

Synthesis, Structural Study and Thermal Expansion of Cesium Ditungsten Tris(Phosphate)

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Abstract

The new phosphate $\text{CsTi}_2(\text{PO}_4)_3$ was synthesized by precipitating method and characterized by scanning electron microscopy with energy-dispersive X-ray microanalyzer, X-ray powder diffraction and IR-spectroscopy. The structure refinement of the phosphate was carried out by a Rietveld analysis. $\text{CsTi}_2(\text{PO}_4)_3$ crystallizes with the cubic system (space group $Ia\bar{3}d$), its unit-cell parameters: $a = 19.909(5)$ Å, $V = 7892(1)$ Å³. It has the framework structure formed by TiO_6 octahedra and PO_4 tetrahedra, the two type positions of Cs^+ cations are in the cavities of the structure. $\text{CsTi}_2(\text{PO}_4)_3$ structure features are discussed. The results of the undertaken study showed that cesium ditungsten tris(phosphate) crystal structure differs from its isoformic analogues $\text{CsZr}_2(\text{PO}_4)_3$ and $\text{AM}_2(\text{PO}_4)_3$ ($A = \text{Na, K, Rb}$; $M = \text{Ti, Zr}$), crystallizing in the trigonal system (space group $R\bar{3}c$) with the kosnarite type. Thermal expansion of the $\text{CsTi}_2(\text{PO}_4)_3$ was studied: $\alpha_a = 7.85 \cdot 10^{-6} \text{ }^\circ\text{C}^{-1}$, $\alpha_v = 23.5 \cdot 10^{-6} \text{ }^\circ\text{C}^{-1}$ in the range 25–800°C.

Introduction

At present there are several commercial methods for reprocessing nuclear fuels [1]. Cesium-137, a β -emitter with the half-life of 30.2 years (its decay-product is barium-137m with the half-life of about 2.6 min), is one of the major radionuclides in spent nuclear fuels. Alumophosphate and borosilicate glasses are generally accepted as the first generation waste form. A drawback of the immobilization of cesium with nuclear waste glasses is the requirement of thermal treatment at over 1000°C, which can cause partial evaporation of radioactive cesium. In addition, they are not stable against the attack by acids and alkalis.

A wide variety of synthetic crystalline inorganic materials have been found to fix high-level nuclear wastes. One of them is ceramic phosphate forms, since they are non-leachable and very stable to high temperatures and radioactive environment. $\text{CsZr}_2(\text{PO}_4)_3$ has been proposed as a perspective candidate for the immobilization of the radiocesium

from nuclear wastes [2]. This compound is characterized by the framework structure related to the mineral kosnarite $\text{KZr}_2(\text{PO}_4)_3$ (trigonal system, space group $R\bar{3}c$, $Z = 6$, $a = 8.687$ Å, $c = 23.87$ Å) [3], synthetic analog is $\text{NaZr}_2(\text{PO}_4)_3$, known as NZP/NASICON. The basis of $\text{CsZr}_2(\text{PO}_4)_3$ structure is the framework built up of corner-sharing ZrO_6 octahedra and PO_4 tetrahedra [4] Cs^+ cations are distributed in the cavities situated in the ribbons of the octahedra and tetrahedra. The inclusion of lighter cations (e.g. titanium instead of zirconium) in the phosphate structure leads to cesium content increase in the crystalline matrices.

In the present work we report results on the synthesis, phase formation, crystal structure and thermal expansion study on $\text{CsTi}_2(\text{PO}_4)_3$ phosphate.

Experimental

The compound was synthesized by the precipitating method. The solutions of the reagent-grade reactants were used for synthesis. The solution of $\text{NH}_4\text{H}_2\text{PO}_4$ taken in accordance with the stoichiometry of the phosphate was dropped into the solution containing CsCl and TiOCl_2 under stirring. The mixture was dried at 80°C, thermally

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treated at 200, 600, 700, 800 and 900°C with 24 h plateaus at each step. All the thermal treatment stages were alternated with careful grinding.

The obtained sample was a white polycrystalline powder. Its chemical composition and homogeneity were checked with the aid of a CamScan MV-2300 (VEGA TS 5130MM) scanning electron microscope (YAG secondary and scattered electron detectors) and an energy-dispersive X-ray microanalyzer equipped with a Link INCA Energy 200C semiconductor Si(Li) detector operated at 20.0 kV. The uncertainty of determination was within 2.5 mass %.

The phase purity was established by powder X-ray diffraction at a Shimadzu XRD-6000 diffractometer ($\text{CuK}_{\alpha 1+\alpha 2}$ radiation). X-ray pattern for the structure refinement was collected in the angular range $10 - 90^\circ$ in 2θ with the step size of 0.02° . The structure refinement was carried out by a Rietveld analysis [5] using RIETAN-97 program [6]. For thermal expansion study the X-ray patterns were obtained in temperature interval $25 - 800^\circ\text{C}$.

Functional composition of the sample was confirmed by IR spectroscopy on an IR Fourier spectrometer FSM 1201 (OOO NPF "Spectranalitpribor") within range $1400 - 400 \text{ cm}^{-1}$.

Results and discussion

Synthesis and spectral characterization

The sample of $\text{CsTi}_2(\text{PO}_4)_3$ began to crystallize at 800°C , the single-phase phosphate was obtained at 900°C . The results of the electron microprobe analysis confirmed the homogeneity of the sample (Fig. 1) and indicated that its composition was close to the theoretical value for the formula within the uncertainty of determination (Table 1).

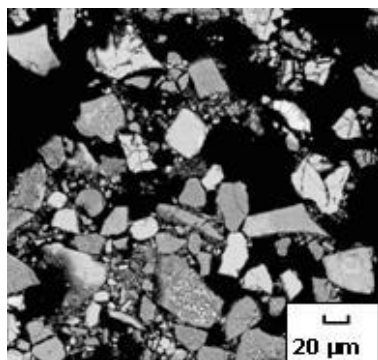


Fig. 1. Microphotograph of the synthesized sample $\text{CsTi}_2(\text{PO}_4)_3$

Table 1

Results of electron microprobe analysis of the synthesized sample $\text{CsTi}_2(\text{PO}_4)_3$

Site number	$n(\text{Cs})$	$n(\text{Ti})$	$n(\text{P})$	$n(\text{O})$
1	1.02	1.98	3.01	12
2	0.97	2.01	3.00	12
3	1.02	1.98	3.01	12
4	0.99	2.02	2.99	12
5	1.01	1.97	3.02	12
Average	1.00	1.99	3.01	12

The X-ray pattern of the cesium ditungsten tris(phosphate) differed from those of $\text{CsZr}_2(\text{PO}_4)_3$ and was analogue to the X-ray pattern of $\text{CsTi}_2(\text{AsO}_4)_3$ (cubic system, space group $Ia\bar{3}d$) [7]. This compound has a framework structure based on $[\text{Ti}_2(\text{AsO}_4)_3]^-$ framework, but TiO_6 and PO_4 polyhedra are linked another way than in $\text{CsZr}_2(\text{PO}_4)_3$ structure. Cs^+ ions are situated in the framework cavities.

The IR spectrum of the synthesized sample (Fig. 2) is typical of orthophosphates with the structural-forming rings of polyhedra. From the symmetry of the sample, 3 ν_3 bands of the characteristic PO_4 vibrations are allowed in the spectrum (1202 , 1070 and 1007 cm^{-1}), one ν_1 band (962 cm^{-1}), 3 ν_2 bands (2 of them are observed in the spectrum, 642 and 567 cm^{-1}), band with maximum at 484 cm^{-1} is relative to ν_2 vibrations.

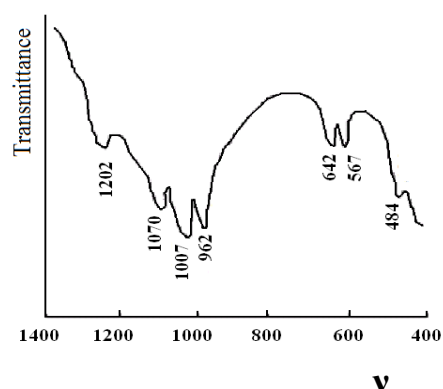


Fig. 2. IR spectrum of the phosphate $\text{CsTi}_2(\text{PO}_4)_3$

Structural description of $\text{CsTi}_2(\text{PO}_4)_3$

For the initial fractional coordinates for structural refinement we used those of $\text{CsTi}_2(\text{AsO}_4)_3$. The observed, calculated and difference XRD patterns are shown in Fig. 3. It is seen that the observed and calculated profiles are in

good agreement. The experimental and refinement conditions, unit cell parameters and R factors are presented in Table 2. The final fractional coordinates and isotropic atomic displacement parameters are listed in Table 3.

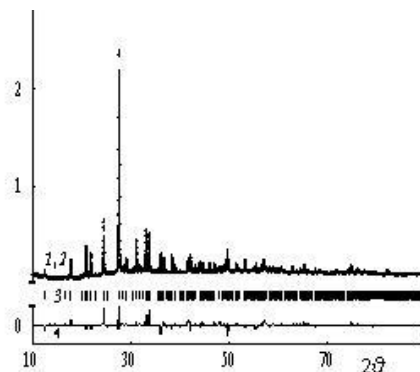


Fig. 3. The Rietveld refinement profiles for $\text{CsTi}_2(\text{PO}_4)_3$: observed (1), calculated (2), Bragg reflections (3), difference of XRD patterns (4)

Table 2

Conditions of X-ray diffraction experiment and part of refinement results for $\text{CsTi}_2(\text{PO}_4)_3$

Space group	$Ia\bar{3}d$ (No. 230)
Z	32
2θ range, °	10-90
Unit cell parameters:	
a , Å	19.909(5)
V , Å ³	7892(1)
Number of reflections	270
Variables:	
Structural	29
Other	22
Reliable factors, %	
R_{wp} ; R_p	7.35; 4.16
S	2.81

Table 3

Fractional coordinates, isotropic atomic displacement parameters (B) and occupancies of the positions (g) in the structure of $\text{CsTi}_2(\text{PO}_4)_3$

Atom	Site	g	x	y	z	B , Å ²
Cs(1)	16b	0.725(2)	0.125	0.125	0.125	1.9(2)
Cs(2)	48g	0.275(2)	0.0173(4)	0.7673(3)	0.375	1.2(2)
Ti(1)	48g	1.0	0.2805(5)	0.0395(5)	0.375	1.1(1)
Ti(2)	16a	1.0	0.0	0.0	0.0	1.9(1)
P	96h	1.0	0.0350(4)	0.3516(5)	0.4569(3)	1.3(4)
O(1)	96h	1.0	0.0108(7)	0.4703(5)	0.3181(5)	1.6(3)
O(2)	96h	1.0	0.2888(7)	0.1271(7)	0.4011(5)	2.0(3)
O(3)	96h	1.0	0.1940(6)	0.0235(7)	0.4090(6)	2.4(2)
O(4)	96h	1.0	0.5731(5)	-0.0257(8)	0.4527(5)	2.7(3)

The unit cell of the studied compound is rather large for inorganic substances: $Z = 32$. The framework sites 48g and 16a in the structure of $\text{CsTi}_2(\text{PO}_4)_3$ are occupied by Ti^{4+} ions, the framework sites 96h are occupied by P and O atoms. In the studied structure Cs^+ ions may be distributed between the two types of sites in the cavities of the framework: 16b and 18g. The occupancies of these sites were found by their varying.

In the chosen model all obtained B parameters are positive and reasonable. The bond lengths and angles in structure-forming polyhedra (Table 4) agree with the corresponding data for other framework phosphates [7-9]. The Ti-O bond lengths for the octahedrally coordinated sites (Ti1

and Ti2) range between 1.81 and 2.12 Å, the P-O distances in the phosphate tetrahedral – between 1.49 and 1.59 Å. The average Cs1-O (3.43 Å) and Cs2-O (3.22 Å) distances are typical of 12- and 8-coordinated Cs^+ ions.

The structure of $\text{CsTi}_2(\text{PO}_4)_3$ is shown in Fig. 4. Its structural framework is formed by columns of TiO_6 octahedra and PO_4 tetrahedra. The heart of every column consists of alternating Ti(2)O_6 octahedra and 12-fold Cs(1)^+ cations situated on the trigonal axis of the unit cell of space group $Ia\bar{3}d$. The rings of PO_4 tetrahedra, Ti(1)O_6 octahedra and then PO_4 tetrahedra are situated around them. The octahedrally coordinated framework sites between these columns are occupied by Ti(1)^{4+} and Ti(2)^{4+} cations.

Table 4
Bond lengths and angles in $\text{CsTi}_2(\text{PO}_4)_3$

Bonds	$d, \text{Å}$	Angles	$\omega, ^\circ$
Cs(1)–O(3) ($\times 6$)	3.330(12)	O(1)Ti(1)O(1)'	170.5(4)
Cs(1)–O(4) ($\times 6$)	3.530(15)	O(1)Ti(1)O(2)	90.9(4)
<Cs(1)–O>	<3.43>	O(1)Ti(1)O(2)'	86.8(5)
Cs(2)–O(1) ($\times 2$)	3.034(14)	O(1)Ti(1)O(3)	102.0(5)
Cs(2)–O(1) ($\times 2$)	3.203(13)	O(1)Ti(1)O(3)'	86.4(4)
Cs(2)–O(3) ($\times 2$)	3.241(14)	O(1)Ti(1)O(2)	88.3(5)
Cs(2)–O(3) ($\times 2$)	3.389(14)	O(1)Ti(1)O(2)'	83.7(4)
<Cs(2)–O>	<3.22>	O(1)Ti(1)O(3)	87.5(5)
Ti(1)–O(2)	1.827(17)	O(1)Ti(1)O(3)'	94.0(5)
Ti(1)–O(3)	1.878(15)	O(2)Ti(1)O(2)'	89.6(6)
Ti(1)–O(2)'	1.992(17)	O(2)Ti(1)O(3)	98.2(6)
Ti(1)–O(1)	2.019(11)	O(2)Ti(1)O(3)'	176.8(5)
Ti(1)–O(3)'	2.023(15)	O(2)Ti(1)O(3)	168.0(5)
Ti(1)–O(1)'	2.118(11)	O(2)Ti(1)O(3)'	88.4(6)
<Ti(1)–O>	<1.98>	O(3)Ti(1)O(3)'	84.2(6)
Ti(2)–O(4) ($\times 6$)	1.807(11)	O(4)Ti(2)O(4)' ($\times 2$)	87.5(5)
<Ti(2)–O>	<1.81>	O(4)Ti(2)O(4)'' ($\times 2$)	92.5(5)
P–O(3)	1.490(15)	O(4)Ti(2)O(4)'''	180.0(6)
P–O(4)	1.558(14)	O(1)PO(2)	115.4(8)
P–O(1)	1.587(13)	O(1)PO(3)	104.2(8)
P–O(2)	1.591(15)	O(1)PO(4)	116.2(8)
<P–O>	<1.56>	O(2)PO(3)	101.9(8)
		O(2)PO(4)	104.3(8)
		O(3)PO(4)	114.2(9)

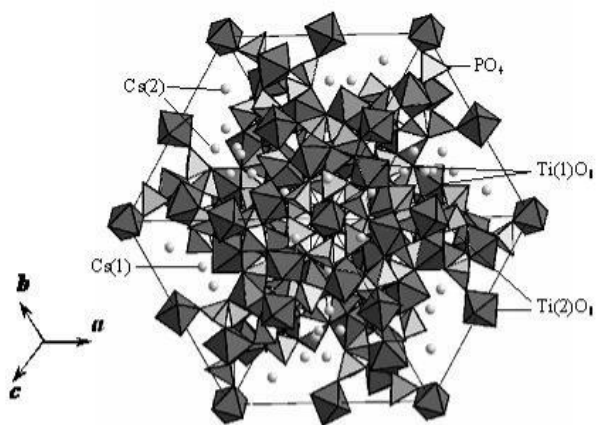


Fig. 4 The projection of $\text{CsTi}_2(\text{PO}_4)_3$ structure on the [111] direction

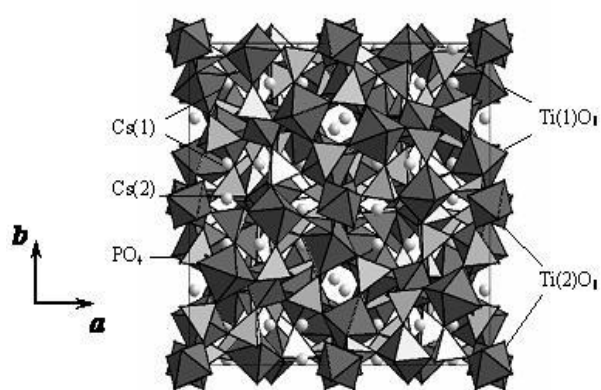


Fig. 5. The projection of $\text{CsTi}_2(\text{PO}_4)_3$ structure on the (001) plane

The large framework cavities partially occupied by cesium ions are shown on the (001) projection (Fig. 5). Every cavity is rounded by vertex-sharing 8 TiO₆ octahedra and 8 PO₄ tetrahedra. The cavities are interconnected to form three-dimensional channels in the framework. Cs(1) sites are in the crossing of the channels and Cs(2) sites are within the cavities.

The structure of CsTi₂(PO₄)₃ has two important features: differently coordinated cesium ions positions in the [Ti₂(PO₄)₃] framework holes and significantly distorted TiO₆ octahedra with six different bond lengths.

The coordination of Cs⁺ ions is often irregular in a large variety of substances. In the studied phosphate structure (Fig. 6), Cs(1) has six nearest oxygen neighbors within 3.33 Å and the other six neighbors within 3.53 Å. Six of eight nearest oxygen atoms are located at the distances between 3.03 and 3.24 Å for Cs(2), the other two are within 3.39 Å.

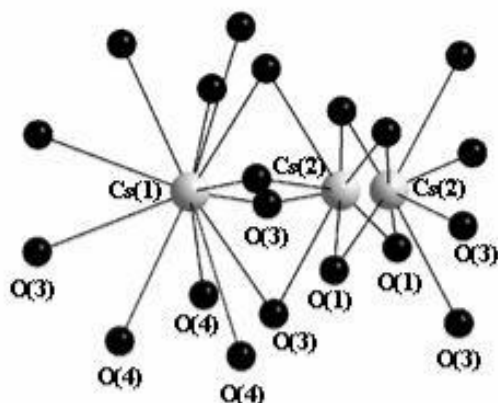


Fig. 6. Cs⁺ sites in CsTi₂(PO₄)₃ structure

The pronounced distortions in TiO₆ polyhedra can be attributed to the difficulty of accommodating common atoms in the titanium octahedra and the phosphate tetrahedra. The Ti–O bonds are longer and weaker than the P–O bonds, and so are more easily distorted from their ideal distances and angles than the P–O bonds.

Thermal expansion behavior

Thermal expansion is an important property, generally considered for any material to be used at elevated temperatures. An increase in an-harmonic potential with increasing temperature causes the thermal expansion of chemical bonds, which in turn

results in dilation of crystal lattice. Fig. 7a shows plot of thermal evolution of unit-cell *a* parameter within range 25–800°C. It is seen that CsTi₂(PO₄)₃ has no phase transitions in the studied temperature interval, and the *a* parameter increase with *T* by linear dependence (correlation coefficient 0.99).

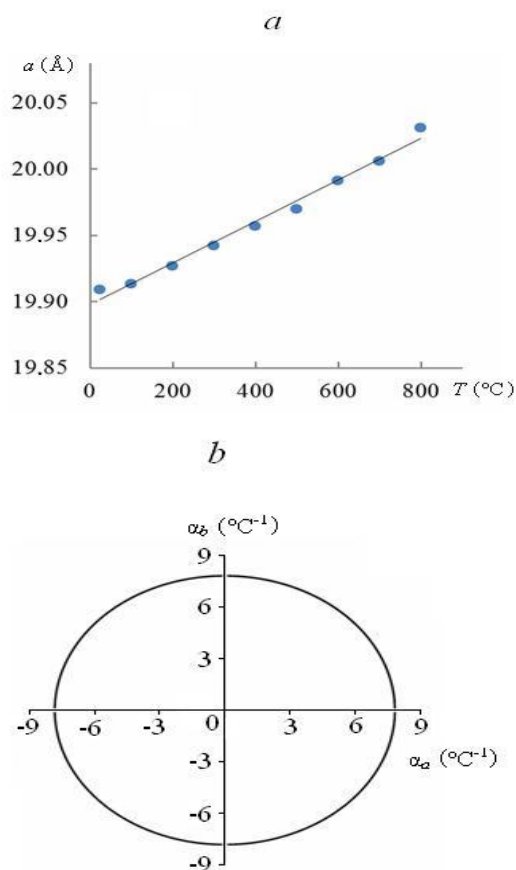


Fig. 7. Unit-cell *a* parameter of CsTi₂(PO₄)₃ as function of temperature (*a*) and thermal expansion diagram in the *a* – *b* plane (*b*)

Thermal expansion diagram [10] allows showing anisotropy of thermal expansion coefficients and characterizing their evolution with temperature. It is shown in Fig. 7b, that thermal expansion of CsTi₂(PO₄)₃ has isotropic behavior and doesn't not depend on temperature. Values of its linear and volume thermal expansion coefficients were $\alpha_a = 7.85 \cdot 10^{-6} \text{ } ^\circ\text{C}^{-1}$, $\alpha_V = 23.5 \cdot 10^{-6} \text{ } ^\circ\text{C}^{-1}$ in the range 25–800°C. So it may be classified as middle-expanding material.

Conclusions

The results of the undertaken study showed that cesium dititanium tris(phosphate) crystal structure

differs from its isoformulic analogues $\text{CsZr}_2(\text{PO}_4)_3$ and $\text{AM}_2(\text{PO}_4)_3$ ($A = \text{Na}, \text{K}, \text{Rb}; M = \text{Ti}, \text{Zr}$). From [2, 4, 11], these phosphates crystallize in the trigonal system (space group $R\bar{3}c$) with the kosnarite type structure. It also has a framework structure with the framework made up of MO_6 octahedra and PO_4 tetrahedra. Framework polyhedra in the kosnarite structure are not so distorted than in $\text{CsTi}_2(\text{PO}_4)_3$: MO_6 octahedra have three equivalent shortest M–O distances and three equivalent longer ones. All alkali cations (including Cs^+) have regular coordination and occupy 6-fold sites in the framework cavities. Therefore atoms in kosnarite-type compounds have more symmetric positions.

$\text{CsTi}_2(\text{PO}_4)_3$ and kosnarite structures differ by the framework polyhedra linking and type of alkali cation position. Zr^{4+} is quite a large cation, which forms framework-building polyhedra with Zr–O bond lengths up to 2.3 Å. This kosnarite-type framework is able to accommodate alkali cations with a wide variety of radii in the cavities. Ti^{4+} is quite a small cation; Ti–O bonds don't exceed 2.1 Å in length. So $[\text{Ti}_2(\text{PO}_4)_3]^-$ framework is able to accommodate Na^+ , K^+ and Rb^+ ions in the cavities of kosnarite structure, but the large size of Cs^+ ion precludes its disposition in such cavities. The ability of a cesium ion to have different coordination with radius of 1.70...1.88 Å (depending on a coordination number) makes conditions to structural type changing.

Thermal expansion of $\text{CsTi}_2(\text{PO}_4)_3$ was studied. It is connected with expansion of Cs–O, Ti–O and P–O bonds with the increase of temperature, and its value is characteristic for middle-expanding materials including nuclear waste glasses and ceramics.

The phosphate ceramics of the framework structure exhibit high stability to the action of aggressive media, radiation damage and thermal-shock resistance [12]. The potential of the removal of radionuclide and stable ions (including $^{137}\text{Cs}^+$, Ti^{4+} , Zr^{4+} and etc.) from spent U-Pu nuclear fuels is based on the knowledge of the basic chemistry and crystal chemistry of the compounds of variable compositions. The knowledge of the structural relations within the morphotropic series $\text{AM}_2(\text{PO}_4)_3$ ($A = \text{Li}, \text{Na}, \text{K}, \text{Rb}, \text{Cs}; M = \text{Ti}, \text{Zr}$) and the formation of different framework Cs-containing phases allow us to choose the compositions and structural type of phosphate matrices depending on the waste compositions.

Acknowledgments

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References

1. I.W. Donald, B.L. Metcalfe, R.N. Taylor, J. Mater. Sci., 1997, 32, 5851–5857.
2. E.A. Asabina, V. I. Pet'kov, V. N. Loshkarev et al., Radiochemistry, 2006, 48, 205–210.
3. M. Brownfield, E. Foord, S. Sutley, T. Botinelly, Am. Mineral., 1993, 78, 653–656.
4. E.R. Gobechiya, Yu.K. Kabalov, V.I. Pet'kov, M.V. Sukhanov, Crystallogr. Rep., 2004, 49, 741–746.
5. H.M. Rietveld, Acta Crystallogr., 1967, 22, 151–152.
6. Y.I. Kim, F. Izumi, J. Ceram. Soc. Jpn., 1994, 102, 401–404.
7. Kwang-Hwa Lii, Inorg. Chem., 1995, 34, 1700–1704.
8. E. A. Asabina, V. I. Pet'kov, M.V. Boguslavsky et al., Russian J. Inorg. Chem., 2006, 51, 1167–1175.
9. S. Senbhagaraman, T.N. Guru Row, A.M. Umarji, J. Mater. Chem., 1993, 3, 309–314.
10. R.I. Belousov, S.K. Filatov, Glass Physics and Chemistry, 2007, 3, 271–275.
11. M. Šljukić, B. Matković, B. Prodić, S. Šcavnicar, Croatica Chem. Acta, 1967, 39, 145–148.
12. B.E. Scheetz, D.K. Agrawal, E. Breval, R. Roy, Waste Management, 1994, 14, 489–505.

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