Phase Equilibria in the MgS–In$_2$S$_3$ System

A. V. Kertman
Tyumen State University, Tyumen, 625003 Russia
e-mail: akertman@utmn.ru
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Abstract—Phase equilibria in the MgS–In$_2$S$_3$ system were studied. This system is of the dystectic type with a limited region of a solid solution based on β-In$_2$S$_3$. In the MgS–In$_2$S$_3$ system, a compound of the composition MgIn$_2$S$_4$ forms, which forms congruently at 1 180 K and crystallizes in the cubic system (space group Fd$3$m) with the unit cell parameter $a = 1.0689$ nm. Eutectics have the compositions 47 and 62 mol % In$_2$S$_3$ and the melting points 1150 and 1120 K, respectively. The MgS solubility in β-In$_2$S$_3$ at 1070 K reaches 9 mol % MgS.

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Sulfides of composition AIn$_2$S$_4$ (where A is an alkaline-earth metal), which form in the AS–In$_2$S$_3$ systems and are the closest analogs of indium sesquisulfide, are of scientific and practical interest. These ternary compounds have practically promising optical and electrophysical properties [1].

Phase equilibria in the MgS–In$_2$S$_3$ system have not been studied before. There are literature data that, in the system at an equimolar ratio between the initial sulfides, there exists a phase of the composition MgIn$_2$S$_4$, which crystallizes in the cubic system (space group Fd$3$m) with the unit cell parameter $a = 1.0615$ nm [2]. The melting point and nature of melting of MgIn$_2$S$_4$ were not determined. Magnesium sulfide MgS crystallizes in the NaCl-type cubic lattice with the unit cell parameter $a = 0.5190$ nm and melts congruently at 2200 K [3] or 2270 K [4]. The congruent melting point of In$_2$S$_3$ is 1360 K [5]. The compound exists in two polymorphic modifications: the low-temperature modification α-In$_2$S$_3$ has a cubic sphalerite structure with the unit cell parameter $a = 0.5360$ nm and a disordered arrangement of vacancies and, at 570 K, transforms to the high-temperature modification β-In$_2$S$_3$, which crystallizes in the tetragonal system (space group I$4$/amd) with the unit cell parameters $a = 0.762$ and $c = 3.232$ nm [6]. It was reported [6] that the β-modification of In$_2$S$_3$ can be considered a quaternary compound that comprises indium atoms, sulfur atoms, and ordered vacancies in voids in the cell.

The purpose of this work was to study the MgS–In$_2$S$_3$ system by physicochemical analysis methods and construct its phase diagram.

EXPERIMENTAL

The initial binary sulfides MgS and In$_2$S$_3$ were synthesized according to standard procedures [3, 7] and identified by chemical and X-ray powder diffraction analyses. Ternary samples were obtained by melting the corresponding mixtures of powders of the initial sulfides in a sulfur vapor with subsequent homogenizing annealing in quartz ampules that were evacuated to a residual pressure of 0.1–0.01 Pa and sealed. The homogenizing annealing was carried out in two isothermal sections at 1070 and 870 K. The annealing times were 700 and 1000 h, respectively, which ensured reaching the equilibrium state of the samples.

The X-ray powder diffraction analysis of the obtained samples was made with a DRON-6 X-ray diffractometer (CuK$_\alpha$ radiation, Ni filter). The recording was calibrated using a single-crystalline silicon powder. The unit cell parameters of MgS in two-phase samples were determined from reflections within the angle 2$\theta$ range 120°–150° with an accuracy of ±0.0001 nm; and for the β-phase of In$_2$S$_3$, from near angles to 2$\theta$ = 60°–80° with an accuracy of ±0.001 nm using the POWDER2 software and data of the PDF-2 database.

Microstructural analysis and phase microhardness measurements were performed on polished and etched sections according to standard procedures with a METAM PB–22 metallographic microscope and PMT-3M microhardness meter, respectively.

Differential thermal analysis and visual thermal analysis were conducted on setups with VR 5/20 and PP-1 thermocouples, respectively. The signals from the thermocouples were converted by analog-to-digital converters of the ADAM type and recorded with a computer. The errors in determining temperature by differential and visual thermal analyses were 0.4 and
0.7% of a measured value, respectively. The phase transition temperatures were determined using a complex of computer programs.

RESULTS AND DISCUSSION
The phase diagram of the MgS–In$_2$S$_3$ system was constructed using a set of physicochemical analysis methods (Fig. 1). The diagram is characterized by the presence of a congruently melting compound of the composition MgIn$_2$S$_4$, which forms eutectics with the initial sulfides $\beta$-In$_2$S$_3$ and MgS.

The fact that the sample obtained by melting and annealing equimolar amounts of magnesium and indium sulfides consists of a single phase was proven by X-ray powder diffraction and microstructural analyses. The X-ray powder diffraction pattern of a sample comprising 50 mol % MgS and 50 mol % In$_2$S$_3$ shows reflections of the phase MgIn$_2$S$_4$ crystallizing in the cubic system (space group $Fd\bar{3}m$) (Fig. 2a). The unit cell parameter is $a = 1.0689$ nm. No reflections of either the phases MgS or $\beta$-In$_2$S$_3$, or the other polymorphic modifications of In$_2$S$_3$ were detected. The microstructure of the sample of this composition is represented by a uniform light-yellow field without foreign inclusions. The melting point of the phase MgIn$_2$S$_4$ as determined by reconciling the results of the differential and visual thermal analyses is 1180 K.

The line describing the phase MgIn$_2$S$_4$ divides the state diagram into two subordinate systems, MgS–MgIn$_2$S$_4$ and MgIn$_2$S$_4$–In$_2$S$_3$.

The MgS–MgIn$_2$S$_4$ subsystem is of the eutectic type and shows no solubility based on the initial compounds. The eutectic is a finely divided mixture of crystals of two phases being in equilibrium and complies with the most universally accepted notions. The composition of the eutectic is 47 mol % In$_2$S$_3$, and its melting point is 1150 K. According to the X-ray powder diffraction analysis data, all the samples obtained in the MgS–MgIn$_2$S$_4$ subsystem within the range 0–50 mol % In$_2$S$_3$ are two-phase, and there are reflections of the phases MgS and MgIn$_2$S$_4$ (Fig. 2b). The unit cell parameters and microhardnesses of MgS and MgIn$_2$S$_4$ in the two-phase samples did not change with varying composition and were $a = 0.5200$ nm and $H = 3500$ MPa for MgS and $a = 1.0689$ nm and $H = 3000$ MPa for MgIn$_2$S$_4$ (Figs. 3 and 4), which suggests