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A new way of phase identification, of $AgGaGeS_4 \bullet nGeS_2$ crystals

R.E. Nikolaev *, I.G. Vasilyeva

Nikolaev Institute of Inorganic Chemistry, Siberian Branch of RAS, 630090 Novosibirsk, Russian Federation,

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ABSTRACT

The phase identification of $AgGaGeS_4 \cdot nGeS_2$ (n=0–4) crystals grown by vertical Bridgman–Stockbarger technique was carried out to find the boundary value n between a homogeneous solid solution and its mixture with GeS_2. To obtain reliable results, the conventional methods of X-ray diffraction (XRD) and energy dispersive X-ray spectroscopy (EDX) were completed by less common vapor pressure measurement in a closed volume and precise density measurements, which are very sensitive to the detection of small amounts of crystalline and glassy GeS_2 and heterogeneous state of the crystals. The boundary value n=1.5 at 1045 K and the coexistence of the solid solution $AgGaGeS_4 \cdot 1.5GeS_2$ with the β-GeS_2 phase for $n > 1.5$ was found. Glassy GeS_2 (~2 mol%) was revealed by vapor pressure measurement and XRD studies in all the crystals. This is discussed in terms of the supersaturated solid solution decomposition upon temperature decreasing and the microphase separation of overcooled melt near the melting point under non-equilibrium crystallization. For the first time, the p–T dependence for glassy GeS_2 was measured by the vapor pressure measurements.

1. Introduction

The solid solutions of $AgGaGeS_4 \cdot nGeS_2$ with related selenides are promising materials for quantum electronics, and their dispersive refractive indices and the transparency region depend strongly on the composition determined by the n value [1–10]. Much attention was drawn to the solubility of GeS_2 in $AgGaGeS_4$, which is a key factor for such materials, and different ways were used to determine it [11–13]. A conventional study of the $AgGaS_2$–GeS_2 section including $AgGaGeS_4$–GeS_2 as its component in the quasi-ternary system Ag_2S–Ga_2S_3–GeS_2 is performed by physical–chemical analysis. Using the same XRD technique, different results of the boundary of the homogeneity range for $AgGaGeS_4$ from GeS_2 side are reported [11–13]. In Ref. [11], $AgGaGeS_4$ is classified as a linear phase with n=0, in Ref. [12] the boundary composition is determined by n=0.22 that corresponds to 55 mol% GeS_2 in the $AgGaS_2$–GeS_2 section, and in Ref. [13] the respective values are n=3.88 and 83 mol% GeS_2. This disagreement is connected with a specific behavior of GeS_2: its volatility may change the given composition and GeS_2 may occur as glass or amorphous phase in compact or thin layered forms [14,15]. Both of the factors manifest during the non-equilibrium high-temperature crystallization from a melt depending on the temperature gradient and crystallization rate. The observation of non-crystalline GeS_2 embedded in the crystalline matrix of $AgGaGeS_4$ and GeS_2 phases is very difficult, and a new approach and new tools are required to determine precisely the total amount of GeS_2 in the crystals.

The present study is focused on a new way of phase identification of as-grown $AgGaGeS_4 \cdot nGeS_2$ (n=0–4) crystals to define exactly the highest n value provided the homogeneous solid solutions free of crystalline or amorphous GeS_2. For this purpose, XRD and EDX were supplemented with two less conventional methods. The vapor pressure measurement in a closed volume is very sensitive tool for the detection of small amounts of volatile GeS_2 and might distinguish GeS and the various forms of GeS_2 using the of p–T functions earlier reported for these phases [16,17]. Another tool intended for accurate density measurements is very sensitive to the crystal phase state [18]. Here, this technique was used to discriminate homogeneous state of the solid solutions from heterogeneous one with a small amount of the GeS_2 phase.

2. Experimental

2.1. Preparation

The $AgGaGeS_4 \cdot nGeS_2$ crystals with n=0–4 (or 50.0, 66.7, 75.0, 80.0 and 83.3 mol% GeS_2) were grown by the conventional vertical Bridgman–Stockbarger technique using high-purity Ge, Ga, Ag and S (all of semiconducting purity). Just before the crystal growth, the mixtures were melted and homogenized for several hours at the upper temperature of 1170 K, which is 30–50 K higher than the reported melting point of $AgGaGeS_4$ known from [12,13]. The growth was performed with the thermal gradient of 20 K/cm and

* Corresponding author. Fax:+7 383 330 94 89.
E-mail addresses: nikolaev@niic.nsc.ru, r.nikolaev@ngs.ru (R.E. Nikolaev).

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growth rate of 5 mm/d. All as-grown crystals were light yellow in color and quite uniform according to light optics, except the crystals containing 80.0 and 83.3 mol% GeS_2 which had inclusions. For the study, the 0.1–0.4 cm^3 (~1 g) portions without visible voids and cavities were cut from the initial part of bulk crystals.

2.2. Techniques

X-ray powder diffraction data were collected on a DRON-UM1 diffractometer (Burevestnik, USSR) employing Ni filtered Cu$K\alpha$ radiation with $\lambda = 1.54178$ Å, using the step width of 0.02°, a 2θ scanning range between 5° and 60°, and silicon as an external standard. Lattice constants were refined by the full-profile analysis of all reflections using Cell Program (version 03.12.2003); the initial structural data for $AgGaGeS_4$ were taken according to No. 20153-ICSD.

The microstructure and composition were determined on fresh chips of size ~50×60 μm^2 using a scanning electron microscope (SEM, JEOL JSM-6700F, Japan) coupled with an EX-23000 BU attachment at 15 kV.

Total pressure above the crystals was measured as a p–T dependence by the vapor pressure measurement with a quartz Bourdon gauge and membrane as a null-point instrument described in [16,19]. The gauge chamber was placed into a furnace with an isothermal profile (± 0.5 K), the vapor pressure was balanced by equal pressure of argon that was measured by U-shaped manometer with an accuracy of 0.1 Torr (1 Torr = 133.3 Pa), and readings were made through a km-8 type cathetometer. A step-by-step heating procedure was used to measure the temperature and vapor pressure with the accuracy of 2 K and 3 Torr, respectively. Before the vapor pressure measurement, membrane with a crystal was annealed at 523 K under 10^{-2} Torr vacuum to remove uncontrolled volatile species. The solid–vapor equilibrium was achieved when it was kept constant within 1 Torr/d.

The density of homogeneous crystals (d_{exp}) was measured with an accuracy of ≤0.01 g/cm^3 by hydrostatic weighing [18] and calculated by the equation:

$$d_{exp.} = \frac{m \times d_l}{m - m_l} \quad (1)$$

where d_l is the ethanol density; m and m_l are the weights of the crystal in the air and in ethanol.

For heterophase crystals, density is calculated by the equation:

$$d_{calc.} = d_1 \times \omega + d_2 \times (1-\omega) \quad (2)$$

where d_1 and d_2 are the densities of main (solid solution) and impurity GeS_2 phases, ω and $(1-\omega)$ are their mass fractions in the crystals of known total composition. Values required for the calculation were obtained in this study by XRD and vapor pressure measurements, whereas density of the crystalline and glassy GeS_2 was taken from the literature [15].

3. Results and discussion

EDX data for the examined $AgGaGeS_4 \cdot nGeS_2$ crystals are listed in Table 1. The difference between the nominal and real compositions was within a reasonable range (< 10 at%), further the nominal compositions are used. But it was important that the crystals were chemically homogeneous, without segments with the Ge and sulfur content higher than the average value. The color and transparency of the crystals containing 50–75 mol% GeS_2 pointed also at the homogeneous state. However, optical transparency for them is not a strong evidence of the single-phase state because glassy GeS_2 has the same range of transmission as $AgGaGeS_4$ crystals and its $E_g = 2.7$ eV is very close to $E_g = 2.78$ eV for the crystals.

Table 1
EDX composition of crystals.

Nominal composition	Content of elements, at%				Found composition
	Ag	Ga	Ge	S	
$AgGaGeS_4$	14.7	12.6	16.5	56.2	$Ag_{1.0}Ga_{0.9}Ge_{1.2}S_{4.0}$
$AgGaGe_2S_6$	10.3	9.6	21.0	59.2	$Ag_{1.0}Ga_{1.0}Ge_{2.1}S_{5.9}$
$AgGaGe_3S_8$	8.0	7.1	24.2	60.7	$Ag_{1.0}Ga_{0.9}Ge_{3.2}S_{7.9}$
$AgGaGe_4S_{10}$	6.9	5.2	27.8	60.2	$Ag_{1.1}Ga_{0.8}Ge_{4.4}S_{9.6}$
$AgGaGe_5S_{12}$	5.9	4.5	29.7	59.9	$Ag_{1.1}Ga_{0.9}Ge_{5.6}S_{11.4}$

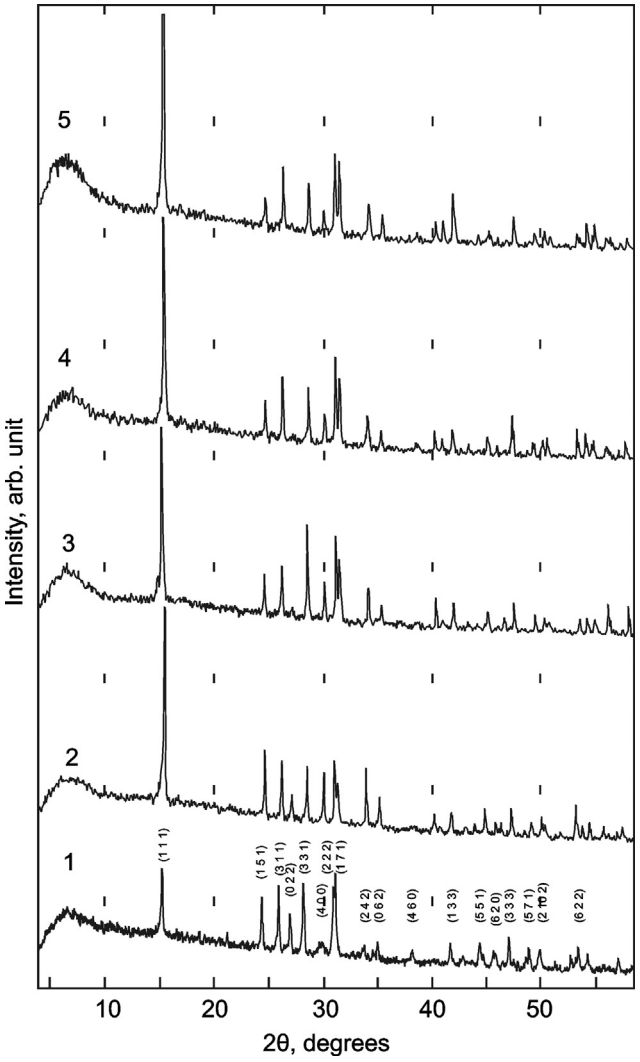

Fig. 1. Indexed powder XRD patterns of *Fdd*2 crystals $AgGaGeS_4 \cdot nGeS_2$: 1: $n=0$, 2: $n=1$, 3: $n=2$, 4: $n=3$, 5: $n=4$.

XRD patterns shown in Fig. 1 demonstrate the reflections characteristic of orthorhombic phase $AgGaGeS_4$ (No. 20153-ICSD), and the intense narrow peaks indicate the high crystallinity state of as-prepared crystals. However, the X-ray patterns vary with the increase of n. Indeed, intensity of the peaks at $2\theta = 15.3$, 31.4, 34.0, 40–41 and 44.9° rises, the peaks at $2\theta = 50$–51° split, and a broad peak of increasing area occurs at 5–10°. As to β-GeS_2, the characteristic peaks are absent in Fig. 1. There is only the peak intensity variation because the parameters of β-GeS_2 are very close