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COORDINATION COMPOUNDS

Crystal Structure of $EuCeCuS_3$

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Abstract—The crystal structure of $EuCeCuS_3$, a complex sulfide synthesized for the first time, has been solved using X-ray powder diffraction data. Crystals are rhombic, space group *Pnma*, Ba_2MnS_3 structural type, $a = 8.1023(1)$ Å, $b = 4.0386(1)$ Å, $c = 15.9022(2)$ Å, $V = 520.36(1)$ Å^3, $Z = 4$, $\rho_{calcd} = 5.767$ g/cm^3. The Eu,CeS_7 polyhedron incorporates the Eu and Ce atoms, which are randomly disordered over two crystallographic sites. The bond lengths $d_{Eu,Ce-S}$ range from 2.885 to 3.044 Å.

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The crystal structures of $ACeCuS_3$ (A = Sr, Ba) were solved using X-ray powder diffraction data [1–3]. $BaCeCuS_3$ is isostructural to Eu_2CuS_3 [1, 2]. $SrCeCuS_3$ has two polymorphs of rhombic symmetry (space group *Pnma*): α-$SrCeCuS_3$ of $BaLaCuS_3$ structural type (at 970 K) with unit cell parameters $a = 11.1626(2)$ Å, $b = 4.0970(2)$ Å, and $c = 11.5307(1)$ Å and β-$SrCeCuS_3$ of Ba_2MnS_3 structural type (at 1170 K) with $a = 8.1393(3)$ Å, $b = 4.0587(2)$ Å, and $c = 15.9661(2)$ Å. The Sr and Ce atoms in α- and β-$SrCeCuS_3$ are observed to be disordered over two crystallographic sites. The site occupancy is 0.84:0.16 (α-) and 0.58:0.42 (β-), respectively [3]. The ratio between the radii of seven-coordinated ions $r_{Ba^{2+}} : r_{Sr^{2+}} : r_{Eu^{2+}} = 1.38 : 1.21 : 1.2$ [4] allows us to predict the formation of $EuCeCuS_3$. Close values of $r_{Sr^{2+}}$ and $r_{Eu^{2+}}$ enable $EuCeCuS_3$ to crystallize in one of the Ba_2MnS_3/$BaLaCuS_3$ structural types, and there is also some probability for the existence of polymorphs. No crystallographic data were found for $EuCeCuS_3$ in the literature.

Here, we report some results of solving the crystal structure of $EuCeCuS_3$ with the use of X-ray powder diffraction data.

EXPERIMENTAL

Cu_2S was synthesized from elementary copper (11-4 high purity grade) and sulfur (15-3 high purity grade) in ampoules. Ce_2S_3 and EuS were synthesized from oxides of TseO-L and EvO-Zh grade in an H_2S and CS_2 flow at 1300 K [5]. According to X-ray powder diffraction data, the synthesized sulfides were single phases and had a stoichiometric composition within chemical analysis error. $EuCeCuS_3$ was prepared by alloying a mixture of initial sulfides EuS, Ce_2S_3, and Cu_2S at a ratio 2 : 1 : 1 in a graphite crucible placed into an evacuated and sealed quartz ampoule. The ampoule was heated in an electrical furnace to 1570 K and allowed to stand for 30 min. Cooling was performed in the switch-off furnace. Samples were annealed at 970 K for 4 months and at 1170 K for 2 months [6, 7].

X-ray powder diffraction analysis of $EuCeCuS_3$ was performed on a PANalytical X'Pert PRO diffractometer (CoK_α radiation, graphite monochromator, PIXcel detector) within the angle range of $10° \le 2\theta \le 140°$. Samples were prepared by pounding with addition of octane in an agate mortar. The unit cell parameters were determined with the ITO software [8].

According to the data of X-ray powder diffraction and microstructural analysis (METAM LV-31 microscope), the 2EuS: 1Ce_2S_3: 1Cu_2S sample annealed at 1170 K contained $EuCeCuS_3$ alone. Element distribution spectra were determined on a Philips SEM JEOL JSM-6510 LM scanning electron microscope at five different points on the surface of a sample. The compositions of all the analyzed areas corresponded to $EuCeCuS_3$. X-ray spectral microanalysis results coincided with theoretical values within a measurement accuracy of 0.2 wt %. The crystal structure of $EuCeCuS_3$ (annealing at 1170 K) was refined by the derivative difference minimization (DDM) method in the anisotropic approximation for all atoms with the reliability factors R-DDM = 4.88% and $R_F = 1.61\%$. The data for isostructural $PbLaCuS_3$ were used as an initial structural model [9]. Refinement was performed taking into account the effects of preferred orientation, anisotropic broadening of peaks, and sample surface roughness and displacement. Anion–cation distances and selected bond angles are given in Tables 1 and 2, respectively. The experimental, calculated, and differ-

Table 1. Interatomic distances (*d*) in the structure of β-$EuCeCuS_3$

Bond	*d*, Å	Bond	*d*, Å	Bond	*d*, Å
(Ce1,Eu2)–S1	2 × 2.923(3)	(Eu1,Ce2)–S1	3.014(4)	Cu–S1	2 × 2.354(2)
(Ce1,Eu2)–S1	3.044(4)	(Eu1,Ce2)–S2	2 × 2.925(3)	Cu–S2	2.365(5)
(Ce1,Eu2)–S2	2.969(5)	(Eu1,Ce2)–S2	2 × 2.984(3	Cu–S3	2.356(5)
(Ce1,Eu2)–S3	2 × 2.885(3)	(Eu1,Ce2)–S3	2 × 3.058(4)	⟨Cu–S⟩	2.357(2)
(Ce1,Eu2)–S3	3.052(5)	⟨(Eu1,Ce2–S)⟩	2.992(2)		
⟨(Ce1,Eu2)–S⟩	2.954(2)				

ence X-ray powder diffraction patterns after DDM refinement are shown in comparison in Fig. 1. The crystal structures were visualized using the Diamond 3 software suite [10].

The 2EuS : $1Ce_2S_3$: Cu_2S sample annealed at 970 K contained two $EuCeCuS_3$ polymorphs, namely, 73.8% of Ba_2MnS_3 structural type (a = 8.0991(1) Å, b = 4.03978(4) Å, c = 15.8979(1) Å) and 20.1% of $BaLaCuS_3$ structural type (a = 11.1174(2) Å, b = 4.07142(9) Å, c = 11.4837(2) Å), which were denoted as β- and α-modifications, respectively, alongside with some admixtures, such as 0.6% of EuS, 0.9% of $CuCeS_2$, and 4.6% of Eu_2CuS_3. Since the sample represented a mixed phase and was poorly crystallized, no refinement was performed for the structure of $EuCeCuS_3$ (coordinates, thermal parameters, atomic site occupancies). Longer annealing is required for the synthesis of a homogeneous α-$EuCeCuS_3$ sample.

RESULTS AND DISCUSSION

The X-ray powder diffraction pattern of β-$EuCeCuS_3$ (annealing at 1170 K) was indexed in in terms of orthorhombic crystal system, Ba_2MnS_3 structural type, with unit cell parameters a = 8.1023(1) Å, b = 4.0386(1) Å, c = 15.9022(2) Å; V = 520.36(1) Å^3, Z = 4, and ρ_{calcd} = 5.767 g/cm^3. β-$EuCeCuS_3$ has a layered-block structure (Fig. 2). Continuous chains of distorted CuS_4 tetrahedra sharing apical S1 atoms along direction [010] are spaced by seven-coordinated Sr and Ce atoms, which form one-capped trigonal $(Eu,Ce)S_7$ prisms. The crystallographic sites of europium and cerium are mixed by 35%. Similar disorder-

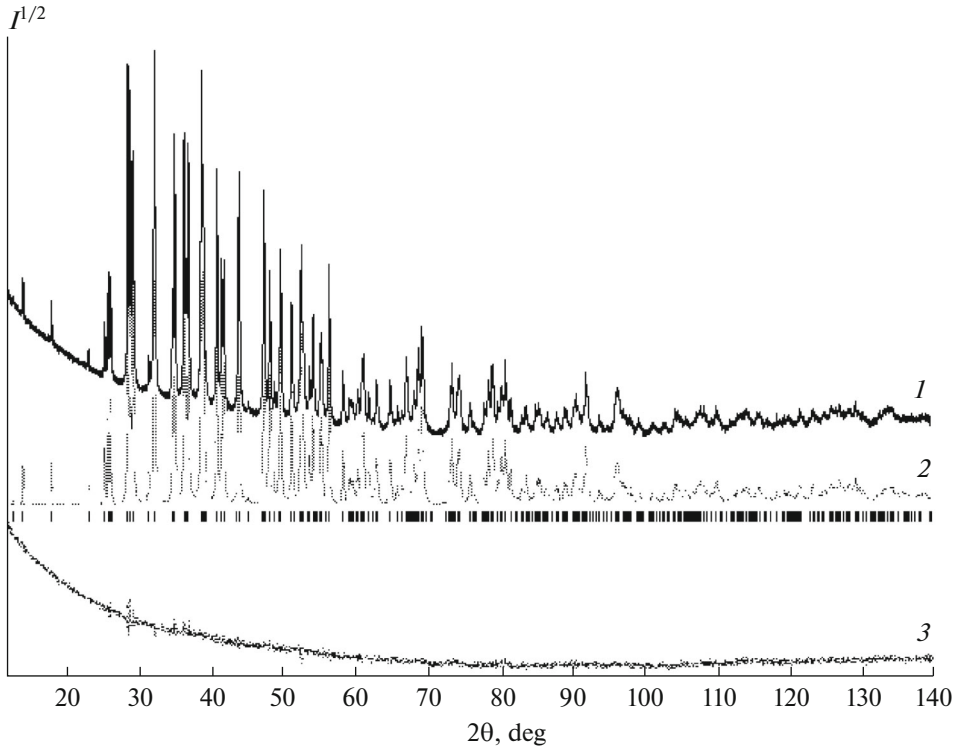

Fig. 1. (*1*) Experimental, (*2*) calculated, and (*3*) difference X-ray powder diffraction patterns of the 2EuS : $1Ce_2S_3$: $1Cu_2S$ sample after DDM refinement of its structure. Main phase peak positions are shown with strokes.

Table 2. Selected bond angles in the structure of β-$EuCeCuS_3$

Angle	ω, deg	Angle	ω, deg	Angle	ω, deg
S1(Ce1,Eu2)S1	87.40(9)	S1(Eu1,Ce2)S3	138.35(10)	S1CuS1	118.12(13)
S1(Ce1,Eu2)S1	78.00(8)	S2(Eu1,Ce2)S1	79.63(9)	S1CuS3	108.64(13)
S1(Ce1,Eu2)S2	78.47(9)	S2(Eu1,Ce2)S1	77.71(9)	S1CuS2	108.96(13)
S1(Ce1,Eu2)S3	125.12(10)	S2(Eu1,Ce2)S2	157.30(10)	S3CuS2	102.36(14)
S1(Ce1,Eu2)S3	143.98(10)	S2(Eu1,Ce2)S2	87.34(10)		
S2(Ce1,Eu2)S1	147.24(10)	S2(Eu1,Ce2)S2	89.3(10)		
S2(Ce1,Eu2)S3	68.78(10)	S2(Eu1,Ce2)S2	85.18(10)		
S3(Ce1,Eu2)S1	80.34(9)	S2(Eu1,Ce2)S3	131.86(10)		
S3(Ce1,Eu2)S1	158.33(10)	S2(Eu1,Ce2)S3	75.84(98)		
S3(Ce1,Eu2)S1	87.84(10)	S2(Eu1,Ce2)S3	121.82(10)		
S3(Ce1,Eu2)S2	121.12(10)	S2(Eu1,Ce2)S3	68.50(10)		
S3(Ce1,Eu2)S3	74.19(10)	S3(Eu1,Ce2)S3	82.65(10)		
S3(Ce1,Eu2)S3	88.83(10)				

ing also appears in isostructural $ALnCuS_3$ crystals (A = Eu, Sr, Pb; Ln = La, Ce, Pr) [3, 5, 9, 11, 12].

A one-capped trigonal $Ce1S_7$ prism is built of 2S1 + S1 + S2 + 2S3 + S3 atoms with an average Ce1–S distance of 2.954 Å (Table 1) at a theoretical value of 2.955 Å calculated from the ionic radii $r_{Ce^{3+}} = 1.07$ and $r_{Eu^{2+}} = 1.20$ Å (CN = 7) [4] with consideration for the site occupancy Ce1 : Eu2 = 0.652 : 0.348. One-capped trigonal $Ce1S_7$ prisms share 2 × S1S1 and 2 × S3S3 edges along axis *a* and 2 × S3S1 edges along axis *b* to form two-dimensional networks in plane *ab*. A one-capped trigonal $Eu1S_7$ prism is built of S1 + 2S2 + 2S2 + 2S3 atoms with an average Eu1–S distance of 2.992 Å (theoretical value, 2.994 Å). $Eu1S_7$ prisms share 2 × S2S2 edges along axis *a* and 2 × S2S2S3 faces along axis *b* to form two-dimensional networks in plane *ab*. One-capped trigonal $Eu1S_7$ and $Ce1S_7$ prims share edges to form a three-dimensional network with channels accommodating Cu^{2+} ions.

The structural characteristics of β-$EuCeCuS_3$ are intermediate between $EuLaCuS_3$ [11] and β-$EuPrCuS_3$ [12]. The unit cell parameters of $EuLnCuS_3$ (Ln = La [11], Ce, Pr [12]) annealed at 1170 K naturally decrease:

$$a = 8.1366\ (EuLaCuS_3\ [11]) \rightarrow 8.1023\ (\beta\text{-}EuCeCuS_3) \rightarrow 8.0786\ (\beta\text{-}EuPrCuS_3\ [12])\ Å;$$

$$b = 4.0586\ (EuLaCuS_3\ [11]) \rightarrow 4.0386\ (\beta\text{-}EuCeCuS_3) \rightarrow 4.0288\ (\beta\text{-}EuPrCuS_3\ [12])\ Å;$$

$$c = 15.9822\ (EuLaCuS_3\ [11]) \rightarrow 15.9022\ (\beta\text{-}EuCeCuS_3) \rightarrow 15.8389\ (\beta\text{-}EuPrCuS_3\ [12])\ Å.$$

The average values of d_{Ln-S} and d_{Cu-S} are also observed to sustain a natural decrease with descending $r_{Ln^{3+}}$ in the series of $EuLnCuS_3$:

$$d_{Ln-S}: 2.975\ (d_{La1-S}\ [11]) \rightarrow 2.954\ (d_{Ce1-S}, \text{Table 1}) \rightarrow 2.719\ (d_{Pr1-S}\ [12])\ Å;$$

$$3.003\ (d_{La2-S}\ [11]) \rightarrow 2.992\ (d_{Ce2-S}, \text{Table 1}) \rightarrow 2.983\ (d_{Pr1-S}\ [12])\ Å;$$

$$d_{Cu-S}: 2.359\ [11] \rightarrow 2.357\ (\text{Table 1}) \rightarrow 2.348\ [12]\ Å.$$

Hence, the established X-ray and structural parameters of β-$EuCeCuS_3$ agree with a natural change in the parameters, bond lengths, and structural types obtained for the series of $EuLnCuS_3$ (Ln = La, Pr, Nd, Sm–Dy, Tm–Lu) correlated with a change in the Ln^{3+} ionic radius in the earlier works [5–7, 11–13].

The crystal structures of $ACeCuS_3$ (A = Sr, Eu) are observed to have some similarity due to close $r_{Sr^{2+}}$ and $r_{Eu^{2+}}$. The various bond lengths $d_{(A,Ce)-S}$ in $ACeCuS_3$ (A = Sr, Eu) produce a difference between their unit cell parameters and volumes and X-ray densities. Small values of the average bond lengths d_{Eu1-S} = 2.992(2) Å and d_{Ce1-S} = 2.954(2) Å ($EuCeCuS_3$) in comparison with d_{Sr1-S} = 3.004(2) Å and d_{Ce1-S} = 2.971(2) Å ($SrCeCuS_3$ [3]) are due to the facts that

(1) The covalent component of the (Eu,Ce)–S bond is less pronounced than for the (Sr,Ce)–S bond. This agrees with the theoretical notions about that rare-earth elements (as transition metals) have an insufficient bond ionicity in comparison with alkali-earth elements [14]; and

(2) $r_{Eu^{2+}} < r_{Sr^{2+}}$. This in turn is caused by the electron structure of Sr ($5s^2$) and Eu ($4f^7 5d^0 6s^2$) and the lanthanide contraction effect.

It is likely that small differences between $r_{A^{2+}}$ and $r_{Ce^{3+}}$ ($\Delta r_{Sr-Ce} = 11.5\%$, $\Delta r_{Eu-Ce} = 10.8\%$) cause the displacement of A^{2+} and Ce^{3+} crystallographic sites.

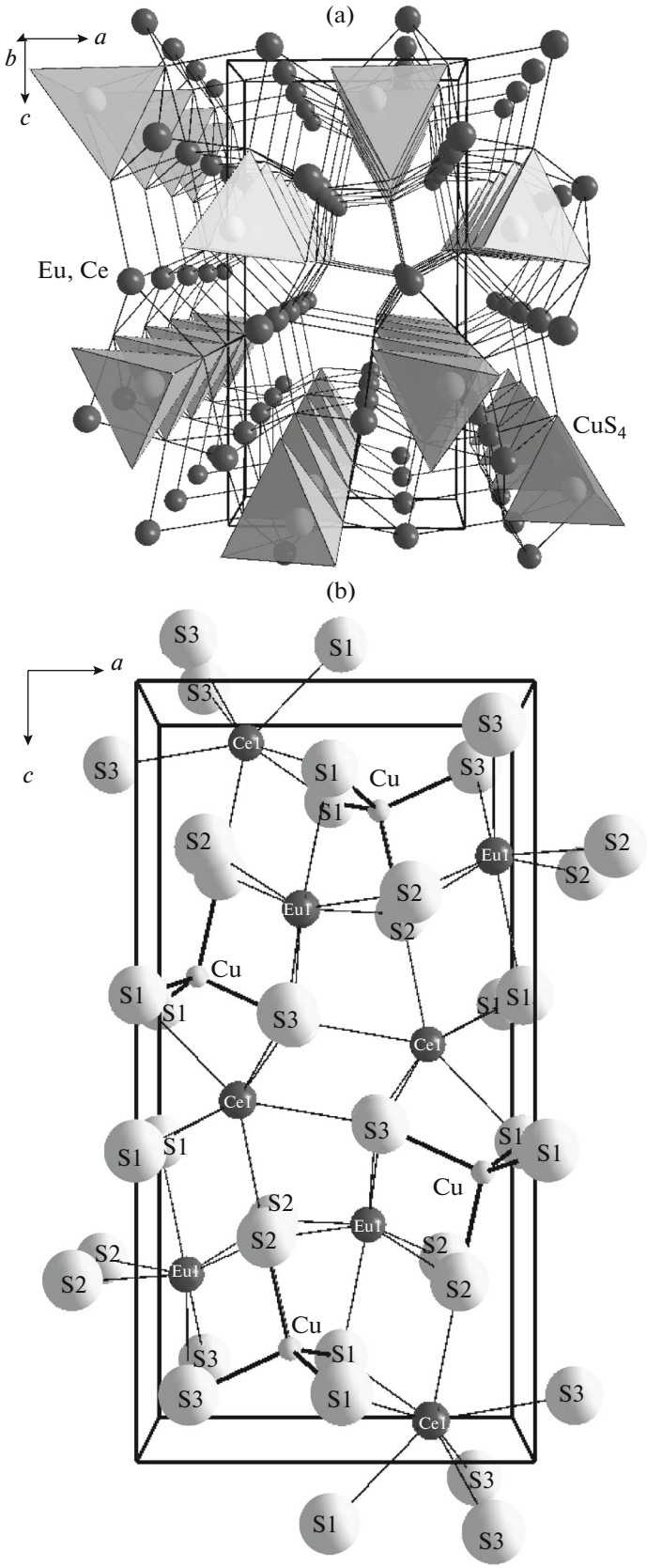

Fig. 2. Projections [010] for the structure of β-$EuCeCuS_3$.

Hence, two polymorphs have been revealed for $EuCeCuS_3$: low-temperature α-$EuCeCuS_3$ ($BaLaCuS_3$ structural type) and high-temperature β-$EuCeCuS_3$ (Ba_2MnS_3 structural type), which are similar to the modifications appearing for $EuPrCuS_3$ [12] and $SrCeCuS_3$ [3]. The crystal structure of β-$EuCeCuS_3$ (annealing at 1170 K) has been solved. The cerium and europium atoms in this structure are randomly disordered over two crystallographic sites. It should be expected that the disordering of rare-earth element atoms over sites will be retained at a lower annealing temperature (970 K) as for $SrCeCuS_3$ [3]. Longer annealing is required for the synthesis of a homogeneous α-$EuCeCuS_3$ sample (annealing at 970 K).

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