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PHASE RELATIONS IN THE $PbTe$-$AgSbTe_2$ SYSTEM

Shabnam Hamlet Mansimova

Baku State University
23, Z.Khalilov str., AZ-1148 Baku, Azerbaijan; e-mail: sebnem.mensimova86@gmail.com

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Abstract: *Phase equilibria in the PbTe-$AgSbTe_2$ section of the quasiternary Ag_2Te-PbTe-Sb_2Te_3 system were studied by means of differential-thermal and X-ray analyses, as well as microhardness measurements. For investigations, two series of alloys of the explored section were prepared by two different ways. Based on the experimental data, the T-x diagram of the PbTe-$AgSbTe_2$ section was constructed. It found that a wide area (30-100 mol% PbTe) of solid solutions based on lead telluride was formed in the system. A characteristic feature of this system is a large temperature range (up to 150 °) of crystallization (melting) of solid solutions which leads to strong segregation and heterogeneity of solid solutions.*

Keywords: *PbTe-$AgSbTe_2$ system, phase diagram, solid solutions, silver-lead-antimony tellurides*
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Introduction

In recent years, thermoelectric (TE) materials have been widely studied to be used as alternative energy sources and in novel energy conversion applications. In this respect, many semiconducting chalcogenides have attracted much attention for the development of TE materials [1-3]. Various complex tellurides such Ag-A^{IV}-B^{V}-Te (A^{IV}- Ge, Sn, Pb; B^{V}-Sb, Bi) alloys have high ZT values and are mentioned among the most promising thermoelectric materials [4-6]. It must be noted that the $AgSbTe_2$ alloy has been used as an important component to construct the TE materials with excellent TE properties, such as $(PbTe)_m(AgSbTe_2)$ (denoted as LAST) and $(GeTe)_x(AgSbTe_2)_{100-x}$ (named as TAGS). The ZT value of LAST reaches 2.2 at 800 K when *m* is 18. The TAGS-x has a ZT value over 1.5 at 800 K when *x* is 80 or 85 [7-11].

Recent studies showed that complex tellurides of heavy p-metals exhibit topological surface states as well, and can be used in spintronics and quantum computing [12-14].

It has to be kept in mind that optimization of functional properties of these materials can be achieved by changing their composition. This is based, in turn, on the research into phase equilibriums in relevant systems [15-17]. In the case of Ag_2Te-A^{IV}Te-$B^{V}{}_2Te_3$ systems, it would be very interesting to look for new complex phases because binary and ternary compounds in these systems have already been recognized as promising matrix phases.

The phase equilibriums in the Ag_2Te-SnTe-Sb_2Te_3, Ag_2Te-SnTe-Bi_2Te_3 and Ag_2Te-PbTe-Bi_2Te_3 systems had already been described in communications [18-21]. For the both systems, several new non-stoichiometric phases were found, and their primary crystallization and homogeneity fields determined. It revealed that the homogeneity region of solid solutions formed along A^{IV}Te-Ag $B^{V}Te_2$ sections expanded greatly in both directions.

Herein, we present the phase relationships in the Ag_2Te-PbTe-Sb_2Te_3 system over the PbTe-$AgSbTe_2$ section. In [22], it was shown that the compound of the $AgSbTe_2$ composition previously mentioned in the literature [23, 24] did not exist, and the cubic phase in the Ag_2Te-Sb_2Te_3 system had a slightly different composition ($Ag_{19}Sb_{29}Te_{52}$). According to [25], $Ag_{19}Sb_{29}Te_{52}$ decomposed by solid-phase reaction upon cooling does not exist below 250 K. Thus, the results of [22, 25] cast doubt on the existence of continuous solid solutions in the PbTe-$AgSbTe_2$ system.

Experimental part

For the experiments, binary tellurides Ag_2Te, PbTe, and Sb_2Te_3 were first synthesized. These compounds were prepared through melting high-purity elements (99.999 wt. %) in evacuated (~10^{-3} Pa) silica ampoules at a temperature of~50 K higher than their melting points [26]. The Ag_2Te was additionally annealed at 1200 K for 3 hours and then quenched with cold water in order to obtain a homogeneous stoichiometric composition. All starting compounds were identified through the use of differential thermal analysis and powder X-ray diffraction techniques.

More than ten alloys of the PbTe-$AgSbTe_2$ section were prepared from the pre-synthesized binary compounds also by means of vacuum alloying. Two series of alloys were obtained in two ways. One series of samples after fusion was slowly cooled to 750 K and annealed at this temperature for 700 hours. The second series of samples were quenched by injecting ampoules into cold water from 1150 K (alloys with compositions of 70, 80 and 90 mol% PbTe) and from 1000 K (other alloys), and then annealed at 750 K for 700 h.

Results and discussion

Fig. 1 shows thermograms for heating alloys of both series with compositions 60, 80 and 90 mol% PbTe. As can be seen, the melting onset temperatures of the two series of alloys are greatly different. For samples of the 1st series (red curves) obtained by slow cooling, the melting onset temperatures are significantly (up to 100º) lower than those of the 2nd series (blue curves). Note that rise in the annealing time up to 1000 h did not change the DTA curves of the alloys of the 2nd series, whereas for those of the 1st series some (~ 10–20 °) rise in the temperatures of the onset of melting was observed.

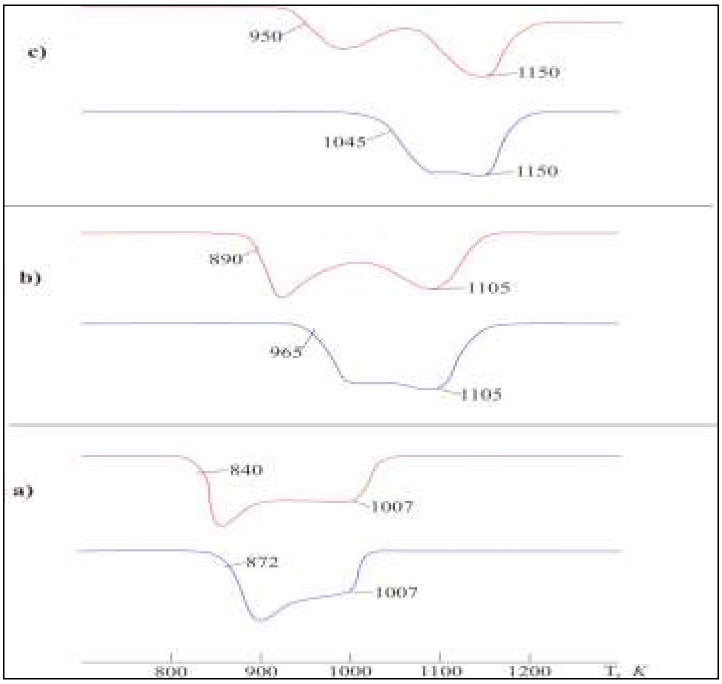


Fig.1. Fragments of the DTA curves for the PbTe-“$AgSbTe_2$” system alloys with the compositions 60 (**a**), 80 (**b**) and 90 (**c**) mol% PbTe. DTA curves for samples from the 1st series are red, and those from the 2nd series are blue.

The results above are indicative that the Series II samples can be considered practically in equilibrium. Therefore, to construct the phase diagram (**Fig. 2**) of the PbTe-“AgSbTe2” system, data from DTA alloys of series II were used (**see Table**). According to **Fig. 2**, the PbTe-“$AgSbTe_2$” system is characterized by the formation of about 70 mol% of solid solutions based on PbTe (β-phase); however, as a whole, the system is generally non-quasi-binary. This is due to the fact that one of the starting components, i.e. “$AgSbTe_2$”, is not an individual compound but a two-phase alloy Ag_2Te+$Ag_{19}Sb_{29}Te_{52}$ [11,14]. This goes to show that the solid phase (Ag_2Te+$Ag_{19}Sb_{29}Te_{52}$) not located on its T-x plane of the PbTe-«$AgSbTe_2$» section is involved in the phase equilibria of this section along the of <30 mol% PbTe composition area.

Table. DTA and microhardness measurement data for the PbTe-“$AgSbTe_2$” system

Composition, *mol % PbTe*	Thermal effect, *K*	H_μ, *MPa*
0	500; 635; 813; 813-840	580;750
5	500; 620; 805; 805-827	
10	500; 603; 805; 805-820	580;790
20	808-825	580;820
30	815-853	
40	827-885	840
50	848-935	
60	872-1007	730
70	913-1058	
80	965-1105	620
90	1045-1150	

The powder X-ray analysis results confirmed the formation of a wide area (30-100 mol% PbTe) of solid solution with a cubic structure in the explored system. PbTe-poor alloys are three-phase (β+Ag_2Te+ Sb_2Te_3).

A characteristic feature of the PbTe-“$AgSbTe_2$” system is a very large temperature range of crystallization (melting) of the β-phase (up to 150 °). For this reason, slow cooling of melts leads to strong segregation and heterogeneity of solid solutions which makes it difficult to achieve an equilibrium state of the samples. The heterogeneity of solid solutions in the 1st series alloys is clearly apparent by a powder X-ray patterns of an alloy with a composition of 70 mol% PbTe (**Fig. 3**). As can be seen, X-ray patterns of samples of this alloy obtained through the use of two different ways, differ strongly. The alloy from the 1st series has very diffuse reflection peaks while the alloy from the 2nd series has a very high quality X-ray pattern.

The results of microhardness measurements (**Table, Fig.2**) are in accordance with the phase diagram. The microhardness values of the β-phase are due to continuous function of the composition and expressed by a curve with a gentle maximum. In alloys with compositions of 10 and 20 mol% PbTe in addition to the β-phase, there are two more phases with microhardness values of ~ 380 and 590 MPa. Following the results of X-ray diffraction analysis of these alloys, these microhardness values refer to Ag_2Te and Sb_2Te_3 compounds.

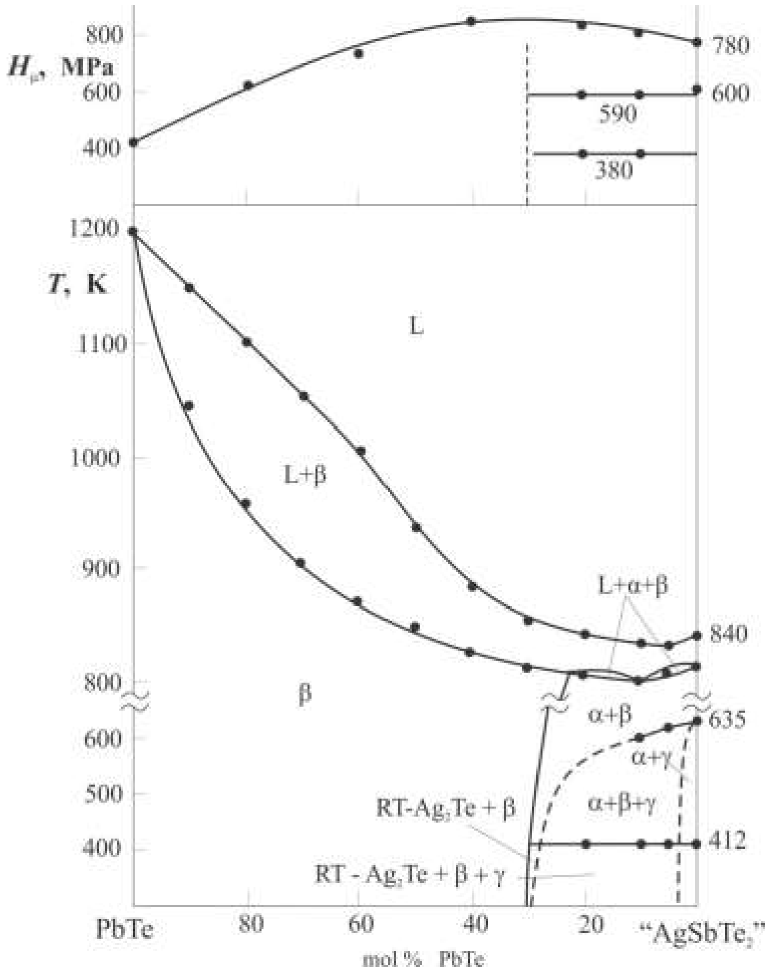
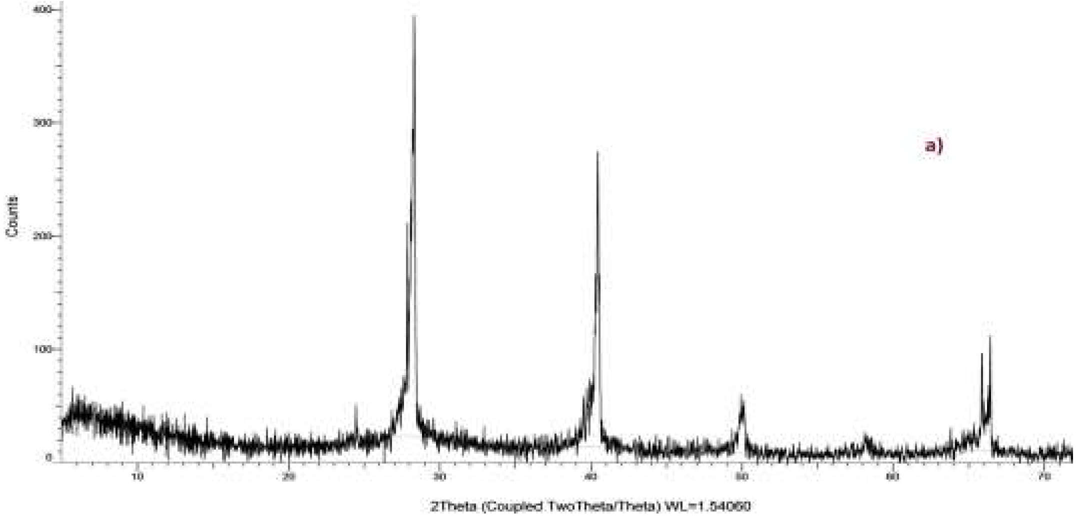


Fig.2. Phase diagram and concentration dependence of microhardness for the PbTe-"$AgSbTe_2$" system



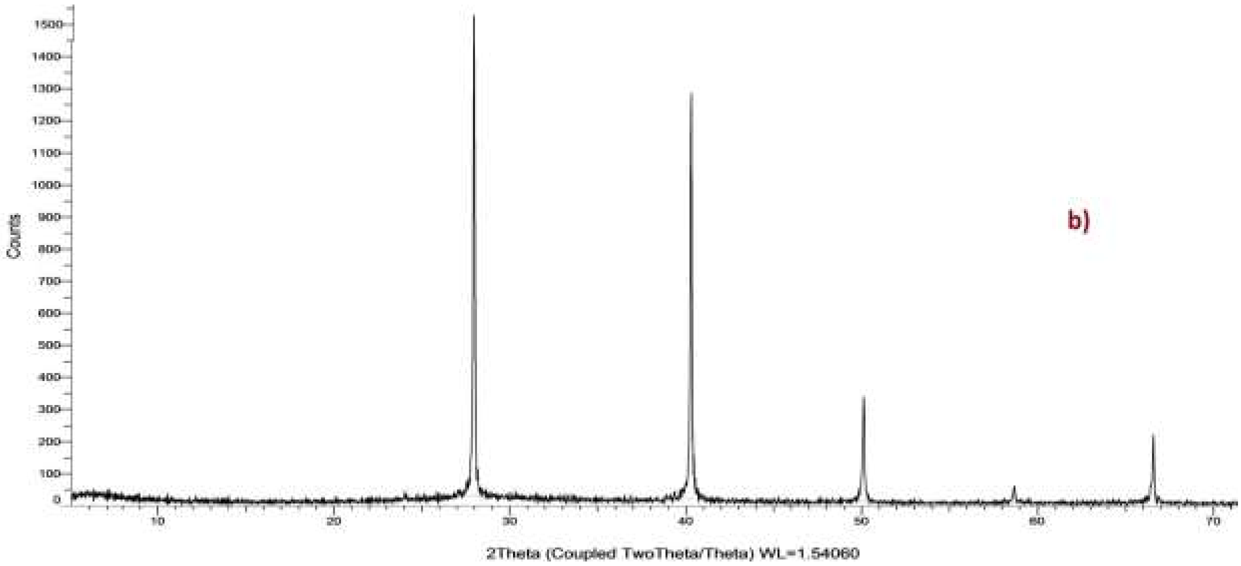


Fig.3. Powder X-ray patterns of alloy with composition of 70 mol% PbTe:
a) a sample from the 1st series; **b)** a sample from the 2nd series

Conclusion

Based on the data of DTA, XRD and microhardness measurements, the nature of phase equilibriua in the $PbTe-AgSbTe_2$ section of the $Ag_2Te-PbTe-Sb_2Te_3$ quasi-ternary system was uncovered. In particular, it found that this section is partially quasi-binary and characterized by the formation of a wide (up to 70 mol %) PbTe (β-phase)-based solid solutions region. Within the 0-30 mol% PbTe composition range the alloys of the system consist of a three-phase mixture $Ag_2Te+Sb_2Te_3+\beta$. A characteristic feature of this system is a large temperature range (up to 150°) of crystallization (melting) of the β-phase that involves a strong segregation and heterogeneity of solid solutions in composition. The obtained solid solutions are of practical interest as medium-temperature thermoelectric materials.

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$PbTe-AgSbTe_2$ SİSTEMİNDƏ FAZA TARAZLIQLARI

Şəbnəm Hamlet qızı Mənsimova

Bakı Dövlət Universiteti
Z. Xəlilov 23, Az-1148 Bakı, e-mail: sebnem.mensimova86@gmail.com

İşdə DTA, RFA və mikrobərkliyin ölcülməsi ilə $Ag_2Te-PbTe-Sb_2Te_3$ kvaziüçlü sistemin kəsiyi üzrə faza tarazlıqları öyrənilmiş və T-x diaqramı qurulmuşdur. Göstərilmişdir ki, sistemdə qurğuşun tellurid əsasında geniş bərk məhlul sahəsi (30-100 mol% PbTe) əmələ gəlir. Bu sisitemin əsas xüsusiyyəti bərk məhlulların kristallşma (ərimə) temperatur intervalının böyük olmasıdır. Bu isə bərk məhlulların güclü likvasiyası və qeyri-bircinsliyi ilə nəticələnir.
Açar sözlər: *$Ag_2Te-PbTe-Sb_2Te_3$ sistemi, faza diaqramı, bərk məhlullar, gümüş-qurğuşun-stibium telluridləri*

ФАЗОВЫЕ РАВНОВЕСИЯ В СИСТЕМЕ $PbTe-AgSbTe_2$

Ш.Г. Мансимова

Бакинский Государственный Университет
AZ 1148 Баку, ул. З.Халилова, 23; e-mail: sebnem.mensimova86@gmail.com

Методами дифференциально-термического и рентгенфазового анализов, а также измерением микротвердости изучены фазовые равновесия по разрезу $PbTe-AgSbTe_2$ квазитройной системы $Ag_2Te-PbTe-Sb_2Te_3$. Для проведения исследований были приготовлены две серии сплавов исследуемого разреза двумя различными способами. На основании экспериментальных данных построена T-x диаграмма разреза $PbTe-AgSbTe_2$. Показано, что в системе образуется широкая область (30-100 мол% PbTe) твердых растворов на основе теллурида свинца. Характерной особенностью данной системы является большой температурный интервал (до 150°) кристаллизации (плавления) твердых растворов, что приводит к сильной ликвации и неоднородности твердых растворов.
Ключевые слова: *система $PbTe-AgSbTe_2$, фазовая диаграмма, твердые растворы, теллуриды серебра-свинца-сурьмы.*