ISSN 0036-0236, Russian Journal of Inorganic Chemistry, 2018, Vol. 63, No. 11, pp. 1494–1500. © Pleiades Publishing, Ltd., 2018. Original Russian Text © A.V. Ruseikina, O.V. Andreev, 2018, published in Zhurnal Neorganicheskoi Khimii, 2018, Vol. 63, No. 11, pp. 1476–1482.

> PHYSICOCHEMICAL ANALYSIS OF INORGANIC SYSTEMS

Phase Equilibria in Systems DyCuS₂-EuS and Cu₂S-Dy₂S₃-EuS

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Abstract—The phase diagram of system $DyCuS_2$ —EuS has been first constructed, and the phase equilibria in the $Cu_2S-Dy_2S_3$ —EuS triangle at 970 K have been studied. Compound EuDyCuS_3 (1DyCuS_2 : 1EuS), space group *Pnma*, a = 10.1901(3) Å, b = 3.9270(1) Å, c = 12.8468(3) Å, melts incongruently at 1727 ± 7 K according to the reaction: EuDyCuS_{3solid} $\leftrightarrow 0.17$ SS EuS (90 mol % EuS, 10 mol % DyCuS_2) + 0.83 liq (42 mol % EuS, 58 mol % DyCuS_2), $\Delta H = 2.9 \pm 0.6$ kJ/mol; microhardness of the phase is 3080 ± 35 MPa. Compound EuDyCuS_3 is transparent in the range 3000–1800 cm⁻¹. In system DyCuS_2–EuS, the solid solution (SS) based on EuS extends from 91 to 100 mol % at 1770 K and from 92 to 100 mol % at 1170 K. In γ -DyCuS_2, 2 mol % EuS, $T = 1487 \pm 8$ K. In system $Cu_2S-Dy_2S_3$ –EuS, 10 secondary systems have been isolated. At 970 K, tie-lines are located between compound EuDyCuS_3 and solid solutions based on compounds β -Cu₂S, EuS, DyCuS_2, β -(DyCu₃S_3), and EuDy₂S_4; between DyCuS_2 and the solid solution of α -Dy₂S_3, DyCuS_2, and EuDy₂S_4.

Keywords: phase equilibria, incongruent melting, complex sulfides, microstructural analysis, differential scanning calorimetry

DOI: 10.1134/S0036023618110141

Compounds EuLnCuS₃ (Ln = Gd–Lu) are nonmetallic magnetic materials [1, 2]. Phase diagrams of systems $Cu_2S-Ln_2S_3-EuS$ (Ln = La, Nd) constructed allowed us to select conditions for the preparation of crystals of incongruently melting compounds EuLnCuS₃ directly from melt [3]. A similarity of phase equilibria was determined in $Cu_2S-Ln_2S_3-EuS$ systems formed by elements of the cerium subgroup [4].

As far as we know, phase equilibria have not been studied in systems $Cu_2S-Ln_2S_3-EuS$ (Ln = Gd-Lu). Dysprosium Dy ($4f^{10}5d^06s^2$) exhibits a stable valence of 3; it is a typical rare-earth element of the yttrium subgroup [5], which allows us to consider the $Cu_2S-Dy_2S_3$ -EuS system as a model.

In system Cu₂S–Dy₂S₃–EuS, compound EuDy-CuS₃ (1Cu₂S : 1Dy₂S₃ : 2EuS) is formed. Samples were obtained by the solid-phase reaction by heating a stoichiometric mixture of rare-earth sesquioxides Ln₂O₃ and copper oxide CuO in a graphite boat at 1170–1320 K in a flow of a CS₂ and N₂ gas mixture [2]. The crystals of EuDyCuS₃ belong to the orthorhombiccrystal system, the structural type (ST) Eu₂CuS₃ [6], space group *Pnma*, the unit cell parameters are a = 10.1904(3) Å, b = 3.9267(1) Å, c = 12.8471(4) Å [2]. Compound EuDyCuS₃ contains magnetic ions Dy^{3+} and exhibits a ferrimagnetic transition at 5.3 K [1, 2].

In system $Cu_2S-Dy_2S_3$, complex sulfides $DyCuS_2$ [7-10] and DyCu₃S₃ [8, 11, 12] are formed, which exist as three polymorphous modifications. Compound α -DyCuS₂ has an orthorhombic crystal structure, space group Pnma, ST 2 [13], the unit cell parameters are a = 13.4251 Å, b = 3.9796 Å, c = 6.2743 Å [9]; α -DyCuS₂ undergoes polymorphic transitions α -DyCuS₂ \rightarrow β -DyCuS₂ at 1175 K and β -DyCuS₂ \rightarrow γ -DyCuS₂ at 1260 K. High-temperature polymorphs are not recorded by quenching [8]. The $DyCu3S_3$ phase of the berthollide type has a shallow maximum of melting at 1590 K and a composition of 37 mol % Dy_2S_3 [8, 14]. The coordinates of the eutectic between the Cu₂S and DyCu₃S₃ phases are 1.3 mol % Dy₂S₃, T = 1390 K [8]. In system Cu₂S-EuS, a eutectic is formed between the initial sulfides at 24.5 mol % EuS, T = 1069 K [3, 4]. In the Dy₂S₃-EuS system, compound $EuDy_2S_4$ is observed to form with the orthorhombic crystal system, ST CaV₂O₄, space group *Pnma*; unit cell parameters are a = 11.87 Å, b = 3.94 Å, c = 14.17 Å [15–17]. Compound EuDy₂S₄ melts incongruently at 2150 ± 40 K according to the scheme: $EuDy_2S_4 \leftrightarrow SS EuS + liq$. The extent of solid solutions (SS) based on EuS and γ -Dy₂S₃ at 1770 K is 9 mol % Dy₂S₃ and 8 mol % EuS, respectively [18].

Phase equilibria in the quasi-triple system Cu_2S – Dy₂S₃–EuS were studied in the Cu₂S–EuDyCuS₃ section [19]. The Cu₂S–EuDyCuS₃ system is of eutectic type with the eutectic coordinates of 10 mol % EuDyCuS₃, T = 1191 K. On the basis of β -Cu₂S, a solid solution of the open type is formed with a peritectic point in the coordinates of 4 mol % EuDyCuS₃, T = 1248 K [18].

The phase diagram of the $DyCuS_2$ -EuS section has not been studied. The mass balance equations of the phases involved in the invariant transformations have not been compiled. There are no data on the enthalpies of phase transformations. Triangulation of the triple system $Cu_2S-Dy_2S_3$ -EuS has not been carried out. The study of phase equilibria in the system $Cu_2S-Dy_2S_3$ -EuS will allow one to determine the intervals of compositions and temperatures for obtaining samples of compound EuDyCuS₃ by crystallization from the melt.

The aims of this work are to construct a phase diagram of system $DyCuS_2$ -EuS, determine the enthalpies of phase transformations in the system, and study phase equilibria in the Cu_2S - Dy_2S_3 -EuS triangle.

EXPERIMENTAL

Compound Cu₂S was obtained from elementary Cu (special purity grade 11-4) and elemental S (special purity grade 15-3) in sealed evacuated quartz tubes [3, 4]. Sulfides Dy_2S_3 and EuS were synthesized from appropriate oxides (DiO-L and EvO-Zh grade, respectively) in a flow of H₂S and CS₂ at 1300 K [20]. According to X-ray powder diffraction analysis, the sulfides obtained are single-phase and have a stoichiometric composition within the error of the chemical analysis. In system Cu₂S–Dy₂S₃–EuS, 80 samples of the inner part of the concentration triangle of sulfides Cu_2S , EuS, and Dy_2S_3 were synthesized according to the previously described procedures [21]. The samples were annealed in evacuated sealed quartz ampules at 970 K for 3000 h and at 1170 K for 1440 h. The annealing temperature in the muffle furnaces was set with a Thermolux thermostat with the accuracy of \pm 5 K. At 1770 K, the samples were annealed for 30 min in an open reactor with induction heating of a graphite crucible. The results of X-ray powder diffraction, microstructural analysis, and DSC samples in the course of annealing make it possible to conclude that an equilibrium state was reached.

DSC was performed on a Setsys Evolution 1750 device (TGA–DSC 1600). Recording conditions: a PtRh 6%–PtRh 30% DSC sensor, heating rate 5 K/min, argon purge rate 25 mL/min, crucible volume 100 μ L, sample weight 100–110 mg [22]. The temperature of the beginning of heat absorption was determined using

the Setsoft Software 2000 program package when performing the linear baseline from the first to the last point and fixed as the point of intersection of the tangent line with the baseline.

IR spectroscopic studies of compound EuDyCuS₃ were carried out on an FT-IR spectrometer in the range 4000-400 cm⁻¹. The polycrystalline sample was ground in an agate mortar and mixed with powder potassium bromide an annealed at 720 K to a homogeneous mass [23, 24]. The mixture was placed in a PF13 mold and pressed into a pellet using an Autotouch hydraulic press with a force of 8 tons; loading time was 4 min.

Microstructural analysis of the polished samples was carried out on an Axio Vert.A1 microscope; durometric analysis (DMA) was performed on an HMV-G21 device using the Vickers method with an error not exceeding 1.5%. Holding time, 15 s; load, 10 kG (98.07 N). Graphical constructions were performed using the Edstate 2D and Edstate 3D programs. X-ray powder diffraction data was obtained on a Dron-7 and a D2 Phaser diffractometers equipped with a Lynxeye¹ detector (Cu K_{α} radiation, Ni-filter). Samples were prepared by grinding in an agate mortar with ethane added. The unit cell parameters of the lower crystal systems were determined using the ITO program [25].

RESULTS AND DISCUSSION

The phase diagram of system DyCuS₂-EuS is first constructed showing complex sulfide EuDvCuS₂ to be formed. The X-ray powder diffraction pattern of compound EuDyCuS₃ is indexed on the basis of a orthorhombic crystal system, ST Eu₂CuS₃, space group *Pnma*; the unit cell parameters are a = 10.1901(3) Å, b = 3.9270(1) Å, c = 12.8468(3) Å (Fig. 1a), which agrees with the data reported [2]. The structure of compound EuDyCuS₃ is described by two-dimensional layers $(DyCuS_3)$ in the *ba* plane formed by distorted CuS₄ tetrahedra and DyS_6 octahedra with ions Eu^{2+} residing between the layers. In the temperature range 770–1170 K, the structural type of compound EuDyCuS₃ remains unchanged, which corresponds to the theoretical idea of the presence of dysprosium in the region of crystallochemical stability [26]. The crystals of complex sulfide EuDyCuS₃ have a gray-brown color, $H = 3080 \pm$ 35 MPa. Compound EuDyCuS₃ is transparent for IR radiation in the range $3000-1800 \text{ cm}^{-1}$ (Fig. 1b), which is typical for EuLnCuS₃ compounds [27]. Absorption bands are observed in the ranges 3800-3000 and $1700-1400 \text{ cm}^{-1}$ attributed to stretching and bending vibrations of hydroxyl groups. The presence of water sorbed can be caused by the water sensitivity of powder EuDyCuS₃.

¹ The studies were carried out at the Earth Cryosphere Institute, Siberian Branch of the Russian Academy of Sciences (Tyumen).



Fig. 1. Panel (a): (1) Experimental X-ray powder diffraction pattern and (2) the [010] projection of the EuDyCuS₃ structure. Panel (b): IR spectrum of EuDyCuS₃ annealed at 970 K. Panel (c): differential thermal curves for EuDyCuS₃.

Three thermal events are observed on the DSC curves of the EuDyCuS₃ samples (Fig. 1c, Table 1), which are completely reproduced in the heating– cooling cycles. When the sample is heated after the last thermal event, the sample is in a polycrystalline state, the appearance of a liquid phase in the sample was not detected. The thermal effects are reproduced in the region 17–80 mol % EuS at the same temperatures as in the EuDyCuS₃ sample and in the Cu₂S–EuDyCuS₃ section [19]. The fixed thermal events are caused by phase transitions of the first kind, namely, the polymorphous transformations of EuDyCuS₃ are not fixed by the quenching method (cooling rate ~ 10^3 – 10^4 K/min).

Similar polymorphic transitions were found to exist in isostructural compound SrDyCuS₃ [22].

Compound EuDyCuS₃ melts at temperatures close to the liquidus of system DyCuS₂–EuS (Fig. 2). The peaks of the thermal events of incongruent melting of compound EuDyCuS₃ and melting of EuS crystals are superimposed upon heating (Fig. 3). When the samples are cooled immediately after the thermal event of the beginning of crystallization of the EuS phase appeared, the peak of EuDyCuS₃ crystallization is manifested explicitly. According to the data of heating and cooling, the average temperature of the incongruent melting of compound EuDyCuS₃ is taken equal to 1727 \pm 7 K. The equation of the material balance of

Phase transformation	Coordinates of invariant points		Mass balance equations	$\Delta H_{ m melt}$, kJ/mol
	composition	<i>T</i> , K		
Incongruent melting of compound	EuDyCuS ₃ (1DyCuS ₂ :1EuS)	1727	$\begin{array}{l} EuDyCuS_{3solid} (50 \text{ mol }\% \text{ EuS}; 50 \text{ mol }\% \text{ DyCuS}_2) \leftrightarrow \\ 0.17SS \text{ EuS } (90 \text{ mol }\% \text{ EuS}; 10 \text{ mol }\% \text{ DyCuS}_2) + \\ 0.83liq (42 \text{ mol }\% \text{ EuS}; 58 \text{ mol }\% \text{ DyCuS}_2) \end{array}$	(2.9)
Melting of the eutectic	12 mol % EuS	1487	$\begin{array}{l} 0.79 \mathrm{DyCuS}_2 \left(2 \ \mathrm{mol} \ \% \ \mathrm{EuS}; 98 \ \mathrm{mol} \ \% \ \mathrm{DyCuS}_2\right) + \\ 0.21 \mathrm{EuDyCuS}_3 \left(50 \ \mathrm{mol} \ \% \ \mathrm{EuS}; 50 \ \mathrm{mol} \ \% \ \mathrm{DyCuS}_2\right) \leftrightarrow \\ \mathrm{liq} \left(12 \ \mathrm{mol} \ \% \ \mathrm{EuS}; 88 \ \mathrm{mol} \ \% \ \mathrm{DyCuS}_2\right) \end{array}$	7.6 ± 0.8
Polymorphic transition α -EuDyCuS ₃ \leftrightarrow β -EuDyCuS ₃	EuDyCuS ₃ (1DyCuS ₂ :1EuS)	1500	$\begin{aligned} & \text{EuDyCuS}_{3\text{solid}} (50 \text{ mol } \% \text{ EuS}; 50 \text{ mol } \% \text{ DyCuS}_2) \leftrightarrow \\ & 0.48\text{SS EuS} (91 \text{ mol } \% \text{ EuS}; 9 \text{ mol } \% \text{ DyCuS}_2) + \\ & 0.52\text{liq} (12.5 \text{ mol } \% \text{ EuS}; 87.5 \text{ mol } \% \text{ DyCuS}_2) \end{aligned}$	4.4 ± 0.5
Polymorphic transition β -EuDyCuS ₃ \leftrightarrow γ -EuDyCuS ₃	EuDyCuS ₃ (1DyCuS ₂ :1EuS)	1543	$\begin{split} & \text{EuDyCuS}_{3\text{solid}} (50 \text{ mol } \% \text{ EuS}; 50 \text{ mol } \% \text{ DyCuS}_2) \leftrightarrow \\ & 0.46\text{SS} \text{ EuS} (90.8 \text{ mol } \% \text{ EuS}; 9.2 \text{ mol } \% \text{ DyCuS}_2) + \\ & 0.54\text{liq} (15.5 \text{ mol } \% \text{ EuS}; 84.5 \text{ mol } \% \text{ DyCuS}_2) \end{split}$	1.0 ± 0.1
Polymorphic transition γ -EuDyCuS ₃ \leftrightarrow δ -EuDyCuS ₃	EuDyCuS ₃ (1DyCuS ₂ :1EuS)	1568	$\begin{split} & \text{EuDyCuS}_{3\text{solid}} \text{ (50 mol \% EuS; 50 mol \% DyCuS}_{2} \text{)} \leftrightarrow \\ & 0.45\text{SS EuS (90.5 mol \% EuS; 9.5 mol \% DyCuS}_{2} \text{)} + \\ & 0.55\text{liq (17 mol \% EuS; 83 mol \% DyCuS}_{2} \text{)} \end{split}$	2.0 ± 0.2

Table 1. Mass balance equations for the phases participating in invariant transformations in system $DyCuS_2$ -EuS

the phases participating in the invariant transformation is shown in Table 1.

Compound DyCuS₂ melts incongruently at 1587 K.

T, K

° 1 $\square 2$ △ 3

pound DyCuS₂ and melting of crystals Dy₂S₃ are superimposed on the heating curve but resolved on the cooling curve. The melting enthalpy of compound DyCuS₂ was determined to be $\Delta H = 11.9 \pm 2$ kJ/mol.

2520

The thermal events of incongruent melting of com-

1900 1900 + SS EuS 42%_AB مفصف 1727 $\Delta\Delta$ Dy₂S DvCuS₂ L + δ-EuDyCuS₃ δ-EuDyCuS₃ EuS SS 1568 90.5% 1587 -2 R -82 <u>1543</u> 1500 20.8% 1500 1500 0___09 Shonac γ -Dy₂S₃ + γ -DyCuS₂ γ-EuDyCuS3 + SS EuS β-EuDyCuS3 + SS EuS γ -DyCuS₂ + α -EuDyCuS₃ 1239 125 α-EuDvCuS: 1174 116 1100 1100 α-EuDyCuS3 + SS EuS ~~~ ممظمم Λ Δ α -DyCuS₂ + α -EuDyCuS₃ DyCuS₂ EuS 40 60 80 20 mol %

EuDvCuS

Fig. 2. Phase diagram of the DyCuS₂-EuS system: (1) DSC data, (2) single-phase sample, and (3) two-phase sample (according to X-ray powder diffraction pattern and microscopic analysis).

RUSSIAN JOURNAL OF INORGANIC CHEMISTRY Vol. 63 2018 No. 11



The thermal events of polymorphic transformations are recorded: α -DyCuS₂ $\leftrightarrow \beta$ -DyCuS₂ at 1174 K, $\Delta H =$ 1.44 kJ/mol; β -DyCuS₂ $\leftrightarrow \gamma$ -DyCuS₂ at 1251 K, $\Delta H =$ 0.41 kJ/mol. The temperatures of polymorphic transitions are consistent with the results of [8]. According to DSC, a decrease in the temperature of the polymorphic transitions $\alpha \leftrightarrow \beta$ to 1167 ± 2 K and $\beta \leftrightarrow \gamma$ to 1239 ± 2 K was recorded in the samples of compositions 5– 30 mol % EuS, which indicates the eutectoid phase transformations in the solid solution based on compound DyCuS₂. In γ -DyCuS₂, 2 mol % EuS dissolves at 1487 K.

A region of solid solution is formed on the base of EuS, the extent of which depends on the temperature being 91–100, 92–100, and 93–100 mol % EuS at 1770, 1170, and 970 K, respectively. The decrease in the unit cell parameter for the EuS phase from a = 5.967 Å to a = 5.951 Å at 970 K is consistent with the value of the reduced radius $r(Cu^+, Dy^{3+}) = (0.600 + 0.912)/2 = 0.756$ Å for cations replacing the Eu²⁺ ions $(r_{Eu}^{2+} = 1.17$ Å, CN = 6) in the EuS structure [28]. A negative deviation from Vegard's law indicates that the interaction force between the components of the EuS matrix is less than the interaction force between sulfur anions and doping cations [29, 30].

An eutectic is formed between the $DyCuS_2$ and $EuDyCuS_3$ phases, the melting peak of which is fixed in 15 samples of various compositions at 1487 ± 8 K. According to the microscopic analysis and the construction of the Tammann triangle, the composition of the eutectic is 12 mol % EuS. The equation of the material balance of the phases participating in the invariant transformation was derived (Table 1). The liquidus line in the $DyCuS_2$ -eutectic region was constructed by approximating the DSC data by polynomials of the second and third degree.

In the region of 50-100 mol % EuS at temperatures below the incongruent decomposition temperature of compound EuDyCuS₃, phases EuDyCuS₃ and a EuSbase solid solution are in equilibrium. Only reflections of conjugated phases are observed on the X-ray powder diffraction patterns of the samples annealed. According to microstructure analysis of samples of different chemical compositions, there are brown oval EuS grains sized from 10×30 to $75 \times 120 \,\mu\text{m}$ located in the EuDyCuS₃ phase field. The liquidus branch in the range 42–100 mol % EuS was approximated by a polynomial of the third degree. There is a negative deviation from the linear dependence.

In system $DyCuS_2$ -EuS, primary formed crystals of compound EuDyCuS₃ are observed in the samples with the composition 13–41 mol % EuS crystallized from melt.

In the quasi-triple system $Cu_2S-Dy_2S_3-EuS$ at 970 K, complex sulfide $EuDyCuS_3$ is in equilibrium with the following phases: SS β -Cu₂S, SS EuS,



Fig. 3. Differential thermal curves for samples of system $DyCuS_2$ -EuS. The compositions of the samples are expressed in mol % EuS.

DyCuS₂, EuDy₂S₄, SS β-DyCu₃S₃. The positions of the tie-lines in the triangle are indicated (Fig. 4). The following phases also exist in equilibrium: DyCuS₂– SS α-Dy₂S₃, DyCuS₂–EuDy₂S₄. The position of the tie-lines in the ternary Cu₂S–Dy₂S₃–EuS system makes it possible to separate 10 secondary systems: EuS–EuDyCuS₃–Cu₂S (I), compositions from the region SS β-Cu₂S–EuDyCuS₃ (II), Cu₂S–EuDy-CuS₃–β-DyCu₃S₃ (III), compositions from the region SS β-DyCu₃S₃–EuDyCuS₃ (IV), β-DyCu₃S₃– EuDyCuS₃–α-DyCuS₂ (V), α-DyCuS₂–EuDy₂S₄– EuDyCuS₃ (VI), α-DyCuS₂–α-Dy₂S₃–EuDy₂S₄ (VII), α-DyCuS₂–compostions from the region SS α-Dy₂S₃ (VIII), EuS–EuDy₂S₄–EuDyCuS₃ (IX), compositions from the region SS EuS–EuDyCuS₃ (X).

The phase equilibria in the polythermal sections of the ternary system are characterized.

System DyCuS₂-EuDy₂S₄ is of the eutectic type. The thermal event of melting of the eutectic was found at 1515 \pm 3 K. The change in the unit cell parameters of compound DyCuS₂ from a = 13.425 Å, b = 3.979 Å, c = 6.274 Å to a = 13.420 Å, b = 4.007 Å, c = 6.256 Å indicates a solid solution based on DyCuS₂ to exist. The temperatures of the eutectoid transformations in the region of the solid solution of DyCuS₂ were recorded to be 1167 \pm 1 and 1245 \pm 2 K. The microhardness of the EuDy₂S₄ phase grains is 3400 \pm 40 MPa.

In system $EuDyCuS_3-EuDy_2S_4$ at 970 K, phases $EuDyCuS_3$ and $EuDy_2S_4$ are in equilibrium. Changes in the unit cell parameters of the conjugated phases in the two-phase region were not found.



Fig. 4. Positions of the tie-linetie-lines in system $Cu_2S-Dy_2S_3-EuS$ at 970 K. The dots indicate the samples studied; the Roman numerals indicate the secondary systems.

In the sections of the ternary system $Cu_2S-Dy_2S_3-EuS_3$, the eutectic temperature decreases regularly from the high-temperature part of the system to the low-temperature part: 1515 K (system $DyCuS_2-EuDy_2S_4$) \rightarrow 1487 K (system $DyCuS_2-EuDyCuS_3$) \rightarrow 1480 K (secondary system V) \rightarrow 1469 K (system $DyCu_3S_3-EuDyCuS_3$) \rightarrow 1400 K (secondary system IV, composition $60Cu_2S: 24.8Dy_2S_3: 15.2EuS) \rightarrow$ 1363 K (secondary system IV, composition $69.7Cu_2S:$ $20.4Dy_2S_3: 9.9EuS) \rightarrow$ 1191 K (system $Cu_2S-EuDy-CuS_3$). It is possible that the point of the triple eutectic is shifted to the eutectic in the $Cu_2S-EuDyCuS_3$ system.

Similar phase equilibria are observed in system $Cu_2S-Gd_2S_3-EuS$ [18] and system $Cu_2S-Dy_2S_3-EuS$. Isostructural compounds $EuGdCuS_3$ and $EuDyCuS_3$ are formed in the systems, in which such high-temperature polymorphic transitions are fixed; the compounds melt incongruently. In systems $LnCuS_2-EuS$, a complex sulfide and a eutectic are formed. In ternary systems at 970 K, compounds

RUSSIAN JOURNAL OF INORGANIC CHEMISTRY Vol. 63 No. 11 2018

EuLnCuS₃ and solid solutions based on phases of the systems forming a triangle are in equilibrium. We should expect similarity of phase equilibria in all systems $Cu_2S-Ln_2S_3-EuS$ (Ln = Gd-Lu).

ACKNOWLEDGMENTS

The authors are grateful to Zh.A. Demchuk, the deputy head of the testing laboratory of the Tyumen section of quality control, metrology, and electrometry of Gazpromneft' Krasnoyarsk, for microstructural and X-ray powder diffraction analysis of samples of the ternary system.

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Translated by V. Avdeeva