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SOLID-PHASE EQUILIBRIA IN THE $GeSb_2Te_4$-$SnSb_2Te_4$-Sb_2Te_3 SYSTEM

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Solid-phase equilibria in the $GeSb_2Te_4$-$SnSb_2Te_4$-Sb_2Te_3 subsystem of the GeTe-SnTe-Sb_2Te_3 system were investigated by powder X-ray diffraction method. Alloys were synthesized from previously prepared binary compounds by melting, quenching from the liquid state, and subsequent annealing at 800 K for 800 h. It was established that the $GeSb_2Te_4$-$SnSb_2Te_4$ and $GeSb_4Te_7$-$SnSb_4Te_7$ sections form continuous series of substitutional solid solutions with tetradymite-like layered structures. In both systems, the lattice parameters increase systematically with increasing Sn content, consistent with Vegard's law. In contrast, the $GeSb_6Te_{10}$–"$SnSb_6Te_{10}$" section is characterized by limited solid solubility. Based on the experimental results and literature data, the solid-phase equilibrium diagram of the $GeSb_2Te_4$-$SnSb_2Te_4$-Sb_2Te_3 system at 300 K was constructed. The diagram contains four single-phase regions, four two-phase regions, and one three-phase region. The obtained results provide new information on phase relations and compositional stability in the Ge-Sn-Sb-Te system and are useful for the development of functional layered chalcogenide materials.

Keywords: tetradymite-like structure, layered materials, phase diagram, chalcogenides, solid solutions.

INTRODUCTION

Heavy p-element binary and multicomponent chalcogenides have been widely studied as functional materials for various applications. In this respect, a number of ternary compounds formed in the A^{IV}-B^{V}-Te systems (A^{IV}- Ge, Sn, Pb; B^{V}- Sb, Bi) are of considerable interest [1-4]. These phases, which form homologous series compounds with the general formula $A^{IV}Te{\cdot}mB_2^{V}Te_3$, crystallize in a tetradymite-like layered structure. Among these systems, the $nGeTe{\cdot}B_2^{V}Te_3$ sections are particularly noteworthy, since, in addition to the above-mentioned homologous series, they also give rise to compounds belonging to the $nGeTe{\cdot}B_2^{V}Te_3$ homologous series [5,6]. Analysis of the available literature indicates that these ternary compounds are currently being intensively investigated as thermoelectric materials, topological insulators, optoelectronic materials, and phase-change materials

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[7-11]. At present, the main focusof research in this area is the preparation of various substitutional solid solutions based on these phases, with the aim of optimizing their functional properties and enabling their controlled modification [12-17].

The solution of this problem is closely related to the investigation of phase equilibria in the corresponding systems. Such studies make it possible both to determine the compositional ranges over which the existing phases remain stable and to identify new solid-solution regions. In particular, the study of phase equilibria in multicomponent chalcogenide systems provides a deeper understanding of the crystal structure-property relationships.

From this standpoint, the GeTe-SnTe–Sb_2Te_3 system is of particular interest. The isostructural ternary phases present in its boundary systems possess a tetradymite-like layered structure, exhibit mutual solubility, and therefore are expected to form extensive solid-solution regions. This, in turn, opens up favorable opportunities for tuning their functional properties.

In the present work, the solid-phase equilibria in the $GeSb_2Te_4$-$SnSb_2Te_4$-Sb_2Te_3 subsystem of the GeTe-SnTe-Sb_2Te_3 system were investigated by X-ray diffraction (XRD).

EXPERIMENTAL

The alloys of the investigated system were prepared by a special procedure using previously synthesized and identified GeTe, SnTe, and Sb_2Te_3 binary compounds as starting materials. Stoichiometric amounts of the binary compounds were loaded into quartz ampoules, which were then evacuated to a residual pressure of 10^{-2} Pa and sealed by melting the ampoule neck in an oxygen–natural gas flame. At the next stage, the alloys were melted in a muffle furnace and, while in the liquid state inside the ampoules, were quenched in ice water. Subsequently, the alloys were heat-treated at 800 K for 800 h and then slowly cooled by switching off the furnace power supply.

Studies devoted to the synthesis of phases with a tetradymite-like structure, as well as analysis of the literature data, show that interlayer diffusion in such layered structures is weak. For this reason, even after prolonged heat treatment, the excess amounts of neighboring phases and starting compounds present in the alloys do not dissolve completely, and the preparation of homogeneous samples by conventional synthesis methods becomes practically difficult. Therefore, in the present work, the synthesis was carried out by quenching from the liquid phase, followed by additional heat treatment. The formation of incompletely crystallized or weakly crystallized samples during quenching facilitates the subsequent formation of the desired phases more readily and effectively during the heat-treatment stage.

The well heat-treated alloys were investigated by powder XRD. XRD measurements were carried out using a Bruker D2 Phaser diffractometer ($CuK\alpha_1$ radiation, 2θ = 5-75° angular range). The diffraction patterns were analyzed using the Match! 3 and HighScore Plus software. Crystal Impact software package with reference to the ICDD and COD databases.

RESULTS AND DISCUSSION

The powder X-ray diffraction patterns of the $Ge_{1-x}Sn_xSb_2Te_4$ samples synthesized by the special procedure and heat-treated at 800 K for 800 h are shown in Fig. 1. As can be seen, all diffraction patterns are single-phase and exhibit features characteristic of materials with a tetradymite-like structure. The XRD patterns of the intermediate compositions are similar to those of the boundary ternary compounds $GeSb_2Te_4$ and $SnSb_2Te_4$. As the composition changes from Ge to Sn, the diffraction peaks shift slightly toward lower angles, which can be attributed to the larger ionic radius of Sn (0.69 Å) compared with that of Ge (0.53 Å). Thus, the X-ray diffraction results indicate the formation of a continuous solid-

solution series (γ-phase) between the parent ternary compounds in the $GeSb_2Te_4$ system. Based on the powder diffraction data, the unit-cell parameters of the solid solutions were refined by the Le Bail method. It was established that all reflections are fully indexed in the hexagonal crystal system (space group *R*-3*m*). The results are presented in Table 1.

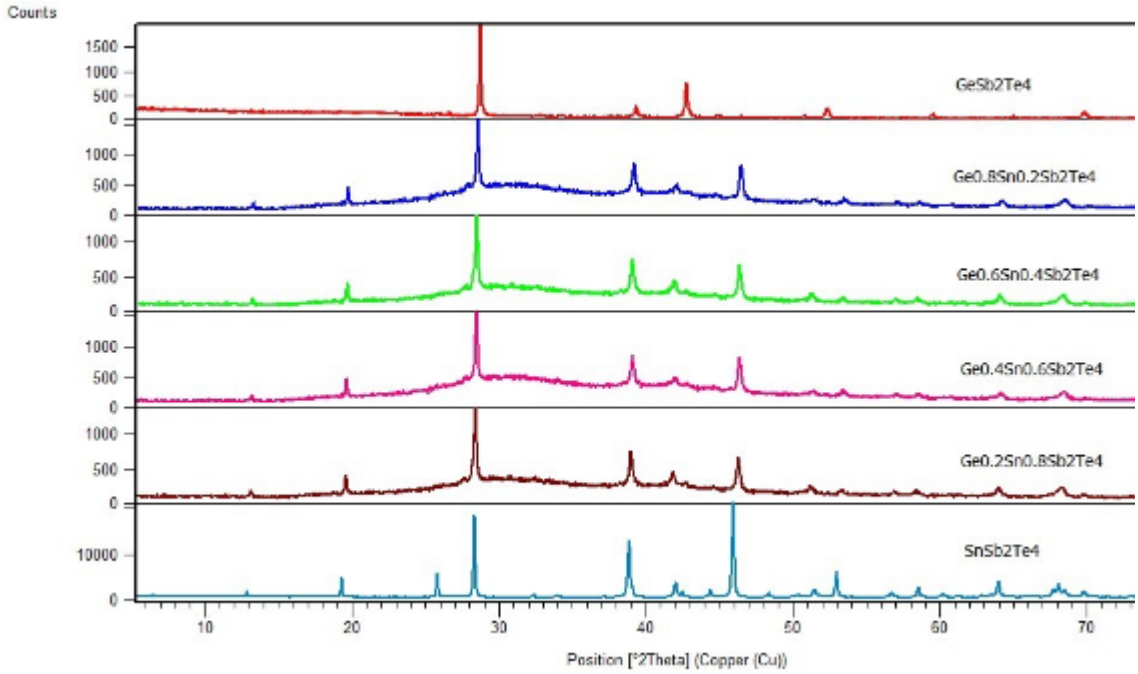

Figure 1. Powder XRD patterns of $Ge_{1-x}Sn_xSb_2Te_4$ solid solutions.

Table 1. Crystal lattice parameters of the for $Ge_{1-x}Sn_xSb_2Te_4$, $Ge_{1-x}Sn_xSb_4Te_7$, and $Ge_{1-x}Sn_xSb_6Te_{10}$ solid solutions**.**

Composition, mol%	Space Group	Lattice parameters, Å		Ref.
		a	*c*	
$Ge_{1-x}Sn_xSb_2Te_4$				
x=0.0	*R*-3*m*	4.252(7)	41.13(5)	[6]
x=0.2	*R*-3*m*	4.263(4)	41.22(2)	This work
x=0.4	*R*-3*m*	4.272(6)	41.31(3)	This work
x=0.6	*R*-3*m*	4.284(4)	41.42(5)	This work
x=0.8	*R*-3*m*	4.291(2)	41.51(1)	This work
x=1.0	*R*-3*m*	4.298(1)	41.57(1)	[18]
$Ge_{1-x}Sn_xSb_4Te_7$				
x=0.0	*P*-3*m*1	4.27(2)	23.84(2)	[6]
x=0.2	*P*-3*m*1	4.275(3)	23.86(4)	This work
x=0.4	*P*-3*m*1	4.281(3)	23.88(1)	This work
x=0.6	*P*-3*m*1	4.287(6)	23.9(2)	This work
x=0.8	*P*-3*m*1	4.291(2)	23.93(5)	This work

x=1.0	*P*-3*m*1	4.2951(2)	23.973(8)	[19]
$Ge_{1-x}Sn_xSb_6Te_{10}$				
x=0.0	*R*-3*m*	4.261(2)	102.12(5)	[6]
x=0.2	*R*-3*m*	4.274(3)	102.19(7)	This work
x=0.4	*R*-3*m*	4.285(3)	102.26(2)	This work

A similar behavior was observed for the $Ge_{1-x}Sn_xSb_4Te_7$ compositions. The XRD patterns of the synthesized and heat-treated samples are presented in Fig. 2. As in the $GeSb_2Te_4$-$SnSb_2Te_4$ section, the diffraction patterns of both end-member compounds and all intermediate compositions are qualitatively identical, indicating the formation of a continuous solid-solution series (δ-phase) over the entire composition range under investigation. With increasing tin content, a slight shift of the diffraction lines toward lower angles is again observed, reflecting the difference in the crystallographic radii of Ge(II) and Sn(II) atoms. Therefore, both the $GeSb_2Te_4$-$SnSb_2Te_4$ and $GeSb_4Te_7$-$SnSb_4Te_7$ sections are characterized by complete mutual solubility in the solid state.

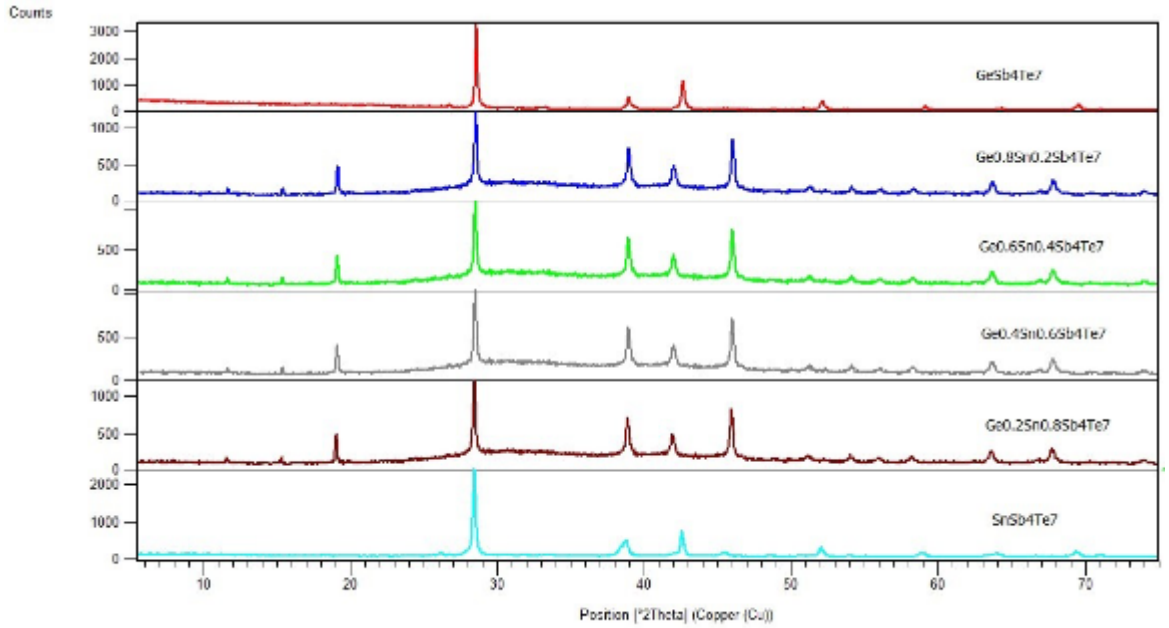

Figure 2. Powder XRD patterns of $Ge_{1-x}Sn_xSb_4Te_7$ solid solutions.

In contrast, the phase relations in the $GeSb_6Te_{10}$-"$SnSb_6Te_{10}$" section are more complex. The powder XRD patterns of the samples equilibrated along this section are presented in Fig. 3. As seen, the diffraction patterns of the samples containing 20 and 40 mol% "$SnSb_6Te_{10}$" are identical to that of the $GeSb_6Te_{10}$ compound, indicating that these compositions remain within the single-phase ε-field. In the powder diffractogram of the sample containing 50 mol% "$SnSb_6Te_{10}$" , in addition to the diffraction lines of $GeSb_6Te_{10}$, reflection peaks corresponding to the β-phase based on Sb_2Te_3 and the δ-phase based on $SnSb_4Te_7$ are observed, indicating that the sample is three-phase (β + δ + ε). Samples with higher tin contents (>65 mol% "$SnSb_6Te_{10}$") are two-phase (β + δ), as confirmed by the powder diffractogram of the sample containing 80 mol% "$SnSb_6Te_{10}$" (Fig. 3). The lattice parameters of solid solutions 0-40 mol% "$SnSb_6Te_{10}$" are listed in Table 1. Overall, unlike the $GeSb_2Te_4$-$SnSb_2Te_4$ and $GeSb_4Te_7$-$SnSb_4Te_7$ systems, which form continuous solid solutions, the $GeSb_6Te_{10}$-"$SnSb_6Te_{10}$" section is characterized by a limited homogeneity

range of the ε-phase and the appearance of two- and three-phase regions.

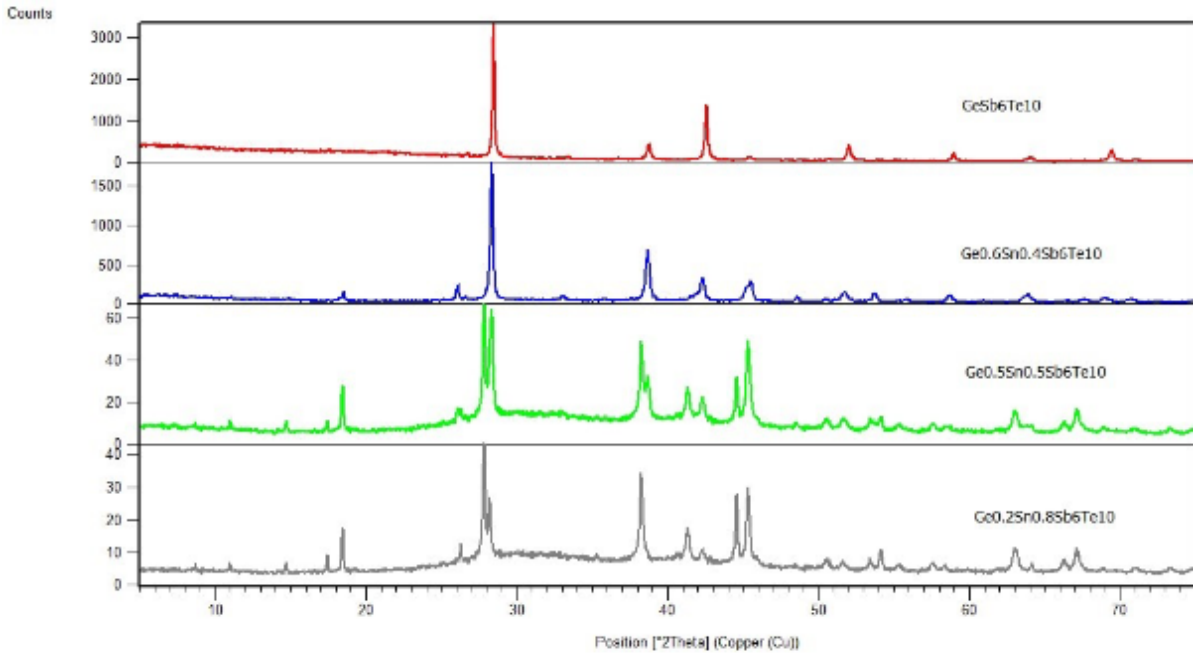

Figure 3. Powder XRD patterns of alloys from $GeSb_6Te_{10}$-"$SnSb_6Te_{10}$" polythermal section.

The concentration dependence of lattice parameters for all three series of substituted solid solutions is shown ib Fig. 4. It is evident that both lattice parameters increase systematically with increasing Sn content. For the $Ge_{1-x}Sn_xSb_2Te_4$ and $Ge_{1-x}Sn_xSb_4Te_7$ series, the variation is close to linear throughout the entire composition range, in accordance with Vegard's law and indicative of continuous substitutional solid-solution formation. In contrast, for $GeSb_6Te_{10}$-"$SnSb_6Te_{10}$" alloys , the linear dependence is preserved only up to approximately 40 mol% Sn, which corresponds to the solubility limit in this series. These results confirm the substitution of Ge by Sn and the consequent increase in unit-cell dimensions.

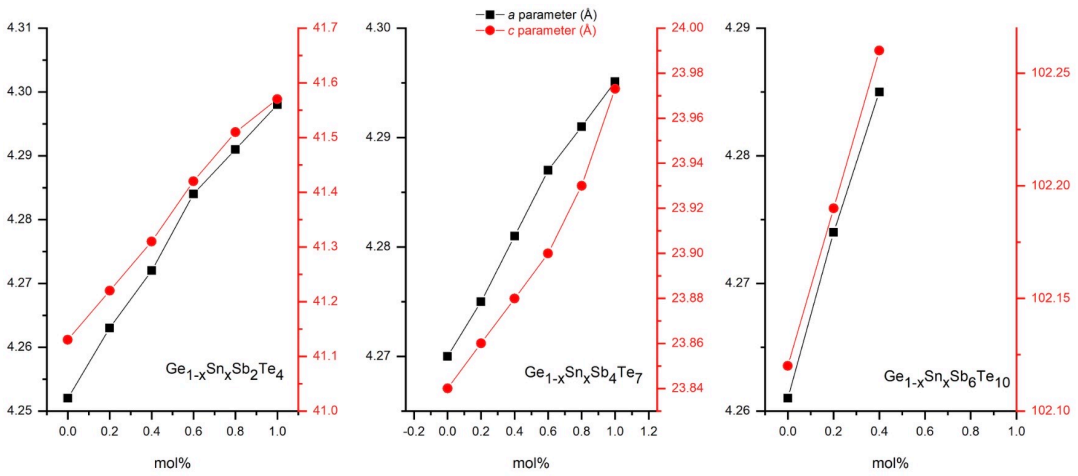

Figure 4. The concentration dependence of lattice parameters for $Ge_{1-x}Sn_xSb_2Te_4$, $Ge_{1-x}Sn_xSb_4Te_7$, and $Ge_{1-x}Sn_xSb_6Te_{10}$ solid solutions**.**

Fig. 5 presents the solid-phase equilibrium diagram of the the $GeSb_2Te_4$-$SnSb_2Te_4$-Sb_2Te_3 system at 300 K, established using the present experimental data in combination with literature results. The diagram contains four single-phase fields, four two-phase fields and one three-phase field. As discussed above, three of the single-phase fields correspond to continuous solid-solution series, designated as the g-, d-, and e-phases, whereas the fourth field, β, corresponds to the homogeneity range of Sb_2Te_3 . The presence of the heterogenous regions was confirmed by XRD. Alloy #1 revealed the equilibrium between the g- and d-phases, as evidenced by the diffraction pattern in Fig. 6. Likewise, alloy #2 was shown to consist of the e- and β-phases in equilibrium. XRD pattern of alloy #3 is fully indexed with reflection line of Sb_2Te_3 with sligh shift which means it is located in the homogeneity field of Sb_2Te_3 as seen in Fig. 6.

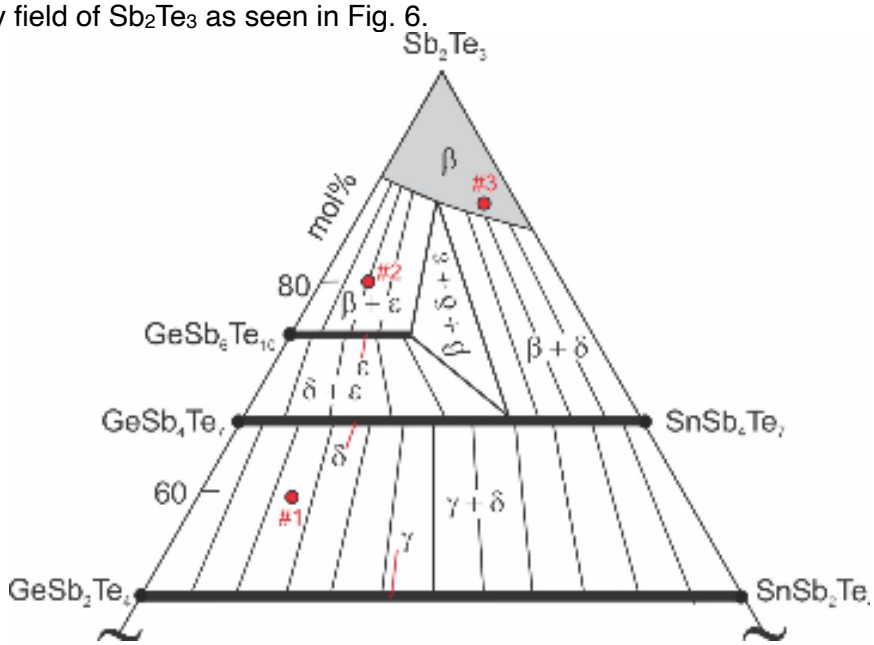

Figure 5. The solid-phase equilibrium diagram of the the $GeSb_2Te_4$-$SnSb_2Te_4$-Sb_2Te_3 system at 300 K. Red circles show alloy compositions for XRD in Fig. 6.

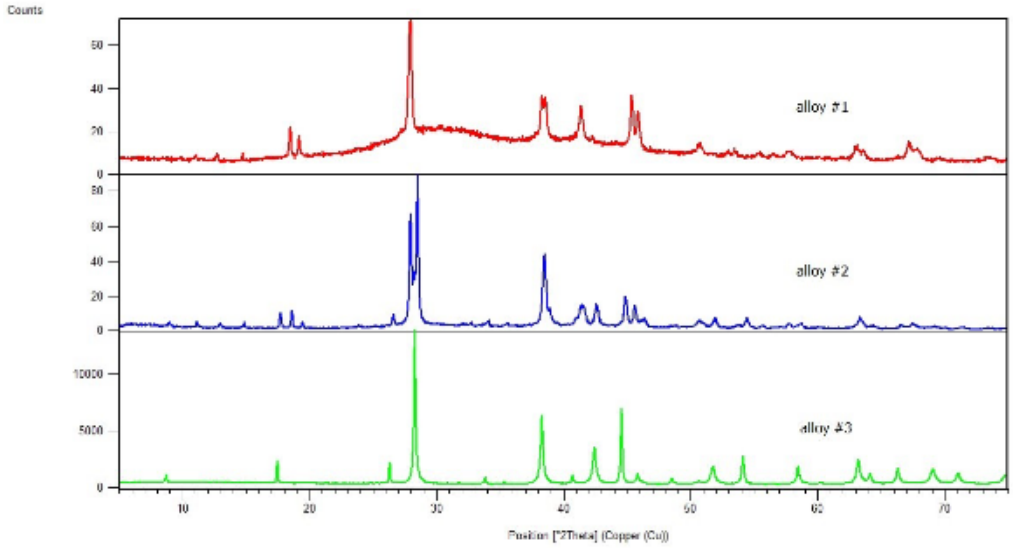

Figure 6. Powder XRD patterns of alloys #1, #2, and #3.

CONCLUSION

The solid-phase equilibria in the $GeSb_2Te_4$-$SnSb_2Te_4$-Sb_2Te_3 subsystem at 300 K were studied by powder X-ray diffraction. Complete mutual solubility was observed for the $GeSb_2Te_4$–$SnSb_2Te_4$ and $GeSb_4Te_7$–$SnSb_4Te_7$sections, indicating broad compositional flexibility of these tetradymite-like phases. By contrast, the $GeSb_6Te_{10}$–"$SnSb_6Te_{10}$" section displays only a restricted homogeneity range, and the appearance of multiphase regions at higher Sn contents points to reduced structural tolerance toward substitution in this case. The increase of lattice parameters with increasing Sn concentration further supports the incorporation of Sn into the crystal structure of the corresponding solid solutions. The constructed isothermal section at 300 K clarifies the phase relations in this subsystem and provides a useful foundation for the compositional design of layered chalcogenide materials with potentially tunable properties.

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