



Phase equilibria in the Tl–TlI–Te system and thermodynamic properties of the $Tl_5Te_{3-x}I_x$ solid solution



Dunya M. Babanly^{a,*}, Ilham M. Babanly^b, Samira Z. Imamaliyeva^b, Vaqif A. Gasimov^a,
Andrei V. Shevelkov^{c,*}

^a Institute of Chemical Problems of ANAS, Baku, Azerbaijan

^b Department of Chemistry, Baku State University, Azerbaijan

^c Department of Chemistry, Lomonosov Moscow State University, Russia

ARTICLE INFO

Article history:

Received 2 September 2013

Received in revised form 25 November 2013

Accepted 29 November 2013

Available online 13 December 2013

Keywords:

Ternary system

Thallium tellurides

Thallium telluride-iodides

Solid solutions

Phase diagram

Thermodynamic properties

ABSTRACT

The Tl–TlI–Te ternary system was investigated by using the DTA and XRD analyses, microhardness and EMF measurements, leading to the construction of important polythermal and isothermal sections as well as the projection of the liquidus surface. Determined were the fields of primary crystallization and the types and coordinates of non- and monovariant equilibria. The system features the formation of continuous solid solutions (δ -phase) between the Tl_5Te_3 and Tl_5Te_2I compounds. The homogeneity area of the δ -phase completely covers the Tl_5Te_2I – Tl_5Te_3 – Tl_2Te subsystem. The partial molar thermodynamic functions ($\Delta\bar{G}$, $\Delta\bar{H}$, $\Delta\bar{S}$) of thallium as well as the standard integral thermodynamic functions of the $Tl_5Te_{3-x}I_x$ solid solution (for various x) were calculated based on the results of the EMF measurements.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Complex chalcogenides and chalcogen-halides of heavy p metals are considered perspective functional materials. Many of them exhibit semiconductor, thermoelectric, photoelectric, and magnetic properties [1,2]. According to recent investigations, Tl_6SeI_4 and Tl_5Se_2I are promising materials for efficient X-ray and γ -ray detection, outperforming the current state-of-the-art material for room temperature operation, CdZnTe (CZT) [3,4]. Given the promising performance of thallium-based chalcogenides and chalcogenide-halide, these compounds continue to attract attention despite of toxicity of thallium derivatives.

The synthesis and growth of the single crystals from the melt requires the knowledge of the respective phase diagrams, which makes the investigation of phase equilibria very important in course of the material development. This is particularly true for quaternary phases, which frequently present wide homogeneity fields based on complex substitutional patterns. Typically, their functional properties can be tuned by varying the composition, which in turn calls for the development of a synthetic approach

toward the preparation of a required stoichiometry within a homogeneity range.

In our previous works, phase equilibria and thermodynamic properties of the systems Tl–TlCl–S [5], Tl–TlBr–S [6], Tl–TlI–S [7], Tl–TlCl–Se [8], Tl–TlBr–Se [9], Tl–TlCl–Te [10], and Tl–TlBr–Te [11] were investigated. A number of polythermal and isothermal sections as well as projections of liquidus surfaces were constructed. The homogeneity fields of the intermediate phases were fixed and their fundamental thermodynamic functions were calculated.

In this work, we report the results of the complete investigation of phase equilibria and thermodynamic properties of the Tl–TlI–Te system. The layout of this paper is as follows. We start with reviewing the literature data on this system and compounds in it, follow with the description of the experimental procedure, and then discuss our results on the phase equilibria, polythermal sections, liquidus surface, and thermodynamic properties of the $Tl_5Te_{3-x}I_x$ solid solution.

1.1. Review of the literature data

The ternary system Tl–Te–I was investigated along various polythermal sections [12–15].

For the Tl–Te boundary system, 4 compounds have been reported; they are Tl_2Te , Tl_5Te_3 , TlTe, and Tl_2Te_3 . The former two

* Corresponding authors. Address: H. Javid 32, Baku, Azerbaijan (D.M. Babanly). Leninskie Gory 1–3, Moscow 119991, Russia. Tel.: +7(495)9392074 (A.V. Shevelkov).

E-mail addresses: babanly_mb@rambler.ru (D.M. Babanly), shev@inorg.chem.msu.ru (A.V. Shevelkov).

melt congruently at 698 and 726 K, respectively, whereas the latter two decompose upon melting at 573 and 511 K, respectively [16,17]. The quasi-binary system TlI–Tl₂Te is characterized by the formation of a ternary compound Tl₅Te₂I that melts by a synthetic reaction at 775 K [12]. The immiscibility area occupies the 20–80 mol% TlI concentration interval at a synthetic temperature. Eutectic is degenerated near TlI and crystallizes at 713 K. Authors of [12] assume the presence of the peritectic equilibrium between Tl₅Te₂I and Tl₂Te at ~730 K. The homogeneity region of Tl₅Te₂I at ~600 K is in the range ~65–745 mol% Tl₂Te. The homogeneity areas of TlI and Tl₂Te were not determined in that work.

This compound forms a continuous solid solution with Tl₅Te₃ [13]. The polythermal sections TlI–TlTe and TlI–Tl₂Te₃ [14] are stable in subsolidus, i.e., consist of heterogeneous mixtures of primary compounds, but they are non-quasi-binary because of the peritectic decomposition of TlTe and Tl₂Te₃. There are wide areas of immiscibility in the phase diagrams of both systems. The phase diagram of the quasi-binary system TlI–Te is characterized by monotectic and eutectic equilibria [15]. The *T*–*x* diagrams of the boundary systems Tl–TlI [18] and TlI–Te [15] are of the monotectic type. The binary compound TlI constituting one of the corners of the ternary system Tl–TlI–Te melts congruently at 715 K and undergoes the Tl_I ⇌ Tl_{II} polymorph transformation at 451 K [18]. Also, the preparation, stability regions, and properties of Tl₂TeI₆ were reported [19].

The following structural information is available from the literature regarding the binary and ternary compounds of the Tl–Te–I system (see Table 1). The low-temperature modification of TlI crystallizes in the orthorhombic symmetry and has a molecular-like crystal structure, whereas the high-temperature modification belongs to the CsCl structure type [20,21].

Tl₂Te crystallizes in the monoclinic space group *C*₂/*c* with 44 formulas per unit cell and has an unusually complex structure composed of Tl¹⁺ and Te²⁻ [17]. TlTe and Tl₂Te₃ possess less complex crystal structures [22,23], however, they exhibit systems of homonuclear Tl–Tl or Te–Te bonds that make their structure somewhat similar to cluster halides of bismuth and tellurium [24,25]. Tl₅Te₃ and Tl₅Te₂I belong to a structural family of compounds crystallizing in the In₅Bi₃ structure type and its less symmetric analogs [26,27]. Crystal structures of other thallium selenohalides and tellurohalides of the 5:2:1 stoichiometry also belong to this structure family [8–11,28,29].

Finally, the crystal structure of Tl₂TeI₆ features Te⁴⁺ cations in a distorted octahedral environment of iodine atoms [30]. Note that this compound does not belong to the ternary Tl–TlI–Te system studied in this work.

2. Experimental

2.1. Synthesis

Elemental thallium (Tl-99.999%, Alfa Aesar), tellurium (Te-99.999%, Alfa Aesar) and iodine (I-99% resublimed pearls, PA-ACS) were used as received. At the first step, they were used for the preparation of binary compounds Tl₂Te, Tl₅Te₃, TlTe, Tl₂Te₃, TlI, and Tl₅Te₂I.

Table 1

Structural data for compounds of the Tl–TlI–Te system.

Compound	Space group	Unit cell parameters	Ref.
TlI	<i>Cmcm</i> (LT) <i>Pm</i> –3 <i>m</i> (HT)	<i>a</i> = 4.57, <i>b</i> = 12.92, <i>c</i> = 5.24 Å <i>a</i> = 4.201 Å	[20,21]
Tl ₂ Te	<i>C</i> ₂ / <i>c</i>	<i>a</i> = 15.662, <i>b</i> = 8.987, <i>c</i> = 31.196 Å, β = 100.76°	[17]
Tl ₅ Te ₃	<i>I4/mcm</i>	<i>a</i> = 8.929, <i>c</i> = 12.620 Å	[26]
TlTe	<i>P4</i> ₂ / <i>nmc</i>	<i>a</i> = 18.229, <i>c</i> = 6.157 Å	[22]
Tl ₂ Te ₃	<i>Cc</i>	<i>a</i> = 17.413, <i>b</i> = 6.552, <i>c</i> = 7.910 Å, β = 133.6°	[23]
Tl ₅ Te ₂ I	<i>I4/mcm</i>	<i>a</i> = 9.026; <i>c</i> = 13.324 Å	[27]
Tl ₂ TeI ₆ ^a	<i>P2</i> ₁ / <i>c</i>	<i>a</i> = 7.765, <i>b</i> = 8.174, <i>c</i> = 13.756 Å, β = 124.2°	[30]

^a Composition out of the Tl–TlTe–I system; see text.

Congruently melting compounds Tl₂Te and Tl₅Te₃ were prepared from the stoichiometric amounts of the corresponding elements by one-step melting in vacuum-sealed (~10⁻² Pa) silica ampoules at 800 K, followed by cooling in a switched-off furnace. For incongruently melting TlTe and Tl₂Te₃ after fusing at 800 K the ampoules were slowly cooled to 560 ± 5 K (TlTe) or 500 ± 5 K (Tl₂Te₃), annealed for 500 h, and then slowly cooled in a switched-off furnace.

TlI was synthesized from the elements following a specially designed procedure, which takes into account high volatility of iodine, describes in detail elsewhere [27].

Ternary compound Tl₅Te₂I was synthesized by melting appropriate amounts of the synthesized TlI and Tl₂Te in a vacuum-sealed quartz ampoule. This compound decomposes by a synthetic reaction upon melting [12]. Accordingly, the ampoule after fusing at 800 K was cooled slowly to 730 K and held at this temperature for ~800 h.

Samples for the investigation of phase equilibria and thermodynamic properties were prepared from Tl₂Te, Tl₅Te₃, TlTe, Tl₂Te₃, TlI, and Tl₅Te₂I. The total mass was 1 g. In most cases, after determining the solidus temperature, samples were annealed at 20–30 K below the solidus for 800–1000 h.

2.2. Analysis

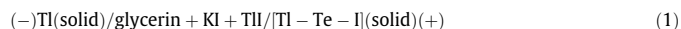
X-ray powder diffraction (XRD), differential thermal analysis (DTA), measurement of microhardness, and electromotive force were used to characterize the samples.

The XRD analysis was performed on a Bruker D8 ADVANCE diffractometer with the Cu Kα₁ radiation. The lattice parameters were refined using the Topas V3.0 software. XRD confirmed that the pre-synthesized binary and ternary compounds were phase-pure, and that the unit cell parameters perfectly matched the literature data for binary compounds. The powder XRD pattern for Tl₅Te₂I was indexed using Topas V3.0 software. It was confirmed that Tl₅Te₂I crystallizes in the tetragonal Tl₅Te₃ structure type with the space group *I4/mcm* and the following unit cell parameters: *a* = 9.026(1), *c* = 13.324(3) Å, *z* = 4, which perfectly matches the literature data (see Table 1).

DTA was carried out with a Termoskan-2 device. The temperature was monitored by a Chromel–Alumel thermocouple. The ramp rate was 5 K min⁻¹. Temperatures of thermal effects were taken mainly from the heating curves. The melting point of the ternary compound Tl₅Te₂I was found to be in agreement with the literature data [12,27].

Microhardness was measured with a PMT-3 tester, the typical loading being 20 g.

For the electromotive force (EMF) measurements, the following concentration chains were assembled:



In the chains of type (1), metallic thallium was used as the left electrode, while equilibrium alloys of the system Tl–Te–I were exploited as the right electrode. A saturated glycerin solution of KI with the addition of 0.1 mass% TlI was used as an electrolyte. The electrodes were prepared by pressing the powdered alloys in the form of pellets (0.5 g) in a molybdenum wire. The temperature was stabilized at 350 K for 40–50 h. EMF was measured by the compensation method in the temperature range of 300–400 K with the accuracy of ±0.1 mV, using a high-resistance universal B7–34A digital voltmeter. The detailed description of the methods of assembling the electrochemical cell and carrying out the EMF measurements are given in [31,32].

3. Results and discussion

To obtain complete a picture of phase equilibria in the system Tl–TlI–Te we have prepared and investigated a number of samples in the sections Tl₂Te–TlI, [Tl₂I]–Tl₂Te, and Tl₅Te₂I–Te(Tl), and also several additional samples out of the given sections. The results are given in Figs. 1–8 and Tables 2–6.

Download English Version:

<https://daneshyari.com/en/article/1611590>

Download Persian Version:

<https://daneshyari.com/article/1611590>

[Daneshyari.com](https://daneshyari.com)