

PHYSICAL METHODS
OF INVESTIGATION

Synthesis and X-ray Crystallographic and IR Spectroscopic Study of Complex Alkaline Earth Zirconium Arsenates

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Abstract—Arsenates $A_{0.5}Zr_2(AsO_4)_3$ ($A = Mg, Ca, Sr, Ba$), synthesized through sol–gel route with subsequent heat treatment, have been studied by X-ray diffraction, electron probe microanalysis, and IR spectroscopy. $Mg_{0.5}Zr_2(AsO_4)_3$ crystallizes in the $Sc_2(WO_4)_3$ structure type (space group $P2_1/n$). $A_{0.5}Zr_2(AsO_4)_3$ ($A = Ca, Sr, Ba$) crystallize in the $NaZr_2(PO_4)_3$ structure type (space group $R\bar{3}$). The $Ca_{0.5}Zr_2(AsO_4)_3$ and $Ba_{0.5}Zr_2(AsO_4)_3$ structures have been refined by the full-profile analysis. The structure frameworks are composed of ZrO_6 octahedra and AsO_4 tetrahedra. The alkaline earth metal atoms occupy one of the two extra-framework positions inside the structure columns. The internal vibrational frequencies of the AsO_4^{3-} tetrahedron have been assigned. The number of the observed bands corresponds to the number predicted by the factor group analysis of vibrations for space groups $R\bar{3}$ and $P2_1/n$.

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The high capacity of the $NaZr_2(PO_4)_3$ (NZP, NASICON) structure type toward metal cations is favorable for the formation of $A_xM_2(EO_4)_3$ ($0 \leq x \leq 4$) compounds of the same structure, where A stands for cations mainly in oxidation states 1+ or 2+, M stands for cations in oxidation states from 2+ to 5+, and E designates anion-forming elements with a tetrahedrally arranged chemical bonds [1]. Letters A, M, and E not only denote a definite set of cations but also correspond to definite structure positions (or groups of positions if they split).

As distinct from the actively studied phosphates and silicates with NZP structure, only a few studies have been dedicated to their arsenate analogues: $ATi_2(AsO_4)_3$ ($A = Li, Na, Ag, K$) and $A_{0.5}Ti_2(AsO_4)_3$ ($A = Mg, Ca, Sr$) [2], $AZr_2(AsO_4)_3$ and $AZr_2(As_xP_{1-x}O_4)_3$ ($A = Li, Na, K, Rb, Cs$), $Sr_{0.5}Zr_2(AsO_4)_3$, $Na_3Sc_2(AsO_4)_3$ [3–8]. The $A^+ \rightarrow 0.5A^{2+}$ substitution can lead to new arsenates $A_{0.5}Zr_2(AsO_4)_3$ ($A = Mg, Co, Ni, Cu, Zn, Mn, Cd, Ca, Ba$), and their structure will depend in the size of the A^{2+} cation and its coordination ability.

With a high degree of probability, the crystal structures of arsenates $A_{0.5}Zr_2(AsO_4)_3$ will be of the NZP

and scandium tungstate $Sc_2(WO_4)_3$ structure types [1]. These structures are based on a three-dimensional $\{Zr_2(AsO_4)_3\}_{3\infty}$ framework composed of vertex-sharing ZrO_6 octahedra and AsO_4 tetrahedra [3, 6]. Differences in framework configuration—spatial arrangement of the Zr and As polyhedra—have an effect on the character of filling of cavities and their number and shape. The NZP-type framework has a more “rarefied” topology responsible for the formation of cavities in the framework that can accommodate bulky cations. The cavities in the $Sc_2(WO_4)_3$ structure are suitable for relatively small ions.

The aim of the present work was to synthesize arsenates $A_{0.5}Zr_2(AsO_4)_3$ ($A = Mg, Ca, Sr, Ba$), refine their structures, and study their IR spectra and thermal behavior.

EXPERIMENTAL

Synthesis. To synthesize $A_{0.5}Zr_2(AsO_4)_3$ ($A = Mg, Ca, Sr, Ba$), stoichiometric amounts of 1 M aqueous solutions of an alkaline earth salt and zirconium oxychloride $ZrOCl_2$ (to prevent hydrolysis, the latter was dissolved in distilled water acidified with hydrogen

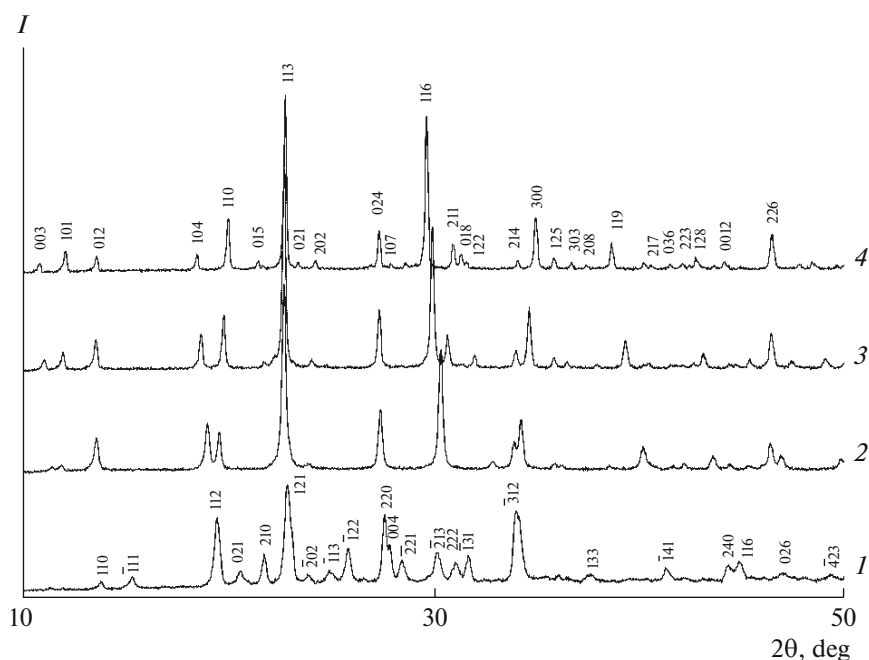


Fig. 1. X-ray powder diffraction patterns of $A_{0.5}Zr_2(AsO_4)_3$, where A is (1) Ba, (2) Sr, (3) Ca, and (4) Mg.

chloride) were poured together under continuous stirring at room temperature. Then, an arsenic acid solution was added under stirring to achieve the required stoichiometry. An arsenic acid solution was prepared from elemental arsenic by dissolving it on heating in a solution of nitric acid and hydrogen chloride taken in a 1 : 1 (v/v) ratio. The resulting gel was dried at 90°C, heated, and kept successively at 270, 600, 800, and 850°C for 12–24 h at each stage. During isothermal annealing, samples were intermittently ground to achieve homogenization.

The chemical composition and homogeneity of the resulting complex alkaline earth zirconium arsenates was monitored by a JEOL JSM-7600F scanning electron microscope with a thermal field emission electron gun (Schottky cathode). The microscope was equipped with an OXFORD X-Max 80 (Premium) energy dispersive spectrometer with a semiconductor silicon-drift detector. The error of determination of the elemental composition was no more than 2 mol %. The results of electron probe microanalysis showed that the grains had a homogeneous composition corresponding to the specified one within the error of the method.

X-ray diffraction. X-ray powder diffraction patterns of the samples were recorded on a Shimadzu XRD-6000 diffractometer (CuK_{α} radiation, $\lambda = 1.54178 \text{ \AA}$, angle range $2\theta = 10^{\circ} - 50^{\circ}$). The X-ray diffraction patterns were indexed by the structural analogy method with the use of crystallographic data for compounds described in the literature. Unit cell parameters were refined by least-squares calculation. The X-ray dif-

fraction patterns for refining the structures of arsenates $A_{0.5}Zr_2(AsO_4)_3$ ($A = Ca, Ba$) were recorded in the angle range $2\theta = 10^{\circ} - 110^{\circ}$ at a scan step of 0.02° and a counting time of 8 s per point. The structure was refined by the Rietveld method [9] with the RIETAN-97 software [10]. The peak profiles were approximated using the modified pseudo-Voigt function (Mod-TCHpV [11]). The coordinates of atoms in $Sr_{0.5}Zr_2(AsO_4)_3$ [7] were taken as a basis model for crystal structure refinement.

IR transmission spectra were recorded on an FSM-1201 Fourier spectrophotometer in the range $400 - 4000 \text{ cm}^{-1}$.

RESULTS AND DISCUSSION

XRD data demonstrate that the crystalline $A_{0.5}Zr_2(AsO_4)_3$ ($A = Ca, Sr, Ba$) phases with NZP structure form at 800°C (Fig. 1). The samples are stable up to 1000°C. In the series $Ca_{0.5}Zr_2(AsO_4)_3 - Sr_{0.5}Zr_2(AsO_4)_3 - Ba_{0.5}Zr_2(AsO_4)_3$, there is a linear dependence of the hexagonal unit cell parameters (space group $R\bar{3}$) on the size of an alkaline earth metal cation: as the radius of the A^{2+} cation increases, a decreases, while c increases (Fig. 2). This feature of the NZP structure is related to accommodation of alkaline earth metal cations in extra-framework cavities inside the columns (between two surfaces of neighboring ZrO_6 octahedra) extended along the c axis. When these cavities are occupied by a larger alkaline earth metal cation, the c parameter increases.

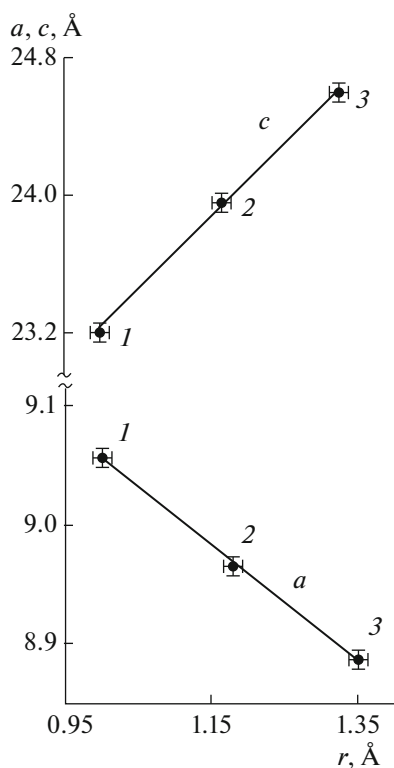


Fig. 2. Unit cell parameters of arsenates $A_{0.5}Zr_2(AsO_4)_3$, where A is (1) Ca, (2) Sr, and (3) Ba, as a function of the alkaline-earth metal size.

Simultaneously, the ZrO_6 octahedra and AsO_4 tetrahedra linking parallel columns turn, which leads to a decrease in the distance between the columns and in the a parameter.

Crystalline $Mg_{0.5}Zr_2(AsO_4)_3$ with a scandium tungstate structure (space group $P2_1/n$) forms at $800^\circ C$ (Fig. 1). Heating above $850^\circ C$ leads to the decomposition of the compound:



Figure 3 shows the IR spectra of the synthesized arsenates crystallized in two space groups, $P2_1/n (C_{2h}^5)$ and $R\bar{3} (C_{3i}^2)$. The arsenic atoms in the monoclinic arsenate structure occupy three positions of symmetry C_1 (4e). For the IR spectrum of $Mg_{0.5}Zr_2(AsO_4)_3$ with space group $P2_1/n$, selection rules allow the existence of eight stretching vibration bands ($\nu_1 - A_u + B_u$, $\nu_3 - 3A_u + 3B_u$) and ten bending vibration bands ($\nu_2 - 2A_u + 2B_u$, $\nu_4 - 3A_u + 3B_u$) of AsO_4^{3-} ion for each of the unique positions. In the internal crystal field with symmetry $R\bar{3}$ (arsenates $A_{0.5}Zr_2(AsO_4)_3$, where A = Ca, Sr, Ba), the local symmetry of the complex ion AsO_4^{3-} is also reduced to C_1 (one structural position of As atoms, 18f). Factor group analysis predicts the fol-

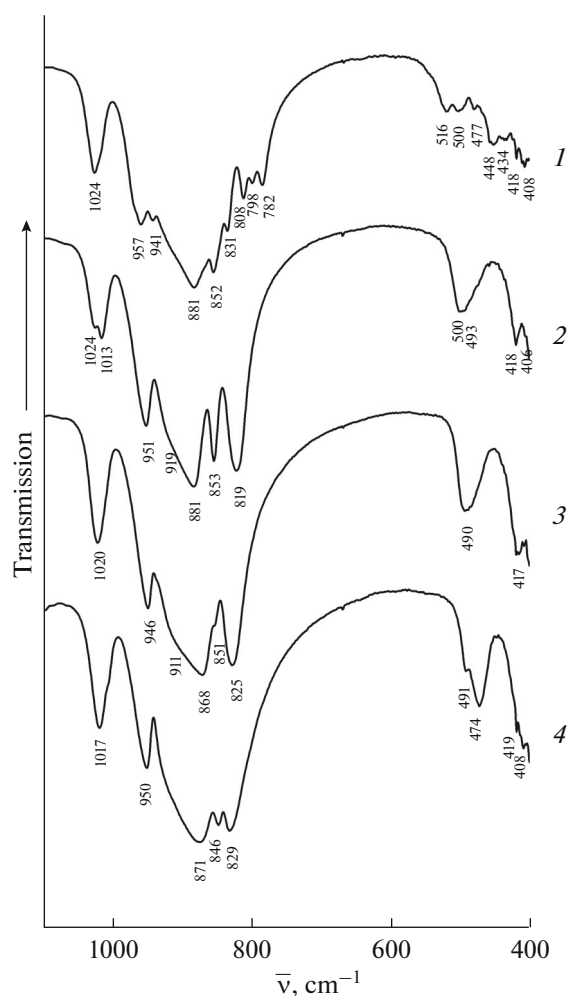


Fig. 3. IR spectra of the $A_{0.5}Zr_2(AsO_4)_3$ arsenates, where A is (1) Mg, (2) Ca, (3) Sr, and (4) Ba.

lowing IR-active internal vibrations of AsO_4^{3-} tetrahedra: eight stretching vibration bands ($\nu_1 - A_u + E_u$, $\nu_3 - 3A_u + 3E_u$) and ten bending vibration bands ($\nu_2 - 2E_u + 2E_u$, $\nu_4 - 3A_u + 3E_u$).

The range of stretching vibrations of rhombohedral zirconium arsenates with calcium, strontium, and barium ($1020 - 820 \text{ cm}^{-1}$) contains up to seven of the eight predicted bands (Fig. 3, spectra 2–4). The IR spectra of these arsenates are similar to the corresponding spectra of arsenates with alkali metal cations [12]. The difference is the appearance of a second low-frequency vibration band ν_1 : in addition to the band $\nu_1 \sim 850 \text{ cm}^{-1}$, the spectra show a lower frequency band at $\sim 825 \text{ cm}^{-1}$. Group-theoretical analysis predicts two bands of ν_1 vibrations of the AsO_4^{3-} ion in arsenate crystals with space group $R\bar{3} (C_{3i})$. The bending vibrations of the arsenate tetrahedron are observed below 500 cm^{-1} and are represented by four bands: ~ 490 ,

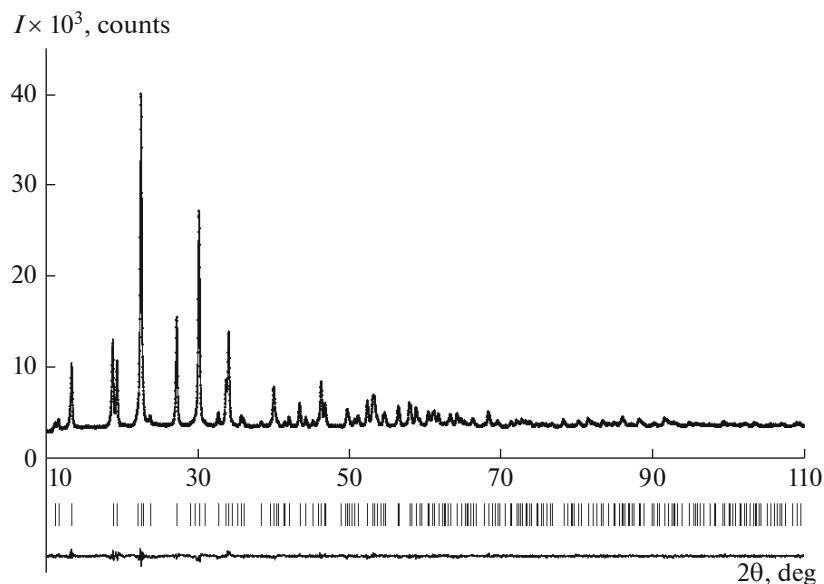


Fig. 4. Experimental (circles) and calculated (solid line) X-ray powder diffraction patterns of $\text{Ca}_{0.5}\text{Zr}_2(\text{AsO}_4)_3$. The vertical ticks correspond to the reflection positions of the theoretical pattern; the lowest trace is the difference curve of the intensities of the experimental and theoretical spectra.

~480, ~418, and ~408 cm^{-1} . All these bands are due to asymmetric bending vibrations ν_4 . The bands of symmetric bending vibrations ν_2 are observed at lower frequencies.

In the IR spectrum of $\text{Mg}_{0.5}\text{Zr}_2(\text{AsO}_4)_3$ with space group $P2_1/n (C_{2h})$, the number of bands in all spectral ranges increases (Fig. 3, spectrum *I*). The increase in the number of bands due to the stretching vibrations of

AsO_4^{3-} is caused by splitting of the high-frequency band at ~950 cm^{-1} into two components at 957 and 941 cm^{-1} , as well as by the appearance of three new ν_1 vibration bands at low frequencies: 808, 798, and 782 cm^{-1} . The

Table 1. Experimental details, unit cell parameters, and selected refinement data for the $\text{A}_{0.5}\text{Zr}_2(\text{AsO}_4)_3$ (A = Ca, Ba) structures

Compounds	$\text{Ca}_{0.5}\text{Zr}_2(\text{AsO}_4)_3$	$\text{Ba}_{0.5}\text{Zr}_2(\text{AsO}_4)_3$
Space group, Z	$R\bar{3}, 6$	
2θ range, deg	10.00–110.00	
Unit cell parameters:		
a , Å	9.0567(3)	8.8877(2)
c , Å	23.2050(6)	24.5944(6)
V , Å ³	1648.36(8)	1682.46(8)
Number of reflections	233	238
Number of refined parameters:		
structural	27	24
other	18	19
Reliability factors R_{wp} , R_p , S , %	2.27, 1.79, 1.43	3.34, 2.41, 2.25

Table 2. Atomic coordinates and isotropic thermal parameters in the $\text{A}_{0.5}\text{Zr}_2(\text{AsO}_4)_3$ (A = Ca, Ba) structures

Atom	Position	x	y	z	B , Å ²
$\text{Ca}_{0.5}\text{Zr}_2(\text{AsO}_4)_3$					
Ca	3b	0	0	0	1.8(2)
Zr1	6c	0	0	0.1402(2)	1.6(1)
Zr2	6c	0	0	0.6460(2)	0.6(1)
As	18f	0.2805(3)	0.9901(5)	0.2478(1)	1.09(6)
O1	18f	0.145(2)	0.931(1)	0.1884(5)	1.3(4)
O2	18f	−0.010(1)	0.812(1)	0.6893(5)	1.1(3)
O3	18f	0.204(1)	0.146(1)	0.0912(4)	0.4(3)
O4	18f	0.814(1)	0.816(1)	0.5818(4)	1.7(3)
$\text{Ba}_{0.5}\text{Zr}_2(\text{AsO}_4)_3$					
Ba	3b	0	0	0.5	2.1(1)
Zr1	6c	0	0	0.1470(2)	1.6(1)
Zr2	6c	0	0	0.6483(2)	0.6(1)
As	18f	0.2818(3)	0.9974(5)	0.2503(2)	0.73(6)
O1	18f	0.135(2)	0.936(2)	0.1974(5)	1.9(2)
O2	18f	0.035(2)	0.815(2)	0.6928(6)	1.9(3)
O3	18f	0.201(1)	0.129(2)	0.0949(5)	1.9(3)
O4	18f	0.808(1)	0.820(2)	0.5934(4)	1.9(3)

spectrum also shows seven bands in the range 520–400 cm^{-1} , which we assign to the ν_4 vibrations. Since the bands are closely spaced and partially overlapped, the number of the bands in the ranges of both the stretching and bending vibrations is considerably smaller than the number allowed by the selection rules. Analogous spectra are typical of framework arsenate $\text{LiZr}_2(\text{AsO}_4)_3$ and $\text{A}_{0.5}\text{Zr}_2(\text{PO}_4)_3$ ($\text{A} = \text{Mg}, \text{Ni}, \text{Cu}, \text{Co}, \text{Zn}, \text{Mn}$) phosphates with space group $P2_1/n$ [12, 13].

The $\text{Ca}_{0.5}\text{Zr}_2(\text{AsO}_4)_3$ and $\text{Ba}_{0.5}\text{Zr}_2(\text{AsO}_4)_3$ structures were refined by the Rietveld method based on the X-ray powder diffraction data. Experimental details, unit cell parameters, and selected refinement results are summarized in Table 1. Figure 4 shows, as an example, the experimental and calculated X-ray powder diffraction patterns of $\text{Ca}_{0.5}\text{Zr}_2(\text{AsO}_4)_3$. The atomic coordinates, isotropic atomic displacement parameters, and population of cationic positions are presented in Table 2.

The refinement results for the $\text{Ca}_{0.5}\text{Zr}_2(\text{AsO}_4)_3$ and $\text{Ba}_{0.5}\text{Zr}_2(\text{AsO}_4)_3$ structures are evidence that they belong to the NZP structure type. The compounds have trigonal symmetry with rhombohedral R -lattice. The crystal structures are based on a three-dimensional framework composed of vertex-sharing discrete ZrO_6 octahedra and AsO_4 tetrahedra (Fig. 5). Two ZrO_6 octahedra and three AsO_4 tetrahedra constitute a topological unit of the framework, a lantern. The lanterns form columns parallel to axis 3. The Ca^{2+} and Ba^{2+} ions occupy one of the two extra-framework positions ($3a$ and $3b$) inside the columns between ZrO_6 octahedra: the $3b$ positions are completely occupied, and the $3a$ positions are partially vacant.

The Zr–O bond lengths in the structures are close to the values calculated from the ionic radii of Zr^{4+} and O^{2-} [14] (2.07 Å) and are typical of the six-coordinate zirconium: for $\text{Ca}_{0.5}\text{Zr}_2(\text{AsO}_4)_3$, Zr(1)–O, 2.00–2.05 Å, and Zr(2)–O, 1.94–2.24 Å; for $\text{Ba}_{0.5}\text{Zr}_2(\text{AsO}_4)_3$, Zr(1)–O, 2.00–2.02 Å, and Zr(2)–O, 2.12–2.14 Å. The coordination polyhedron Zr(2) O_6 in the $\text{Ca}_{0.5}\text{Zr}_2(\text{AsO}_4)_3$ structure is very distorted: three bonds (Zr(2)–O(4)) are 0.3 Å longer than the other three bonds (Zr(2)–O(2)) because of the O–O repulsion in the vacant $3a$ positions inside the columns extended along the c axis. In both arsenates, the difference between the Zr(1)–O(1) and Zr(1)–O(3) bond lengths in Zr(1) O_6 octahedra is small because of the attraction between the oxygen atoms and ions in the oxidation state 2+. In the AsO_4 tetrahedra, the bond lengths and angles are, respectively, 1.55–1.74 Å and 102.70° – 114.72° in $\text{Ca}_{0.5}\text{Zr}_2(\text{AsO}_4)_3$ and 1.60–1.77 Å and 99.34° – 116.19° in $\text{Ba}_{0.5}\text{Zr}_2(\text{AsO}_4)_3$; the bond length calculated from the ionic radii of As^{5+} and O^{2-} is 1.68 Å [14]. The Ca–O (2.53 Å) and Ba–O (2.83 Å) bond lengths are somewhat larger than the values cal-

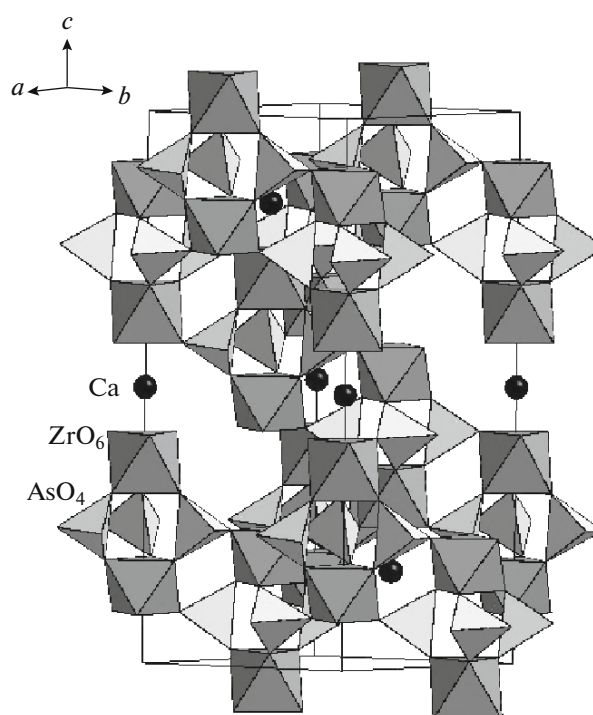


Fig. 5. A fragment of the $\text{Ca}_{0.5}\text{Zr}_2(\text{AsO}_4)_3$ structure.

culated from the ionic radii [14] (2.35 and 2.70 Å, respectively) and point to the ionic character of the Ca–O and Ba–O bonds.

The unit cell parameters of the $\text{A}_{0.5}\text{Zr}_2(\text{AsO}_4)_3$ ($\text{A} = \text{Ca}, \text{Sr}, \text{Ba}$) arsenates are larger than analogous values for isostructural phosphates of the same formula (Table 3). Since the ionic radius of As^{5+} (0.33 Å) is larger than that of P^{5+} (0.17 Å), the O–O distances in AsO_4 tetrahedra are larger than in PO_4 tetrahedra. The anion-forming elements with tetrahedrally arranged chemical bonds connect the columns in framework structures; therefore, the unit cell parameters of the $\text{A}_{0.5}\text{Zr}_2(\text{AsO}_4)_3$ arsenates are larger than the corresponding values for the $\text{A}_{0.5}\text{Zr}_2(\text{PO}_4)_3$ phosphates.

Table 3. Crystallographic characteristics of arsenates and phosphates [13]

Chemical formula	a , Å	c , Å	V , Å ³
$\text{Ca}_{0.5}\text{Zr}_2(\text{AsO}_4)_3$	9.0567(3)	23.2050(6)	1648
$\text{Ca}_{0.5}\text{Zr}_2(\text{PO}_4)_3$	8.780(1)	22.653(3)	1512
$\text{Sr}_{0.5}\text{Zr}_2(\text{AsO}_4)_3$	8.965(2)	23.955(6)	1667
$\text{Sr}_{0.5}\text{Zr}_2(\text{PO}_4)_3$	8.701(1)	23.370(4)	1532
$\text{Ba}_{0.5}\text{Zr}_2(\text{AsO}_4)_3$	8.8877(2)	24.5944(6)	1682
$\text{Ba}_{0.5}\text{Zr}_2(\text{PO}_4)_3$	8.638(1)	23.950(3)	1548

Thus, framework arsenates $A_{0.5}Zr_2(AsO_4)_3$ ($A = Mg, Ca, Sr, Ba$), have been synthesized, their phase formation has been examined, the crystals structures has been refined, IR spectroscopic analysis has been performed, and thermal stability has been studied.

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