# Preparation and Thermal Expansion of Calcium Iron Zirconium Phosphates with the NaZr$_2$(PO$_4$)$_3$ Structure

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**Abstract**
Ca$_{0.5(1+x)}$Zr$_{2-x}$Fe$_x$(PO$_4$)$_3$ phosphates have been synthesized by a sol–gel process. The individual compounds and solid solutions obtained crystallize in the NaZr$_2$(PO$_4$)$_3$ structure (trigonal symmetry, sp. gr. $R\bar{3}$). Using high-temperature X-ray diffraction, we have determined their thermal expansion parameters in the temperature range from 25 to 800°C. With increasing $x$, the magnitudes of their linear thermal expansion coefficients and thermal expansion anisotropy decrease. Most of the synthesized phosphates can be rated as low-thermal-expansion compounds and can be regarded as materials capable of withstanding thermal "stress."

*Keywords:* NZP, phosphate, sol–gel process, X-ray diffraction, solid solution, thermal expansion.

## INTRODUCTION

Owing to the wide isomorphism characteristic of the NaZr$_2$(PO$_4$)$_3$ (NZP) structure [1–3], structural analogs of NZP are of interest for designing new inorganic materials for a variety of purposes: radioactive waste consolidation [4, 5], minor actinide transmutation [6, 7], thermally stable ceramics [8, 9], ionic conductors [10, 11], phosphors [12, 13], and other applications.

Such compounds have a framework structure and can be described by the general crystal-chemical formula (M1)(M2)$_3$[T$_2$(XO$_4$)$_3$]. Their structural framework is made up of TO$_6$ octahedra and XO$_4$ tetrahedra, which share oxygens. The blocks linked in this manner have the form of helical ribbons running along the crystallographic axis $c$. The framework contains M1 and M2 voids, differing in size, which are capable of accommodating a wide variety of cations compensating its charge [2, 3].

Various iso- and heterovalent substitutions allow one to control the properties of the resulting compounds, making them respond in the desired manner. One such property is the thermal expansion of materials. A crystal-chemical approach makes it possible to create materials of particular compositions with low and controlled thermal expansion, which are capable of withstanding thermal "stress" and combining with other materials without additional deformation.

Most studies concerned with the high-temperature crystal chemistry of NZP-type orthophosphates deal with double phosphates containing tetravalent elements on the T site of the framework and alkali-metal or alkaline-earth cations on the M sites.

In the $AZr_2(PO_4)_3$ [14] and $AHf_2(PO_4)_3$ [15] (A = Na, K, Rb, Cs) series, the magnitudes of the thermal expansion and anisotropy coefficients decrease as the ionic radius of the alkali metal cation increases in going form Na to Cs; that is, the cesium-containing orthophosphates have the smallest thermal expansion coefficients (TECs) and lowest anisotropy [15].

In the $B_{0.5}Zr_2(PO_4)_3$ (B = Mg, Ca, Sr, Ba) zirconium phosphates, containing the doubly charged cations on the M1 site, increasing the size of the $B^{2+}$ cation leads to a change in the sign of their thermal expansion coefficients. In particular, the calciumcontaining phosphates have thermal expansion coefficients $\alpha_a < 0$ and $\alpha_c > 0$, whereas the strontium- and barium- containing phosphates have $\alpha_a > 0$ and $\alpha_c < 0$ [16].

In the $Na_{2x}R_{0.5+x}Nb_{1.5-x}(PO_4)_3$ (R = Al, Fe) systems, the magnitude of the linear thermal expansion coefficient was shown to decrease with decreasing Msite occupancy [8].

Many of the NZP-type phosphates have low thermal expansion [8, 9, 14–19]. This can be accounted for in terms of the unique behavior of their structure on heating: expansion and compression in different crystallographic directions [20]. In designing materials stable to thermal "stress," not only a small average thermal expansion coefficient but also low thermal expansion anisotropy are important.

According to experimental data [8, 9, 14, 15, 18, 20] and theoretical simulation results [21], the main factors influencing the thermal expansion of NZP-type compounds are (1) the interstices positions occupancy [8, 9] and (2) the radius of the ions on the interstices positions [9, 14, 15, 18, 20]. The reason for this is that the weakest bonds, namely, the metal–oxygen bonds in out-framework positions, make a predominant contribution to the behavior of the crystal structure on heating. Because of this, the incorporation of cations with a large ionic radius into the M sites of these compounds or a reduction in the occupancy of these sites leads to a reduction in the magnitude of their linear thermal expansion coefficients.

Examples of how these principles work are the compounds $Al_{0.5}Nb_{1.5}(PO_4)_3$ [8] (factor 1), $CsHf_2(PO_4)_3$ [15], and $Nd_{0.33}Zr_2(PO_4)_3$ [9] (factor 2). However, not many such substances are currently known, and most of them contain expensive cations, such as Cs, Nb, and lanthanides, so the use of such substances is commercially unviable. In connection with this, there is currently great practical interest in a search for new ways of reducing thermal expansion coefficients.

In this work, using $Ca_{0.5(1+x)}Zr_{2-x}Fe_x(PO_4)_3$ phosphates as an example, we demonstrate how substitutions of cations with a smaller ionic radius in comparison with zirconium on the T site enable controlled changes in the volume of the framework in the NZP structure. This should ensure a decrease in the volume of the framework and, consequently, in the volume of the framework voids. As a result, principle 2 would be expected to be operative (for the cations with the smaller ionic radius), which would lead to an increase in the number of low-thermal-expansion compounds. Moreover, varying the Zr : Fe ratio in the composition of the compounds under consideration will allow one to resolve an issue of no less importance: controlled changes in thermal expansion characteristics.

# EXPERIMENTAL

**Subjects of investigation.** As subjects of investigation, we used $Ca_{0.5(1+x)}Zr_{2-x}Fe_x(PO_4)_3$ phosphates with $x = 0–1.25$. The ionic radius of iron cations is smaller than that of zirconium: $R(Zr^{4+}) = 0.72$ Å and $R(Fe^{3+}) = 0.55$ Å.

**Synthesis.** The compounds were synthesized by a sol–gel process, using ethanol as a salting-out agent. Starting chemicals were mixed in stoichiometric ratios. To a 1 M $Ca(NO_3)_2$ solution was added a weighed amount of $ZrOCl_2 \cdot 8H2O$ and a 0.5 M $Fe(NO_3)_3$ solution. Next, a 1 M $NH_4H_2PO_4$ solution was added dropwise to the resultant mixture with constant stirring. This led to the formation of a gel-like precipitate. After that, ethanol was added to the precipitate. After brief mixing, the gel was dried at 90°C for 20 h. The resultant powder was thermostated at temperatures of 600 and 800°C for 20 h in each step, with intermediate grinding in an agate mortar and X-ray diffraction characterization.

**Characterization techniques.** X-ray diffraction measurements were performed on a Shimadzu LabX XRD 6000 X-ray diffractometer (Cu$K\alpha$ radiation, $\lambda$ =1.54056 Å) in the angular range $2\theta = 10°–50°$. Hightemperature X-ray diffraction data were collected in the temperature range 25–800°C on a Panalytical X'Pert Pro diffractometer equipped with an Anton Paar HTK 1200 N high-temperature oven chamber. Differential scanning calorimetry (DSC) curves were obtained on a SETARAM LABSYS DSC 1600 differential scanning calorimeter in the temperature range from 25 to 1000°C at a heating rate of 10°C/min.

# RESULTS AND DISCUSSION

The synthesized samples had the form of polycrystalline powders ranging in color from white to dark brown, depending on Fe content. According to X-ray diffraction data (Fig. 1), the compounds under study crystallize in the $NaZr_2(PO_4)_3$ structure, as expected (trigonal symmetry, sp. gr. $R\bar{3}$, analog of $Ca_{0.5}Zr_2(PO_4)_3$ [16]). Figure 2 shows the unit-cell parameters as functions of $x$ for the phosphates under consideration. As expected, the unit-cell parameters decrease with increasing $Fe^{3+}$ content.

The high-temperature X-ray diffraction data in Fig. 3 demonstrate that, over the entire composition range studied, the unit-cell parameters of the phosphates vary on heating in a similar manner: the $a$ parameter decreases, whereas the $c$ parameter rises. This behavior is typical of the NZP phosphate family. The only exception is the end-member of the series under consideration, $Ca_{1.125}Zr_{0.75}Fe_{1.25}(PO_4)_3$ ($x = 1.25$): both of its unit-cell parameters increase with increasing temperature.

For some of the samples, these dependences deviate from linear behavior. This shows up as a change in the slope of the temperature dependence of the $a$ cell parameter above 700°C for the samples with $x = 0.25$ and 0.5. For clarity, these curves are presented in Fig. 4 on a different scale.
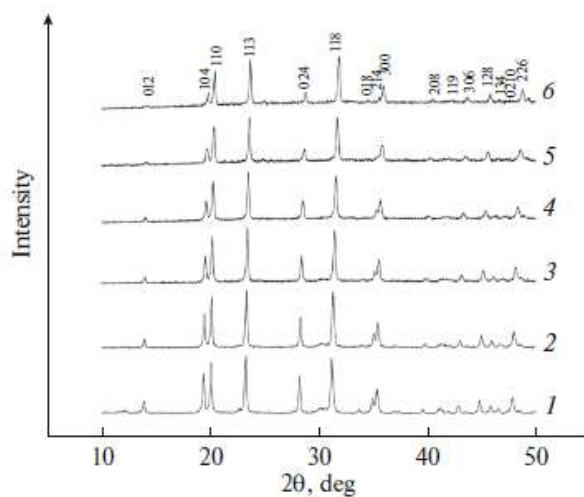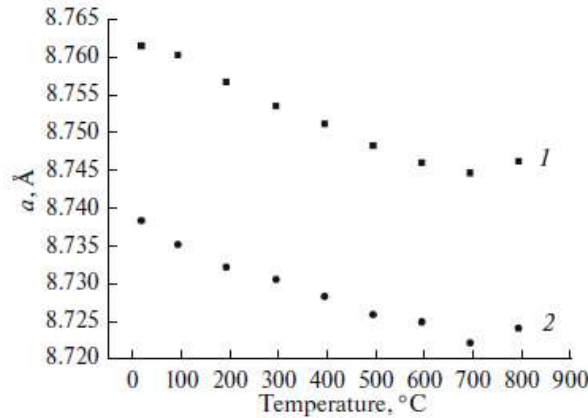
**Fig. 1.** X-ray diffraction patterns of the $Ca_{0.5(1+x)}Zr_{2-x}Fe_x(PO_4)_3$ phosphates with $x =$ (*1*) 0, (*2*) 0.25, (*3*) 0.5, (*4*) 0.75, (*5*) 1, and (*6*) 1.25.
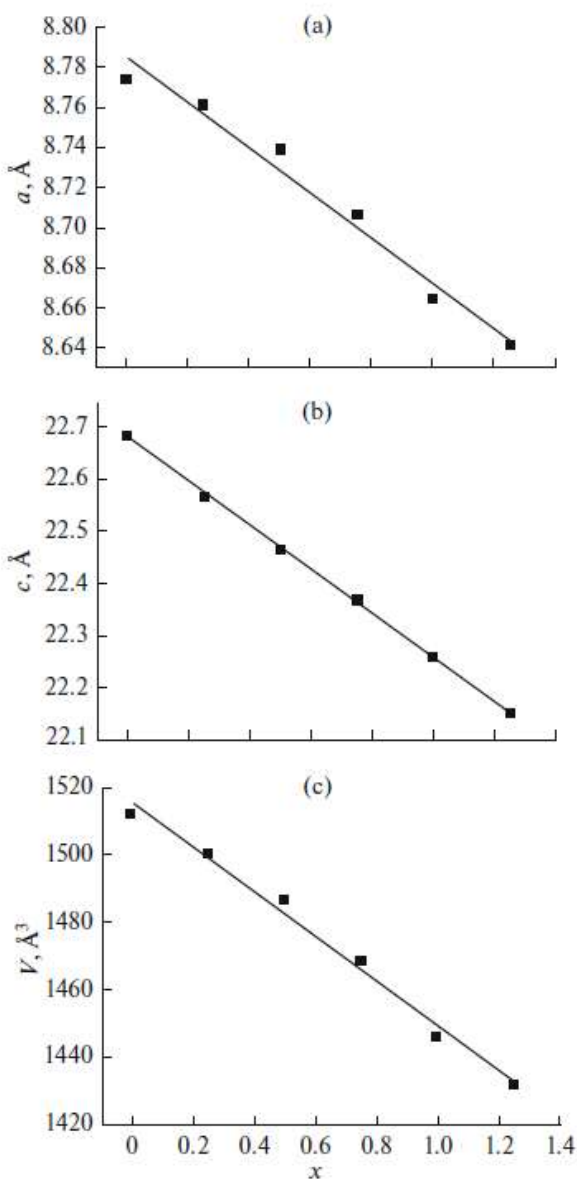


**Fig. 2.** Composition dependences of the unit-cell parameters (a) $a$, (b) $c$, and (c) $V$ for the $Ca_{0.5(1+x)}Zr_{2-x}Fe_x(PO_4)_3$ phosphates.
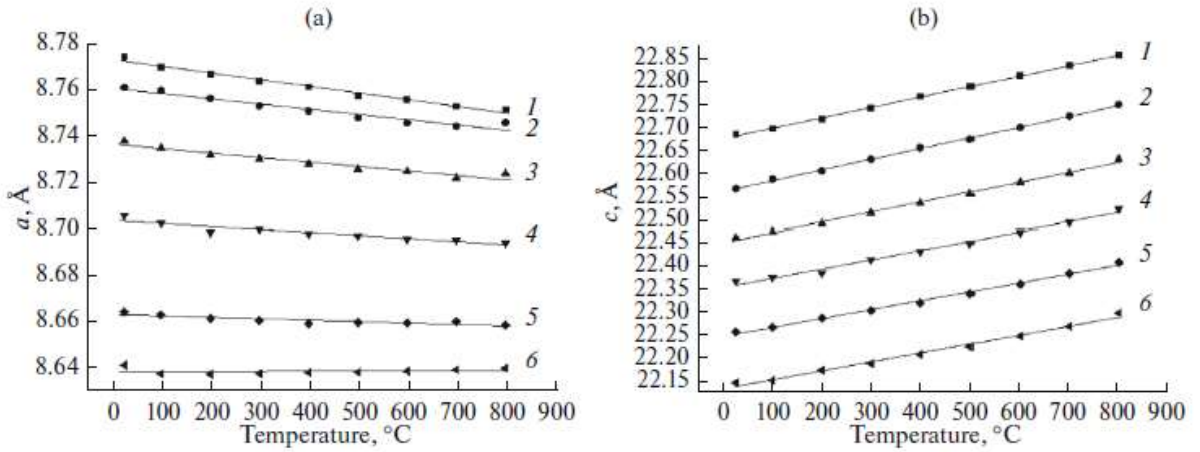
**Fig. 3.** Temperature dependences of the unit-cell parameters (a) $a$ and (b) $c$ for the $Ca_{0.5(1+x)}Zr_{2-x}Fe_x(PO_4)_3$ phosphates with $x =$ (*1*) 0, (*2*) 0.25, (*3*) 0.5, (*4*) 0.75, (*5*) 1, and (*6*) 1.25.



**Fig. 4.** Temperature dependences of the unit-cell parameter $a$ for the $Ca_{0.5(1+x)}Zr_{2-x}Fe_x(PO_4)_3$ phosphates with $x =$ (*1*) 0.25 and (*2*) 0.5.

To find out the cause of this behavior, we performed a DSC scan of the $Ca_{0.75}Zr_{1.5}Fe_{0.5}(PO_4)_3$ compound in the temperature range from 25 to 1000°C (Fig. 5). The DSC curve shows a thermal event at temperatures from 600 to 800°C, which seems to be a phase transition. It seems likely that it is this transition which is responsible for the increase in the unit-cell parameter $a$ of the samples. Further research is needed to gain insight into the structural changes due to the assumed phase transition.

We calculated the axial ($\alpha_a$ and $\alpha_c$), average ($\alpha_{av}$), and volumetric ($\beta$) thermal expansion coefficients and thermal expansion anisotropy ($\Delta\alpha$) of the phosphates under investigation in the temperature range from 25 to 800°C (from 25 to 700°C for the samples with $x =$ 0.25 and 0.5) (Table 1, Fig. 6).

Most of the synthesized phosphates can be rated as low-thermal-expansion compounds. Analysis of the composition dependences of the thermal expansion parameters in Fig. 6 indicates that increasing the Fe content of the $Ca_{0.5(1+x)}Zr_{2-x}Fe_x(PO_4)_3$ samples and, as a consequence, reducing the unit-cell volume reduce the magnitude of the linear thermal expansion coefficients ($\alpha_a$ and $\alpha_c$) and, accordingly, thermal expansion anisotropy ($\Delta\alpha$), whereas the average and volumetric thermal expansion coefficients ($\alpha_{av}$ and $\beta$) increase.
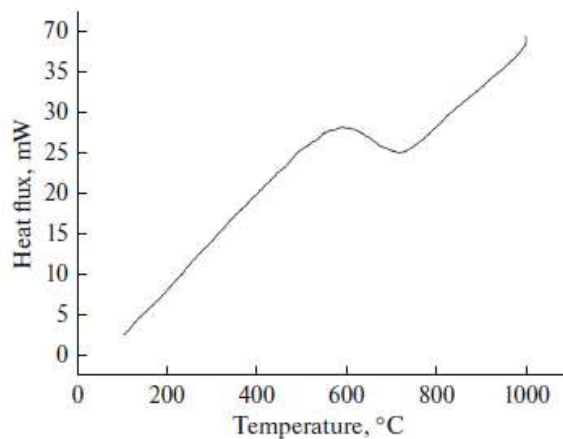
**Fig. 5.** DSC data for the $Ca_{0.75}Zr_{1.5}Fe_{0.5}(PO_4)_3$ phosphate.

**Table 1.** Thermal expansion parameters of the $Ca_{0.5(1+x)}Zr_{2-x}Fe_x(PO_4)_3$ phosphates

| x | $\alpha_a \cdot 10^6$ °C$^{-1}$ | $\alpha_c \cdot 10^6$ °C$^{-1}$ | $\alpha_{cp} \cdot 10^6$ °C$^{-1}$ | $\beta \cdot 10^6$ °C$^{-1}$ | $\Delta\alpha \cdot 10^6$ °C$^{-1}$ |
|---|---|---|---|---|---|
| 0 | -3,31 | 9,88 | 1,09 | 3,33 | 13,19 |
| 0,25 | -2,97 | 10,16 | 1,41 | 4,15 | 13,13 |
| 0,5 | -2,52 | 9,10 | 1,35 | 3,95 | 11,62 |
| 0,75 | -1,49 | 8,87 | 1,96 | 5,80 | 10,36 |
| 1 | -0,69 | 8,64 | 2,42 | 7,21 | 9,34 |
| 1,25 | 0,46 | 8,73 | 3,22 | 8,86 | 8,27 |
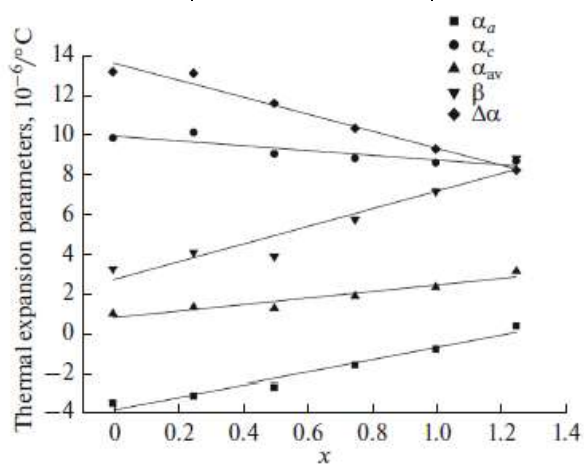


**Fig. 6.** Composition dependences of the thermal expansion parameters $\alpha_a$, $\alpha_c$, $\alpha_{av}$, $\beta$, and $\Delta\alpha$ for the $Ca_{0.5(1+x)}Zr_{2-x}Fe_x(PO_4)_3$ phosphates.

Thus, the proposed crystal-chemical principle of controlled changes, including a reduction, in thermal expansion parameters (linear coefficients and anisotropy) has been demonstrated in this study.

## CONCLUSIONS

A crystal-chemical principle of a reduction and controlled changes in thermal expansion characteristics of NZP-type compounds through a reduction in the volume of their framework by introducing smaller cations has been used to model the composition of $Ca_{0.5(1+x)}Zr_{2-x}Fe_x(PO_4)_3$ phosphates ($R(Zr^{4+}) = 0.72$ Å and $R(Fe^{3+}) = 0.55$ Å). The phosphates of this series with $x = 0$–1.25 have been synthesized by a sol–gel process. According to X-ray diffraction data, they have the $NaZr_2(PO_4)_3$ structure (trigonal symmetry, sp. gr. $R\bar{3}$). With increasing $x$ (Fe content), the unit-cell parameters and volume of the phosphates decrease.

According to high-temperature X-ray diffraction data obtained in the range 25–800°C, the lattice parameters $a$ and $c$ are linear functions of $t$: $a$ decreases and $c$ rises with temperature. In the case of the phosphates with $x = 0.25$ and 0.5, there is a deviation from linear behavior at temperatures above 700°C. This finding correlates with the present DSC results, which point to a phase transition in the range 600–800°C. As expected, the thermal expansion characteristics $\alpha_a$, $\alpha_c$, and $\Delta\alpha$ tend to zero with increasing Fe content in the NZP frameworks of the phosphate series studied.

Thus, the crystal-chemical approach used here has made it possible to increase the number of known lowthermal- expansion NZP-type compounds capable of withstanding thermal "shocks" in a wide temperature range. It is promising to apply this approach to isostructural framework compounds containing different tetrahedral anions, similar to $NaZr_2(PO_4)_3$.

## ACKNOWLEDGMENTS

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