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THE SOLID-STATE PHASE DIAGRAM OF THE PbTe-PbSe-Bi_2Se_3-Bi_2Te_3 RECIPROCAL SYSTEM

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Abstract. The solid-phase eqilibria in the Pb-Bi-Te-Se quaternary system along the reciprocal PbTe-PbSe-Bi_2Se_3-Bi_2Te_3 sub-system was investigated experimentally using Scanning Electron Microscope equipped with energy dispersive X-ray detector (SEM-EDS) and X-ray diffraction XRD analyses of the equilibrated alloys. It was shown that the system featured by the formation of the tetradymite-type solid solutions based on the $n(PbTe)\cdot m(Bi_2Te_3)$ compounds (γ_1, γ_2 and γ_3-phases)in the wide range of concentration. The narrow solid solutions having monoclinic structure fields were also revealed from the PbSe-Bi_2Se_3 boundary system based on its ternary $[(PbSe)_5]_n[(Bi_2Se_3)_3]_m$ compounds (δ_1, δ_2 and δ_3-phases). The system has a quite complex phase equilibria scheme with numerous biphasic and triphasic phase areas.

Keywords: *tetradymit-type solid solutions, layered materials, bismuth selenide, lead bismuth telluride, phase diagram*.

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1. Introduction

Recently, binary or more complex layered van der Waals compounds have attracted a lot of interest thanks to their simultaneously thermoelectric and topological insulator properties (Müchler *et al.*, 2013; Okamota *et al.*, 2012; Okuda *et al.*, 2013; Eremeev *et al.*, 2012). Both of these materials are functional materials of enormous interest, as they promise solutions for waste-heat recovery and applications in spintronics, optoelectronics and quantum computing. Among the perspective 3D van der Waals layered tellurides, the most studied materials are ternary ones those in crystal structures, each atomic layer consists of only one type of atoms. However, it was predicted that design the disordered alloys with statistical distribution of different types of atoms would be more attractive from the point of view tuning the electronic surface and band properties (Shvets *et al.*, 2017; Shikin *et al.*, 2014; Klimovckikh *et al.*, 2017; Souma *et al.*, 2012). Up to now, a series of the similar compounds like $PbBi_4Te_7$, $PbBi_6Te_{10}$, $Sn(Bi,Sb)_4Te_7$ etc., formed by alternation of quintuples (five-layered blocks) $[A^V{}_2Te_3]$ and septuples (seven-layered blocks) $[A^{IV}A^V{}_2Te_4]$ (X=Bi, Sb; Y=Pb, Sn) blocks of TIs have been theoretically (Eremeev *et al.*, 2012; Neupane *et al.*, 2012; Verginory *et al.*, 2013, 2015) and experimentally investigated (Okuda *et al.*, 2013; Eremeev *et al.*, 2012; Papagno *et al.*, 2016). Obviously, they are "pure" thellurium-based heterostructured campounds. From the chemical and crystallographic aspects, there is no any impediment to partial substitution of the Te by Se, that leads to

significant modication in the electronic structure. For example, it was shown in Souma *et al.* (2012) that the substitution of Te by Se in septuples of the $PbBi_2Te_{4-x}Se_x$ compound results by significant increase of the bulk band gap.

The boundary quasi-binary systems of the title system were studied very well so far. The phase diagram of the PbTe-Bi_2Te_3 system and its layered ternary compounds are investigated in numerous of works. According to first appeared report by Elagina *et al.* (1959), this system hosts only one intermediate ternary phase, $PbBi_4Te_7$ that melts incongruently at 850 K. Later, the new version of the phase diagram was appeared by Hirai *et al.* (1967) in which new metastable compound, $Pb_2Bi_2Te_5$ was shown instead of stable $PbBi_4Te_7$. This compound was found to be melt peritectially at 851 K and to stable until 668 K. Below, it eutectoidally decomposes into PbTe+Bi_2Te_3 eutectoid mixture. The existence of this compound was confirmed in Refs. (Petrov *et al.*, 1969) as thin films state and its crystal lattice parameters were reported. The latest version of the phase diagram of the PbTe–Bi_2Te_3 system and ternary compounds formed in this system which are belong to $n(PbTe)\cdot m(Bi_2Te_3)$ homologous series, can be found in the series of publications by Shelimova *et al.* (2004) and Karpinskii *et al.* (2002). In these works, shown that the compound $PbBi_4Te_7$ melts congruently at 858 K, whereas $PbBi_2Te_4$ has a peritectic melting point at 856 K. Furthermore, three ternary layered compounds belonging to the homologous series $n(PbTe)\cdot m(Bi_2Te_3)$ were found along this section: $Pb_2Bi_6Te_{11}$, $PbBi_6Te_{10}$, and $PbBi_8Te_{13}$.

Unlike PbTe-Bi_2Te_3 system, in the PbSe-Bi_2Se_3 compounds, the PbSe bilayers are not incorporated into Bi_2Se_3 quintuples to form $PbBi_2Se_4$ seven-layered blocks where Pb atoms take positions in the central atomic plane (Se-Bi-Se-Pb-Se-Bi-Se) (Shelimova *et al.*, 2010). Instead, the composition of the PbSe-Bi_2Se_3 alloys can be expressed by the general formula $[(PbSe)_5]_n[(Bi_2Se_3)_3]_m$. Their monoclinic crystal structures can be described as mBi_2Se_3 quintuple layers sandwiched by adjacenting of n bilayers of rocksalt structured PbSe (Shelimova *et al.*, 2010), forming a natural multilayer heterostructure that consisted by topological insulator and an ordinary insulator. One can see that, would be very interesting to study solubility limit of selenium in the entire PbTe-Bi_2Te_3 compounds. According to Liu *et al.* (1994), within the PbSe-PbTe-Bi_2Se_3-Bi_2Te_3 reciprocal system, the tetradymite structured layered phases extends from initial $PbBi_2Te_4$ up to $PbBi_2Te_{0.88}Se_{3.12}$, however, at higher concentrations for selenium, alloys transform to monoclinic structure from hexagonal. Therefore, in order to rational design of these type new materials strongly requires the investigation of the phase diagram of the respective element systems in order to determine solubility limit, synthesis condition for the poly- and single crystalline alloys, annealing regime, crystallization sequence from liquid phase etc. (Babanly *et al.*, 2017).

In this paper, we present the experimental investigation of the phase relationships in the Pb-Bi-Te-Se system along the PbTe-PbSe-Bi_2Se_3-Bi_2Te_3 reciprocal plane in order to search new quaternary alloys with variable compositions.

2. Experimental Part

2.1. Synthesis

Bismuth, lead, selenium and tellurium (not less than 99.999 mass % purity) purchased from Alfa Aesar were used for the synthesis of starting binary and ternary compounds. The binary Bi_2Te_3, Bi_2Se_3, PbSe and PbTe, as well as the three $[(PbSe)_5]_n[(Bi_2Se_3)_3]_m$ and three $n(PbTe)\cdot m(Bi_2Te_3)$ ternary compounds were

synthesized by melting stoichiometric amounts of the elements in sealed quartz containers at temperatures 1050 and 1380 K for former four binaries and 1050 and 950 K for the latter two families of the compounds. Due to the fact that except binary compounds and $PbBi_4Te_7$, other ternary compounds melt by peritectic reactions, they were additionally annealed at 800 K and 1000 K for 500 h to complete the homogenization. All the alloys were melted at 1200 K for about 10-12 h and were then kept at 800-810 K for about 1000 h. Most of the alloys were then slowly cooled down to room temperature with the furnace, but in some cases, alloys were quenched at 800 K in cold water after annealing to keep the equilibrium state.

2.2. Analysis

XRD and SEM-EDS techniques were used to verify the purity of the synthesized starting compounds and to analyze the alloys. The XRD patterns were recorded on a Bruker D2 PHASER diffractometer with Cu-$K\alpha_1$ radiation within the range of $2\theta=5°\div80°$. The unit cell parameters were calculated by indexing of powder patterns using Topas V3.0 software. The microstructures and equilibrium compositions for some selected samples were determined by Tescan Vega 3 SBH scanning electron microscope equipped with Thermo Scientific Ultra Dry Compact EDS detector.

3. Results and discussion

The solid-state phase diagram of the title system (Fig. 1) was constructed based on the experimental data from XRD analysis and SEM-EDS measurements of the equilibrated alloys. Since the tetradymite-type layered ternary compounds $PbBi_2Te_4$ (I), $PbBi_4Te_7$ (II) and $PbBi_6Te_{10}$ (III), as well as solid-solutions fields based on them are located in the compositional range of ≥75 mol% Bi_2Te_3, the scale of the phase diagram to be extended up twice in vertical direction.

The experimental data shows that in the given reciprocal system exist the wide range of Te→Se substituted solid-solutions based on the ternary compounds (I)-(III) (γ_1, γ_1 and γ_3-phases). The ultimate compositions for the given solid-solutions fields were measured to be as ~70 mol%, ~58 mol% and ~55 mol% Bi_2Se_3 for the γ_1-, γ_1- and γ_3-phases, respectively.

As can be seen from the phase diagram, the measured homogeneity fields of the δ_1, δ_2 and δ_3-phases based on $Pb_5Bi_6Se_{14}$, $Pb_5Bi_{12}Se_{23}$, and $Pb_5Bi_{18}Se_{32}$, respectively, do not excess ~10 mol% along the composition rectangle.

According to literature data, the boundary systems PbSe-PbTe (Liu *et al.*, 1994(1)) and Bi_2Se_3-Bi_2Te_3 (Bounani *et al.*, 1996) of the PbTe-PbSe-Bi_2Se_3-Bi_2Te_3 reciprocal system featured by the formation of the continuous α- and β solid-solution fields, respectively.

The existence of the γ_1-phase based on the compound (I) was experimentally confirmed in our previous work (Aliev, 2019). The existences of the other two solid-solutions fields, γ_2- and γ_3 were also confirmed by the same way.

Thanks to the presence of the aforementioned phases with variable compositions, the numerous bi-and triphasic areas appear in the system (Fig. 1). Most of the biphasic areas shown in the phase diagram ($\alpha+\gamma_1$, $\gamma_1+\gamma_2$, $\gamma_2+\gamma_3$, $\gamma_3+\beta$, $\alpha+\delta_1$, $\delta_1+\delta_2$, $\delta_2+\delta_3$ and $\beta+\delta_3$) experimentally confirmed by means of XRD and SEM-EDS techniques. In order to confirm the tentatively plotted phase diagram, here we present SEM images and XRD patterns of the some alloys taken from the various phase areas. For instance, biphasic content of the alloy #1 (*for alloy composition see Fig. 1*) according to α- and γ_1-phases

based on the $PbBiTe_{1-x}Se_x$ and $PbBi_2Te_{4-x}Se_x$ systems clearly seen from the SEM image (Fig. 2).

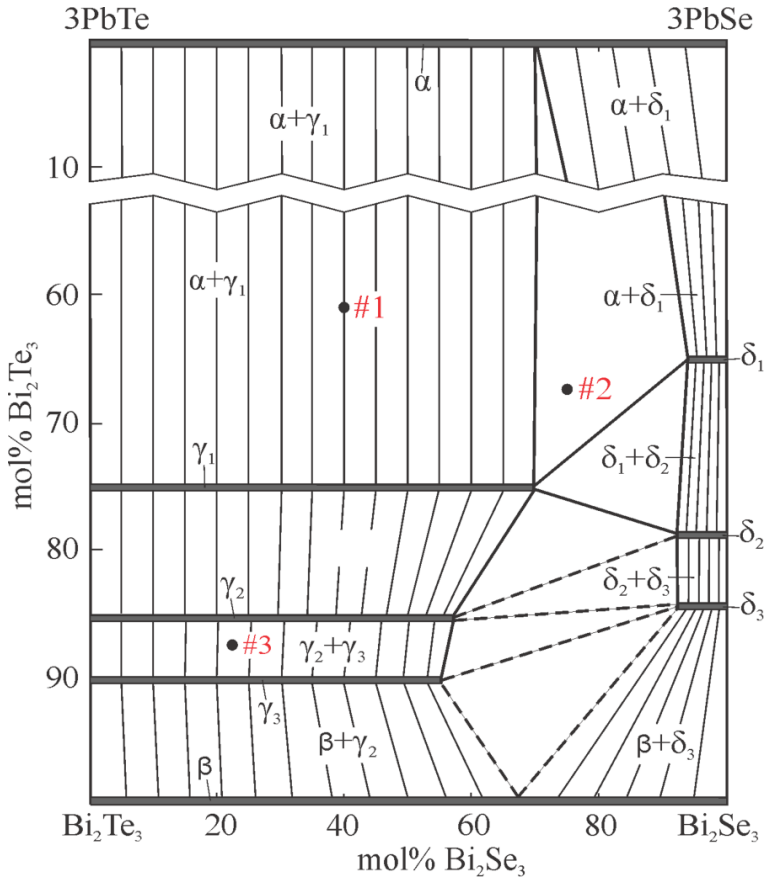

Figure 1. The solid-state phase diagram of the reciprocal PbTe-PbSe-Bi_2Se_3-Bi_2Te_3 system

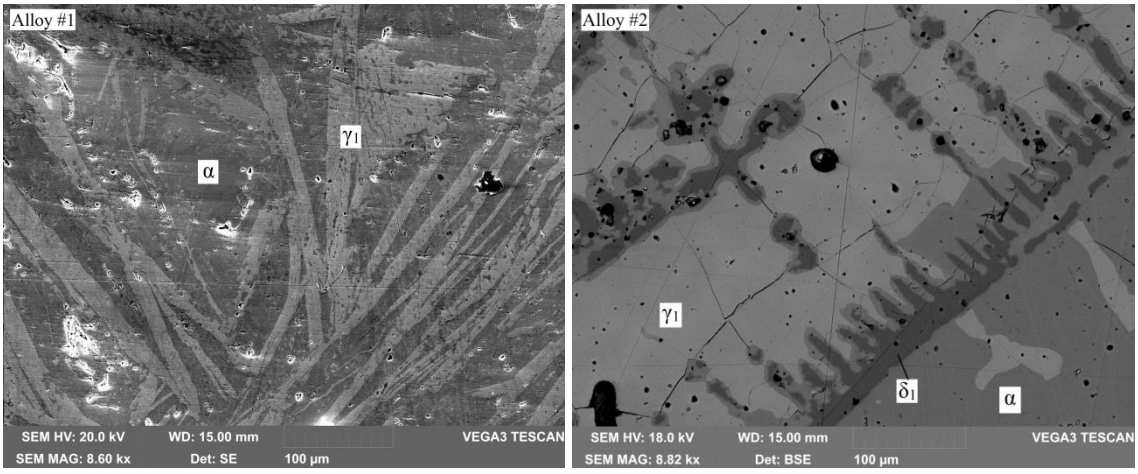

Figure 2. SEM micrographs of the alloys #1 and #2. The alloys compositions are shown on Fig. 1

The SEM micrograph of the alloy #2 selected from three-phase $\alpha+\gamma_1+\delta_1$ area agree very well with its clearly seen triphasic content according to very good crystallized cubic α, tetradymite-type layered γ_1 and monoclinic δ_1-solid solutions. The XRD pattern of the alloy #3 clearly show the biphasic content of its according the γ_2 and

γ_3 based on the $PbBi_4Te_7$ and $PbBi_6Te_{10}$ compounds. The existence of the $\alpha+\gamma_1+\delta_1$ and $\gamma_1+\delta_1+\delta_2$ was also confirmed experimentally. Nevertheless, unfortunately we were not able to detect other triphasic areas which are possible to appear close to Bi_2Se_3 corner of the composition rectangle. An assumed several triphasic areas in these part was drawn tentatively by dot-lines. The confirmation of these areas requires further carefully investigations in the narrow composition areas.

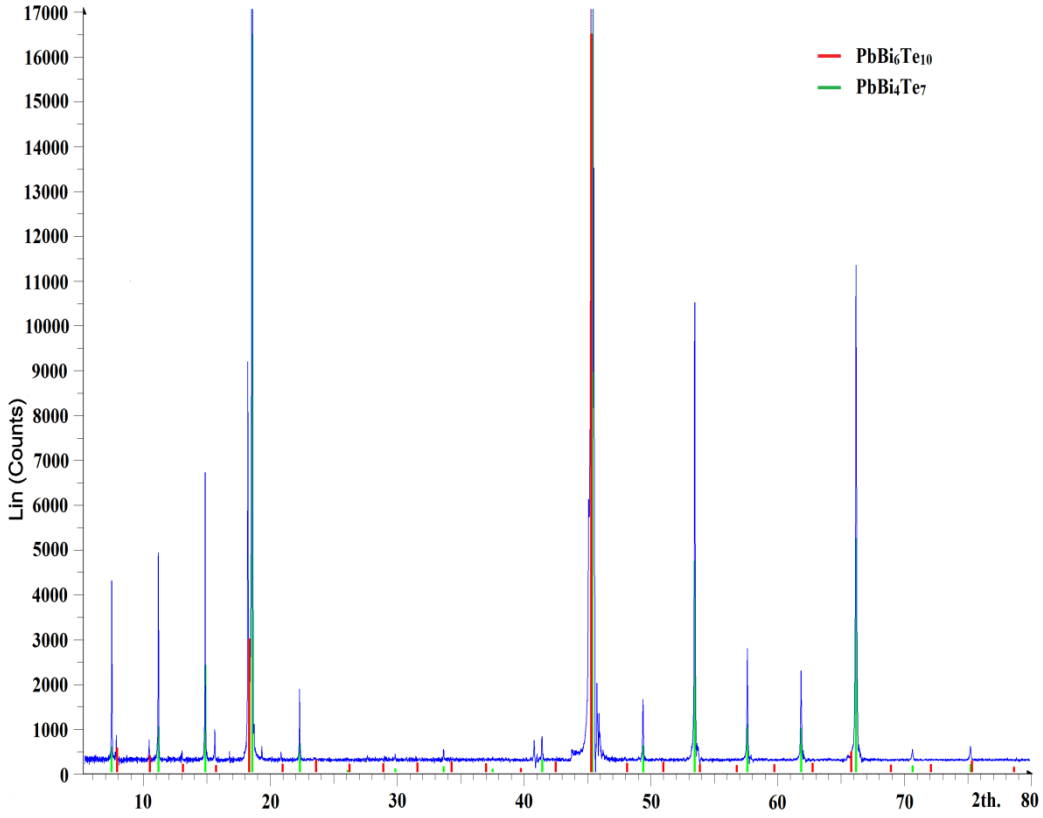

Figure 3. XRD patterns alloy #3. The alloy composition is shown on Fig. 1

4. Conclusion

Using the SEM-EDS and XRD techniques, the solid-state phase diagram of the reciprocal PbTe-PbSe-Bi_2Se_3-Bi_2Te_3 system was investigated experimentally. The system host two type of the solid-solutions fields. One of them is the tetradymite-type solid solutions based on the $n(PbTe)\cdot m(Bi_2Te_3)$ compounds (γ_1, γ_2 and γ_3-phases) in the wide range of concentration. Second one is the monoclinic structured solid-solutions based on the ternary $[(PbSe)_5]_n[(Bi_2Se_3)_3]_m$ compounds (δ_1, δ_2 and δ_3-phases). The given phase diagram can shed light on the design of the $n(PbTe_{1-x}Se_x)\cdot m(Bi_2Te_{3-x}Se_x)$ disordered alloys where tellurium atoms in the quintuple and septuple blocks substituted by the selenium. Substitution of the tellurium by selenium in such structures can significantly modify the electronic structure of the materials.

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