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PHASE EQUILIBRIA IN THE SYSTEM SbTeI-BiTeI

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Abstract. The phase equilibria in the system SbTeI-BiTeI were studied and the T-x phase diagram of the system was constructed using DTA and XRD methods. It was established that, the system is stable in subsolidus area and forms substitutional solid solutions based on the initial compounds. There are ~67 mol% and ~10 mol% solubility regions on the basis of BiTeI and SbTeI compounds, accordingly. New solid solutions obtained based on the BiTeI compound are of interest as topological insulator materials and Rashba semiconductors.

Keywords: *SbTeI-BiTeI system, phase diagram, solid solutions, Rashba semiconductors.*

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1. Introduction

One of the most pressing problems in inorganic material science in recent years is the acquisition of new functional materials for quantum computing and spintronics. Such materials include topological insulators, substances exhibiting 3D Rashba Spin Splitting (RSS) (Eremeev *et al*., 2012, 2017; Papagno *et al*., 2016; Viti *et al.*, 2016; Landolt *et al.*, 2012). The most typical representative of RSS samples is the BiTeI compound (Wu *et al.*, 2016; Kanou & Sasagawa, 2013; Ideue et al., 2014; Maa et al., 2016).

Compounds of type $B^{V}XHal$ (B^{V} - As, Sb, Bi, X - S, Se, Te, Hal - Cl, Br, I) have been in the center of the researchers' attention from the middle of the last century (Gerzanich & Fridkin, 1982; Dönges, 1950). In the course of numerous research, their interesting thermoelectric, photoelectric, optical, ferroelectric, and so on. properties have been detected (Audzijonis *et al*., 2008; Koc *et al*., 2017; Rusinov *et al*., 2016; Tablero, 2016; Ozer & Cabuk, 2018; Guo & Zhang, 2017; Dubey *et al*., 2014, Khan *et al*., 2017). Many of these substances are applied or are considered promising for the application in different areas of the technique. Because in such phases there is high possibility to change the composition at large intervals, which opens up great opportunities for the optimization of the properties.

One of the rational ways to optimize the properties of known compounds with functional properties is obtention of new multi-component phases of variable composition by studying phase equilibrium in relevant systems (Babanly *et al*., 2017; Imamaliyeva *et al*., 2018; Babanly & Tagiyev, 2018). Because in such phases it is

possible to change the composition at large intervals, which opens up great opportunities for the optimization of the properties.

The BiI_3-SbI_3-Bi_2Te_3-Sb_2Te_3 system is of interest in the search for new materials with RSS properties, since formation of wide substitution solid solutions is expected in the SbTeI-BiTeI cross section.

This contribution presents results of the study of phase equilibrium in the SbTeI-BiTeI system. Initial compounds of this system have been studied in detail. It has been established that SbTeI melts incongruently by peritectic reaction at 645K (Aleshin *et al*., 1974), and BiTeI - congruently at 828K (Tomokiyo *et al*., 1977). Complete phase diagrams of the Sb(Bi)-Te-I systems were constructed, primary crystallization regions of phases in both systems, as well as types and coordinates of non- and monovariant equilibria were determined, and thermodynamic properties of SbTeI and BiTeI compounds were studied (Aliev *et al.*, 2012; Babanly *et al*., 2009). It was established that SbTeI has a monoclinic structure with a = 13.7008, b = 4.2418, c = 9.2005, β = 128.631º, and z = 4, whereas BiTeI has a hexagonal composition with a = 4.3392, c = 6.854, z = 1 cell parameters (Papazoglou & Rentzeperis, 1983; Shevelkov *et al*., 1995).

2. Experimental. Materials and syntheses

Elements of high purity (99.999% by weight) from Alpha Aesar company were used for synthesis of the initial ternary compounds. Synthesis was carried out by co-melting the stoichiometric proportions of these compounds in an inclined two-zone furnace under vacuum condition (10^{-2} Pa). Methods of synthesis are described in detail (Aliev *et al*., 2012; Babanly *et al*., 2009). The temperature of the "cold" zone was 400 K (the sublimation temperature of iodine is 386K (Leenson, 2005)), whereas the temperature of the "hot" zone was kept at a temperature 30–50 K higher than the melting points of the corresponding compounds. At the next stage, the SbTeI compound was powdered, pressed as pellets, and annealed at 600 K for 1000 hours. Congruently melting BiTeI compound was processed for 20 hours at 780 K.

Two sets of samples of different composition (0.5 g each) of the SbTeI-BiTeI system were prepared under vacuum by melting preliminarily synthesized and identificated ternary compounds and thermally treated for 1000 hours at 600 K. 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 10 K / min), and XRD - in the Bruker D8 diffractometer (CuK_α radiation) at 2θ = 10° -70°.

3. Results and discussion

Figure 1 shows powder X-rays diffraction patterns of thermally treated alloys. As can be seen, diffraction patterns of all the samples between pure BiTeI and the alloy of the 40 mol% BiTeI composition are similar to each other and differs only by a slight shift of the diffraction lines. This means that, up to 60% of bismuth atoms can be replaced by stibium atoms while maintaining the crystal structure of the BiTeI compound. On the other hand, the diffraction pattern of the 10 mol% BiTeI sample consists mainly of the SbTeI diffraction peaks and lines of the most intense peaks (27.1, 35.2 and 39.1º) of the solid solutions based on BiTeI are also observed. The powder X-

ray diffractograms of the 20 and 30 mol% BiTeI-containing samples consist of peaks of both mutually saturated solid solutions (Fig.1).

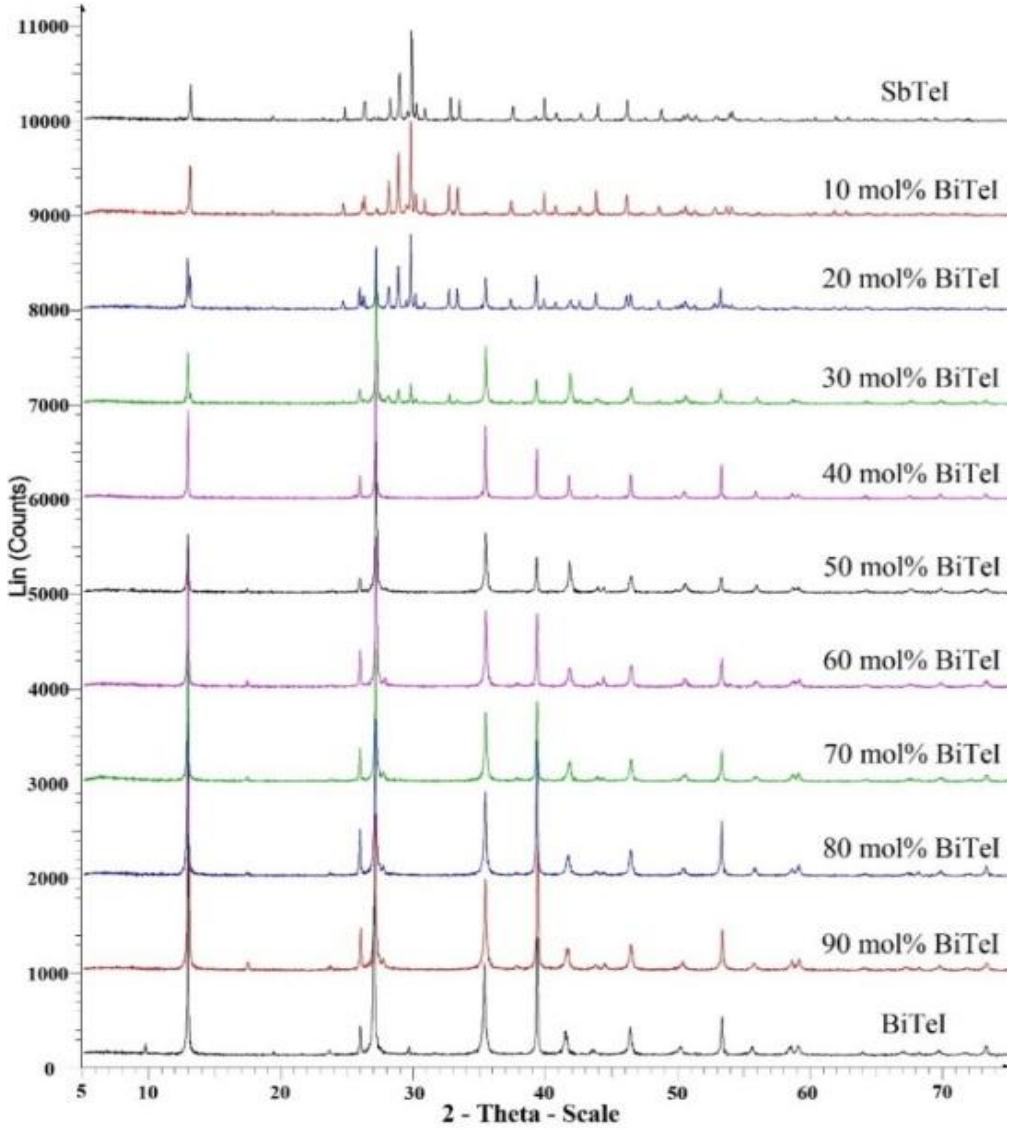

Figure 1. X-ray images of some alloys of the BiTeI-SbTeI system

T-x phase diagram of the system was constructed using DTA results (Table 1). The system is non-quasibinary due to the incongruent melting character of the SbTeI. However, it is stable in subsolidus and forms wide substitutional solid solutions based on the primary compounds (Fig.2). Liquidus consists of two curves. A solid phase of $Sb_{2-x}Bi_xTe_3$ composition (α-phase) primarily crystallizes in the the 0-80 mol% BiTeI composition intervale, while solid solutions based on BiTeI (γ_2-phase) crystallize in the >80 mol% BiTeI phase region. Crystallization in the L + α field continues with monovariant L + α↔γ_1 perithetic (PU curve) and L↔a + γ_2 eutectic (10-80 mol% BiTeI) reactions (Fig.2,3; Table1). Horizontal line at 668 K conforms the transition reaction (U): L + α ↔ γ_1 + γ_2. The γ_1 + γ_2 phase is formed as a result of this reaction below the solidus. At the transition reaction temperature, the homogeneity area of the γ_1 phase is ~ 15 mol%, and the homogeneity area of the γ_2 - phase is ~ 73 mol%.

Table 1. DTA results for the SbTeI-BiTeI system

Composition, mol% BiTeI	**Thermal effects, *K***
0 (SbTeI)	645; 845
5	648; 843
10	653-668; 842
15	668-715-841
20	668-738-840
25	668-760-839
30	739-772-838
40	776-794-836
50	793-805-833
60	797-809-823
70	805-822
80	815-820
90	814
100 (BiTeI)	828

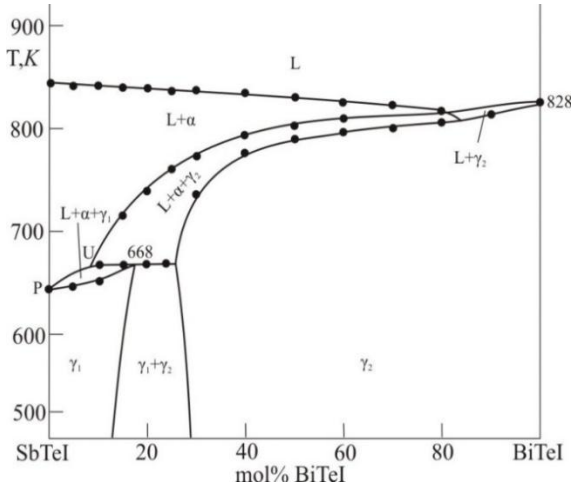

Figure 2. Phase diagram of the SbTeI-BiTeI system

Table 2. Crystal lattice parameters of the initial compounds and γ_2-phase in the SbTeI-BiTeI system

Composition, mol%BiTeI	**Phase content**	**Lattice parameters, Å**
20	$\gamma_1+\gamma_2$	*a=4.3139(4) c=6.8635(6)*
30	$\gamma_1+\gamma_2$	*a=4.3143(4) c=6.8633(6)*
40	γ_2	*a=4.3172(3) c=6.8627(5)*
50	γ_2	*a=4.3214(3) c=6.8612(5)*
60	γ_2	*a=4.3257(3) c=6.8601(6)*
70	γ_2	*a=4.3302(4) c=6.8585(6)*
80	γ_2	*a=4.3346(4) c=6.8569(6)*
90	γ_2	*a=4.3387(3) c=6.8558(5)*
100 (BiTeI)	γ_2	*a=4.3430(3) c=6.8547(5)*

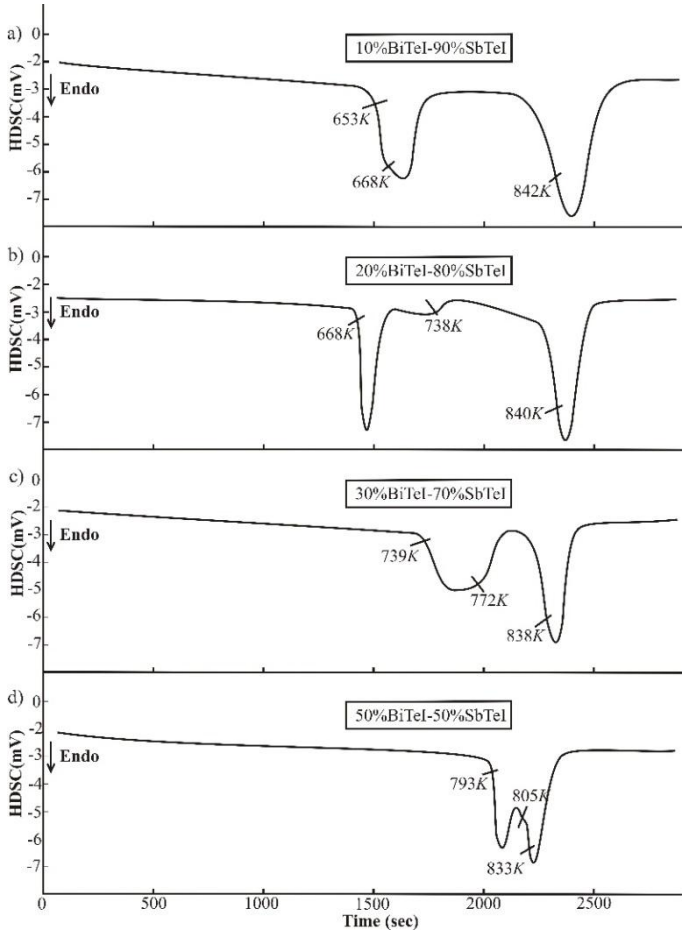

Figure 3. DTA curves of some alloys of the BiTeI-SbTeI system

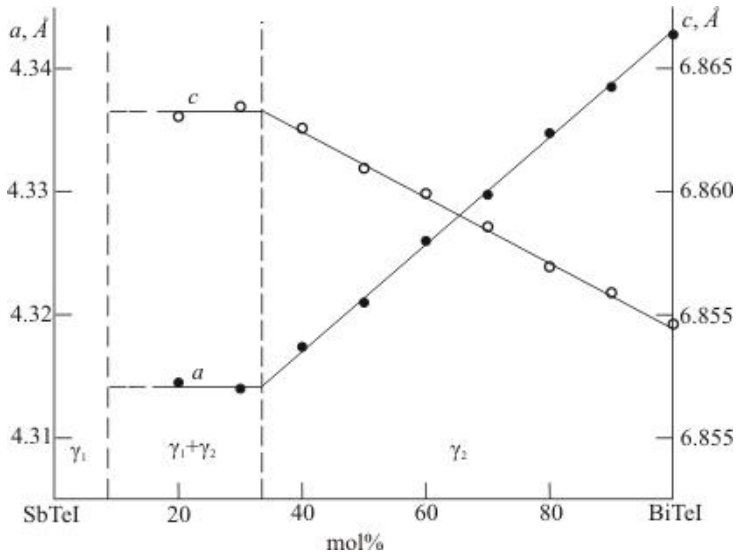

Figure 4. Dependence of lattice parameters of the γ_2- phase upon composition

Crystal lattice parameters of the γ_2-solid solutions were calculated using Topaz V 3.0 computer software based on powder X-ray patterns (Table 2). As can be seen from the dependence graph of the lattice parameters upon composition (Fig.4), they change as a linear function of composition within the homogeneity area of the γ_2- phase and remain constant within the γ_1+ $\gamma_2$two-phase area. Test points have ~ 67 mole% BiTeI composition. This composition corresponds to the maximum concentration of the γ_2 - phase at room temperature.

4. Conclusion

For the first time, the interaction between the SbTeI and BiTeI compounds were investigated using DTA and XRD methods and the phase diagram of the system was constructed. It has been established that, although the system is non-quasibinary, it is stable in subsolidus and is characterized by formation of wide solid solutions based on the initial compounds. The solubility is ~ 67 mol% on the basis of BiTeI and about ~ 10 mol% based on the SbTeI at room temperature. Obtained new solid solutions based on the BiTeI are of great practical interest as potential Rashba semiconductors and topological insulator materials.

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