Phase Diagram of the TlGaSe$_2$–CuGaSe$_2$ System


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Abstract—The phase equilibria in the TlGaSe$_2$–CuGaSe$_2$ system are studied for the first time over the entire composition range using differential thermal analysis, x-ray diffraction, and conductivity measurements. The system is shown to contain TlGaSe$_2$ and CuGaSe$_2$-based solid solutions extending to 2 mol % CuGaSe$_2$ and 1.5 mol % TlGaSe$_2$, respectively.

INTRODUCTION

TlGaSe$_2$ and CuGaSe$_2$ belong to the III–III–VI$_2$ and I–III–VI$_2$ families of semiconductors and are of considerable practical interest as attractive materials for optoelectronic applications [1–16].

TlGaSe$_2$, a typical incomplete-valence semiconductor, has a specific crystal structure in which Ti$^+$ is in octahedral coordination, and Ga$_{3+}$ is in tetrahedral coordination [1–3].

CuGaSe$_2$ has the chalcopyrite structure, in which Cu and Ga form an ordered sublattice. The unit cell of CuGaSe$_2$ contains eight atoms (2Cu, 2Ga, and 4Se) and has a c/a ratio close to 2 [11, 12].

In this paper, we report phase relations in the TlGaSe$_2$–CuGaSe$_2$ system over the entire composition range.

EXPERIMENTAL

TlGaSe$_2$–CuGaSe$_2$ alloys were prepared from pre-synthesized TlGaSe$_2$ and CuGaSe$_2$. The starting chemicals used were 3N thallium, OSCh 11–4 copper, OSCh 17–4 selenium, and 3N gallium. To remove the oxide film and other contaminations, Cu was etched in 5% HNO$_3$ for 8–10 min and then washed with running distilled water. Thallium was distilled in vacuum.

Ampules (thick-walled silica, 25-mm inner diameter) were cleaned in 40% HF for 5 min, rinsed with distilled water, and then calcined in vacuum at 1400 K. The inner wall of the ampules was graphitized to prevent reaction with the melt. TlGaSe$_2$ and CuGaSe$_2$ were synthesized by reacting stoichiometric elemental mixtures at 1150 and 1450 K, respectively, for 5 h at a residual pressure of 10$^{-3}$ Pa in two-zone furnaces. The melt was homogenized by vigorous stirring. The TlGaSe$_2$ and CuGaSe$_2$ samples thus prepared were then equilibrated by annealing for 240 h at 1000 and 900 K, respectively.

The phase purity and homogeneity of TlGaSe$_2$ (dark cherry) and CuGaSe$_2$ (dark gray) were checked by differential thermal analysis (DTA) and x-ray diffraction (XRD).

TlGaSe$_2$–CuGaSe$_2$ samples (6 g) were prepared by a similar procedure.

DTA was carried out at a heating rate of $\pm 10^\circ$C/min using a programmed temperature controller [17], N-306 XY recorder, and high-sensitivity amplifier. The temperature was measured by PR-30/6 Pt/Pt–Rh thermocouples calibrated against the melting points of Bi, Pb, Se, Te, Sb, KCl, NaCl, Na$_2$SO$_4$, Ag, and Cu. The accuracy in temperature measurements was $\pm 5^\circ$C. The samples (1 g) were sealed under vacuum in silica Stepanov vessels 5 mm in inner diameter. As a reference substance, we used calcined alumina.

Electrical resistivity was measured using Shch 31 and V7–30 multirange voltmeters with an accuracy of 0.05 and 5%, respectively. Fine-particle samples for resistivity measurements were pressed into silica capillaries 10 mm in length and 2.7 mm in diameter. The ends of the capillaries were soldered with indium, to which copper leads were attached.

Phase compositions were determined by XRD on a DRON-3 powder diffractometer (Ni-filtered CuK$_\alpha$ radiation, 40 kV, 20 mA, continuous scan rate of 1°(20)/min, rotating sample).

RESULTS AND DISCUSSION

The T–x phase diagram of the TlGaSe$_2$–CuGaSe$_2$ system, inferred from DTA, XRD, and conductivity data, is displayed in Fig. 1. The system contains one eutectic and one peritectic. The TlGaSe$_2$-based ($\alpha$) solid solution undergoes no phase transformations. With decreasing temperature, its stoichiometry range becomes narrower. The eutectic is located at 18 mol % CuGaSe$_2$, with a melting point of 1048 K.
The limit of the α solid solution at the eutectic temperature is at 3 mol % CuGaSe₂. Just as CuGaSe₂, the CuGaSe₂-based solid solutions undergo a transformation from the chalcopyrite to sphalerite structure [11, 12]. The peritectic point is located at 86 mol % CuGaSe₂ and 1328 K. The limit of the β solid solution at the peritectic temperature is at 98.1 mol % CuGaSe₂.

The TlGaSe₂–CuGaSe₂ phase diagram falls into type VI in Roozeboom’s classification [18].

The XRD data (Fig. 2) agree well with the DTA results. The XRD peaks from the alloys containing ≤2 mol % CuGaSe₂ and >98 mol % CuGaSe₂ are slightly shifted in comparison with the end members, attesting to the formation of solid solutions. The XRD patterns of the other alloys contain reflections from the two end members. As follows from the XRD data, the room-temperature solubility limits in the TlGaSe₂–CuGaSe₂ system are 2 and 1.5 mol % on the TlGaSe₂- and CuGaSe₂-rich sides, respectively.

The conductivity data (Fig. 3) fit well with the XRD and DTA results.

CONCLUSIONS

Phase relations in the TlGaSe₂–CuGaSe₂ system were studied over the entire composition range. The system contains restricted solid-solution series (type VI in Roozeboom’s classification). At room temperature, TlGaSe₂ dissolves 2 mol % CuGaSe₂, and CuGaSe₂ dissolves 1.5 mol % TlGaSe₂.

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REFERENCES