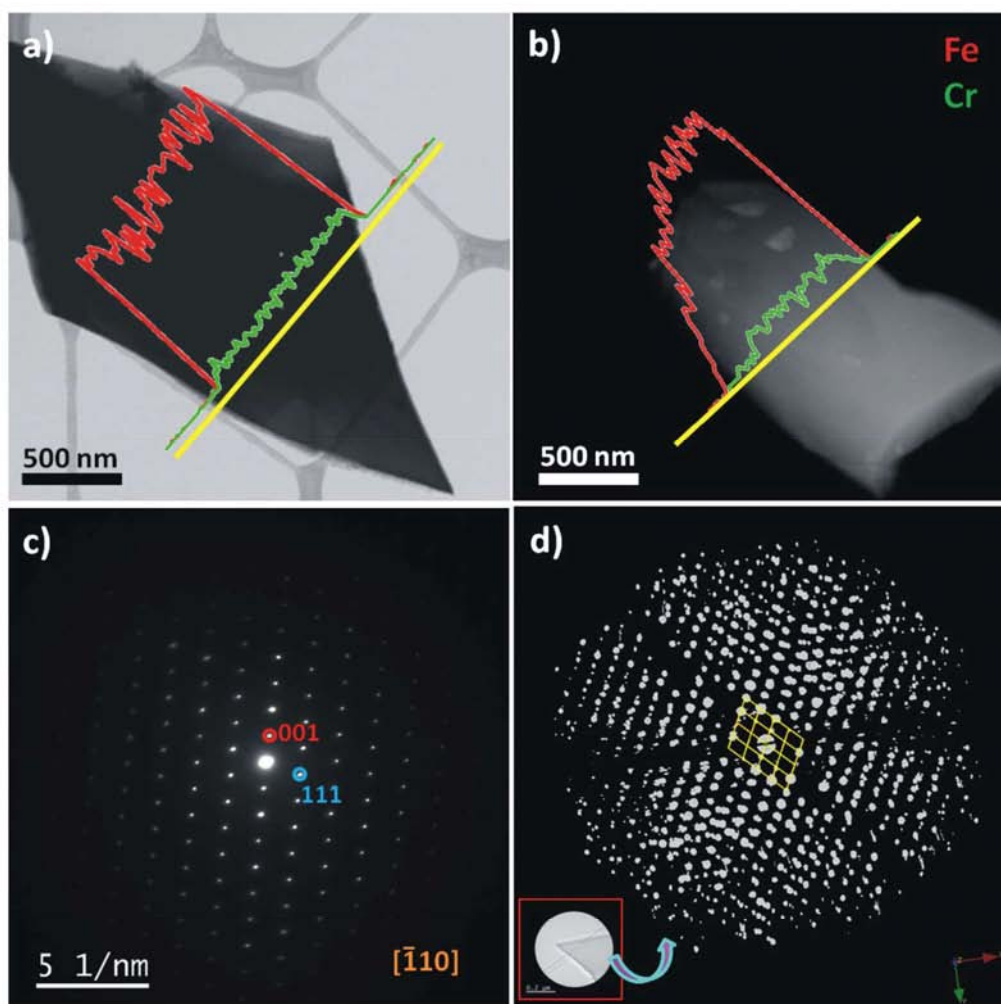


Fig. 2. TEM images for CrFeNP: (a) BF-STEM and (b) DF-STEM images and the corresponding composition profiles of Cr (green) and Fe (red) referred to the yellow line (EDX line scan). (c) Selected area electron diffraction (SAED) pattern along $[-110]$ zone. (d) The 3D electron diffraction tomography of a nanocrystal reveals a similar cell to that obtained by X-ray single crystal.

in extensive hydrogen bonding.

3.2. Thermal decomposition: thermogravimetric and kinetic analysis

The TG-DTG-DTA profiles in an inert atmosphere for CrFeNP depicted in Fig. 5a, show that the compound is stable up to ca. 600 K; then, two mass losses occur, the second one at ca. 900 K. The on-line mass spectrometric analysis of the evacuated vapors in the thermogravimetric experiment indicates that the mass spectrometric curve related to water has two maxima, while that associated with ammonia has only one coinciding with the second stage of water loss, see Fig. 5b. Comparing Fig. 5a and c one can observe that the substitution of Fe^{3+} for Cr^{3+} ions in the parent compound has an insignificant effect on the thermal stability. Note that the thermal decomposition of FeNP is shown in Fig. 5c.

The determination of the kinetic parameters of thermal decomposition of CrFeNP was performed from thermogravimetric data obtained in the temperature range 298–1273 K, under a nitrogen atmosphere, using different heating rates $\beta = 2.5, 5, 10, 15$ and 20 K min^{-1} . The isoconversional methods MFR and Vyaz were applied to

evaluate the activation energy as a function of the extent of conversion. An increment $\Delta\alpha = 0.01$ was considered for the computation. In Fig. 6 two zones for the activation energy are observed. In the $0.05 \leq \alpha \leq 0.30$ conversion range, the E is about 150 kJ mol^{-1} , concerning to the first step of water loss. In the $0.70 \leq \alpha \leq 0.90$ conversion range, using the Vyazovkin method, the values obtained for E are about 300 kJ mol^{-1} that correspond to the second step of water and ammonia loss. The values of E calculated by the MFR method in the second α -range are slightly greater than 300 kJ mol^{-1} , a similar behaviour was observed in the activation energy values of FeNP. Although the shape of the $E - \alpha$ curves is quite similar, the activation energy values calculated by differential and non-linear isoconversional methods are slightly higher for CrFeNP than FeNP compound [26]. The thermal decomposition of CrFeNP is less smooth than that for FeNP as shown the TG curves, see Fig. 5a (CrFeNP) and 5c (FeNP). This fact is better noticed by the Friedman method because, in general, the differential isoconversional methods are more sensitive to experimental variations than other procedures. The product $Af(\alpha)$ has been computed by the two aforementioned isoconversional methods [27]. Then, the general kinetic differential Eq. (2) could be solved. The experimental and recon-

Table 1
Crystal data and structure refinements at room temperature for CrFeNP and FeNP.

	CrFeNP	FeNP
Empirical formula	Cr _{1.02} Fe _{1.98} N ₃ O ₂₄ P ₆	Fe _{1.5} H ₁₁ N _{1.5} O ₁₂ P ₃
Crystal system	Triclinic	Triclinic
Space group	<i>P</i> -1 (No. 2)	<i>P</i> -1 (No. 2)
Crystal size (mm)	0.18 × 0.08 × 0.06	0.06 × 0.04 × 0.02
<i>a</i> (Å)	7.1661(3)	7.1685(6)
<i>b</i> (Å)	8.8377(5)	8.8447(7)
<i>c</i> (Å)	9.4544(6)	9.4625(8)
<i>α</i> (°)	64.810(6)	64.812(8)
<i>β</i> (°)	70.213(5)	70.227(8)
<i>γ</i> (°)	69.397(5)	69.436(8)
<i>V</i> (Å³)	494.42(5)	495.53 (7)
<i>Z</i>	1	2
<i>D_x</i> (g cm⁻³)	2.605	2.686
<i>F</i>(000)	379	403
Reflections	2994	2963
Restraints	1	15
Parameters	168	193
w<i>R</i> (F²)	0.0907	0.1112
R[F² > 2σ(F²)]	0.0383	0.0578
<i>S</i> (°)	1.089	1.045

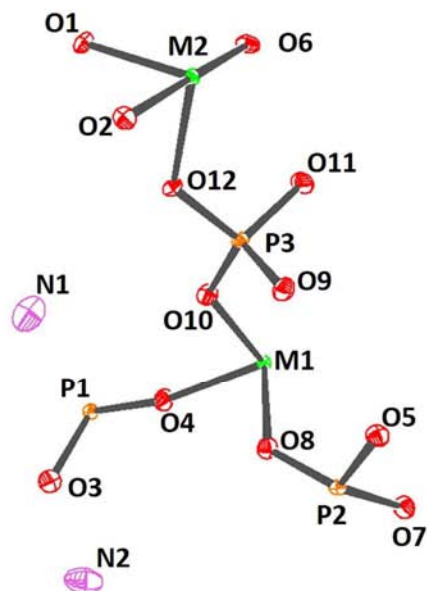


Fig. 3. ORTEP diagram of the asymmetric unit of CrFeNP.

structured extent of conversion as a function of temperature curves for $\beta = 2.5$ and 20 K min^{-1} are shown in Fig. 7a and b, respectively. A good agreement with the experimental data for both MFR and Vyaz methods has been achieved.

3.3. Magnetic properties

To understand the current magnetic results of CrFeNP we have to compare with those of polycrystalline FeNP previously described in Refs. [5,6]. At first glance, the temperature dependence of the magnetic susceptibility of both materials seems to be similar. Fig. 8 presents the temperature dependence of the magnetic molar susceptibility χ_M as well as the temperature dependence of M/H under 10 Oe and 1 kOe measured in ZFC and FC conditions. Firstly, χ_M increases below ca 18 K (T_C) until $T_f \approx 3 \text{ K}$, then sharply decreases down to our measurement temperature 2 K. This behaviour is consistent with a sequence of

magnetic states (similar to that found previously in FeNP), i.e., paramagnetic (PM), ferrimagnetic (FI) and antiferromagnetic (AF) states with decreasing temperature. The Curie temperature, defined by the minimum on dM/dT curve, has been determined to be $T_C = 17.9 \text{ K}$ and the temperature of the second magnetic phase transition $T_f = 3.1 \text{ K}$. Secondly, concerning to the ZFC and FC measurements (see the inset (a) of Fig. 8), the low magnetic data collected under 10 Oe show thermomagnetic irreversibility below the Curie temperature $T_C = 17.9 \text{ K}$ down to $T_f = 3.1 \text{ K}$, within the ferrimagnetic phase. A sharp change in the magnetization is observed at T_C under 10 Oe when compared to that found under 1 kOe (see the inset (b) of Fig. 8), even the 10 Oe ZFC seems to indicate the presence of a small broaden Hopkinson peak, which would be related to domain wall pinning effects and domain wall displacement under low applied magnetic fields. However, no divergence between the ZFC and FC magnetic susceptibilities is observed under a magnetic field of 1 kOe (see the inset (b) of Fig. 8), indicating that for a value of the magnetic field larger than that the Zeeman energy is overcoming the magneto-crystalline one.

The paramagnetic susceptibility follows a Curie-Weiss law in the temperature range of 300–50 K, but on approaching T_C , the susceptibility deviates from the universal Curie-Weiss (C-W) law. A more appropriate way to identify the magnetic order comes from Neel's mean field theory of ferrimagnetism [28], which suggests a hyperbolic shape for the temperature dependence of the inverse of paramagnetic susceptibility for a ferrimagnet and a straight line for a ferromagnet. Then, the inverse molar magnetic susceptibility was fitted to the Néel expression of a ferrimagnetic material, see Fig. 9.

$$\frac{1}{\chi_M} = \frac{T - \Theta_p}{C} - \frac{\gamma}{T - \Theta} \quad (8)$$

The obtained parameters are $\Theta_p = -58.63 \text{ K}$, $C = 3.63 \text{ emu K (mol Oe)}^{-1}$, $\gamma = 37.03 \text{ mol Oe (emu K)}^{-1}$, $\Theta = 16.43 \text{ K}$. These values are close to those found previously in FeNP, suggesting that the magnetic orderings involved in FeCrNP could be similar to those found in the parent compound FeNP, although the exchange interactions may be slightly modified. The negative value of Θ_p indicates antiferromagnetic interactions between the two sublattice magnetic moments corresponding to two different crystallographic sites of M^{3+} ions, i.e., those ions that are located in different sublattices, while the positive value of Θ implies the development of ferromagnetic coupling between ions in the same sublattice. A numerical measure of the error of the fit is given by the sum of the square errors

$$SSE = \frac{1}{n} \sum_{i=1}^n (y_i^* - y_i)^2 \quad (9)$$

that can be normalized to

$$R^2 = 1 - \frac{SSE}{SST} \quad (10)$$

where

$$SST = \frac{1}{n} \sum_{i=1}^n (y_i - \bar{y})^2 \quad (11)$$

with $y_i^* = f(x_i)$ and $\bar{y} = \sum_{i=1}^n y_i / n$, the average. When $R^2 = 1$, all points lie on the curve with no scatter. The value of R^2 coefficient is 0.9999.

The effective magnetic moment $\mu_{\text{eff}} = 5.4 \mu_B$ calculated from the Eq. (8) is very close to the theoretically calculated value $\mu_{\text{eff}}^{\text{calc}} = 5.3 \mu_B$, obtained applying the expression

$$\mu_{\text{eff}}^{\text{calc}} = \sqrt{x\mu_{Cr}^2 + (1-x)\mu_{Fe}^2} \quad (12)$$

when considering the experimental values of the paramagnetic moments of Fe^{3+} ($5.9 \mu_B$) and Cr^{3+} ($3.7 \mu_B$) [29]. In contrast, for FeNP the effective paramagnetic moment was found to be around $5.8 \mu_B$, which is quite close to the free-ion value of Fe^{3+} , $5.92 \mu_B$.

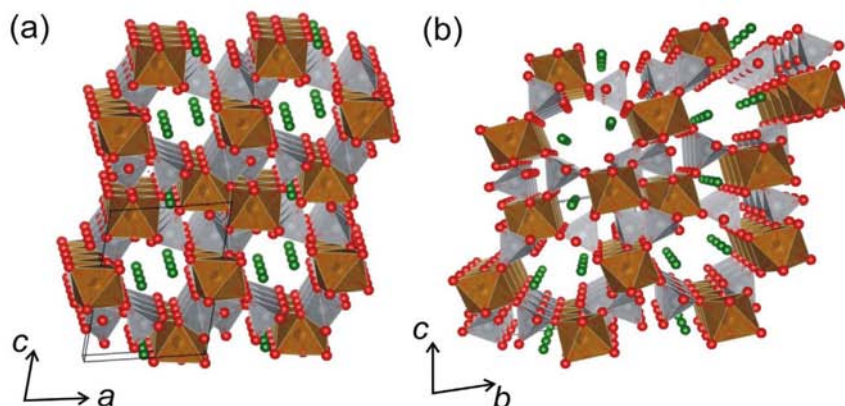


Fig. 4. Projection of the structure of CrFeNP viewed down (a) the *b*-axis and (b) the *a*-axis. PO₄ tetrahedra, Cr/FeO₆ octahedra, and N green circles.

Table 2
Selected hydrogen-bond geometry for CrFeNP.

D – H...A	D – H (Å)	H...A (Å)	D...A (Å)	D – H...A (deg.)
N1–H1...O10 ⁱ	0.98(2)	2.07(2)	3.048(4)	171(4)
N1–H2...O7 ⁱⁱ	0.99(2)	1.97(3)	2.920(4)	158(3)
N1–H3...O1 ⁱⁱⁱ	0.98(3)	2.05(4)	2.849(4)	138(1)
N1–H4...O4 ^{iv}	0.98(4)	2.72(4)	3.613(6)	152(5)
N1–H4...O8 ^{iv}	0.97(3)	2.61(5)	3.289(5)	127(5)
P1–O3–H5...O8 ^{iv}	0.99(3)	1.76(4)	2.731(3)	167(4)
P2–O7–H6...O1 ^v	0.97(5)	1.73(5)	2.699(4)	172(4)

Symmetry code: (i) *x*, *y*, *z*; (ii) *x* + 1, *y* – 1, *z*; (iii) –*x* + 1, –*y* – 1, –*z* + 1; (iv) –*x* + 1, –*y*, –*z* + 1; (v) *x* – 1, *y* + 1, *z*.

In order to understand the magnetic response of CrFeNP we have also performed magnetization measurements up to applied magnetic fields of 140 kOe. Fig. 10 shows isothermal magnetization curves at 2, 3, 10, 19, 30 and 50 K temperatures (the upper-part inset of Fig. 10 shows the magnetization curves in the first quadrant for $0 \leq H$ (kOe) ≤ 2.5 at 2, 3, 10 and 19 K). As can be seen from Fig. 10 the magnetization does not saturate even at 140 kOe, in the same way as was also observed in FeNP. Besides that, the smaller value of the magnetic moment under 140 kOe for FeCrNP ($1.2 \mu_B/\text{fu}$ at 2 K) when compared to that of FeNP ($1.5 \mu_B/\text{fu}$ at 2 K) could be explained in the following way: owing to the existence of two non-equivalent magnetic sublattices and assuming that the magnetic structure at 2 K in FeCrNP within the AF phase is the same as that of FeNP, i.e., a full compensated AF structure with a magnetic block unit consisting of two-up magnetic moments and one-down magnetic moment, the preferential substitution of one-Fe³⁺ magnetic moment ($\sim 4.8 \mu_B$) which is parallelly coupled in the block unit by one-Cr³⁺ magnetic moment ($\sim 3 \mu_B$) could lead to a smaller magnetic moment per formula unit, which is what is observed experimentally. This fact could indicate that the substitution of Fe by Cr in this compound is not totally random and that the Cr³⁺ ions prefer to occupy the 2i sites rather than the 1e ones within the crystallographic unit cell. Further experiments using neutron diffraction will be needed to elucidate this issue.

On the other hand, the latter remark is concerning to the nature of the metamagnetic process detected in the magnetization curves at low temperatures (see Fig. 10). The existence of magnetic hysteresis, as the direction of the magnetic field sweep is reversed (see inset of Fig. 10), is related to a first-order magnetic phase transition from the full compensated AF ordering to a ferrimagnetic phase when increasing the magnitude of the applied magnetic field. The critical values of the applied magnetic field decrease when the temperature rises, passing

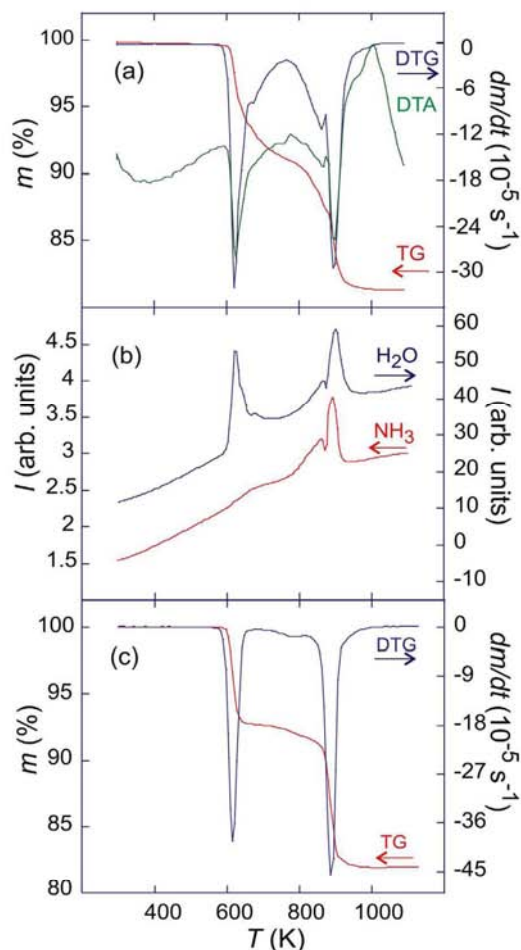


Fig. 5. (a) TG, DTG and DTA curves of CrFeNP obtained at 10 K min⁻¹ heating rate. (b) MS signals of evacuated vapors on the TG-experiment: *m/z* 15, NH₃ and *m/z* 18, H₂O for CrFeNP. (c) TG and DTG curves of FeNP.

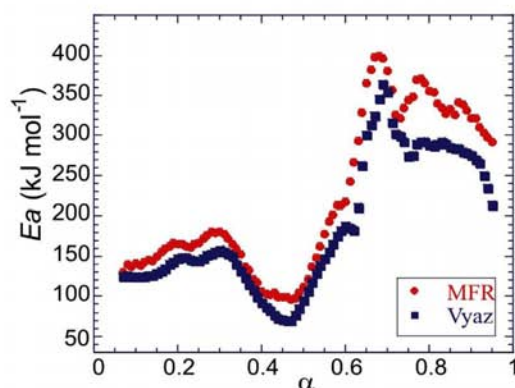


Fig. 6. Activation energy versus extent of conversion of CrFeNP.

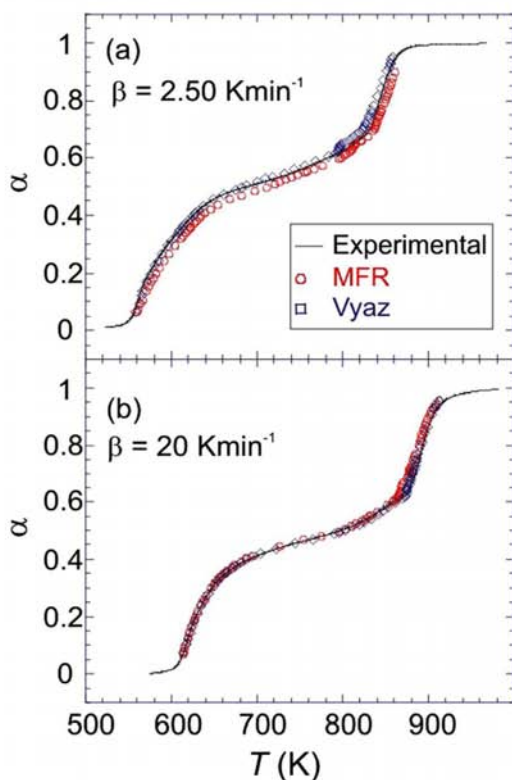


Fig. 7. Experimental and reconstructed $\alpha - T$ curves for CrFeNP (a) at 2.5 K min^{-1} and (b) at 20 K min^{-1} .

from around 1 kOe (2 K) to less than 0.5 kOe for temperatures in the interval $3 \text{ K} < T < 10 \text{ K}$ (see inset of Fig. 10).

As a result, we have seen that the magnetic properties of FeCrNP, when the substitution of $1/3$ of Fe^{3+} ions in FeNP [4] for Cr^{3+} ions is performed, can be understood in a simple way just comparing the present results with those found previously in FeNP. Beyond this fact, what the present findings really highlight is the interest in investigating different Fe/Cr substitutions in order to explore the modifications in the exchange interactions caused by this Fe-Cr substitution in this hydrogenphosphate $\text{FeNH}_4(\text{HPO}_4)_2$.

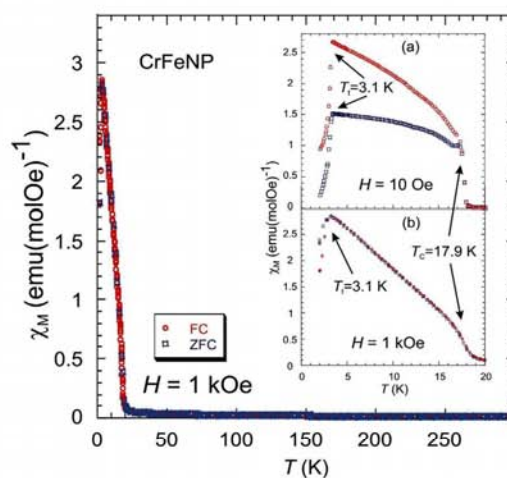


Fig. 8. Temperature dependence of the molar magnetic susceptibility (χ_M) for CrFeNP. The inset shows the temperature dependence of χ_M measured under 10 Oe (a) and 1 kOe (b) between 2 K and 20 K.

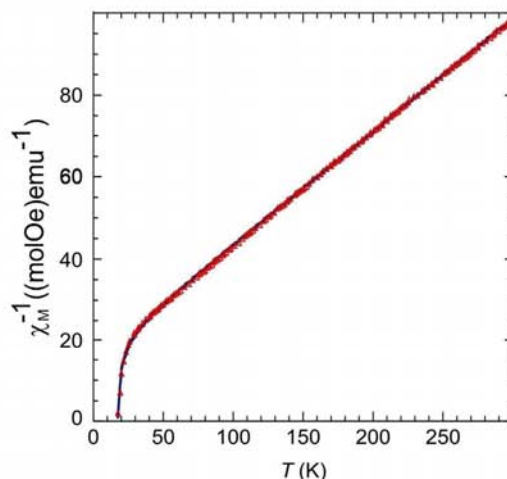


Fig. 9. Temperature dependence of the reciprocal molar magnetic susceptibility (χ_M^{-1}) for CrFeNP.

4. Conclusions

We report the hydrothermal synthesis and characterization of a new crystalline ammonium-chromium(III)-iron(III) bis(hydrogenphosphate), $\text{Cr}_{0.34}\text{Fe}_{0.66}\text{NH}_4(\text{HPO}_4)_2$. This compound is isostructural with the ammonium-iron(III) bis(hydrogenphosphate), $\text{FeNH}_4(\text{HPO}_4)_2$. It crystallizes in the triclinic system, space group $P-1$. The TG-DTG curves show that CrFeNP possesses good thermal stability and the mass spectrometric curves related to water and ammonium indicate that the mass losses are in two steps. The application of isoconversional methods (MFR and Vyaz) allowed us to evaluate the activation energy in each step as a function of the extent of conversion for the compounds. The reconstructed $\alpha - T$ curves show a good agreement with the experimental data. It undergoes two magnetic phase transitions: paramagnetic to ferrimagnetic at $T_c = 17.9 \text{ K}$ and ferrimagnetic to antiferromagnetic at $T_i = 3.1 \text{ K}$ as the temperature decreases. These transition temperatures are lower than the corresponding ones for $\text{FeNH}_4(\text{HPO}_4)_2$. We attribute the double magnetic phase transition and the reduction of the magnetization values at low temperatures to the

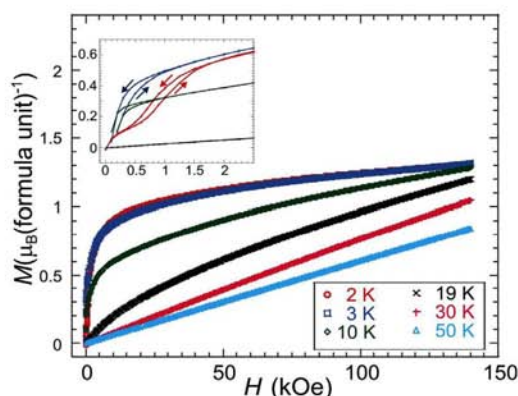


Fig. 10. Magnetization isotherms for CrFeNP measured up to magnetic fields of 140 kOe at selected temperatures. The upper-part inset shows the magnetization curves for $0 \leq H$ (kOe) ≤ 2.5 at 2, 3, 10 and 19 K.

role of the two non-equivalent magnetic sublattices of the Fe^{3+} and $\text{Cr}^{3+}/\text{Fe}^{3+}$ ions. In brief, the presence of chromium in the iron lattice positions in the FeNP structure causes changes in both the thermal behaviour and the magnetic properties of the compounds.

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4. CONCLUSIONES

4. Conclusiones

Las publicaciones recogidas en esta memoria muestran los resultados relativos a la obtención y caracterización de fosfatos metálicos y al estudio cinético de su descomposición térmica. Las conclusiones más relevantes se presentan a continuación.

En la investigación realizada para la determinación y validación de los parámetros cinéticos destacan los siguientes aspectos:

1. Se ha desarrollado una modificación al método isoconversional diferencial de Friedman.
 - El método modificado de Friedman es menos sensible al ruido experimental que el método de Friedman.
 - El método modificado no necesita utilizar ninguna aproximación para la determinación de los parámetros cinéticos, y su implementación es similar al método sin modificar.
 - La evaluación del método modificado se realizó aplicándolo a casos simulados teóricamente. Los resultados mostraron que proporciona valores más precisos de la energía de activación que el método de Friedman.
 - Se calculó la dependencia de la energía de activación con el grado de conversión en el proceso de descomposición térmica de la sal $\gamma\text{-Ti}(\text{PO}_4)(\text{NH}_4\text{HPO}_4)$ mediante los métodos isoconversionales de Friedman, modificado de Friedman (utilizando tres y cinco puntos) y el método integral de Kissinger-Akahira-Sunose. Los resultados obtenidos para la conversión utilizando el método modificado de Friedman están más próximos a los experimentales que los obtenidos con los otros métodos.
2. Se ha presentado un procedimiento para obtener un modelo discreto que describa la velocidad de reacción de un proceso térmico en función del grado de conversión y la temperatura.
 - Este procedimiento puede aplicarse siempre independientemente del método usado para determinar la energía de activación.
 - El modelo discreto permite chequear los parámetros cinéticos obtenidos por cualquier método y predecir los comportamientos (cinéticos) a

velocidades de calentamiento diferentes a las utilizadas experimentalmente.

- Se evaluó el comportamiento del modelo aplicándolo a simulaciones teóricas, siendo su respuesta completamente satisfactoria.
 - Se utilizó el modelo discreto para chequear los valores de la energía de activación obtenida aplicando los métodos isoconversionales de: Friedman, modificado de Friedman, Kissinger-Akahira-Sunose y Vyazovkin en la descomposición térmica del fosfato $(\text{NH}_4)_2\text{Th}(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$. El procedimiento propuesto describe, en todos los casos, adecuadamente la cinética de la reacción de descomposición.
3. En relación con el estudio de fosfatos de metales de transición con más de un átomo magnético se ha sintetizado hidrotermalmente y caracterizado un nuevo compuesto cristalino, el bis(hidrogenofosfato) de amonio-cromo(III)-hierro(III), $\text{Cr}_{0.34}\text{Fe}_{0.66}\text{NH}_4(\text{HPO}_4)_2$. Se resumen sus propiedades más relevantes en los puntos siguientes:
- Cristaliza en el sistema triclinico, grupo espacial $P-1$. Su estructura está formada por octaedros $(\text{Fe}/\text{Cr})\text{O}_6$ que comparten vértices con tetraedros PO_4 . La celda primitiva está formada por tres iones M^{3+} ($\text{Fe}^{3+}/\text{Cr}^{3+}$) que ocupan dos posiciones cristalográficas diferentes. La estructura cristalina presenta dos túneles infinitos en las direcciones $[0\ 1\ 0]$ y $[1\ 0\ 0]$ donde se localizan los cationes amonio.
 - Se han determinado los parámetros cinéticos de la descomposición térmica aplicando diferentes métodos isoconversionales, obteniéndose modelos cinéticos muy similares. El cálculo de la energía de activación de su descomposición térmica muestra dos zonas diferenciadas que coinciden con las pérdidas de agua y amoniaco que experimenta el compuesto.
 - Los parámetros cinéticos, obtenidos por los métodos: modificado de Friedman y Vyazovkin se han chequeado, reconstruyendo las curvas $\alpha - T$. Los valores obtenidos muestran una alta coincidencia con las experimentales.

- Desde el punto de vista magnético se observan dos transiciones, al disminuir la temperatura, de paramagnético a ferrimagnético a $T_C = 17.9$ K y de ferrimagnético a antiferromagnético a $T_I = 3.1$ K.

5. REFERENCIAS

5. Referencias

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6. INFORMACIÓN SUPLEMENTARIA

Artículo S1

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Modeling Chemical Kinetics in Solid State Reactions

J.A. Huidobro, I. Iglesias, B.F. Alfonso, C. Trobajo, and J.R. Garcia

Abstract This work deals with the kinetics of thermally stimulated processes which take place in the solid state phases. The activation energy of the solid is calculated using several methods of different families of isoconversional methods (differential, integral and incremental). A model of the kinetics is obtained by a method independent from the procedure used to compute the activation energy and it is analysed in three theoretical simulations as well as the thermal degradation of $\text{FeNH}_4(\text{HPO}_4)_2$. The reconstructed $\alpha - T$ curves of the simulations and the experimental case indicates that the model works properly.

1 Modeling Kinetics

The study of kinetics in solid state reactions explains the mechanism of the chemical processes as well as the meaning of the related parameters. It provides qualitative and quantitative information on phase transformations, crystallization, thermal decomposition, etc. Several analysis techniques such as Thermogravimetric Analysis (TGA), have been developed to measure physical and chemical changes.

A simple stimulated thermal reaction follows a scheme in the form $Re \rightarrow P + S$ where Re is the reactant, P the solid product and S is the solvent or water vapour. The reaction progress is given by the extent of conversion $\alpha(t) = (m_0 - m(t))/(m_0 - m_f)$

J.A. Huidobro (✉)
Departamento de Matematicas, Universidad de Oviedo, Gijón, Spain
e-mail: jahuidobro@uniovi.es

I. Iglesias • B.F. Alfonso
Departamento de Física, Universidad de Oviedo, Gijón, Spain
e-mail: iis@uniovi.es; mbafernandez@uniovi.es

C. Trobajo • J.R. Garcia
Departamento de Química Organica e Inorganica, Universidad de Oviedo, Oviedo, Spain
e-mail: ctf@uniovi.es; jrgm@uniovi.es

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jahuidobro@uniovi.es

where $m(t)$ is the mass of *Re* at time t and m_0 and m_f are the initial and final masses, respectively. These reactions are commonly described by the equation

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E}{RT}\right) f(\alpha) \quad (1)$$

where T is the temperature, R the universal gas constant, A the pre-exponential factor, E the activation energy and $f(\alpha)$ the model function [5].

The knowledge of A , E and $f(\alpha)$, the called kinetic triplet, allows solving Eq. (1) and so a description of the process can be obtained. In the model-fitting methods, the obtention of the kinetic triplet is based on the determination of the model function by fitting several reaction models to the experimental data and then the coefficients A and E are computed. But different forms of $f(\alpha)$ with disparate values of A and E can be fitted to the data and then these methods are not recommended [6].

In isoconversional methods the activation energy is computed without knowing the model function or the pre-exponential factor [7]. Consequently, a model of the process based on Eq. (1) cannot be obtained. Some authors [4, 8] have proposed different methods in order to calculate the product $Af(\alpha)$, considered as a sole factor, depending on how the activations energy has been computed. The main purpose of this study is to analyse the behaviour of a method to compute $Af(\alpha)$, independent of the procedure used to compute the activation energy, when it is applied to three theoretical simulations as well as the thermal degradation of $\text{FeNH}_4(\text{HPO}_4)_2$.

Mechanisms of chemical transformations are indeed complicated, they usually involve more than a single reaction. Then, Eq. (1) must be understood as an approximation to describe the process, the kinetic parameters are considered as apparent parameters and their physical meaning should be carefully analysed.

One of the simplest isoconversional methods is that proposed by Friedman (FR) [2], which is a differential isoconversional method. For a constant heating rate program of temperature $T = T_0 + \beta t$ and taking logarithms, Eq. (1) turns into

$$\ln\left(\frac{d\alpha(T)}{dT} \beta\right) = \ln(Af(\alpha(T))) - \frac{E}{RT} \quad (2)$$

where now $\alpha(T)$ represents the dependence of the extent of conversion respect to the temperature. Several runs with different heating rates β_i , $i = 1, \dots, n$ with $n \geq 3$ are carried out and n experimental $\alpha - T$ curves are obtained. Thus, for a fixed value of α and from each experimental curve, values for T_i and $d\alpha(T_i)/dT$ are obtained. Then, from Eq. (2), the points $(1/T_i, \ln(d\alpha(T_i)/dT)\beta_i)$ belong to a straight line whose slope is $-E_\alpha/R$. The activation energy E_α can be obtained by fitting to the experimental data.

Wu et al. [8] extended this method by computing not only E but also $\ln(Af(\alpha(T)))$ and then, the product $Af(\alpha)$ is known and the differential Eq. (1) can be solved.

Generally, one drawback of this method is its sensitivity to noise that can come from numerical differentiation or experimental measures. A method (MFR) to

diminish this effect was proposed in [3] where Eq. (2) is considered for more values of α . Then, by fitting to the experimental data, the activation energy is computed.

Less sensitive to noise are integral isoconversional methods that consider an integral form of Eq. (1) but $\exp(-E/(RT))$ does not have a suitable antiderivative and some approximations have been proposed. They are based on assuming E is constant over the whole process and this is not very common. One of these is the generalized Kissinger method [1] (KAS), widely used. Vyazovkin [5] introduced a non-linear method (Vyaz) by integration of Eq. (1) over $[\alpha^* - \Delta\alpha^*, \alpha^*]$ and Samuelsson [4] computed $Af(\alpha)$, assuming it is constant over the interval.

A different idea, where this assumption is not necessary, is to compute the factor $Af(\alpha)$ directly from Eq. (1). Assuming the activation energy is known, for a fixed value of α , the product $Af(\alpha)$ can be obtained by fitting to the experimental data. Then, the differential Eq. (1) can be solved and a model is obtained. In this work, the four aforementioned methods were used to determine the activation energy and four set of values $E_\alpha - \alpha$ were obtained. For each method, the corresponding values of $Af(\alpha)$ were computed and model of the kinetics was achieved.

2 Results and Conclusions

This procedure to obtain a kinetic model has been implemented in Matlab and it was applied to three theoretical simulations. In all cases four constant heating rates were applied to generate the simulated data. In the first case, a one-step model with a first-order model function $f(\alpha) = 1 - \alpha$ and Arrhenius parameters $A = 10^9 \text{ min}^{-1}$ and $E = 10^2 \text{ kJ mol}^{-1}$ were considered. The four methods used to compute the activation energy provide similar values. Using them, the product $Af(\alpha)$ was computed and then $\alpha - T$ curves were plotted by solving the general kinetic differential equation.

In the second simulation, a parallel two-step, equally weighted, case was analysed being $f_1(\alpha) = 1 - \alpha$, $A_1 = 10^{12} \text{ min}^{-1}$ and $E_1 = 167 \text{ kJ mol}^{-1}$ and $f_2(\alpha) = 1 - \alpha$, $A_2 = 10^{26} \text{ min}^{-1}$ and $E_2 = 352 \text{ kJ mol}^{-1}$. The third simulation analysed an Avrami-Erofeev model function $f(\alpha) = 4(1 - \alpha)[- \ln(1 - \alpha)^{3/4}]$ with $A = 10^2 \text{ min}^{-1}$ and $E = 20.9 \text{ kJ mol}^{-1}$. Figure 1 shows the simulated and the reconstructed $\alpha - T$ curves for the three simulations. In all cases a good agreement was achieved.

Finally, thermogravimetric analysis of the thermal degradation of $\text{FeNH}_4(\text{HPO}_4)_2$ was conducted in a N_2 dynamic atmosphere, using a Mettler-Toledo TGA/SDTA851^e, at four different heating rates. As can be seen in Fig. 2a, the process occurs in two consecutive stages, the on-line mass spectrometric analysis indicates that the material firstly loses water about 600 K and secondly, at about 900 K, water and ammonia. The $E - \alpha$ plot, displayed in Fig. 2b, shows this behaviour. The experimental data are satisfactorily reconstructed (Fig. 2c)

In conclusion, the product $Af(\alpha)$ has been computed by a method independent of how the activation energy has been obtained. Then, the general kinetic differential

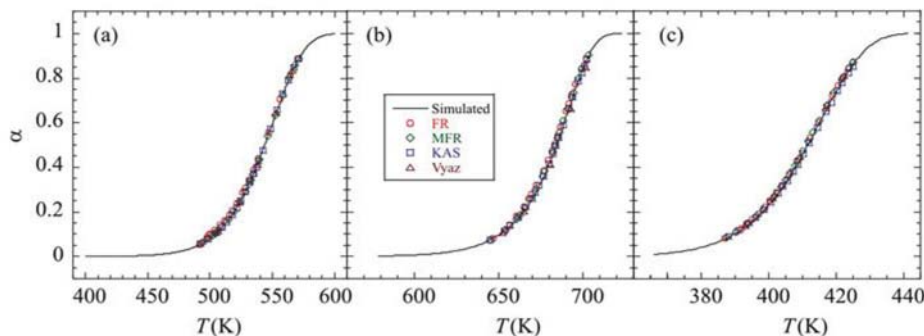


Fig. 1 Comparison of the simulated and reconstructed $\alpha - T$ curves for $\beta = 8 \text{ K min}^{-1}$. Simulations 1, 2 and 3 in (a), (b) and (c), respectively

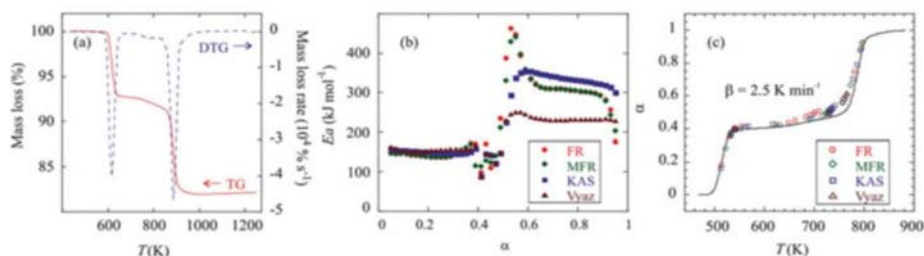


Fig. 2 TG and DTG curves of $\text{FeNH}_4(\text{HPO}_4)_2$ obtained at 10 K min^{-1} heating rate (a); activation energy versus extent of conversion (b); experimental (line) and reconstructed (points) $\alpha - T$ curves for $\beta = 2.5 \text{ K min}^{-1}$ (c)

equation can be solved overcoming the ambiguity of the model-fitting methods. In this way, a discrete model that can be used to describe kinetics in solid state processes. This model has worked efficiently in the description of the theoretical simulations studied and in the thermal decomposition of $\text{FeNH}_4(\text{HPO}_4)_2$.

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Artículo S2

Thermal behavior of layered α -titanium phosphates:
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Thermal behavior of layered α -titanium phosphates: from the titanium(IV) bis(hydrogenphosphate) monohydrate to an europium(III)-phase via propylamine intercalation

Jorge García-Glez¹ · Olena Khainakova¹ · Isabel Iglesias² · Belén F. Alfonso² · José A. Huidobro³ · Zakariae Amghouz⁴ · Aránzazu Espina⁵ · Camino Trobajo¹

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Abstract

Polycrystalline layered α -titanium phosphate, α -Ti(HPO₄)₂·H₂O, has been obtained under H₃PO₄(aq) reflux conditions, and its intercalation compound with propylamine, α -Ti(HPO₄)₂·2C₃H₇NH₂·H₂O, was used for trapping luminescent Eu-centers in two-dimensional confined space. All materials were characterized by X-ray powder diffraction, scanning electron microscopy, solid-state nuclear magnetic resonance (SS-NMR, ³¹P MAS and ¹³C CPMAS) and thermogravimetric analysis coupled with mass spectrometry. Moreover, the activation energy of thermal decomposition has been calculated as a function of the extent of conversion, applying both a modified Friedman method developed in our laboratory and the advanced nonlinear method proposed by Vyazovkin.

Keywords Titanium phosphate · Propylamine · Europium · Thermal decomposition · Kinetic analysis

Introduction

α -Ti(HPO₄)₂·H₂O (α -TiP) was the subject of continuous study over the past 50 years. The pioneering studies on this material were conducted by Alberti in his laboratory at the University of Perugia (Italy) [1, 2] and emerged in the wake of the work of the Clearfield Lab (USA) on zirconium phosphates [3]. The contributions of the Soviet school, particularly the Chernukov Lab in Nizhni

Nóvgorod (Russia) have also to be mentioned [4]. In this context, our group at the University of Oviedo (Spain), published its first articles on this topic at the beginning of the 1980s [5–7].

According to the excellent review of Clearfield and Díaz [8], the first report of a crystalline form of zirconium phosphate was in 1964. Up to that time, only an amorphous white fine powder was known. The transformation from the amorphous to crystalline form is a slow process. It is therefore possible to control the size of the particles from very small, approximately 50 nm, up to micro-size and even to large crystals. These particles are layered and exhibit the ability to exchange positively charged species for protons, to undergo intercalation behavior and exfoliation of the layers. In addition, it has been shown that the surface of the particles may be functionalized by bonding to silanes, isocyanates and epoxides, and this bonding may even be extended to phosphates and phosphonic acids after replacing the surface protons by Zr⁴⁺ or Sn⁴⁺. Attachment of a functional group to the surface bonding ligands including phosphates or phosphonic acids, allows using this large class of functionalized materials for a variety of applications. Because of the extraordinary properties of this compound, a great variety of potential and realized uses

✉ Zakariae Amghouz
amghouzzakariae@uniovi.es

¹ Departamento de Química Orgánica e Inorgánica, Universidad de Oviedo-CINN, 33006 Oviedo, Spain

² Departamento de Física, Escuela Politécnica de Ingeniería, Universidad de Oviedo, 33204 Gijón, Spain

³ Departamento de Matemáticas, Escuela Politécnica de Ingeniería, Universidad de Oviedo, 33204 Gijón, Spain

⁴ Departamento de Ciencia de los Materiales e Ingeniería Metalúrgica, Escuela Politécnica de Ingeniería, Universidad de Oviedo, 33204 Gijón, Spain

⁵ Servicios Científico-Técnicos, Universidad de Oviedo, 33006 Oviedo, Spain

have been invoked. As a result, from 1964 to the present, more than 10,000 scientific papers have been published describing the chemistry and applications of this remarkable compound. This phenomenon continues as every year a few hundred new papers appear in the chemical literature.

In our laboratory, both α -TiP [9, 10] and its propylamine intercalation product, α -Ti(HPO₄)₂·2C₃H₇NH₂·H₂O (α -TiPPr) [11–13], have been previously synthesized and characterized. On the other hand, the treatment of α -TiPPr with europium(III) nitrate solutions, involving an ion-exchange process between propylammonium cations, C₃H₇NH₃⁺, and hexahydrate europium(III) species, [Eu(H₂O)₆]³⁺, has led to a new luminescent material (α -EuTiPPr) [14].

Despite the large volume of information obtained in recent decades, the kinetic studies on the thermal decomposition processes of layered titanium phosphates are relatively scarce [15–18]. This contribution reports the kinetic features of thermo-oxidative decomposition processes of the three aforementioned materials: α -TiP, α -TiPPr, and α -EuTiPPr.

Experimental

All chemicals used were of reagent grade. MilliQ water was used throughout the experiments. α -TiP was obtained by the method described by Alberti et al. [1], using 10 M H₃PO₄ and amorphous titanium phosphate (PO₄/Ti = 1.3) heated under reflux for 50 h. Propylamine intercalation compound, α -TiPPr, was obtained by placing α -TiP in an atmosphere saturated with propylamine vapor for 6 days at room temperature [11]. α -EuTiPPr was prepared by equilibrating α -TiPPr with 0.1 M europium nitrate Eu(NO₃)₃·5H₂O solution ($T = 25.0 \pm 0.1$ °C, $t = 72$ h, solution/solid ratio = 20 mL g⁻¹) [14].

The phosphorus and titanium contents of the solids were determined by inductively coupled plasma mass spectrometry (ICP-MS) analysis (Finnigan, Element model) after dissolving a weighed amount in HF(aq). Microanalytical data (C and N) were determined by an Elemental Model Vario MACRO elemental analyzer. Elemental analysis (mass %) for α -TiP: P 23.9, Ti 18.6 (calculated for Ti(HPO₄)₂·H₂O: P 24.03, Ti 18.56), α -TiPPr: P 16.7, Ti 12.8, C 18.8, N 7.3 (calculated for Ti(HPO₄)₂·2C₃H₇NH₂·H₂O: P 16.47, Ti 12.73, C 19.16, N 7.45), and α -EuTiPPr: P 13.7, Ti 10.8, Eu 24.0, C 2.5, N 0.9 (calculated for [Eu(H₂O)₆]_{2/3}Ti(PO₄)₂·[(H₂O)₆]_{1/3}: P 14.85, Ti 11.47, Eu 24.28).

Powder diffraction studies

Room temperature X-ray powder diffraction (XPD) patterns were collected on an X'Pert PRO MPD X-ray diffractometer with PIXcel detector, operating in the Bragg–Brentano ($\theta/2\theta$) geometry and using CuK _{α} radiation ($\lambda = 1.5418$ Å).

Electron microscopy studies

SEM images were obtained by using JEOL 6610VL scanning electron microscope operating at 20 kV and equipped with an X-Max Silicon Drift Detector for EDX analysis.

Solid-state nuclear magnetic resonance studies

Room temperature SS-NMR spectra were collected on a Bruker AVANCE III 400 equipped with a 4-mm wide-bore MAS probe, operating at ³¹P resonating frequency of 161.97 MHz and ¹³C resonating frequency of 100.64 MHz. Samples were packed in zirconia rotor with Kel-F tape. ³¹P MAS NMR spectra were acquired at 8 kHz spin rate. The relaxation delays were 20 s and number of scans of 100. All the spectra were referred to NH₄H₂PO₄ ($\delta = 0.9$ ppm) as external standard for chemical shift calibration. ¹³C CPMAS NMR spectra were acquired at 5 kHz spin rate. The relaxation delays for all spectra were 5 s and number of scans 100. Chemical shift was externally referenced to the 43.5 ppm resonance of glycine.

Thermal analysis

A Mettler-Toledo TGA/SDTA851^c was used for the thermal analyses in a dynamic oxygen atmosphere (50 mL min⁻¹) at several heating rates ($\beta = 2.5, 5, 10, 20, 40$ K min⁻¹). In all cases, ca. 15 mg of powder sample was thermally treated, and blank runs were performed. A Pfeiffer Vacuum ThermoStarTM GSD301T mass spectrometer was used to determine the evacuated vapors. The masses 18 (H₂O), 44 (CO₂) and 59 (C₃H₇NH₂) were tested by using a detector C-SEM, operating at 1200 V, with a time constant of 1 s.

Determination of kinetic parameters

The kinetics of many solid-state reactions involving a change of mass can be described by the basic equation

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E}{RT}\right) f(\alpha) \quad (1)$$

where α is the extent of conversion, t is the time, T is the temperature, A is the Arrhenius factor, E is the activation

energy, R is the universal gas constant and $f(\alpha)$ is the reaction model. Although the mechanisms in solid-state reactions are usually very complex and tend to involve several steps, Eq. (1) represents a simple kinetic model which can be used to describe an approximation of the kinetics of the process [19–21].

Many methods have been developed in order to estimate the kinetic parameters and nowadays, one can say that the most reliable results are provided by isoconversional methods. These methods are based on the isoconversional principle that states that the reaction rate depends only on the temperature for a given value of the extent of conversion. Several runs with different heating programmes, usually with constant heating rates $T = T_0 + \beta_i t$, are carried out and then the values of the activation energy are computed from experimental data.

The differential method of Friedman comes from Eq. (1) by taking logarithms

$$\ln\left(\left(\frac{d\alpha}{dt}\right)_{\alpha,i}\right) = \ln(Af(\alpha)) - \frac{E_\alpha}{RT_{\alpha,i}} \quad (2)$$

where $T_{\alpha,i}$ denotes the temperature at which α is reached for the i th heating program. Then, by plotting $\ln\left(\left(\frac{d\alpha}{dt}\right)_{\alpha,i}\right)$ against $1/T_{\alpha,i}$, the value of E_α can be estimated. As is well-known, a drawback of this procedure is its sensitivity to noise, in particular, when it is applied to data coming from thermogravimetric analysis (TG).

In order to decrease the effects of noise, a modified procedure (MFR) was proposed by Huidobro et al. [22]. The underlying idea is, for a given value of α , to consider not only the data corresponding to α but including data of surrounding points. So, five points $\alpha_1 = \alpha - 2\Delta\alpha$, $\alpha_2 = \alpha - \Delta\alpha$, $\alpha_3 = \alpha$, $\alpha_4 = \alpha + \Delta\alpha$, $\alpha_5 = \alpha + 2\Delta\alpha$, for n heating programmes, are considered and Eq. (2) leads to

$$\ln\left(\frac{d\alpha(t_{k,i})}{dt}\right) = \ln(Af(\alpha_k)) - \frac{E}{RT_{k,i}}, \quad k = 1, \dots, 5 \quad (3)$$

These five points are very close and assuming that variations of the activation energy over the interval $[\alpha_1, \alpha_5]$ are neglected, Eq. (3) involves five different straight lines with the same slope $m = -E/R$. Thus, we can find the slope by fitting to the experimental data for all these points simultaneously rather than only for α . This method can be applied to a different number of points.

Integral isoconversional methods are based on an integral of Eq. (1)

$$g(\alpha) = \int_{t_0}^{t_\alpha} \exp\left(-\frac{E}{RT}\right) dt \quad (4)$$

where $g(\alpha) = \int [1/(Af(\alpha))]d\alpha$. The integral on the right-hand side of Eq. (4) is known as temperature integral and does not have an analytical solution and, for this reason, several approximations have been proposed giving rise to different methods. Although some of them are very popular [23], they have been criticized because of the inconsistency of their formulation, particularly when the activation energy changes with the extent of conversion [24, 25].

The nonlinear advanced method proposed by Vyazovkin [24, 26] is one of the most accurate procedures for kinetic analysis. For a small increment of conversion $\Delta\alpha$ and assuming that A is constant over the interval $[\alpha - \Delta\alpha, \alpha]$, integration of Eq. (1) with respect to t gives

$$\int_{\alpha-\Delta\alpha}^{\alpha} \frac{1}{Af(\alpha)} d\alpha = J(E_\alpha) \quad (5)$$

where $J(E_\alpha) = \int_{t_{\alpha-\Delta\alpha}}^{t_\alpha} \exp(-E_\alpha/RT) dt$. Then, for a given value of α and several runs $i = 1, \dots, n$, the $J_{\alpha,i}$'s should be equal. To obtain E_α Vyazovkin proposed the minimization of the function.

$$\Phi(E_\alpha) = \sum_{i=1}^n \sum_{j \neq i}^n \frac{J_i(E_\alpha)}{J_j(E_\alpha)} \quad (6)$$

Numerical integration has been used to evaluate $J(E_\alpha)$.

Results and discussion

XPD analysis shows that α -TiP is highly crystalline (Fig. 1a) with the first characteristic peak at $2\theta = 11.65^\circ$ ($d_{002} = 7.58 \text{ \AA}$) corresponding to its interlayer distance. In

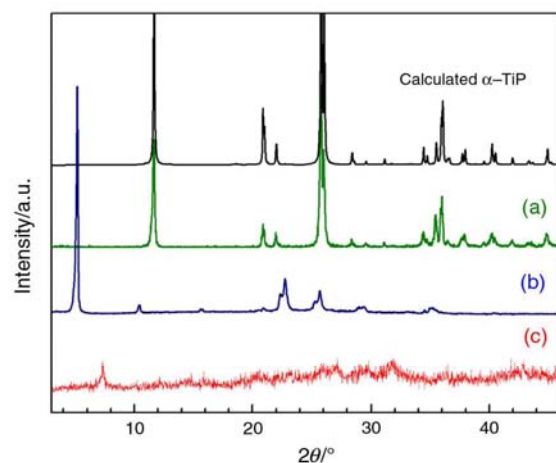


Fig. 1 XPD patterns for α -TiP (a), α -TiPPr (b) and α -EuTiPPr (c)

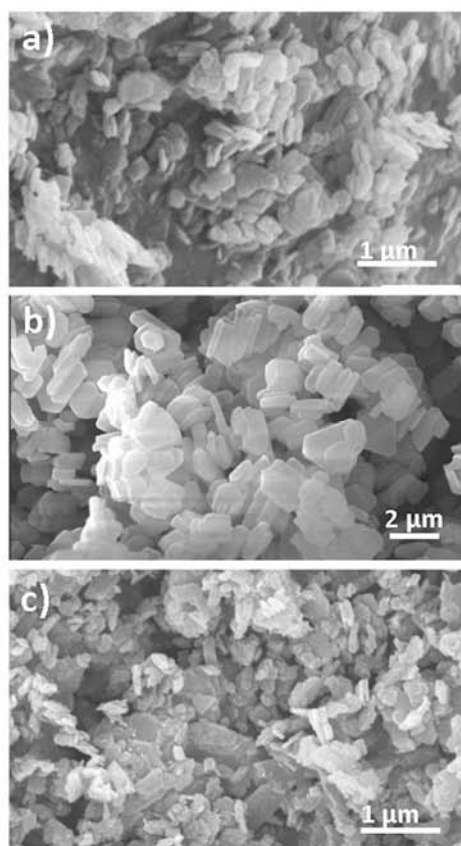


Fig. 2 SEM images for α -TiP (a), α -TiPPr (b) and α -EuTiPPr (c)

α -TiPPr, the basal spacing increases up to 16.9 Å (Fig. 1b) as a consequence of the propylamine intercalation as a bimolecular film [11] in which the terminal amino groups are protonated by the POH groups and the carbon chains are roughly inclined by 59° to the titanium phosphate layers, showing a similar packing to that reported for γ -titanium phosphate intercalation compounds [27, 28]. α -EuTiPPr presents a structural order in the direction perpendicular to the plane of the sheet with a diffraction peak at $2\theta = 7.33^\circ$ corresponding to a d -spacing of 12.0 Å (Fig. 1c). This new peak was attributed to the formation of an Eu-phase with the idealized formula $[\text{Eu}(\text{H}_2\text{O})_6]_{2/3}\text{-Ti}(\text{PO}_4)_2\cdot[(\text{H}_2\text{O})_6]_{1/3}$, where $[\text{Eu}(\text{H}_2\text{O})_6]^{3+}$ occupying 2/3 of the pseudo-zeolitic cavities so as to counteract the negatively charged titanium phosphate layer, while the rest of the pseudo-zeolitic cavities (1/3 of the total) are supposed to be occupied by water molecules [14].

SEM images (Fig. 2) show that all three samples present a platelet-like pseudo-hexagonal morphologies typical of the layered metal phosphates [29], indicating that in this

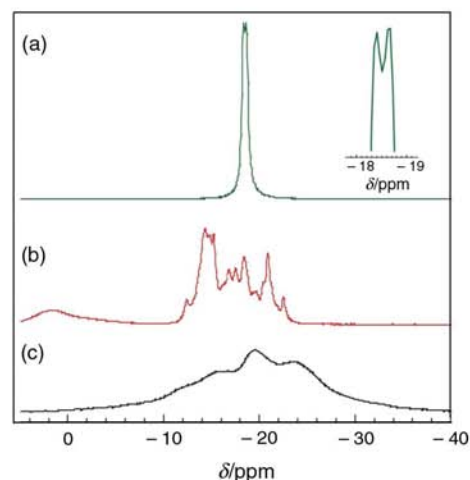


Fig. 3 ^{31}P MAS NMR spectra for α -TiP (a), α -TiPPr (b) and α -EuTiPPr (c). These spectra show the number of observed peaks in each sample (a: 2 peaks, b: 11 peaks, c: 4 peaks) and the chemical shift for each peak is illustrated in Table 1

Table 1 ^{31}P MAS NMR chemical shift values of the peaks observed in the spectra shown in Fig. 3

α -TiP	α -TiPPr	α -EuTiPPr
- 18.4	1.5	- 11.4
- 18.7	- 12.4	- 15.0
	- 14.3	- 19.6
	- 14.8	- 23.6
	- 15.2	
	- 16.9	
	- 17.5	
	- 18.4	
	- 19.7	
	- 20.9	
	- 22.5	

case both intercalation and ion-exchange processes preserve the sheets integrity of the α -titanium phosphate.

The ^{31}P MAS NMR spectrum of α -TiP (Fig. 3a, Table 1) shows two partially resolved peaks that according to the crystal data, correspond to two inequivalent HPO_4 groups in titanium phosphate layers [10]. After treatment with propylamine, the ^{31}P MAS NMR spectrum became substantially different for α -TiPPr. The former two signals transformed into a dozen peaks (Fig. 3b, Table 1), indicating a high disorder of the propylamine molecules in the interlayer space. The ^{13}C CPMAS NMR spectrum of α -TiPPr (Fig. 4a) displays three resonances at ca. 41.3, 21.8 and 11.6 ppm, which correspond to three different carbon types (α , β and γ) in the propylamine, indicating that the intercalated propylamine is protonated [30]. However, the

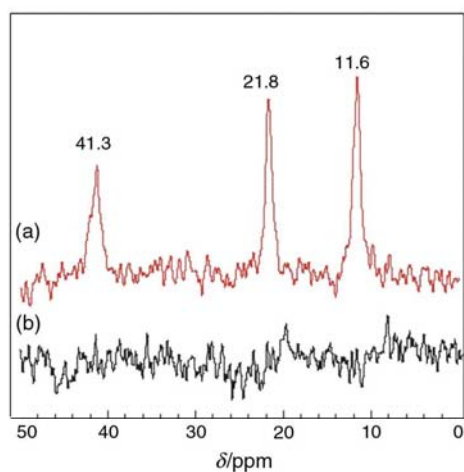


Fig. 4 ^{13}C CPMAS NMR spectra for α -TiPPr (a) and α -EuTiPPr (b). Spectrum (a) shows 3 peaks and in the spectrum (b) no relevant peak is observed

titanium phosphate sample containing europium (α -EuTiPPr) does not present any relevant signal in the ^{13}C CPMAS NMR experiment (Fig. 4b). The carbon content in the sample is below the sensitivity of the NMR experiment used in the measurements of ^{13}C . The ^{31}P MAS NMR spectrum of α -EuTiPPr shows fairly broad peaks in the range between 0 and -40 ppm (Fig. 3c, Table 1) and provides very little information, probably as a result of two assistant effects: the disorder in the interlayered space occupied by one layer of cationic species and the local magnetic field in the environment of the europium(III) cations.

Figure 5 displays the TG-DTG curves for the three studied materials. The DTG curve of α -TiP (Fig. 5a) shows two minima, the first corresponds to the loss of hydration water at ca. 495 K and the second is due to the elimination of condensation water at 795 K, with a total mass loss of 14.5% (calculated for $\text{Ti}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$: 13.95%). The TG-DTG curves of α -TiPPr (Fig. 5b) show a complex decomposition behavior from the beginning of the process up to obtaining the final titanium diphosphate phase (TiP_2O_7) with a total mass loss of 39.5% (calculated: 40.96%), and the probable formation of several α - $\text{Ti}(\text{HPO}_4)_2 \cdot x\text{C}_3\text{H}_7\text{NH}_2$ ($x = 2.0, 1.7, 1.3, 1.0,$ and 0.5) intermediate phases [31]. The first DTG peak at 353 K is associated with the loss of the hydration water, while the signals in the 400–1000 K range are related to the loss of both propylamine and condensation water (see MS-data: H_2O and $\text{C}_3\text{H}_7\text{NH}_2$ signals, in Fig. 6a). Finally, the last peak (at 1173 K) corresponds to the combustion of organic matter occluded in the compound (see CO_2 -signal, in

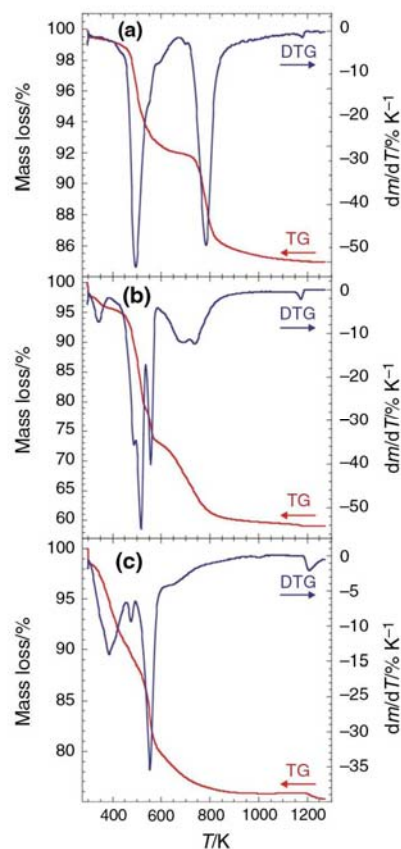


Fig. 5 TG (red line) and DTG (blue line) curves for α -TiP (a), α -TiPPr (b) and α -EuTiPPr (c) obtained at 10 K min^{-1} heating rate in O_2 -atmosphere

Fig. 6a), as previously reported for other amine-metal phosphates [32].

The TG-DTG curves of α -EuTiPPr (Fig. 5c) show that the material decomposes in several overlapping steps with water evacuation from room temperature up to 1000 K (see MS-data, in Fig. 6b). In addition to the loss of water, at 500–600 K, the loss of propylamine is also observed according to the elemental composition data (see Table 1 in Ref. [14] where the residual amounts of organic matter in α -EuTiPPr are reported). Again, the combustion of small amounts of organic matter trapped on the collapsed solid is also observed at high temperatures (ca. 1200 K).

The kinetic study for the thermo-oxidative decomposition of the three materials (α -TiP, α -TiPPr, and α -EuTiPPr) was performed using thermogravimetric data obtained in air atmosphere at several constant heating rates ($\beta = 2.5, 5, 10, 20, 40 \text{ K min}^{-1}$). The kinetic evaluation was carried out by using the modified method of Friedman (MFR) [22] and the advanced nonlinear method proposed by

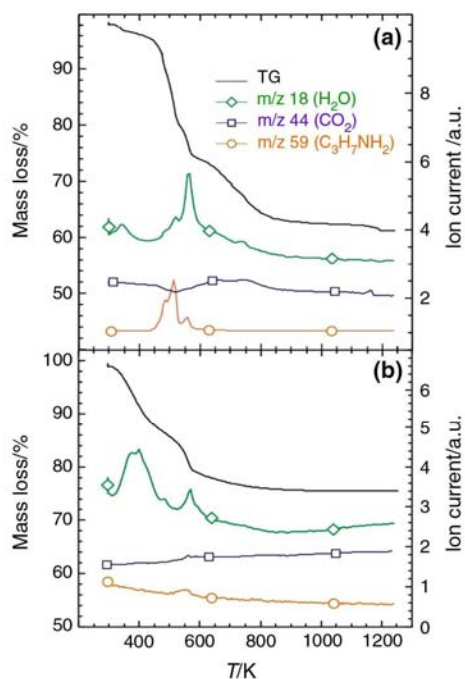


Fig. 6 MS-signals of evacuated vapors on the TG-experiment [m/z 18 for H_2O , m/z 44 for CO_2 , and m/z 59 for $\text{C}_3\text{H}_7\text{NH}_2$] for α -TiPPr (a) and α -EuTiPPr (b)

Vyazovkin (Vyaz) [24, 26]. The apparent activation energy as a function of the extent of conversion was calculated considering an increment $\Delta\alpha = 0.01$. In all cases, the E values obtained by applying both the MFR and Vyaz methods are very close to each other.

For α -TiP sample, Fig. 7 shows two distinguished zones for the activation energy corresponding to the loss of water. The first zone, for the conversion range $0.15 \leq \alpha \leq 0.50$, is

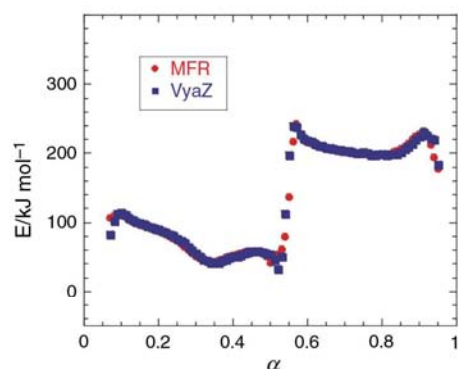


Fig. 7 Dependence of the apparent activation energy on the extent of conversion for α -TiP

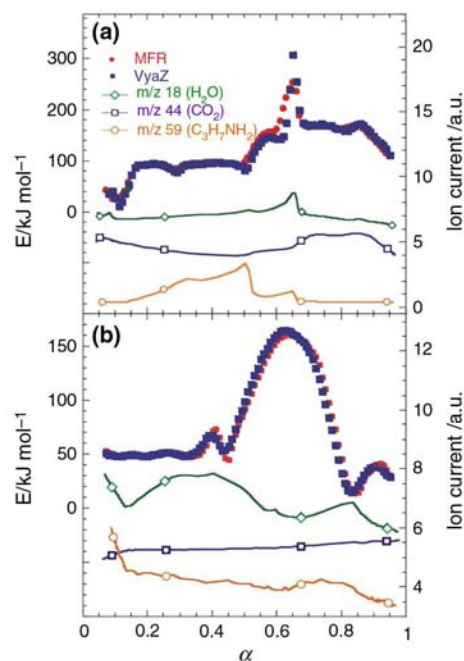


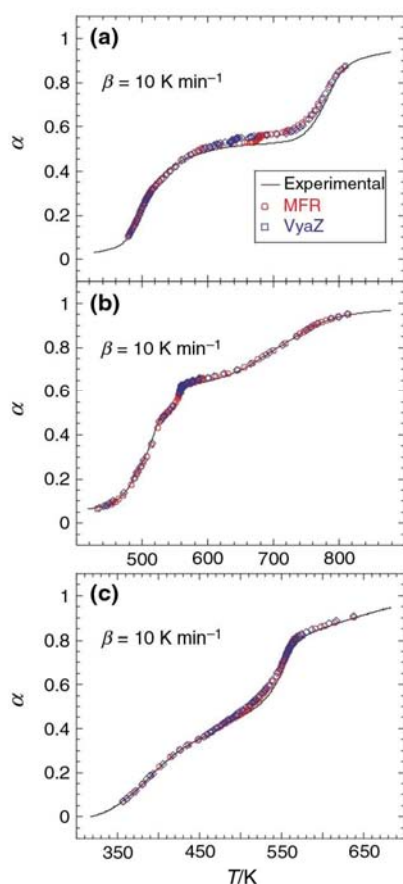
Fig. 8 Apparent activation energy and MS-signals of evacuated vapors [m/z 18 for H_2O , m/z 44 for CO_2 , and m/z 59 for $\text{C}_3\text{H}_7\text{NH}_2$] versus extent of conversion for α -TiPPr (a) and α -EuTiPPr (b)

associated with the evacuation of hydration water with an average activation energy of 70 kJ mol^{-1} . The second conversion range, $0.60 \leq \alpha \leq 0.90$, corresponds to the loss of condensation water and the activation energy is relatively higher, about 205 kJ mol^{-1} . These results show a good agreement with the experimental TG-DTG curves (Fig. 5a).

The $E - \alpha$ curves for the other two materials, α -TiPPr in Fig. 8a and α -EuTiPPr in Fig. 8b, have a more irregular shape due to the overlapping mass loss processes. For a better understanding of this behavior, we have plotted both the apparent activation energy and the mass spectrometry signals (m/z 18 H_2O , m/z 44 CO_2 , and m/z 59 $\text{C}_3\text{H}_7\text{NH}_2$) versus the extent of conversion for these two compounds. In the case of α -TiPPr, Fig. 8a, a part of the hydration water is lost for $\alpha < 0.2$, and then, over the extent of conversion range $0.2 \leq \alpha \leq 0.5$, a part of the propylamine is lost and the value obtained for the apparent activation energy is ca. 95 kJ mol^{-1} . The first loss of water takes place in two overlapping steps, which are difficult to distinguish by thermogravimetric analysis, and the intercalated propylamine is lost in several overlapping steps [31]. When $\alpha = 0.65$ (see Fig. 8a), E reaches a maximum value of 300 kJ mol^{-1} that can be associated with the loss of the remaining hydration water and propylamine. For α ranging

Table 2 Correlation factor in the fitting of the conversion obtained for the MFR and Vyaz methods, as a function of the heating rate (β , in K min^{-1})

Sample	Method	$\beta = 2.5$	$\beta = 5$	$\beta = 10$	$\beta = 20$	$\beta = 40$
α -TiP	MFR	0.98564	0.95813	0.96282	0.96941	0.99771
	Vyaz	0.99251	0.96500	0.96589	0.96760	0.99475
α -TiPPr	MFR	0.99897	0.99886	0.99930	0.99909	–
	Vyaz	0.99820	0.99886	0.99924	0.99879	–
α -EuTiPPr	MFR	0.99833	0.97167	0.99662	0.99935	–
	Vyaz	0.99694	0.96757	0.99518	0.99904	–

**Fig. 9** Experimental and reconstructed $\alpha - T$ curves at 10 K min^{-1} heating rate for α -TiP (a), α -TiPPr (b) and α -EuTiPPr (c)

approximately between 0.65 and 0.85, the apparent activation energy is about 160 kJ mol^{-1} and attributed to the loss of the condensation water. These experimental results match with the theoretically calculated extent of conversion: α between 0.12 and 0.69 for the loss of hydration water and propylamine, and $\alpha = 0.88$ for the loss of condensation water.

For α -EuTiPPr, the $E - \alpha$ and $m/z - \alpha$ curves are shown in Fig. 8b. In the first stage, for α between ca. 0.1

and 0.4, the apparent activation energy is practically constant (ca. 50 kJ mol^{-1}). It corresponds to the largest loss of the hydration water. In the second stage, for α between ca. 0.45 and 0.65, the loss of hydration water is finished and the loss of propylamine is detected. Finally, when $\alpha > 0.65$, the $m/z - \alpha$ curves show the loss of both condensation water and propylamine.

When a collection of values y_i , $i = 1, \dots, n$, is approximated by the values y_i^* , the correlation factor given by $R^2 = 1 - \frac{\sum_{i=1}^n (y_i - y_i^*)^2}{\sum_{i=1}^n (y_i - \bar{y})^2}$, where $\bar{y} = \frac{\sum_{i=1}^n y_i}{n}$, informs about the goodness of the approximation. In this study, the excellent agreement of both MFR and Vyaz methods with the experimental data, in the whole temperature range and for several heating rates, is illustrated by the values of the correlation factor R^2 summarized in Table 2. As can be seen, in all cases R^2 is near 1. Apart from that, Fig. 9 shows the reconstructed conversion curves and the experimental ones obtained in the laboratory for the three compounds at a heating rate $\beta = 10 \text{ K min}^{-1}$.

Conclusions

We have shown that the chemical modifications of the parent α -TiP compound could be successfully performed by taking advantage of its intercalation and ion-exchange properties. The morphology of the particles for the intercalated and ion-exchange forms (α -TiPPr, and α -EuTiPPr) is apparently similar to the parent α -TiP compound. However, solid-state NMR and thermal analysis were able to detect structural differences between these three compounds. In addition, the apparent activation energy was estimated for the thermo-oxidative decomposition stages observed in TG experiments for all the studied materials. An excellent agreement between the both applied MFR and Vyaz methods and the experimental data was obtained.

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Artículo S3

Kinetic analysis of the thermal decomposition of iron(III) phosphates:

$\text{Fe}(\text{NH}_3)_2\text{PO}_4$ and $\text{Fe}(\text{ND}_3)_2\text{PO}_4$

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 and Fe(ND₃)₂PO₄**
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Corresponding Author:	Isabel Iglesias Universidad de Oviedo Gijon, Asturias SPAIN
Corresponding Author Secondary Information:	
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Corresponding Author's Secondary Institution:	
First Author:	Isabel Iglesias
First Author Secondary Information:	
Order of Authors:	Isabel Iglesias José A Huidobro Belén F. Alfonso Camino Trobajo Aránzazu Espina Rafael Mendoza José R. García
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Kinetic analysis of the thermal decomposition of iron(III) phosphates: Fe(NH₃)₂PO₄ and

Fe(ND₃)₂PO₄

Isabel Iglesias¹, José A. Huidobro², Belén F. Alfonso¹, Camino Trobajo³, Aránzazu Espina⁴, Rafael Mendoza⁴, José R. García³

¹*Dpto. de Física, Universidad de Oviedo, 33007 Oviedo, Spain.*

²*Dpto. de Matemáticas, EPI Gijón, Universidad de Oviedo, 33204 Gijón, Spain.*

³*Dpto. de Química Orgánica e Inorgánica, Universidad de Oviedo-CINN, 33006 Oviedo, Spain.*

⁴*Servicios Científico-Técnicos, Universidad de Oviedo, 33006 Oviedo, Spain.*

Email corresponding author: iis@uniovi.es

Abstract

The hydrothermal synthesis and the chemical-physical characterization of a diamine iron phosphate (hydrogen and deuterated forms) are reported. A new synthetic route, by using *n*-butylammonium dihydrogen phosphate as precursor, leads to the largest crystals described so far for this compound. Its crystal structure (hydrogen-form) was determined from single-crystal X-ray diffraction data. It crystallizes in the orthorhombic system (*Pnma*, *a* = 10.1116(2) Å, *b* = 6.3652(1) Å, *c* = 7.5691(1) Å, *Z* = 4) at room temperature, and below 220 K changes towards monoclinic *P2₁/n*. The *in situ* powder X-ray thermo-diffraction monitoring for the hydrogen compound is also included. Thermal analysis shows that the solid is stable up to ca. 440 K. The kinetic analysis of the thermal decomposition (hydrogen and deuterated forms) was performed by using the isoconversional methods of Vyazovkin and a modified version of Friedman. Similar values of the activation energy were achieved by both methods and they were found to be consistent.

Keywords: Metal phosphates, hydrothermal synthesis, crystal structure, thermal decomposition, kinetics.

Introduction

In the last decades, structures and properties of open-framework transition metal phosphates have attracted the interest of many researchers because of their possible utilization in different areas such as catalysis, adsorption, ion exchange and battery electrodes [1, 2]. The olivine-phosphate LiFePO₄ started the way for a new class of materials like an alternative to cathodes for rechargeable lithium batteries [3]. To date, the interest in this kind of compounds continues due to its potential technical applications such as electric vehicles and grid storage [4, 5]. Moreover, the possibility of different oxidation states and coordination geometries of iron causes that iron phosphates exhibit interesting magnetic properties [6, 7]. Hydrothermal synthesis conditions play an important

role on the products obtained because of the influence of the precursors, molar ratio, pH, reaction time, etc. [8].

For instance, the direct synthesis of iron(III) phosphates under mild hydrothermal conditions by the reaction of $\text{FeCl}_3(\text{aq})$ and $\text{H}_3\text{PO}_4(\text{aq})$ in presence of urea has been reported [9]. As was observed, the compounds obtained depend on the presence and the concentration of urea in the reaction system. Without urea or at low urea concentration only $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ is formed and as the concentration of urea and the pH in the reaction media increase, the sequential formation of $\text{NH}_4\text{Fe}(\text{HPO}_4)$, $\text{NH}_4\text{Fe}_2(\text{PO}_4)_2(\text{OH}) \cdot 2\text{H}_2\text{O}$, and $\text{Fe}(\text{NH}_3)_2\text{PO}_4$, take place.

The polycrystalline diamine iron(III) phosphate, $\text{Fe}(\text{NH}_3)_2\text{PO}_4$, and its deuterated phase $\text{Fe}(\text{ND}_3)_2\text{PO}_4$ had been previously synthesized and structurally characterized in our laboratory [10, 11]. The nuclear diagram obtained from the powder neutron diffraction data (PND) of the deuterated sample between 30 and 300 K, complementary to the powder X-ray diffraction (PXRD), allowed us to analyze in depth the structural phase transition: Orthorhombic ($Pnma$) crystal structure at room temperature and monoclinic ($P2_1/n$) below 226(5) K [11]. PND experiments between 1.8 and 30 K revealed a magnetic phase transition at the temperature of 22 K towards a helimagnetic arrangement with an incommensurate propagation vector $\vec{k}_{inc} = (1/2 - \tau, 0, \tau)$, being $\tau \sim 0.04$ rlu (reciprocal lattice units). The magnitude of the Fe(III) magnetic moments is close to $\mu_{Fe} = 4.5 \mu_B$ at $T = 2$ K [12].

This paper reports the hydrothermal synthesis of $\text{Fe}(\text{NH}_3)_2\text{PO}_4$ with an adequate size of crystallites to address the first structural characterization of this material from single-crystal X-ray diffraction. At room temperature, the compound shows orthorhombic symmetry, $Pnma$ space group. The thermal decomposition of the hydrogen and the deuterated samples has been analyzed and kinetic parameters computed by using isoconversional methods.

Experimental

The synthesis of $\text{Fe}(\text{NH}_3)_2\text{PO}_4$ large crystals was carried out by a hydrothermal route in a stainless steel Teflon-lined vessel under autogenous pressure from a mixture of $\text{C}_4\text{H}_9\text{NH}_3(\text{H}_2\text{PO}_4)$ [13], $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (1 M, Merck), and $(\text{NH}_2)_2\text{CO}$ (solid, Merck) in the molar ratio 1:1:16. The total volume of the reaction mixture was 15 mL, and the autoclave was sealed and heated at 453 K during 6 days. The solid product was filtered off, thoroughly washed with an excess of ionized water until neutral pH, and dried in air at room temperature. The phosphorus and iron contents of the solids were determined by inductively coupled plasma mass spectrometry (ICP-MS) analysis (Finnigan, Element model) after dissolving a weighed amount in $\text{HF}(\text{aq})$. Microanalytical data for nitrogen was obtained with a Perkin Elmer 2400B elemental analyser.

Powder diffraction studies

1 Powder X-ray diffraction (PXRD) patterns were recorded on a Panalytical X'pert PRO MPD X-ray
 2 diffractometer with PIXcel detector, operating in the Bragg-Brentano ($\theta/2\theta$) geometry, using CuK α radiation (λ
 3 = 1.5418 Å). Data were collected at room temperature between 5° and 80° in 2θ with a step size of 0.02° and
 4 count time of 10 s per step. In the X-ray thermodiffraction studies each powder pattern was recorded in the 10°–
 5 60° range (1 h) with a scan step size of 0.0131 and a counting time of 0.424 s⁻¹. Temperature intervals of 20 K,
 6 from room temperature up to 1073 K, were chosen. The temperature ramp between two consecutive
 7 temperatures was 10 K min⁻¹.
 8

9
 10 Data collection of single crystal X-ray diffraction was performed at 298 K on an Oxford Diffraction Xcalibur
 11 Nova single crystal diffractometer, using CuK α radiation. Images were collected at a 65 mm fixed crystal-
 12 detector distance, using the oscillation method, with 1° oscillation and variable exposure time per image (10-60
 13 s). Data collection strategy was calculated with the program CrysAlis Pro CCD [14]. Data reduction and cell
 14 refinement was performed with the program CrysAlis Pro RED (Oxford Diffraction Ltd., 2008). The unit cell
 15 dimensions were determined from 4187 reflections between $\theta = 4^\circ$ and 74° and multiple observations were
 16 averaged, $R_{\text{merge}} = 0.02$, resulting in 538 unique reflections of which 529 were observed with $I > 2\sigma(I)$. An
 17 empirical absorption correction was applied using the SCALE3 ABSPACK algorithm as implemented in the
 18 program CrysAlis Pro RED [14]. Crystal structure was solved by direct methods, using the program SIR-92 [15]
 19 and anisotropic least-squares refinement was carried out with SHELXL-97 [16]. All non-hydrogen atoms were
 20 anisotropically refined while hydrogen atoms were located in a Fourier difference map and then isotropically
 21 refined riding on their parent atom.
 22

23 Thermal analysis and kinetic data

24 A Mettler-Toledo TGA/SDTA851e was used for the thermal analysis in a dynamic oxygen atmosphere (50 mL
 25 min⁻¹) at several heating rates. In all cases, ca. 15 mg of powder sample was thermally treated, and blank runs
 26 were performed.
 27

28 The kinetics of heterogeneous condensed phase reactions, in conditions far from equilibrium and assuming the
 29 temperature dependence is given by the Arrhenius equation [17, 18], can be described by the general equation
 30

$$31 \frac{d\alpha}{dt} = A \exp\left(-\frac{E}{RT}\right) f(\alpha) \quad (1)$$

32 where α is the degree of conversion, t (s) is the time, A (s⁻¹) is the pre-exponential factor, T (K) is the
 33 temperature, E (J mol⁻¹) is the activation energy, R (J mol⁻¹ K⁻¹) is the gas constant and $f(\alpha)$ is the reaction
 34 model function. For a non-isothermal process with a constant heating rate β , $T = T_0 + \beta t$, equation (1) can be
 35 written as
 36

$$\beta \frac{d\alpha}{dT} = Af(\alpha)\exp\left(-\frac{E}{RT}\right) \quad (2)$$

Isoconversional methods are based on the isoconversional principle which states that the reaction rate, at a given extent of conversion, is only a function of temperature [19]. A large number of computational methods have been developed to perform the kinetic analysis that can be achieved without determining the pre-exponential factor or the model function [18]. One of the most popular and simplest method is that proposed by Friedman [20] that is included in the family of isoconversional differential methods. For a given value of the extent of conversion and for several runs with different constant heating rates $\beta_i, i = 1, \dots, n$, taking logarithms in the general kinetic equation (2) one obtains

$$\ln\left[\beta_i \left(\frac{d\alpha}{dT}\right)_{\alpha,i}\right] = \ln[A_\alpha f(\alpha)] - \frac{E_\alpha}{RT_{\alpha,i}} \quad (3)$$

Then, the value of activation energy can be determined from the slope of the plot of $\ln[\beta_i(d\alpha/dT)_{\alpha,i}]$ against $1/T_{\alpha,i}$. A general drawback of differential methods is that they are very sensitive to experimental noise and tend to be numerically unstable, especially when the rate is estimated by numerical differentiation [18]. A modified version of the Friedman method (MFR) has been proposed by Huidobro et al. which is less sensitive to noise effects [21].

Numerical differentiation can be avoided by using integral isoconversional methods. Integration in equation (1) leads to

$$g(\alpha) = \frac{A}{\beta} \int_0^{T_\alpha} \exp\left(-\frac{E}{RT}\right) dT = \frac{A}{\beta} I(E, T) \quad (4)$$

where $g(\alpha) = \int_0^\alpha \frac{1}{f(\alpha)} d\alpha$. The integral on the right hand side, known as the temperature integral, has no analytical solution and several procedures have been proposed in order to overcome this difficulty. Some approximations have been suggested in order to estimate the value of the temperature integral but they should be carefully applied because of possible intrinsic inconsistencies, particularly when the activation energy changes with α , [18, 22]. Further increase in the accuracy have been accomplished by using numerical integration over small segments of either temperature or time. Vyazovkin proposed an advanced non-linear method (Vyaz) [23, 24] where the activation energy is obtained by minimization of the function

$$\Phi(E_\alpha) = \sum_{i=1}^n \sum_{j \neq i}^n \frac{J_i(E_\alpha)}{J_j(E_\alpha)} \quad (5)$$

where

$$J_i(E_\alpha) = \int_{t_{\alpha_i-\Delta\alpha}}^{t_{\alpha_i}} \exp\left(-\frac{E_\alpha}{RT_{\alpha,i}}\right) dt \quad (6)$$

In this study, the modified Friedman and the Vyazovkin methods have been applied. In order to obtain a model describing the kinetic process, a way of calculating the factor $c_\alpha = Af(\alpha)$ has been proposed [25]. After computing the activation energy, for a fixed value of α , the product $Af(\alpha)$ can be obtained by using equation (2) and fitting to the experimental data

$$\beta_i \frac{d\alpha(T_{\alpha,i})}{dT} = c_\alpha \exp\left(-\frac{E_\alpha}{RT_{\alpha,i}}\right), \quad i = 1, \dots, n \quad (7)$$

This means the points $\left(\exp\left(-\frac{E_\alpha}{RT_{\alpha,i}}\right), \beta_i \frac{d\alpha(T_{\alpha,i})}{dT}\right)$ are on a straight line passing through the origin and whose slope $Af(\alpha)$ can be obtained by the least-squares method. After knowing the activation energy E and the factor $c_\alpha = Af(\alpha)$, for a given heating rate β , differential equation (2) can be solved and so, the kinetic parameters can be checked, for instance, by reconstructing $\alpha - T$ curves for the same heating rates as those used for the runs and comparing these values with those obtained in the laboratory [21, 25, 26].

Results and discussion

Morphological and structural results

SEM image of $\text{Fe}(\text{NH}_3)_2\text{PO}_4$ is shown in Figure 1 suggesting the morphology of the sample is constituted by fibers forming compact blocks unlike polycrystalline phases [10,12].

A summary of crystallographic data and refinement parameters is listed in Table 1. Final atomic coordinates and isotropic displacement parameters are reported in Table 2 and the selected bond lengths and angles of the monocrystalline compound are listed in Table 3. The crystal system of $\text{Fe}(\text{NH}_3)_2\text{PO}_4$ at room temperature is orthorhombic, the space group is $Pnma$ (No. 62), unit cell dimensions are $a = 10.1116(2)$ Å, $b = 6.3652(1)$ Å, $c = 7.5691(1)$ Å, $\alpha = \beta = \gamma = 90^\circ$ and $Z = 4$. At room temperature, the structure of monocrystalline phase can be described by isolated iron octahedrons which are sharing corners with four phosphate tetrahedrons and two ammonia molecules in relative *cis* position (see Fig. 2). The ammonia molecules are placed in the channels along the b axis. There is only one crystallographically independent iron per unit cell. In Figure 3, a projection of the monocrystalline structure down the b axis is shown.

The evolution of the cell parameters with temperature was analysed from the sequential refinement of the profiles obtained from the single crystal X-ray diffraction by using the Rietveld method and the FullProf program. From 290 K to 250 K, a and b keep constant and c linearly decreases 0.1 %. Then, the parameters a

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and b decrease and c raises until 100 K and they keep constant from 100 K to 2 K. The angle β of the unit cell varies from 90° at 250 K to 92.5° at 100 K showing the orthorhombic structure changes towards monoclinic $P2_1/n$ one (see Fig. 4). Basic structural characteristics maintain stable although symmetry is lost because of strong hydrogen bonds.

The *in situ* HT-PXRD patterns suggest (see Fig. 5) that the starting phase is stable up to 440 K. The ammonium evacuation finishes at ca. 680 K. After this temperature, an intermediate phase occurs until ca. 940 K, when the α -FePO₄ is formed [27].

Thermogravimetric and kinetic analysis

The TG-DTG profiles in an inert atmosphere for Fe(NH₃)₂PO₄ (large crystals) depicted in Figure 6 show that the material is stable up to ca. 440 K. Then it decomposes in three steps with ammonium evacuation up to ca. 680 K giving a total weight loss of 18.5% (calc. 18.4%) in the formation of FePO₄. According to the weight loss of 9.6% (calc. 9.2%) and DTG peaks position, the first step, up to ca. 560 K, can be attributed to the evacuation of one ammonium molecule. The weight loss of 5.9% (calc. 6.1%) accompanying the next step, up to ca. 610 K, amounts to the evacuation of 2/3 ammonium molecules. In the latest step, up to ca. 680 K, the weight loss, 3.0% (calc. 3.1%), is closely corresponding with 1/3 of ammonium molecules.

The determination of the kinetic parameters of thermal decomposition of Fe(NH₃)₂PO₄ (large crystals) was performed from thermogravimetric data obtained in the temperature range from 298 to 1173 K, under a nitrogen atmosphere, using the heating rates $\beta = 1.25, 2.5, 5, 10$ and 20 K min^{-1} . The isoconversional methods MFR and Vyaz were applied to evaluate the activation energy as a function of the extent of conversion with an increment $\Delta\alpha = 0.01$. For comparison, the same study has been carried out for samples previously synthesized (hydrogen and deuterated forms) with smaller crystallite size: Fe(NH₃)₂PO₄ [10] and Fe(ND₃)₂PO₄ [11]. The dependence of the activation energy of the extent of conversion is similar for all samples, there are three different zones that occur in the same conversion range (see Fig. 7). For the large crystals, in the $0.05 < \alpha < 0.50$ conversion range, the apparent activation energy E is about 100 kJ mol^{-1} , concerning to the first step of ammonium loss. For $0.50 < \alpha < 0.70$, the values obtained for E are about 110 kJ mol^{-1} that correspond to the second step of ammonium loss, and finally, in the $0.70 < \alpha < 0.90$ conversion range, E is about 100 kJ mol^{-1} related with the third step of ammonium loss. The shape of the $E - \alpha$ curves are slightly less smooth in the second and third α -range for the other two samples. The difference may be due to a partial overlap of the last two ammonium losses. The values of the activation energy computed by the MFR and Vyaz methods hardly show variations.

Using these values, the product $Af(a)$ was calculated and the general kinetic differential equation (2) could be solved for $\beta = 1.25, 2.5, 5, 10$ and 20 K min^{-1} . The reconstructed $\alpha - T$ curves, obtained with the computed kinetic parameters, were compared with the experimental ones and as can be observed, Figure 8, a good agreement for both MFR and Vyaz methods, has been achieved. A numerical measure of the difference between the reconstructed and experimental curves is given by $R^2 = 1 - SSE/SST$ where $SSE = \sum_{i=1}^n (\alpha_i^* - \alpha_i)^2/n$ and $SST = \sum_{i=1}^n (\alpha_i - \bar{\alpha})^2/n$, being α_i the experimental data, α_i^* the computed values and $\bar{\alpha} = \sum_{i=1}^n \alpha_i/n$ [25]. The obtained values are: 0.999557, 0.992676, 0.999179, 0.997144 and 0.998747 for MFR method, and 0.998384, 0.992278, 0.999071, 0.996493 and 0.998995 for Vayz method, for $\beta = 1.25, 2.5, 5, 10$ and 20 K min^{-1} , respectively.

Conclusions

A new hydrothermal route for the synthesis of a diamine iron(III) phosphate is reported. It leads to a crystalline form in the orthorhombic system, space group $Pnma$, at room temperature, however it undergoes a structural phase transition towards monoclinic $P2_1/n$, from 250 K to 100 K. The TG-DTG curves show that three mass losses occur. The application of isoconversional methods MFR and Vyaz allowed us to evaluate the activation energy in each step as a function of the extent of conversion for the both hydrogen (two samples, with different crystal size) and deuterated forms. A similar behaviour of the activation energy was observed for the three samples. In order to test the kinetic parameters, $\alpha - T$ curves were reconstructed and compared with the experimental data showing a good agreement.

Acknowledgements

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Figure captions

1
2 **Fig. 1.** SEM image showing the morphology of $\text{Fe}(\text{NH}_3)_2\text{PO}_4$ sample.
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4 **Fig. 2.** Crystal structure of $\text{Fe}(\text{NH}_3)_2\text{PO}_4$. Octahedrons FeO_4N_2 in brown, and tetrahedrons PO_4 in grey colour.
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6 Atoms of nitrogen in blue and hydrogen in white.
7

8 **Fig. 3.** The channels along the b axis are fully occupied by the ammonia molecules in the crystal packing of
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10 $\text{Fe}(\text{NH}_3)_2\text{PO}_4$.
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12 **Fig. 4.** Variation of cell parameters with temperature for $\text{Fe}(\text{NH}_3)_2\text{PO}_4$.
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14 **Fig. 5.** HT-PXRD diffraction patterns evolution of $\text{Fe}(\text{NH}_3)_2\text{PO}_4$ under thermal treatment.
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16 **Fig. 6.** TG and DTG curves of $\text{Fe}(\text{NH}_3)_2\text{PO}_4$ obtained at 10 K min^{-1} heating rate.
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18 **Fig. 7.** Dependence of the activation energy on the extent of conversion for (a) $\text{Fe}(\text{NH}_3)_2\text{PO}_4$ (large crystals), and
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20 pre-synthesized materials: (b) $\text{Fe}(\text{NH}_3)_2\text{PO}_4$ [10] and (c) $\text{Fe}(\text{ND}_3)_2\text{PO}_4$ [11].
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22 **Fig. 8.** Comparison of the experimental (solid lines) and reconstructed (points) $\alpha - T$ curves for monocrystalline
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Figure1

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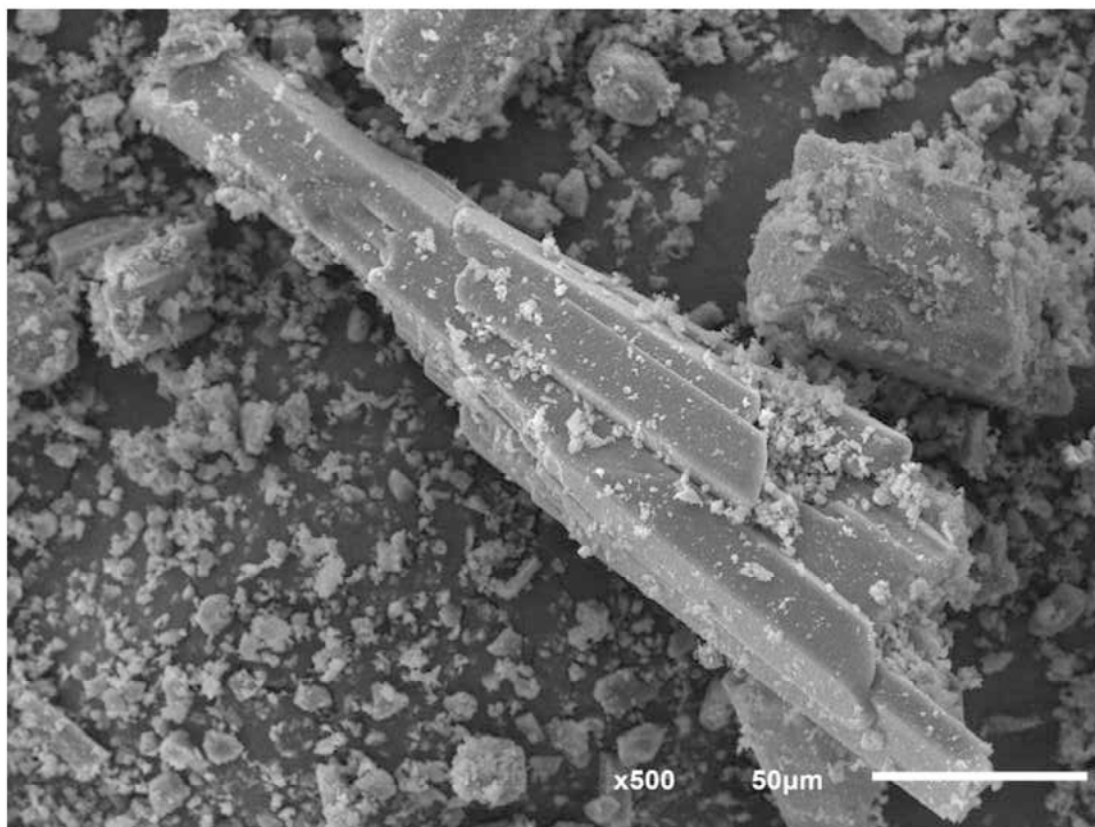


Figure2

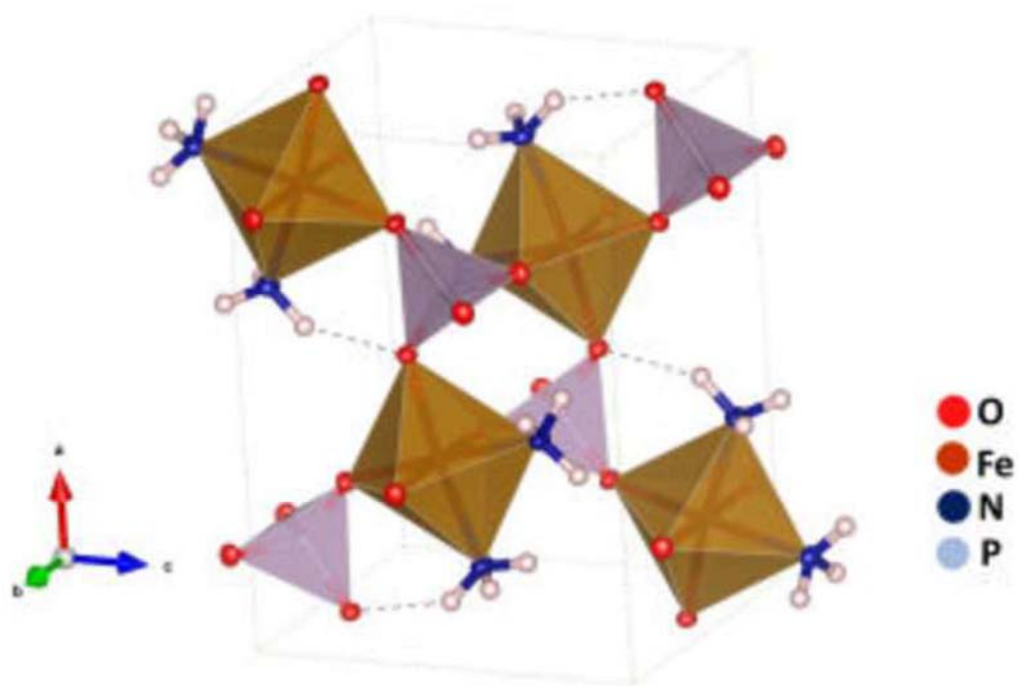
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Figure3

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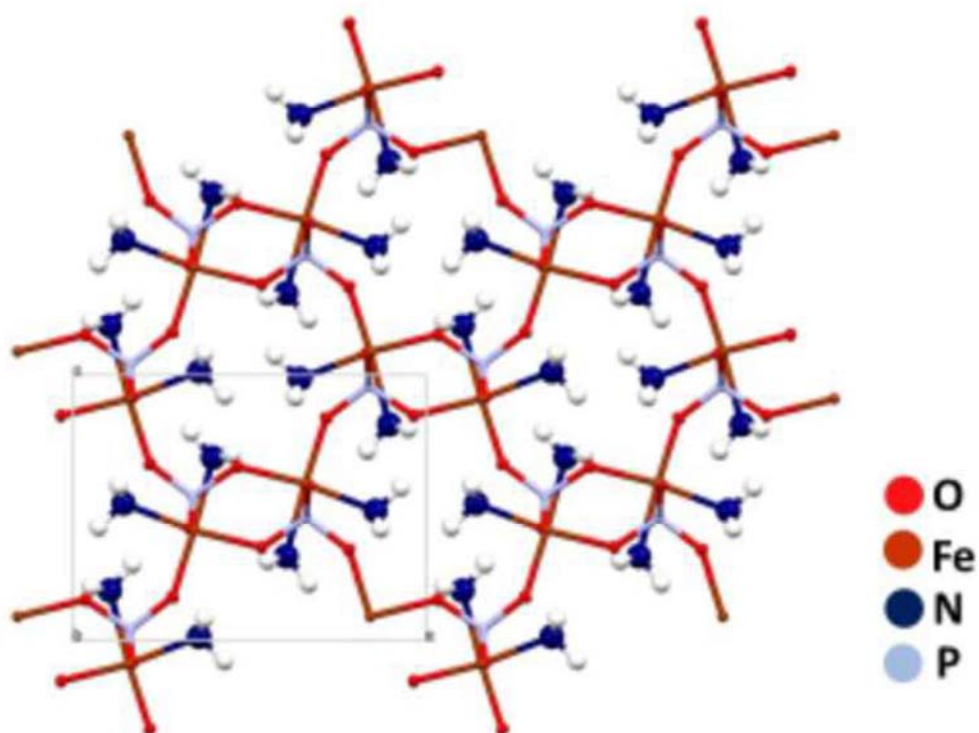


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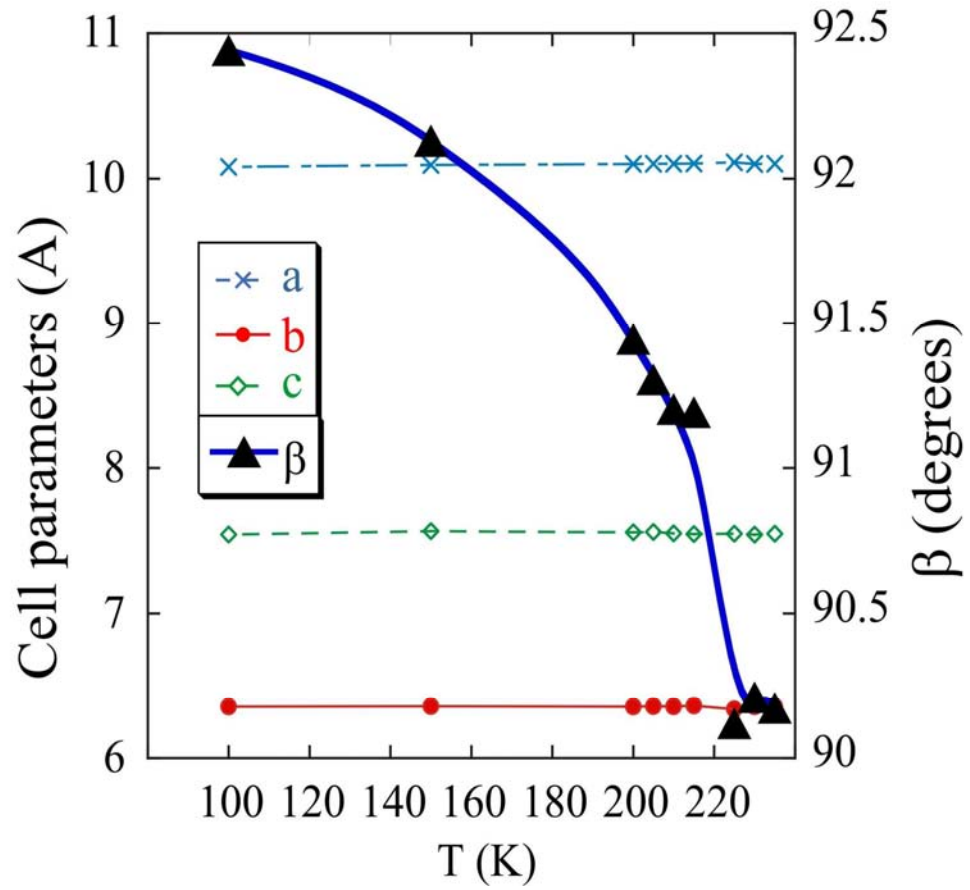
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Figure5

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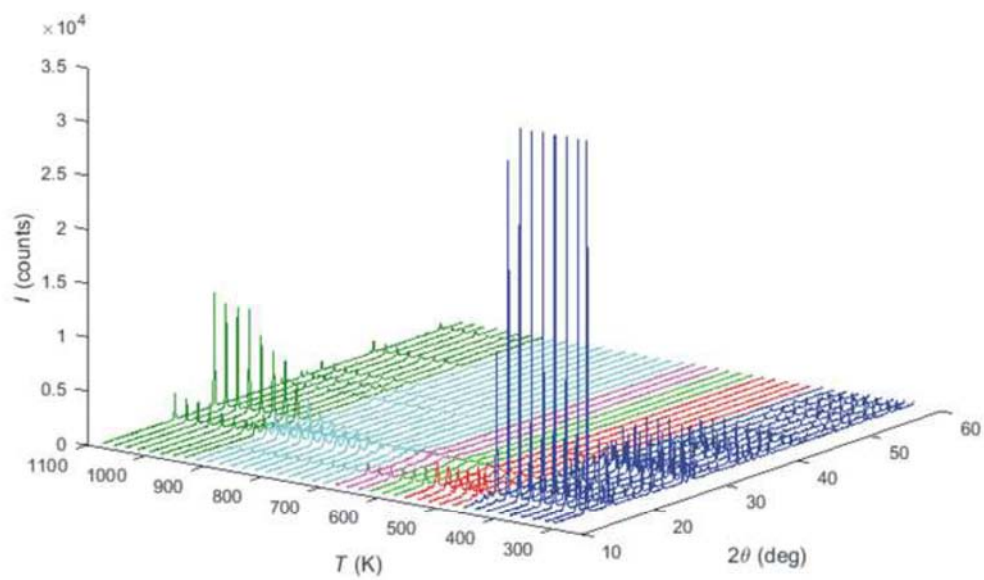


Figure6

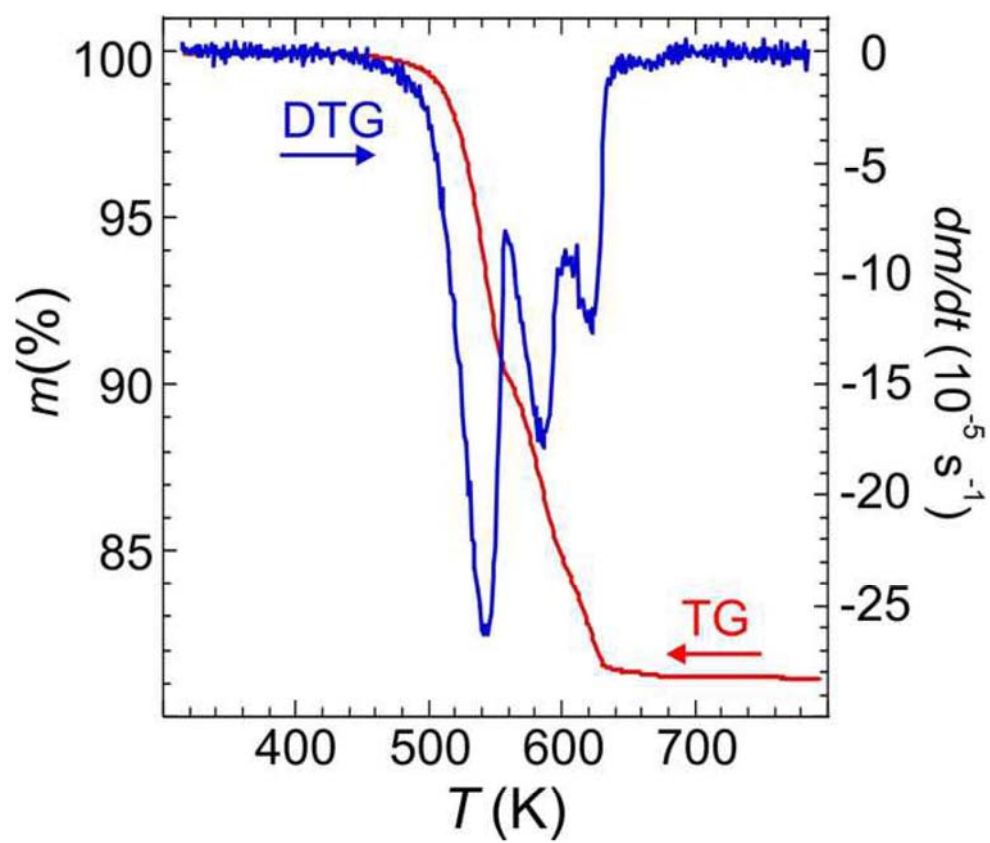
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Figure7

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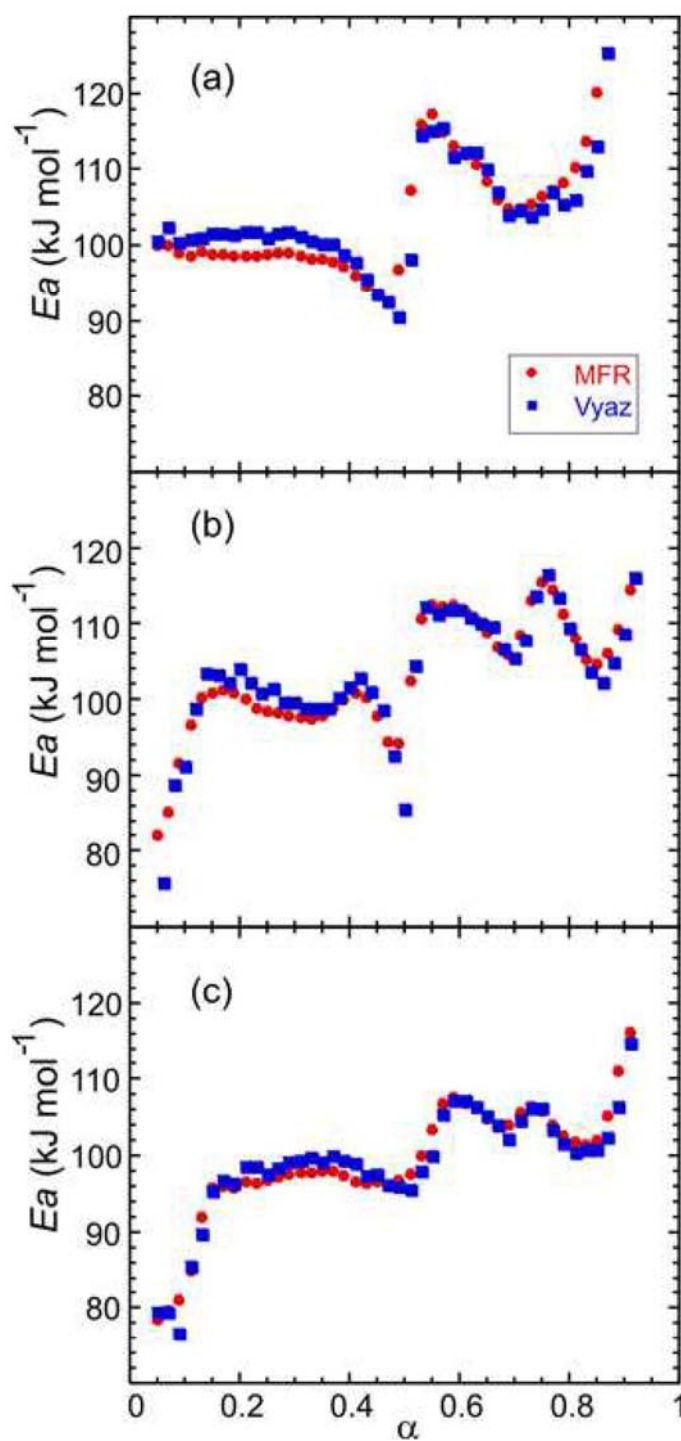


Figure8

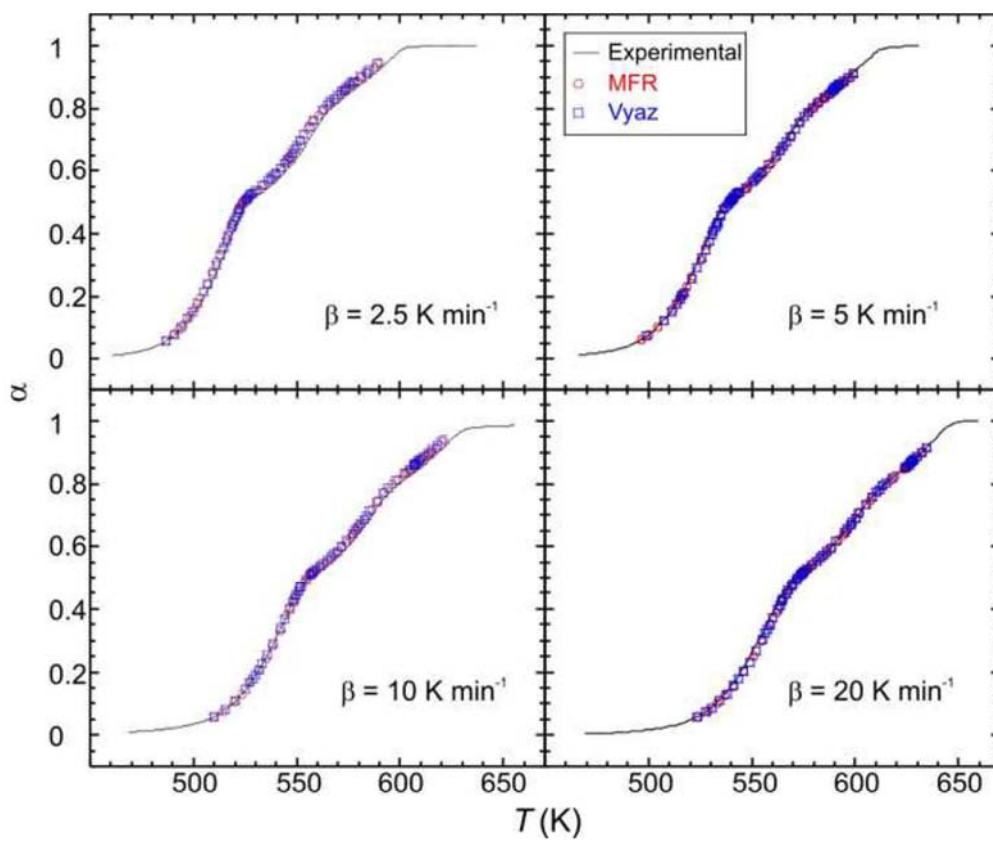
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Table1

Table 1. Crystal data and structure refinement

Molecular formula	FeN ₂ H ₆ PO ₄
Formula mass/g mol ⁻¹	184.89
Color	Green
Wavelength/Å	1.5418
Crystal system	Orthorhombic
Space group	Pnma n° 62
a/Å	10.1116(2)
b/Å	6.3652(1)
c/Å	7.5691(1)
Z	4
Calculated density/g cm ⁻³	2.521
Volume/Å ³	487.165(14)
Crystal size/mm ³	0.08x0.02x0.01
θ range/deg	7.0 to 74°
Absorption coefficient/mm ⁻¹	27.462
F(000)	372
Index ranges	-12<=h<012 -7<=k<=7 -9<=l<=9
Reflections collected	4187
Independent reflections	538 [R(int)=0.02]
Completeness θ = 70.00°	100.0%
Refinement method	Full-matrix least-squares on F ²
Data/restraints/parameters	538/0/50
Goodness-of-fit on F ²	1.143
Final R ind.[I > 2sigma(I)]	R1 = 0.0215 wR2 = 0.0613
R indices (all data)	R1 = 0.0217 wR2 = 0.0614
Largest diff. Peak and hole	0.289 and -0.816 e.Å ⁻³

Table2

Table 2. Fractional coordinates for the $\text{Fe}(\text{NH}_3)_2\text{PO}_4$

Atom	x	y	z	U(eq)
Fe	0.8422(1)	$\frac{3}{4}$	0.0896(1)	10(1)
P	0.8384(1)	$\frac{1}{4}$	-0.0412(1)	10(1)
O(1)	0.8348(1)	0.4416(2)	0.0819(1)	16(1)
O(2)	0.7826(1)	$\frac{3}{4}$	0.3369(2)	16(1)
O(3)	1.0343(1)	$\frac{3}{4}$	0.1536(2)	16(1)
N(1)	0.6428(2)	$\frac{3}{4}$	-0.0137(3)	22(1)

Table3

Table 3. Bond lengths [Å] and angles [deg] for Fe(NH₃)₂PO₄

Fe-O(1)	1.9652(14) x 2	O(1)-Fe(1)-O(1)	174.45(6)
Fe-O(2)	1.9663(16)	O(1)-Fe(1)-O(2)	90.96(3)
Fe-O(3)	2.0021(15)	O(1)-Fe(1)-O(3)	92.53(3)
		O(2)-Fe(1)-O(3)	93.87(6)
Fe-N(1)	2.1624(19)	O(1)-Fe(1)-N(1)	87.34(3)
Fe-N(2)	2.1661(18)	O(2)-Fe(1)-N(1)	93.34(8)
P-O(1)	1.5354(13) x 2	O(3)-Fe(1)-N(1)	172.79(8)
P-O(2)	1.5318(15) x 2	O(1)-Fe(1)-N(2)	88.90(3)
P-O(3)	1.5427(15) x 2	O(2)-Fe(1)-N(2)	176.68(7)
N(1)-H(11)	0.9612	O(3)-Fe(1)-N(2)	89.45(6)
N(1)-H(12)	0.9913	N(1)-Fe(1)-N(2)	83.34(8)
N(2)-H(21)	0.9534	O(2)-P(1)-O(1)	110.29(5)
N(2)-H(22)	0.9752	OO(1)-P(1)-O(1)	105.20(10)
		O(2)-P(1)-O(3)	109.51(10)
		O(1)-P(1)-O(3)	110.74(5)
		P(1)-O(1)-Fe(1)	144.16(8)
		P(1)-O(2)-Fe(1)	144.90(10)
		P(1)-O(3)-Fe(1)	132.56(9)
		Fe(1)-N(1)-H(11)	109.3
		Fe(1)-N(1)-H(12)	115.6
		H(11)-N(1)-H(12)	105.1
		Fe(1)-N(2)-H(21)	104.8
		Fe(1)-N(2)-H(22)	124.6
		H(21)-N(2)-H(22)	106.4

Symmetry transformations used to generate equivalent atoms:

#1 x,-y+3/2,z #2 -x+3/2,-y+1,z-1/2 #3 x,-y+1/2,z

#4 -x+2,-y+1,-z #5 -x+3/2,-y+1,z+1/2