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Phase diagram for the quasi-binary thallium(I) selenide–indium(III) selenide system

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ABSTRACT

The Tl_2Se–In_2Se_3 cross section of the Tl–In-Se system was studied by both the common thermal analysis (TA) and the X-ray diffraction (XRD). From the results of the studies the phase diagram for the quasi-binary Tl_2Se–In_2Se_3 system was delineated for the first time. Numerical values of the phase transition temperatures at different alloy compositions within the whole concentration range have been listed in a table. The existence of two ternary compounds $TlInSe_2$ and $TlIn_5Se_8$ was established.

1. Introduction

A ternary system of the type M–M′–X, where M and M′ are any metals and X is a chalcogen, focused interest of many researches in the last three decades, because of the possibility of forming ternary chemical compounds embodying advantageous semiconductive properties. The greater electronegativity of the element X (as e.g. selenium and tellurium), the higher is probability of the compound formation. The best way of searching for the compounds are phase equilibrium studies on the quasi-binary systems $M_aX_b - M'_cX_d$, which are polythermal cross-sections (isopleths) of the corresponding ternary systems.

As yet, only two cross sections of the Tl–In-Se system were studied, namely TlSe–InSe and Tl_2Se–In_2Se_3. Results of the studies on the TlSe–InSe system have been reported by many authors [1–3] but the knowledge of the Tl_2Se–In_2Se_3 system is still poor. Although the latter system was studied formerly twice [4,5], its phase diagram has not been published to date. In the work [4] the title system was studied by electromotive force (*emf*) measurement of concentration cells at 750–873 K in the compositions range 0.30–0.80 mol% In_2Se_3. From the results reported in [4] the dependence of the *emf* values vs. concentration (Fig. 1) was constructed. It followed that only one stoichiometric compound $TlInSe_2$ was formed in this system. The paper [5] is rather one-page communication where it was mentioned that in the Tl_2Se–In_2Se_3 system the $TlInSe_2$ compound was formed (melting congruently at 1053 K), homogeneity region which extends from 0.45 mol% In_2Se_3 to 0.55 mol% In_2Se_3 and that solidus temperatures and heats of melting of alloys were measured. The paper [5] includes neither experimental data nor phase equilibrium diagram.

However, in an analogous system Tl_2Te–In_2Te_3 [6,7], that was studied by thermal analysis, *emf* measurement of concentration cells and X-ray diffraction, the existence of two ternary compounds was showed. Because of a very small difference in the radii of selenium and tellurium, it may be supposed that in the Tl_2Se–In_2Se_3 system also two chemical compounds may be formed. This is the reason why the aim of the present work was determination of the phase equilibrium diagram for the thallium(I) selenide–indium(III) selenide system within the whole concentration range.

2. Experimental

2.1. Materials

The components of the system examined, i.e. thallium selenide and indium selenide, were prepared from pure elements: thallium 99.9 mass%, indium 99.9 mass% and selenium 99.9 mass% (all from Aldrich Chemical Co.). The metal chalcogenides were synthesized by simple fusing stoichiometric quantities of the elements, weighed with an accuracy of ±0.0001 g, in quartz tubes in a purified argon atmosphere (5 N pure, BOC Gazy, Poznan) and then mixed for 15 min at temperature about 100 K higher than the melting point of the respective metal chalcogenide.

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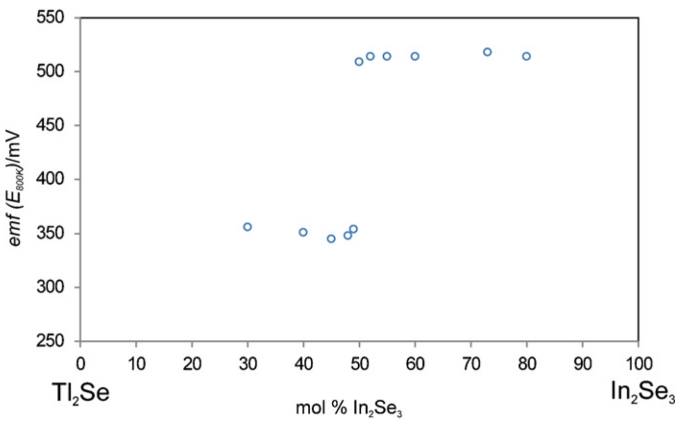

Fig. 1. The *emf* values of the cells with alloy electrodes of compositions covering the 0.30–0.80 mol% In_2Se_3 concentration range of the system Tl_2Se–In_2Se_3 at 750–873 K (constructed from the results reported in [4]).

2.2. Apparatus and measurements

The phase studies on the Tl_2Se–In_2Se_3 system were performed by making use of the TA method (cooling curve technique) in a quartz apparatus designed for phase and cryometric investigations at high temperatures [8]. The phase transition temperatures of the examined samples were determined by using a thermopile Pt/Pt, Rh calibrated at the freezing points of standards (lead, zinc, aluminum, potassium chloride and silver). The molten samples (no less than 25 g) were vigorously stirred throughout the experiments with a quartz stirrer to maintain equilibrium conditions of crystallization of the melts. The cooling rate was 0.8–1.2 K/min, the accuracy of measurements was ±0.5 K. The examples of cooling curves are shown in Fig. 2 (alloy samples with composition 85.68 mol% In_2Se_3 and 32.37 mol% In_2Se_3). The thermopile was connected to a dual display multimeter Fluke 45 which was joined to a computer for the processing and display of the experimental data.

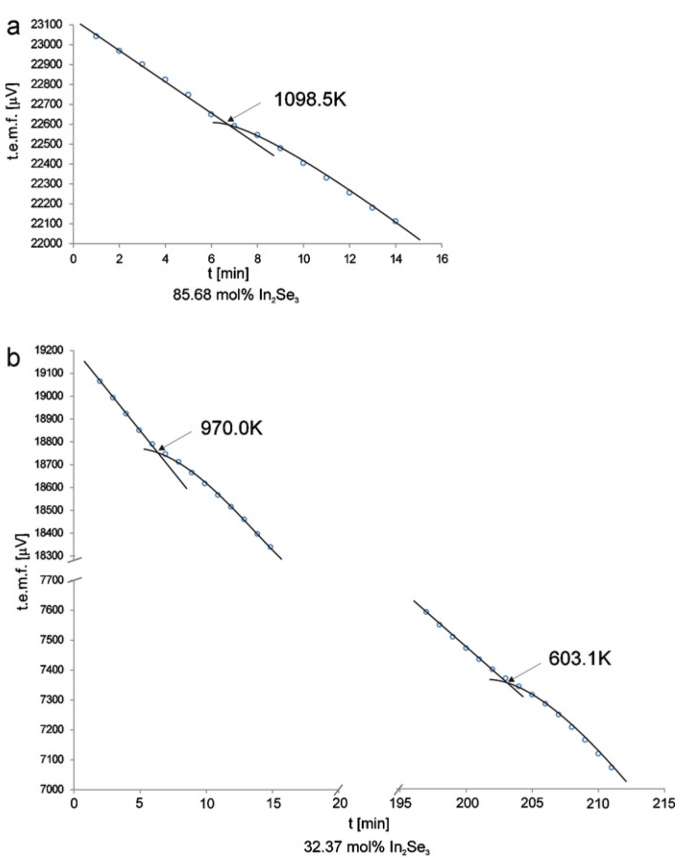

Fig. 2. Examples of the cooling curves (t.e.m.f., thermoelectromotive force of a thermopile).

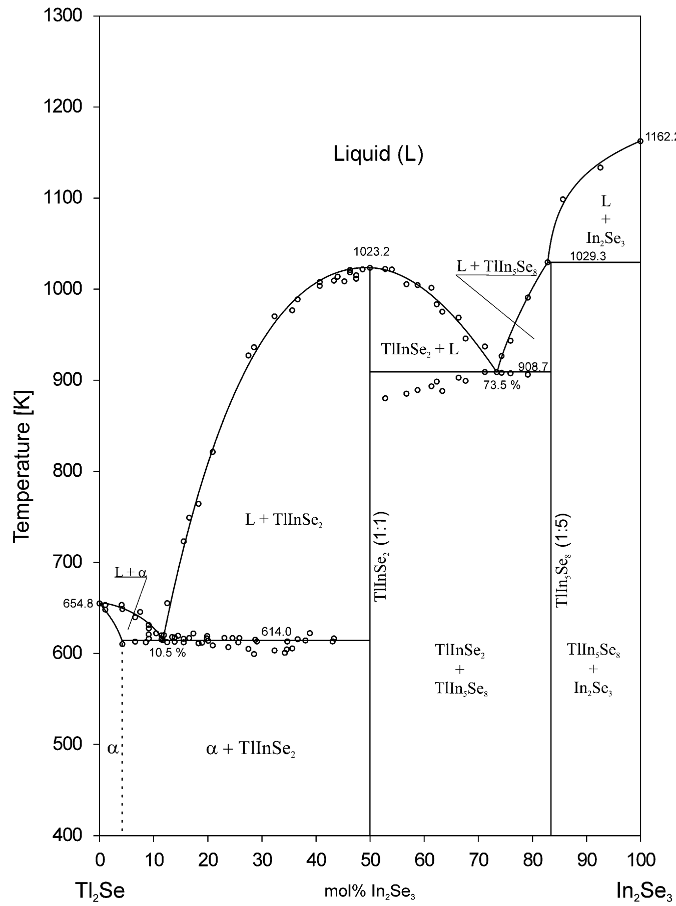

Fig. 3. Phase diagram for the system Tl_2Se–In_2Se_3 (this work).

The composition of the eutectics was determined by a graphical method i.e. by a simple extrapolation of the liquidus curves up to their intersection with the solidus line, accordingly, the compositions were given with an accuracy of ±1 mol%.

To confirm the results of the TA, use was also made of the XRD method. Alloy samples with compositions 2.5, 7, 30, 48, 50, 52, 60, 70, 80, 83.3 and 95 mol% In_2Se_3 were prepared in the same way as metal chalcogenides (Section 2.1). The solidified samples were powdered in an Analysette 3 Spartan pulverisette 0 vibration mill (Fritsch) and homogenized for 7 days under vacuum at 573 K, then quenched in a cooling bath (ice + methanol). The XRD examinations of the alloys as well as of pure components (Tl_2Se and In_2Se_3) were performed using a Siemens D 5000 diffractometer, employing Cu Kα, Kβ radiation (20 mA, 35 kV). The measurements were made in 2θ angle range of 15–60° with a 0.04° step and at least 2 s per step.

3. Results

The measurements of phase transformation temperatures in the system thallium(I) selenide–indium(III) selenide were effected by common thermal analysis within the whole concentration range. Results of these measurements have been listed in Table 1 to enable other authors to employ them in future computational treatment of the system. Based on these data, the phase equilibrium diagram