

© ANNA V. RUSEIKINA, EVGENY O. GALENKO,  
LEONID A. SOLOVIEV, ANNA M. ZHERNOVNIKOVA

adeschina@mail.ru, jonny3452@mail.ru, leosol@icct.ru, annushka\_kot@mail.ru

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**PHYSICOCHEMICAL ANALYSIS OF THE 2SrS:  
1Ln<sub>2</sub>S<sub>3</sub>:1Ag<sub>2-x</sub>S (Ln = La, Nd, Dy, Er, Lu) COMPOUNDS\***

**SUMMARY.** The phase composition of the 2SrS:1Ln<sub>2</sub>S<sub>3</sub>:1Ag<sub>2-x</sub>S (Ln = La, Nd, Er, Lu) samples annealed at 1,170 K is determined by the X-ray study and micrographic investigation; the conoids in the SrS–Ln<sub>2</sub>S<sub>3</sub>–Ag<sub>2</sub>S triangles are preliminarily determined. The 2SrS:1Ln<sub>2</sub>S<sub>3</sub>:1Ag<sub>2-x</sub>S (Ln = La, Nd, Er, Lu) samples contain three basic phases: SrS, Ag<sub>2</sub>S, and SrLn<sub>2</sub>S<sub>4</sub>. The compositions are within the SrS–SrLn<sub>2</sub>S<sub>4</sub>–Ag<sub>2-x</sub>S triangle, the conoids in the SrS–Ln<sub>2</sub>S<sub>3</sub>–Ag<sub>2</sub>S triangles pass between the Ag<sub>2-x</sub>S–SrLn<sub>2</sub>S<sub>4</sub> phases. No new compounds, such as SrLnAg<sub>2</sub>S<sub>3</sub> (Ln = La, Nd, Lu), are formed. Having studied the cooled samples from the Ag<sub>2-x</sub>S–Dy<sub>2</sub>S<sub>3</sub>–SrS melt system in the ratios of 1: 2; 1: 1: 3; 2: 1: 2; 1: 1: 1, we discover the phases forming the triangle and occurring within the systems, making the triangle: Ag<sub>2-x</sub>S, AgDy<sub>2</sub>S<sub>2</sub>, SrDy<sub>2</sub>S<sub>4</sub>. The samples have a set of reflexes not characteristic of any of the main phases occurring in the system; the maximum intensity is registered in the ratio of 1:1:2, which allows us to pre-assign the chemical formula of SrDyAg<sub>2</sub>S<sub>3</sub> to the forming phase. The phase composition of 1:2:1 sample is the following: AgDy<sub>2</sub>S<sub>2</sub> and SrDy<sub>2</sub>S<sub>4</sub>. The conoid in the SrS–Dy<sub>2</sub>S<sub>3</sub>–Ag<sub>2</sub>S triangle goes between the AgDy<sub>2</sub>S<sub>2</sub>–SrDy<sub>2</sub>S<sub>4</sub> phases.

**KEY WORDS.** X-ray study, micrographic investigation, ALnBS<sub>3</sub> (A = Sr, Ba, Pb, Eu; Ln = La–Lu) complex sulfides, quasi-triangular systems, phase equilibria.

The poorly studied systems containing d-, f-elements are prospective targets to search for new complex sulfide phases where really significant properties should be predicted. Derived in the ratio of the original sulfides of 1Ln<sub>2</sub>S<sub>3</sub>: 2AS: 1Cu<sub>2</sub>S, LnBS<sub>3</sub>, the sulfides are formed in the quasi-triangular systems of AS–Ln<sub>2</sub>S<sub>3</sub>–Cu<sub>2</sub>S (A = Sr, Ba, Pb, Eu; Ln = La–Lu) [1], [2], [3], [4], [5], [6], [7]. The phase equilibria in isothermal and polythermal sections in the BaS–Ln<sub>2</sub>S<sub>3</sub>–Cu<sub>2</sub>S (Ln = La, Gd, Dy) [1], SrS–Ln<sub>2</sub>S<sub>3</sub>–Cu<sub>2</sub>S (Ln = La–Lu) [2], EuS–Ln<sub>2</sub>S<sub>3</sub>–Cu<sub>2</sub>S (Ln = La, Nd) [8] systems were studied comprehensively. At high-temperature synthesis (1,070–1,320 K), a change in structure type of the AL<sub>n</sub>CuS<sub>3</sub>-compounds of the orthorhombic system, BaLaCuS<sub>3</sub>, ST [2] or Ba<sub>2</sub>MnS<sub>3</sub>, ST [4], which are specific to Ln = La–Nd → Eu<sub>2</sub>CuS<sub>3</sub>,

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(Ln = Sm-Dy) [2], [3], [5]  $ST \rightarrow KZrCuS_3$  (Ln = Er-Lu) [2], [3]  $ST$ , is observed in the rare earth element series.

The similar properties of  $Cu_2S$  and  $Ag_2S$  (argentum and cuprum are similar in electrons) suggest that the sulfides of isoformular composition,  $ALnAgS_3$ , are formed in the  $AS-Ln_2S_3-Ag_2S$  systems, thus,  $BaLnAgS_3$  compound [7], [9] is formed in the  $BaS-Ln_2S_3-Ag_2S$  systems.

The published data on the nature of phase equilibria and compound formation in the  $SrS-Ln_2S_3-Ag_{2-x}S$  (Ln = La-Lu) systems were not found. The quasi-triangular  $SrS-Ln_2S_3-Ag_{2-x}S$  systems are limited by the binary  $Ag_{2-x}S-Ln_2S_3$ ,  $Ag_{2-x}S-SrS$ ,  $Ln_2S_3-SrS$  systems. The data on the  $Ag_{2-x}S-SrS$  systems were not found. The congruently melting compounds of the monoclinic and tetragonal  $AgLnS_2$  (Ln = Sm, Gd-Yb), cubic (NaCl  $ST$ )  $AgLnS_2$  (Ln = Er-Lu) systems are formed in  $Ag_{2-x}S-Ln_2S_3$  [10]. The incongruently melting  $SrLn_2S_4$  compounds of the cubic  $Th_3P_4$  (Ln = La-Gd)  $ST$  system and the congruently melting  $SrLn_2S_4$  (Ln = Tb-Lu) compounds of the orthorhombic  $CaFe_2O_4$   $ST$  system are formed in  $Ln_2S_3-SrS$  [2].

As the structure of compounds in the lanthanide family can change, to create an integrated view of the occurrence of the  $SrLnAgS_3$  type compounds, we should analyze the samples from three different areas in the rare earth element series: La, Nd, Dy, Er, Lu, after the rare earth element series is j, S and s full — close to Nd, Gd and Ho [11].

The purpose of this paper is to determine whether new compounds of the  $SrLnAgS_3$  type occur in the  $SrS-Ln_2S_3-Ag_{2-x}S$  (Ln = La, Nd, Dy, Er, Lu) systems or not.

**The experiment.** Exactly stoichiometric  $Ag_2S$  is not formed, the composition of the sulfide phase is  $Ag_{1.99-1.97}S$  [10]. The  $Ag_{1.985}S$  compound is prepared from elementary Ag of 11-4 extra pure grade and S of 15-3 extra pure grade by the direct synthesis method.

The melted samples of the composition:  $2SrS: 1Ln_2S_3: 1Ag_{1.985}S$  (Ln = La, Nd, Dy, Er, Lu) were obtained by the technique described in [12]. The samples were annealed at 1,170 K in the vacuum-sealed quartz ampoules during 2 months. The microstructural analysis (MSA) of the polished samples was carried out using the *METAM LV-31* optical metallographic microscope.

The X-ray study was carried out using the *PANalytical X'Pert PRO* diffractometers equipped with the *PIXcel* and *DRON 7* detectors ( $CuK\alpha$  emission, Ni-filter). The powder samples were prepared by triturating with octane in the agate mortar. The X-ray diagrams were taken in the following range of diffraction angles:  $5^\circ \leq 2\theta \leq 140^\circ$ . The phase identification was performed using the ICDD PDF4+ 2012 database. The lattice parameters of lower crystal systems were determined by the ITO program [13]. The parameter specification and quantitative phase analysis were performed on the basis of powder data by the quasi-Newton method for the derivative difference minimization (DDM) [14].

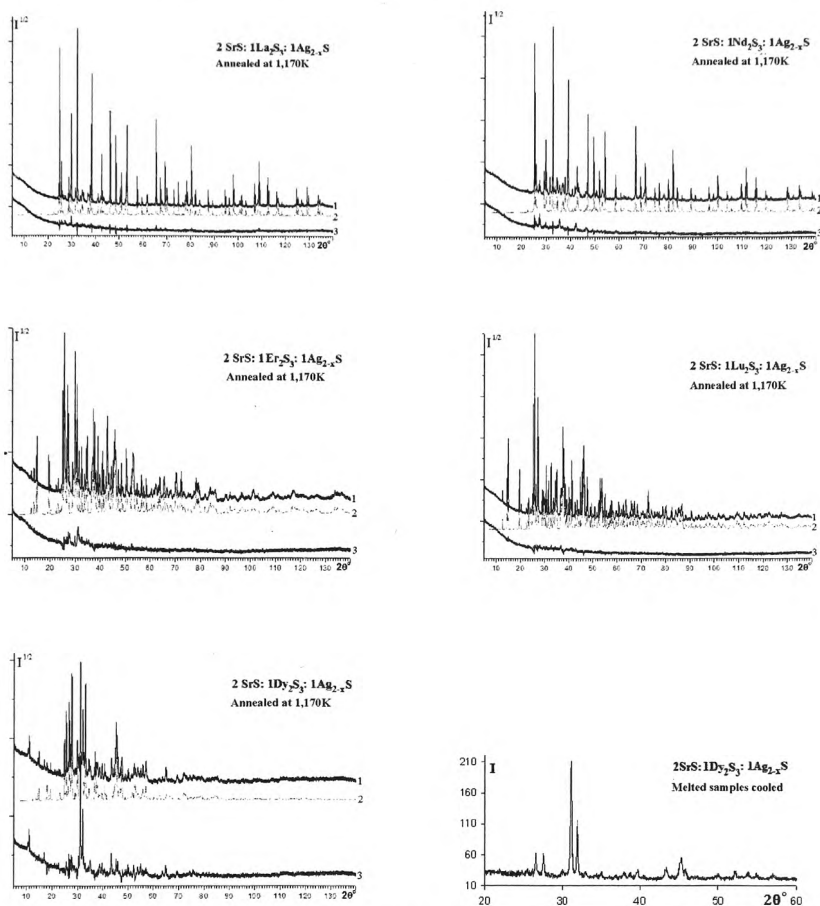
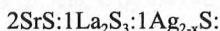


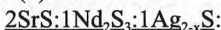
Fig.1. Experimental (1), predicted (2) and differential (3) diffraction patterns of 2SrS: 1Ln<sub>2</sub>S<sub>3</sub>: 1Ag<sub>2-x</sub>S samples after structure specification by the DDM method. The phase composition of the samples is described in the text of the paper.

**Results and discussion.** The geometric characteristics to energetic characteristics ratio exercises a decisive influence on the complex compound formation. In accordance with “the characteristic-to-characteristic ratio rule”, the quantity differences of the Sr–Ln–Ag (La–Lu) component characteristic higher than 15% predetermine the probability of a new compound formation [15]. The differences in the ionic radii ( $\Delta r$ ) Ag<sup>+</sup> ( $r_{\text{Ag}^+} = 0.67 \text{ \AA}$ , EN 1.93 [16], [17]) and Ln<sup>3+</sup> are 35–22 %; the electronegativity difference is (EN) 34–22 % (Ln = La–Lu). The differences in  $\Delta r$  and EN Sr<sup>2+</sup> ( $r_{\text{Sr}^{2+}} = 1.18 \text{ \AA}$  (CN = 6), EN 0.92) and Ag<sup>+</sup> are 43 and 52 %, and for Sr<sup>2+</sup> and Ln<sup>3+</sup>, they are from 13 to 27 % and from 28 to 39 %, respectively.

In the systems forming the  $\text{SrS}-\text{Ln}_2\text{S}_3-\text{Ag}_{2-x}\text{S}$  ( $\text{Ln} = \text{La}, \text{Nd}$ ) triangle, the following sulfides congruently melt:  $\text{SrS}$ ,  $\text{Ln}_2\text{S}_3$ ,  $\text{Ag}_{2-x}\text{S}$ ,  $\text{SrLn}_2\text{S}_4$ , so in the ternary system, it is theoretically possible to draw a conoid joining the conjugate phases  $\text{Ag}_{2-x}\text{S}-\text{SrLn}_2\text{S}_4$ . According to RFA (Fig. 1) and MSA,  $2\text{SrS}:1\text{Ln}_2\text{S}_3:1\text{Ag}_{2-x}\text{S}$  ( $\text{Ln} = \text{La}, \text{Nd}$ ) samples contain three major phases.



62.2%  $\text{SrLa}_2\text{S}_4$ ,  $I-43d$ ,  $a = 8.78473 \text{ \AA}$ ;  
 13.1%  $\text{Ag}_2\text{S}$ ,  $P2_1/c$ ,  $a = 4.2264(6)$ ,  $b = 6.9294(9)$ ,  $c = 9.534(1) \text{ \AA}$ ,  $\beta = 3125.59(1)^\circ$ ;  
 24.7%  $\text{SrS}$ ,  $\text{Fm}3m$ ,  $a = 6.0062(1) \text{ \AA}$ .



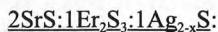
59.3%  $\text{SrNd}_2\text{S}_4$ ,  $I-43d$ ,  $a = 8.64294(4) \text{ \AA}$ ;  
 20.8%  $\text{Ag}_2\text{S}$ ,  $P2_1/c$ ,  $a = 4.2280(4)$ ,  $b = 6.9286(8)$ ,  $c = 9.534(1) \text{ \AA}$ ,  $\beta = 125.58(1)^\circ$ ;  
 19.9%  $\text{SrS}$ ,  $\text{Fm}3m$ ,  $a = 5.9878(3) \text{ \AA}$ .

The mass ratios of the identified phases are given without the amorphous component and unidentified phases appearing in the difference curve. Due to imperfect phase stoichiometry, the metals in the phases are partially substituted (according to the lattice parameter variations); to make a consistent evaluation of amorphous and unidentified component quantity is difficult.

The  $2\text{SrS}:1\text{Ln}_2\text{S}_3:1\text{Ag}_{2-x}\text{S}$  ( $\text{Ln} = \text{La}, \text{Nd}$ ) compositions lie within the  $\text{SrS}-\text{SrLn}_2\text{S}_4-\text{Ag}_{2-x}\text{S}$  triangle, the conoid goes between the  $\text{Ag}_{2-x}\text{S}-\text{SrLn}_2\text{S}_4$  phases. No new compounds of the  $\text{SrLnAgS}_3$  type are formed in the  $\text{SrS}-\text{Ln}_2\text{S}_3-\text{Ag}_{2-x}\text{S}$  ( $\text{Ln} = \text{La}, \text{Nd}$ ) systems.

As the  $\text{SrS}$ ,  $\text{Ln}_2\text{S}_3$ ,  $\text{Ag}_{2-x}\text{S}$ ,  $\text{SrLn}_2\text{S}_4$ ,  $\text{AgLnS}_2$  compounds congruently melt in the systems forming the  $\text{SrS}-\text{Ln}_2\text{S}_3-\text{Ag}_{2-x}\text{S}$  ( $\text{Ln} = \text{Dy}, \text{Er}, \text{Lu}$ ) triangle, in the ternary system it is theoretically possible to draw a conoid joining the conjugate phases:  $\text{AgLnS}_2-\text{SrLn}_2\text{S}_4$ ,  $\text{Ag}_{2-x}\text{S}-\text{SrLn}_2\text{S}_4$ ,  $\text{AgLnS}_2-\text{SrS}$ .

The  $2\text{SrS}:1\text{Ln}_2\text{S}_3:1\text{Ag}_{2-x}\text{S}$  compositions lie on the  $\text{AgLnS}_2-\text{SrS}$  conoid. According to RFA, the mass ratios, s.g. (space group), phase composition and u.n. parameters of identified phases in the  $2\text{SrS}:1\text{Ln}_2\text{S}_3:1\text{Ag}_{2-x}\text{S}$  ( $\text{Ln} = \text{Er}, \text{Lu}$ ) samples annealed at 1,170 K are as follows (Fig. 1):



47.0%  $\text{SrEr}_2\text{S}_4$ ,  $P_{nma}$ ,  $a = 11.9590(4)$ ,  $b = 3.9569(2)$ ,  $c = 14.2333(5) \text{ \AA}$ ;  
 21.7%  $\text{Ag}_2\text{S}$ ,  $P2_1/c$ ,  $a = 4.2267(3)$ ,  $b = 6.9277(6)$ ,  $c = 9.530(1) \text{ \AA}$ ,  $\beta = 125.59(1)^\circ$ ;  
 23.3%  $\text{SrS}$ ,  $\text{Fm}3m$ ,  $a = 5.9840(2) \text{ \AA}$ ;  
 8.1%  $\text{Er}_2\text{SO}_2$ ,  $P-3m1$ ,  $a = 3.7613(1)$ ,  $c = 6.5456(2) \text{ \AA}$ .  
 $2\text{SrS}:1\text{Lu}_2\text{S}_3:1\text{Ag}_{2-x}\text{S}:$   
 68.2%  $\text{SrLu}_2\text{S}_4$ ,  $P_{nma}$ ,  $a = 11.8972(1)$ ,  $b = 3.92357(5)$ ,  $c = 14.1187(2) \text{ \AA}$ ;  
 29.6%  $\text{Ag}_2\text{S}$ ,  $P2_1/c$ ,  $a = 4.2270(2)$ ,  $b = 6.9280(4)$ ,  $c = 9.5321(6) \text{ \AA}$ ,  $\beta = 125.58(1)^\circ$ ;  
 2.2%  $\text{SrS}$ ,  $\text{Fm}3m$ ,  $a = 5.9840(6) \text{ \AA}$ .

According to RFA, the  $2\text{SrS}:1\text{Ln}_2\text{S}_3:1\text{Ag}_{2-x}\text{S}$  ( $\text{Ln} = \text{Er}, \text{Lu}$ ) samples belong to the  $\text{SrS}-\text{SrLn}_2\text{S}_4-\text{Ag}_{2-x}\text{S}$  triangle (for Er, there is an oxisulfide inclusion), which fits the

MSA data. In the metallographic samples, the needle formations permeate through the SrS phase, indicating the decomposition of SrS-based solid solutions (SS). Thus, the conoid goes between the  $\text{Ag}_{2-x}\text{S}-\text{SrLn}_2\text{S}_4$  phases.

According to the differential diffraction pattern of the  $2\text{SrS}:1\text{Lu}_2\text{S}_3:1\text{Ag}_{2-x}\text{S}$  sample in the  $\text{SrS}-\text{Ln}_2\text{S}_3-\text{Ag}_{2-x}\text{S}$  system, no new compound formation is observed, and in the diffraction pattern of the  $2\text{SrS}:1\text{Er}_2\text{S}_3:1\text{Ag}_{2-x}\text{S}$  sample, there are unidentified reflexes which are specific to none of the phases present in the system.

To determine the occurrence or non-occurrence of new phases and to predetermine the quasi-binary sections in the  $\text{SrS}-\text{Dy}_2\text{S}_3-\text{Ag}_{2-x}\text{S}$  system, the phase composition of the samples cooled after melting (Fig. 1-3) was determined by the MSA and RFA methods as follows: p. 1 ( $1\text{Ag}_{2-x}\text{S}:2\text{Dy}_2\text{S}_3:1\text{SrS}$ ); p. 2 ( $1\text{Ag}_{2-x}\text{S}:1\text{Dy}_2\text{S}_3:2\text{SrS}$ ); p. 3 ( $1\text{Ag}_{2-x}\text{S}:1\text{Dy}_2\text{S}_3:3\text{SrS}$ ); p. 4 ( $2\text{Ag}_{2-x}\text{S}:1\text{Dy}_2\text{S}_3:2\text{SrS}$ ); p. 5 ( $1\text{Ag}_{2-x}\text{S}:1\text{Dy}_2\text{S}_3:1\text{SrS}$ ). The phases forming the  $\text{SrS}-\text{Dy}_2\text{S}_3-\text{Ag}_{2-x}\text{S}$  triangle were in the samples, and  $\text{Ag}_{2-x}\text{S}$ ,  $\text{AgDyS}_2$ ,  $\text{SrDy}_2\text{S}_4$  were identified in the systems making a triangle. There is a set of reflexes, which are specific to none of the phases in the system and which cannot be obtained by their addition, in the samples of p. 2, p. 3, p. 4, p. 5. The comparison of the diffraction patterns disclosed that the sample of p.2 had the maximum intensity of these lines (Fig. 1). In the metallographic samples, a new phase is represented by the bright field permeated with honeycomb formations. The relationship between the basic sulfides in the sample composition is presented as  $1\text{Ag}_{2-x}\text{S}:1\text{Dy}_2\text{S}_3:2\text{SrS}$ , which allows pre-attributing the chemical formula of  $\text{SrDyAgS}_3$  to a resulting phase.

According to RFA and MSA, the samples of p. 1, p. 4 are two-phase:  $\text{AgDyS}_2 + \text{SrDy}_2\text{S}_4$  and  $1\text{Ag}_{2-x}\text{S} +$  a new phase, respectively, and the sample of p. 5 is three-phase:  $\text{AgDyS}_2 + \text{SrDy}_2\text{S}_4 +$  a new compound. In the metallographic samples, there are the  $\text{SrDy}_2\text{S}_4$  primary crystals, up to  $15 \times 200 \mu\text{m}$  in size, and the eutectics between the  $\text{AgDyS}_2$  and  $\text{SrDy}_2\text{S}_4$  phases in the sample of p.1; there are grains of a new phase, up to  $30 \times 130 \mu\text{m}$  in size, and the eutectics between a phase and  $\text{Ag}_{2-x}\text{S}$  in the sample of p. 4; there are the  $\text{AgDyS}_2$  grains, up to  $10 \times 40 \mu\text{m}$  in size,  $\text{SrDy}_2\text{S}_4$  up to  $50 \times 180 \mu\text{m}$  in size, and a new compound, up to  $30 \times 120 \mu\text{m}$  in size (Fig. 2) in the sample of p.5. The X-ray patterns of p. 2 and p. 4 are similar (Fig. 1). In the metallographic sample of p. 2, a new phase is presented by long oblong primary crystals and eutectic ones forming a honeycomb-shaped pattern. After annealing at 1,170 K, according to the MSA and RFA data,  $2\text{SrS}:1\text{Dy}_2\text{S}_3:1\text{Ag}_{2-x}\text{S}$  sample is at least three-phase (Fig. 1)/

The samples under investigation are marked with points.

1. 40.9%  $\text{SrDy}_2\text{S}_4$ ,  $P_{\text{max}}$ ,  $a = 11.994(5)$ ,  $b = 3.992(2)$ ,  $c = 14.325(5)$  E;
2. 59.1%  $\text{AgDyS}_2$ ,  $P_{21}$ ,  $a = 7.657(3)$ ,  $b = 7.673(3)$ ,  $c = 12.002(6)$  E,  $\beta = 90.44(6)^\circ$ .
3. an unidentified phase (demonstrated in the difference curve).

The new compound is likely to be stable at high temperatures and to decompose when the temperature falls.

Therefore, it is stated that there is an equilibrium between the  $\text{AgDyS}_2-\text{SrDy}_2\text{S}_4$  compounds (Fig. 3). At this stage, it is difficult to determine the nature of the other phase equilibria. Forming new compounds is likely to be specific to the  $\text{SrS}-\text{Ln}_2\text{S}_3-\text{Ag}_{2-x}\text{S}$  ( $\text{Ln} = \text{Dy}, \text{Er}$ ) systems.

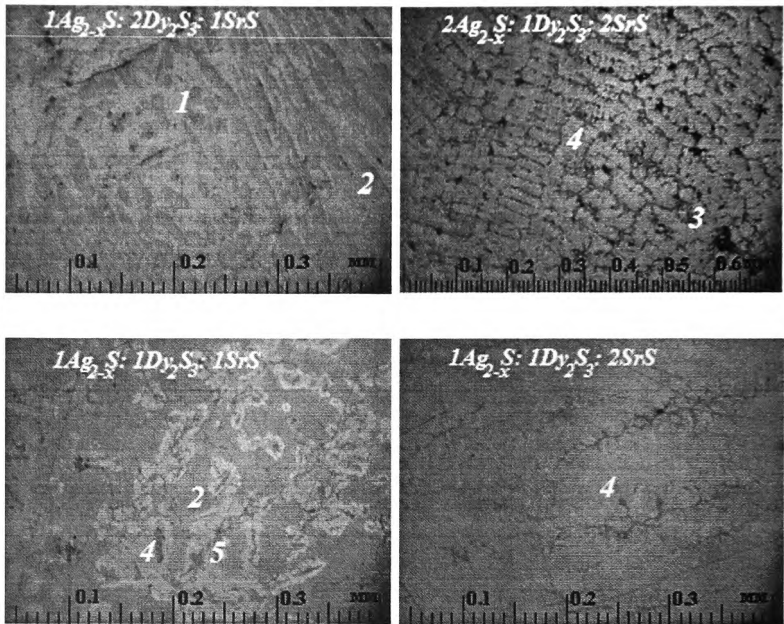


Fig. 2. The photographs of the sample microstructure in the SrS-Dy<sub>2</sub>S<sub>3</sub>-Ag<sub>2-x</sub>S system. The phases presented in the system are as follows: 1 — the eutectics between the AgDyS<sub>2</sub> and SrDy<sub>2</sub>S<sub>4</sub> phases; 2 — SrDy<sub>2</sub>S<sub>4</sub>; 3 — Ag<sub>2-x</sub>S; 4 — an unidentified phase; 5 — AgDyS<sub>2</sub>

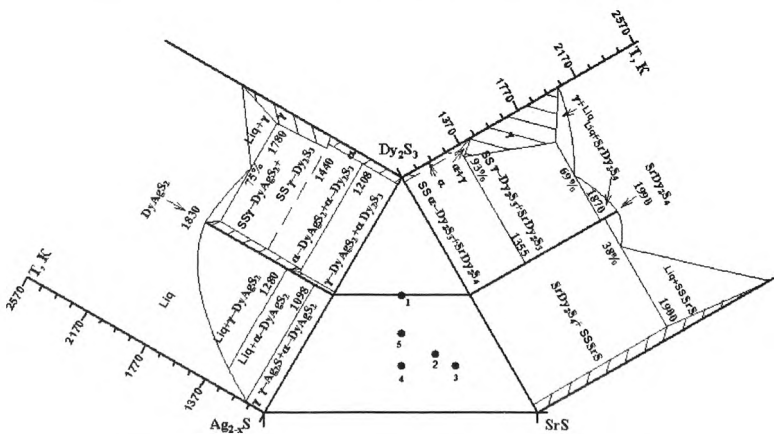


Fig. 3. The search for complex sulfides in the SrS-Dy<sub>2</sub>S<sub>3</sub>-Ag<sub>2-x</sub>S system.

The samples under investigation are marked with points.

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