Journal of Alloys and Compounds 671 (2016) 109–113

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Phase diagrams of novel Tl_4SnSe_4–$TlSbSe_2$–Tl_2SnSe_3 quasi-ternary system following DTA and X-ray diffraction

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ARTICLE INFO

Article history:
Received 12 November 2015
Received in revised form
6 February 2016
Accepted 8 February 2016
Available online 11 February 2016

Keywords:
Thallium
Tin
Stibium
Selenide
Phase diagrams
Thermal analysis
X-ray diffraction
Solid state reaction

ABSTRACT

Phase relation in the Tl_4SnSe_4–$TlSbSe_2$–Tl_2SnSe_3 quasiternary system were studied by the DTA and X-ray diffraction in combination with mathematical modeling. The phase diagrams of the Tl_4SnSe_4–$TlSbSe_2$ and Tl_2SnSe_3–$TlSbSe_2$ systems, the perspective views of the phase interaction in the ternary system, the liquidus surface projection, the isothermal section at 423 K were built for the first time. The Tl_4SnSe_4–$TlSbSe_2$–Tl_2SnSe_3 system is of the invariant eutectic type and is characterized by the formation of limited solid solutions following initial ternary compounds. New complex compounds are not formed.

1. Introduction

The one of the main tasks for the semiconductor materials science and engineering consists the development of new functional materials. Particular interest present complex Tl chalcogenide crystals and their alloy derivatives. Among them particular interest is attracted to the Tl_2Se–$SnSe_2$–Sb_2Se_3 ternary system. These ternary system are interesting for investigation due to formation of ternary compounds which reveal unusual optical, thermoelectric and photoelectrical behaviors. They have broad practical application in infrared optoelectronics, thermoelectricity, spirometry, optical triggering, gratings etc. Tl-containing structures are expected to possess low thermal conductivity due to effective scattering of phonons that are responsible for the transfer of heat in the materials. Thallium complex compounds have recently attracted interest as promising thermoelectric materials [1,2]. Thallium is similar in crystal chemical behavior to some of the alkali metals. It forms preferentially compounds in oxidation state +1 and its ionic radius is very close to the ionic radius of potassium, however the electronegativity is higher. Replacement of potassium by thallium may enhance the electrical conductivity of a compound, as a result of substantial reduction of the ionicity of the chemical bonds. Also, thallium is a heavy element and its introduction into a semiconductor will lead to a decrease of the thermal conductivity.

The Tl_2Se–$SnSe_2$ system is characterized by the formations of Tl_4SnSe_4, Tl_2SnSe_3 ternary compounds, which congruently melt at 718 K and 738 K [3–6], respectively. In the Tl_2Se–Sb_2Se_3 system there are formed two congruently melting compounds: Tl_9SbSe_6 (743 K) and $TlSb_2Se_2$ (730 K) [7–9]. The $SnSe_2$–Sb_2Se_3 system is of the eutectic type [10]. The Tl_2Se–$SnSe_2$–Sb_2Se_3 ternary system is divided into the five separate secondary subsystems Tl_2Se–Tl_4SnSe_4–Tl_9SbSe_6, Tl_4SnSe_4–$TlSbSe_2$–Tl_9SbSe_6, Tl_2SnSe_3–Tl_4SnSe_4–$TlSbSe_2$, Tl_2SnSe_3–$TlSbSe_2$–$SnSe_2$, $SnSe_2$–$TlSbSe_2$–Sb_2Se_3 with the four quasi-binary sections Tl_4SnSe_4–Tl_9SbSe_6, Tl_4SnSe_4–$TlSbSe_2$, Tl_2SnSe_3–$TlSbSe_2$ and $SnSe_2$–$TlSbSe_2$ [11,12]. The knowledge of the structure plays a crucial role for the design of crystals with advanced optoelectronic features [12–17] including infrared photo-transparency, multi-photon excitation, optical

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http://dx.doi.org/10.1016/j.jallcom.2016.02.078
0925-8388/

modulators in the Ir spectral range. In the present work we will present the data of the DTA and X-ray diffraction studies in combination with mathematical modeling of the phase diagrams for the Tl_4SnSe_4–$TlSbSe_2$ and Tl_2SnSe_3–$TlSbSe_2$ systems. Furthermore, the perspective views of the phase interaction in the ternary system, the liquidus surface projection, the isothermal section will be explored.

2. Materials and methods

As educts we used thallium (I), tin (IV) and stibium (III) selenides. Synthesis of these binary compounds was carried out with high-purity elements (better than 99.99 wt.%). $T1_2Se$, $SnSe_2$ and Sb_2Se_3 binary compounds were prepared by the single-temperature method from stoichiometric amounts of the initial elements in evacuated quartz containers. The binary compounds were purified by zone crystallization methods. The Tl_4SnSe_4, Tl_2SnSe_3 and $TlSbSe_2$ ternary compounds were obtained from stoichiometric amounts of initial binary selenides. Identification of binary and ternary compounds was done by the DTA and X-ray analysis.

The multicomponent alloys were synthesized from ternary complex selenides in quartz ampoules evacuated to a residual pressure of 0.13 Pa. After thermal treatment at highest temperature (823 K) for 24 h the samples were slowly cooled (25–30 K per hour) down to 423 K and homogenized at this temperature for 336 h. Subsequently the ampoules were quenched into cold water.

The phase equilibria in the ternary system were investigated by the differential thermal (DTA), X-ray powder diffraction, microstructure (MSA) analyses. More details about the performed DTA, XRD diffraction and microstructure are given in the Supplement 1. The classical methods of physico-chemical analysis were used in combination with the simplex method of mathematical modeling of phase equilibria in multicomponent systems [18]. More details about this modeling approach are given in the Supplement 2. The differential thermal analysis was carried out by means of a device including an *x-y* recorder PDA-1 and a chromelalumel thermocouple, with an accuracy of ±5 K. The samples were heated and cooled in a furnace using an RIF-101 programmer, which provided a linear temperature variation. X-ray powder diffraction was carried out on a DRON-3-13 diffractometer (Cu Kα radiation, Ni filter). Rietveld refinements of X-ray powder diffraction data were performed by using the WinCSD program [19]. The microstructure analysis was carried out with a metallographic microscope Lomo Metam R1.

3. Results and discussion

3.1. Tl_4SnSe_4–$TlSbSe_2$ quasibinary system

Tl_4SnSe_4–$TlSbSe_2$ quasibinary system is characterized by the eutectic processes $L \leftrightarrow Tl_4SnSe_4 + htmTlSbSe_2$ (see Fig.1). The lines of primary crystallization are intersected in the invariant point with coordinates 62 mol./% $TlSbSe_2$, 619K. Limited solid solutions are formed in the system: β on the base of Tl_4SnSe_4 and δ, δ′ following low-, high-temperature polymorphic modification of $TlSbSe_2$, respectively. Eutectical processes $\delta' \leftrightarrow \beta + \delta$ is observed at 595 K. The solid solution range based on $TlSbSe_2$ do not exceed 14 mol.% at 423 K.

3.2. Tl_2SnSe_3–$TlSbSe_2$ quasibinary system

The phase diagram of the Tl_2SnSe_3–$TlSbSe_2$ system is presented in Fig.2. This system belongs to the Rozeboom type V and is

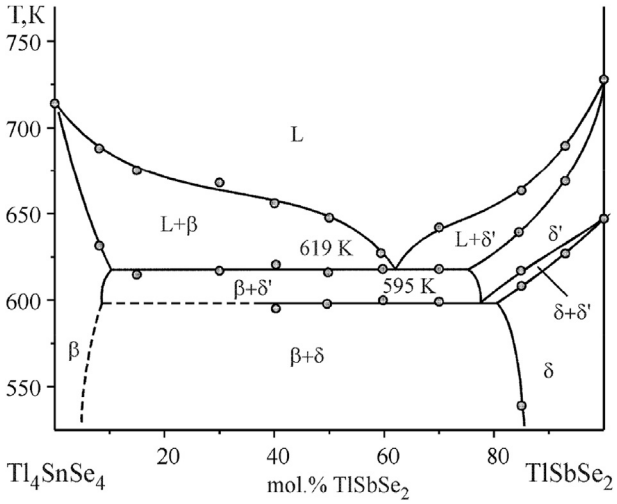

Fig. 1. Phase diagram of the Tl_4SnSe_4–$TlSbSe_2$ system (the accuracy of the points corresponds to 5 K).

characterized by the invariant eutectic processes $L \leftrightarrow ltmTl_2SnSe_3 + htmTlSbSe_2$. The coordinates of the eutectic point correspond to 70 mol.% $TlSbSe_2$ at 635K. In this system are formed ε, ε′ solid solutions based on low-, high-temperature polymorphic modifications of Tl_2SnSe_3 and δ, δ′ solid solutions based on low-, high-temperature polymorphic modifications of $TlSbSe_2$, respectively. The metatectic processes $\varepsilon' \leftrightarrow L + \varepsilon$ based on the polymorphic transformation of the ternary compound Tl_2SnSe_3 is observed at 693 K, eutectic processes $\delta' \leftrightarrow \varepsilon + \delta$ based on the polymorphic transformation of $TlSbSe_2$ takes place at 597 K. At 423 K the existence of the solid solution range of low-temperature polymorphic modification of $TlSbSe_2$ is less than 11 mol.%. The lattice parameters of initial ternary compounds and solid solutions based on $TlSbSe_2$ are shown in Table 1.

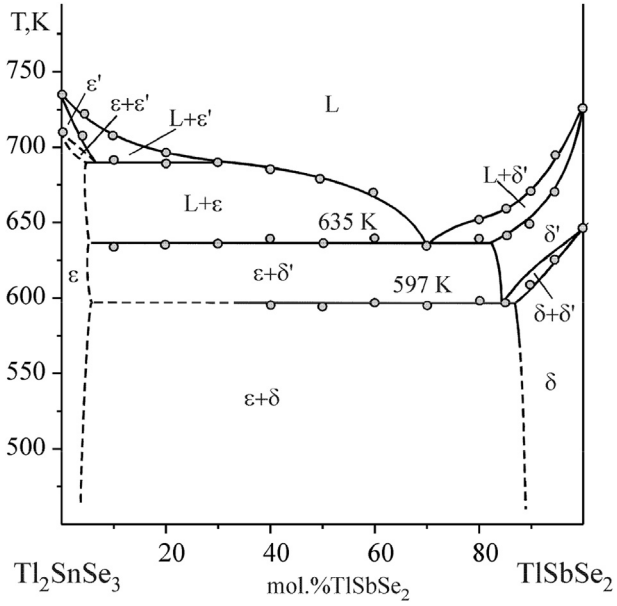

Fig. 2. Phase diagram of the Tl_2SnSe_3–$TlSbSe_2$ system (the accuracy of the points corresponds to 5 K).