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SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF SOLID SOLUTIONS IN THE $GeBi_2Te_4$–$MnBi_2Te_4$ AND $GeBi_4Te_7$–$MnBi_4Te_7$ SYSTEMS

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This study reports the synthesis and comprehensive characterization of layered solid solutions in the $GeBi_2Te_4$–$MnBi_2Te_4$ and $GeBi_4Te_7$–$MnBi_4Te_7$ systems, which belong to the tetradymite family of compounds known for their thermoelectric and topological insulator properties. Alloys with varying Ge–Mn ratios were prepared using a two-stage thermal treatment involving melt quenching followed by prolonged annealing. Powder X-ray diffraction confirmed the formation of single-phase solid solutions across the full compositional range in both systems. A systematic shift in diffraction peaks with increasing Mn content indicates lattice parameter variation consistent with Vegard's law, reflecting the substitution of Ge^{2+} by larger Mn^{2+} ions. Le Bail refinement was employed to determine precise lattice parameters, revealing smooth trends without structural anomalies. Scanning electron microscopy further confirmed the microstructural homogeneity of the samples. The findings demonstrate the formation of continuous solid solutions in both systems, offering a basis for future exploration of their electronic and magnetic properties.

Keywords: layered materials, tetradymite-type structure, germanium bismuth tellurides, manganese bismuth tellurides, solid solutions

INTRODUCTION

Ternary compounds with the general formula $A_nBi_{2n}Te_{3n+1}$ (A – Mn, Sn, Ge, Pb; n = 1, 2, 3, ...) have a layered structure belonging to the tetradymite family and have garnered significant attention for their promising applications in mainly thermoelectric devices and topological insulators [1-5]. The unique crystallography of these compounds is characterized by a periodic stacking of quintuple (n = 1), septuple (n = 2), and more complex layered units along the *c*-axis, which gives rise to strong anisotropy in their electronic and thermal transport properties [6-8]. This structural feature facilitates two-dimensional charge carrier confinement and supports the emergence of topologically protected surface states, making these materials highly attractive for both fundamental studies and practical device applications. However, studies related to these materials indicate that overcoming the limitations of their applications in various fields requires fine-tuning their bulk band structure, which can be achieved through

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chemical substitution, doping, or strain engineering, thereby optimizing their functional performance.

The substitution effects in Sn(Mn)↔Mn, Sn↔Pb, and Sb↔Bi pairs within *A*-Sb-Bi-Te quaternary systems have already been investigated [9-16], highlighting their role in structural compatibility and phase stability across extended solid solution ranges. These findings provide a valuable framework for exploring analogous substitution behavior in the $GeBi_2Te_4$–$MnBi_2Te_4$ and $GeBi_4Te_7$–$MnBi_4Te_7$ systems, where similar atomic size and valence characteristics suggest the potential for continuous solid solution formation and fine-tuning of intrinsic material properties.

In the present work, tetradymite-type layered solid solutions in the title systems were synthesized and systematically characterized to investigate the phase formation, structural evolution, and the extent of mutual solubility between the end-member compounds. The study aims to clarify the influence of Ge↔Mn substitution on crystal structure and stability, providing insights into the potential tailoring of electronic and magnetic properties in these complex layered tellurides.

EXPERIMENTAL

A total of six alloys in each system, including the end-member ternary compounds, were synthesized and thoroughly homogenized at compositions of 0, 20, 40, 60, 80, and 100 mol% for experimental studies in the $GeBi_2Te_4$–$MnBi_2Te_4$ and $GeBi_4Te_7$–$MnBi_4Te_7$ systems. As part of the synthesis methodology development, we assumed that bulk samples of layered phases obtained by the widely used fusion method do not reach thermodynamic equilibrium, even after prolonged thermal annealing (more than 2000 hours) [17-21]. This behavior is attributed to the nature of van der Waals phases, which, unlike conventional bulk materials, are formed under non-equilibrium crystallization conditions (e.g., standard melt cooling). These phases exhibit extremely slow interlayer diffusion, resulting in minimal structural evolution during subsequent annealing. To address this, we quenched the alloys from the melt to suppress the formation of large crystals and promote homogeneity. A subsequent annealing step was employed to facilitate the formation of the target equilibrium phases.

Powder X-ray diffraction analysis was performed for alloys in both the $GeBi_2Te_4$–$MnBi_2Te_4$ and $GeBi_4Te_7$–$MnBi_4Te_7$ systems. In all cases, the diffractograms confirm the formation of single-phase materials, with no evidence of secondary or impurity phases. Representative XRD patterns for selected compositions from each system are shown in Fig. 1 and 2. The diffraction profiles of the intermediate compositions closely resemble those of the respective end-member compounds, indicating the formation of continuous solid solutions. A systematic shift of the diffraction peaks toward lower 2θ angles with increasing Mn content is observed, reflecting lattice expansion due to the substitution of smaller Ge^{2+} ions with larger Mn^{2+} ions. All reflections for the $GeBi_2Te_4$–$MnBi_2Te_4$ series are indexed to a rhombohedral structure with space group *R*-3*m* (No. 166), while those for the $GeBi_4Te_7$–$MnBi_4Te_7$ series correspond to a trigonal structure with space group *P*-3*m*1 (No. 164), confirming structural consistency within each system across the compositional range.

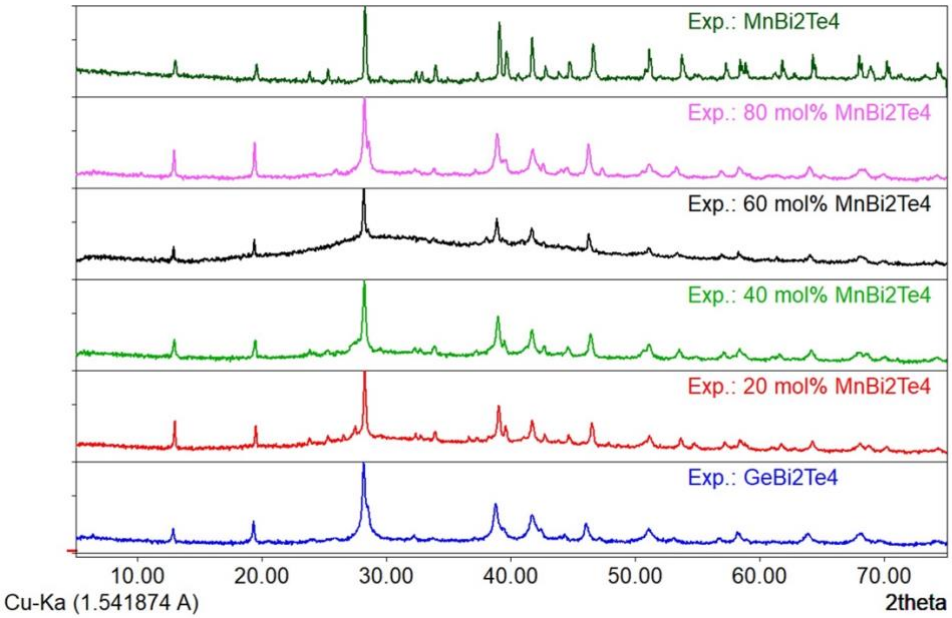

Figure 1. Powder XRD patterns of alloys of $GeBi_2Te_4$–$MnBi_2Te_4$ system.

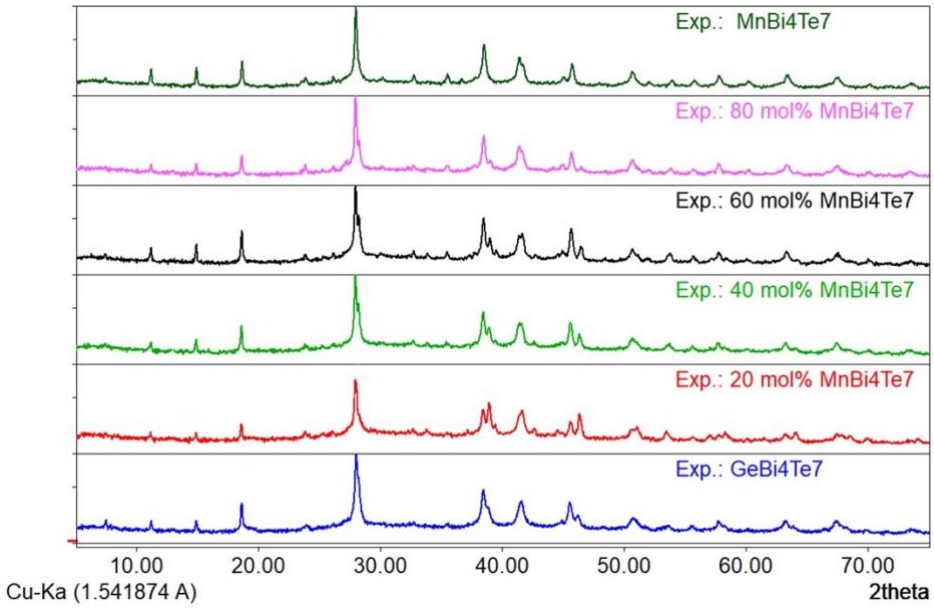

Figure 2. Powder XRD patterns of alloys of $GeBi_4Te_7$–$MnBi_4Te_7$ system.

Preliminary SEM observations of selected alloys reveal homogeneous microstructures without visible phase segregation, supporting the XRD results that confirm the formation of single-phase solid solutions.

The lattice parameters of the solid solutions were accurately determined from the powder XRD data using the Le Bail refinement method, which allows for the extraction of reliable structural information from complex diffraction patterns. The calculations were done using the hexagonal unit cell setting for all samples. Figure 3 presents the final refinement for the alloy with 20 mol% $MnBi_4Te_7$, displaying both the observed and calculated diffractograms, along with the residual difference curve, which reflects the quality of the fit. The refined lattice parameters, including the unit cell dimensions and corresponding uncertainties, are summarized in Table 2.

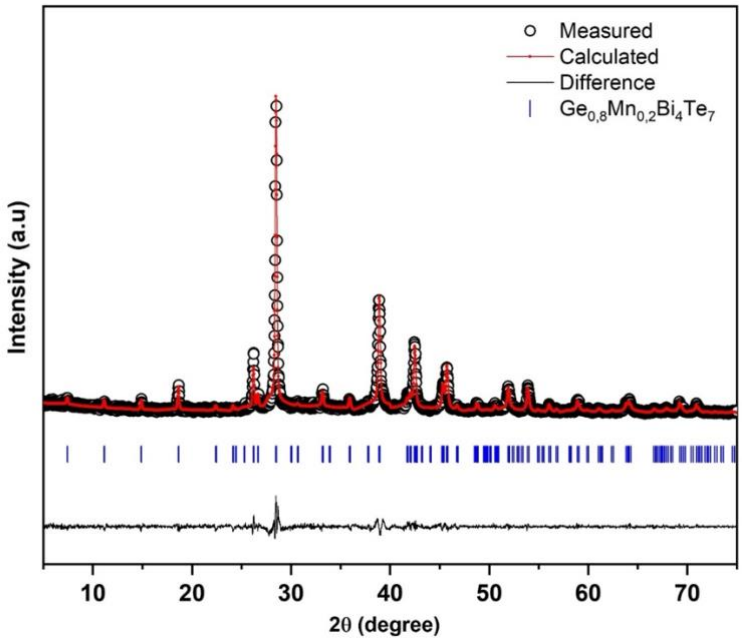

Figure 3. Le Bail profile of alloy with composition $Ge_{0.8}Mn_{0.2}Bi_4Te_7$.

The compositional dependence of the lattice parameters for the solid solution series in the $GeBi_2Te_4$–$MnBi_2Te_4$ and $GeBi_4Te_7$–$MnBi_4Te_7$ systems was determined from the refined values presented in Table 2. As illustrated in Figures 4(a) and 4(b), *a* lattice parameter increases, while the *c* parameter decreases systematically with increasing Mn content. This behavior is consistent with Vegard's law and reflects the gradual substitution of smaller Ge^{2+} ions by larger Mn^{2+} ions, leading to anisotropic changes in the crystal structure. The smooth and continuous variation of the lattice parameters over the entire compositional range confirms the formation of complete solid solutions without evidence of phase separation or structural distortion.

Table 2. The compositional dependence of the lattice parameters for the solid solution series in the $GeBi_2Te_4$–$MnBi_2Te_4$ and $GeBi_4Te_7$–$MnBi_4Te_7$ systems was determined from the refined values

Composition, mol%	Space Group	Lattice parameters, Å		Ref.
		a	*c*	
$Ge_{1-x}Mn_xBi_2Te_4$				
x=0.0	*R*-3*m*	4.3176(3)	41.259(5)	[8]
x=0.2	*R*-3*m*	4,3199	41,17	This work
x=0.4	*R*-3*m*	4,3235	41,104	This work
x=0.6	*R*-3*m*	4,3257	41,022	This work
x=0.8	*R*-3*m*	4,3281	40,975	This work
x=1.0	*R*-3*m*	4.3304(4)	40.919(4)	[21]
$Ge_{1-x}Mn_xBi_4Te_7$				
x=0.0	*P*-3*m*1	4.3556(2)	23.928(4)	[8]
x=0.2	*P*-3*m*1	4,3567	23,901	This work
x=0.4	*P*-3*m*1	4,3576	23,875	This work
x=0.6	*P*-3*m*1	4,3585	23,851	This work
x=0.8	*P*-3*m*1	4,3595	23,824	This work
x=1.0	*P*-3*m*1	4.3601(1)	23.798(2)	[21]

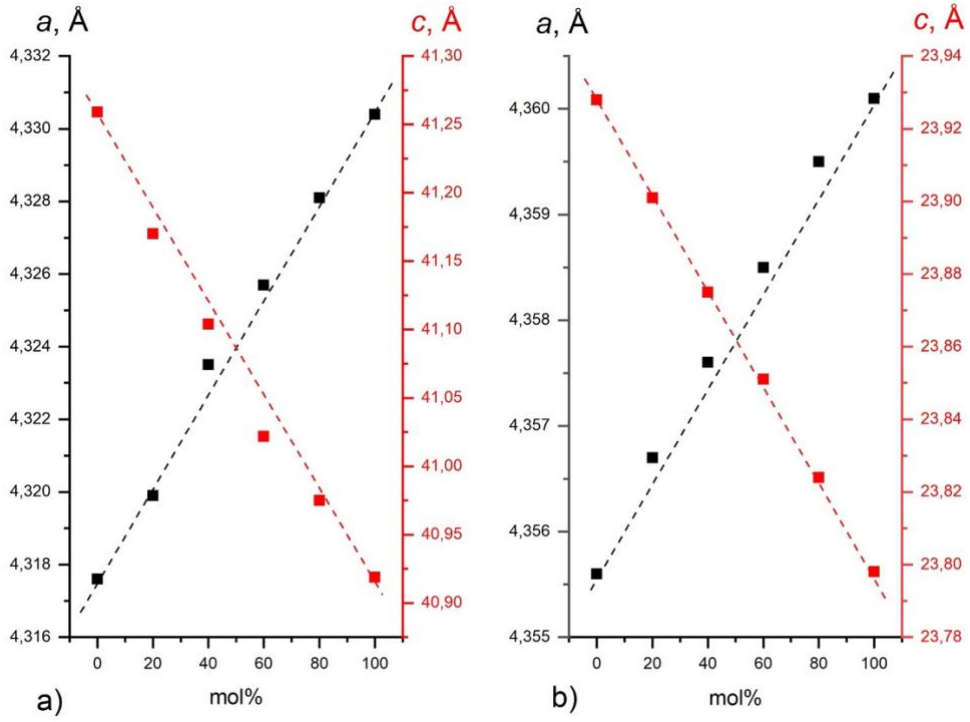

Figure 4. Concentration of lattice parameters of $Ge_{1-x}Mn_xBi_2Te_4$ and $Ge_{1-x}Mn_xBi_4Te_7$ solid solutions.

CONCLUSION

Continuous solid solutions were successfully synthesized in the $GeBi_2Te_4$–$MnBi_2Te_4$ and $GeBi_4Te_7$–$MnBi_4Te_7$ systems through a melt-quenching and multi-stage annealing process. XRD analysis confirmed the formation of single-phase materials throughout the full composition range, with structural transitions consistent with rhombohedral (*R*-3*m*) and trigonal (*P*-3*m*1) symmetry, respectively. Le Bail refinement of the powder XRD patterns revealed a linear variation of lattice parameters with increasing Mn content, in agreement with Vegard's law, indicating the successful substitution of Ge^{2+} by Mn^{2+} ions. SEM analysis supported the homogeneity of the synthesized alloys. These results not only confirm the structural compatibility of Ge and Mn in these layered telluride systems but also provide a platform for further studies into their functional properties, particularly concerning thermoelectric and topological applications.

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