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*PHASE EQUILIBRIA IN THE BaF2 — SmSF SECTION OF THE BaF2-SmF3-Sm2S3-BaS QUADRANGLE**

SUMMARY. The X-ray and microstructural analyses of the samples of the BaF_2 — SmSF section located in the irregular BaF_2–SmF_3–Sm_2S_3–BaS quadrangle are carried out. When the SmSF content changes, the phase composition of samples in the section also changes. Six areas are identified in the section according to the phase composition of the samples. The phases of nonstoichiometric composition are formed in the BaF_2 — SmSF section based on barium fluoride: $Ba_{1-x}Sm_xF_{2+x}$ of 25 mol.% SmSF is replaced by the phase of the $Ba_{4\pm x}Sm_{3\pm x}F_{17\pm x}$ composition. The increase in the concentration of samarium ions results in the monotonic decrease in the cube cell parameters of the nonstoichiometric phases. It is discovered that a phase of unknown composition is formed in the samples of BaF_2— SmSF from 25 to 55 mol.% SmSF section of 25-55 mol.% SmSF. It is supposed that there are cations and anions of two types in the compound and, on the basis of this compound, the solid solution area is formed. The further study of the BaF_2_SmF_3_Sm_2S_3_BaS quadrangle is required to determine the composition and structure of the compounds formed. The $BaSm_2S_2F_4$ compound is not formed in this section. In the BaF_2 — SmSF section, the BaS, TP $Ba_{1-x}SmxF_{2+x}$, TP $Ba_{4\pm x}Sm_{3\pm x}F_{17\pm x}$, Sm_3S_4 compounds are in equilibrium with the compounds of unknown composition located in different areas of the tetrahedron; therefore, the section is not a quasi-binary cut of the quadrangle. The approximate positions of the conoids in the BaF_2-SmF_3-Sm_2S_3_BaS quadrangle and the area of the unknown composition phase are registered.

KEY WORDS. Phase equilibria, complex $A^{II}Sm_2S_2F_4$ (A^{II}= Ca, Sr, Ba) fluorosulfides.

The AIISm$_2$S$_2$F$_4$ compounds are formed in the $A^{II}F_2$ – SmSF (A^{II} = Ca, Sr) systems at the initial ratio of 1 $A^{II}F_2$: 2 SmSF. The $A^{II}Sm_2S_2F_4$ compounds crystallize in the tetragonal system of the PbFCl structure type (the I4/mmm space group), and melt congruently: $CaSm_2S_2F_4$ a = 0.3916, c = 1.9250, T_{melt}. = 1,620 K; $SrSm_2S_2F_4$ a = 0.3997, c = 1.9480, T_{melt}. =1,625 K [1-4]. The quasibinary sections are distinguished in the Ba–Sm–F–S tetrahedron, the BaF_2, BaS, SmF_3, and Sm_2S_3 compounds are the vertexes of the BaS–BaF_2–SmF_3–Sm_2S_3 irregular quadrangle (Fig.1). The compositions of the initial and forming compounds are coplanar. The BaF_2 compound of the cubic system,

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CaF_2 structure type (ST), the Fm3m space group, with the following parameter of unit cell (u.c.): a = 0.6200 nm, melts congruently at 1,641 K. BaS of the cubic system (NaCl - ST, the Fm3m space group), melts congruently at 2,502 K. SmF3 crystallizes in the orthorhombic system (β–YF_3 - ST, the Pnma space group) and melts congruently at 1,578 K. Sm_2S_3 of the cubic system (high-temperature γ-modification, Th_3P_4 - ST, the I43d space group), melts congruently at 2,200 K. SmSF of the tetragonal system (PbFCl - ST, the P4/nmm space group), melts congruently at 1,695 K. $BaSm_2S_4$ of the orthorhombic system ($CaFe_2O_4$ –ST, the Pnam space group), melts congruently at 1,990 K [5-7].

The ionic radii ratios of alkaline-earth elements (for the coordination number of 8, rCa^{2+} = 0.112 nm, rSr^{2+} = 0.126 nm, rBa^{2+} = 0.142 nm [8]) suggest that the compounds of the $BaLn_2S_2F_4$ composition are likely to be formed in the BaF_2 – LnSF systems. There are no data published on the investigation of the BaF_2 – SmSF system and the phase diagram construction. The BaF_2 – SmSF system generates interest in the formability of a new $BaSm_2S_2F_4$ compound, consisting of both cations and anions of two types, which provides its potential use in optical instrument-making and laser technology.

The purpose of this research is to study the phase equilibria in the BaS–BaF_2–SmF_3–Sm_2S_3 system, the BaF_2 – SmSF section.

The experiment and data processing. The commercial BaF_2 powder of extra pure grade and the SmSF compound obtained by standard methods [1], [4], were used as original substances, the second sample set of the predetermined composition in the BaF_2 – SmSF system was prepared from the SmSF powder synthesized by the technique [9]. To produce SmSF, the SmF_3 powder produced by the technique [10-11] and the Sm_2S_3 powder synthesized from the commercial Sm_2O_3 oxide of the SmO-L type in H_2S and CS_2 sulfidizing gas flow by the standard technique [12] were used. To remove hygroscopic water, the BaF_2 powder was thermally processed in the fluoridizing atmosphere of teflon pyrolysis products at 773 K [13].

The samples of the predetermined compositions were obtained by melting the original component mixture (BaF_2 and SmSF) in the black-lead crucibles in the re-vacuumized quartz argon-filled reactors with induction heating. The substances were threefold melted, however, they were not heated 15–20 K higher than the complete melting temperature for the sample. The samples were annealed in the vacuum-sealed quartz ampoules at 973 K. The annealing time was experimentally determined: the samples from different annealing stages were hardened and analyzed by the microstructure, durometric, and X-ray phase methods. The total annealing time of the samples was 5,500 hours.

The X-ray phase analysis (RPA) was carried out using the *DRON-7* diffractometer (the CuKα-radiation, the Ni-filter). The parameters for the u.c. phases were calculated using the *PDWin-4, Powder-2* software, within the accuracy of 0.001-0.0005 nm for the orthorhombic system, and within the accuracy of 0.0001 nm for the cubic system. The microstructure analysis (MSA) was carried out using the *METAM LV-1* microscope.

The results and discussion. To study the phase equilibria in the BaF_2 — SmSF system, 11 samples of various compositions (Table 1) were synthesized. A total of 24 test samples were studied by the complex of physicochemical methods.

Table 1

Chemical and phase composition of the melted samples of the BaF_2–SmSF system annealed at 973 K during 5,500 hours

Chemical composition, mol.%			Phase composition		
Sample No.	BaF_2	SmSF			
3	95	5	$Ba_{1-x}Sm_xF_{2+x}$	BaS	
4	90	10	$Ba_{1-x}Sm_xF_{2+x}$	BaS	X*
5	75	25	$Ba_{1-x}Sm_xF_{2+x}$	$Ba_{4\pm x}Sm_{3\pm}xF_{17\pm x}$	X*
6	60	40		$Ba_{4\pm}xSm_{3\pm}xF_{17\pm x}$	X*
11	55	45		$Ba_{4\pm}xSm_{3\pm}xF_{17\pm x}$	X*

*) X-phase of unknown composition

Chemical composition, mol.%			Phase composition			
Sample No.	BaF_2	SmSF				
1	50	50	$Ba_{4\pm}xSm_{3\pm}xF_{17\pm x}$	X*	$BaSm_2S_4$	
8	45	55	$Ba_{4\pm x}Sm_{3\pm x}F_{17\pm x}$	X*	$BaSm_2S_4$	
9	40	60	$Ba_{4\pm x}Sm_{3\pm x}F_{17\pm x}$	SmSF	$BaSm_2S_4$	
2	33.3	66.7	$Ba_{4\pm x}Sm_{3\pm x}F_{17\pm x}$	SmSF	$BaSm_2S_4$	
7	20	80	$Ba_{4\pm x}Sm_{3\pm x}F_{17\pm x}$	SmSF	$BaSm_2S_4$	
10	10	90	$Ba_{4\pm x}Sm_{3\pm x}F_{17\pm x}$	SmSF	$BaSm_2S_4$	Sm_3S_4

The BaF_2 — SmSF section is located in the BaF_2— SmF_3— Sm_2S_3— BaS irregular quadrangle (Fig. 1A). According to the RPA and MSA data, the compounds located in different areas of the tetrahedron are in equilibrium in the BaF_2— SmSF section (Table 1), therefore, the BaF_2— SmSF section is not a quasibinary one of the quadrangle.

As the SmSF content changes, the phase composition of the system samples also does. Six areas should be distinguished according to the phase composition of the samples in the section (Table 1).

According to the data in [14], an open barium fluoride solid solution (SS) range with the compounds of nonstoichiometric compositions, $Ba_{1-x}Sm_xF_{2+x}$ and $Ba_{4\pm x}Sm_{3\pm x}F_{17\pm x}$, are formed in the BaF_2 — SmF_3 system, therefore, these compounds are formed in the BaF_2 — SmSF section under study.

According to the RPA and MSA data, the SmSF samples containing 5, 10 mol.% are two-phase. The BaS and $Ba_{1-x}Sm_xF_{2+x}$ compounds are in equilibrium in the 5, 10 mol.% SmSF samples, Fig. 1A demonstrates probable conoid positions marked with a dashed line between these compounds (the horizontal interval joining phase compositions, being in equilibrium).

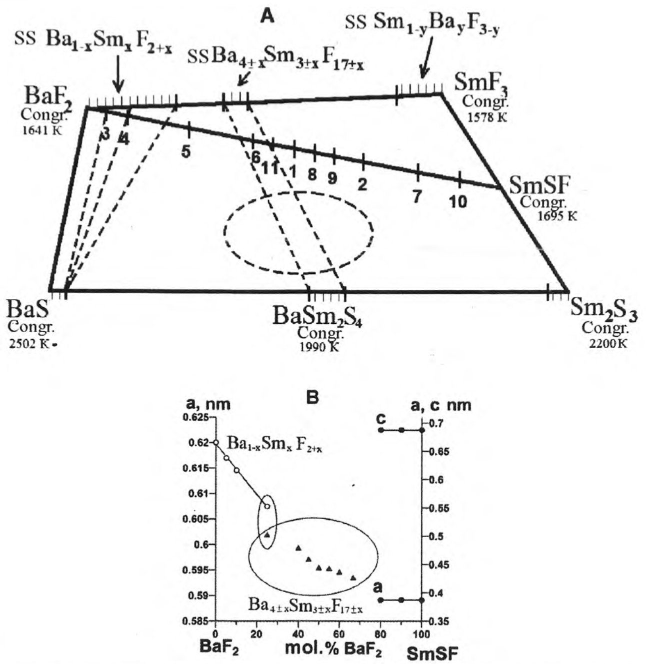

Fig. 1. A — the $BaS–BaF_2–LaF_3–La_2S_3$ quadrangle in the plane. The phase composition of the quadrangle quasibinary sections at the temperature of 973 K [6], [7], [14]. The compound homogeneity areas are hatched. The conoid position and the new X phase area are marked with a dashed line;
B — The dependence of the composition on the unit cell parameters for the samples of the BaF_2 – SmSF system annealed at 973 K during 5,500 hours.

The compound having a defect fluorite structure of the $Ba_{1-x}Sm_xF_{2+x}$ composition is formed in the samples containing 5, 10, 25 mol.% BaF_2-based SmSF. The increase in samarium ion concentration (for the coordinate number of 8 rBa^{2+} = 0.142 nm, rSm^{3+}=0.1079 nm [6]) results in monotonic decreasing the cubic u.c. parameter from 0.6200 nm to 0.6075 nm at 25 mol.% SmSF (Fig. 1B).

According to the RPA data, the $Ba_{1-x}Sm_xF_{2+x}$ SS reflexes split in the sample containing 25 mol.% SmSF. In this sample, there are two solid solutions with the fluorite-derivative structure: SS of $Ba_{1-x}Sm_xF_{2+x}$ (a = 0.6075 nm) and SS of $Ba_{4\pm x}Sm_{3\pm x}F_{17\pm x}$ (a = 0.6018 nm). The solid solution of $Ba_{4\pm x}Sm_{3\pm x}F_{17\pm x}$ composition is formed both in the cooled melt and annealed samples in the whole range of compositions under investigation: from 25 to 90 mol.% SmSF. As the samarium ion concentration increases, the cubic u.c. parameter monotonically decreases from 0.6018 nm in the sample with 25 mol.% SmSF to 0.5934 nm in the sample with 66.6(6) mol.% SmSF. The minimum parameter spread for the $Ba_{4\pm x}Sm_{3\pm x}F_{17\pm x}$ SS u.c. (0.0008 nm spread) is obtained in the range from 50 to 60 mol.% SmSF, the perfect formula for $Ba_4Sm_3F_{17}$ compounds may be obtained in these compositions (Fig. 1B).

The change in the BaF_2-based SS grains is observed in the microstructure of 5–90 mol.% SmSF samples: the $Ba_{1-x}Sm_xF_{2+x}$ grains are brown in reflected light; while forming $Ba_{4\pm x}Sm_{3\pm x}F_{17\pm x}$, the grains become dark-brown. The primary dark brown oval grains of the $Ba_{4\pm x}Sm_{3\pm x}F_{17\pm x}$ compound are observed in the samples containing 25-55 mol.% SmSF. As the samarium ion concentration increases, the primary grains decrease and the substance passes into a fine-grained eutectic mixture in the samples of 60–90 mol.% SmSF composition.

In the samples containing 25-55 mol.% SmSF, the BaF_2-based solid solutions and a compound of unknown composition are in equilibrium. The sample of 40 mol.% SmSF is two-phase. According to the RPA data, the reflexes belonging to the $Ba_{4\pm x}Sm_{3\pm x}F_{17\pm x}$ SS are distinguished, the other reflexes are not indicated, the diffraction pattern demonstrates the position of the reflexes of the unknown composition phase (Fig. 2). Depending on the SmSF contents, the reflexes are shifted from the specified positions, so we suppose that the new compound consists of cations and anions of two types, and a solid solution based on this compound is formed. To determine the composition and structure of the newly-formed compound, the advanced study of the BaF_2–SmF_3–Sm_2S_3–BaS quadrangle is required. The area where the new phase may exist and the probable conoids between the $Ba_{4\pm x}Sm_{3\pm x}F_{17\pm x}$ SS and the new phase are distinguished in the quadrangle (Fig. 1A).

Occasional primary dark-brown oval grains (5-10 μm in size) of the $Ba_{4\pm x}Sm_{3\pm x}F_{17\pm x}$ SS and light-brown oval grains of the unknown compound occur in the microstructure of the sample containing 40 mol.% SmSF. The bulk of the sample is eutectic mixture between these compounds (Fig. 3A). In the samples containing 50–55 mol.% SmSF, the number of the dark-brown $Ba_{4\pm x}Sm_{3\pm x}F_{17\pm x}$ grains decreases, the unknown phase content increases, and, according to the RPA data, the fine bright-yellow oval grains forming thin prolate clusters over the entire sample surface appear. As the SmSF content increases, so does the $BaSm_2S_4$ phase in the samples.

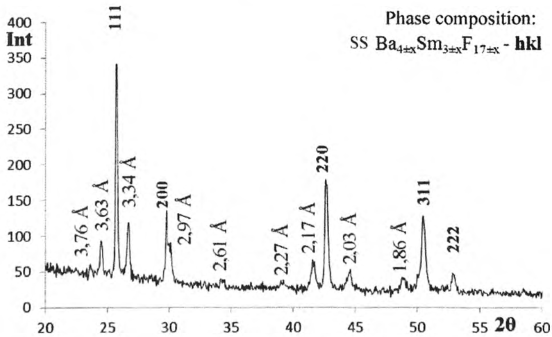

Fig. 2. The diffraction pattern of the 60 mol.% BaF_2 — 40 mol.% SmSF sample annealed at 973 K during 5,500 hours. The reflexes the positions of which are indicated in Å belong to the phase of an unknown composition. The case: Cu K_α — radiation, Ni — filter.

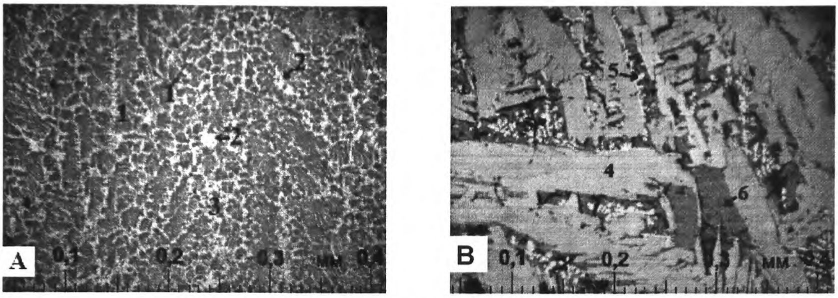

Fig. 3. The microstructure photos of the BaF_2 — SmSF system samples annealed at 973 K during 5,500 hours.
A — 40 mol.% SmSF; B — 90 mol.% SmSF. The phases existing in the system: 1 — the BaF_2 –based SS of the $Ba_{4\pm x}Sm_{3\pm x}F_{17\pm x}$ composition; 2 — the phase of an unknown composition; 3 — the eutectic mixture of the $Ba_4\pm xSm_{3\pm x}F_{17\pm x}$ grains and the unknown phase; 4 — SmSF; 5 — Sm_3S_4; 6 — the eutectic formed by the crystals of the $Ba_{4\pm x}Sm_{3\pm x}F_{17\pm x}$ and $BaSm_2S_4$ phases

The samples containing 60–80 mol% SmSF, are three-phase and similar to each other. According to the RPA data, three phases are in equilibrium: SS of the $Ba_{4\pm x}Sm_{3\pm x}F_{17\pm x}$, $BaSm_2S_4$, and SmSF composition. When the ratio of the original components is 1 BaF_2 to 2 SmSF, the $BaSm_2S_2F_4$ compounds are not formed. The samples containing 66.6(6) mol.% SmSF crystallized from a melt and annealed at 973 K have no reflexes, which can be referred to the $BaSm_2S_2F_4$ phase during the assignment of indices. The long-time annealing at 973 K results in no change in the sample phase composition. When the microstructure is analyzed, three phases are also found in these samples, the nature of microstructure is similar over the whole range from 60 to 80 mol.% SmSF. The microstructure of the 60 mol.% SmSF sample is presented as a fine-grained eutectic mixture of the dark-brown crystals of the $Ba_{4\pm x}Sm_{3\pm x}F_{17\pm x}$ SS and yellow ones of the $BaSm_2S_4$ compound, in which the occasional prolate yellow SmSF grains appear. While the SmSF content increases, the increase in the primary samarium fluorosulfide grains and the regular decrease in the eutectic crystal number occur.

The sample, containing 90 mol.% SmSF, is four-phase. According to the RPA data, there are such phases as: SmSF, $BaSm_2S_4$, Sm_3S_4 and $Ba_{4\pm x}Sm_{3\pm x}F_{17\pm x}$ SS. The sample microstructure is presented as coarse elongate yellow crystals of SmSF, clusters of bright-yellow grains ((5–10)x5 μm in size) of Sm_3S_4, which also form a thin film on the surface of SmSF crystals, passing into the oval grains of Sm_3S_4, and as the fine-grained eutectic between the $BaSm_2S_4$ compounds and the nonstoichiometric $Ba_{4\pm x}Sm_{3\pm}xF_{17\pm x}$ phase. The formation of Sm_3S_4 compound located in the Ba–Sm–F–S tetrahedron indicates a shift of equilibrium toward the Sm_3S_4 — Sm_2S_3 solid solution.

The SmSF phase u.c. parameter for the samples containing 80 – 90 mol.% SmSF, does not change (Fig. 1B). The SmSF-based solid solution is not formed in the system.

The BaF_2 – SmSF section is not a quasibinary one of BaS–BaF_2–Sm_2S_3–SmF_3 tetrahedron, as in the system, the $BaSm_2S_4$, BaS, SS $Ba_{1-x}Sm_xF_{2+x}$, SS $Ba_{4\pm x}Sm_{3\pm x}F_{17\pm x}$, Sm_3S_4 compounds located in different areas of the tetrahedron are in equilibrium.

Conclusion. The stable phases are formed in the BaF_2 – SmSF system: SS of $Ba_{4\pm x}Sm_{3\pm x}F_{17\pm x}$, $BaSm_2S_4$ and compounds of unknown composition, which results in adding complexity to the interaction in the BaF_2–SmSF system against the $A^{II}F_2$ — SmSF (A^{II} = Ca, Sr) systems and the non-occurrence of the $BaSm_2S_2F_4$ compound in this section. The possible location of conoids in the BaF_2–SmF_3–Sm_2S_3–BaS quadrangle and the area where the phase of an unknown composition may occur are suggested.

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