

# Condensed Matter and Interphases

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## Synthesis and study of the properties of synthetic analogues of the mineral naffildite with the participation of rare earth elements

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### Abstract

In recent years, there has been a significant increase in interest in ternary and quaternary compounds with the participation of rare earth elements (REE), as well as copper, antimony, and bismuth, which have a wider range of physical properties. Due to their valuable physical properties, they have become promising targets of research for modern materials science. Therefore, the purpose of this work is to study the properties of synthetic analogues of naffildite with the participation of rare earth elements.

The samples were synthesised from ternary sulphides (in the case of obtaining  $\text{Cu}_2\text{LaSb}_3\text{S}_7$ ,  $\text{Cu}_2\text{CeSb}_3\text{S}_7$ ,  $\text{Cu}_2\text{PrSb}_3\text{S}_7$  and  $\text{Cu}_2\text{NdSb}_3\text{S}_7$ ) by fusion in sealed quartz ampoules, preliminarily evacuated to a residual pressure of  $10^{-3}$  mmHg at 950–1100 K for 8 hours. The remaining antimony and bismuth-containing analogues, due to the peritectic nature of formation, were synthesised through batches ( $2\text{Cu} + \text{Ln} + 3\text{Sb}(\text{Bi}) + 7\text{S}$ ) from especially pure elements. After completion of the reaction, homogenizing annealing was carried out for a month at 600–700 K, depending on the composition. The obtained samples were investigated by differential thermal (DTA), X-ray phase (XRD) and microstructural (MSA) analyzes, as well as by measuring the microhardness and determining the density.

Compounds of the  $\text{Cu}_2\text{LnSb}_3\text{S}_7$  or  $\text{Cu}_2\text{LnBi}_3\text{S}_7$  (Ln – REE) type have been synthesised by direct synthesis from elements or from the ligature  $\text{CuSbS}_2(\text{CuBiS}_2)$  and  $\text{LnSbS}_3(\text{LnBiS}_3)$ . It was found that they are isostructural and crystallize in the orthorhombic system ( $\text{Cu}_2\text{LnSb}_3\text{S}_7$  –  $a = 14.490 \div 14.264$ ,  $b = 21.422 \div 21.206$ ,  $c = 3.902 - 3.804$  Å;  $\text{Cu}_2\text{LnBi}_3\text{S}_7$  –  $a = 14.722 \div 14.506$ ,  $b = 21.864 \div 21.564$ ,  $c = 4.142 \div 3.464$  Å;  $Z = 4$ , simple group Pbnm or Pbn2<sub>1</sub>) and belong to the structure type of naffildite  $\text{Pb}_2\text{Cu}(\text{Pb}, \text{Bi})\text{Bi}_2\text{S}_7$ .  $\text{Cu}_2\text{LaSb}_3\text{S}_7$ ,  $\text{Cu}_2\text{PrSb}_3\text{S}_7$  and  $\text{Cu}_2\text{NdSb}_3\text{S}_7$  melt congruently at 975, 985, and 1015 K, respectively, and other compounds are formed by a peritectic reaction.

**Keywords:** compound, crystal structure, naffildite, lattice parameters, electrical conductivity, thermal electromotive force.

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## 1. Introduction

In recent years, there has been a significant increase in interest in ternary and quaternary compounds with the participation of rare earth elements (REE), as well as copper, antimony, and bismuth, which have a wider range of physical properties. Due to their valuable physical properties, they have become promising targets of research for modern materials science [1–3].

Crystal chemical substantiation and obtaining new classes of compounds based on known structures is of great importance. Therefore, obtaining and studying the physicochemical properties of analogues of naffildite allows to expand the range of complex compounds. Therefore, the purpose of this work is to study the properties of synthetic analogues of naffildite with the participation of rare earth elements.

The crystal structure of naffildite was first determined in [4]. Naffildite crystallizes in the orthorhombic syngony and has the following unit cell parameters:  $a = 14.387$  (7),  $b = 21.011$  (5),  $c = 4.46$  (6) Å, space group Pbnm or  $Pbn2_1$ ,  $Z = 4$ .

The bases of the naffildite structure contain ten-element complex ribbons. These ten-element ribbons are connected on both sides with Pb, Bi

and randomly spaced Pb, Bi. The latter consists of aikinite ribbons [5]. It should be noted that the authors of [6], when considering the crystal chemistry of homologues of stibnite  $Sb_2S_3$  also referred to the naffildite structure. They found that stibnite ribbons are the main element of many natural and synthetic sulphosalts. Subsequently, in [9–11], it was established that the crystal structures of a number of synthetic compounds, in particular,  $Pb_4Sb_6S_{13}$ ,  $Pb_{4.75}Bi_{4.1}S_{11.2}$ ,  $Pb_4Sb_4S_{11}$  and others are composed of complex combinations of semi-octahedral ribbons.

When considering the crystal chemistry of complex sulphides [12, 13], it was found that the structure of naffildite is connected on both sides with common sulphur atoms by four elemental ribbons of aikinite  $[CuPb_2Bi_2S_6]_8$ . Here Cu atoms play the role of a cementing cation. However, the monograph [13] lists only the unit cell parameters, interplanar distances, and intensities of diffraction lines of naffildite. Fig. 1a shows ribbon structures and representation of a naffildite structure with Pauling polyhedra is shown in Fig. 1b.

As can be seen from Fig. 1b, four of the lead atoms are arranged in eight-dimensional

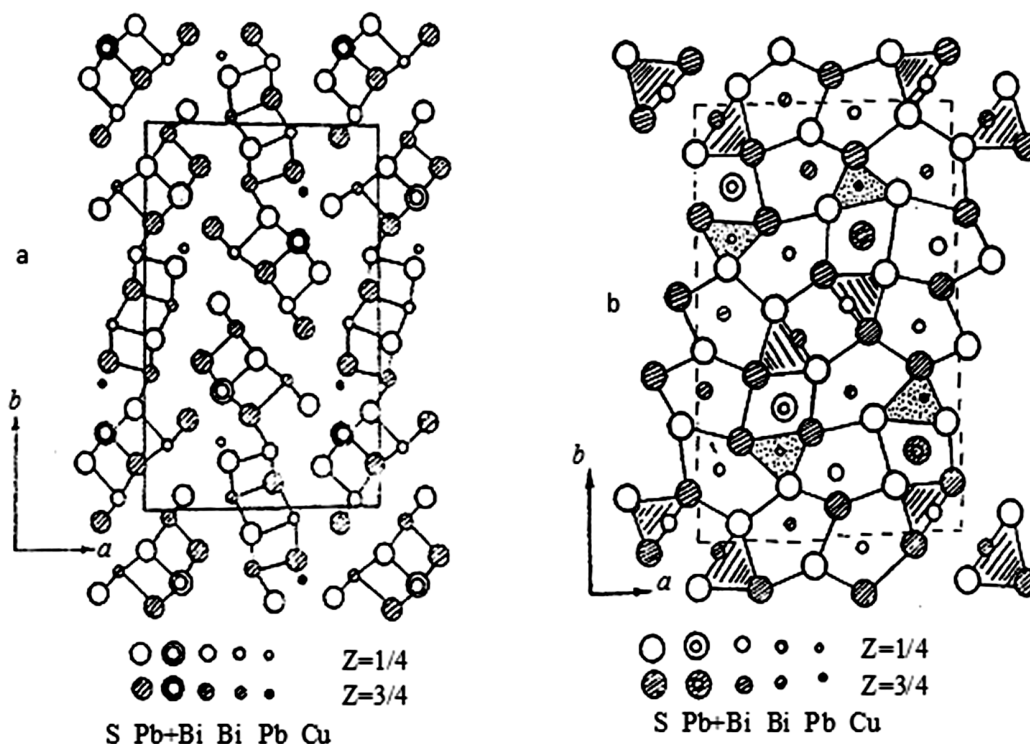
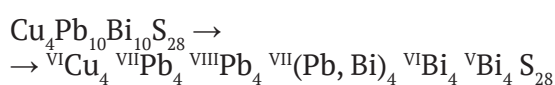


Fig. 1. The crystal structure of naffildite: a – ribbon representation; b – representation with a Pauling polyhedra

(trigonal prisms plus two hemi-octahedrons), four Pb atoms and four Bi atoms are arranged in seven-dimensional (hemi-octahedron plus trigonal prism) coordinations. Four Bi atoms are located in the plane at the centre of the hemi-octahedron and have a five-fold coordination. Two Pb atoms and two Bi atoms randomly fill polyhedra consisting of a hemi-octahedron and a trigonal prism which are parallel in a plane. Four Cu atoms are arranged in tetrahedra. They form a quadruple coordination and play the role of a cementing cation. Taking in consideration the aforementioned, the crystal chemical formula of naffildite can be represented as follows:



Thus, the crystal structure of naffildite consists of several polyhedra with complex configurations. It should be noted that this complexity of the configuration of polyhedra allows us to obtain a synthetic homologous series of naffildite by the substitution of cations with the corresponding atoms.

It is known that the CN of lanthanides in complex sulphides varies from 6 to 9 [14], the coordination polyhedra in them are mainly octahedron, trigonal prism, one-, two- and tricapped trigonal prisms. Therefore, the possibility of obtaining new classes of compounds with substitution of Pb in a naffildite structure, which has sevenfold coordination with  $\text{Eu}^{2+}$  or  $\text{Yb}^{2+}$  cations (statistically arranged Pb, Bi atoms) with compensating  $\text{Bi}^{3+}$  cations, located in hemi-octahedra, substituting  $\text{Sb}^{3+}$  and  $\text{Ln}^{3+}$  with the naffildite structure, was proposed.

Earlier, we synthesised and studied the properties of synthetic lanthanum and neodymium-containing analogues of the mineral naffildite [15], berthierite [16, 17], aikinite,  $\text{CuPbBi}_3\text{S}_6$  [18], and bournonite  $\text{CuPbSbS}_3$  [19,20]. Based on this, this study presents the results of the synthesis, X-ray study, and physiochemical properties of analogues of naffildite with other rare earth elements.

## 2. Experimental

The starting ternary compounds ( $\text{CuSbS}_2$ ,  $\text{CuBiS}_2$ ,  $\text{LnSbS}_3$  and  $\text{LnBiS}_3$ ) were studied in detail in [1, 21, 22]. For the determination of

the optimal mode of synthesis and growth of single crystals of  $\text{Cu}_2\text{LnSb}_3\text{S}_7$  and  $\text{Cu}_2\text{LnBi}_3\text{S}_7$  compounds, derived from the structure of naffildite, differential thermal (DTA), X-ray phase (XRD) and microstructural (MSA) analyses, as well as by determination of the microhardness and density were performed. DTA was performed using an NTR-70 Kurnakov thermograph in the temperature range of 298–1200 K. The heating rate was 10 deg/min. Aluminium oxide was used as a standard [23].

X-ray diffraction patterns were recorded using a Bruker D2 PHASER diffractometer ( $\text{CuK}_\alpha$ -radiation, Ni - filter); MSA was performed using an MIM-8 microscope. The microhardness was measured using a PMT-3 microhardness tester with the loads selected as a result of measuring the microhardness of each phase, and the density was determined by the pycnometric method.

Samples were synthesised from ternary sulphides (in the case of obtaining  $\text{Cu}_2\text{LaSb}_3\text{S}_7$ ,  $\text{Cu}_2\text{CeSb}_3\text{S}_7$ ,  $\text{Cu}_2\text{PrSb}_3\text{S}_7$  and  $\text{Cu}_2\text{NdSb}_3\text{S}_7$ ) in sealed quartz ampoules, preliminarily evacuated to a residual pressure of  $10^{-3}$  mmHg at 950–1100 K for 8 hours. The rest of the antimony and bismuth-containing analogues, due to the peritectic nature of the formation, were synthesised through batches ( $2\text{Cu} + \text{Ln} + 3\text{Sb}(\text{Bi}) + 7\text{S}$ ) from extra pure elements. After completion of the reaction, homogenizing annealing was carried out for a month at 600–700 K, depending on the composition.

## 3. Results and discussion

Phase diagram of  $\text{CuSbS}_2$ - $\text{PrSbS}_3$  system, plotted based on the results of physico-chemical analysis, is shown in Fig. 2. As can be seen, with a ratio of components of 2:1, a quaternary sulphosalt of composition  $\text{Cu}_2\text{PrSb}_3\text{S}_7$  was formed in the  $\text{CuSbS}_2$ - $\text{PrSbS}_3$  system. This compound melts congruently at 985 K and divides the system into two subsystems:  $\text{CuSbS}_2$ - $\text{Cu}_2\text{PrSb}_3\text{S}_7$  and  $\text{Cu}_2\text{PrSb}_3\text{S}_7$ - $\text{PrSbS}_3$ . Both subsystems are of the eutectic type. Coordinates of eutectic points: 15 mol. %  $\text{PrSbS}_3$  and  $T = 700$  K, 55 mol. %  $\text{PrSbS}_3$  and  $T = 825$  K. The solubility based on the original sulphides was limited and was 5 mol. %  $\text{PrSbS}_3$  based on  $\text{CuSbS}_2$  and 5 mol. %  $\text{CuSbS}_2$  based on  $\text{PrSbS}_3$ .

The quaternary compound  $\text{Cu}_2\text{PrSb}_3\text{S}_7$  is a phase of variable composition and exists in the range of compositions 32÷37 mol. %  $\text{PrSbS}_3$ .

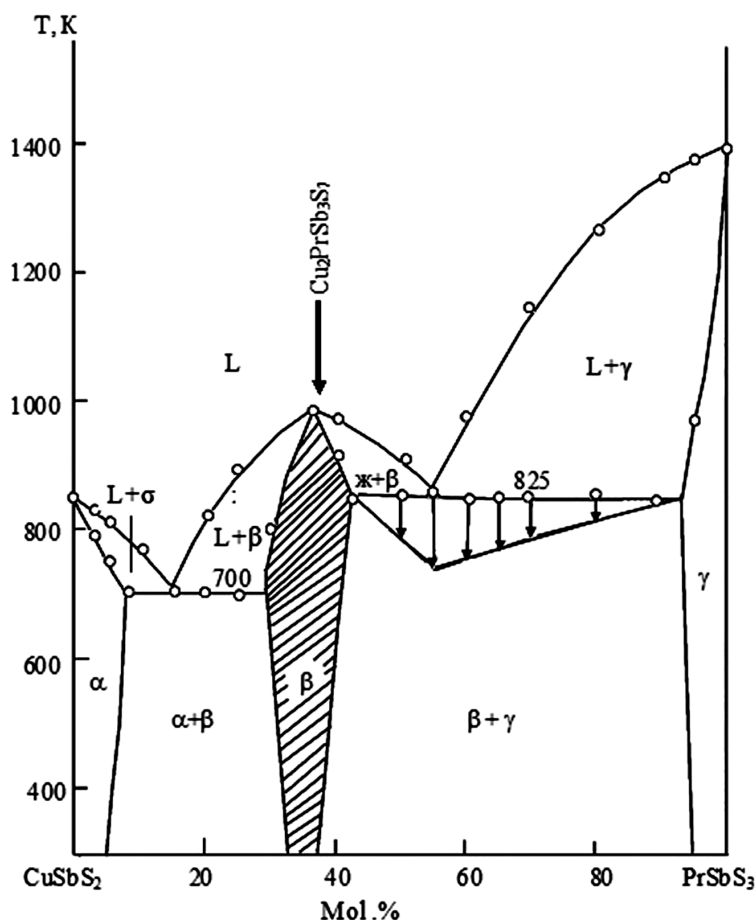


Fig 2.  $T$ - $x$  diagram of the  $\text{CuSbS}_2 - \text{PrSbS}_3$  system

The formation of a new phase in the system was also confirmed by microhardness measurement data. Depending on the composition in  $\text{CuSbS}_2 - \text{PrSbS}_3$  system there are three sets of microhardness values  $2300 \div 2450$ ,  $2100 \div 2200$  and  $2900 \div 3100$  MPa related to microhardness  $\alpha$ ,  $\beta$  and  $\gamma$ -phases, respectively.

As we noted above, all systems in the La-Nd series have the same character, i.e., the quaternary compounds melt congruently. Other similar systems involving antimony and bismuth are also quasi-binary, in all cases with a component ratio of 2:1, naffildite-like compounds are formed. However, they melt incongruently.

The XRD data were in complete agreement with the DTA and MSA data and confirm the formation of a compound of  $\text{Cu}_2\text{LnSb}_3(\text{Bi})_3\text{S}_7$  type.

Crystallographic data and some physico-chemical properties of compounds of  $\text{Cu}_2\text{LnSb}_3(\text{Bi})_3\text{S}_7$  type are shown in Table 1 and the calculations of X-ray diffraction patterns for some compounds of this type are presented in Table 2.

The resulting quaternary compounds are isostructural with each other, crystallize in the orthorhombic syngony, and belong to the naffildite structural type. In the unit cell  $\text{Cu}_2\text{LnSb}_3(\text{Bi})_3\text{S}_7$ ,  $Z = 4$ , a  $\text{Pbnm}$  or  $\text{Pbnm}2_1$  space group is located. As can be seen from Table 1, the parameters and volume of the elementary cell naturally decrease in the series of lanthanides with an increase in the charge of  $\text{Ln}^{3+}$ .

The temperature dependences of the electrical conductivity coefficients and thermal electromotive force of some compounds of the  $\text{Cu}_2\text{LnBi}_3\text{S}_7$  ( $\text{Ln} = \text{La}, \text{Nd}, \text{Sm}, \text{Gd}, \text{Er}$ ) type were investigated and shown in Fig. 3 and 4.

The measurement results showed that these crystals are characterised by a dependence inherent in impurity semiconductors. In the impurity region (315–343 K), the electrical conductivity gradually increases and, upon transition to the intrinsic region (450–525 K), increases abruptly. The band gap calculated from this region increases in the series  $\text{Cu}_2\text{LaSb}_3\text{S}_7 -$

**Table 1.** Crystallographic and some physicochemical properties of compounds of the  $\text{Cu}_2\text{LnSb}_3\text{S}_7$  and  $\text{Cu}_2\text{LnBi}_3\text{S}_7$  types

Compound	Lattice parameters, Å			V, Å <sup>3</sup>	Density, g/cm <sup>3</sup>	Microhardness, MPa	$\Delta E$ , eV
	a	b	c				
$\text{Cu}_2\text{LaSb}_3\text{S}_7$	1.4490	21.422	3.902	1232.92	4.38	1950	0.53
$\text{Cu}_2\text{CeSb}_3\text{S}_7$	14.462	21.414	3.972	1230.08	4.46	2000	–
$\text{Cu}_2\text{PrSb}_3\text{S}_7$	14.441	21.460	3.931	1218.23	4.512	2010	–
$\text{Cu}_2\text{NdSb}_3\text{S}_7$	14.460	21.406	3.964	1226.98	4.64	2100	0.60
$\text{Cu}_2\text{SmSb}_3\text{S}_7$	14.392	21.362	3.940	1211.32	4.82	2200	0.73
$\text{Cu}_2\text{GdSb}_3\text{S}_7$	14.362	21.454	3.922	1208.45	4.78	2370	0.80
$\text{Cu}_2\text{ErSb}_3\text{S}_7$	14.303	21.284	3.884	1182.39	4.90	2350	–
$\text{Cu}_2\text{YbSb}_3\text{S}_7$	14.271	21.252	3.842	1152.86	4.96	2400	–
$\text{Cu}_2\text{LuSb}_3\text{S}_7$	14.264	21.206	3.804	1150.64	5.36	2450	–
$\text{Cu}_2\text{LaBi}_3\text{S}_7$	14.722	21.864	4.142	1333.23	5.70	1850	0.38
$\text{Cu}_2\text{CeBi}_3\text{S}_7$	14.704	21.806	4.104	1315.89	5.92	1900	–
$\text{Cu}_2\text{NdBi}_3\text{S}_7$	14.661	21.784	4.046	1292.19	6.16	1940	0.40
$\text{Cu}_2\text{SmBi}_3\text{S}_7$	14.606	21.706	4.022	1275.3	6.32	2080	0.45
$\text{Cu}_2\text{GdBi}_3\text{S}_7$	14.584	21.664	4.00	1263.79	6.54	2150	0.69
$\text{Cu}_2\text{ErBi}_3\text{S}_7$	14.522	21.606	3.486	1093.77	6.70	2200	0.86
$\text{Cu}_2\text{LuBi}_3\text{S}_7$	14.506	21.564	3.464	1083.56	6.83	2360	0.90

**Table 2.** Calculation of X-ray diffraction patterns of compounds  $\text{Cu}_2\text{GdSb}_3\text{S}_7$ ,  $\text{Cu}_2\text{LuSb}_3\text{S}_7$ , and  $\text{Cu}_2\text{NdBi}_3\text{S}_7$ 

$\text{Cu}_2\text{GdSb}_3\text{S}_7$				$\text{Cu}_2\text{LuSb}_3\text{S}_7$				$\text{Cu}_2\text{NdBi}_3\text{S}_7$			
$d_{\text{exp}}$	$I/I_0$	$hkl$	$d_{\text{calc}}$	$d_{\text{exp}}$	$I/I_0$	$hkl$	$d_{\text{calc}}$	$d_{\text{exp}}$	$I/I_0$	$hkl$	$d_{\text{calc}}$
7.184	20	200	7.182	7.134	10	200	7.132	7.336	18	200	7.331
4.373	10	320	4.372	5.918	10	230	5.918	5.110	18	230	5.109
3.980	8	330	4.979	4.340	8	320	4.338	4.174	10	150	4.176
3.684	30	250	3.684	4.066	8	150	4.065	4.054	10	330	4.054
3.577	15	060	3.575	3.638	15	250	3.645	3.662	15	400	3.664
3.440	10	031	3.434	3.537	15	060	3.535	3.631	15	060	3.633
3.280	5	221	3.278	3.356	10	201	3.358	3.432	10	131	3.434
3.193	5	260	3.192	3.208	7	221	3.201	3.269	34	430	3.272
3.062	100	141	3.062	3.166	20	280	3.167	3.172	100	141	3.172
2.984	30	440	2.984	3.130	100	147	3.139	3.041	75	440	3.042
2.898	5	241	2.896	2.954	30	440	2.958	2.798	30	450	2.805
2.794	60	331	2.793	2.941	10	241	2.939	2.369	20	470	2.373
2.649	28	401	2.648	2.861	45	331	2.861	2.334	40	271	2.338
2.310	8	511	2.304	2.601	30	401	2.602	2.280	25	560	2.281
2.240	30	560	2.239	2.550	8	161	2.547	2.120	5	650	2.120
2.122	12	1.10.0	2.122	2.271	10	511	2.269	2.093	8	601	2.092
2.034	12	611	2.034	2.226	40	560	2.220	2.050	15	720	2.057
1.958	80	002	1.961	2.120	25	371	2.118	2.023	10	002	2.023
1.875	35	132	1.875	2.100	6	0.10.0	2.098	1.860	30	312	1.862
1.827	8	142	1.827	2.009	8	611	2.007	1.848	35	711	1.853
1.689	12	690	1.689	1.900	10	002	1.902	1.774	25	830	1.778
1.619	8	362	1.618	1.838	6	202	1.837	1.716	8	352	1.718
1.574	5	452	1.597	1.819	30	222	1.811	1.581	8	691	1.583
1.530	10	940	1.530	1.776	8	142	1.776	1.335	26	113	1.333
1.479	5	901	1.478	1.748	20	491	1.747	1.310	10	692	1.310
				1.703	10	741	1.701				
				1.693	10	840	1.690				
				1.670	8	690	1.673				
				1.580	8	362	1.580				
				1.560	10	452	1.560				
				1.520	5	940	1.519				

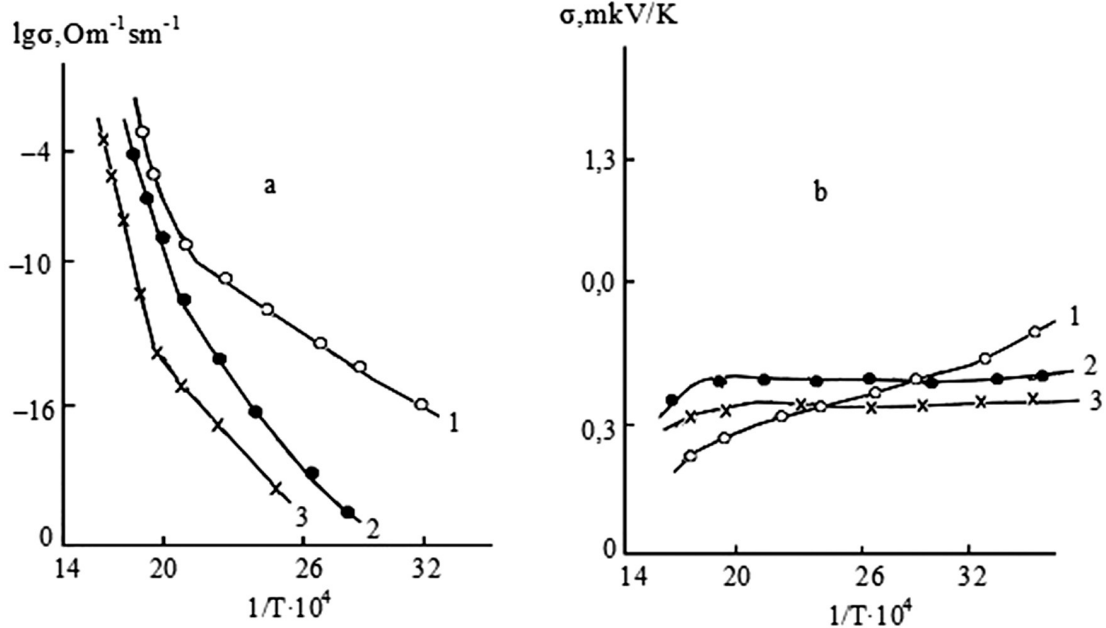


Fig. 3. Temperature dependences of electrical conductivity (a) and thermal electromotive force (b) of compounds of  $\text{Cu}_2\text{LaBi}_3\text{S}_7$  (1),  $\text{Cu}_2\text{NdBi}_3\text{S}_7$  (2), and  $\text{Cu}_2\text{GdBi}_3\text{S}_7$  (3)

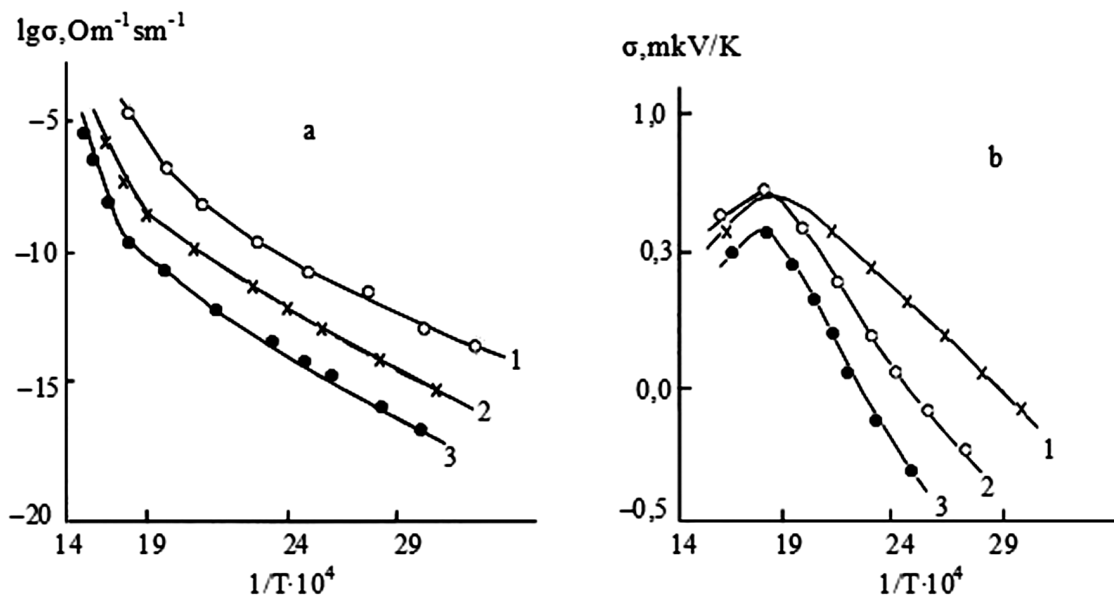


Fig. 4. Temperature dependences of electrical conductivity (a) and thermal electromotive force (b) of compounds of  $\text{Cu}_2\text{SmBi}_3\text{S}_7$  (1),  $\text{Cu}_2\text{ErBi}_3\text{S}_7$  (2), and  $\text{Cu}_2\text{LuBi}_3\text{S}_7$  (3)

$\text{Cu}_2\text{GdSb}_3\text{S}_7$  from  $\Delta E = 0.53$  (for  $\text{Cu}_2\text{LaSb}_3\text{S}_7$ ) to  $\Delta E = 0.80$  eV (for  $\text{Cu}_2\text{GdSb}_3\text{S}_7$ ) and  $\Delta E = 0.38$  eV (for  $\text{Cu}_2\text{LaBi}_3\text{S}_7$ ) to  $\Delta E = 0.90$  eV (for  $\text{Cu}_2\text{LuBi}_3\text{S}_7$ ).

The nature of the change of thermal electromotive force ( $\alpha$ ) for  $\text{Cu}_2\text{LaBi}_3\text{S}_7$ ,  $\text{Cu}_2\text{NdBi}_3\text{S}_7$ , and  $\text{Cu}_2\text{GdBi}_3\text{S}_7$  compounds is similar to a change in electrical conductivity, i.e. in its own region  $\alpha$  decreases sharply. In the case of  $\text{Cu}_2\text{SmBi}_3\text{S}_7$ ,  $\text{Cu}_2\text{ErBi}_3\text{S}_7$ , and  $\text{Cu}_2\text{LuBi}_3\text{S}_7$  compounds with an

increase in electrical conductivity, the thermal electromotive force also increases, and in the intrinsic conduction region it decreases, which was probably due to their complex band structure.

#### 4. Conclusions

Technological conditions have been developed and compounds of the  $\text{Cu}_2\text{LnSb}_3\text{S}_7$  and  $\text{Cu}_2\text{LnBi}_3\text{S}_7$  types have been synthesised. It was

established that they are isostructural, crystallize in the orthorhombic syngony ( $\text{Cu}_2\text{LnSb}_3\text{S}_7$  –  $a = 14.490 \div 14.264$ ,  $b = 21.422 \div 21.206$ ,  $c = 3.902 - 3.804$  Å;  $\text{Cu}_2\text{LnBi}_3\text{S}_7$  –  $a = 14.722 \div 14.506$ ,  $b = 21.864 \div 21.564$ ,  $c = 4.142 \div 3.464$  Å;  $Z = 4$ , space group Pbnm or Pbn<sub>2</sub>) and belong to the naffildite structural type.

The crystal lattice parameters of the obtained compounds were calculated and some physico-chemical and electrophysical properties were studied. It was established that these compounds are *p*-type semiconductors.

### Author contributions

Mammadov Sh. H. – writing of the article and head of scientific research. Aliyev O. M. – idea for the scientific work and writing of the article. Azhdarova D. S. – scientific editing of the text, final conclusions. Agaeva R. M. – conducting research. Ragimova V. M. – conducting research.

### Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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