

SYNTHESIS AND PROPERTIES OF INORGANIC COMPOUNDS

Synthesis, Structure, and Thermal Expansion of Sodium Zirconium Arsenate Phosphates

M. V. Sukhanov^a, V. I. Pet'kov^a, D. V. Firsov^a, V. S. Kurazhkovskaya^b, and E. Yu. Borovikova^b

^a Nizhni Novgorod State University, pr. Gagarina 23, Nizhni Novgorod, 630950 Russia

^{**} Moscow State University, Vorob'evy gory, Moscow, 119899 Russia

Received March 29, 2010

Abstract—Sodium zirconium arsenate phosphates $\text{NaZr}_2(\text{AsO}_4)_x(\text{PO}_4)_{3-x}$ were synthesized by precipitation technique and studied by X-ray diffraction and IR spectroscopy. In the series of $\text{NaZr}_2(\text{AsO}_4)_x(\text{PO}_4)_{3-x}$, continuous substitution solid solutions are formed ($0 \leq x \leq 3$) with the mineral kosnarite structure. The crystal structure of $\text{NaZr}_2(\text{AsO}_4)_{1.5}(\text{PO}_4)_{1.5}$ was refined by full-profile analysis: space group $R\bar{3}c$, $a = 8.9600(4)$ Å, $c = 22.9770(9)$ Å, $V = 1597.5(1)$ Å³, $R_{\text{wp}} = 4.55$. The thermal expansion of the arsenate–phosphate $\text{NaZr}_2(\text{AsO}_4)_{1.5}(\text{PO}_4)_{1.5}$ and the arsenate $\text{NaZr}_2(\text{AsO}_4)_3$ was studied by thermal X-ray diffraction in the temperature range of 20–800°C. The average linear thermal expansion coefficients ($\alpha_{\text{av}} = 2.45 \times 10^{-6}$ and 3.91×10^{-6} K^{−1}, respectively) indicate that these salts are medium expansion compounds.

DOI: 10.1134/S0036023611090294

The family of the mineral kosnarite $\text{KZr}_2(\text{PO}_4)_3$, often called NZP after the first synthesized analog with similar composition $\text{NaZr}_2(\text{PO}_4)_3$, comprises compounds and solid solutions described by the crystal-chemical formula $(\text{M1})_{0 \rightarrow 1}(\text{M2})_{0 \rightarrow 3} \{[\text{L}_2(\text{TO}_4)_3]^{p-}\}_{3\infty}$, where $\{[\text{L}_2(\text{TO}_4)_3]^{p-}\}_{3\infty}$ is the structure framework (p is the framework charge) and $(\text{M1})_{0 \rightarrow 1}$, $(\text{M2})_{0 \rightarrow 3}$ are the types of extraframework cationic positions with indication of the number of occupied sites [1–3]. The kosnarite structure framework $\text{KZr}_2(\text{PO}_4)_3$ is composed of vertex-sharing isolated PO_4 tetrahedra and ZrO_6 octahedra [4]. The structural fragments $[\text{Zr}_2(\text{PO}_4)_3]$ form columns extended along the c axis. The potassium atoms occupy extraframework positions M1 located between the $[\text{Zr}_2(\text{PO}_4)_3]^-$ fragments and have C.N. = 6. The extraframework M2 cavities between the $[\text{Zr}_2(\text{PO}_4)_3]$ columns are vacant in the kosnarite structure.

Most of the studies dealing with the synthesis, structure, and properties of compounds with the kosnarite structure were performed for complex phosphates and sulfates with variable cationic composition [5, 6]. The works devoted to compounds with mixed anionic composition consider the replacement of phosphorus by silicon $\text{Na}_{1+x}\text{Zr}_2(\text{SiO}_4)_x(\text{PO}_4)_{3-x}$ ($0 \leq x \leq 3$) [7, 8], phosphorus by arsenic $\text{AZr}_2(\text{AsO}_4)_x(\text{PO}_4)_{3-x}$ ($\text{A} = \text{Na}, \text{K}, x = 1.5, 3.0$) and $\text{NaTi}_2(\text{AsO}_4)_x(\text{PO}_4)_{3-x}$ ($0 \leq x \leq 1.2$) [9, 10], phosphorus by molybdenum $\text{A}_{1-x}\text{Zr}_2(\text{MoO}_4)_x(\text{PO}_4)_{3-x}$ ($\text{A} = \text{Na}, \text{K}, \text{Rb}, \text{Cs}, 0 \leq x \leq 0.1\text{--}0.6$) [11, 12], phosphorus by boron $\text{Na}_{1+2x}\text{Zr}_2(\text{BO}_4)_x(\text{PO}_4)_{3-x}$ ($0 \leq x \leq 0.9$) [13], and phosphorus by sulfur $\text{Zr}_2(\text{SO}_4)(\text{PO}_4)_2$ [14]. For some of them, the crystal structure was refined and the ionic conductivity was investigated [15].

The effect of the nature of the atom (size, electronegativity) in the positions M1, M2, L, and the occupancies of the extraframework positions on the thermal expansion of NZP phosphates is widely discussed in the literature; this gave rise to a set of empirical regularities of the thermal expansion of their lattice, which allow targeted prediction of phosphates with controlled, including ultrasmall thermal expansion [3]. The effect of the anion-forming atom T other than phosphorus on the thermal expansion of compounds with the kosnarite structure has not been studied. The issues of crystal chemical modeling and synthesis of different-anion compounds and solid solutions, the effect of anion substitutions on the practically valuable properties of materials with the kosnarite structure (ionic conductivity and magnetic, luminescence, and catalytic properties) remain topical.

The similar chemical properties of phosphorus and arsenic, which are located in the same Group of the Mendeleev Table, the slight difference between the As–O and P–O bond lengths in the AsO_4 and PO_4 tetrahedra (1.69 and 1.53 Å, respectively) and electronegativities (2.1 and 2.2) allow one to hope for broad isomorphism in the series of arsenate phosphates.

This work is devoted to the synthesis, structure refinement, and elucidation of the fields of concentration and temperature stability of compounds and solid solutions of the kosnarite structural type and to study of the thermal expansion of new arsenate phosphates described as $\text{NaZr}_2(\text{AsO}_4)_x(\text{PO}_4)_{3-x}$.

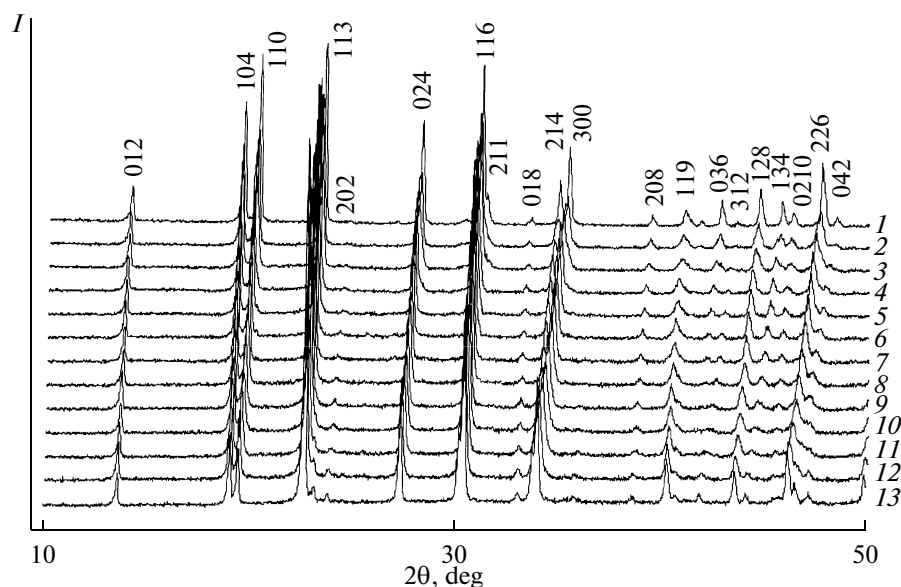


Fig. 1. X-Ray diffraction patterns of the arsenate phosphates $\text{NaZr}_2(\text{AsO}_4)_x(\text{PO}_4)_{3-x}$: $x = (1) 0, (2) 0.25, (3) 0.5, (4) 0.75, (5) 1.0, (6) 1.25, (7) 1.5, (8) 1.75, (9) 2.0, (10) 2.25, (11) 2.5, (12) 2.75, (13) 3.0$.

EXPERIMENTAL

It was planned to synthesize arsenate–phosphate samples $\text{NaZr}_2(\text{AsO}_4)_x(\text{PO}_4)_{3-x}$ with $x = 0, 0.25, 0.5, 0.75, 1.0, 1.25, 1.5, 1.75, 2.0, 2.25, 2.5, 2.75$, and 3.0 covering the whole range of existence of the putative phases with the kosnarite structure. The synthesis was carried out by the precipitation technique. For this purpose, stoichiometric amounts of 1 M aqueous solutions of sodium nitrate and zirconium oxychloride ZrOCl_2 were mixed. Then stoichiometric amounts of 1 M phosphoric and 0.5 M arsenic acids were added with stirring and heating. The solution of arsenic acid was prepared by dissolving elemental arsenic with heating in a solution of nitric and hydrochloric acids present in 1 : 1 ratio (by volume).

The mixtures obtained were dried at 90 and 270°C and heat treated at 600 and 900°C for 24 h. The step-wise heating of the samples was alternated with dispersion for maintenance of sample homogenization.

The chemical composition and uniformity of samples were determined by a CamScan MV-2300 raster electron microscope (VEGA TS 5130MM) equipped with secondary and reflected electron YAG detectors and energy-dispersive X-ray microanalyzer with a Link INCA ENERGY 200C semiconductor Si(Li) detector. For calculating the compositions, the PAP correction method was used. The error of determination of the sample composition was not more than 2 at. %. The results of microprobe analysis showed that monophase arsenate–phosphate samples are uniform and consist of crystallites of size 1 to 20 μm; their composition corresponds to the theoretical one to within the inaccuracy of the method.

Powder X-ray diffraction patterns of the samples were measured on an XRD-6000 X-ray diffractometer ($\text{CuK}\alpha$ radiation, $\lambda = 1.54178 \text{ \AA}$, angle range $2\theta = 10^\circ - 50^\circ$). The X-ray diffraction spectrum for refining the structure of the arsenate–phosphate $\text{NaZr}_2(\text{AsO}_4)_{1.5}(\text{PO}_4)_{1.5}$ was measured in the range of angles $2\theta = 10^\circ - 110^\circ$ with a scanning step of 0.02° and exposure of 2.5 s. The diffractogram processing and structure refinement were performed by the Rietveld method [16] using the RIETAN-97 program [17]. The peak profiles were approximated using the modified pseudo-Voigt function (Mod-TCH pV [18]). As the base model for refining the crystal structure of the arsenate–phosphate, the atom coordinates of the arsenate $\text{NaZr}_2(\text{AsO}_4)_3$ (space group $R\bar{3}c$, the structural type of kosnarite) were used [19]. The high-temperature measurements were carried out in the temperature range of 25–800°C using the HA-1001 Shimadzu attachment. The heating rate was 10 K/min. Prior to the measurements, the sample was kept at a specified temperature for 10 min.

The functional composition of the samples was confirmed by IR spectroscopic studies. IR absorption spectra were recorded on an FSM-1201 FT IR spectroscopy in the wavelength range of 400–1400 cm^{-1} .

RESULTS AND DISCUSSION

The results of powder X-ray diffraction indicate that in the $\text{NaZr}_2(\text{AsO}_4)_x(\text{PO}_4)_{3-x}$ system, the crystal phases with the kosnarite structure are formed at 600°C. The increase in the annealing temperature to 900°C resulted in their higher crystallinity. The single-

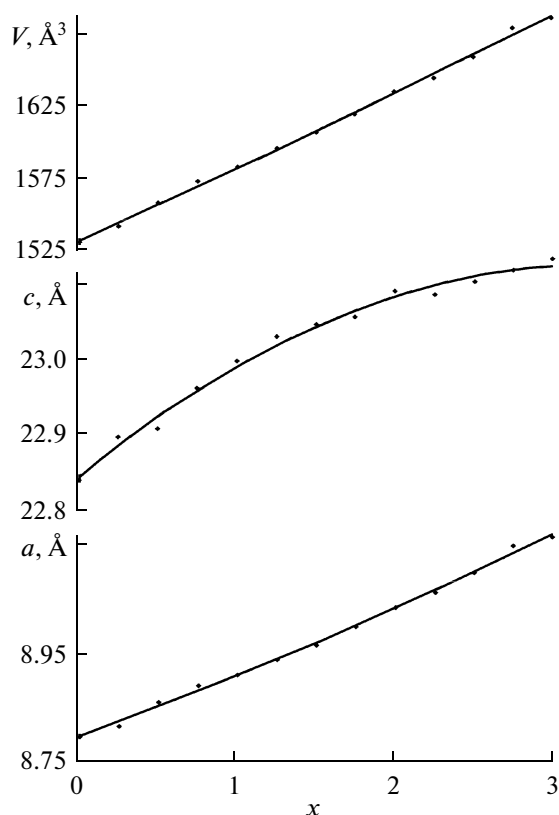


Fig. 2. Unit cell parameters of $\text{NaZr}_2(\text{AsO}_4)_x(\text{PO}_4)_{3-x}$ vs. composition.

phase samples were obtained in the composition range of $0 \leq x \leq 0.5$ and $2.5 \leq x \leq 3.0$. The compositions with $1.0 \leq x \leq 2.5$ are characterized, according to powder X-ray diffraction, by the presence of two phases with the kosnarite structure in the samples. Further increase in the annealing temperature to 950°C resulted in the appearance of zirconium oxide reflections in the X-ray diffraction patterns of all arsenic-containing samples.

According to the preliminary conclusion concerning the miscibility of phosphorus and arsenic in the arsenate–phosphate systems, one should expect broad limits of isomorphous miscibility of $\text{NaZr}_2(\text{PO}_4)_3$ and $\text{NaZr}_2(\text{AsO}_4)_3$, which contradicted the obtained experimental data, apparently due to the low reactivity of the solid-state reactants. The solid-state reaction can be initiated by trace additives able to change the concentrations of point and extended defects and thus affect the diffusion processes and reactions at interfaces. In the case of NZP compounds, the metal oxide additives forming low-melting compounds ensure the active shrinkage of the pressed powders on heating and the formation of samples with nearly theoretical density [20–22]. As a result, the contact surface between the reacting particles in the solid reaction mixtures

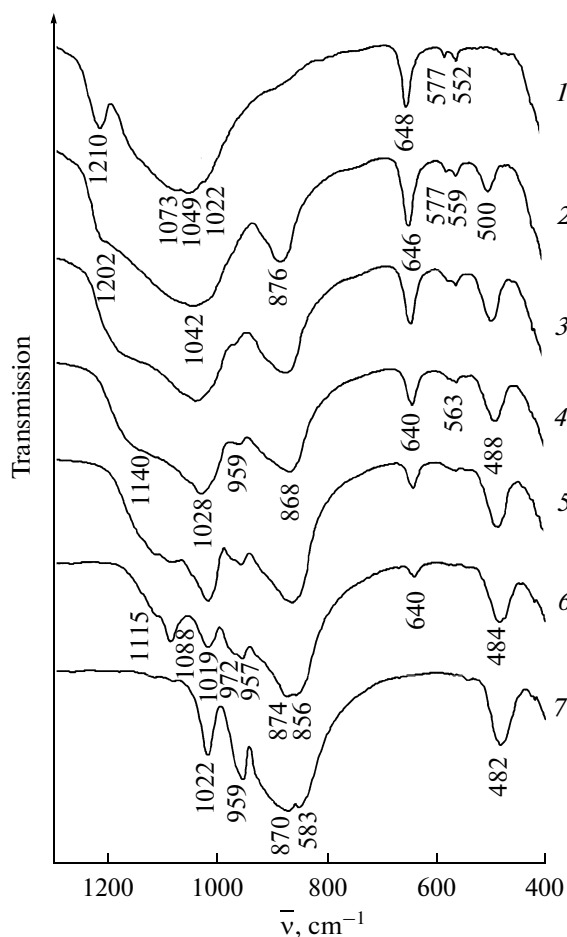


Fig. 3. IR spectra of arsenate phosphates $\text{NaZr}_2(\text{AsO}_4)_x(\text{PO}_4)_{3-x}$: $x = (1) 0, (2) 0.5, (3) 1.0, (4) 1.5, (5) 2.0, (6) 2.5, (7) 3.0$.

increases and the reaction rate grows. As the sintering additive, we used ZnO (0.75 wt %).

The powders obtained by precipitation and annealed at 800°C were mixed with ZnO, pressed at 300 MPa, and annealed at $850\text{--}900^\circ\text{C}$ for 24 h. The use of sintering trace additive provided single-phase sodium zirconium arsenate–phosphate samples, $\text{NaZr}_2(\text{AsO}_4)_x(\text{PO}_4)_{3-x}$, over the whole range of compositions (Fig. 1). Powder X-ray diffraction analysis of the arsenate–phosphate sample $\text{NaZr}_2(\text{AsO}_4)_{1.5}(\text{PO}_4)_{1.5}$ pressed and annealed under the same conditions but without zinc oxide showed the presence of two NZP phases, as in the case of synthesis without the sintering additive or pressing.

The X-ray diffraction patterns of arsenate phosphates show a smooth displacement of the diffraction maxima with gradual change in their relative intensities upon increase in x (Fig. 1). The calculated parameters of their unit cells increase monotonically following an increase in the content of larger arsenic atoms (compared to phosphorus atoms), which attests to the formation of continuous substitution solid solutions in

Table 1. Details of the X-Ray diffraction experiment and results of crystal structure refinement of $\text{NaZr}_2(\text{AsO}_4)_{1.5}(\text{PO}_4)_{1.5}$

Space group	$R\bar{3}c$ (no. 167)
Z	6
2 θ range, deg	10–110
Unit cell parameters:	
a , Å	8.9600(4)
c , Å	22.9770(9)
V , Å ³	1597.5(1)
Number of reflections	227
Number of refined parameters:	
structural	15
other	18
Reliability factors, %	
R_{wp}^a , R_p^b	4.55, 3.41

$$^a R_{wp} = \{(\sum w_i [y_{iexp} - y_{icalc}]^2 / (\sum w_i [y_{iexp}]^2))^{1/2}\}.$$

$$^b R_p = (\sum |y_{iexp} - y_{icalc}|) / (\sum y_{iexp}).$$

this system (Fig. 2). The dependences of the unit cell parameters a and c of arsenate phosphates on the composition are described by parabolic equations: $a = 0.0055x^2 + 0.1079x + 8.7941$ (± 0.004 Å), $c = -0.0264x^2 + 0.1742x + 22.842$ (± 0.007 Å), $V = 0.5586x^2 + 49.293x + 1530.0$ (± 1 Å³). The deviations of the dependences of unit cell parameters from the Vegard's rule are apparently due to the flexibility of the structure framework and distortion of the anion packing of the solid solution as compared with the anion packing in the pure components.

IR spectra of the solid solutions of $\text{NaZr}_2(\text{AsO}_4)_x(\text{PO}_4)_{3-x}$ are presented in Fig. 3. In the IR

spectra of the arsenate phosphates $\text{NaZr}_2(\text{AsO}_4)_x(\text{PO}_4)_{3-x}$, the selection rules allow five asymmetric ν_3 stretching modes, one symmetric ν_1 stretching mode, five asymmetric ν_4 bending modes, and two symmetric ν_2 bending modes for each tetrahedral ion. The absorption bands at 1020–1210 cm^{-1} in the IR spectrum of $\text{NaZr}_2(\text{PO}_4)_3$ ($x = 0$) are asymmetric stretching bands, those at 550–650 cm^{-1} are asymmetric P–O bending modes in the PO_4 tetrahedron. The symmetric stretching modes are not manifested in the spectrum, while the symmetric bending modes occur below 400 cm^{-1} . Out of the five ν_3 bands allowed by the selection rules, four bands were found in the spectrum, one with a maximum at 1210 cm^{-1} and three overlapping bands at 1073, 1049, and 1022 cm^{-1} . The high-frequency band at 1210 cm^{-1} , which is not typical of anhydrous phosphates, comes from the contribution of the electron density of small highly charged Zr^{4+} ion to the P–O bond. The ν_4 bending region has three bands (out of five bands allowed by the selection rules) with maxima at 648, 577, and 522 cm^{-1} . The IR spectrum of the second terminal member of the series, $\text{NaZr}_2(\text{AsO}_4)_3$, is characterized by considerable shift of all bands in both vibration regions to lower frequencies, which is caused by larger size and weight of the arsenic atom as compared with the phosphorus atom. The IR spectrum of $\text{NaZr}_2(\text{AsO}_4)_3$ shows a doublet of intense high-frequency bands at 1022 and 959 cm^{-1} . The bending region contains one medium-intensity band at 482 cm^{-1} . The other bands are apparently below 400 cm^{-1} and cannot be observed by the instrument used.

In the IR spectra of intermediate members of the series, as the content of arsenic increases, the bands of AsO_4^{3-} ion appear at 876 and 500 cm^{-1} and their intensity increases. Simultaneously, the PO_4^{3-} absorption bands shift to lower frequencies: the high-frequency band at 1210 cm^{-1} shifts by ~ 100 cm^{-1} , and the most intense ν_3 band of the phosphate ion shifts by ~ 30 cm^{-1} (1049 $\text{cm}^{-1} \rightarrow 1020$ cm^{-1}). The bands of bending ν_4 vibrations also shift to lower frequencies. On the other hand, the AsO_4^{3-} bands shift to higher frequencies as the arsenic content in the intermediate compounds

Table 2. Coordinates and isotropic thermal parameters of atoms in the structure of $\text{NaZr}_2(\text{AsO}_4)_{1.5}(\text{PO}_4)_{1.5}$

Atom	Position	x	y	z	B , Å ²
Na	6b	0	0	0	3.59(3)
Zr	12c	0	0	0.14450(5)	0.48(5)
As, P	18e	0.2911(2)	0	0.25	1.13(8)
O1	36f	0.1779(6)	−0.0171(6)	0.1903(6)	0.6(2)
O2	36f	0.1878(5)	0.1617(5)	0.0866(2)	0.4(1)

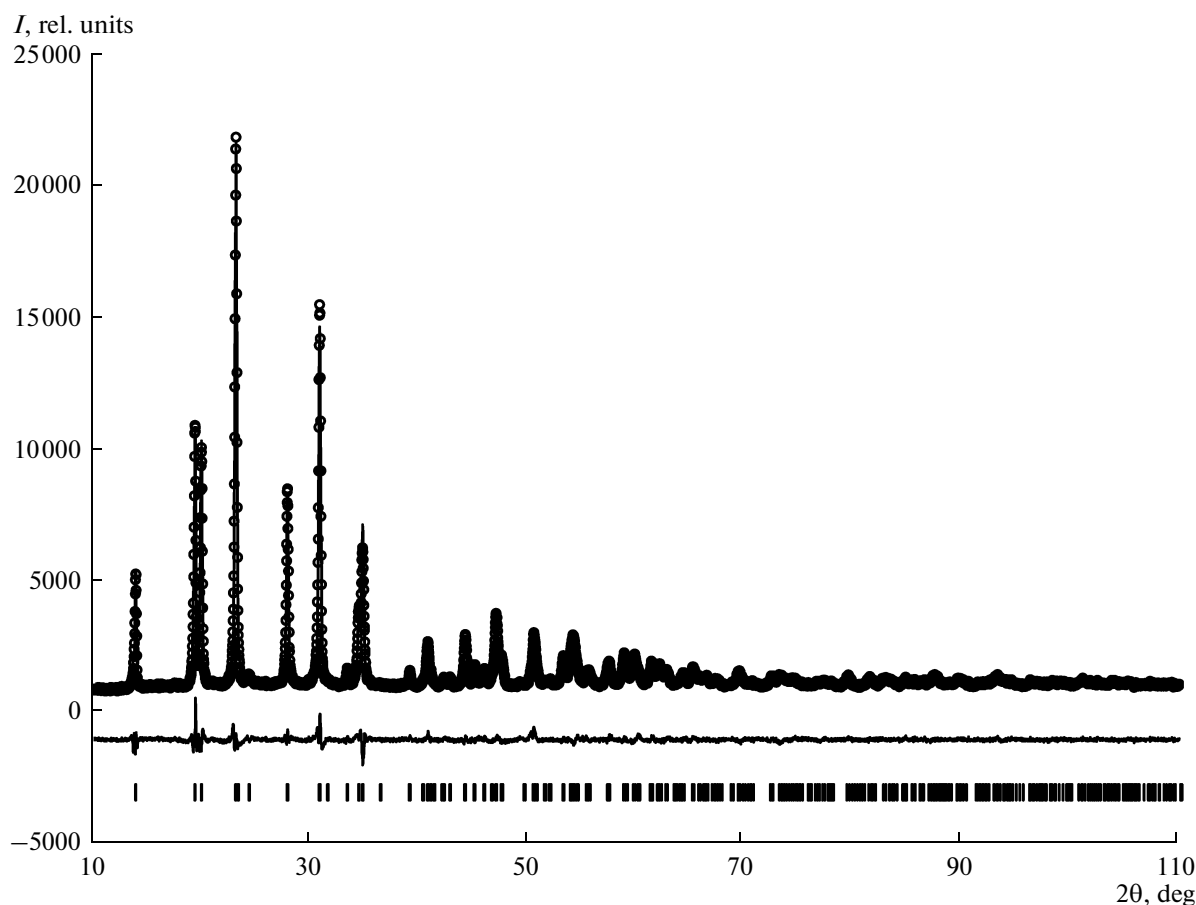


Fig. 4. Experimental (circles) and calculated (continuous line) X-ray diffraction spectra of $\text{NaZr}_2(\text{AsO}_4)_{1.5}(\text{PO}_4)_{1.5}$. The vertical dashes show the positions of reflections of the theoretical X-ray diffraction pattern $\text{NaZr}_2(\text{AsO}_4)_{1.5}(\text{PO}_4)_{1.5}$, the curve in the lower part of the figure is the difference curve of the intensities of experimental and theoretical spectra.

decreases. Thus the doublet of principal ν_3 bands of the AsO_4^{3-} anion at 870, 853 cm^{-1} is converted to one band at 876 cm^{-1} for compound with $x = 0.5$. The AsO_4^{3-} bending band at 482 cm^{-1} shifts by $\sim 20 \text{ cm}^{-1}$ to higher frequencies: 482 \rightarrow 500 cm^{-1} . The spectrum of the $x = 1.5$ compound exhibits the second band of the arsenate ion at 959 cm^{-1} . The IR spectrum of the arsenate phosphate with $x = 2.5$ acquires the features of the final member of the series, $\text{NaZr}_2(\text{AsO}_4)_3$. The smooth shifts of the PO_4^{3-} and AsO_4^{3-} anions to lower and higher frequencies, respectively, attest to the formation of continuous substitution solid solutions in the series of $\text{NaZr}_2(\text{AsO}_4)_x(\text{PO}_4)_{3-x}$.

To confirm the structure of mixed sodium zirconium arsenate phosphates, the structure of $\text{NaZr}_2(\text{AsO}_4)_{1.5}(\text{PO}_4)_{1.5}$ was studied by the Rietveld method. The experiment details, unit cell parameters, and structure refinement details are presented in Table 1. The structure of the arsenate phosphate $\text{NaZr}_2(\text{AsO}_4)_{1.5}(\text{PO}_4)_{1.5}$, like that of the terminal members of the series, $\text{NaZr}_2(\text{PO}_4)_3$ and $\text{NaZr}_2(\text{AsO}_4)_3$, cor-

responds to the kosnarite type and is composed of tetrahedra statistically occupied by arsenic and phosphorus atoms and ZrO_6 octahedra connected by vertices

Table 3. Selected interatomic distances and bond angles in the polyhedra ZrO_6 and $(\text{As,P})\text{O}_4$ in the structure of $\text{NaZr}_2(\text{AsO}_4)_{1.5}(\text{PO}_4)_{1.5}$

Bond	$d, \text{\AA}$	Angle	ω, deg
Na—O2 ($\times 6$)	2.540(4)	O1(As,P) O1'	111.5(5)
Zr—O1 ($\times 3$)	1.979(9)	O1(As,P)O2 ($\times 2$)	106.9(2)
Zr—O2 ($\times 3$)	2.065(4)	O1(As,P)O2 ($\times 2$)	110.2(2)
(As,P)—O1 ($\times 2$)	1.667(12)	O2(As,P)O2'	111.2(2)
(As,P)—O2 ($\times 2$)	1.617(3)	O1ZrO1' ($\times 3$)	94.4(2)
		O1ZrO2 ($\times 3$)	89.5(2)
		O1ZrO2 ($\times 3$)	92.7(2)
		O1ZrO2 ($\times 3$)	171.7(2)
		O2ZrO2' ($\times 3$)	82.9(2)

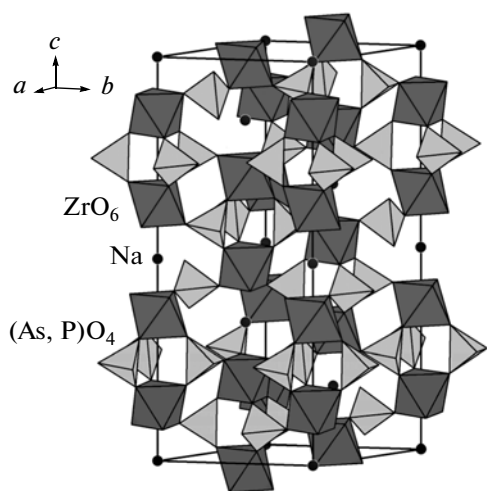


Fig. 5. Crystal structure of $\text{NaZr}_2(\text{AsO}_4)_{1.5}(\text{PO}_4)_{1.5}$.

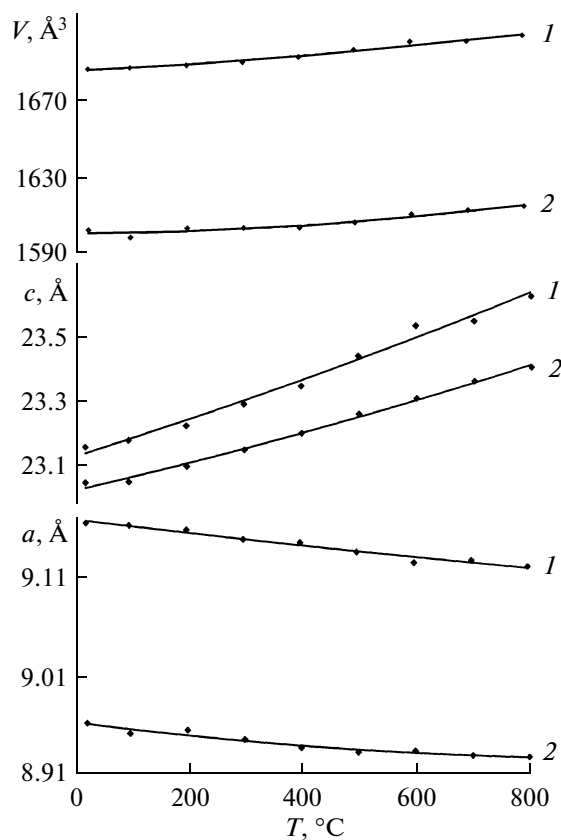


Fig. 6. Unit cell parameters of (1) $\text{NaZr}_2(\text{AsO}_4)_3$ and (2) $\text{NaZr}_2(\text{AsO}_4)_{1.5}(\text{PO}_4)_{1.5}$ vs. temperature.

(Table 2, Fig. 4, 5). The sodium atoms occupy the extraframework M1 positions. The calculated bond lengths and angles are typical of phosphates and arsenates with the kosnarite structure (Table 3).

The occupancy of the tetrahedral positions in $\text{NaZr}_2(\text{AsO}_4)_{1.5}(\text{PO}_4)_{1.5}$ by larger arsenic cations results in expansion of the cell along crystallographic axes. This is accompanied by deformation tetrahedra. The (P,As)—O1 bond length along the c axis is longer than the bond lengths at the O2—(P,As)—O2 angle located in the horizontal plane. This difference between the interatomic distances is maximum for the arsenate—phosphate $\text{NaZr}_2(\text{AsO}_4)_{1.5}(\text{PO}_4)_{1.5}$ (0.05 Å) and less than 0.03 Å for the terminal members of the series, $\text{NaZr}_2(\text{PO}_4)_3$ and $\text{NaZr}_2(\text{AsO}_4)_3$. The difference between the bond lengths results in shortening of the distance between the parallel columns along a axis and their stretching along the c axis and accounts for the deviation of the behaviors of the parameters a and c from the Vegard's law in the arsenate—phosphate series.

The thermal expansion of the arsenate $\text{NaZr}_2(\text{AsO}_4)_3$ and the arsenate—phosphate $\text{NaZr}_2(\text{AsO}_4)_{1.5}(\text{PO}_4)_{1.5}$ was studied by thermal X-ray diffraction. An increase in the temperature results in a decrease in the parameter a of their cells and increase in the parameter c (Fig. 6, Table 4), which is due to the correlated rotation of the tetrahedra and octahedra around the c axis typical of NZP compounds. The values of linear thermal expansion coefficients of the arsenate $\text{NaZr}_2(\text{AsO}_4)_3$ are $\alpha_a = -6.65 \times 10^{-6}$, $\alpha_c = 25.04 \times 10^{-6}$, $\alpha_{av} = 3.91 \times 10^{-6} \text{ deg}^{-1}$; those for the arsenate—phosphate $\text{NaZr}_2(\text{AsO}_4)_{1.5}(\text{PO}_4)_{1.5}$ are $\alpha_a = -5.82 \times 10^{-6}$, $\alpha_c = 18.99 \times 10^{-6}$, $\alpha_{av} = 2.45 \times 10^{-6} \text{ deg}^{-1}$. Both compounds can be classified as medium expansion compounds. An increase in the arsenic content in the compound results in increase in the absolute values of the thermal expansion coefficients, which is attributable to an increase in the bond lengths of the tetrahedral atoms to oxygen and the bond ionicity and, as a consequence, lower strength at thermal deformations of the crystal structure. The opposite directions of variation of the cell parameters on heating results in a considerable anisotropy of the thermal expansion, which increases with increase in the content of arsenic in the compound: the $|\alpha_a - \alpha_c|$ value is $31.7 \times 10^{-6} \text{ deg}^{-1}$ for $\text{NaZr}_2(\text{AsO}_4)_3$ and $24.8 \times 10^{-6} \text{ deg}^{-1}$ for $\text{NaZr}_2(\text{AsO}_4)_{1.5}(\text{PO}_4)_{1.5}$.

Thus, sodium zirconium arsenate phosphates $\text{NaZr}_2(\text{AsO}_4)_x(\text{PO}_4)_{3-x}$ were synthesized by the precipitation method with addition of ZnO for sintering at the final stage. In this system, continuous substitution solid solutions with the kosnarite structure are formed. The tetrahedral positions in the arsenate phosphates are statistically occupied by phosphorus and arsenic atoms. The high-temperature X-ray diffraction studies of $\text{NaZr}_2(\text{AsO}_4)_{1.5}(\text{PO}_4)_{1.5}$ and $\text{NaZr}_2(\text{AsO}_4)_3$ allow one to assign these compounds to medium expansion compounds.

Table 4. $p = p_2t^2 + p_1t + p_0$ polynomials for the unit cell parameters (a , c , V) of $\text{NaZr}_2(\text{AsO}_4)_{1.5}(\text{PO}_4)_{1.5}$ and $\text{NaZr}_2(\text{AsO}_4)_3$ on temperature

	p_2	p_1	p_0
$\text{NaZr}_2(\text{AsO}_4)_{1.5}(\text{PO}_4)_{1.5}$			
a (± 0.002 Å)	0.039×10^{-6}	-0.080×10^{-3}	8.964
c (± 0.008 Å)	0.114×10^{-6}	0.393×10^{-3}	23.021
V (± 1 Å ³)	21.613×10^{-6}	-1.399×10^{-3}	1602.0
$\text{NaZr}_2(\text{AsO}_4)_3$			
a (± 0.002 Å)	0.013×10^{-6}	-0.077×10^{-3}	9.171
c (± 0.014 Å)	0.095×10^{-6}	0.559×10^{-3}	23.125
V (± 0.7 Å ³)	10.540×10^{-6}	12.913×10^{-3}	1684.5

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research, project no. 11-03-00032.

REFERENCES

1. M. E. Brownfield, E. E. Foord, S. J. Sutley, et al., *Am. Mineral.* **78**, 653 (1993).
2. L. Hagman and P. Kierkegaard, *Acta Chem. Scand.* **22**, 1822 (1968).
3. V. I. Pet'kov and A. I. Orlova, *Neorgan. Mater.* **39**, 1177 (2003).
4. M. Sljukic, B. Matkovic, B. Prodic, and D. Anderson, *Z. Kristallogr., Kristalloggeom., Kristallophys., Kristallochem.* **130**, 148 (1969).
5. J. Alamo, *Solid State Ionics* **63–65**, 547 (1993).
6. P. R. Slater and C. Greaves, *J. Mater. Chem.* **4** (9), 1463 (1994).
7. L. B. Goodenough H. Y.-P. Hong, and J. A. Kafalas, *Mater. Res. Bull.* **11** (2), 203 (1976).
8. A. K. Ivanov-Shits and I. V. Murin, *Solid-State Ionics* (St.-Peterb. Gos. Univ., St. Petersburg, 2001), Vol. 1 [in Russian].
9. D. Mazza, M. Lucco-Borlera, and S. Ronchetti, *Powder Diffraction* **13** (4), 227 (1998).
10. R. Shimanouchi-Futagami, M. Nishimori, and H. Nishizawa, *J. Mater. Sci. Lett.* **20**, 1881 (2000).
11. V. I. Pet'kov, M. V. Sukhanov, and V. S. Kurazhkovskaya, *Radiokhimiya* **45** (6), 560 (2003) [*Radiochemistry* **45** (6), 620 (2003)].
12. M. V. Sukhanov, V. I. Pet'kov, V. S. Kurazhkovskaya, et al., *Zh. Neorg. Khim.* **51** (5), 773 (2006) [*Russ. J. Inorg. Chem.* **51** (5), 706 (2006)].
13. R. Shimanouchi-Futagami, M. Nishimori, and H. Nishizawa, *J. Mater. Sci. Lett.* **19**, 405 (2000).
14. J. Alamo and R. Roy, *J. Solid State Chem.* **51** (2), 270 (1984).
15. E. Breval, H. A. McKinstry, and D. K. Agrawal, *British Ceram. Transact.* **93** (6), 239 (1994).
16. H. M. Rietveld, *Acta Crystallogr.* **22**, 151 (1967).
17. Y. I. Kim and F. Izumi, *J. Ceram. Soc. Jpn.* **102**, 401 (1994).
18. F. Izumi, *The Rietveld Method*, Ed. by R. A. Young (Oxford Univ. Press, New York, 1993), Ch. 13.
19. M. Chakir, A. El. Jazouli, and D. de Waal, *Mater. Res. Bull.* **38**, 1773 (2003).
20. E. Breval, G. Harshe, and D. K. Agrawal, *Ceram. Trans.* **38**, 837 (1993).
21. N. Chakraborty, D. Basu, and W. Fischer, *J. Eur. Ceram. Soc.* **25**, 1885 (2005).
22. M. V. Sukhanov, V. I. Pet'kov, and D. V. Firsov, *Neorg. Mater.* **47**, 753 (2011) [*Inorg Mater.* **47**, 753 (2011)].