T–x Phase Diagram of the TlGaS2–TlFeS2 System and Band Gap of TlGa1–xFexS2 (0 ≤ x ≤ 0.01) Single Crystals

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Abstract—We have constructed the T–x phase diagram of the TlGaS2–TlFeS2 system (simple eutectic system, eutectic at 80 mol % TlFeS2 with a melting point of 953 K). The system contains limited series of monoclinic solid solutions based on the ternary end-members. At an annealing temperature of 933 K, the TlGaS2-based solid solution extends to ≤5 mol % TlFeS2 and the TlFeS2-based solid solution extends to ≤10 mol % TlGaS2. We have examined the effect of partial iron substitution for gallium on the optical properties of melt-grown single crystals of the TlGaS2-based solid solutions and determined their band gap as a function of temperature and Fe concentration.

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INTRODUCTION

The use of compound semiconductors, including TlMX2 (M = Ga, In; X = S, Se, Te), which crystallize in a variety of polytype structures, in many practical applications stems from the fact that varying their chemical composition allows one to obtain materials ranging widely in physical properties. This offers the possibility of controlling the band gap, energy position of emission bands, majority carrier type, and electrical conductivity of such semiconductors. Nevertheless, the ability to produce optical and electronic instruments with reproducible performance parameters using compound semiconductors is still a challenging problem. The reason for this is that the formation conditions of the materials in question and the phase equilibria in related systems have not yet been studied in sufficient detail, and defect formation in these materials is an uncontrolled process. The possibility of preparing solid solutions in the TlGaS2–TlFeS2 system, with smoothly varying physical properties, leads to a new look at the practical use of these materials.

The unit cell of TlGaS2 semiconductor crystals, which have a structure made up of layers of chains, is composed of layered slabs. Each layer comprises a sequence of Ga4S10 structural units in the form of a pyramid, which are in turn made up of GaS4 tetrahedra. The pyramids in the layers thus formed share corners, with the thallium atoms accommodated in the resultant trigonal interstices. The unit-cell parameters of TlGaS2 crystals (monoclinic symmetry, sp. gr. C2/c) are [1] a = 10.772, b = 10.772, c = 15.638 Å, and β = 100.06°, and their density is ρ = 5.560 g/cm³. The error of determination is 0.002 Å in the a cell parameter and 0.004 Å in the c parameter.

The ternary compound TlFeS2 is a magnetic semiconductor. TlFeS2 crystals have a chain structure (monoclinic symmetry, sp. gr. C2/m = C2h) with the following unit-cell parameters: a = 11.643, b = 5.306, c = 6.802 Å, β = 116.75°, Z = 16 [2, 3].

The objectives of this work were to construct the T–x phase diagram of the pseudobinary system TlGaS2–TlFeS2 and investigate the physical properties of the solid solutions in this system.

EXPERIMENTAL

The starting chemicals used in our preparations were high-purity constituent elements: thallium (Tl-00), gallium (5N Ga), sulfur (OSCh 16-5), and iron (3N Fe). The ternary compounds TlGaS2 and TlFeS2 were synthesized by reacting stoichiometric elemental mixtures, which were melted in silica tubes sealed off under a vacuum of 10⁻³ Pa. The completion of the synthesis of the ternary compounds TlGaS2 and TlFeS2 was checked by differential thermal analysis (DTA) and X-ray diffraction (XRD). The results were compared to earlier data [1–3].

DTA characterization of the TlGaS2–TlFeS2 system was carried out using 12 alloys, with x varied in steps of 0.1. The alloys were prepared by reacting appropriate mixtures of the ternary compounds TlGaS2 and TlFeS2 at 1000 K for 5–7 h in silica tubes sealed off under a vacuum of 10⁻³ Pa. Next, the alloys were vacuum-annealed in two steps: first at 953 K for
200 h and then at 933 K for 500 h. The annealed alloys were furnace-cooled to room temperature.

The 7–x phase diagram of the TlGaS₂–TlFeS₂ system was mapped out using DTA and XRD data. DTA of the alloys was carried out at a heating rate of 10 K/min using an NTR–73 pyrometer. Phase transition temperatures were determined with an accuracy of ±3 K. Prior to DTA scans, the samples were placed in Stepanov vessels of fused silica, which were then pumped down to a residual pressure of 10⁻³ Pa. The sample weight was 1 g. The reference substance used was calcined aluminum oxide, which was placed in a Stepanov vessel. The temperature was monitored with a Pt/Pt–Rh thermocouple, connected to a V7-34 voltmeter.

The phase composition of the alloys was determined by XRD at room temperature on a DRON-2 diffractometer with CuKα radiation.

To examine the effect of partial Fe³⁺ → Ga³⁺ cation substitution on the properties of the TlGa₁₋ₓFeₓS₂ (x = 0; 0.005; 0.01) solid solutions, single crystals of these solid solutions were grown from the melt by the Bridgman–Stockbarger method. To this end, the synthesized alloys were ground, and the resultant powders were charged into conical-bottom silica ampules 8–10 cm in length and 1 cm in inner diameter. The ampoules were pumped down to 10⁻³ Pa, sealed off under vacuum, and placed in a two-zone furnace. The temperature in the upper zone of the furnace was maintained at 1165 ± 10 K (that is, above the melting point of TlGaS₂), and that in the lower zone was 1110 ± 10 K (below the melting point of TlGaS₂). The ampoule lowering rate in the furnace was 0.3–0.5 cm/h, and the temperature difference across the crystal–melt interface was 25 ± 5 K. The above ampoule lowering rate in the furnace turned out to be optimal for the seeding process.

X-ray microanalysis of single-crystal TlGa₁₋ₓFeₓS₂ samples on a CAMECA MS-46 X-ray microanalyzer showed that the samples were homogeneous. Optical absorption spectra were measured using samples in the form of platelets ≈10–100 μm thick, cleaved from the single-crystal ingots. Light was incident along the normal to the layers of the samples, that is, along the crystallographic axis c of the crystals. Optical transmission spectra were measured as functions of temperature using an experimental setup built around a KSVU-6M system and UTREKS helium cryostat, which ensured temperature stabilization with an accuracy of ±0.01 K. The setup included an MDR-6 monochromator and FEU-100 photomultiplier tube. The spectral resolution of the experimental configuration was ≈2 Å.

RESULTS AND DISCUSSION

The 7–x phase diagram of the TlGaS₂–TlFeS₂ system is presented in Fig. 1. The system contains limited series of solid solutions based on the ternary end-members TlGaS₂ and TlFeS₂. The melting point of the TlGaS₂ compound, which has a structure made up of layers of chains, is 1165 K, and that of TlFeS₂, which has a chain structure, is 900 K. The liquidus in the 7–x phase diagram of the system under consideration comprises two primary crystallization regions: those of the solid solutions based on the end-members TlGaS₂ and TlFeS₂. Its solidus includes one eutectic horizontal, situated at 953 K. The phase diagram has one eutectic, with a melting point of 953 K. The eutectic composition is 80 mol % TlFeS₂ + 20 mol % TlGaS₂. The extent of the solid solutions in the alloys annealed at 933 K for 500 h was determined by microstructural analysis.

The XRD data for the TlGaS₂–TlFeS₂ alloys agree with the 7–x phase diagram obtained in this study. The XRD patterns of the solid solutions were similar to those of the ternary end-members.

The extent of the solid solutions in the 7–x phase diagram of the TlGaS₂–TlFeS₂ system was inferred from microstructural analysis data. It is seen in Fig. 1 that, at an annealing temperature of 933 K, the solid solutions based on the end-members extend to ≈5 mol % TlFeS₂ and ≈10 mol % TlGaS₂.

The unit-cell parameters of the TlGaS₂-based solid solution were found to vary slightly with increasing Fe³⁺ content, which is attributable to the larger ionic radius of Fe³⁺ in comparison with Ga³⁺. In particular, the unit-cell parameters of TlGa₀.₉₉Fe₀.₀₁S₂ were determined to be a = 10.760, b = 10.758, c = 15.625 Å, and β = 100.6° (Z = 16).

\[ T – x \text{ PHASE DIAGRAM OF THE TlGaS}_2–\text{TlFeS}_2 \text{ SYSTEM} \]