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New NZP-based phosphates with low and controlled thermal expansion

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In the present work thermal expansion of niobium phosphates with framework structure belonging to the structure type of $NaZr_2(PO_4)_3$ (NZP) was (examined). Among the big number of complex orthophosphates with framework structure $[T_2(PO_4)_3]^{p-}$, the phosphates belonging to $NaZr_2(PO_4)_3$ structure family are investigated more widely. $NaZr_2(PO_4)_3$ itself is of rhombohedral structure (sp. gr. $R\,\bar{3}\,c$). Its framework $\{[Zr_2(PO_4)_3]^{p-}\}_{3\infty}$ is a three-dimensional lattice consisting of PO_4-tetrahedra vertex-linked to ZrO_6-octahedra. 3D linked-voids, penetrating the framework, can be vacant and also partially or fully occupied by cations compensating framework charge p. There are two types of voids: M1- and M2-sites that are different by location, shape, and size [1]. The general crystal chemical formula of these compounds is $\{(M1)(M2)_3[L_2(PO_4)_3]^{p-}\}_{3\infty}$, where L are framework sites. One of the remarkable and useful properties of NZP-phosphates is its low thermal expansion [2–10]. Low NZP-structure deformations on heating are due to the presence of firmly linked TO_6- and PO_4-polyhedra in its framework and depend on the number of vacant M-sites and also nature of cations occupying them. They tend to decrease when the number of vacant interstitial sites increases.

We have synthesized phosphates $Na_2R_{0.5+x}Nb_{1.5-x}(PO_4)_3$, where R = A1, Fe; $0 \leq x \leq 0.5$. The examination of the influence of M1—site occupation on the behavior of the above mentioned phosphates was carried out for the purpose of further prediction of compositions with controlled thermal characteristics.

The samples were prepared by solid-state reaction. The samples were prepared from stoichiometric quantities of Fe_2O_3, Al_2O_3, Nb_2O_5, NaCl, and $NH_4H_2PO_4$. Thoroughly grounded mixtures were heated at 450 °C followed by subsequent heat treatments at 600, 800, and 1000 °C (under X-ray diffraction control) with intermediate regrinding at each stage. The Al samples were white powders and Fe samples were pink-colored.

The samples were characterized by X-ray powder diffraction, IR-spectroscopy, and high temperature X-ray powder diffraction. As follows from X-ray powder diffraction data the single-phase products were obtained for compositions with $0.1 \leq x \leq 0.5$. In the diffraction pattern of $Al_{0.5}Nb_{1.5}(PO_4)_3$ and $Fe_{0.5}Nb_{1.5}(PO_4)_3$ low-intensive reflections of impurity phase ($NbOPO_4$) were detected. The hexagonal lattice parameters were calculated from indexing data. They do not change significantly in the series with x changing for Al: $a = 8.484$–8.577 Å, $c = 21.72$–21.98 Å, and for Fe: $a = 8.592$–8.615 Å, $c = 22.04$–22.09 Å. The phosphates were found to crystallize in NZP structure type with $R\,\bar{3}\,c$ space group. IR-spectroscopy data were in full agreement with X-ray diffraction data. IR-spectra show that investigated compounds belong to orthophosphate class.

Structure refinement of $Fe_{0.5}Nb_{1.5}(PO_4)_3$ phosphate was carried out by powder neutronography. Neutron diffraction spectrum of powder sample, inserted into cylindric can ($d = 10$ mm) was detected at room temperature on time-of-flight diffractometer DN-2 (maximal resolution $\Delta d/d = 0.01$), installed on impulse reactor IQR-2 JINR, Dubna. Structure refinement was made by Rietveld technigue using computer programme Mria [11].

Structure refinement of $Fe_{0.5}Nb_{1.5}(PO_4)_3$ phosphate was carried out in space group $R\,\bar{3}\,c$ taking the structure of titanium niobium phosphate as a structural analogue [12]. The portion of the structure is shown in Fig. 1: $a = 8.6298(6)$ Å, $c = 22.1221(15)$ Å. It is a three-dimensional framework of mixed type with general formula $[Fe_{0.5}Nb_{1.5}(PO_4)_3]$ built up from discrete TO_{6-} octahedra (here $(Fe/Nb)O_6$) and phosphate PO_4-tetrahedra. Ferric and niobium cations are located on the threefold axis and statistically occupy a 12-fold site ($00z$) being coordinated by six oxygen atoms. Typical fragment of this framework is $\{T_2(PO_4)_3\}$ unit (dimmer) consisting of two octahedra linked by three bridging tetrahedra. The presence of this unit is typical for a big number of framework orthophosphates with Nasicon-like structure [13, 14]. These units are joined together in turn by common oxygen atoms to form three-dimensional lattice having large interstitial voids. So, the three-dimensional mixed framework $[Fe_{0.5}Nb_{1.5}(PO_4)_3]$ is formed, covering all cations of the structure.

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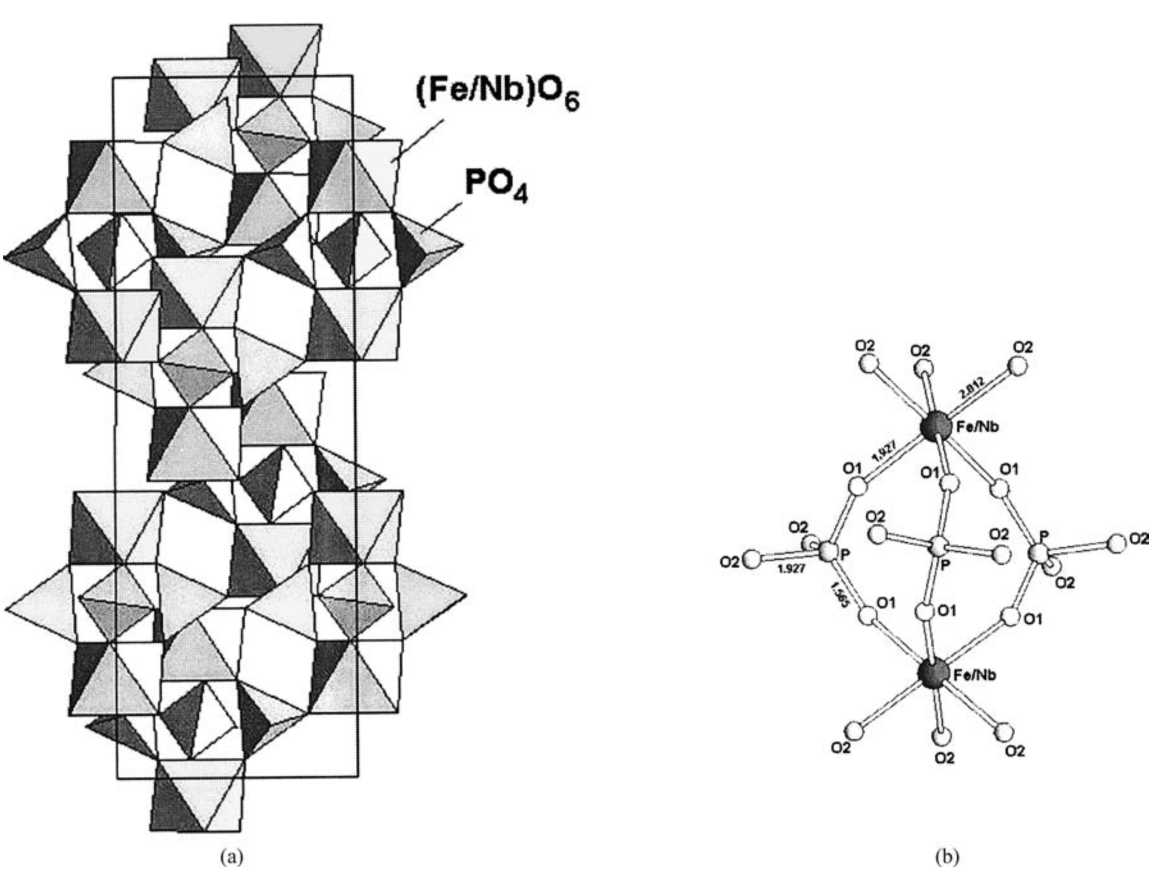

Figure 1 Portion of $Fe_{0.5}Nb_{1.5}(PO_4)_3$ structure: (a) projection on [100] plane, (b) bonds location in $T_2(PO_4)_3$ "dimmer".

The behavior of phosphates on heating was examined by high temperature X-ray powder diffraction method. The data were collected on X-ray powder diffractometer with Co K_α radiation ($\lambda = 1.78892$ Å) fitted with high temperature attachment by a technique described in [15]. The samples were heated at the rate of 10 K/min. The reflections were registered in the temperature range of 20–800 °C in steps of 100 °C. The temperature was measured by Pt-Pt/Rh thermocouple the readings of which were checked by simultaneous measurement of lattice parameters of Al_2O_3 as a reference substance.

From obtained results, the axial coefficients of thermal expansion α_a and α_c and also average coefficients of thermal expansion were determined (Table I).

As it was expected, the phosphates $Al_{0.5}Nb_{1.5}(PO_4)_3$ and $Fe_{0.5}Nb_{1.5}(PO_4)_3$ with all vacant M-sites posses near-zero thermal expansion. Intercalation of Na into M-site of phosphates leads to the increase of the expansion along the c-axis, because among other bonds in the structure, namely Na—O bond is the most undergoing to the deformation on heating. At the same time along the a-axis the contraction of the structure takes place (Fig. 2). Due to anisotropy of α-values ($\alpha_a < 0$, $\alpha_c > 0$), the average coefficients of thermal expansion are not high. The anisotropy $\Delta\alpha = |\alpha_a - \alpha_c|$ increases with increasing x and becomes maximal for phosphate $NaAlNb(PO_4)_3$ and $NaFeNb(PO_4)_3$ ($\Delta\alpha = 23.9 \times 10^{-6}$ and 22.2×10^{-6} 1/K, respectively) and minimal for phosphate $Al_{0.5}Nb_{1.5}(PO_4)_3$ and $Fe_{0.5}Nb_{1.5}(PO_4)_3$ ($\Delta\alpha = 1.1 \times 10^{-6}$ and 3.9×10^{-6} 1/K, respectively). It should be noticed that the phosphate $Al_{0.5}Nb_{1.5}(PO_4)_3$ is one of the rare representatives of compounds having near-zero thermal expansion combined with near-zero anisotropy of thermal expansion. Ceramics based on these compounds should not undergo mickocracking under temperature stress conditions (thermal "shock"). The same behavior on heating is observed for $CsZr_2(PO_4)_3$ ($\alpha_a = -0.6 \times 10^{-6}$ 1/K, $\alpha_c = 0.5 \times 10^{-6}$ 1/K, $\alpha_{av} = -0.2 \times 10^{-6}$ 1/K, and $\Delta\alpha = 1.1 \times 10^{-6}$ 1/K) and $CsHf_2(PO_4)_3$ ($\alpha_a < |-1| \times 10^{-6}$ 1/K, $\alpha_c < 1 \times 10^{-6}$ 1/K, $\alpha_{av} \sim 0 \times 10^{-6}$ 1/K, and $\Delta\alpha \sim 0 \times 10^{-6}$ 1/K) [16]. They show the decrease of α- and $\Delta\alpha$-values for $AM_2^{IV}(PO_4)_3$ com-

TABLE I Parameters of thermal expansion of $Na_{2x}R_{0.5+x}Nb_{1.5-x}(PO_4)_3$ phosphates

Phosphate	Coefficients of thermal expansion ($\alpha \times 10^6$ K^{-1}) α_a	α_c	α_{av}	Anisotropy ($\Delta\alpha \times 10^6$ K^{-1})
$Al_{0.5}Nb_{1.5}(PO_4)_3$	−1.1	0	<0	−1.1
$Na_{0.2}Al_{0.6}Nb_{1.4}(PO_4)_3$	−2.7	9.8	1.48	12.5
$Na_{0.4}Al_{0.7}Nb_{1.3}(PO_4)_3$	−3.1	11.0	1.60	14.1
$Na_{0.6}Al_{0.8}Nb_{1.2}(PO_4)_3$	−3.1	13.5	2.43	16.6
$Na_{0.8}Al_{0.9}Nb_{1.1}(PO_4)_3$	−3.9	17.0	3.06	20.9
$NaAlNb(PO_4)_3$	−4.9	19.0	3.07	23.9
$Fe_{0.5}Nb_{1.5}(PO_4)_3$	−2.6	1.3	−1.31	3.9
$Na_{0.2}Fe_{0.6}Nb_{1.4}(PO_4)_3$	−2.9	8.0	0.73	10.9
$Na_{0.4}Fe_{0.7}Nb_{1.3}(PO_4)_3$	−2.9	10.6	1.60	13.5
$Na_{0.6}Fe_{0.8}Nb_{1.2}(PO_4)_3$	−4.1	13.2	1.67	17.3
$Na_{0.8}Fe_{0.9}Nb_{1.1}(PO_4)_3$	−4.9	15.2	1.80	20.1
$NaFeNb(PO_4)_3$	−4.6	17.6	2.60	22.2

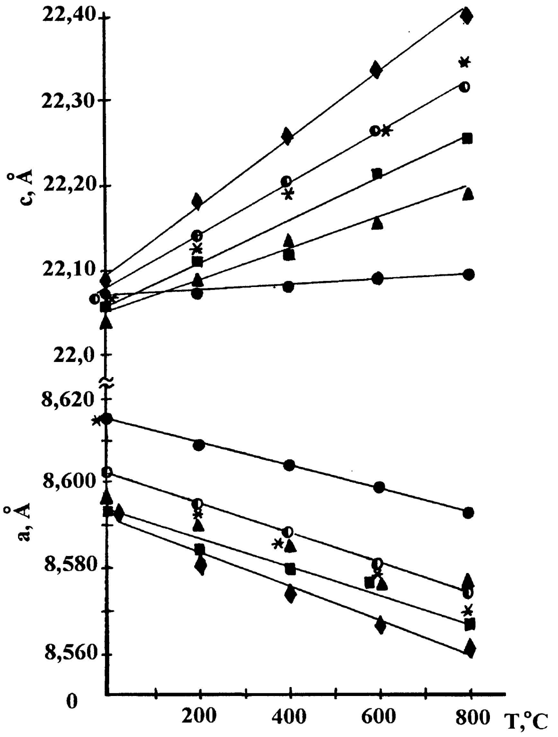

Figure 2 Thermal evolution of lattice parameters of $Na_{2x}Fe_{0.5+x}Nb_{1.5-x}(PO_4)_3$ phosphates.

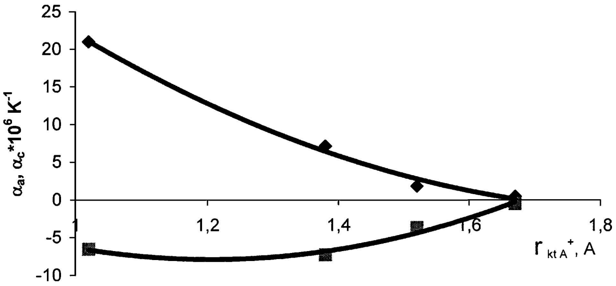

Figure 3 Dependence of thermal expansion coefficients on the size of cations in M1-site for $A^IHf_2(PO_4)_3$; A = Li, Na, K, Rb, Cs [7].

pounds, A = Na, K, Rb, Cs when the substitution of small cations by large ones takes place in interstitial voids (Fig. 3).

Both empirically established regularities of α- and $\Delta\alpha$-values decreasing.

– The decrease of number of interstitial cations in series $Na_2Al_{0.5+x}Nb_{1.5-x}(PO_4)_3$ (Fig.4);

– the increase of size of interstitial cations in series $AM_2^{IV}(PO_4)_3$ (Fig. 3)

illustrate crystallochemical principles, the use of which, when simulating new NZP-based compounds, allows to extend the number of compounds with such unigue thermomechanic properties.

These principles also allow to simulate compounds with controlled and desired characteristics of thermal expansion.

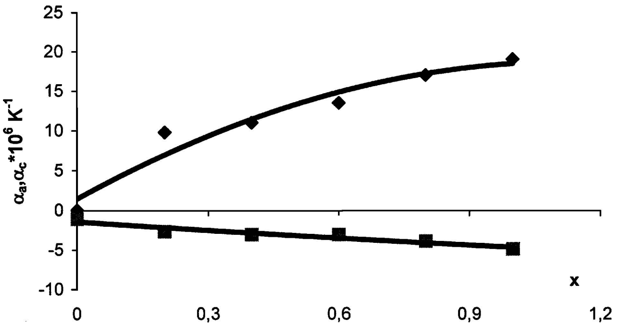

Figure 4 Dependence of thermal expansion coefficients on the number of occupied M1-site for $Na_{2x}Al_{0.5+x}Nb_{1.5-x}(PO_4)_3$.

The need of such properties in materials exists. They are materials applying in space and laser technology, catalysts and catalytic carriers, and other materials with different functionalities, possessing size-keeping ability in a wide themperature range.

Acknowledgments

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