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System $SrGa_2S_4$–$LaGaS_3$

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Abstract—Phase relations in the $SrGa_2S_4$–$LaGaS_3$ system were studied by physicochemical analysis, and the $SrGa_2S_4$–$LaGaS_3$ phase diagram was mapped out. The system was found to contain the quaternary compound $SrLaGa_3S_7$, which melts congruently at 1290 K and has a tetragonal structure. The composition ranges of the $SrGa_2S_4$- and $SrLaGa_3S_7$-based solid solutions were determined.

In earlier studies [1, 2], the $EuGa_2S_4$–$LaGaS_3$ and $CaGa_2S_4$–$LaGaS_3$ systems were found to contain quaternary compounds with the $MLaGa_3S_7$ stoichiometry, These compounds were shown to be wide-gap *p*-type semiconductors [3]. $CaLaGa_3S_7$ has a tetragonal structure with $a = 9.50$ Å and $c = 6.16$ Å [4].

In this communication, we report our results on the $SrGa_2S_4$–$LaGaS_3$ system.

$SrGa_2S_4$ (S_1) is known to crystallize in the orthorhombic system with $a = 20.64$ Å, $b = 20.49$ Å, and $c = 12.21$ Å ($\rho_{meas} = 3.62$ g/cm^3, $\rho_x = 3.64$ g/cm^3) [5]. $LaGaS_3$ (S_4) has a monoclinic structure with $a = 10.33$ Å, $b = 12.82$ Å, $c = 10.56$ Å, and $\gamma = 98.90°$ ($\rho_{meas} = 4.32$ g/cm^3, $\rho_x = 4.35$ g/cm^3) [6, 7].

According to Petere and Baglie [8], $SrGa_2S_4$ melts congruently at 1400 K. $LaGaS_3$ was reported to form peritectically [7].

In our preparations, $SrGa_2S_4$ and $LaGaS_3$ were presynthesized from SrS, Ga_2S_3, and La_2S_3. Quaternary alloys were prepared by reacting appropriate mixtures at 1200 K for 8–10 h in evacuated quartz tubes, followed by homogenization at 900–950 K for 130–135 h, depending on composition. The samples ranged in color from yellow to yellow-orange.

The alloys were characterized by differential thermal analysis (NTR-70 unit), x-ray diffraction (DRON-3 powder diffractometer, CuK_α radiation), microstructural analysis (MIM-7 optical microscope), microhardness tests, and density measurements.

The temperature was measured with an accuracy of ±5 K. Lattice parameters were determined to within ±0.01 Å. The accuracy in density and microhardness measurements was ±10% or better.

Microstructural examination showed that the melted alloys containing 0–4 and 47–54 mol % $LaGaS_3$ were single-phase, with sharp grain boundaries (Fig. 1). The other alloys were two-phase. The same was evidenced by microhardness measurements: the measured microhardness values were found to fall in three distinct ranges, 3000–3120, 2740–2890, and 3090–3130 MPa, corresponding to the α-phase ($SrGa_2S_4$-based solid solution), β-phase ($SrLaGa_3S_7$-based solid solution), and $LaGaS_3$.

The $SrGa_2S_4$–$LaGaS_3$ phase diagram constructed on the basis of the present results is displayed in Fig. 2b. The system contains the quaternary compound $SrLaGa_3S_7$ (S_2) and narrow composition ranges of the α- and β-phases. $SrLaGa_3S_7$ melts congruently at 1293 K.

The $SrGa_2S_4$–$LaGaS_3$ phase diagram can be regarded as consisting of two partial phase diagrams: $SrGa_2S_4$–$SrLaGa_3S_7$ and $SrLaGa_3S_7$–$LaGaS_3$. $SrGa_2S_4$ and $SrLaGa_3S_7$ form a eutectic at 25 mol % $LaGaS_3$ with the melting point at 1010 K. The composition range of the α-phase extends to 10 mol % $LaGaS_3$ at 1010 K. With decreasing temperature, the solubility of $SrLaGa_3S_7$ in $SrGa_2S_4$ decreases to 4 mol %, which leads to precipitation of the β-phase in the form of small platelets embedded in the α-phase matrix. $SrLaGa_3S_7$ exists in the composition range 47–54 mol % $LaGaS_3$ and has a tetragonal structure with $a = 9.45$–9.54 Å and $c = 6.14$–6.18 Å.

The $SrLaGa_3S_7$–$LaGaS_3$ join is nonpseudobinary, because of the incongruent melting of $LaGaS_3$. This

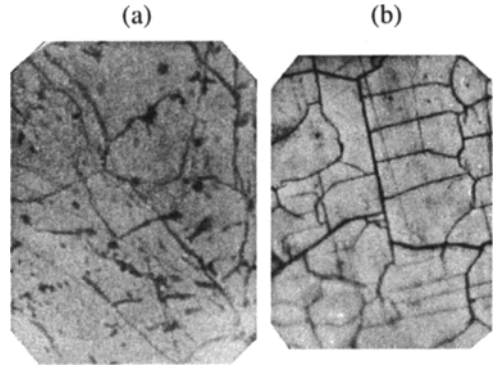

Fig. 1. Microstructures of $SrGa_2S_4$–$LaGaS_3$ alloys containing (a) 4 and (b) 50 mol % $LaGaS_3$; ×57.5.

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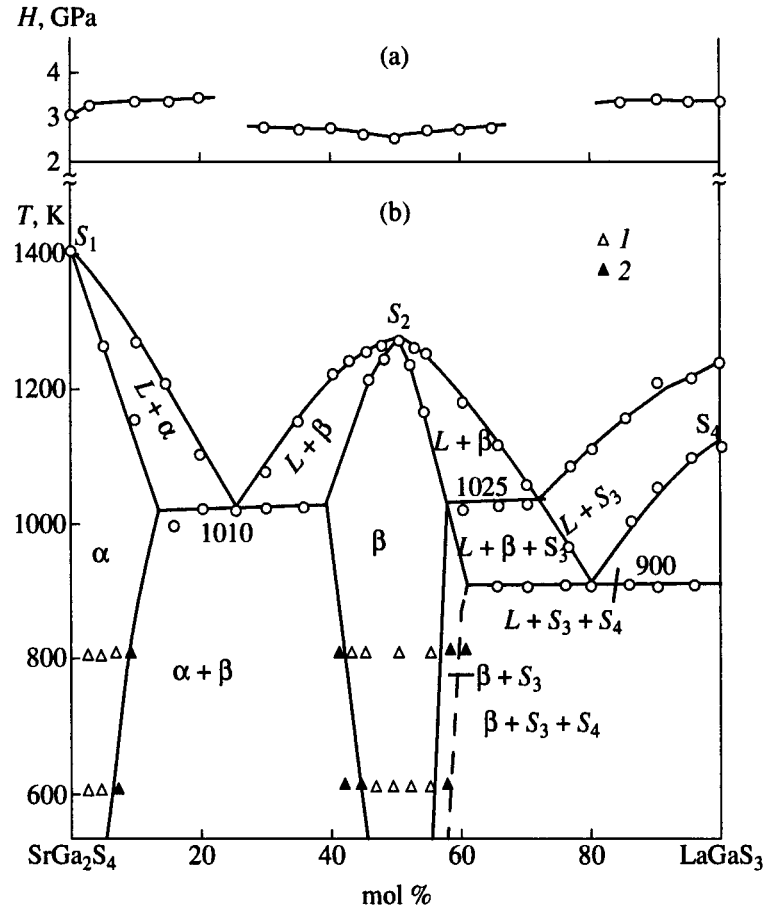

Fig. 2. (a) Composition dependence of microhardness; (b) $SrGa_2S_4$–$LaGaS_3$ phase diagram: (*1*) single-phase alloys, (*2*) two-phase alloys; $S_1 = SrGa_2S_4$, $S_2 = SrLaGa_3S_7$, $S_3 = La_6Ga_{10/3}S_{14}$, $S_4 = LaGaS_3$.

join intersects two primary-crystallization fields—those of the β-phase and $La_6Ga_{10/3}S_{14}$. The corresponding branches of the liquidus intersect at 71.5 mol % $LaGaS_3$ (1025 K). The primary crystallization of S_3 is followed by the three-phase peritectic reaction $L + S_3 = S_4$.

Note that, in the composition range 70–100 mol % $SrGa_2S_4$, liquid quenching yielded glassy alloys. The DTA curves of these alloys showed prominent endotherms between 840 and 850 K. According to DTA data, the glass-transition temperature of the $SrGa_2S_4$-rich alloys rises from 820 to 830 K with increasing $SrLaGa_3S_7$ content. The glass of composition $SrGa_2S_4$ was found to crystallize most readily.

X-ray diffraction data demonstrate that $SrLaGa_3S_7$ is isostructural with $CaLaGa_3S_7$ and has a tetragonal structure with a = 9.54 Å and c = 6.18 Å (V = 562.45 Å^3, sp. gr. $P\bar{4}2_1m$, $Z = 2$).

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