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SYNTHESIS AND X-RAY DIFFRACTION STUDY OF $Pb_4Yb_2S_7$ COMPOUND

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Abstract: *Crystallographic characteristics of ternary lanthanide sulfide compounds of lead were collected and their crystallochemical analysis was performed. New compounds were synthesized in PbS- Yb_2S_3 (2:1, 3:1, 4:1) systems. In the ratio PbS-Yb_2S_3 (4:1) there was detected the formation of a new compound $Pb_4Yb_2S_7$. X-ray diffraction studies revealed that this compound was crystallized in the orthorhombic structure and had crystallographic characteristics as follows: a = 13.630Å, b = 23.481Å, c= 4.025Å, $V_{u.c}$ = 1288.18Å^3, Z = 4. A new possible structural motive was proposed for the $Pb_4Yb_2S_7$ compound.*
Keywords: *X-ray phase analysis, lanthanides, polyhedron, structural motif.*
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Introduction

Owing to the variety of unique properties, ternary and complex chalcogenides containing lanthanides have been the main object of intensive research in terms of both synthesis and study into physicochemical characteristics, including structural studies and crystal-chemical analysis.

Crystallochemical analysis of the structures of ternary sulfide compounds of lanthanides shows that the coordination numbers of lanthanides are mainly changing from 6 to 9 (6- trigonal prism, 7- one-cap, 8- two-cap, 9- three-cap trigonal prism) and coordination number of Pb changes from 6 to 8 (6- octahedron, 7- one-cap, 8- two-cap trigonal prism). When the basic conditions of the formation are the same, new structural motifs are formed, and the larger the coordination numbers of the chemical element create a chance to form new compounds. In this regard, the investigation of structural properties of existing compounds in the Pb-Ln-S system, the development of new possible structural motifs, and their synthesis are very important in crystal chemistry. There are very few scientific studies into crystal structure of ternary sulfides of Pb lanthanides. Crystallographic characteristics of compounds of the considered class were collected, and all these data were entered in table by adding some crystal-chemical properties (V_S- volume on sulfur. $V_{u.c}$ - the volume of the unit cell) (Table1).

As a result of the crystal-chemical analysis of ternary sulfides of the lead lanthanides, it was found that there are only two types of compounds with the chemical formula Ln_2PbS_4. Thus, these compounds were crystallized in the cubic lattice from La to Dy [1] and in the rhombic lattice from Ho to Lu. These compounds were obtained with a components ratio of 1:1 in the Ln_2S_3 - PbS system. As can be seen from the Table, the Dy element does not form Ln_2PbS_4 type compound but forms two solid solutions ($Dy_{8.46}Pb_{3.36}S_{16}$ and $Dy_{2.333}Pb_{0.5}S_4$). The Ho element froms both Ho_2PbS_4 compound and $Ho_{4.56}Pb_{1.14}S_8$ solid solution. The Eu element does not form any compound. The Lu_2PbS_4 compound was studied by two different authors [2-4] and differs from each other in the accuracy of calculation of unit cell parameters. Cell parameters of Ln_2PbS_4 type compounds of Ho, Er, and Tm are as twice as bigger than Yb and Lu. As can be seen, the study of lanthanoid ternary sulfides of Pb has been poorly studied. The current work deals with synthesis and X-ray diffraction of new compounds with (3:1) and (4:1) ratios of components in the PbS-Yb_2S_3 system.

Table 1. Crystallographic characteristics of ternary sulfides of Pb lanthanides.

Composition	*syngonia*	*Space group*	*Cell parameters*			*Z*	$V_{u.c}$	V_S	*Literature*
			a, Å α^o	*b, Å* β^o	*c, Å* γ^o				
La_2PbS_4	cubic	I43d	8.767	-	-	4	673.83	42.114	1
$CePbS_4$	cubic	I43d	8.705	-	-	4	659.64	41.227	1
Pr_2PbS_4	cubic	I43d	8.675	-	-	4	652.84	40.802	1
Nd_2PbS_4	cubic	I43d	8.632	-	-	4	643.18	40.198	1
Sm_2PbS_4	cubic	I43d	8.572	-	-	4	629.86	39.366	1
Gd_2PbS_4	cubic	I43d	8.522	-	-	4	618.91	38.681	1
Tb_2PbS_4	cubic	I43d	8.405	-	-	4	610.88	38.180	1
$Dy_{8.46}Pb_{3.36}S_{16}$	cubic	I43d	8.445	-	-	1	603.14	37.696	2
$Dy_{2.333}Pb_{0.5}S_4$	cubic	I43d	8.405	-	-	4	594.02	37.126	1
$Ho_{4.56}Pb_{1.14}S_8$	cubic	I43d	8.366	-	-	2	585.54	36.596	3
Ho_2PbS_4	orthorombic	Cmc2	7.908	28.622	12.022	16	2721.15	42.517	3
Er_2PbS_4	orthorombic	Cmc2	7.863	28.525	11.995	16	2690.38	42.037	3
Tm_2PbS_4	orthorombic	Cmc2	7.842	28.418	11.966	16	2666.56	41.665	2
Lu_2PbS_4	orthorombic	Pnma	11.919	3.889	14.103	4	653.72	40.857	2
Yb_2PbS_4	orthorombic	Pnma	11.899	3.902	14.127	4	655.83	40.989	1,4
Lu_2PbS_4	orthorombic	Pnma	11.926	3.893	14.123	4	655.77	40.985	3,4

Experimental part

In the study of the PbS-Yb_2S_3 system, $Pb_3Yb_2S_6$ (3:1 ratio of components) was synthesized by using elements, and $Pb_4Yb_2S_7$ (4:1 ratio of components) was synthesized by using binary sulfides.

Synthesis of $Pb_3Yb_2S_6$ was carried out in a single-zone furnace in an evacuated quartz ampoule using high purity (99.99%) elements. After keeping for 4 hours at 940 °C the sample was additionally subjected to heat treatment at 450 ° C for 144 hours to ensure homogeneity.

The synthesis of the sample containing $Pb_4Yb_2S_7$ was carried out in a single-zone furnace in an evacuated quartz ampoule with simultaneous melting of binary sulfides. After keeping for 4 hours at 950 ° C, the sample was further subjected to heat treatment at 450 ° C for 172 hours to obtain a homogenous sample.

The resulting alloys were studied by means of differential thermal analysis and X-ray diffraction analysis. DTA measurements were performed with the help of NETZSCH 404 F1 Pegasus device at 10 °C/min rate, and X-ray diffraction analysis was carried out with D2Phaser diffractometer (CuK_α-emission, in the range of $5^0 \leq 2\theta \geq 75^0$ degrees).

The diffractogram of the sample containing $Pb_3Yb_2S_6$ and synthesized from the elements are shown in Fig. 1.

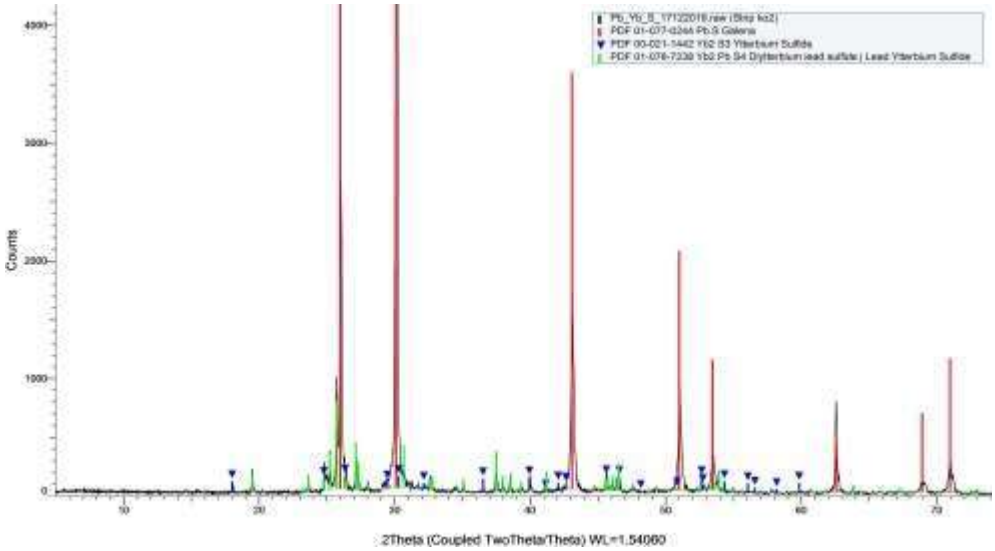

Fig. 1. Diffraction pattern of the Pb-Yb-S system

X-ray diffraction analysis showed that the sample contains several phases - PbS, Yb_2S_3, and $PbYb_2S_4$. The calculated distances between the planes in line with results of the analysis and interpretation of the X-ray diffraction pattern of the sample containing $Pb_4Yb_2S_7$ (Fig. 2) are indexed as a single value (Table 2). As a result of X-ray diffraction studies, it was found that the compound $Pb_4Yb_2S_7$ was crystallized in a rhombic cell and had the following crystallographic characteristics. a = 13.630Å, b = 23.481Å, c = 4.025Å, $V_{u.c}$ = 1288.18Å^3, Z = 4. Also the volume of the anion was calculated, one of the parameters of the internal control [5]. Thus, the volume of sulfur in this compound obtained V_S= 46.006 Å^3.

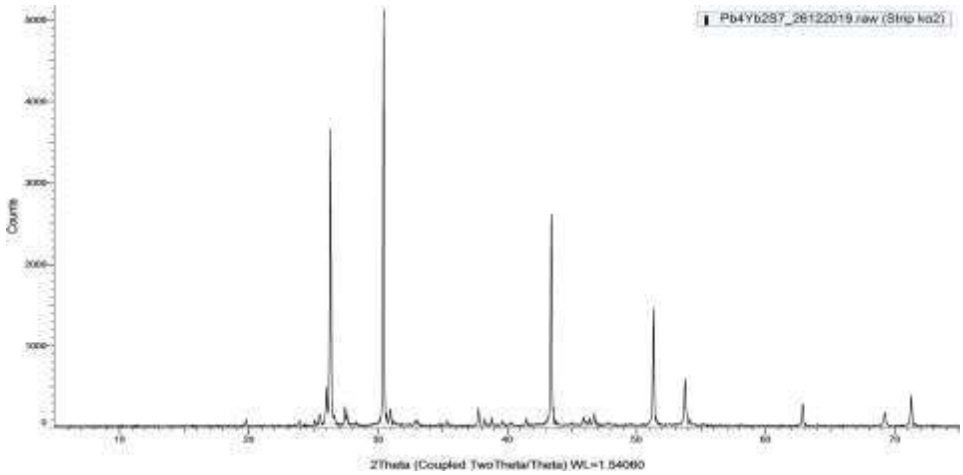

Fig. 2. Diffraction pattern of the $Pb_4Yb_2S_7$ compound

Crystallographic characteristics of the $Pb_4Yb_2S_7$ compound were compared with unit cell parameters of already known sulfide compounds of Pb, Sb, and Bi. As a result of the comparison, it found that the parameters of $Pb_4Yb_2S_7$ went well with the parameters of the mineral $Pb_4Yb_2S_7$ (gungarrite) [5].

Table 2. X-ray diffraction pattern of the $Pb_4Yb_2S_7$ compound

№	*2θ*	d_{exp}	I/I_0	*hkl*
1	19.777	4.4855	2	310
2	24.018	3.7023	1	121
3	25.063	3.5502	1	031
4	25.504	3.4897	3	201
5	26.033	3.4201	7	400
6	26.320	3.3834	71	260
7	27.486	3.2425	3	141
8	30.431	2.9350	100	080
9	30.952	2.8868	4	180
10	32.934	2.7184	1	370
11	35.347	2.5371	1	171
12	37.784	2.3790	4	081
13	38.222	2.3522	1	0.10.0
14	39.557	2.2714	1	600
15	41.508	2.1733	2	461
16	43.407	2.0830	52	490
17	45.004	2.0126	1	002
18	45.912	1.9750	2	660
19	46.397	1.9565	1	710
20	46.733	1.9422	2	631
21	47.890	1.8990	1	590
22	51.317	1.7789	28	162
23	53.774	1.7033	11	4.12.0
24	54.110	1.6935	1	820
25	62.868	1.4770	5	940
26	69.219	1.3562	3	10.0.0
27	71.268	1.3222	7	990

Thus, Craig I.R. in the analysis of minerals containing Ag-Pb-Bi-S [6], discovered a mineral containing $Pb_4Bi_2S_7$, and called it gungarrit. However, the crystallographic characteristics of this mineral have not been determined. In works devoted to the study and

crystallochemical analysis of $Pb_nBi_2S_{3+n}$ compounds [7,8], the synthesis of $Pb_4Bi_2S_7$ (n = 4) was carried out, the crystallographic characteristics were calculated, and a structural motif consisting of 12 semi-octahedra consisting of $Pb_8Bi_4S_{14}$ was proposed.

With regard to the above, it is possible to say that the new connection $Pb_4Bi_2S_7$ will have the following possible structure when replacing Bi in the tape $Pb_8Bi_4S_{14}$ on Yb (Fig. 3).

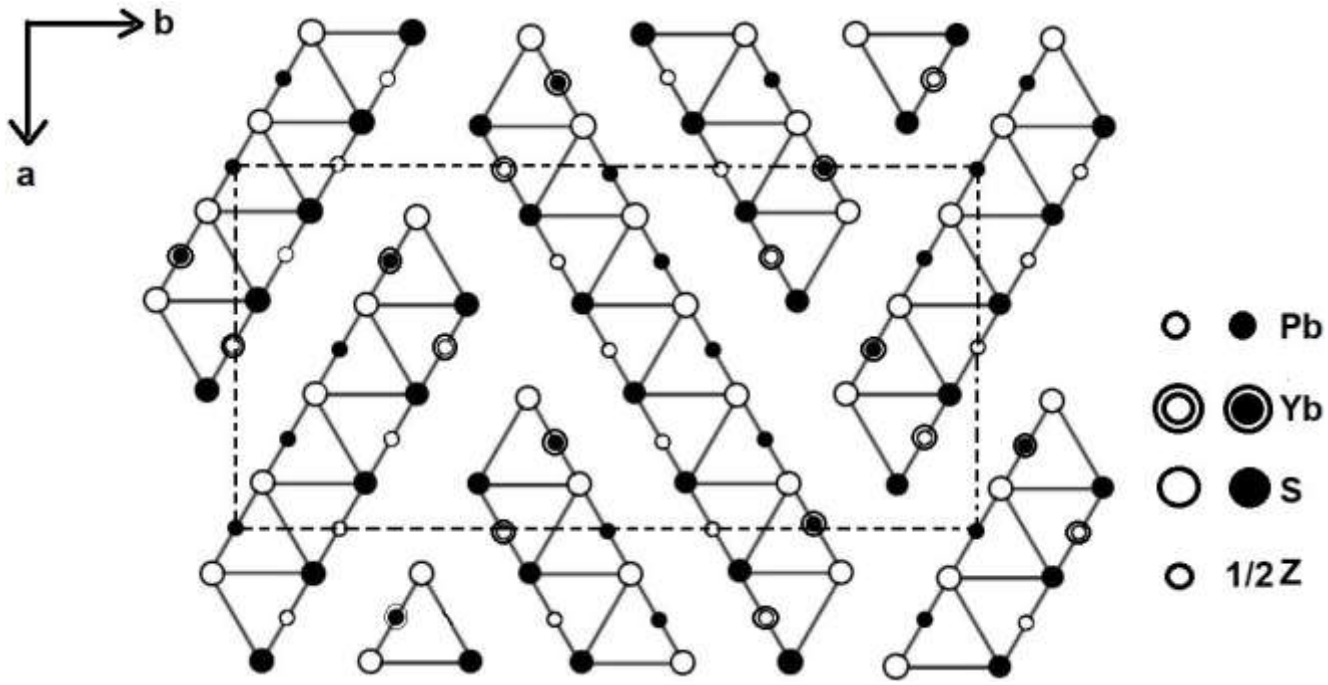

Fig. 3. Possible structural motive for Proposed $Pb_4Yb_2S_7$ compound

References

1. Patrie M., Guittard M., Pardo M.P. Systèmes L2X3-PbX (L = lanthanides, X = S, Se, Te). *Bull. Soc. Chem. Fr*. 1969, pp. 3832–3837.
2. Gulay.L.D., Shemet V.Ya R_2S_3-PbS systems. *J.Alloys Compounds*. 2007, p. 431.
3. Gulay L.D., Daszkieüicz M., Shemet V.Ya. Crystal architecture of RE_2PbS_4. *Z.Anorg. Allg Chem 2008, vol.* 634, pp. 1887-1895.
4. Gulay L.D., Daszkieüicz M., Shemet V.Ya., Pietraszko A. Crystal structure of the R_2PbS_4 (R=Yb and Lu) compounds. *J.Alloys Compounds*., 2008, vol. 453, pp. 143-146.
5. Gasymov V.A., Huseynov G.G. About ehpress control of intrastructural parameters. *II Rep. conf "Physicochemical analysis and inorganic. Materials Science"*, col. art. Baku, 1996, pp. 85-86.
6. Craig J.R. Phase relation and mineral assemblages in the Ag-Bi-Pb-S system. *Mineral Deposita*. 1967, vol. 1, pp. 278-326.
7. Gasymov V.A., Mamedov Kh.S. Crystal chemical characteristics of compounds with the general formula $Pb_nBi_2S_{3+n}$. *Azerbaijan Chemical Journal*. 1978, no. 5, pp. 115-119.
8. Gasymov V.A., Mamedov Kh.S. About the expected structure of the gungarrite $Pb_4Bi_2S_7$. V conf. in chemistry, physics and technical. approx. chalcogenides, *Abstracts of reports*, Baku, 1979, p. 49.

$Pb_4Yb_2S_7$ BİRLƏŞMƏSİNİN SİNTEZİ VƏ RENTGENOQRAFİK TƏDQİQİ

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Qurğuşunun lantanoidli üçlü sulfidli birləşmələrin kristalloqrafik xarakteristikaları toplanmış və kristallokimyəvi analizi aparılmışdır. PbS-Yb_2S_3 (2:1, 3:1, 4:1) sistemlərində yeni birləşmələr sintez olunmuşdur. PbS-Yb_2S_3 (4:1) nisbətində - yeni $Pb_4Yb_2S_7$ birləşməsinin əmələ gəlməsi aşkar olunmuş və rentgenoqrafik tədqiqatlar nəticəsində bu birləşmənin ortorombik qəfəsdə kristallaşdığı və aşağıdakı kristalloqrafik xarakteristikalara malik olduğu müəyyənləşdirilmişdir: a= 13.630Å, b= 23.481Å, c= 4.025Å, $V_{e.q}$= 1288.18Å^3, Z= 4. $Pb_4Yb_2S_7$ birləşməsi üçün yeni mümkün quruluş motivi təklif olunmuşdur.

Açar sözlər: rentgen faza analizi, lantanoidlər, poliedr, quruluş motivi.

СИНТЕЗ И РЕНТГЕНОГРАФИЧЕСКОЕ ИССЛЕДОВАНИЕ СОЕДИНЕНИЯ $Pb_4Yb_2S_7$

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Кристаллографические характеристики лантаноидных тройных сульфидных соединений свинца были собраны и проведен кристаллохимический анализ. Новые соединения были синтезированы в системах PbS- Yb_2S_3 (2:1, 3:1, 4:1). В соотношении PbS- Yb_2S_3 (4:1) - было обнаружено образование нового соединения $Pb_4Yb_2S_7$, и рентгенографические исследования показали, что это соединение кристаллизуется в ромбической решетке и имеет следующие кристаллографические характеристики: a = 13,630Å, b = 23,481Å, c= 4.025Å, $V_{э.я}$ = 1288,18Å^3, Z = 4. Для соединения $Pb_4Yb_2S_7$ был предложен новый возможный структурный мотив.

Ключевые слова: рентгенофазовый анализ, лантаноиды, полиэдр, структурный мотив