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PHASE RELATIONS AND CHARACTERIZATION OF SOLID SOLUTIONS IN THE $SnSb_2Te_4$–$MnSb_2Te_4$ SYSTEM

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Abstract. The phase relations in the $SnSb_2Te_4$–$MnSb_2Te_4$ system were investigated employing differential thermal analysis, X-ray diffraction and scanning electron microscope equipped with energy dispersive x-ray spectroscopy techniques. The system in non-quasibinary and continuous tetradymite-like solid solutions with $Sn_{1-x}Mn_xSb_2Te_4$ formula is formed in the whole concentration range. The hexagonal lattice parameters, *a* and *c* decrease linearly in direct proportion to *x* following Vegard's law. Besides, the peritectic decomposition temperatures of solid solutions increase with increasing content of Mg^{2+} ion. Due to the complex interaction between the $SnSb_2Te_4$ and $MnSb_2Te_4$ compounds, the SnTe–MnTe–Sb_2Te_3 composition triangle needs to be studied for a phase identification above the solidus line.

Keywords: *$SnSb_2Te_4$–$MnSb_2Te_4$ system, phase equilibria, solid solutions, tetradymite-like structure, topological insulator.*

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1. Introduction

Apart from conventional insulators and semiconductors, topological insulators (TI) exhibit many novel physical phenomena which creates huge potential for electronic and spintronic applications (Hasan *et al*., 2010; He *et al*., 2020; Tokura *et al*., 2019; Mong *et al*., 2019). Doping known TIs with magnetic element is considered to be a simple route to induce magnetism in these materials. However, both magnetic and Tl layer contained materials showing the intrinsically magnetic behaviors make possible to realize the formation of axion insulators and topological magnetoelectric effect, and so on (Babanly *et al*., 2017; Niesner *et al*., 2014; Kou *et al*., 2015; Li *et al*., 2019; Teng *et al*., 2019). Particularly, fabrication of the manganese layer contained heterostructures is experimentally verified as a promising material platform (Murakami *et al*., 2019; Ding *et al*., 2020; Li *et al*., 2020; Chen *et al*., 2019; Otrokov *et al*., 2019; Aliev *et al*., 2019), e.g., the first antiferromagnetic TI recently has been confirmed (Otrokov *et al*., 2019).

In this contribution, it was an attempt to investigate the phase relations in the $SnSb_2Te_4$–$MnSb_2Te_4$ system. Since both constituents have identical structures and close valued lattice parameters, the system is considered to be a promising candidate for obtention of substitutional solid solutions which were experimentally observed in similar systems (Yan *et al*., 2019; Orujlu, 2020; Seidzade, 2019; Seidzade *et al*., 2019; Pan *et al*., 2015). Substitution solid solutions are found to be an effective strategy to control novel properties by changing the concentration of starting components.

A review of the literature data showed that $MnSb_2Te_4$ is the only an

experimentally observed ternary compound in the $MnTe–Sb_2Te_3$ pseudo-binary system. Similar to well-known isostructural analog $MnBi_2Te_4$, it is a tetradymite-like layered compound of the rhombohedral lattice (*a*=4.2445 Å, *c*=40.870 Å (Yan *et al*., 2019)) with the *R-3m* (#166) space group. Crystal structure of this compound is comprised of alternation of septuple layered blocks along the *c* axis separated by van der Waals spacing. The observed antiferromagnetic ordering temperature for $MnSb_2Te_4$ (19 K (Yan *et al*., 2019)) is lower comparing to $MnBi_2Te_4$ (24 K (Otrokov *et al*., 2019)).

Up to know, the phase relations of the $SnTe–Sb_2Te_3$ pseudo-binary system were reported in (Elagina *et al*., 1959), and only one ternary compound - $SnSb_2Te_4$ was experimentally observed forming with a peritectic reaction at 594°C (Seidzade *et al*., 2019) or 603°C (Elagina *et al*., 1959). The $SnSb_2Te_4$ compound crystallizes in *R-3m*-type hexagonal structure with the lattice parameters *a* = 4.2957 Å, *c* = 41.542 Å (Seidzade *et al*., 2019), and is a three-dimensional topological insulator (Menshchikova *et al*., 2013).

2. Experimental part

The samples of the $Sn_{1-x}Mn_xSb_2Te_4$ system were synthesized under vacuum conditions by using elemental components (supplied by Alfa Aesar) in glassy carbon crucibles inside the quartz tubes at 750°C for 5 hours. The purity of the elements was higher than 99.99%. The resulting ingots were homogenized at 450°C for 45 days and then quenched in icy water.

After annealing, all equilibrated samples were examined using powder X-ray diffraction (PXRD), differential thermal analysis (DTA) and scanning electron microscope (SEM) equipped with energy-dispersive X-ray spectroscopy (EDX) techniques. The PXRD analysis was performed on a Bruker D2 PHASER diffractometer using CuK_α radiation (scanned in the 2θ range of 5°-75°). TOPAS 4.2 and EVA software were used for the determination of lattice parameters and pattern indexing. Thermal analysis was carried out by LINSEIS HDSC PT1600 system with a heating rate of 10 $°C \cdot min^{-1}$, and microstructure and chemical homogeneity were investigated using a HITACHI SU8030 scanning electron microscope with Bruker EDX detector.

3. Result and discussion

The PXRD patterns of homogenized alloys are present in Fig. 1a. It was observed that all intermediate compositions have a set of diffraction lines that have similar reflections with end-member compositions of the system corresponding to the tetradymite-like hexagonal structure with space group *R-3m* (#166). With increasing the manganese content (x=0-1.0), diffraction peaks showed shift of reflections to the higher angles related to ionic radius differences.

Determined structural parameters of some $Sn_{1-x}Mn_xSb_2Te_4$ alloys from PXRD patterns are listed in the Table. Values for initial compounds, $SnSb_2Te_4$ and $MnSb_2Te_4$ which were obtained in this work are in a good agreement with those reported by Yan *et al*., (2019) and Seidzade *et al*., (2019). Both parameters of $SnSb_2Te_4$ is bigger compared to $MnSb_2Te_4$ due to $r(Sn^{2+})=118$ pm > $r(Mn^{2+})=70$ pm. From Fig. 1b. it is seen that the lattice parameters *a* and *c* decrease linearly with increasing *x* value following Vegard's law. These results provide strong evidence for the formation of complete solid solution

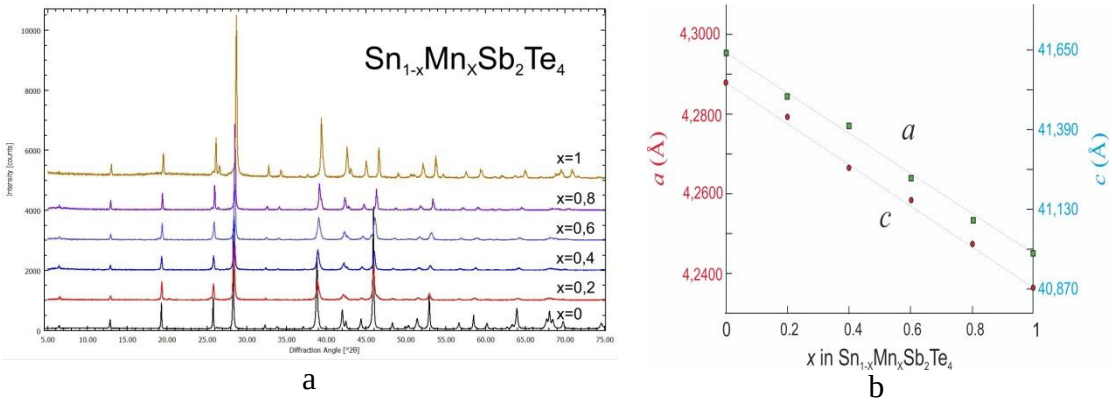

Figure 1. RFA results (a) and concentration dependence of lattice parameters (b) of alloys

areas in the $SnSb_2Te_4$–$MnSb_2Te_4$ system. Obtention of the observed solid solutions has furtherly been confirmed by the SEM-EDX measurements. Fig. 2a and 2b depict SEM images of the powder $Sn_{0.6}Mn_{0.4}Sb_2Te_4$ alloy with clearly segregated layers, confirming that synthesized material is a tetradymite-like layered structure integrated by van der Waals spacing. The EDX spectroscopy (Fig. 2c) presents the existence of Sn, Mn, Sb and Te atoms in the analyzed area and resulting chemical composition agreeing with the nominal formula $Sn_{0.6}Mn_{0.4}Sb_2Te_4$.

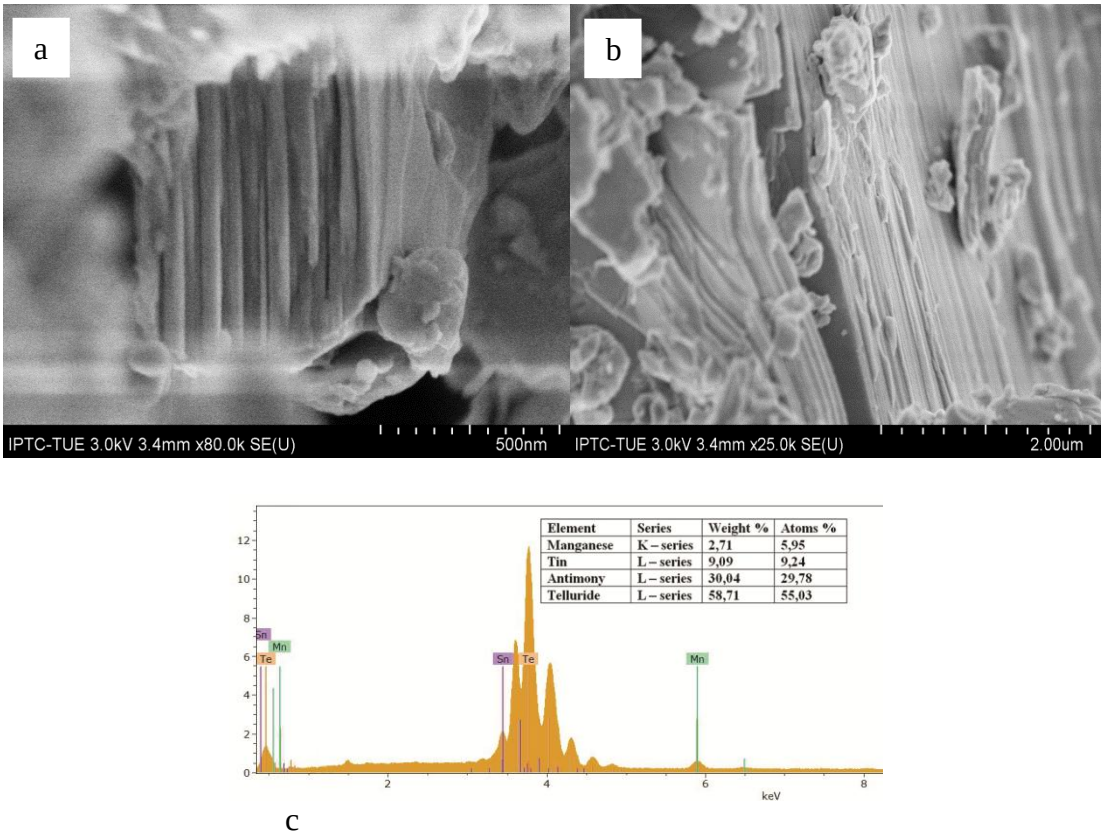

Figure 2. SEM images (a,b) and EDX analysis (c) for the elemental distribution of the powder $Sn_{0.6}Mn_{0.4}Sb_2Te_4$ alloy annealed at 450°C for 45 days

DTA examinations of some selected $Sn_{1-x}Mn_xSb_2Te_4$ compositions are shown in the Table. Thermal effects evaluated from the onset point of an endothermic peak on heating thermograms correspond to peritectic decomposition temperatures. Their onset temperatures increase with the increasing amount of Mn^{2+}. However, liquidus temperatures of some alloys could not be observed during the cooling and heating processes.

The phase diagram of the $SnSb_2Te_4$–$MnSb_2Te_4$ system constructed as a result of the obtained data from DTA, RFA, and SEM-EDX measurements is presented in Fig. 3. It has been found that the system is non-quasibinary due to the incongruent melting character of $SnSb_2Te_4$ and $MnSb_2Te_4$. It is stable up to the peritectic decomposition temperatures and forms a continuous series of solid solutions.

Table 1. DTA results and lattice parameters of some $Sn_{1-x}Mn_xSb_2Te_4$ alloys

***x* in $Sn_{1-x}Mn_xSb_2Te_4$**	**Thermal effects (°C)**	**Lattice parameters (Å)**	
		a	**c**
0	595; 625	4.2958(3)	41.546(4)
0.2	602-609	4.2844(2)	41.438(1)
0.4	607-613	4.2768(2)	41.264(4)
0.6	617-624	4.2642(4)	41.162(4)
0.8	630-636	4.2538(3)	41.019(2)
1.0	640; 1017	4.2451(4)	40.872(3)

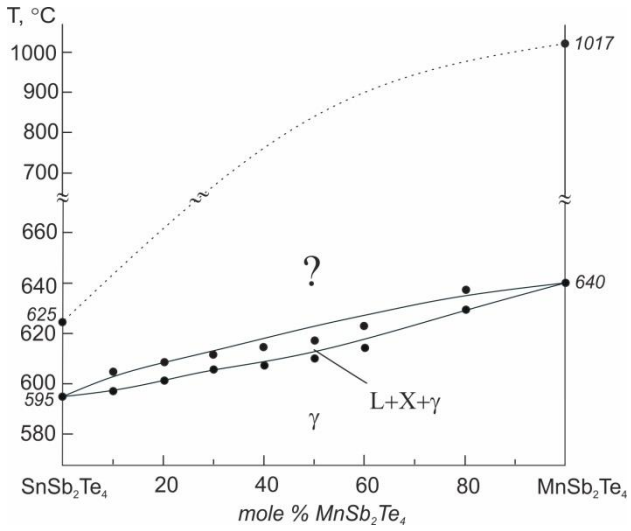

Figure 3. Phase diagram of the $SnSb_2Te_4$–$MnSb_2Te_4$ system

However, these results are only enough to draw an accurate phase diagram of the system below the solidus curve. Due to complex interaction of the $SnSb_2Te_4$ and $MnSb_2Te_4$ compounds, it is impossible to identify a phase composition between the liquidus and solidus curves. In this regard, the concentration triangle SnTe–MnTe–Sb_2Te_3 should be studied to identify phase composition in the $SnSb_2Te_4$–$MnSb_2Te_4$ system above the solidus.

4. Conclusion

The phase relations in the $SnSb_2Te_4$–$MnSb_2Te_4$ system have been studied based on XRD, DTA and SEM-EDS methods. The system is non-quasibinary and characterized by formation of the continuous solid solution series with a tetradymite-like hexagonal structure. Both lattice parameters of solid solutions vary linearly depending on composition following the Vegard's law. The melting temperature of $Sn_{1-x}Mn_xSb_2Te_4$ alloys was found to increase with increasing *x*. Obtained solid solutions are of great interest as a prospect of magnetic topological materials.

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