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Inorganic chemistry**SYNTHESIS AND STUDY OF SYNTHETIC ANALOGUES OF NUFFIELDITE
MINERAL WITH RARE EARTH ELEMENTS****O.M.Aliyev, R.M.Agayeva, D.S.Ajdarova, T.F.Maksudova,
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(Presented by Academician of NAS of Azerbaijan A.M.Aliyev)

*Cu₂LnSb₃S₇ and Cu₂LnBi₃S₇ type compounds were synthesized by direct ampullary method and their monocrystals were grown by crystallization. It was determined that these compounds are isostructural and crystallize in orthorhombic syngony (Cu₂LnSb₃S₇ – $a = 14.26 \div 14.43$, $b = 21.20 \div 21.42$, $c = 3.80 \div 3.90 \text{ \AA}$; Cu₂LnBi₃S₇ – $a = 14.50 \div 14.72$, $b = 21.56 \div 21.86$, $c = 3.96 \div 4.14 \text{ \AA}$; $Z = 4$) and are semi-conductors with *p*-type conductivity. Their band gap varies at $\Delta E - 0.53 \div 0.90 \text{ eV}$ interval.*

Keywords: compound, synthesis, nuffieldite, semiconductors

Rapid development of modern science and technology stimulates the search of functional complex compounds. In that sense synthesis and study of structural analogues of natural minerals which is known before to science is of great importance, because it is possible to produce materials of which the properties are controlled due to important cation and anion changes by keeping general valence balance in basic structure. It is known that sulfides of copper, antimony, bismuth and lanthanide draw much attention as an optically-sensitive material. Thus, diode and triodes prepared on the basis of Cu₂S (Cu₂O), Sb₂S₃, Bi₂S₃ and Ln₂S₃ (Ln₂O₂S) are used as a rectifier or considered to be perspective materials [1-4]. From this point obtaining and investigation of Cu₂LnSb₃S₇ and Cu₂LnBi₃S₇ type compounds based on the chalcogenides is an actual problem.

Experimental part

CuSbS₂ and LnSbS₃ type initial components were synthesized in vacuum quartz ampoules by using especially pure elements. Temperature mode of the synthesis was conducted as it was shown in the work [5,6]. By using CuSbS₂ and LnSbS₃ ligands we synthesized alloys of LaSbS₃-CuSbS₂, NdSbS₃ – CuSbS₂ and other systems. Quaternary alloys were obtained from alloys or 2Cu₂S+3Sb₂S₃+2Ln+6S burden. Synthesis was conducted in quartz ampoule at 675-700K, then at 950-1300K when sulphur totally entered into reaction. After keeping the ampoule in this mode for 1-1.5 hours temperature was decreased to 650-675K

and was homogenized 25-27 days. It should be noted that Cu₂LnSb₃S₇ type compounds and alloys synthesized on their basis have a negative coefficient of volume expansion. That's why synthesis was conducted in graphitized or special double walled quartz ampoule. As Cu₂LnBi₃S₇ type compounds are formed by peritectic reaction they were synthesized from elements by direct method. Monocrystals of congruently melting Cu₂LnBi₃S₇ type compounds were obtained by directed crystallization method (Brickman-Stockbarger). For this purpose two-stage electric furnace was used. In the first stage (T₁) the temperature was 45-50° higher than melting temperature of the compound, in the second stage (T₂) it was 60-75° lower. Ampoule was lowered with 5mm/h speed to the furnace, when entered to T₁-stage it melted, in T₂-stage it crystallized. The process proceeded two days, and needle-shaped crystals suitable for optical, X-ray studies were obtained.

Research results of Cu₂LnSb₃S₇ type compounds

According to the results of X-ray analysis it was determined that Cu₂LnSb₃S₇ type compounds are isostructural, crystallize in the orthorhombic syngony and belong to nuffieldite structure type.

4 molecules ($Z=4$) are located in elementary cell, space group is *Pbnm* or *Pbn2*. Crystallographic and some physical-chemical properties of synthesized compounds are given in table 1.

Table 1

Crystallographic and physical-chemical properties of $\text{Cu}_2\text{LnSb}_3\text{S}_7$ type compounds

Compound	Lattice parameters, Å			Volume of elementary lattice, V, Å ³	Density, g/cm ³		Microhardness, kg/mm ²
	a	b	c		experimental	calculated	
$\text{Cu}_2\text{LaSb}_3\text{S}_7$	14.43	21.42	3.90	1205.45	4.38	4.72	195
$\text{Cu}_2\text{CeSb}_3\text{S}_7$	14.46	21.41	3.968	1228.44	4.46	4.64	200
$\text{Cu}_2\text{PrSb}_3\text{S}_7$	14.44	21.46	3.965	1225.59	4.516	4.65	207
$\text{Cu}_2\text{NdSb}_3\text{S}_7$	14.463	21.404	3.962	1226.50	4.64	4.67	210
$\text{Cu}_2\text{SmSb}_3\text{S}_7$	13.39	21.36	3.94	1211.04	4.82	4.76	220
$\text{Cu}_2\text{GdSb}_3\text{S}_7$	14.36	21.35	3.92	1201.82	4.78	4.84	237
$\text{Cu}_2\text{ErSb}_3\text{S}_7$	14.30	21.28	3.86	1174.61	4.90	5.08	235
$\text{Cu}_2\text{YbSb}_3\text{S}_7$	14.27	21.25	3.84	1164.44	4.96	5.10	240
$\text{Cu}_2\text{LuSb}_3\text{S}_7$	14.26	21.20	3.80	1148.78	5.36	5.16	245

The structure of nuffieldite consists of ten element complex chain. This ten element band consists of four element aikinite $[\text{CuPb}_2\text{Bi}_2\text{S}_6]_\infty$ band connected on both sides by general S atom with ternary $[\text{PbBi}(\text{Pb},\text{Bi})\text{S}_5]_\infty$ bands. Here Cu atoms located in tetrahedrons act as a cementing kation. In fig.1 description of nuffieldite $\text{Cu}_4\text{Pb}_{10}\text{Bi}_{10}\text{S}_{28}$ structure with band and Pauling polyhedrons was given. As it is seen from figure four Pb atoms are located in eight, and four Pb and four Bi atoms are located in seven coordination. Four Bi atoms are located nearly in the cen-

ter of square base of semi-octahedron. Two Pb and two Bi atoms disorderly fill polyhedrons which consist of semi-octahedron and trigonal prism parallel to the plane. Four Cu atoms are located in tetrahedrons and have four coordinations and act as a cementing kation. Considering the above mentioned we can express crystalline chemical formula of nuffieldite $\text{Cu}_4\text{Pb}_{10}\text{Bi}_{10}\text{S}_{28}$ by the following way:

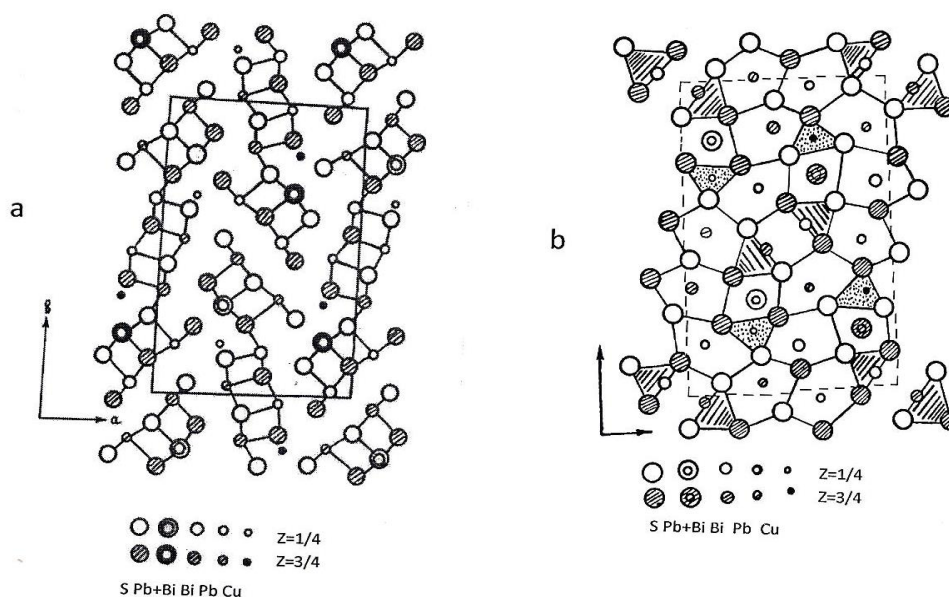


Fig 1. Structure of nuffieldite $\text{Pb}_2\text{Cu}(\text{Pb}, \text{Bi})\text{Bi}_2\text{S}_7$: a- band description; b- description with pauling polyhedrons

Thus, structure of nuffildite has a complex configuration consisting of several polyhedrons. This complexity allows us to substitute nuffildite kations with geometrically near kations and to obtain new analogues. It is known that coordination numbers of lanthanides in complex chalcogenides of rare earth elements change from 6 to 9 and coordination polyhedrons consist of seven and eight vertexes as well as nine vertexes (trigonal prism + three semi-octahedrons) and octahedrons in nuffildite. So, by substituting Pb kation in seven and eight coordination with relevant lanthanides (Er^{2+} , Yb^{2+}) or Pb kation in eight vertexes with relevant lanthanides or by replacing compensating kation instead of disorderly distributed (Pb, Bi), and substituting Sb^{3+} with Bi^{3+} atoms in semi-octahedron we may say our opinion about the possibility of synthesizing new type analogues of nuffildite.

According to thermal analysis results majority of $\text{Cu}_2\text{LnSb}_3\text{S}_7$ type compounds melt congruently. Their melting temperature varies at 910-1010K range in $\text{Cu}_2\text{LnSb}_3\text{S}_7$ - $\text{Cu}_2\text{LuSb}_3\text{S}_7$

row. Variation of microhardness and density changes regularly and completes each other in lanthanide row like in melting temperature. Temperature dependences of electric conductivity and electromotive force of $\text{Cu}_2\text{LnSb}_3\text{S}_7$ type compounds at 300-600K range were investigated. It was defined that they are p-type semi-conductors and band gap varies at 0,53-0.90 eV range in a row.

Research results of $\text{Cu}_2\text{LnBi}_3\text{S}_7$ (Lu= La, Ce, Nd, Sm, Gd, Er, Lu) type compounds and their discussion

According to the results of thermal analysis unlike $\text{Cu}_2\text{LnSb}_3\text{S}_7$ type compounds $\text{Cu}_2\text{LnBi}_3\text{S}_7$ type compounds are formed by peritectic reactions, decompose and melt. Their melting temperature varies at 815-940K range in $\text{Cu}_2\text{LaBi}_3\text{S}_7$ - $\text{Cu}_2\text{LuBi}_3\text{S}_7$ row.

By X-ray powder analysis it was determined that $\text{Cu}_2\text{LnBi}_3\text{S}_7$ type compounds is isostructural with $\text{Cu}_2\text{LnSb}_3\text{S}_7$ type compounds and crystallize at orthorhombic syngony (table 2).

Table 2

Crystallographic and physical-chemical properties of $\text{Cu}_2\text{LnBi}_3\text{S}_7$ type compounds

Compound	Lattice parameters, Å			Volume of elementary lattice, V, Å ³	Density, g/cm ³		H, kg/mm ²	ΔE , eV
	a	b	c		experimental	calculated		
$\text{Cu}_2\text{LaBi}_3\text{S}_7$	14.72	21.86	4.14	1332.16	5.57	5.70	185	0.48
$\text{Cu}_2\text{CeBi}_3\text{S}_7$	14.70	21.80	4.10	1313.88	5.66	5.92	190	0.50
$\text{Cu}_2\text{NdBi}_3\text{S}_7$	14.66	21.78	4.04	1289.95	5.78	6.16	194	0.56
$\text{Cu}_2\text{SmBi}_3\text{S}_7$	14.60	21.70	4.00	1267.28	5.92	6.32	208	0.58
$\text{Cu}_2\text{GdBi}_3\text{S}_7$	14.58	21.66	4.00	1263.21	5.97	6.54	215	0.62
$\text{Cu}_2\text{ErBi}_3\text{S}_7$	14.52	21.60	3.98	1248.25	6.10	6.70	220	0.65
$\text{Cu}_2\text{LuBi}_3\text{S}_7$	14.50	21.56	3.96	1237.97	6.19	6.83	236	0.78

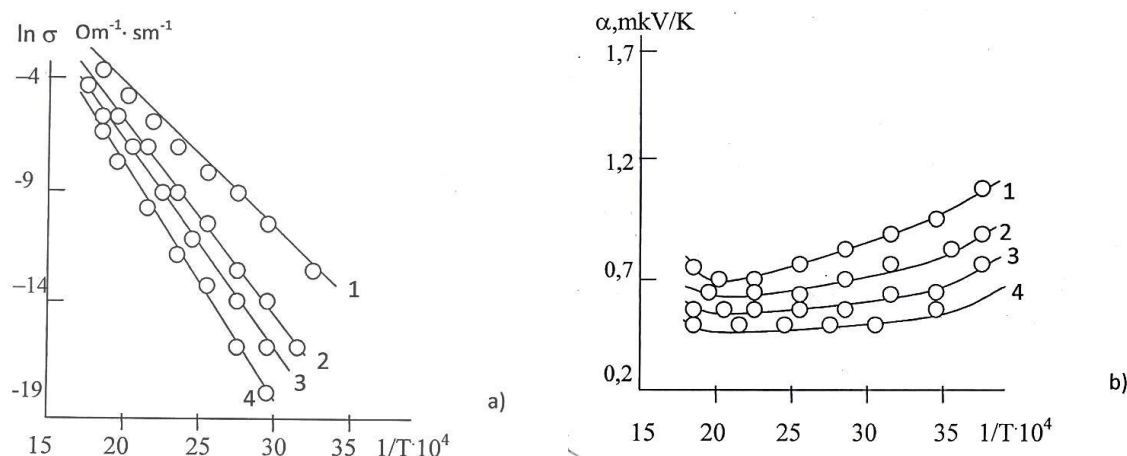


Fig.2. Temperature dependences of electric conductivity (a) and electromotive force (b) of $\text{Cu}_2\text{LnBi}_3\text{S}_7$ type compounds:
1- $\text{Cu}_2\text{LaBi}_3\text{S}_7$; 2- $\text{Cu}_2\text{NdBi}_3\text{S}_7$; 3- $\text{Cu}_2\text{GdBi}_3\text{S}_7$; 4- $\text{Cu}_2\text{ErBi}_3\text{S}_7$

Temperature dependence of α and σ - $\text{Cu}_2\text{LnBi}_3\text{S}_7$ type compounds was studied at 293-573K range (fig.2). As it is seen, electric conductivity of studied compounds acts as common semiconductors, in other words when temperature increases electric conductivity of the sample rises. Band gap varies at $\Delta E = 0.48 \div 0.57$ eV range. Electric conductivity of the compounds is found to be $\sigma \approx 10^{-7} \text{ ohm}^{-1}\text{cm}^{-1}$ at room temperature, but at 573K it is $\sigma \approx 10^{-3} \text{ ohm}^{-1}\text{cm}^{-1}$. Curves of temperature dependence of electromotive force $\alpha \sim \alpha(1/T)$ of compounds are characterized by weakly expressed minimum (fig. 2b).

The sign of electromotive force conforms to electron conductivity. It should be noted that $\lg \sigma \sim f(1/T)$ dependence does not allow us to confirm the dominance of additive conductivity by stoichiometric impurity of samples due to particular conductivity of $\text{Cu}_2\text{LnBi}_3\text{S}_7$ type compounds or additives. In the latter case we may expect the lattice to transfer to the special conductivity at high temperature. Electric conductivity of $\text{Cu}_2\text{LnBi}_3\text{S}_7$ type compounds varies at $\Delta E = 0.48 \div 0.75$ eV range calculated from $\lg \sigma \sim f(1/T)$ dependence at 295-800K interval. When the compounds are heated from 673 to 695 K in vacuum and then cooled till room temperature, n-type changes and is substituted with p-type conductivity. We suppose that this can be explained by the deviations of samples' compositions from stoichiometry. As it is seen, $\text{Cu}_2\text{LnBi}_3\text{S}_7$ type compounds are formed as a

result of interaction of copper, rare earth elements, bismuth, sulphur. Main physical and chemical and crystallochemical properties of these compounds have an intermediate position between CuBiS_2 and LnBiS_3 compounds. The reason is that nuf-fieldite mineral keeps the structural motives in crystal structures of these compounds. All of the phases formed in $\text{CuSbS}_2 - \text{LnSbS}_3$ and $\text{CuBiS}_2 - \text{LnBiS}_3$ systems are characterized with the mixed coordination (tetrahedral and octahedral) of atoms. Different type of filling order of tetrahedral and octahedral spaces in the structure causes $\text{Cu}_2\text{LnSb}_3\text{S}_7$ and $\text{Cu}_2\text{LnBi}_3\text{S}_7$ type compounds to show different physical properties. We may suppose that variation of physical properties in $\text{CuSbS}_2 - \text{LnSbS}_3$ and $\text{CuBiS}_2 - \text{LnBiS}_3$ systems is related to the rise of covalent bond in tetrahedrons. As it was noted covalent part of chemical bond in antimony (bismuth) octahedrons exceeds ion part, but in lanthanide part ion degree of the bond exceeds covalent part. In some cases there are some distinctions in physical properties of different crystals of phase grown in similar ampoule. We think that this is due to deviations in regulation of layers of sulphur atoms in growth process of the crystal. Different needle-shaped crystals show various properties and their elementary lattice constants do not change and in all cases they are homogeneous. Different physical properties of crystals with similar parameters can be explained by regulation degree of layer of

sulphur atoms. This case is also observed in ZnIn_2S_4 crystal which is formed in $\text{ZnS-In}_2\text{S}_3$ system [7]. In other cases difference in physical properties may be related to various sizes of crystal lattice, in other words different mixed regulation. As it was noted in all cases lattice constants of crystals remain steady. To clarify this object we must conduct detailed structural analysis and wide physical researches. But it is known that dependence of physical and chemical and physical properties of the compounds on the structure is doubtless.

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NAFİLDİT MİNERALININ NADİR TORPAQ ELEMENTLƏRİ İLƏ SİNTETİK ANALOQLARININ ALINMASI VƏ TƏDQİQİ

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$\text{Cu}_2\text{LnSb}_3\text{S}_7$ və $\text{Cu}_2\text{LnBi}_3\text{S}_7$ tipli birləşmələr birbaşa ampul metodu ilə sintez olunmuş və istiqamətlənmiş kristallaşma metodu ilə onların monokristalları yetişdirilmişdir. Müəyyən edilmişdir ki, göstərilmiş birləşmələr izostruktur olub ortorombik sinqoniyada ($\text{Cu}_2\text{LnSb}_3\text{S}_7$ – $a = 14.26 \div 14.43$, $b = 21.20 \div 21.42$, $c = 3.80 \div 3.90 \text{ Å}$; $\text{Cu}_2\text{LnBi}_3\text{S}_7$ – $a = 14.50 \div 14.72$, $b = 21.56 \div 21.86$, $c = 3.96 \div 4.14 \text{ Å}$; $Z = 4$) kristallaşırlar və p-tip keçiriciliyə malik yarımkeçiricidirlər. Onların qadağan olunmuş zolaq eni $\Delta E = 0.53 \div 0.90 \text{ eV}$ intervalında dəyişir.

Açar sözlər: birləşmə, sintez, nafildit, yarımkeçirici

СИНТЕЗ И ИССЛЕДОВАНИЕ СИНТЕТИЧЕСКИХ АНАЛОГОВ МИНЕРАЛА НАФИЛДИТА С УЧАСТИЕМ РЕДКОЗЕМЕЛЬНЫХ ЭЛЕМЕНТОВ

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Прямой ампульным методом синтезированы и методом направленной кристаллизации выращены монокристаллы соединений типа $\text{Cu}_2\text{LnSb}_3\text{S}_7$ и $\text{Cu}_2\text{LnBi}_3\text{S}_7$. Установлено, что указанные соединения изоструктурны и кристаллизуются в орторомбической сингонии ($\text{Cu}_2\text{LnSb}_3\text{S}_7$ – $a = 14.26 \div 14.43$, $b = 21.20 \div 21.42$, $c = 3.80 \div 3.90 \text{ Å}$; $\text{Cu}_2\text{LnBi}_3\text{S}_7$ – $a = 14.50 \div 14.72$, $b = 21.56 \div 21.86$, $c = 3.96 \div 4.14 \text{ Å}$; $Z = 4$) и являются полупроводниками с р-типом проводимости. Их ширина запрещенной зоны изменяется в интервале $\Delta E = 0.53 \div 0.90 \text{ эВ}$.

Ключевые слова: соединение, синтез, нафилдит, полупроводник