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The solid-phase equilibria in the $\mathbf{GeBi}_2\mathbf{Te}_{_4}\text{-}\mathbf{SnBi}_2\mathbf{Te}_{_4}\text{-}\mathbf{Bi}_2\mathbf{Te}_{_3}$ system **at 300 K and the characterization of tetradymite-type layered solid solutions**

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Abstract

The GeTe-SnTe-Bi $_{2}$ Te $_{3}$ system is of great interest due to the potential formation of a series of cation-substituted solid solutions based on ternary layered compounds with a tetradymite-type structure, which have significant potential as valuable thermoelectric materials and topological insulators. This study presents the results of investigating this system in the composition range of GeBi $_2$ Te $_4$ -SnBi $_2$ Te $_4$ -Bi $_2$ Te $_3$ using powder X-ray diffraction analysis. Particular attention is given to obtaining equilibrium alloys.

An isothermal section of the phase diagram at 300 K has been constructed, consisting of four single-phase regions separated by three two-phase regions. The X-ray diffraction patterns of the equilibrium alloys were refined using the Rietveld method. The obtained diffraction results clearly indicate the presence of continuous series of solid solutions along the sections $\rm{GeBi_{2}Te_{4}\text{-}SnBi_{2}Te_{4}\text{-}GeBi_{4}Te_{7}\text{-}SnBi_{4}Te_{7}\text{-}snBi_{6}Te_{10}\text{-}SnBi_{6}Te_{10}\text{-}The lattice parameters for all the solid solution series were$ determined, showing a linear increase with the rise in Sn concentration.

Keywords: Solid solutions, Germanium bismuth tellurides, Tin bismuth tellurides, Topological insulators, Isothermal section, XRD

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1. Introduction

The quest for advanced materials with enhanced properties has led to extensive research in the field of multi-component chalcogenides, particularly those based on *M*-Bi-Te (*M* – Ge, Sn, Pb, and Mn) systems [1–8]. These materials, which have attracted great interest due to their thermoelectric properties, have been intensively studied in recent years again as materials exhibiting properties of a new quantum state of matter – topological insulators [9–14]. Topological insulators (TIs) are a class of materials that have garnered significant interest due to their ability to conduct electricity on their surfaces while remaining insulating in their bulk [15–18].

Recently, a homologues series of layered ternary compounds with a general formula of $n\text{A}^{\text{\tiny{IV}}}$ Te $\cdot m\text{Bi}_{2}$ Te₃ have gained great attention for their unique electronic structures. Systhematic investigations into ternary compounds in these chalcogenides systems show that these tetradymite-type layered van der Waals phases are 3D Tls and hold potential for revolutionary applications in spintronics, quantum computing, and low-power electronics [19–24]. All these compounds share a structural similarity as they belong to the tetradymite-type layered structure which is composed of repeating units of quintuple or septuple layers, typically consisting of alternating atomic layers such as chalcogenides (e.g., Se or Te) and metals (e.g., Bi or Sb with *M* – Ge, Sn, Pb, and Mn) [1–4; 14]. Research on existing layered topological insulator phases indicates that addressing the limitations of their applicability across various fields necessitates the precise tuning of their bulk band structure. An effective approach to promoting electron transport dominated by topologically protected states is through targeted chemical substitution, whereby specific atomic sites in the material's crystal lattice are replaced to modify its electronic structure and enhance the prevalence of these states. This type of topological engineering has been previously studied in numerous works and has demonstrated significant potential for tuning material properties and improving performance for application prospects [25–30].

In this study, by means of differential thermal analysis (DTA) and powder X-ray diffraction (XRD) methods, we studied solid-phase equilibria diagram in the GeBi $_{2}$ Te $_{4}$ -SnBi $_{2}$ Te $_{4}$ - $Bi₂Te₃$ system at 300 K and characterized the $\rm{Ge}_{1-x}\rm{Sn}_{x}\rm{Bi}_{2}\rm{Te}_{4}$, $\rm{Ge}_{1-x}\rm{Sn}_{x}\rm{Bi}_{4}\rm{Te}_{7}$, and $\rm{Ge}_{1-x}\rm{Sn}_{x}\rm{Bi}_{6}\rm{Te}_{10}$ continuous series of solid solutions with examining compositional effects on the material's crystalline behaviours. Our findings provide insights into the phase diagrams of the GeTe-SnTe-Bi₂Te₃ pseudoternary system and contribute to understanding the influence of $Ge \leftrightarrow Sn$ substitution on the thermodynamic and structural properties of these topological insulator compounds. Data on phase equilibria in the boundary systems GeTe-Bi $_2$ Te $_3$ and SnTe- $Bi₂Te₃$ are taken from [2, 5].

2. Experimental

The starting materials for the preparation of alloys were high-purity germanium pieces (Alfa Aesar, CAS 7440-56-4), tin lump (Alfa Aesar, CAS 7440-31-5), bismuth shots (Alfa Aesar, CAS 7440-69-9), and tellurium lump (Alfa Aesar, CAS 13494-80-9). During the first stage, GeTe, SnTe, and Bi_2Te_3 binary compounds were synthesized. The phase purity of the synthesized binary compounds was checked via DTA and powder XRD methods. Alloys of the studied systems with different compositions were prepared using presynthesized binary compounds. The weighed three components were sealed in quartz ampoules, then melted at 1050 K for 6 h, followed by rapid quenching in ice water. All the ampoules were then placed in a muffle furnace at a temperature of 770 K for 720 hours to achieve a state close to equilibrium. After heat treatment, the alloys were cooled in a switched off furnace.

Powder XRD and DTA techniques were used to characterize the products. The temperatures of the phase transformations were determined by DTA using the LINSEIS HDSC PT1600 system (heating rate of 10 °C/min) and a multichannel DTA device based on a TC-08 Thermocouple Data Logger. Powder X-ray diffraction (XRD) was examined on Bruker D2 PHASER diffractometer using $\text{Cu}\text{K}\alpha_{_1}$ radiation within a scanning range of 2θ = 5÷75. COD and PDF-2 databases were used for the interpretation of the powder diffraction patterns. Both qualitative and quantitative assessments of the XRD patterns were carried out using Rietveld analysis with FullProf and HighScore Plus software package.

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3. Results and discussion

The powder XRD patterns of annealed alloys of $\text{Ge}_{1\text{-x}}\text{Sn}_{\text{x}}\text{Bi}_2\text{Te}_4$ systems are shown in Fig. 1. The observed peaks of the XRD patterns indicate a trigonal symmetry with the *R*-3*m* space group. As can be seen, the diffraction peaks exhibit a systematic shift towards lower 2θ angles as the Sn content increases, indicating an expansion of the lattice due to the larger atomic radius of Sn compared to Ge. Additionally, the absence of any new peaks or the splitting of existing peaks suggests that no phase separation occurs, confirming the formation of a continuous solid solution. The broadening of peaks with increasing Sn content may also be attributed to microstrains or slight variations in crystallite size as the alloy composition changes. Overall, these patterns confirm the successful incorporation of Sn

into the Ge-Bi-Te matrix, leading to a tunable modification of the crystal structure without disrupting the overall phase stability.

Similarly, the XRD patterns of $Ge_{1-x}Sn_xBi_4Te_7$ exhibit a comparable trend (see Fig. 2) with a systematic shift of diffraction peaks towards lower 20 angles as the Sn concentration increases. This shift, like in the $\text{Ge}_{1\text{-x}}\text{Sn}_{x}\text{Bi}_{2}\text{Te}_{4}$ system, indicates an expansion of the lattice due to the substitution of Sn for Ge. The consistency of this shift across the entire compositional range supports the formation of a continuous solid solution along the GeBi₄Te₇-SnBi₄Te₇ section.

The XRD patterns of alloys of the $\text{GeBi}_{6}\text{Te}_{10}$ - $SnBi₆Te₁₀$ section also show a similar shift towards lower 2θ angles with increasing Sn content, indicating lattice expansion and the formation of a continuous solid solution without

Fig. 1. Powder XRD patterns of $\text{Ge}_{_{1\text{-x}}} \text{Sn}_{_{\text{x}}} \text{Bi}_{_{2}} \text{Te}_{_{4}}$ alloys

Fig. 2. Powder XRD patterns of $\text{Ge}_{_{1\text{-x}}} \text{Sn}_{_\text{x}} \text{Bi}_{_4} \text{Te}_{_{7}}$ alloys

phase separation, as seen in Fig. 3. Thus, based on the obtained results, it can be stated that the $\text{GeBi}_2 \text{Te}_4$ -Sn $\text{Bi}_2 \text{Te}_4$, $\text{GeBi}_4 \text{Te}_7$ -Sn $\text{Bi}_4 \text{Te}_7$, and GeBi $_{\rm 6}$ Te $_{\rm 10}$ -SnBi $_{\rm 6}$ Te $_{\rm 10}$ sections of the GeTe-SnTe- ${\rm Bi}_{_2}{\rm Te}_{_{\rm 3}}$ system are characterized by the formation of continuous series of solid solutions below the subsolidus temperature.

The structural parameters of all the alloys were refined by the Rietveld technique. Powder XRDbased Rietveld refinements yield the final lattice parameter values by showing good agreement between the experimental and calculated profiles across all compositions. Calculated lattice parameters for the $Ge_{1-x}Sn_xBi_2Te_4$, $Ge_{1-x}Sn_xBi_4Te_7$, and $\rm Ge_{1.5}Sn_{x}Bi_{6}Te_{10}$ solid solutions were listed in Table 1. It can been seen that the values obtained by our refinements for all ternary end-member compounds are in good agreement with the values of the literature [2, 5]. Results for intermediate compositions are consistent with Vegard's law, which describes the linear relationship between lattice parameters and composition in solid solutions. The variation of lattice parameters *a*, and *c* with the Sn content is presented in Fig. 4 (a), (b), and (c). As expected,

Fig. 3. Powder XRD patterns of $\text{Ge}_{\text{\tiny{1-x}}} \text{Sn}_{\text{\tiny{x}}} \text{Bi}_{\text{\tiny{6}}} \text{Te}_{\text{\tiny{10}}}$ alloys

 ${\bf Fig. 4.}$ Dependence of lattice parameters a and c for alloys of $\rm Ge_{1-x}Sn_xBi_2Te_4$ (a), $\rm Ge_{1-x}Sn_xBi_4Te_7$ (b), and $\rm Ge_{1-x}Sn_x$ ${\rm Bi}_{_6}{\rm Te}_{_{10}}$ (a) systems versus Sn content

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Composition, mol%	Lattice parameters, Å		Ref.
	$\mathfrak a$	\mathcal{C}_{0}	
$Ge_{1-x}Sn_xBi_2Te_4$			
$x = 0.0$	4.3176(3)	41.259(5)	$\lceil 5 \rceil$
	4.3181(4)	41.217(5)	This work
$x = 0.2$	4.3384(2)	41.288(3)	This work
$x = 0.4$	4.3508(7)	41.332(5)	This work
$x = 0.6$	4.3691(4)	41.396(4)	This work
$x = 0.8$	4.3892(3)	41.462(5)	This work
$x = 1.0$	4.4035(3)	41.511(2)	$[25]$
	4.4029(3)	41.528(5)	This work
$Ge_{1-x}Sn_xBi_{4}Te_{7}$			
$x = 0.0$	4.3556(2)	23.928(4)	$\lceil 5 \rceil$
	4.3525(4)	23.939(2)	This work
$x = 0.2$	4.3637(2)	23.949(4)	This work
$x = 0.4$	4.3735(5)	23.956(3)	This work
$x = 0.6$	4.3809(7)	23.967(7)	This work
$x=0.8$	4.3884(1)	23.977(1)	This work
$x = 1.0$	4.3998(2)	23.981(3)	$[31]$
	4.3992(5)	23.988(6)	This work
$Ge_{1-x}Sn_xBi_6Te_{10}$			
$x = 0.0$	4.3572(3)	101.911(2)	$\lceil 5 \rceil$
	4.3566(1)	101.918(4)	This work
$x = 0.4$	4.3676(8)	102.128(3)	This work
$x = 0.8$	4.3799(5)	102.335(1)	This work
$x = 1.0$	4.3873(8)	102.431(1)	[32]
	4.3867(2)	102.438(4)	This work

Table 1. Crystal structure parameters of some phases

both lattice parameters increase with increasing concentration of Sn content due to the larger ionic radius of Sn^{2+} compared to Ge^{2+} .

Fig. 5 shows the solid-phase equilibrium diagram of the GeBi $_2$ Te₄-SnBi $_2$ Te₄-Bi $_2$ Te₃ system at 300 K constructed using the above experimental results and literature data. The isothermal section consists of four monophasic and three two-phase regions. As mentioned above, three out of four single-phase regions belong to a continuous series of solid solutions which are the ε -, φ -, and χ -phases. The β -phase corresponds to the homogeneity region of $\mathrm{Bi}_2\mathrm{Te}_3$, which we delimited taking into account the data from [2, 5]. The formation of biphasic areas is confirmed with XRD. Alloy #1 clearly demonstrated that the ε -phase is in equilibrium with the φ -phase, as shown in Fig. 6 (a). Similarly, alloy #2 (Fig. 2(b)) had two equilibrium phases, which were identified as the φ - and χ - phases. Since both alloy

compositions located on the Ge-rich side of the diagram (see Fig. 5), reference XRD lines shown in Fig. 6 (a) and (b) were chosen for comparison from germanium ternary compounds.

Fig. 5. The solid-phase equilibrium diagram of the $\text{GeBi}_{2}\text{Te}_{4}$ - $\text{SnBi}_{2}\text{Te}_{4}$ - $\text{Bi}_{2}\text{Te}_{3}$ system at 300 K. Red circles show alloy compositions for XRD in Fig. 6

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Fig. 6. Powder XRD patterns of alloys #1 and #2 in Fig. 5

4. Conclusions

In this work, based on the results of XRD of equilibrium alloys, a solid-phase equilibrium diagram of the GeTe-SnTe-Bi₂Te₃ system in the $\text{composition range of } \text{GeBi}_2 \text{Te}_4\text{-SnBi}_2 \text{Te}_4\text{-Bi}_2 \text{Te}_3$ at 300 K was constructed. It was established that this subsystem is characterized by the formation of continuous series of substitution solid solutions with the general formula $\rm{Ge}_{1-x}\rm{Sn}_{x}\rm{Bi}_{2}\rm{Te}_{4}$, $\rm{Ge}_{1-x}\rm{Sn}_{x}\rm{Bi}_{4}\rm{Te}_{7}$ and $\rm{Ge}_{1-x}\rm{Sn}_{x}\rm{Bi}_{6}\rm{Te}_{10}$ with a layered tetradymite-type structure and a wide homogeneity region based on ${\rm Bi}_{_2}{\rm Te}_{_{3}}.$ The lattice parameters of the above-mentioned series of solid solutions were refined based on powder diffraction patterns using the Rietveld method. It is shown that their concentration dependences are in good agreement with Vegard's law. The solid solutions obtained in this work are of practical interest from the point of view of developing new topological insulators and thermoelectric materials with adjustable properties.

Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

Contribution of the authors

The authors contributed equally to this article.

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