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PHYSICAL METHODS OF INVESTIGATION

Crystal Structure of $EuLaCuS_3$

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Abstract—The crystal structure of the $EuLaCuS_3$complex sulfide synthesized for the first time has been solved by X-ray powder diffraction. Crystals are orthorhombic, space group *Pnma*, Ba_2MnS_3-type structure, $a = 8.1297(3)$ Å, $b = 4.0625(1)$ Å, $c = 15.9810(4)$ Å, $V = 527.80(3)$ Å^3, $Z = 4$, and $\rho_{calc} = 5.669$ g/cm^3. The La and Eu atoms are randomly disordered over two crystallographic positions with a coordination number of 7, and the Eu(La)–S bond lengths range from 2.892(6) to 3.078(6) Å. The CuS_4 tetrahedra with Cu–S interatomic distances of 2.358(5)–2.40(1) Å form chains running along the *b* axis.

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Some powder X-ray diffraction data on the crystal-chemical characteristics of the $SrLaCuS_3$ complex sulfide are available from [1]: orthorhombic crystal system, space group *Pnma*, $a = 11.157(2)$ Å, $b = 4.1003(6)$ Å, and $c = 11.545(2)$ Å. In a single-crystal X-ray diffraction experiment, the crystal structure of $PbLaCuS_3$ was solved by Brennan and Ibers [2]. Crystals are orthorhombic, space group *Pnma*, $a = 8.091(3)$ Å, $b = 4.093(1)$ Å, and $c = 15.996(5)$ Å. The ratio of the ionic radii of seven-coordinated ions ($r\mathrm{Sr}^{2+}$: $r\mathrm{Pb}^{2+}$: $r\mathrm{Eu}^{2+}$ = 1.21 : 1.23 : 1.2 Å [3]) allows us to predict the formation of $EuLaCuS_3$. No information on the $EuLaCuS_3$ crystal structure has been found. The presence of *d*- and *f* elements in the crystal lattice gives rise to practically valuable properties. Brennan and Ibers [2] noted that $PbLaCuS_3$ is a diamagnetic and a semiconductor with a bandgap energy of 1.5 eV. In $EuLnCuS_3$ compounds (Ln = Eu–Lu) [4] containing nonmagnetic Ln ions, the ferromagnetic alignment of Eu^{2+} momentums occurs at 3.4–4.4 K. The ferromagnetic transition in $EuLnCuS_3$ compounds containing magnetic Ln ions occurs at 5.0 K. The present paper presents the solution of crystal structure $EuLaCuS_3$ based on powder X-ray diffraction data.

EXPERIMENTAL

Cu_2S was synthesized from elementary copper (11-4 high purity grade) and sulfur (15-3 high purity grade) in sealed evacuated double-walled quartz ampoules. EuS and La_2S_3 were synthesized from oxides of EvO-Zh and LaO-D grades in a H_2S and CS_2 flow at 1300 K [5]. According to X-ray powder diffraction, the simple sulfides were single phases. Within the error of chemical analysis, the sulfides had the stoichiometric compositions. $EuLaCuS_3$ samples were prepared by alloying the initial sulfides mixed in the ratio 2EuS : $1La_2S_3$: Cu_2S in a graphite crucible placed into a sealed evacuated double-walled quartz ampoule. The ampoule was heated in an electrical furnace up to 1570 K and allowed to stay for 30 min. Cooling was conducted in the switch-off furnace. The samples were annealed in sealed evacuated quartz ampoules at 970 K for 3000 h.

The identity of the synthesized compound was confirmed by microstructural analysis (a METAM PB microscope) and X-ray powder diffraction (PANalytical X'Pert PRO diffractometer equipped with a PIXcel detector, CoK_α radiation, graphite monochromator, 298 K). A powdery sample was prepared by pounding with addition of octane in an agate mortar. The X-ray diffraction pattern was taken within the diffraction angle range of $10° \le 2\theta \le 125°$. The $EuLaCuS_3$ unit cell parameters were determined with the ITO software [6]. In addition to the main phase, La_3S_4, EuS, and $CuLaS_2$ impurities were found in the sample. The crystal structure was refined by the derivative difference minimization (DDM) method [7] using X-ray powder diffraction data with consideration for the effects of preferred orientation, the anisotropic broadening of peaks, and the surface roughness (*R*-DDM = 8.67%, R_{Bragg} = 4.39%). The data for isostructural $PbLaCuS_3$ [2] was used as the initial model. The experimental, calculated, and difference X-ray diffraction patterns of the studied sample are compared in Fig. 1. Atomic coordinates and isotropic thermal parameters are listed in Table 1. The shortest selected cation–anion distances (Table 2) were calculated on the basis of the structural data. The selected bond angles are given in Table 3. The crystal structures were visualized with the use of the Diamond 3 software [8].

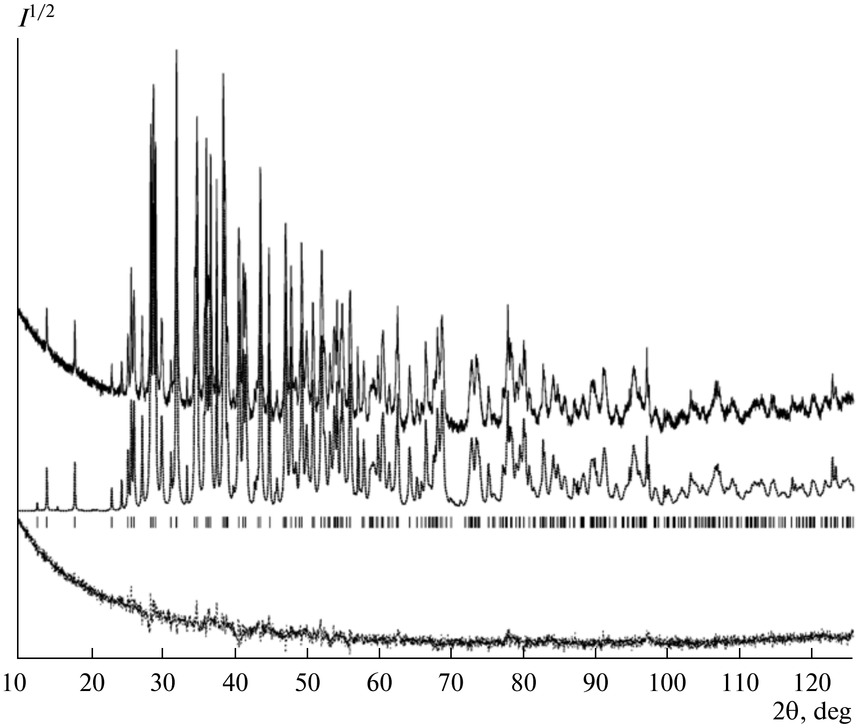

Fig. 1. Experimental (solid line), calculated (dashed line), and difference (points) X-ray diffraction patterns of an $EuLaCuS_3$ sample after the refinement of its structure by the DDM method (R-DDM = 8.67%). The peak positions for the major phase are indicated with strokes.

RESULTS AND DISCUSSION

The X-ray diffraction pattern of the studied compound was indexed in terms of orthorhombic crystal system, space group *Pnma*, a = 8.1297(3) Å, b = 4.0625(1) Å, c = 15.9810(4) Å, V = 527.80(3) Å^3, Z = 4, and ρ_{calc} = 5.669 g/cm^3. The crystal has a layered-block structure (Fig. 2). The copper ion is coordinated by four sulfur ions with the formation of a distorted tetrahedron. A CuS_4 tetrahedron is formed of the 2 × S(1) + S(2) + S(3) atoms, and the average Cu—S distance is 2.369 Å (Table 2).

In the $EuLaCuS_3$ structure, CuS_4 tetrahedra share the S(1) vertices to form continuous chains running in the direction [010]. The chains are spaced by rare-

Table 1. Atomic coordinates and thermal parameters and site occupancy factors in the $EuLaCuS_3$

Atom	x	y	z	Occupancy	U_{iso}, Å^2
Eu(1)	0.2536(3)	0.25	0.0383(1)	0.55(5)	0.012(1)
Eu(2)	0.0908(3)	0.25	0.7851(1)	0.45(5)	0.013(1)
La(1)	0.2536(3)	0.25	0.0383(1)	0.45(5)	0.012(1)
La(2)	0.0908(3)	0.25	0.7851(1)	0.55(5)	0.013(1)
Cu	0.1180(6)	0.25	0.3661(3)	1	0.025(2)
S(1)	0.014(1)	0.25	0.6002(5)	1	0.017(3)
S(2)	0.181(1)	0.25	0.2194(6)	1	0.011(2)
S(3)	0.381(1)	0.25	0.4291(5)	1	0.012(2)

Table 2. Interatomic distances (*d*) in the $EuLaCuS_3$ structure

Bond	*d*, Å	Bond	*d*, Å	Bond	*d*, Å
Eu(1)–S(1)	2 × 2.948(7)	Eu(2)–S(1)	3.022(9)	Cu–S(1)	2 × 2.358(5)
Eu(1)–S(1)	3.059(9)	Eu(2)–S(2)	2×2.942(6)	Cu–S(2)	2.400(9)
Eu(1)–S(2)	2.954(9)	Eu(2)–S(2)	2×3.005(6)	Cu–S(3)	2.361(9)
Eu(1)–S(3)	2 × 2.892(6)	Eu(2)–S(3)	2×3.078(6)	**<Cu–S>**	**2.369**
Eu(1)–S(3)	3.076(9)	**<Eu(2)–S>**	**3.010**		
<Eu(1)–S>	**2.967**				

Average values are boldfaced.

Table 3. Selected bond angles (ω) in the $EuLaCuS_3$ structure

Angle	ω, deg	Angle	ω, deg	Angle	ω, deg
S(1)Eu(1)S(1)	87.2(2)	S(1)Eu(2)S(3)	138.3(2)	S(1)CuS(1)	118.8(3)
S(1)Eu(1)S(1)	78.4(2)	S(2)Eu(2)S(1)	77.4(2)	S(1)CuS(3)	108.3(3)
S(1)Eu(1)S(2)	78.4(2)	S(2)Eu(2)S(1)	79.9(2)	S(1)CuS(2)	108.7(3)
S(1)Eu(1)S(3)	143.5(2)	S(2)Eu(2)S(2)	157.2(2)	S(3)CuS(2)	102.9(3)
S(1)Eu(1)S(3)	125.1(2)	S(2)Eu(2)S(2)	87.2(2)		
S(2)Eu(1)S(1)	147.8(2)	S(2)Eu(2)S(2)	89.3(2)		
S(2)Eu(1)S(3)	68.7(2)	S(2)Eu(2)S(2)	85.2(2)		
S(3)Eu(1)S(1)	87.8(2)	S(2)Eu(2)S(3)	76.4(2)		
S(3)Eu(1)S(1)	158.4(2)	S(2)Eu(2)S(3)	121.3(2)		
S(3)Eu(1)S(1)	80.0(2)	S(2)Eu(2)S(3)	132.4(2)		
S(3)Eu(1)S(2)	121.0(2)	S(2)Eu(2)S(3)	68.1(2)		
S(3)Eu(1)S(3)	89.2(2)	S(3)Eu(2)S(3)	82.6(2)		
S(3)Eu(1)S(3)	74.3(2)	S(1)Eu(2)S(3)	138.3(2)		

earth metal atoms that coordinate sulfur atoms. A characteristic feature of the $EuLaCuS_3$ structure is that Eu and La atoms are disordered over two positions in a manner similar to that in isostructural $PbLaCuS_3$ [2] and $SrLaCuSe_3$ [9].

Both rare-earth ions in the structure $EuLaCuS_3$ coordinate seven sulfur ions to form two coordination polyhedra (monocapped trigonal prisms $Eu(1)S_7$ and $Eu(2)S_7$) with coordination numbers of 6 + 1 (Fig. 3). The $Eu(1)S_7$ prism is formed of the 2S(1) + S(1) + S(2) + 2S(3) atoms with an average Eu(1)–S distance of 2.967 Å. The theoretical value calculated from the ionic radii of La^{3+} and Eu^{2+} (for CN = 7) with consideration for the site occupancy (Eu : La = 0.55 : 0.45) is 2.995 Å [3]. The $Eu(2)S_7$ prism is formed of the S(1) + 2S(2) + 2S(3) atoms with an average Eu(2)–S distance of 3.010 Å (theoretical value with consideration of site occupancies is 2.985 Å).

The $Eu(1)S_7$ prisms are linked to one another by common 2 × S(1) and 2 × S(3) edges along the *a* axis and with common S(3)S(1) edges along the *b* axis to form two-dimensional networks in the *ab* plane. The

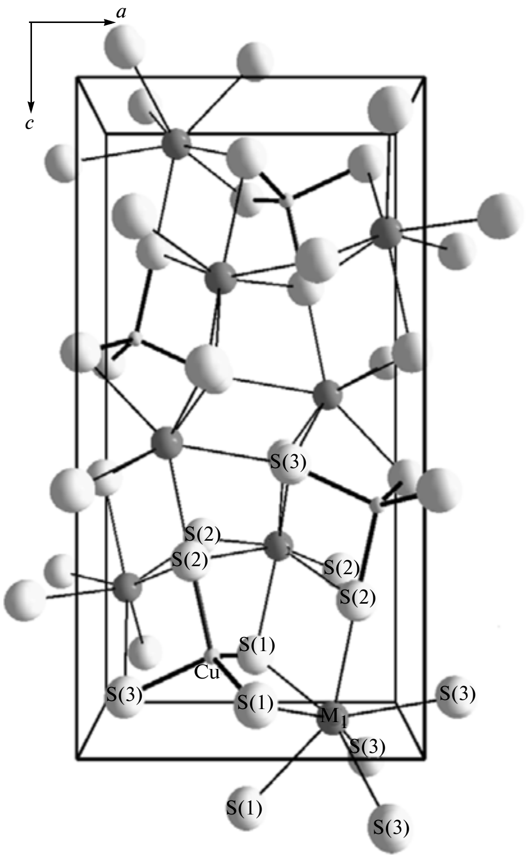

Fig. 2. Geometrical projection [010] of the $EuLaCuS_3$ structure. The Cu, Eu(La), and S atoms are denoted by small-, medium-, and large-diameter circles, respectively. M_1 is Eu(1)La(1) and M_2 is La(2)Eu(2). The Cu–S interatomic distances are denoted by semi-bold lines.

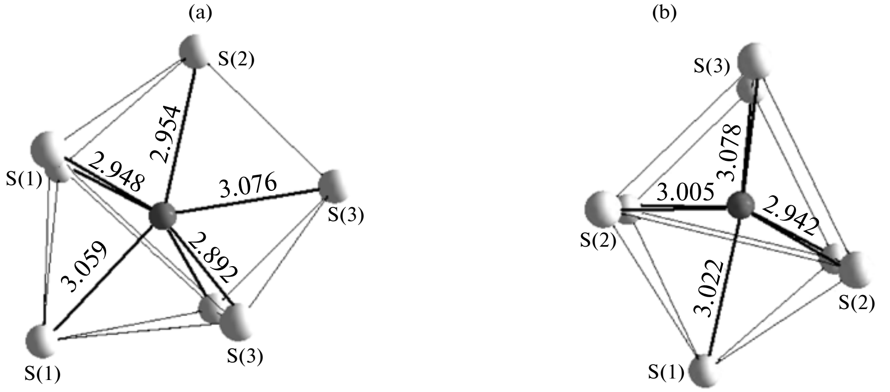

Fig. 3. Coordination geometry of (a) Eu(1)La(1) atoms and (b) La(2)Eu(2) atoms in $EuLaCuS_3$. The interatomic distances in single-cup trigonal prisms are given in Å.

$Eu(2)S_7$ prisms are linked by 2 × S(2) edges along the *a* axis and by S(2)S(2)S(3) faces along the *b* axis, and also form two-dimensional networks in the *ab* plane. The $Eu(1)S_7$ and $Eu(2)S_7$ prisms are linked by the S(2)S(1) and S(2)S(3) edges along the *c* axis to form a three-dimensional structure with channels accommodating copper ions. As noted in [2], an analogous arrangement is typical of α-La_2S_3 and some other compounds with a similar composition. Thus, the $EuLaCuS_3$ structure may be considered as a result of the replacement of some La atoms in α-La_2S_3 for Eu atoms and the incorporation of Cu atoms into approximately tetrahedral positions between the LaS_7 prisms, this providing an explanation, in particular, for the distorted structure of CuS_4 tetrahedra and the random distribution of Eu^{2+} and La^{3+} ions, which have close sizes, over two crystallographic positions.

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