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THERMAL EXPANSION IN THE Zr AND 1-, 2-VALENT COMPLEX PHOSPHATES OF $NaZr_2(PO_4)_3$ (NZP) STRUCTURE*

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Abstract

$A_{5-4x}Zr_xZr(PO_4)_3$ (A=Na, K; $0 \le x \le 1.25$), $Na_{1-x}Cd_{0.5x}Zr_2(PO_4)_3$ ($0 \le x \le 1$), $Na_{5-x}Cd_{0.5x}Zr(PO_4)_3$ ($0 \le x \le 4$) compositions which belong to the NZP structural family were synthesized using the sol-gel method. The lattice thermal expansion of members of these rows were determined up to 600°C by high-temperature X-ray diffractometry. The axial thermal expansion coefficients change from $-5.8 \cdot 10^{-6}$ to $7.5 \cdot 10^{-6}$ $°C^{-1}$ (α_a) and from $2.6 \cdot 10^{-6}$ to $22 \cdot 10^{-6}$ $°C^{-1}$(α_c). These results, in addition to those for other NZP compounds allow us to explain their low thermal expansion. The mechanism can be attributed to strongly bonded three-dimensional network structure, the existence of structural holes capable to damp some of the thermal vibrations and anisotropy in the thermal expansion of the lattice.

Keywords: complex zirconium phosphates, NZP structure, thermal expansion, X-ray diffraction

Introduction

The NZP family of materials attracts wide interest fro its low and tailorable thermal expansion, the ability to immobilize radioactive nuclides, their ionic conductivity, and possible catalytic properties, etc. [1–4].

In the rhombohedral NZP structure PO_4 tetrahedra are linked by corner-sharing with ZrO_6 octahedra forming a three-dimensional framework built up by $[Zr_2(PO_4)_3]^-$ units in which each O atom is bonded to only one P and one Zr atom (Fig. 1). The infinite columns of these units lie along the *c* direction of the hexagonal unit cell parallel to each other and these columns are joined together perpendicular to the *c* axis by PO_4 tetrahedra to develop the three-dimensional framework. Holes within this framework of columns are formed which will accommodate the larger alkali cations. Two kinds of holes are present; one alkali site occurs in the columns of Zr octahedra, M1, which is usually occupied and the other site, M2, located between the columns of Zr

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octahedra. In $NaZr_2(PO_4)_3$ the M1 site is fully occupied while the M2 site is vacant. The M2 sites become populated when additional cations are needed for charge compensation with polyvalent cations other than zirconium.

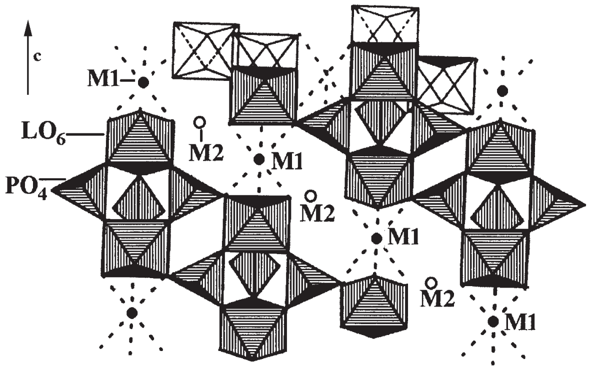

Fig. 1 Simplified schematic figure of the crystal NZP structure type with the projection along *c* axis

The general crystal chemical formulae for compounds in the NZP family is: $(M1)(M2)_3\{[L_2(PO_4)_3]^{p-}\}_{3\infty}$ where M1 and M2 are crystallographic positions in the framework holes, L are positions of the framework. The framework and the ions inserted into the M1 and M2 sites behave as two parts of the structure playing different roles. Chemical bonds between the atoms forming the framework are strong covalent bonds and the inserted ions are bonded to the M1 and M2 sites with relatively weak interactions (the weakest one is for cations having +1 degree of oxidation).

The stability and flexibility of the NZP structure allow the existence iso- and heterovalent substitutions at all non-oxygen lattice sites and give rise to a large number of compounds with identical topology of connections between their structural units.

The thermal expansion of these compounds is anisotropic: the *c* axis positive thermal expansion is coupled with contraction along the *a* and *b* axes. It has been suggested [5] that the framework thermal expansion is close to zero and the largest contribution to the expandability in NZP materials is the expansion of the Na–O bond itself. This controls the size of the site M1 along the *c* axis (i.e. the O–O distance) and causes cooperative rotations of linked PO_4 and LO_6 polyhedra giving rise to bond angle distortions. The O–P–O bond angles spread in the *c* direction, and thus the NZP structure expands along the *c* axis and contracts the *a* axis, leading to low average values of thermal expansion coefficients.

The NZP model has been proposed to describe the thermal behavior of these materials in terms of cooperative rotation of linked polyhedra in the skeleton of the structure [6]. It can be used to predict the evolution of the lattice parameters with temperature in the NZP-type compounds with the $R\bar{3}c$ space group. But the NZP compounds symmetry may be lower depending on the differences in the structural parts of the three-dimensional framework or in the number, size and particular locations of the cations, occupying holes of network [7]. Moreover, this model requires knowledge of the atom coordinates that are only known for the limited number of the NZP-based compounds. That is why new experimental data and more simple models are required for a better understanding of their peculiar behavior.

We have studied the orthophosphates of the rows $A_{5-4x}Zr_x(PO_4)_3$ (A=Na, K; x=0, 0.25, 0.50, 0.75, 1.0, 1.125, 1.25), $Na_{1-x}Cd_{0.5x}Zr_2(PO_4)_3$ (x=0, 0.3, 0.5, 0.7, 1), $Na_{5-x}Cd_{0.5x}Zr(PO_4)_3$ (x=0, 1, 2, 3, 4, 5), and obtained a quantitative thermodynamic information on the axial (α_a, α_c) and average (α_{av}) thermal expansion coefficients. The results obtained are compared with the data on other NZP compounds allow us to propose the mechanism to explain the expansion behavior of such materials.

Experimental

Phosphates of the general formula $A_{5-4x}Zr_xZr(PO_4)_3$ (A=Na, K, $0\leq x\leq 1.125$), $Na_{1-x}Cd_{0.5x}Zr_2(PO_4)_3$ ($0\leq x\leq 1$), and $Na_{5-x}Cd_{0.5x}Zr(PO_4)_3$ ($0\leq x\leq 5$) were synthesized by the sol-gel method. The starting materials $NaNO_3$, KNO_3, $Cd(NO_3)_2\cdot 4H_2O$, $ZrOCl_2\cdot 8H_2O$, and H_3PO_4 were chemically pure reagents. A solution of phosphoric acid, taken in accordance with the stoichiometry of the phosphate, was added to mixtures of the aqueous solutions of salts (alkali nitrates, cadmium nitrate and zirconium oxychloride) taken in the correct ratios under stirring at room temperature. The gel formed was dried at 80°C and then heated at 600, 800 and 1000°C with 24 h at each temperature. The heating steps were alternated with grinding.

The chemical composition and homogeneity of the synthesized powders were checked with the aid of a Camebax microprobe. The results of the electron microprobe analysis confirmed the homogeneity of the samples and indicated that their compositions were close to the theoretical values calculated for the general formula.

We studied the prepared compounds with XRD, DTA, TG and IR spectroscopy. The phases were identified by X-ray powder diffraction at DRON 3M, using the CuK_α line, and thermal expansion coefficients were determined up to 600°C by means of a high temperature diffraction technique. Previously, the thermal behavior of the phosphate samples has been studied by simultaneous DTA-TG measurements performed with a Q-1500D derivatograph. Samples were heated in the temperature interval from 20 to 1000°C under static air, at heating rate of 10°C min^{-1}, using platinum crucibles. Al_2O_3 was used as standard. IR spectra were obtained by means of a Specord-75 IR spectrophotometer in the frequency range 1400–400 cm^{-1}. Samples were prepared as finely dispersed films on a KBr support.

Results and discussion

Because phosphate (PO_4) group fundamental bands were found in the infrared spectra we have been able to identify the prepared compounds as orthophosphates. The characteristic orthophosphate absorption bands of $A_{5-4x}Zr_xZr(PO_4)_3$ (A=Na, K) were similar to the published ones [8]. The IR spectra of the phases crystallizing in the $Na_{1-x}Cd_{0.5x}Zr_2(PO_4)_3$ system change smoothly in passing from sodium to cadmium phase. The IR and XRD studies indicate formation of the continuous series of solid solutions. The IR spectra in the range of absorption of the PO_4 group also showed regular changes in the $Na_{5-x}Cd_{0.5x}Zr(PO_4)_3$ ($0 \leq x \leq 4$) system on substitution of sodium by cadmium cations.

As it was evident from the X-ray data, the prepared phosphates showed an NZP-like structure phase. The calculated lattice parameters were given in Tables 1–3. The lattice parameters for all investigated phases were changing a little from 0.8717 to 0.9160 nm in the case of *a* parameter, and from 2.180 to 2.402 nm in the case of *c* parameter.

The variation of *a* and *c* at room temperature may be explained as follows: the *a* parameter depends on the width of the column and on the distance between the columns, which is determined by the number and size of metal ions in the M2 positions (Fig. 1). Therefore, the greater the number and size of ions in the M2 positions between the columns are, the larger the *a* parameter is. The variation of the *c* parameter is mainly the result of the action of three factors: the size and the content of the metal ions (Zr^{4+}, Cd^{2+}, Na^{+} or K^{+}) inside the column, decreasing the oxygen-oxygen repulsion; electrostatic repulsion Zr^{4+}–Zr^{4+} and metal ion (M1)–Zr^{4+} between the neighbouring polyhedra inside the column.

Table 1 Crystallographic characteristics (T=25°C) of the compounds of $A_{5-4x}Zr_xZr(PO_4)_3$ (A=Na, K) systems

Chemical formula	Space group	m^*	Unit-cell parameters		
			a/nm	c/nm	V/nm^3
$Na_{0.5}Zr_{2.125}(PO_4)_3$	$R\bar{3}c$	0.625	0.8805	2.281	1.531
$NaZr_2(PO_4)_3$	$R\bar{3}c$	1	0.8801	2.287	1.534
$Na_2Zr_{1.75}(PO_4)_3$	$R\bar{3}c$	1.75	0.8795	2.279	1.526
$Na_3Zr_{1.5}(PO_4)_3$	$R\bar{3}c$	2.5	0.8792	2.272	1.521
$Na_4Zr_{1.25}(PO_4)_3$	$R\bar{3}c$	3.25	0.8815	2.276	1.531
$Na_5Zr(PO_4)_3$	R32	4	0.9160	2.180	1.584
$KZr_2(PO_4)_3$	$R\bar{3}c$	1	0.8717	2.381	1.566
$K_3Zr_{1.5}(PO_4)_3$	$R\bar{3}c$	2.5	0.8723	2.391	1.575
$K_5Zr(PO_4)_3$	$R\bar{3}c$	4	0.8741	2.402	1.589

$^*m$ is number of occupied M (M1+M2) positions per formula unit

The introduction of a larger K^+ cation instead of Na^+ in the M1 position increases the *c* parameter (Table 1), since the polyhedral cell of M1 is formed by the triangular faces of two neighbouring ZrO_6 octahedra located along the *c* axis. Hence, when the M1 site is occupied by large ions, bridging PO_4 tetrahedra should be stretched in the *c* direction, and conctracted in the *a* direction in accordance with the O–P–O bond angle spreading described earlier. When the Na content in the M1 site decreased by partial substitution of elements of larger valence (Zr^{4+} or Cd^{2+}) and smaller ionic radius, the *c* parameters are almost independent of the Na content at the M1 site (Tables 1 and 2). In the case of $Na_3CdZr(PO_4)_3$ and $Na_4Cd_{0.5}Zr(PO_4)_3$ phosphates (Table 3) it may be suggested that M2 sites are fully occupied by cations and M1 sites are empty (for $Na_3CdZr(PO_4)_3$) or half filled with the cations (for $Na_4Cd_{0.5}Zr(PO_4)_3$), owing to latter the *c* parameter values of these compounds are minimum in the system $Na_{5-x}Cd_{0.5x}Zr(PO_4)_3$. Alteration in the lattice parameters of rhombohedral NZP compounds shows that the network modifies its dimensions to adapt to the size of the cations occupying the M1 and M2 sites without breaking of the bonds.

Table 2 Crystallographic characteristics (T=25°C) and values for the thermal expansion coefficients (T=25÷600°C) of the compounds in the $Na_{1-x}Cd_{0.5x}Zr_2(PO_4)_3$ system

Chemical formula	Space group	*m*	*a*/nm	*c*/nm	$\alpha_a \cdot 10^{-6}$/°C^{-1}	$\alpha_c \cdot 10^{-6}$/°C^{-1}	$\alpha_{av} \cdot 10^{-6}$/°$C^{-1}$
$Cd_{0.5}Zr_2(PO_4)_3$	$R\bar{3}$	0.5	0.8829	2.223	–3.50	10.20	1.1
$Na_{0.1}Cd_{0.45}Zr_2(PO_4)_3$	$R\bar{3}$	0.55	0.8827	2.222	–5.21	13.41	1.0
$Na_{0.3}Cd_{0.35}Zr_2(PO_4)_3$	$R\bar{3}c$	0.65	0.8800	2.236	–2.82	6.44	0.3
$Na_{0.5}Cd_{0.25}Zr_2(PO_4)_3$	$R\bar{3}c$	0.75	0.8789	2.249	–0.70	6.27	1.6
$Na_{0.7}Cd_{0.15}Zr_2(PO_4)_3$	$R\bar{3}c$	0.85	0.8795	2.256	–2.18	6.27	0.6
$NaZr_2(PO_4)_3$	$R\bar{3}c$	1	0.8801	2.287	–5.50	22.30	3.8

Table 3 Crystallographic characteristics (T=25°C) and values for the thermal expansion coefficients (T=25÷600°C) of the compounds in the $Na_{5-x}Cd_{0.5x}Zr(PO_4)_3$ system

Chemical formula	Space group	*m*	*a*/nm	*c*/nm	$\alpha_a \cdot 10^{-6}$/°C^{-1}	$\alpha_c \cdot 10^{-6}$/°C^{-1}	$\alpha_{av} \cdot 10^{-6}$/°$C^{-1}$
$NaCd_2Zr(PO_4)_3$	$R\bar{3}c$	2	0.8840	2.242	–2.42	15.04	3.4
$Na_2Cd_{1.5}Zr(PO_4)_3$	$R\bar{3}c$	2.5	0.8791	2.277	–1.40	17.40	4.9
$Na_3CdZr(PO_4)_3$	R32	3	0.9061	2.207	7.04	13.90	9.3
$Na_4Cd_{0.5}Zr(PO_4)_3$	R32	3.5	0.9045	2.204	7.53	16.70	10.6

No thermal effects have been observed by means of DTA-TG data of the phosphates investigated (except of $Na_5Zr(PO_4)_3$ compound). Therefore, no chemical or phase transformations occur up to 1000°C.

In the $Na_5Zr(PO_4)_3$ samples structural phase transition was observed at 114–130°C. This transition is clearly detected with high-temperature X-ray diffractometry (particularly it can be seen by means of the 116 reflection reflex profile changing) and corresponds to a centering of off-centered zirconium atoms in octahedral sites and an occupation transfer between sodium sites [9]. The *a* and *c* parameters are increased abruptly at the structural transition temperature. Besides in the case of some $Na_5Zr(PO_4)_3$ samples the thermal effect was observed at 96°C that corresponds to a change of correlation between off-centered zirconium atoms in octahedral sites [9]. Different thermal behavior is caused by some variations of composition of the samples.

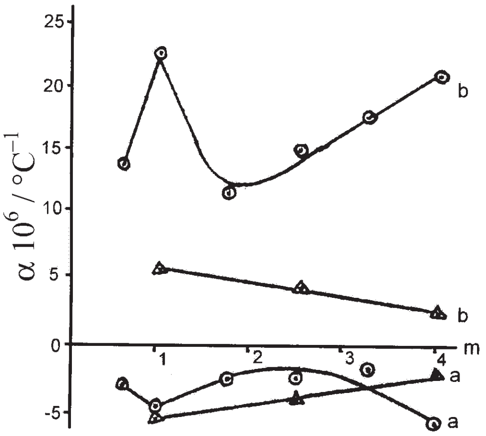

Fig. 2 Axis thermal expansion coefficient α_a (a), and α_c (b) *vs*. number of occupied M positions (*m*) in the rows $A_{5-4x}Zr_xZr(PO_4)_3$ (*A*=Na (o), K (Δ))

The calculated axial thermal expansion coefficients, α_a and α_c, and the average values for the prepared samples of phosphates are shown on Fig. 2 and in Tables 2 and 3. Comparison of our values of the axial thermal expansion coefficients and those from the literature of $AZr_2(PO_4)_3$ (*A*=Na, K) phosphates [1] show good agreement.

From the results shown on Fig. 2 and in Tables 2 and 3 it is evident that the thermal expansion anisotropy is observed for rows of the phosphates studied; that is typical of members of the $NaZr_2(PO_4)_3$ structural family.

All Na–Zr-phosphates (Fig. 2) independent of an occupancy of M positions (*m*) have considerable anisotropy: α_a is negative (up to $-5.82\cdot10^{-6}$ $°C^{-1}$) and α_c is positive (up to $22.02\cdot10^{-6}$ $°C^{-1}$). As to the K-phases it is considerably lower. The maximum value occurs at $m=1$: $\alpha_a=-5.30\cdot10^{-6}$ and $\alpha_c=5.41\cdot10^{-6}$ $°C^{-1}$. The minimum anisotropy is for $K_5Zr(PO_4)_3$ ($m=4$) $\alpha_a=-2.14\cdot10^{-6}$ $°C^{-1}$, $\alpha_c=2.65\cdot10^{-6}$ $°C^{-1}$. From Fig. 2, there is no monotonous dependence on composition and, consequently, on occupancy of the M positions for the sodium compound axial coefficients α_a and α_c. We have observed a bending on the curves $\alpha_a=f(m)$ and $\alpha_c=f(m)$ for sodium–zirconium phosphates. In contrast to the sodium phosphates in the case of potassium phosphates analogues the axial coefficients change as a function of relative content of K cations and, consequently, of the M positions occupancy, monotonously (Fig. 2).

The $Cd_{0.5}Zr_2(PO_4)_3$ compound adopts the lower symmetry $R\bar{3}$ space group owing to alternate ordering of Cd^{2+} and vacancy along the *c* axis leading to crystallographically distinct occupied and vacant M1 sites. Both the Cd site and the vacancy site expand with temperature [10], resulting in expansion along the *c* axis (Table 2).

$Na_{1-x}Cd_{0.5x}Zr_2(PO_4)_3$ phosphates studied had low average thermal expansion coefficients (Table 2). Here low thermal expansion is achieved due to the anisotropy in the thermal expansion of the lattice. The axial coefficients for this system have the opposite signs. Decreasing of the number of sodium atoms and increasing of the cadmium content in the compounds with the $R\bar{3}c$ space group leads to lower values of the axial thermal expansion coefficients. This situation brings about effects of the size, valence of ions at the M1 sites and their occupancy ratio.

Samples made of the $Na_{5-x}Cd_{0.5x}Zr(PO_4)_3$ system also show considerable thermal expansion anisotropy (Table 3). It should be noted that in the case of the samples having high sodium content the α_a and α_c coefficients are positive, and for the compositions with low sodium content the coefficients have opposite signs; the coefficients α_c are positive and α_a are negative. The average volume expansion coefficients decrease with decreasing of the Na content in the system and with increasing of number of vacant M2 positions. Among the phosphates of this system it could be regarded as middle thermal expansion coefficients samples such phosphates which have x=3 and 4, and as phosphates having high values of thermal expansion coefficients which have x=0, 1 and 2.

The model which allows us and others [11, 6] to explain thermal expansion in the NZP compounds is based on the major contribution of the large thermal stretching of the weaker bonds into thermal expansion coefficients. The axial expansion behavior and the change of the lattice parameters of the compounds at room temperature are mainly determined by the interactions between the NZP network and the inserted ions, the chemical nature of the atoms forming the network and inserted into holes (ionic radii, charges, and the type of electron shell), the number of inserted ions and their distribution among crystallographic positions in the framework holes of the NZP structure.

The position M1 of the basic NZP structure has a symmetry of $\bar{3}$ and a coordination number of 6. It is the most stable position and is usually partly or completely occupied with cations. An exception is the case when the total number of ions compensating the framework negative charge is close to three, and then the M2 position is occupied. M2 site is very large having irregular form, and coordinational number of the cations situated in the sites can be changing as a function of the framework of $[L_2(PO_4)_3]$ deformation and temperature. The framework may accept cations having different enough sizes and oxidation degrees into its holes, and at the same time it is able not to change considerably its geometry.

Incorporation of a larger cation into the M1 position accompanies expansion of the framework structure along the *c* axis (so as the M1 positions are situated in the columns which are parallel to the *c* axis) and to contraction along the *a* axis, that caused by correlated rotation of the LO_6 octahedra and PO_4 tetrahedra having shared tops. The parameter *c* increases and the parameter *a* decreases in the row of phosphates $AZr_2(PO_4)_3$ (A=Na, K, Rb, Cs) having completely occupied M1 positions when Na is changed for a bigger cation [12]. Table 1 shows the variation of lattice parameters of $NaZr_2(PO_4)_3$ and $KZr_2(PO_4)_3$ at room temperature. Analogous variation with temperature of *a* and *c* parameters is observed for each of these compounds. Anharmonic vibrations accumulate in the weakest bonds, A(M1)–O, that are lengthened more than the strong L–O and P–O ones with increasing temperature. Due to the position of the lengthening octahedra $A(M1)O_6$ in columns parallel the *c* axis (Fig. 1) the effect of temperature results in structure expansion in the vertical direction ($\alpha_c>0$). In this case there has place deformation of the PO_4 tetrahedra linking the columns. Internal angle O–P–O increases along the *c* axis, the distance between the columns shortens, and the structure in the horizontal direction contracts ($\alpha_a<0$). However temperature influence upon the occupied octahedra, for instance, $Na(M1)O_6$, is consisting of its expansion, but not so much as to get the size of the polyhedra MlO_6 with K, Rb or Cs, as a result of crystal chemical substitution of sodium for a larger cation.

If $M1O_6$ octahedra have been extended along the *c* axis by the incorporation of a larger cation then further enlargement of the structure along the *c* axis under heating will be inhibited by bridged PO_4-tetrahedra linking of the column of the framework structure. For instance, in the row of phosphates $AZr_2(PO_4)_3$ (*A*=Na, K, Rb, Cs) the axial coefficients are in the following limits: $\alpha_a=(-8\div-0.56)\cdot10^{-6}$ °C^{-1}, $\alpha_c=(22.3\div0.45)\cdot10^{-6}$ °C in the temperature interval from 20 up to 800°C going from Na to Cs [1, 13]. Ultra-low axis thermal expansion with very low anisotropy is observed for $CsZr_2(PO_4)_3$. Considering the data presented, we can conclude that crystal chemical effect of substitution and of thermal expansion are not strictly equivalent although both influence upon the same bonds in the structure.

If the M1 position occupancy ratio is less than one as for the phosphates, $B_{0.5}L_2(PO_4)_3$ (*B*=Cd, Ca, Sr, Ba, *L*=Ti, Zr, Hf), it is necessary to take into account the contribution of the occupied and empty M1 positions into relative expansion or contraction of the structure. The occupied M1 positions give a synchronous thermal changing of the cell parameters: namely the structure expansion along the *c* axis is accompanied by contraction along the *a* axis. The empty M1 positions may either expand or contract during heating. From literature and our data, the empty M1 positions in the $Ca_{0.5}Zr_2(PO_4)_3$ [14] and $Cd_{0.5}Zr_2(PO_4)_3$ (Table 2 and [10]) phosphates expand when temperature increases; in the case of $Sr_{0.5}Ti_2(PO_4)_3$ [15] and $Sr_{0.5}Zr_2(PO_4)_3$ [16] they contract.

$Ca_{0.5}Zr_2(PO_4)_3$ ($\alpha_a<0$, $\alpha_c>0$) and $Sr_{0.5}Zr_2(PO_4)_3$ ($\alpha_a>0$, $\alpha_c<0$) exhibit opposite anisotropies in their respective axial thermal expansions. Utilization of NZP solid solutions from components with opposite thermal expansions, for example $Ca_{0.5-x}Sr_xZr_2(PO_4)_3$ ($0\leq x\leq0.5$) [17], present the opportunity to synthesize materials with tailorable and near-zero volume thermal expansion and near-zero axial thermal expansion anisotropy.

The presence of ions in the M2 positions forces the structure to expand along the *a* direction (Fig. 1). In the case when the M1 position is fully occupied α_a is usually negative but sometimes it becomes zero or positive, for example, in the $Na_{1+x}Y_xZr_{2-x}(PO_4)_3$, $Na_{1+2x}Mg_xZr_{2-x}(PO_4)_3$, $Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$ and $Na_{5-x}Cd_{0.5x}Zr(PO_4)_3$ series ([5] and Table 2). This tendency continues to the M2 positions occupancy of 0.75–2. Here we have the least axial anisotropy. Large M2 holes are not situated directly along the *c* axis because α_c has weak dependence on the cation content in the M2 positions, and if the M1 position is completely occupied, for instance, by sodium cations, α_c keeps to be large (Fig. 2). When the occupancies of M2 positions are increasing from 2 up to 3 (here all the M2 positions are occupied) α_a is decreasing and the anisotropy increases again. This observation may be explained as following. When occupancy of M2 positions with cations approaches to the specified value the effect of thermal expansion of the phosphate along the *a* axis becomes comparable with the effect of expansion along the *c* axis, and further extensive expansion along the *c* axis may become dominant.

If the M1 and M2 positions are not occupied, the polyhedra is distorted less and the intensity of thermal expansion of the network of the ‘empty’ framework changes with a variation of the atom L ionic radii. Under thermal deformation the framework contraction along the *a* axis and expansion along the c axis due to presence of vacancies in the *c* direction depends on the O–O and L–O bond energies. The average thermal expansion coefficient α_{av} of the empty network changes from $-0.5\cdot10^{-6}$ up to $0.5\cdot10^{-6}$ °C [18].

The combination of the effect of substitution of the framework L ions with the effect of inserted ions (having larger size than sodium) into the M1 and M2 positions of the NZP structure and the solid solutions making in which the components would have thermal coefficients opposite in sign and close in value, should be useful for designing materials with controllable expansion necessary for applications in high temperature technologies.

Conclusions

Thermal expansion of the $A_{5-4x}Zr_xZr(PO_4)_3$ (A=Na, K; $0\le x\le1.125$), $Na_{1-x}Cd_{0.5x}Zr_2(PO_4)_3$ ($0\le x\le1$), $Na_{5-x}Cd_{0.5x}Zr(PO_4)_3$ ($0\le x\le4$) series was investigated by high-temperature X-ray diffractometry. Low thermal expansion in the rhombohedral NZP-type structures with a flexible framework was caused by the simultaneous thermal changing: the expansion along the *c* axis is accompanied by the contraction along axis *a*. The results obtained being compared with the data for the other NZP-related compounds allow us to propose ideas that successfully explain the mechanism of low thermal expansion in such materials. The thermal expansion behavior of these solids can be presented as a result of cooperative rotations of LO_6 and PO_4 linked polyhedra and the relative expansion (or contraction) of the occupied and vacant M1 and M2 sites of the NZP structure. The mechanism proposed is attributed to the low thermal behavior of strongly bonded three-dimensional network structure, the existence of structural holes capable to damp some of the thermal vibrations and the anisotropy in the thermal expansion of the lattice.

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