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**NOVEL VARIABLE PHASES IN THE QUATERNARY Pb–Bi–Te–Se SYSTEM
ALONG THE PbBi_2Te_4 –“ PbBi_2Se_4 ” ISOPLETH SECTION****Z.S.Aliev***Azerbaijan State Oil and Industry University**Institute of Physics, NAS of Azerbaijan**ziyasaliev@gmail.com; ziya.aliev@asoiu.edu.az*

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The phase equilibria in the Pb–Bi–Te–Se quaternary system along the PbBi_2Te_4 –“ PbBi_2Se_4 ” isopleth section was investigated experimentally using differential thermal analysis and X-ray diffraction analyses of the equilibrated alloys. It was shown that the system is non-quasi-binary one and featured by the formation of the tetradymite-type solid solutions based on the PbBi_2Te_4 in the wide range of concentration. The system has a more complex phase equilibria scheme that comes from its host reciprocal PbTe–PbSe– Bi_2Se_3 – Bi_2Te_3 system. One can see that, in order to reveal the phase equilibria scheme and understand the crystallization scheme, reactions types etc., the thorough investigation of the entire pointed reciprocal PbTe–PbSe– Bi_2Se_3 – Bi_2Te_3 system is very important.

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

*doi***Introduction**

Up to date, numerous binary or more complex compounds have been reported to have topological insulating properties [1–4]. Among them, the most studied materials are tetradymite-like layered compounds in which each atomic layer consists of only one type of atoms. Nevertheless, it has been predicted that it is possible to design the disordered alloys with statistical distribution of different types atoms [5–8]. For instance, a series of the similar heterostructured compounds like PbBi_4Te_7 , $\text{PbBi}_6\text{Te}_{10}$, $\text{Sn}(\text{Bi},\text{Sb})_4\text{Te}_7$ etc., formed by alternation of quintuples (five-layered blocks) $[\text{A}^{\text{V}}_2\text{Te}_3]$ and septuples (seven-layered blocks) $[\text{A}^{\text{IV}}\text{A}^{\text{V}}_2\text{Te}_4]$ ($\text{X}=\text{Bi}, \text{Sb}$; $\text{Y}=\text{Pb}, \text{Sn}$) blocks of TIs have been theoretically [4, 9–11] and experimentally investigated [3, 4, 12]. As can be seen, the mentioned heterostructured compounds are only tellurium-based compounds. However, theoretically there is no any impediment to partial substitution of the tellurium by selenium that leads to significant modification in the electronic structure. For example, it was shown in [9] that the substitution of Te by Se in septuples of the $\text{PbBi}_2\text{Te}_{4-x}\text{Se}_x$ compound results by significant increase of the bulk band gap. In the aforementioned type heterostructures, which are contain alternation of the quintuples and septuples with both Se and Te atoms, the band gaps is expected to be significant wide.

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 [13], 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 [14] in which new metastable compound, $\text{Pb}_2\text{Bi}_2\text{Te}_5$ 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. [15] 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 $n(\text{PbTe})\cdot m(\text{Bi}_2\text{Te}_3)$ homologous series, can be found in the series of publications by Shelimova and Karpinskii [16, 17]. 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 $n(\text{PbTe})\cdot m(\text{Bi}_2\text{Te}_3)$ were found along this section: $\text{Pb}_2\text{Bi}_6\text{Te}_{11}$, $\text{PbBi}_6\text{Te}_{10}$, and $\text{PbBi}_8\text{Te}_{13}$.

Unlike PbTe–Bi₂Te₃ system, in the PbSe–Bi₂Se₃ compounds, the PbSe bilayers are not incorporated into Bi₂Se₃ quintuples to form PbBi₂Se₄ septuples containing Pb atoms in the central atomic plane (Se–Bi–Se–Pb–Se–Bi–Se) [17]. Instead, the composition of the PbSe–Bi₂Se₃ alloys can be expressed as [(PbSe)₅]_n[(Bi₂Se₃)₃]_m, which are the monoclinic crystal structure can be described as *m*Bi₂Se₃ quintuple layers sandwiched by adjacent of *n* bilayers of rocksalt structured PbSe [18], forming a natural multilayer heterostructure that consisted by topological insulator and an ordinary insulator. One can see that, starting from the PbBi₂Te₄ compound it would be very interesting to study solubility limit of selenium in the entire PbTe–Bi₂Te₃ system. According to [19], within the PbSe–PbTe–Bi₂Se₃–Bi₂Te₃ reciprocal system, the tetradymite structured layered phases extends from initial PbBi₂Te₄ up to PbBi₂Te_{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.

In this paper, we present the experimental investigation of the phase relationships in the Pb–Bi–Te–Se system along the PbBi₂Te₄–“PbBi₂Se₄” section in order to search new quaternary alloys with variable compositions.

Experimental Part

Synthesis. Synthesis of the PbBi₂Te₄–“PbBi₂Se₄” alloys was performed from the respective elements of a high purity grade (not less than 99.999%) in sealed ($\sim 10^{-2}$ Pa) silica ampoules at 1200 K according to phase diagram of the PbTe–Bi₂Te₃ [16] and PbSe–Bi₂Se₃ systems [18]. The samples were stirred at this temperature by shaking the furnace and then cooled down to room temperature with the switched-off furnace. The synthesized alloys were further

annealed at 820 K for 200 h in order to get complete homogenization.

Analysis. The equilibrated alloys were analyzed by X-ray powder diffraction (XRD) and differential thermal analysis (DTA). X-ray powder diffraction data were collected at room temperature using a Bruker D8 ADVANCE powder diffractometer with CuK α_1 radiation within the range of $2\theta = 5^\circ$ – 75° . The unit cell parameters were calculated by indexing of powder patterns using Topas V3.0 software. For the DTA measurements, the THERMOSCAN-2 device equipped with chromel–alumel thermocouples was used. The heating rate was 10 K·m⁻¹. Temperatures of thermal effects were taken from the heating curves.

Results and discussion

The phase diagram of the PbBi₂Te₄–“PbBi₂Se₄” isopleth section was plotted based on the DTA and XRD data of the equilibrated alloys. The plotted phase diagram (Figure 1) shows that this system is non-quasi-binary isopleth of the quaternary system Pb–Bi–Te–Se along the PbTe–PbSe–Bi₂Se₃–Bi₂Te₃ plane. As can be seen from the phase diagram, the PbSe_{1-x}Te_x solid solutions (α -phase) primarily crystallizes from the liquid phase.

Obviously from literature data, the boundary PbSe–PbTe sub-system of the PbTe–PbSe–Bi₂Se₃–Bi₂Te₃ reciprocal system featured by the formation of the continuous solid solution field, whereas, other two sub-systems, namely PbTe–Bi₂Te₃ and PbSe–Bi₂Se₃ host ternary compounds PbBi₂Te₄ [16] and Pb₅Bi₆Se₁₄ [18] those melt incongruently with formation of the L+PbTe and L+PbSe biphasic mixtures.

The XRD analysis of the alloys shows that the system hosts tetradymite-type solid-solution field based on the PbBi₂Te₄ (Figure 2) up to ~ 75 mol% “PbBi₂Se₄”.

Within the compositional range up to 75 mol% “PbBi₂Se₄”, the crystallization process below the liquidus continuous on the peritectic L+ $\alpha \leftrightarrow \gamma_1$ reaction, where γ_1 is the solid solution based on PbBi₂Te₄. This monovariant process ends up simultaneously complete consuming of melt and α -phase, consequently the system

transform to monophasic phase of γ_1 . This is due to fact that, all the investigated alloys having chemical composition according to $\text{PbBi}_2\text{Te}_{4-x}\text{Se}_x$ stoichiometry.

Within the compositional range of ~75-100 mol% " PbBi_2Se_4 " one can see the complex physicochemical interaction of the phases,

where only through investigation of the entire reciprocal $\text{PbTe-PbSe-Bi}_2\text{Se}_3\text{-Bi}_2\text{Te}_3$ system can help to understand the crystallization schemes, reactions types etc. The phase diagram illustrated in Figure 2, present an assumed scheme of the phase equilibria in this phase area.

Fig. 1. XRD patterns for different alloys in the PbBi_2Te_4 –" PbBi_2Se_4 " isopleth section. The alloys compositions are given according to their selenium content.

Fig. 2. The phase diagram of the isopleth section PbBi_2Te_4 –" PbBi_2Se_4 ".

According to phase diagram of the PbSe–Bi₂Se₃ system [19], an alloy "PbBi₂Se₄" contains two phases, namely Pb₅Bi₆Te₁₄ and Pb₅Bi₁₂Te₂₃ which are melt incongruently at 993 and 973 K by peritectic reactions $L + \text{PbSe} \leftrightarrow \text{Pb}_5\text{Bi}_6\text{Te}_{14}$ and $L + \text{Pb}_5\text{Bi}_6\text{Te}_{14} \leftrightarrow \text{Pb}_5\text{Bi}_{12}\text{Te}_{23}$ respectively. Along the title isopleth, these processes are monovariant ones. Taking into account high probability of formation solid solutions (δ_1 and δ_2) based on these ternary compounds along the PbBi₂Te₄–"PbBi₂Se₄" isopleth, these processes can be written as $L + \alpha \leftrightarrow \delta_1$ and $L + \delta_1 \leftrightarrow \delta_2$. Taking into account these equilibria, one can assume the presence of the following phase areas $L + \alpha \leftrightarrow \delta_1$, $L + \delta$, $L + \delta_1 \leftrightarrow \delta_2$ and $\delta_1 + \delta_2$. In our opinion, horizontal at 935 K on the phase diagram of the title isopleth section representing an invariant $L + \delta_1 + \delta_2 \leftrightarrow \gamma_1$ equilibrium. In different finishing versions of this reaction, the following mono-, bi- and triphasic areas appear in the system: γ_1 , $\gamma_1 + \delta_1$ (or $\gamma_1 + \delta_2$) and $\gamma_1 + \delta_1 + \delta_2$

Conclusion

The phase diagram of the PbBi₂Te₄–"PbBi₂Se₄" isopleth section of Pb–Bi–Te–Se quaternary system was studied experimentally and wide range of tetradymite-type solid solutions based on PbBi₂Te₄ was revealed. The given phase diagram can shed light on the design of the PbBi₂Te_{4-x}Se_x disordered alloys in which tellurium atoms in the septuple blocks substituted by the selenium. As known, partially substitution of the tellurium by selenium leads to significant modification in the electronic structure of the materials, i.e., introducing Se atoms in the tetradymite-type layered materials significantly increase their bulk band gaps.

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Pb–Bi–Te–Se SİSTEMİNDƏ PbBi_2Te_4 –“ PbBi_2Se_4 ” POLİTERMİK KƏSİYİ ÜZRƏ DƏYİŞƏN TƏRKİBLİ YENİ FAZALAR

Z.S.Əliyev

Pb-Bi-Te-Se dördlü sistemində faza tarazlıqları PbBi_2Te_4 –“ PbBi_2Se_4 ” politermik kəsiyi üzrə təcrübi olaraq differensial termiki analiz və rentgenfaza analizi üsulları ilə tədqiq edilmişdir. Müəyyən edilmişdir ki, qeyd olunan kəsik qeyri-kvazibinar olub, geniş qatılıq intervalında PbBi_2Te_4 əsasında tetradimit quruluşlu bərk məhlulların əmələ gəlməsi ilə xarakterizə olunur. PbBi_2Te_4 –“ PbBi_2Se_4 ” politermik kəsiyi mürəkkəb faza tarazlığı mənzərəsinə sahibdir ki, bu da onun mənsub olduğu $\text{PbTe-PbSe-Bi}_2\text{Se}_3\text{-Bi}_2\text{Te}_3$ qarşılıqlı sisteminin xüsusiyyətləri ilə bağlıdır. Bu kəsik üzrə baş verən bütün tarazlıq proseslərini müəyyən etmək üçün həmin qarşılıqlı sistemin geniş qatılıq və temperatur intervalında öyrənilməsi vacibdir.

Açar sözlər: tetradimitəbənzər bərk məhlullar; laylı quruluşlu materiallar; bismut selenid; qurğuşun bismut telluridləri; faza diagramı.

НОВЫЕ ФАЗЫ ПЕРЕМЕННОГО СОСТАВА ПО РАЗРЕЗУ PbBi_2Te_4 –“ PbBi_2Se_4 ” ЧЕТВЕРНОЙ СИСТЕМЫ Pb-Bi-Te-Se

З.С.Алиев

Методами дифференциального термического и рентгенфазового анализов исследованы фазовые равновесия по политермическому сечению PbBi_2Te_4 –“ PbBi_2Se_4 ” четверной системы Pb-Bi-Te-Se . Установлено, что данный разрез неквазибинарный и характеризуется образованием широкой области твердых растворов с тетрадимитоподобной структурой на основе PbBi_2Te_4 . Данный политермический разрез имеет сложную картину фазовых равновесий, обусловленную особенностями взаимной системы $\text{PbTe-PbSe-Bi}_2\text{Se}_3\text{-Bi}_2\text{Te}_3$. Для точного установления всех равновесных процессов необходимо изучение указанной взаимной системы в широком интервале составов и температур.

Ключевые слова: тетрадимитоподобные твердые растворы, слоистые материалы, селенид висмута, теллуриды свинца висмута, фазовая диаграмма.