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PHASE EQUILIBRIA OF THE Bi_4Se_3-Bi_4Te_3 SYSTEM AND CRYSTALLOGRAPHIC STUDY OF $Bi_4Se_{3-x}Te_x$ SOLID SOLUTIONS

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Abstract. The phase relations in the Bi_4Se_3-Bi4Te_3 system were investigated using the results of DTA and PXRD of balanced alloys. Analysis of the experimental data showed that below the solidus, the system is stable and forms a continuous series of solid solutions with a trigonal structure. The lattice parameters of solid solutions determined from powder diffractograms by the Rietveld method increase linearly with increasing Te concentration which is in accordance with Vegard's rule.

Keywords: *bismuth tellurides, bismuth selenides, tetradymite-type structure, phase equilibria, solid solutions, topological insulators.*

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1. Introduction

Tetradymite-type layered bismuth chalcogenides have long been in the center of close attention of researchers as advanced functional materials. These compounds, especially Bi_2Se_3 and Bi_2Te_3, as well as solid solutions, doped phases, and composites based on them, are intensively studied as thermoelectric materials and are used in the manufacture of portable refrigerators, temperature control devices, and for power generation at space stations, etc (Rowe, 2006; Shevelkov, 2008, Tumelero *et al.*, 2019; Duong *et al.*, 2017; Witting *et al.*, 2020; Goldsmid, 2014). After the discovery of a new quantum state of matter - a topological insulator (TI) (Moore, 2010; Hasan *et al.*, 2010; Kane *et al.*, 2011), it was shown that these phases also exhibit the properties of TI, and are extremely favorable for various applications, including spintronics, quantum computers, medicine, security systems, etc (Sultana *et al.*, 2017; Le *et al.*, 2017; Pesin *et al.*, 2012; Politano *et al.*, 2015; Heremans *et al.*, 2017, Hogan *et al.*, 2019).

However, an analysis of literature data shows that in contrast to Bi_2Te_3, the functional properties of the mixed-layer compounds of the $nBi_2 \cdot mBi_2Te_3$homologous series have been studied very poorly, which is apparently due to the difficulty of obtaining high-quality samples, particularly monocrystals.

The development of methods and optimization of the conditions for the synthesis of compounds and the design of materials, especially in the so-called alloy systems, requires knowledge of phase equilibria and reliable thermodynamic data of the corresponding systems (Babanly *et al.*, 2017, 2019). At same time, systems containing compounds-structural analogs are of particular interest, since one can expect vast regions of solid solutions in them (Orujlu, 2020; Imamaliyeva *et al.*, 2020).

In this work, we present an experimental investigation of phase equilibria in the Bi_4Se_3-Bi_4Te_3 system and crystallographic study of $Bi_4Se_{3-x}Te_x$ solid solution. These

type of solid solutions by selective replacing of atoms on the same sites creates a chance to control tunable properties by adjusting the concentration of substitutional atoms.

According to (Hasanova *et al.*, 2021a), in Bi-Tebinary system, a total of seven tetradymite-type layered compounds are formed according to the newly refined version of the phase diagram constructed by us. Bi_4Te_3 compound melts with peritectic reaction at 435°C and crystallizes in rhombohedral structure (Sp.gr.*R*-3*m*) with following lattice parameters: *a*=4.4440 and *c*=41.890 Å (Bos *et al.*, 2007). Similarly, the Bi-Se binary system contains seven tetradymite-type layered compounds with almost stoichiometric compositions (Hasanova *et al.*, 2021b). Bi_4Se_3 melts peritectically at 556°C. It has the same rhombohedral structure (Sp.Gr.*R*-3*m*) as Bi_4Te_3 with lattice parameters of *a*=4.332 and *c*=40.610 Å (Okamoto 1994).

2. Experimental part

The alloys of the studied system were synthesized by fusing of high purity elemental bismuth, selenium, and tellurium in evacuated (~10^{-2} Pa) quartz ampoules. When developing the synthesis methodology of samples, we assumed that the bulk samples of layered phases obtained by the widely used fusion method do not reach an equilibrium state even after a long period (2000–3000 h) of thermal annealing (Abrikosov *et al.*, 1960; Sher *et al.*, 1986). This is apparently because, unlike conventional bulk samples, van der Waals phases obtained in non-equilibrium crystallization conditions (i.e., ordinary cooling of the melt) practically do not undergo any changes during further thermal treatment due to very low diffusion between layers.

Taking this into account, to ensure a high dispersion of samples, after alloying, samples were quenched by dropping ampoules into the ice water from a liquid state (600ºC). Additionally, all samples were annealed at temperatures of 400-500ºC depending on the compositions to obtain equilibrium compositions.

Studies were carried out by powder X-ray diffraction (PXRD) and differential thermal analysis (DTA) techniques. DTA curves were recorded on a NETZSCH 404 F1 Pegasus system. Powder diffractograms of the initial compounds and intermediate alloys were recorded using Bruker D2 diffractometer with $CuK\alpha_1$ radiation in the range of $2\theta = 5 \div 75°$. The indexing of the PXRD patterns and the refinement of the lattice parameters were implemented using the FullProf software by the Le Bail method.

3. Results and discussion

The PXRD patterns of equilibrated alloys are shown in Fig. 1a. As can be seen, each intermediate alloy has qualitatively identical diffractograms with primary binary compounds. An analysis of these diffraction lines shows that they are fully indexed in rhombohedral structure with space group *R*-3*m*. The lattice parameters of all alloys were determined by the Rietveld technique. The observed and calculated data of the powder diffraction pattern belongs to alloy with 60 mol% Bi_4Te_3 composition are shown in Fig. 1b, and determined lattice parameters of alloys are given in Table. As the composition changes from selenides to tellurides, the diffraction peaks undergo a slight shift in the direction of the small angles, while their total number remains unchanged. It is happened due to an increase in the lattice parameters as the tellurium concentration increases with the Se→Te substitution. It was observed that lattice parameters increase linearly with increasing concentration of Te content according to Vegard's law (Fig.

2a). These results provide strong evidence that a continuous series of solid solutions are formed in Bi_4Se_3-Bi_4Te_3 section.

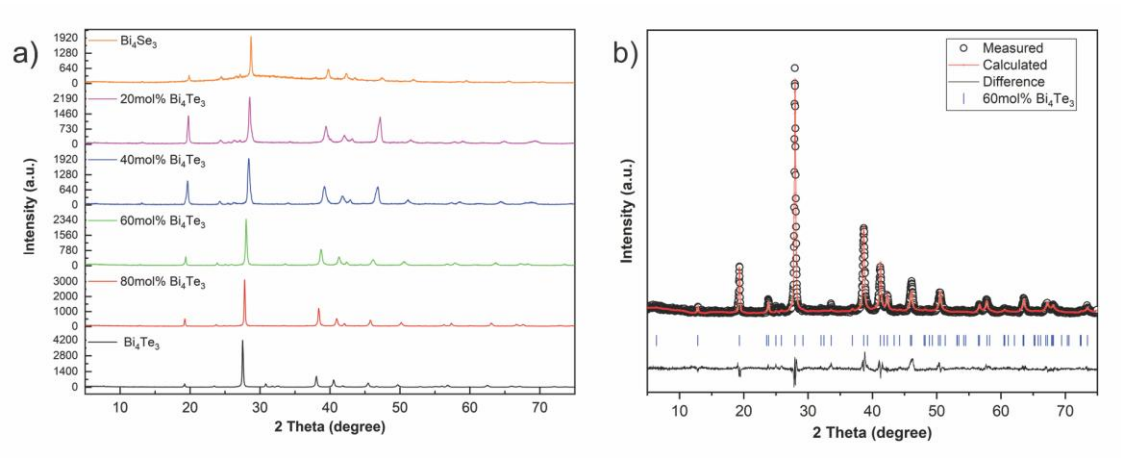
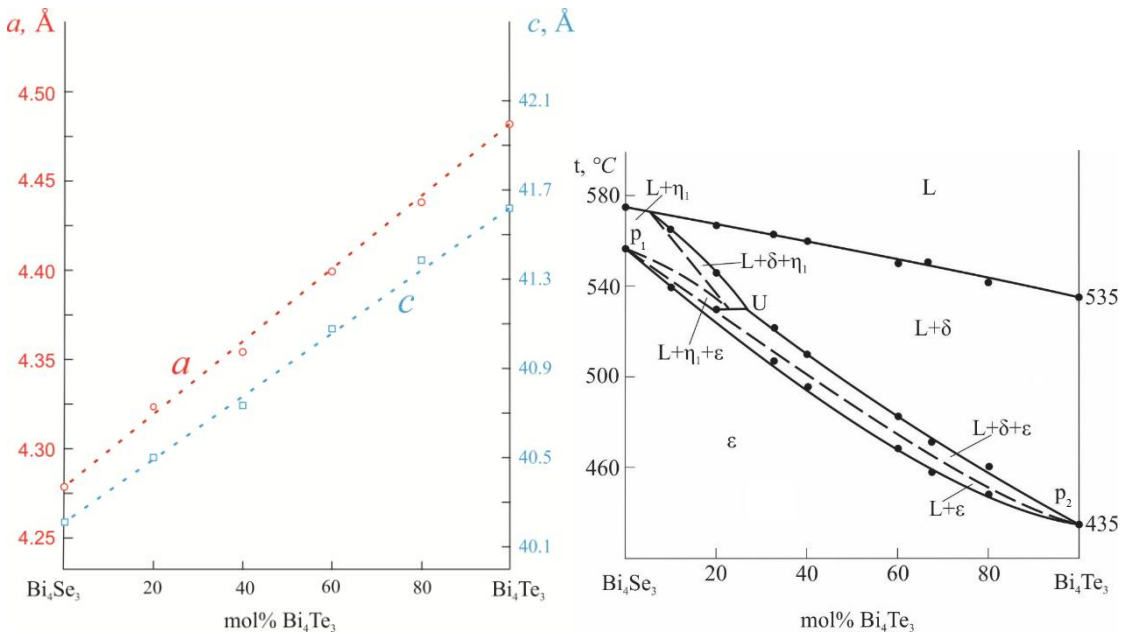


Fig. 1. PXRD patterns of $Bi_4Se_{3-x}Te_x$ alloys (a) and Rietveld refinement profile of alloy with 60 mol% Bi_4Te_3 composition (b)

Table 1. Calculated lattice parameters of $Bi_4Se_{3-x}Te_x$ alloys

Alloys	Lattice parameters (Å)	
	a	***b***
Bi_4Te_3	4.4819	41.618
80mol% Bi_4Se_3	4.4381	41.386
60mol% Bi_4Se_3	4.3993	41.078
40mol% Bi_4Se_3	4.3512	40.734
20mol% Bi_4Se_3	4.3235	40.517
Bi_4Se_3	4.2786	40.211



a) b)

Fig 2. Concentration dependence of lattice parameters of $Bi_4Se_{3-x}Te_x$ alloys(a) and phase diagram of Bi_4Se_3-Bi_4Te_3 system (b)

On the basis of results obtained from DTA and PXRD examination of equilibrated alloys, as well as using liquidus projection data of the Bi_2-Bi_2Se_3-Bi_2Te_3 system (Zeynalova *et al*., 2021), a phase diagram of the Bi_4Se_3-Bi_4Te_3 system were constructed, as presented in Figure 2b.

As can be seen from the constructed diagram, the system is stable below subsolidus and forms continious solid solutions (ε-phase).

Comparation the Fig.2b with the liquidus surface of the Bi_2-Bi_2Se_3-Bi_2Te_3 system (Zeynalova *et al*., 2021), shows that initially, η_1- phase based on Bi_8Te_7 compound crystallizes from the liquid phase, while δ-phase crystallize in 5-100 mol% Bi_4Te_3 concentration range. In Bi_4Se_3 rich side (0-25 mol% Bi_4Te_3) of the phase diagram, below the liquidus line, the crystallization goes by $L+\delta\leftrightarrow\eta_1$ and $L+\eta_1\leftrightarrow\varepsilon$ monovariant peritectic, and $L+\eta_1\leftrightarrow\delta+\varepsilon$ (U) nonvariant transition reactions. As a result, $L+\delta+\eta_1$, $L+\eta_1$, $L+\eta_1+\varepsilon$, and $L+\delta+\varepsilon$ phase regions are formed in the phase diagram. The latter field is formed by the $L+\delta\leftrightarrow\varepsilon$ peritectic reaction on the UP_2 curve in the 25-100 mol% Bi_4Te_3 concentration range. The crystallization process finishes in the entire section by $L\leftrightarrow\varepsilon$ bivariant scheme, and a single-phase region based on ε-solid solutions appears at low temperatures.

It is worth noting that according to constructed phase diagram, both phases entering the reaction with $L+\eta_1\leftrightarrow\varepsilon$ peritectic reaction must be completely consumed and monophasic ε-phase must be obtained in the subsolidus area since the composition is on the corresponding quasi-stable section. However, in this case, the three-phase region along the solidus curve should contact the single-phase region, which would give the impression of a violation of the Gibbs phase rule. Therefore, in phase diagrams, L+ε two-phase region are shown with a dashed line just above the solidus.

4. Conclusion

In the present paper, Bi_4Se_3-Bi_4Te_3 section of the Bi-Se-Te system was experimentally investigated using DTA and PXRD techniques. Based on obtained results, the phase diagram of the studied system was constructed. It was established that the system is stable below subsolidus and forms a continuous series of solid solutions in the system. The lattice parameters of solid solutions were determined using the FullProf software by the Le Bail method. Both *a* and *c* lattice parameters increase linearly with increasing concentration of Te content according to Vegard's law.

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