PHYSICOCHEMICAL ANALYSIS OF INORGANIC SYSTEMS

Phase Equilibria in the Systems SrS-Cu₂S-Ln₂S₃ (Ln = La or Nd)

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Abstract—Phase equilibria in the systems SrS–Cu₂S–Ln₂S₃ (Ln = La or Nd) have been studied along the isothermal section at 1050 K and vertical sections CuLnS₂–SrS and Cu₂S–SrLnCuS₃, which are partially quasibinary joins. Compounds SrLnCuS₃ with Ln = La or Nd have been synthesized for the first time. They crystallize in orthorhombic space group *Pnma*, the BaLaCuS₃ structure type, with the following unit cell parameters: for SrLaCuS₃, *a* = 1.1157(2) nm, *b* = 0.41003(6) nm, *c* = 1.1545(2) nm; for SrNdCuS₃, *a* = 1.1083(1) nm, *b* = 0.40887(7) nm, *c* = 1.1477(2) nm. Noticeable homogeneity regions for SrLnCuS₃ are not found. The compounds melt congruently by the reaction SrLnCuS₃ \leftrightarrow SrS + *L* at 1365 K for SrLaCuS₃ and 1400 K for SrNdCuS₃. The tie-lines at 1050 K in the systems SrS–Cu₂S–Ln₂S₃ radiate from SrLnCuS₃ toward phases SrS, Cu₂S, CuLnS₂, and SrLn₂S₄, lying between the phases CuLnS₂ and compositions from the γ -Ln₂S₃–SrLn₂S₄ solid-solution field. Eutectics are formed between the compounds CuLaS₂ and SrLaCuS₃ at 21.0 mol % SrS, *T* = 1345 K; between the compounds CuNdS₂ and SrNdCuS₃, *T* = 1075 K and 8.0 mol % SrNdCuS₃, *T* = 1055 K.

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No data exist on phase equilibria in the quasi-ternary systems $SrS-Cu_2S-Ln_2S_3$ with Ln = La or Nd. Only their boundary binary systems are described in the literature: $Cu_2S-Ln_2S_3$, $Ln_2S_3-SrS(Ln = La, Nd)$, and Cu₂S–SrS. The systems Cu₂S–La₂S₃ and Cu₂S–Nd₂S₃ form complex sulfides CuLaS₂ and CuNdS₂, which melt incongruently at 1471 and 1465 K, respectively. A eutectic is formed between the phases Cu₂S and CuLnS₂ [1, 2]. The systems La₂S₃-SrS and Nd₂S₃-SrS form the complex compounds SrLa₂S₄ and SrNd₂S₄, which melt incongruently at 2290 and 2255 K, respectively. A continuous solid solution with a Th_3P_4 -type structure is formed between the phases γ -Ln₂S₃ and $SrLn_2S_4$ [3]. The system Cu_2S -SrS has a eutectic phase diagram with limited solubility on the basis of Cu₂S. The melting temperature of the eutectic is 1095 K; the composition is 21.5 mol % SrS [4].

The investigations of phase equilibria in the systems $SrS-Cu_2S-Ln_2S_3$ (Ln = La, Nd) are topical for the following reasons: this combination of *s*-, *d*-, and 4*f*-metal sulfides creates prerequisites for the formation of new compounds; at the same time, this provides the basis for choosing synthesis parameters for these new compounds.

One goal of this work was to study phase equilibria in the systems $SrS-Cu_2S-Ln_2S_3$ with Ln = La or Nd along the 1050 K isothermal section and vertical sections. The other goal was to determine the composition and structurally characterize new complex sulfides.

EXPERIMENTAL

The compound Cu_2S was prepared from the high purity grade constituent elements (copper os.ch. 11-4 and sulfur os.ch. 16.5; Russia) in evacuated and sealed off fused silica ampoules [5]. The sulfides SrS and Ln_2S_3 were synthesized from SrSO₄ (chemically pure grade, Russia) and Ln_2O_3 (LaO-D and NO-D grade samples, Russia) in flowing H₂S and CS₂ at 1300 K [6].

 $SrS-Cu_2S-Ln_2S_3$ (Ln = La, Nd) alloys were alloyed from SrS, Cu_2S , and Ln_2S_3 in a graphite crucible inside an open fused silica reactor. The reactor was preevacuated and purged with argon. The crucible was inductively heated in an RF generator. A sulfur-containing gas atmosphere was created in the reactor, which was necessary for avoiding the thermal dissociation of the starting sulfides [6]. Samples with compositions lying along the joins Cu₂S–SrLnCuS₃ were synthesized in a sealed-off fused silica ampoule. The samples, contained in evacuated and sealed off fused silica ampoules, were annealed at 1050 K for 500 h. At 1350–2000 K, the alloys were exposed for 20–30 min to a sulfur-containing gas atmosphere in a graphite crucible inductively heated inside an open reactor. The annealing time ensured the equilibration of the samples.

Samples of the complex sulfides $SrLaCuS_3$ and $SrNdCuS_3$ were prepared by alloying the constituent sulfides in a graphite crucible placed inside a sealed-off fused silica ampoule.

Powder X-ray diffraction was carried out on a DRON 6 diffractometer using CoK_{α} radiation. Microstructure



Fig. 1. Tie-lines in the systems $SrS-Cu_2S-La_2S_3$ and $SrS-Cu_2S-Nd_2S_3$ at 1050 K. Dots indicate experimentally studied compositions.

was examined on a Metam PB microscope. Visual polythermal analysis (VPA) and differential thermal analysis (DTA) were carried out as described previously [6]. The precision was up to 1% of the measured value in VPA and 0.1–0.2% in DTA. Edstate 2D and Edstate 3D software was used for graphic design. The unit cell parameters were calculated using Powder2 software. The phases SrLaCuS₃ and SrNdCuS₃ were identified with reference to the Powder Diffraction File PDF2 (JCPDS-ICDD, Release 2002). X-ray structure refinement was carried out using GSAS software [7]. The starting model used included data for the isostructural compound BaLaCuS₃ [8].

RESULTS AND DISCUSSION

Previously unknown compounds $SrLnCuS_3$ (Ln = La or Nd) are formed in the systems SrS-Cu₂S-Ln₂S (Ln = Ln or Nd) when the component ratio is 2SrS : $1Cu_2S$: : $1Ln_2S_3$. The compounds SrLaCuS₃ and SrNdCuS₃ have a BaLaCuS₃-type structure, space group *Pnma*. The parameters of the orthorhombic unit cell for SrLaCuS₃ are a = 1.1157(2) nm, b = 0.41003(6)nm, c = 1.1545(2) nm; for SrNdCuS₃, a = 1.1083(1) nm, b = 0.40887(7) nm, c = 1.1477(2) nm. Microstructure observation and powder X-ray diffraction confirmed that complex sulfide SrLnCuS₃ is in equilibrium with simple and complex sulfides of the boundary systems Cu₂S–Ln₂S₃, Ln₂S₃–SrS, and Cu₂S–SrS. This fact enabled us to determine the positions of tie-lines at 1050 K (Fig. 1). The tie-lines were drawn between the conjugate phases $CuLnS_2$ - $SrLn_2S_4$, $SrLnCuS_3$ – $SrLn_2S_4$, SrLnCuS₃–SrS, SrLnCuS₃–CuLnS₂, and Cu₂S–SrLnCuS₃, as well as between the phase CuLnS₂ and compositions from the γ -Ln₂S₃–SrLn₂S₄ solid solution (ss) field. Five subordinate triangles were recognized in each of the systems SrS–Cu₂S–Ln₂S₃; in Fig. 1, they are indicated by figures. The compounds SrLnCuS₃ are in equilibrium with the phases CuLnS₂ and SrS; they are simultaneously formed along the join CuLnS₂–SrS, which makes the investigation of this join pertinent. Of the other phases in equilibrium with the compound SrLnCuS₃, the only congruently melting phase is Cu₂S. The character of phase equilibria along the join Cu₂S–SrLnCuS₃ determines many features of equilibria in the relevant portion of the triangle, which makes it necessary to construct a phase diagram for this join.

Joins CuLaS₂–SrS and CuNdS₂–SrS

In the systems $CuLnS_2$ -SrS (Fig. 2), complex sulfides $SrLnCuS_3$ are formed when the component ratio is $1CuLnS_2$: 1SrS. These complex sulfides melt incongruently by the reaction $SrLnCuS_3 \longrightarrow ssSrS + L$ at 1365 K for $SrLaCuS_3$ and 1400 K for $SrNdCuS_3$.

Homogeneity ranges for compounds $SrLnCuS_3$ and $CuLnS_2$ were not found. Samples with chemical compositions approaching phases $SrLnCuS_3$ and $CuLnS_2$ consist of two phases, and the amount of the second phase correlates the position of the sample in the diagram. The positions of reflections of compounds $SrLnCuS_3$ and $CuLnS_2$ in the two-phase samples were the same as in homogeneous and stoichiometric samples. SrS is the base of a limited solid solution. Within



Fig. 2. $CuLaS_2$ -SrS and $CuNdS_2$ -SrS phase diagrams. (1) DTA data; (2) full melting of the sample according to VPA; (3) singlephase samples; (4) two-phase samples as determined by powder X-ray diffraction and microstructure examination.

the solid solution, the experimental SrS unit cell parameter versus composition data show a scatter of 0.006-0.007 nm; this scatter did not allow us to establish a correlation. The extent of the solid solution was determined from microstructure and powder X-ray diffraction data. The solvus line at 1050 K and the solidus line at 1650 K pass through the point 97.0 mol % SrS. The solubility at the incongruent-melting temperature of compounds SrLnCuS₃ is 5.0 mol % CuLnS₂. The temperature dependence of the position of the solvus line as a function of composition is confirmed by the microstructure of aliquots of the samples. Inside all primary strontium sulfide grains, there are needle-like SrLnCuS₃ crystals that appeared during annealing as a result of the demixing of the SrS ss.

Below the incongruent decomposition temperature of SrLnCuS₃ in the region of 50–100 mol % SrS, phases SrLnCuS₃ and SrS are in equilibrium, and only reflections of these phases appear in the X-ray diffraction patterns of annealed samples. The similarity of the microstructure of aliquots of the samples with compositions in the range 50–100 mol % SrS confirms the incongruent melting of SrLnCuS₃. The samples contain chains of SrS grains in the background of crystals of the phase SrLnCuS₃, which is intrinsic to two-phase fields with a peritectic.

In the region of 0–50 mol % SrS, a eutectic is formed between the phases $CuLnS_2$ and $SrLnCuS_3$. The eutectic composition was determined from microstructure and DTA data. The coordinates of the eutectic formed between $CuLaS_2$ and $SrLaCuS_3$ are 21.0 mol % SrS, T = 1345 K; for the eutectic between $CuNdS_2$ and SrNdCuS₃, the coordinates are 31.0 mol % SrS, T = 1310 K. A characteristic feature of the system $CuLaS_2$ -SrS is the closeness of the temperature of the eutectic between phases $CuLaS_2$ and $SrLaCuS_3$ (1345 K) and the incongruent-decomposition temperature of the phase $SrLaCuS_3(1365 \text{ K})$. Microstructurally, the eutectic between $CuLaS_2$ and $SrLaCuS_3$ appears as an alternation of oval crystals of the conjugate phases $10-20 \ \mu\text{m}$ in size. The eutectic between the phases $CuNdS_2$ and $SrNdCuS_3$ consists of coarse grains both in annealed samples and in those cooled from melt. The eutectic crystals of the phases $CuNdS_2$ and $SrNdCuS_3$ have an oval shape; their sizes are $60-80 \ \mu\text{m}$.

The DTA traces for all aliquots of the samples with compositions lying in the region $CuLnS_2$ -eutectic demonstrate a peak due to the melting of the eutectic and a peak due to the melting of primary gains of the compound $CuLnS_2$. The specific feature of the system $CuNdS_2$ -SrS is the diffuse character of the peaks associated with the melting of primary CuNdS₂ crystals. The cooling traces display well-defined peaks associated with the crystallization of primary CuNdS₂ grains. The liquidus temperatures are set equal to the arithmetic mean between the melting temperatures upon heating and the crystallization temperatures upon cooling.

The CuLnS₂-eutectic and eutectic–SrS liquidus lines consist of two branches, each built by fitting the experimental (DTA or DTA plus VPA) data to a second-order polynomial.

Visual polythermal analysis, to which the systems CuLnS₂–SrS were subjected in order to design parts of the eutectic–SrS liquidus line, confirms the incongruent melting character of SrLnCuS₃. The appearance of a liquid phase in aliquots was observed within a narrow



Fig. 3. Cu₂S–SrLaCuS₃ and Cu₂S–SrNdCuS₃ phase diagrams. For the notation, see Fig. 2.

range of temperatures and coincided with the DTA determinations of the melting temperature for the phase $SrLnCuS_3$.

The systems $CuLnS_2$ -SrS are partially quasi-binary joins of the triangles Cu_2S - Ln_2S_3 -SrS (Ln = La, Nd). The quasi-binary character of the joins is spoiled above the incongruent-melting temperature of $CuLaS_2$ and $CuNdS_2$. Below these temperatures, equilibrium in the systems $CuLnS_2$ -SrS involves the conjugate phases $CuLnS_2$ and $SrLnCuS_3$, and $SrLnCuS_3$ and SrS, respectively.

Thus, complex sulfides $SrLnCuS_3$ are formed in the systems $CuLnS_2$ –SrS. A eutectic is formed between the compounds $CuLnS_2$ and $SrLnCuS_3$. There is a limited solid-solution field on the base of SrS.

Joins Cu₂S–SrLaCuS₃ and Cu₂S–SrNdCuS₃

The system Cu₂S–SrLaCuS₃ (Fig. 3) is a partially quasi-binary join of the system SrS–Cu₂S–La₂S₃. Its quasi-binary character is spoiled near the compound SrLaCuS₃ above its incongruent melting temperature. A field SrS + *L* appears in the phase diagram, and a third phase (SrS) is observed in the microstructure of samples cooled from melt and containing more than 66.7 mol % SrLaCuS₃. After annealing at 750°C, SrS crystals disappear. At temperatures below the SrLaCuS₃ decomposition temperature, the starting phases Cu₂S and SrLaCuS₃ are in equilibrium. The X-ray diffraction patterns of samples annealed at 750 K display only reflections of α -Cu₂S and SrLaCuS₃.

The Cu_2S -SrLaCuS₃ system has a eutectic phase diagram with a limited Cu_2S -base solid solution. The

eutectic coordinates are as follows: 14.0 mol % SrLaCuS₃, T = 1075 K. The microstructure of a eutectic sample displays a eutectic mixture of needle-shaped crystals of Cu₂S and SrLaCuS₃. The eutectic grains are 20–40 µm long. The microstructure observations are confirmed by DTA results. Only one peak at 1075 K due to the melting of the eutectic is observed in the DTA trace for a sample containing 14.0 mol % SrLaCuS₃ in addition to the peak associated with the polymorphic transition α -Cu₂S \longleftrightarrow β -Cu₂S. The shape of this peak implies that in the phase diagram, melting is represented by invariant phase equilibrium.

All DTA traces for the annealed samples of the system Cu₂S-SrLaCuS₃ demonstrate a peak associated with the polymorphic transition α -Cu₂S $\leftrightarrow \beta$ -Cu₂S. The polymorphic-transition temperature decreases slightly from 376 to 370 K, proving the existence of a small field of Cu₂S-base solid solution. The insignificant extent of the solid solution makes microstructure observation difficult. However, we synthesized a sample containing 1.0 mol % SrLaCuS₃ in which needleshaped SrLaCuS₃ crystals have larger sizes than eutectic crystals and are uniformly distributed over the sample. The sizes and distribution of SrLaCuS₃ grains imply that the grains were formed upon the demixing of the primary solid Cu₂S-base solution. The DTA peak associated with the eutectoid transformation β -Cu₂Sss + SrLaCuS₃ $\leftrightarrow \gamma$ -Cu₂S ss is detected at 620 K only in an aliquot of the sample that contains 1.0 mol % SrLaCuS₃. The value of this peak only insignificantly differs from the noise level; this eutectoid transformation is indicated by a dashed line in the diagram.

The liquidus branch from the eutectic to the melting point of Cu_2S is drawn through two intermediate points.

The phase diagrams are designed on the basis of consistent results of independent physicochemical methods, and we consider them adequate. The similarity of phase equilibria in the systems $SrS-Cu_2S-La_2S_3$ and SrS-Cu₂S-Nd₂S₃ is due to the fact that lanthanum and neodymium belong to one tetrad: isostructural compounds SrLaCuS₃ and SrNdCuS₃ are formed in these systems, and the phase diagrams of partially quasi-binary systems are alike.

The trend of the line is nearly linear. The liquidus line between the eutectic and SrLaCuS₃ consists of two

branches, which meet at the incongruent-melting tem-

perature of SrLaCuS₃ (at 1365 K). The branches are the

second-order-polynomial best-fit curves obtained for

the DTA data (until the curves meet the peritectic horizontal of SrLaCuS₃) and DTA and VPTA data (from the

meeting with the peritectic horizontal to the SrLaCuS₃

ilar to the Cu₂S–SrLaCuS₃ phase diagram. A eutectic is formed between phases Cu₂S and SrNdCuS₃; its com-

position, derived from MS and DTA data, is set equal to

8.0 mol % SrNdCuS₃; T = 1055 K. This system is a par-

tial quasi-binary join of the ternary system SrS-Cu₂S-

Nd₂S₃, thanks to the incongruent melting of SrNdCuS₃.

The Cu₂S–SrNdCuS₃ phase diagram (Fig. 3) is sim-

line).

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