Phase Relations in the TlInS₂—TlYbS₂ System and Electrical Properties of Tl₂InYbS₄ Crystals

F. M. Seyidov, E. M. Kerimova, and N. Z. Gasanov

Institute of Physics, Academy of Sciences of Azerbaijan, pr. Javida 33, Baku, AZ1143 Azerbaijan

e-mail: ekerimova@physics.ab.az

Received April 19, 2011

Abstract—We have studied phase relations in the TlInS₂—TlYbS₂ system and showed that it contains a congruently melting compound of composition Tl₂InYbS₄ (1 : 1 ratio of the constituent sulfides). According to X-ray diffraction results, the compound Tl₂InYbS₄ crystallizes in tetragonal symmetry. Temperature-dependent electrical conductivity and Hall data for Tl₂InYbS₄ single crystals demonstrate that this compound is a p-type semiconductor with a band gap of 1.60 eV. The temperature variation of the carrier Hall mobility in Tl₂InYbS₄ corresponds to carrier scattering by acoustic phonons.

DOI: 10.1134/S0020168511110215

INTRODUCTION

Thallium group III–A metal (In, Ga) and thallium rare earth (Yb, Sm, Er) chalcogenides constitute a new class of semiconductor materials [1–19]. It is, therefore, of great interest to study phase relations in the TlInS₂—TlYbS₂ system.

The purpose of this work was to study phase relations in the TlInS₂—TlYbS₂ system and electrical properties of Tl₂InYbS₄ crystals.

EXPERIMENTAL

TlInS₂—TlYbS₂ samples were prepared by melting appropriate high-purity elemental mixtures in silica tubes sealed off under a vacuum of 1.3 × 10⁻² Pa. The mixtures were heated at a rate of 5 K/min to 1490–1570 K, held there for 8–9 h, and then slowly cooled to an annealing temperature. The alloys containing less than 50 mol % TlYbS₂ were annealed at 870 ± 10 K for 490 h, and those containing 50–100 mol % TlYbS₂ were annealed at 1390 ± 20 K for 560 h.

Low-temperature phase relations in the TlInS₂—TlYbS₂ system were studied using an NTR-64 instrument; at high temperatures, we used a VDTA-8 thermal analyzer, which operates at temperatures of up to 2470 K under a spectroscopically pure helium over-pressure.

X-ray diffraction patterns of Tl₂InYbS₄ powder samples were obtained using a URS-55 X-ray generator and 57.3-mm Debye–Scherrer powder camera (CuKα radiation).

In electrical measurements, we used Tl₂InYbS₄ single crystals grown by a modified Bridgman–Stockbarger process in purpose-designed fused silica ampules. The inner walls of the ampules were graphitized. The ampules were mounted in a vertical two-zone furnace. The temperature of the upper, higher temperature zone was stabilized at 25–30 K above the melting point (Tm) of the material to be prepared, and that of the lower temperature zone was 30–40 K below Tm. The temperature gradient in the transition zone was ~20 K/cm.

First, the ampule was lifted by a purpose-designed drive along the furnace axis to the upper, higher temperature zone. After stabilization for 15–20 h, it was lowered at a rate of 0.8 mm/h. The time taken for the ampule to traverse the transition (solidification) zone and reach the lower temperature zone was seven to eight days. Next, the temperatures of both zones were slowly (two to three days) lowered to room temperature. The resultant Tl₂InYbS₄ ingots consisted of long (~9 cm), very thin fibers aligned along the ampule axis, which formed a monolithic crystal.

The electrical conductivity and Hall coefficient of the Tl₂InYbS₄ single crystals were measured by a bridge technique using samples in the form of rectangular parallelepipeds 3 × 4 × 12 mm in dimensions. Electrical contacts with stable Ohmic behavior were made by capacitor discharge welding of tungsten lead wires to the lateral faces of the sample.
RESULTS AND DISCUSSION

The TlInS$_2$–TlYbS$_2$ phase diagram inferred from the present differential thermal analysis data is shown in Fig. 1. It follows from this phase diagram that the TlInS$_2$–TlYbS$_2$ system contains a compound of composition Tl$_2$InYbS$_4$ (1 : 1 ratio of the constituent sulfides), which melts congruently at 1640 K and has no homogeneity range. There is an (invariant) eutectic point at a composition of (TlInS$_2$)$_{0.75}$(TlYbS$_2$)$_{0.25}$ and a temperature of 950 K. Tl$_2$InYbS$_4$ and TlYbS$_2$ form a simple eutectic at (TlInS$_2$)$_{0.41}$(TlYbS$_2$)$_{0.59}$ with a melting point of 1565 K.

According to X-ray diffraction results, the compound Tl$_2$InYbS$_4$ crystallizes in tetragonal symmetry with unit-cell parameters $a = 8.32$ Å and $c = 6.50$ Å. The indexing scheme for a Tl$_2$InYbS$_4$ crystal is presented in the table.

Figure 2 presents temperature-dependent electrical conductivity ($\sigma$) and Hall ($R_H$) data for three samples of single-crystal Tl$_2$InYbS$_4$. The three samples show semiconducting behavior with $p$-type conduction. Their conductivity increases with temperature; that is, the $\sigma(T)$ of Tl$_2$InYbS$_4$ exhibits semiconducting behavior. The exponential growth of the conductivity with temperature at high temperatures is due to the development of intrinsic conduction.

The band gap ($E_g$) of the Tl$_2$InYbS$_4$ crystals was evaluated from the high-temperature $\log(R_HT^{3/2})$ ver-