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PHYSICO-CHEMICAL INTERACTION IN THE BiSI–BiTeI SYSTEM

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Based on the results of the DTA and X-ray phase analysis, the phase equilibria in the BiTeI–BiSI system were studied and the T – x phase diagram was constructed. It was established that the system is stable in the subsolidus area and there are ~7–8 mol % and ~5 mol% solid solution areas based on BiTeI and BiSI compounds at room temperature, accordingly. In 2016 general, the system is non-quasibinary. Bi₁₉S₂₇I₃ (0–33 mol % BiTeI) and tetradymite-Bi₂Te₂S (33–83mol% BiTeI) phases primarily crystallize from the liquid phase in the wide composition ranges.

Keywords: BiTeI–BiSI system, phase diagram, solid solutions, Rashba semiconductors.

doi**Introduction**

Due to their unique properties, B^VXHal (B^V – As, Sb, Bi; X – S, Se, Te; Hal – Cl, Br, I) type compounds have been in the center of the researchers' attention from the middle of the last century [1–3]. These compounds exhibit ferroelectric, thermoelectric, photovoltaic, magnetic, optical etc. properties and are considered a promising material for solar-powered devices [4–12]. In recent years, the topological insulator properties and 3D Rashba spin splitting have been observed in these compounds [13–17], that made these alloys even more attractive.

The phase equilibria in B^V–X–Hal systems were studied, the projection of liquidus surfaces was constructed, melting character and primary crystallization regions of existing phases were determined [18–23].

Obtention of phases of variable compositions on basis of the B^VXHal type compounds is of great importance to find materials with superior functional properties. The BiTeI–BiSeI and BiTeI–SbTeI systems which are interesting in this regard, have been studied by authors [24, 25] and a wide range of solid solutions based on the Rashba semiconductor BiTeI have been detected. Hence, the purpose of the present contribution is to investigate the equilibria in the BiTeI–BiSI system and to search for new phases.

Initial compounds of the BiTeI–BiSI system have been studied in detail. BiTeI melts congruently at 828 K [26]. It has a hexagonal struc-

ture with lattice parameters: $a = 4.3392$ (1), $c = 6.854$ (1) Å, $z = 1$ [27]. BiSI melts incongruently by decomposition at 808 K [28] along the quasi binary Bi₂S₃–BiI₃ system. This compound has orthorhombic crystal structure with: $a = 8519$ (5), $b = 10177$ (8), $c = 4172$ (6) Å, $z = 4$ [29].

Experiments and analyses

The syntheses of the initial BiTeI and BiSI compounds were carried out by co-melting the stoichiometric proportions of high purity (99.999% by weight) elements in an inclined two-zone furnace under vacuum condition (10^{–2} Pa). Initially, the temperature of the "hot" zone was 900 K, whereas the "cold" zone temperature kept at 400 K (the sublimation temperature of iodine is 386 K) considering the high vapor pressure of iodine. After much of the iodine was reacted, the ampoule moved to the "hot" zone. After stirring the homogeneous liquid in the ampoule at this temperature, the furnace cooled gradually. At the next stage, the incongruently melting BiSI compound was annealed at 750 K for 300 h and the congruently melting BiTeI was annealed at 780 K for 20 h, to achieve complete homogenization.

Two sets of samples of different composition (0.5 g each) of the BiTeI–BiSI system were synthesized in evacuated quartz ampoules using initially prepared and identified compounds and annealed at 700 K for 2 weeks. Experimental studies were conducted by differential-thermal analysis (DTA) and X-ray phase analysis (XRD).

The DTA was carried out using the differential-scanning calorimeter "NETZSCH 404 F1 Pegasus system" (speed of heating 10 K/min), and XRD—in the Bruker D8 diffractometer ($\text{CuK}\alpha$ -radiation) at the $2\theta = 5^\circ\text{--}75^\circ$ range.

Discussion of the experimental results

Figure 1 represents the powder X-ray diffraction patterns of thermally treated alloys. As can be seen, the diffraction pattern of the 90 mol% BiSI sample consists mainly of the BiSI diffraction peaks. The lines of the most intense peaks of the solid solutions based on BiTeI are also observed (12.8° , 26.9° , 35.5° and 46.3°). Similarly, the diffraction pattern of the 10 mol% BiSI sample consists mainly of the BiTeI diffraction peaks and lines of the most intense peaks (18° , 20.1° , 22.5° and 28.5°) of the solid solutions based on BiTeI. From this result, we can predict that the solubility regions based on BiTeI and BiSI are $\sim 7\text{--}8$ and 5 mol% respectively. The powder X-ray diffractograms of the 10–90 mol% BiSI-containing samples consist of peaks of both mutually saturated solid solutions.

T - x phase diagram of the system was constructed using DTA results (Table 1). The system is non-quasibinary due to the peritectic melting character of BiSI. However, it is stable in subsolidus and characterized by the for-

mation of limited solid solutions on the basis of initial compounds (Figure 2).

Liquidus consists of three curves. Based on T - x diagrams of the Bi_2S_3 – BiI_3 [18] and Bi_2Te_3 – BiI_3 [19] systems, we can assume that ε (based on $\text{Bi}_{19}\text{S}_{27}\text{I}_3$), δ (based on $\text{Bi}_2\text{Te}_2\text{S}$) and γ_2 (based on BiTeI) phases crystallize in the 0–33 mol% BiTeI, 33–83 mol% BiTeI and >83 mol% composition interval, respectively. Crystallization in the $L+\varepsilon$ field continues with monovariant $L+\varepsilon\leftrightarrow\gamma_1$ peritectic (PU_1 curve) and $L\leftrightarrow\varepsilon+\gamma_2$ eutectic (15–40 mol% BiTeI) reactions. The horizontal line at 775 K conforms the transition reaction (U_1):

Crystallization in the 40–53 mol% BiTeI composition intervals continues with monovariant $L\leftrightarrow\gamma_1+\delta$ and in the 53–83 mol% BiTeI composition intervals – with eutectic $L\leftrightarrow\gamma_2+\delta$ reactions. At about 8–83 mol% BiTeI composition interval crystallization ends by the transition reaction (U_2) (Figure 2):

At the transition reaction temperature, the homogeneity area of the γ_1 phase is ~ 7 mol%, and the homogeneity area of the γ_2 phase is ~ 13 mol%.

Fig. 1. X-ray images of some alloys of the BiTeI–BiSI system.

Fig. 2. Phase diagram of the BiTeI-BiSI system.

DTA results for the system BiTeI-BiSI

Composition, mol% BiTeI	Thermal effects, K
0 (BiSI)	808; 895
5	780-800-873
10	753; 775-788-848
15	753; 775-828
20	753; 775-780-811
25	753; 775-782-801
30	753; 775-785-791
40	753; 775-798
50	733; 758-805
60	753; 766-809
70	753; 782-810
80	753; 796-806
90	788-813
100 (BiTeI)	828

Fig. 3. DTA curves of some alloys of the system BiTeI-BiSI.

Let us explain the phase diagram (Figure 2) in the context of heating curves (Figure 3) of some alloys in the BiTeI–SbTeI system. As it can be seen, a diffused endo effect is observed in the heating thermogram of 90 mol% BiTeI containing sample. This reflects the melting of the γ_2 phase based on BiTeI at 788–813 K. The strong endo effect observed at 753 K in a sample of 80 mol% BiTeI is appropriate to the U_2 transition reaction, subsequent thermal effects reflect the monovariant eutectic $L \leftrightarrow \gamma_2 + \delta$ process and the end of melting. On the thermogram of 40 mol% BiTeI containing sample, the sharp peak at 753 K represents U_2 transition reaction, while the peaks at 775 K and 798 K belong to the melting of $L + \gamma_1 + \delta$ and $L + \delta$ eutectic mixtures, accordingly. Similarly, in 10 mol% BiTeI containing sample the intensive peaks at 753 K and 775 K belong to U_2 and U_1 transition reactions, and the peaks at 788 K and 848 K demonstrate the melting of $L + \epsilon + \gamma_1$ and $L + \epsilon$ eutectic mixtures.

Conclusion

For the first time, the existence of $\text{BiTe}_{1-x}\text{Sb}_x\text{I}$ solid solutions was detected using DTA and XRD methods and the phase diagram of the system was constructed. It was established that, although the system is non-quasibinary, it is stable in subsolidus and is characterized by the formation of limited solid solutions on the basis initial compounds. Maximum solubility was observed at 750 K: ~ 6 mol% on the basis of BiSI and more than ~ 10 mol% based on BiTeI. New solid solutions based on the BiTeI are of great practical interest as potential Rashba semiconductors and topological insulator materials.

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BiSI–BiTeI SISTEMİNDƏ FİZİKİ-KİMYƏVİ QARŞILIQLI TƏSİR

E.C.Əhmədov

DTA və RFA nəticələrinə əsasən BiTeI–BiSI sistemində faza tarazlıqları öyrənilmiş və T – x faza diaqramı qurulmuşdur. Müəyyən olunmuşdur ki, sistem subsolidusda stabildir və otaq temperaturunda BiTeI əsasında 7–8 mol%, BiSI əsasında isə 5 mol%-ə yaxın bərk məhlul sahəsi əmələ gətirir. Bütövlükdə isə sistem qeyri-kvazibinardır. Geniş tərkib intervallarında maye fazadan ilkin olaraq $\text{Bi}_{19}\text{S}_{27}\text{I}_3$ (0–33 mol% BiTeI) və tetradimit – $\text{Bi}_2\text{Te}_2\text{S}$ (33–83 mol% BiTeI) kristallaşır.

Açar sözlər: BiTeI–BiSI sistemi, faza diaqramı, bərk məhlullar, Rashba yarımkəçiriciləri.

ФИЗИКО-ХИМИЧЕСКОЕ ВЗАИМОДЕЙСТВИЕ В СИСТЕМЕ BiSI–BiTeI

Е.Дж.Ахмедов

На основании результатов ДТА и рентгенофазового анализов были изучены фазовые равновесия в системе BiTeI–BiSI и построена фазовая диаграмма T – x . Установлено, что система стабильна в области субсолидуса. На основе соединений BiTeI и BiSI образуются твердые растворы, которые при комнатной температуре занимают области ~7–8 и ~5 мол% соответственно. Однако в общем система – неквазибинарная. В широком диапазоне составов из жидкости кристаллизуются $\text{Bi}_{19}\text{S}_{27}\text{I}_3$ (0–33 мол% BiTeI) и тетрадимит– $\text{Bi}_2\text{Te}_2\text{S}$ (33–83моль% BiTeI).

Ключевые слова: система BiTeI–BiSI, фазовая диаграмма, твердые растворы, полупроводники Рашибы.