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The Crystal Structure of $\text{La}_3\text{Pb}_{0.1}\text{Ga}_{1.6}\text{S}_7$ and $\text{Pr}_3\text{Pb}_{0.1}\text{Ga}_{1.6}\text{S}_7$ Compounds

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The crystal structure of $\text{La}_3\text{Pb}_{0.1}\text{Ga}_{1.6}\text{S}_7$ and $\text{Pr}_3\text{Pb}_{0.1}\text{Ga}_{1.6}\text{S}_7$ compounds was determined by X-ray powder diffraction method. The samples were prepared by solid-solid reactions of the elements at 1370 K. The compounds crystallize in the $\text{La}_3\text{CuSiS}_7$ structure type, space group $P6_3$, with the lattice and computation parameters $a = 1.01902(3)$ nm, $c = 0.60661(2)$ nm, $R_I = 0.0673$, $R_P = 0.1546$ (for $\text{La}_3\text{Pb}_{0.1}\text{Ga}_{1.6}\text{S}_7$) and $a = 1.00034(3)$ nm, $c = 0.60587(3)$ nm, $R_I = 0.0847$, $R_P = 0.1623$ (for $\text{Pr}_3\text{Pb}_{0.1}\text{Ga}_{1.6}\text{S}_7$). The crystalline structure is described with hexagonal system, in which La(Pr) atoms center trigonal prisms with one additional atom. These prisms are formed by S atoms. The atoms of the statistical mixture M1(0.600 Ga + 0.090 Pb) and M2 (0.59(1) Ga + 0.095(7) Pb) are located practically in the centers of the octahedra of S atoms. Ga atoms are located in tetrahedra of S atoms. Asymmetric structure of the studied compounds points out their non-linear properties. Adding Pb atoms to the structure of $\text{La}_3\text{Ga}_{1.67}\text{S}(\text{Se})_7$ compounds increases the probability of formation of the ionic component of the inter-atomic bond, and this in turn improves thermoelectric properties.

Key words: crystal structure, X-ray methods, rare-earth metal chalcogenides.

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Introduction

The scientific and technological progress provides society with good devices which are useful for in daily life. The most important issue is the toxicity of used materials. Of course, sometimes we cannot avoid adding toxic stuff. Instead, scientists try to reduce the presence of toxic elements in composition. On the other hand, such substances sometimes may improve properties and utility of materials which are based on them.

Atoms of sulfides of the rare-earth metals are connected by covalent interactions more than ionic ones. Such a structure is stable for atoms which have a big coordination surrounding. Furthermore, the 4f electron level in rare earth metals is not filled completely. It gives an opportunity for forming ionic bonds with elements which have an unfilled p electronic level, for example, atoms Si, Ge, Sn, and Pb. Using such an approach, we can create new materials with useful properties. According to the work of Samsonov G.V [1], some sulfides of the rare-earth metals are used as high-

temperature and thermal shock-resistant refractories (because of their high melting point), high-temperature semiconductors, high ohmic volume resistors and anti-emission materials.

The rare-earth-containing materials are interesting to study also because they allow synthesizing a wide range of compositions within one type of structure [2-3].

In the work [4] by Loireau-Lozac'h A.M. and others is written that the compound $\text{La}_3\text{Ga}_{1.67}\text{S}_7$, which melts congruently at 1423 K, crystallizes in hexagonal space group $P6_3$ with next unit cell: $a = 1.015$ nm, $c = 0.608$ nm. Also a ternary compound $\text{La}_3\text{Ga}_{1.67}\text{Se}_7$, which is isostructural to $\text{La}_3\text{Ga}_{1.67}\text{S}_7$, is formed in the quasi-binary Ga_2S_3 - La_2S_3 system. Both of the compounds crystallize in the structural type of $\text{La}_3\text{CuSiS}_7$. Structures of the structural type of $\text{La}_3\text{CuSiS}_7$ are interesting because of their promising properties [5]. In this structural type La atom has 8-coordinate geometry to eight S atoms. A spread of La-S bond distance is observed ranging from 2.88 to 3.16 Å. Atom Cu is bonded in a trigonal planar geometry to three equivalent S atoms. All Cu-S bond lengths are 2.26 Å. Atoms Si are

centered tetrahedra, although there are one shorter (2.12 Å) and three longer (2.15 Å) Si–S bond lengths. The Ga–S bond lengths in the tetrahedral geometry to four S atoms are close to those of Si–S in the same coordination. The Pb–S bonds are slightly longer than Cu–S. Therefore, the complete substitution of Cu(II) by Pb(II) in a site is highly unlikely. However, the combination of 0.1Pb + 0.57Ga for the 2a site allows such a substitution. The paper presents the results of the study of the crystal structure of the quaternary compounds $\text{La}_3\text{Pb}_{0.1}\text{Ga}_{1.6}\text{S}_7$ and $\text{Pr}_3\text{Pb}_{0.1}\text{Ga}_{1.6}\text{S}_7$ which are considered as prospective compositions for material sciences.

Compounds which include Gallium, Lanthanum, Praseodymium, and Sulfur have a large interest because of their wide transmission window (0.5 - 10 m), low-phonon energy, good rare-earth solubility, large non-linearity and so on [6]. However, thermoelectric properties are not investigated, although the crystal structure $\text{La}_3\text{Ga}_{1.67}\text{S}_7$ and $\text{Pr}_3\text{Ga}_{1.67}\text{S}_7$ compounds points to possibility such properties. If we consider the second coordination surrounding of these compounds, then we understand that in a cuboctahedron which is formed by $[\text{GaS}_4]^{5-}$ anion sublattice we can include Pb atoms. The presence of heavy metal atoms can improve the thermoelectric properties. In this work, we present the crystal structure of $\text{La}_3\text{Pb}_{0.1}\text{Ga}_{1.6}\text{S}_7$ and $\text{Pr}_3\text{Pb}_{0.1}\text{Ga}_{1.6}\text{S}_7$ compounds.

I. Experimental details

The alloys were synthesized from elementary substances of at least 99.99 wt. % purity in quartz containers in an MP-30 programmable electric muffle furnace. The containers were evacuated to a residual pressure of 10^{-2} Pa and soldered in oxygen-gas burner flame. The alloys were synthesized step-wise as follows:

1) heating the mixtures to 870 K at the rate of 30 K/h; 2) exposure for 100 h; 3) heating to 1370 K at the rate of 12 K/h; 4) exposure for 2 h; 5) cooling to 770 K at the rate of 12 K/h; 6) homogenizing annealing for 500 h. After reaching the equilibrium state the synthesized alloys were quenched into room-temperature water.

The diffraction patterns for X-ray structure analysis were recorded at a DRON 4-13 diffractometer over 2Θ range of 10 - 100° (CuK α radiation, scan step 0.02°, 20 s exposure in each point). Data processing and the determination of the crystal structure utilized WinCSD software package [7].

II. Results and discussion

The crystal structure of the $\text{La}_3\text{Pb}_{0.1}\text{Ga}_{1.6}\text{S}_7$ and $\text{Pr}_3\text{Pb}_{0.1}\text{Ga}_{1.6}\text{S}_7$ compounds was studied by X-ray powder diffraction method, and its belonging to the hexagonal crystal system was established (space group $P6_3$). The conditions of the X-ray experiment and the crystallographic characteristics of the structure of the synthesized compounds are shown in Table 1. The refinement of atom coordinates and isotropic temperature displacement parameters (Table 2) in this model yielded satisfactory values of fit factors. Analysis of hkl reflection indices and their intensity indicates that the structure of the $\text{La}(\text{Pr})_3\text{Pb}_{0.1}\text{Ga}_{1.6}\text{S}_7$ compounds belong to the structural type $\text{La}_3\text{CuSiS}_7$ (space group $P6_3$; $a = 1.028$ nm, $c = 0.575$ nm) [8].

The observed and calculated diffraction patterns of the $\text{La}_3\text{Pb}_{0.1}\text{Ga}_{1.6}\text{S}_7$ and $\text{Pr}_3\text{Pb}_{0.1}\text{Ga}_{1.6}\text{S}_7$ compounds and the differences between them are presented in Fig. 1 and Fig. 2, respectively.

Inter-atomic distances agree well with the sums of the respective ionic radii [9] (Table 3).

The projection of the unit cell and the coordination polyhedra of La(Pr), Ga and M1(M2) atoms in the

Table 1.

Experimental details and crystallographic data for $\text{La}_3\text{Pb}_{0.1}\text{Ga}_{1.6}\text{S}_7$ and $\text{Pr}_3\text{Pb}_{0.1}\text{Ga}_{1.6}\text{S}_7$.

Parameters	$\text{La}_3\text{Pb}_{0.1}\text{Ga}_{1.6}\text{S}_7$	$\text{Pr}_3\text{Pb}_{0.1}\text{Ga}_{1.6}\text{S}_7$
Space group	$P6_3$ (173)	$P6_3$ (173)
a , (nm)	1.01902(3)	1.00034(3)
c , (nm)	0.60661(2)	0.60587(3)
Cell volume (nm ³)	0.54552(5)	0.52505(5)
Number of atoms in cell	23.3	23.3
Calculated Density (g/cm ³)	4.6326(4)	4.8666(5)
Absorption coefficient (1/cm)	1045.82	1162.99
Radiation and wavelength (nm)	Cu 0.154185	
Diffractometer	Dron 4-13	
Mode of refinement	Full Profile	
Program	WinCSD	
Number of atom sites	6	
Number of free parameters	19	
2Θ ; $\sin\Theta/\lambda$ (max.)	99.90; 0.496	100.02; 0.497
R_I	0.0673	0.0847
R_P	0.1545	0.1623
Scale factor	0.20766(1)	0.17847(1)

Table 2.

Atomic coordinates and equivalent displacement parameters for $\text{La}_3\text{Pb}_{0.1}\text{Ga}_{1.6}\text{S}_7$ and $\text{Pr}_3\text{Pb}_{0.1}\text{Ga}_{1.6}\text{S}_7$.

$\text{La}_3\text{Pb}_{0.1}\text{Ga}_{1.6}\text{S}_7$					
Atom	Wyck.	x/a	y/b	z/c	$B_{\text{iso}} \times 10^2 \text{ (nm}^2\text{)}$
La	6(c)	0.3747(1)	0.1410(1)	0.2395(5)	0.85(4)
Ga	2(b)	1/3	2/3	0.1710(7)	0.6(3)
M1	2(a)	0	0	-0.0598(12)	0.8(2)
S1	6(c)	0.1015(6)	0.5229(5)	0.0102(8)	0.8(2)
S2	6(c)	0.1470(7)	0.2358(6)	0.2809(11)	0.4(2)
S3	2(b)	1/3	2/3	0.4949(14)	0.9(3)
M1 – 0.600 Ga + 0.090 Pb					
$\text{Pr}_3\text{Pb}_{0.1}\text{Ga}_{1.6}\text{S}_7$					
Atom	Wyck.	x/a	y/b	z/c	$B_{\text{iso}} \times 10^2 \text{ (nm}^2\text{)}$
Pr	6(c)	0.3745(2)	0.1448(2)	0.2408(6)	0.93(3)
Ga	2(b)	1/3	2/3	0.1562(8)	1.03(14)
M2	2(b)	0	0	-0.0657(12)	1.4(2)
S1	6(c)	0.0965(8)	0.5163(11)	0.0093(11)	1.1(2)
S2	6(c)	0.1518(9)	0.2435(7)	0.2928(10)	0.8(2)
S3	2(b)	1/3	2/3	0.517(2)	0.7(3)
M2 – 0.59(1) Ga + 0.095(7) Pb					

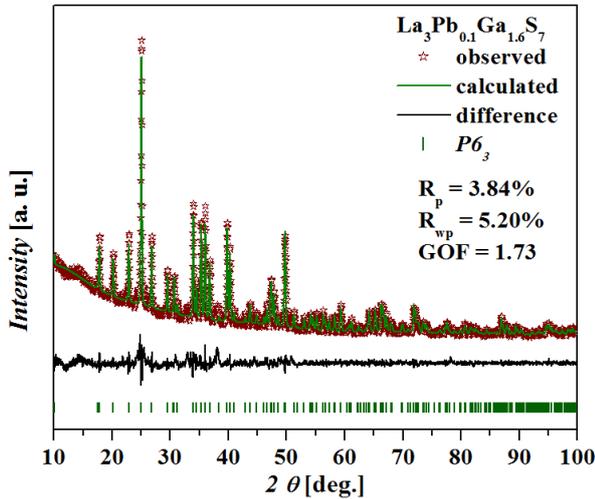


Fig. 1. Observed and calculated diffraction patterns for $\text{La}_3\text{Pb}_{0.1}\text{Ga}_{1.6}\text{S}_7$ and their difference.

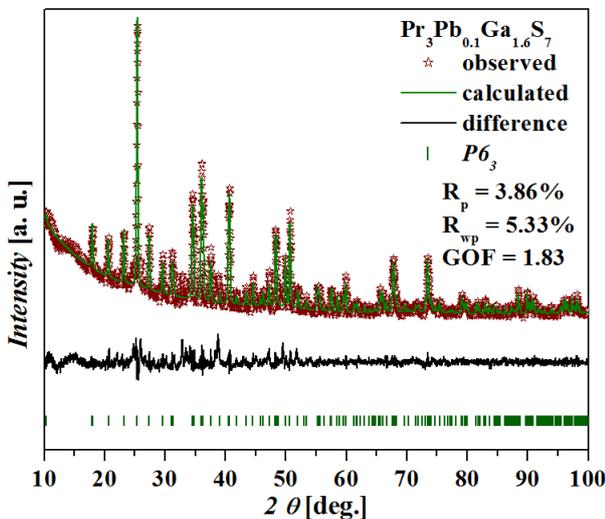


Fig. 2. Observed and calculated diffraction patterns for $\text{Pr}_3\text{Pb}_{0.1}\text{Ga}_{1.6}\text{S}_7$ and their difference.

$\text{La}(\text{Pr})_3\text{Pb}_{0.1}\text{Ga}_{1.6}\text{S}_7$ structure are shown in Fig. 3. $\text{La}(\text{Pr})$ atoms center trigonal prisms with one additional atom. These prisms are formed by S atoms. The atoms of the statistical mixture M1(0.600 Ga + 0.090 Pb) and M2 (0.59(1) Ga + 0.095(7) Pb) are located practically in the centers of the octahedra of S atoms. That is largely controlled by the geometrical requirements of one-dimensional stacks of Ga-centered tetrahedra separated by the La atoms. The site occupations can be understood in a simple way as being driven by the need to satisfy appropriate bond valence sums for both the Ga and Pb atoms. The distribution different atoms which have different occupancy p electronic levels in one site, increases probability thermoelectric properties which are connected to numbers of charge carriers.

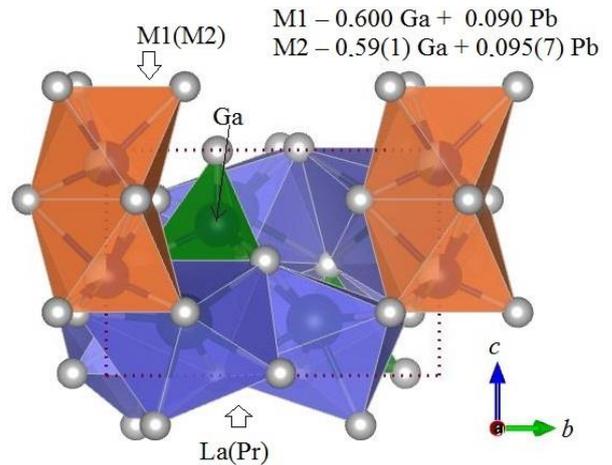


Fig. 3. Packing of polyhedra of cations in the structure of $\text{La}(\text{Pr})_3\text{Pb}_{0.1}\text{Ga}_{1.6}\text{S}_7$ compounds.

The obtained compositions agree well within the standard deviations with the nominal compositions of the synthesized alloys. The elemental composition of compounds was further evaluated by performed EDAX analysis, and the results are presented in Table 4 and

Table 3.

The inter-atomic distances δ (nm) and coordination numbers of atoms in the structure of $\text{La}_3\text{Pb}_{0.1}\text{Ga}_{1.6}\text{S}_7$ and $\text{Pr}_3\text{Pb}_{0.1}\text{Ga}_{1.6}\text{S}_7$ compounds.

$\text{La}_3\text{Pb}_{0.1}\text{Ga}_{1.6}\text{S}_7$			$\text{La}_3\text{Pb}_{0.1}\text{Ga}_{1.6}\text{S}_7$		
Atoms	δ (nm)	CN	Atoms	δ (nm)	CN
La	– S1	0.2831(6)	Pr	– S1	0.2847(9)
	– S2	0.2934(6)		– S1	0.2886(9)
	– S2	0.2937(6)		– S1	0.3015(9)
	– S1	0.2972(6)		– S2	0.2870(8)
	– S3	0.3010(5)		– S2	0.2918(8)
	– S2	0.3044(7)		– S2	0.2945(7)
	– S1	0.3072(6)		– S3	0.2903(6)
Ga	– S3	0.1964(10)	Ga	– S3	0.2184(13)
	– 3S1	0.2284(6)		– 3S1	0.2259(9)
M1	– 3S2	0.2314(7)	M2	– 3S2	0.2297(8)
	– 3S2	0.2948(8)		– 3S2	0.3042(9)
S1	– Ga	0.2284(6)	S1	– Ga	0.2259(9)
	– La	0.2831(6)		– Pr	0.2847(9)
	– La	0.2972(6)		– Pr	0.2886(9)
	– La	0.3072(6)		– Pr	0.3015(9)
S2	– M1	0.2314(7)	S2	– M2	0.2297(8)
	– La	0.2934(6)		– Pr	0.2870(8)
	– La	0.2937(6)		– Pr	0.2918(8)
	– M1	0.2948(8)		– Pr	0.2945(7)
	– La	0.3044(7)		– M2	0.3042(9)
S3	– Ga	0.1964(10)	S3	– Ga	0.2184(13)
	– 3 La	0.3010(5)		– 3Pr	0.2903(6)

Table 4.

Results of the EDX analysis of the $\text{La}_3\text{Pb}_{0.1}\text{Ga}_{1.6}\text{S}_7$ and $\text{Pr}_3\text{Pb}_{0.1}\text{Ga}_{1.6}\text{S}_7$ compounds.

Element	Content, at%	Error, %	Element	Content, at%	Error, %
La	28.43	4.92	Pr	19.53	2.36
Pb	0.61	0.30	Pb	1.67	0.47
Ga	12.22	1.16	Ga	8.12	0.61
S	58.73	3.12	S	70.68	2.57

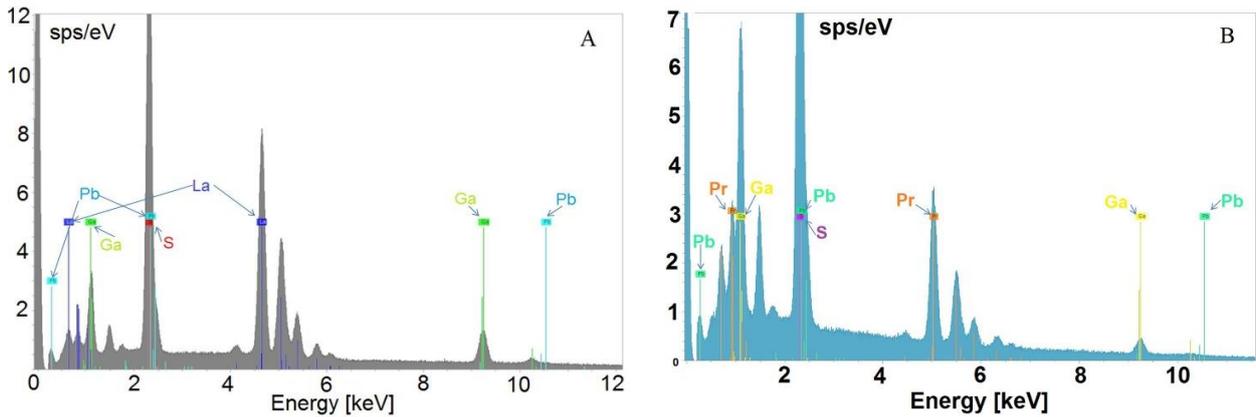


Fig. 4. EDAX spectra for $\text{La}_3\text{Pb}_{0.1}\text{Ga}_{1.6}\text{S}_7$ (A) and $\text{Pr}_3\text{Pb}_{0.1}\text{Ga}_{1.6}\text{S}_7$ (B) compounds.

Fig. 4. One can see that the structure calculation results and elemental analysis are in good agreement.

Conclusions

For the first time, new quaternary compounds of the compositions $\text{La}_3\text{Pb}_{0.1}\text{Ga}_{1.6}\text{S}_7$ and $\text{Pr}_3\text{Pb}_{0.1}\text{Ga}_{1.6}\text{S}_7$ were synthesized, and their crystal structure was studied by X-

ray diffraction methods. It was found that these compounds crystallize in the hexagonal crystal system ($\text{La}_3\text{CuSiS}_7$ structure type, space group $P6_3$) with the unit cell parameters 1.01902(3) nm, 0.60661(2) nm (for $\text{La}_3\text{Pb}_{0.1}\text{Ga}_{1.6}\text{S}_7$) and 1.00034(3) nm, 0.60587(3) nm (for $\text{Pr}_3\text{Pb}_{0.1}\text{Ga}_{1.6}\text{S}_7$).

Asymmetric structure of the studied compounds points out their non-linear properties. Adding Pb atoms to the structure of $\text{La}_3\text{Ga}_{1.67}\text{S}(\text{Se})_7$ compounds increases

the probability of formation of the ionic component of the inter-atomic bond, and this in turn improves thermoelectric properties.

The elemental composition of the synthesized alloys was confirmed by EDAX analysis.

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Кристалічна структура $\text{La}_3\text{Pb}_{0.1}\text{Ga}_{1.6}\text{S}_7$ та $\text{Pr}_3\text{Pb}_{0.1}\text{Ga}_{1.6}\text{S}_7$

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Кристалічна структура сполук $\text{La}_3\text{Pb}_{0.1}\text{Ga}_{1.6}\text{S}_7$ та $\text{Pr}_3\text{Pb}_{0.1}\text{Ga}_{1.6}\text{S}_7$ вивчена рентгенівським методом порошку. Зразки для аналізу отримані методом твердофазних реакцій між вихідними компонентами за температури 1370 К. Отримані сполуки кристалізуються в структурному типі La_3CuSi_7 , просторова група $P6_3$ з наступними параметрами елементарної комірки: $a = 1.01902(3)$ нм, $c = 0.60661(2)$ нм, $R_I = 0.0673$, $R_P = 0.1546$ (для $\text{La}_3\text{Pb}_{0.1}\text{Ga}_{1.6}\text{S}_7$) і $a = 1.00034(3)$ нм, $c = 0.60587(3)$ нм, $R_I = 0.0847$, $R_P = 0.1623$ (для $\text{Pr}_3\text{Pb}_{0.1}\text{Ga}_{1.6}\text{S}_7$). Кристалічна структура сполук описана в гексагональній системі, в якій атоми La(Pr) є центровані в тригональних призмах з одним додатковим атомом. Атоми статистичної суміші M1(0.600 Ga + 0.090 Pb) and M2 (0.59(1) Ga + 0.095(7) Pb) локалізовані практично в октаедричних порожнинах. Атоми Ga займають тетраедри, що утворені атомами Сульфуру. Асиметрична структура вивчених сполук вказує на їхні нелінійно-оптичні властивості. Атоми Pb, що фактично введені в структуру $\text{La}_3\text{Ga}_{1.67}\text{S}(\text{Se})_7$, створюють значну ймовірність зростання іонної складової зв'язків, що в свою чергу сприяє покращенню термоелектричних властивостей.

Ключові слова: кристалічна структура, рентгенівський метод порошку, халькогеніди рідкісноземельних елементів.