Stability Limits and Properties of Tl₂TeBr₆, Cs₂TeBr₆, and Rb₂TeBr₆

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Abstract—The composition stability limits of the compounds Tl_2TeBr_6 , Cs_2TeBr_6 , and Rb_2TeBr_6 were determined from differential thermal analysis, microstructural, and microhardness data. The congruently melting composition was found to differ from the stoichiometric composition for Tl_2TeBr_6 and Cs_2TeBr_6 and to coincide with it for Rb_2TeBr_6 . Single crystals of the compounds studied were prepared using growth charges with the congruently melting compositions, and their properties were investigated.

INTRODUCTION

The compounds existing in the TlHal–Tl₂X (Hal = Br, I; X = S, Se) systems were studied earlier [1–7]. Tl₆SI₄ and Tl₆SeI₄ crystals attracted particular interest, since they were found to exhibit high photosensitivity [4, 7]. According to phase-diagram studies [6], the Tl₆SI₄–Tl₆SeI₄ and Tl₅Se₂Br–Tl₅Se₂I systems contain continuous series of substitutional solid solutions, which opens up possibilities for preparing new materials with gradually varying properties.

There is also considerable scientific interest in the mixed-anion phases existing in the MBr–TeBr₄ (M = Tl, Cs, Rb) systems. The phase equilibria in these systems were investigated in a few works [8–10]. However, data on the composition stability limits of the M_2 TeBr₆ phases are still missing. The properties of these phases have not yet been studied in sufficient detail because of the lack of single crystals.

The purpose of this work was to refine the MBr– TeBr₄ (M = Tl, Cs, Rb) phase diagrams; to determine the stability limits of Tl₂TeBr₆, Cs₂TeBr₆, and Rb₂TeBr₆; to grow single crystals of these compounds; and to investigate their properties.

EXPERIMENTAL

MBr–TeBr₄ (M = Tl, Cs, Rb) alloys were prepared from TlBr, CsBr, RbBr, and TeBr₄. TlBr was synthesized as described in [11, 12]. CsBr and RbBr were prepared by reacting OSCh 18-4 Cs₂CO₃ and Rb₂CO₃ with reagent-grade HBr. The three bromides were additionally purified by directional solidification.

TeBr₄ can be prepared by the procedure described in [13], but, in our opinion, it is more convenient to use a two-compartment reactor represented schematically in Fig. 1. A weighed amount of tellurium 3 was loaded into compartment 1, and a slight excess of bromine placed in glass capillary 4 was introduced into compartment 2. Next, the system was pumped to 0.133 Pa, neck 6 was sealed off, and capillary 4 was locally heated with a gas torch. As a result, bromine vapor filled compartment 2 and partially reacted with tellurium. After a time, by heating compartment 2, bromine was gradually driven to compartment 1, and neck 5 was sealed off. Further synthesis was carried out with no temperature gradient in a resistance furnace. During synthesis (72 h), the temperature did not exceed 659 K (melting point of TeBr₄). The resultant material was furnace-cooled to room temperature.

The TeBr₄ thus prepared was additionally purified by vacuum sublimation. Simultaneously, excess bromine was distilled off. In this way, we obtained orangeyellow TeBr₄ crystals, which were found to be rather stable in air. Their melting point was slightly higher than that reported in the literature. The crystals could be stored for a long time in sealed silica tubes or vials placed in a desiccator. Note that, at atmospheric pressure, TeBr₄ partially decomposes at the melting point [13].

The purity of the binary bromides was 99.999+%, as determined by spectrochemical analysis for Fe, Si, Mg, Ti, Cu, Ag, and Ni.



Fig. 1. Two-compartment reaction vessel: (1, 2) compartments, (3) tellurium, (4) capillary containing bromine, (5, 6) necks.



Fig. 2. (a) TlBr–TeBr₄, (b) CsBr–TeBr₄, and (c) RbBr–TeBr₄ phase diagrams.

The ternary alloys were prepared from appropriate bromide mixtures sealed in silica tubes under a vacuum of 0.2 Pa. The annealing temperature was chosen based on preliminary differential thermal analysis (DTA) data. The annealing duration was 720–900 h.

DTA was carried out with an NTR-62M unit. The temperature was monitored by a Chromel–Alumel thermocouple with an accuracy of ± 5 K. X-ray diffraction (XRD) measurements were performed on a DRON-2 diffractometer (Cu K_{α} radiation, LiF monochromator). The relative intensities of XRD peaks were expressed as a percent. Density was determined by the Archimedes method using toluene as a saturating and suspending medium. Microhardness was measured with a PMT-3 tester at a load of 0.196 N. Optical absorption spectra were recorded on an IKS-14A spectrometer using platelike samples 2–3 mm in thickness.

RESULTS AND DISCUSSION

The TlBr–TeBr₄, CsBr–TeBr₄, and RbBr–TeBr₄ phase diagrams derived from our DTA and XRD data are displayed in Fig. 2.

Each of the systems contains a single intermediate phase with the stoichiometry M_2 TeBr₆, melting congruently at 810, 1040, and 960 K in the Tl, Cs, and Rb systems, respectively. The eutectics are located at 10 and 80 mol % TeBr₄ (melting points of 700 and 630 K, respectively) in the Tl system, 13 and 92 mol % TeBr₄ (848 and 635 K) in the Cs system, and 15 and 70 mol % TeBr₄ (758 and 610 K) in the Rb system. Our results generally agree with those by Grin'ko *et al.* [8], but the melting points of M_2 TeBr₆ determined in this work are somewhat higher (e.g., by 10 K for Cs₂TeBr₆), presumably because of the higher purity of the binary bromides used in our preparations.

The composition stability limits of Tl_2TeBr_6 , Cs_2TeBr_6 , and Rb_2TeBr_6 were determined from DTA, microstructural, and microhardness data for samples quenched after annealing. The results are shown in Fig. 3.

At the eutectic temperatures, the width of the stability range is 4.7, 3.6, and 3.2 mol % TeBr₄ for Tl₂TeBr₆, Cs₂TeBr₆, and Rb₂TeBr₆, respectively. The congruently melting composition is shifted from the M₂TeBr₆ stoichiometry by 0.2 mol % toward TlBr in the TlBr– TeBr₄ system and by 0.2 mol % toward TeBr₄ in the CsBr–TeBr₄ system. In the RbBr–TeBr₄ system, the congruent composition of Rb₂TeBr₆ coincides with its stoichiometric composition. In the three systems, microhardness passes through an extremum at the congruent composition.

Single crystals of the compounds in question were grown by the Bridgman process using growth charges with the congruently melting composition. The solidification rate was 0.3–0.5 mm/h, and the thermal gradient



Fig. 3. Stability regions of (a) Tl_2TeBr_6 , (b) Cs_2TeBr_6 , and (c) Rb_2TeBr_6 : (*1*) single-phase regions, (2) two-phase regions. Composition dependences of microhardness in the systems (a') $TlBr-TeBr_4$, (b') $CsBr-TeBr_4$, and (c') $RbBr-TeBr_4$ near the M_2TeBr_6 stoichiometry.

at the growth interface was 2-4 K/mm. The grown crystals, 25-55 mm in length and 15-22 mm in diameter, were annealed at 473 K for 3 days and then cooled to

room temperature at a rate of 30 K/h. The Tl_2TeBr_6 crystals were dark red, and the Cs_2TeBr_6 and Rb_2TeBr_6 crystals were cherry red.

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Compound	$T_{\rm m}$, K	ρ , g/cm ³	<i>H</i> , MPa	$\Delta_{\rm m}H$, kJ/mol	$\Delta_{\rm m}S$, J/(mol K)	ΔE_0 , eV
Rb ₂ TeBr ₆	960	4.18	32	15	15.7	2.14
Cs ₂ TeBr ₆	1040	4.49	42	14	13.5	2.12
Tl ₂ TeBr ₆	810	5.61	15	21.2	26.2	2.06

Properties of Rb₂TeBr₆, Cs₂TeBr₆, and Tl₂TeBr₆ crystals

All of the crystals were found to be stable in air. They actively react with concentrated HNO_3 and H_2SO_4 and show little or no reaction with toluene, ethanol, acetone, and concentrated HCl. Tl_2TeBr_6 slowly hydrolyzes in water.

The physicochemical and optical properties of the crystals are summarized in the table.

From the position of the fundamental absorption edge, we determined the band gap ΔE_0 of the crystals (table). The optical transmittance of the crystals was found to be fairly high (60–75% for 2- to 3-mm-thick samples). The resistivity of the Tl₂TeBr₆ crystals was ~10⁶ Ω cm.

According to XRD data, Tl_2TeBr_6 has a tetragonal structure with lattice parameters a = 10.63(2) Å and c = 10.72(4) Å. The measured density of Tl_2TeBr_6 (table) is close to its x-ray density (5.56 g/cm³).

CONCLUSION

The phase relations in the MBr–TeBr₄ (M = Tl, Cs, Rb) systems were studied in detail in the regions of Tl_2TeBr_6 , Cs_2TeBr_6 , and Rb_2TeBr_6 . Single crystals of these compounds were grown, and their properties were investigated.

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