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Phase Equilibria of the MnTe-Sb₂Te₃ System and Synthesis of Novel Ternary Layered Compound – MnSb₄Te₇

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By using Differential Thermal Analysis (DTA) and Powder X-ray Diffraction (PXRD) techniques, the phase diagram of the MnTe-Sb₂Te₃ system has been constructed for the first time in the entire composition range. The system features two ternary layered van der Waals (vdW) compounds. Apart from known MnSb₂Te₄, novel MnSb₄Te₇ which a structural analogous of the known MnBi₂Te₄ was found in the system. Crystal structure parameters of both compounds were determined by Rietveld refinement using the fundamental parameter approach. Both compounds were found to decompose via peritectic reactions and possess significant homogeneity ranges. The title system is also characterized by the existence of the wide solid solution field based on the starting Sb₂Te₃. The present results would be useful for the bulk single crystal growth of both compounds from the liquid phase via the determination of primary crystallization areas.

Keywords: MnTe-Sb₂Te₃ system; manganese antimony tellurides; magnetic topological insulators; X-ray diffraction; phase diagram.

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Introduction

VdW materials based on bismuth and antimony chalcogenides have received great interest thanks to the attractive combination of intriguing thermoelectric and topological insulator (TI) properties [1-4]. Non-trivial band topology and complex structures of these materials allow for the realization of many novel topological phenomena, such as quantum Hall effect, quantum spin Hall effect, quantum anomalous Hall effect (QAHE), Majorana fermions, topological axion insulators, magnetoresistance switch effect, etc., which have huge potential for electronic, spintronic applications or other future technologies [5-12].

The most recent research topic in this field concerns materials having both magnetic and topological features. Breaking time-reversal symmetry and open an exchange gap in the Dirac surface states in TIs are key points for the realization of magnetism [13-16]. Results of doping trivial TI materials with magnetic transition metals by Molecular Beam Epitaxy and Bridgman methods show magnetic ordering at extremely low temperatures which is the main factor that prevents its practical use [17-20]. However, layered heterostructures contain both magnetic and TI layers succeed to integrate these seemingly incompatible characters [15, 16, 21], e.g., recently confirmed first intrinsic antiferromagnetic TI - MnBi₂Te₄ [22]. In this connection, other possible ternary compounds containing magnetic transition metals (M) – V, Cr, Mn, and Fe in both MT£–Sb₂Te₃ and MT£–Bi₂Te₃ systems are believed to be an ideal platform to explore interesting topological quantum effects that remains elusive experimentally so far.

The phase diagram of the MnTe-Bi₂Te₃ quasi-binary system was investigated [23]. The system contains three ternary compounds that melt incongruently via peritectic reactions and further research revealed the existence of other homologues series [23-25]. It was also revealed that interlayer antiferromagnetic ordering weakens from MnBi₂Te₄ to MnBi₅Te₁₀ which is ferromagnetic and furtherly disappears in high members of homologues.
series [25]. The temperature-dependent changes in the electronic structure of the MnBi$_2$Te$_4$ were studied in [26].

To our best knowledge, the phase diagram of the MnTe-Sb$_2$Te$_3$ binary system is not yet available in the literature. Crystal structure determination and some theoretical studies devoted to electronic structure, magnetism, etc., of the MnSb$_2$Te$_4$ are reported in [27-32]. The observable antiferromagnetic ordering temperature for MnSb$_2$Te$_4$ (19 K [28]) is lower comparing to MnBi$_2$Te$_4$ (24 K [22]).

In the present work, the phase diagram of the MnTe-Sb$_2$Te$_3$ binary system is determined experimentally for the first time and crystal structure refinement of ternary compounds is presented. The boundary binary compounds of the system have been investigated on several occasions [33-37]. MnTe melts peritectically at 1155 ± 5 °C and crystallizes in the hexagonal crystal structure, space group P6$_3$/mmc (no. 194) with unit cell parameters $a = 4.1429$ Å, $c = 6.7076$ Å [35]. Hexagonal NiAs-type crystal structure undergo several phase transformations. Sb$_2$Te$_3$ melts peritectically at 620 °C and crystallizes in a rhombohedral unit cell having the lattice constants $a = 4.264$ Å, $c = 30.458$ Å (space group, $R$-3$m$ (no. 166)) [36, 37].

I. Experimental details

High purity elemental compounds (99,9999 %, Alfa Aesar and Sigma-Aldrich) were used to synthesize binary starting compounds MnTe and Sb$_2$Te$_3$. Mixture of components inside the vacuum (~10$^{-3}$ Pa residual pressure) sealed quartz ampoules were melted at 1250 °C and 700 °C, respectively. Glassy carbon crucibles were used to synthesize MnTe to prevent manganese reaction with quartz. Both binary compounds were analyzed by DTA and PXRD to check the phase purity and results were close to the values reported in the literature [33-37]. DTA examination of MnTe shows four endothermic peaks at the temperatures 955, 1020, 1055, and 1151 °C, respectively. The first three peaks belong to polymorphic transformations, while the last one indicates the peritectic melting point ($T_m$ = 1155 K) which is formed in similar A$^IV$-Te-Sb$_2$Te$_3$ systems (A$^IV$-Ge, Sn, Pb). Since these two ternary compounds can be easily distinguished in XRD analysis with their characteristic non-overlapping peaks at small angles. In addition, analyzing the PXRD patterns of the equilibrated alloys indicate that, besides Sb$_2$Te$_3$, there is another phase that is not indexed by the database. Clearly distinguishable peaks at low angles allow us to assume that they more likely correspond to the MnSb$_2$Te$_7$ layered compound with similar reflection lines with a negligible shifting compared to pure Sb$_2$Te$_3$. This fact clearly confirms the existence of a solubility field based on Sb$_2$Te$_3$ about 11 - 12 mol%. In Fig. 1.a, the PXRD peaks of alloy 75 mol% Sb$_2$Te$_3$ indicate that, besides Sb$_2$Te$_3$, there is another phase composition was found to be a biphasic mixture of MnTe and Sb$_2$Te$_3$ as expected (Fig. 1.f). All these results strongly prove the existence of a new compound in the system with a stoichiometric ratio of 1:4:7 in addition to 1:2:4. However, we found no evidence for the existence of other ternary compounds in the Sb$_2$Te$_3$-rich region. We believe that the atomic size factor is a dominant structural feature that prevents the formation of more complex members of homologous series in this system. The existence of a wide solubility field based on Sb$_2$Te$_3$ indicates that Sb atoms are relatively easy to substitute Mn atoms up to a certain amount so that we can predict that both ternary compounds should have homogeneity fields.

The Rietveld refinement was done to reveal the crystal structure of both ternary compounds. All refinements showed very good fits. The observed and calculated data of the powder diffraction patterns are shown in Fig. 2 and results of the Rietveld structural refinement are listed in Table 1. The compound MnSb$_2$Te$_4$ has the same trigonal structure as MnBi$_2$Te$_4$ with crystal lattice parameters $a = 4.2445$ Å and $c = 40.862$ Å. For MnSb$_2$Te$_4$, all diffraction patterns are indexed in the trigonal structure with lattice parameters $a = 4.2413$ Å and $c = 23.761$ Å. We note that determined unit cell parameters of MnSb$_2$Te$_4$ are in good agreement with Vesta software.

II. Results and discussion

To identify phase equilibria in the MnTe-Sb$_2$Te$_3$ system over the entire concentration range, fourteen alloys were prepared. Fig. 1 shows the PXRD results of some selected alloys. The diffraction peaks of different phases can be identified by referring to the ICDD and COD databases. Characteristic peaks of different phases are described by different symbols. As can be seen from Fig. 1.a, an alloy having 90 mol% Sb$_2$Te$_3$ has similar reflection lines with a negligible shifting compared to pure Sb$_2$Te$_3$. This fact clearly confirms the existence of a solubility field based on Sb$_2$Te$_3$ about 11 - 12 mol%. In Fig. 1.b, the PXRD peaks of alloy 75 mol% Sb$_2$Te$_3$ indicate that, besides Sb$_2$Te$_3$, there is another phase composition was found to be a biphasic mixture of MnTe and Sb$_2$Te$_3$ as expected (Fig. 1.f). All these results strongly prove the existence of a new compound in the system with a stoichiometric ratio of 1:4:7 in addition to 1:2:4. However, we found no evidence for the existence of other ternary compounds in the Sb$_2$Te$_3$-rich region. We believe that the atomic size factor is a dominant structural feature that prevents the formation of more complex members of homologous series in this system.
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Fig. 1. PXRD patterns of some equilibrated alloys: a) 90 mol% Sb$_2$Te$_3$, b) 75 mol% Sb$_2$Te$_3$, c) 66.7 mol% Sb$_2$Te$_3$, d) 60 mol% Sb$_2$Te$_3$, e) 50 mol% Sb$_2$Te$_3$, f) 40 mol% Sb$_2$Te$_3$.

Fig. 2. Rietveld refinement profiles for the MnSb$_2$Te$_4$ (a) and MnSb$_4$Te$_7$ (b).
with already reported ones elsewhere in [27, 28].
However, the narrow homogeneity field of the MnSb$_2$Te$_4$
compound may cause some deviation from the values of
the $a$ and $c$ parameters which suggests that other results
can also be acceptable.

Both compounds exhibit tetradymite-type layered
structure where unit cells consist of stacked septuple
blocks of Te-Sb-Te-Mn-Te-Sb-Te for MnSb$_2$Te$_4$ (space
group $R-3m$) and repetitions of the same septuple layer
and quintuple layer blocks of Sb$_2$Te$_3$ for MnSb$_4$Te$_7$
(space group $P-3m1$) (Fig. 3). In each block, atomic
layers are covalently bonded, whereas blocks itself
connected via van der Waals interactions.

The phase diagram of the MnTe-Sb$_2$Te$_3$ (Fig. 4)
system was constructed by means of DTA and PXRD
results of annealed alloys. As can be seen from
the figure, this system is a partial quasi-binary section of the

| Table 1 |
| Results of Rietveld refinements for the investigated phases |
| MnSb$_2$Te$_4$ | MnSb$_4$Te$_7$ |
| Space group | $R-3m$ (no. 166) | $P-3m1$ (no. 164) |
| $Z$ | 3 | 1 |
| Temperature (K) | 293 | 293 |
| Unit cell parameter: $a$ (Å) | 4.2445(2) | 4.2513(3) |
| $c$ (Å) | 40.862(3) | 23.761(4) |
| Unit cell volume ($Å^3$) | 637.534 | 371.9108 |
| $R_{Bragg}$% | 2.67 | 1.35 |
| Radiation type | CuK$_{α}$ | CuK$_{α}$ |

Fig. 3. Crystal structures of MnSb$_2$Te$_4$ and MnSb$_4$Te$_7$.

Fig. 4. Phase diagram of the MnTe-Sb$_2$Te$_3$ system.
Conclusion

In this work, the phase relationship in the Mn-Sb-Te system due to the incongruent melting character of manganese telluride. As discussed above, the MnTe-Sb2Te3 system host two ternary intermediate compounds. Both compounds melt by peritectic reactions:

\[ \text{L} + \text{MnTe} \rightarrow \text{MnSb}_2\text{Te}_3 (p_1, 647^\circ \text{C}) \]
\[ \text{L} + \text{MnSb}_2\text{Te}_3 \rightarrow \text{MnSb}_{2.5}\text{Te}_7 (p_2, 628^\circ \text{C}) \]

The composition of the invariant peritectic points corresponds to 75 (p1) and 80 (p2) mol% Sb2Te3, respectively. The system also has eutectic point (e) lies at 85 mol% Sb2Te3 and 614 °C. One can be seen from the phase diagram, both compounds possess significant homogeneity ranges. Besides, there is an approximately 11 - 12 mol% solubility region based on Sb2Te3. On the MnTe rich side, several polymorphic transformations were observed. By using DTA results, we determined that the temperatures of polymorphic transformations were significantly reduced compared to pure MnTe and occur by following metatropic reactions:

\[ (\text{MnTe h}) \Leftrightarrow \text{L} + (\text{MnTe i1}) \]
\[ (\text{MnTe i1}) \Leftrightarrow \text{L} + (\text{MnTe i2}) \]
\[ (\text{MnTe i2}) \Leftrightarrow \text{L} + (\text{MnTe rt}) \]

The reaction temperatures were found to be 1035, 977, and 883 °C, respectively.

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Фазова рівновага системи MnTe-Sb$_2$Te$_3$ та синтез повільної тернарної шаруватої структури – MnSb$_4$Te$_7$

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За допомогою методів диференційного термічного аналізу (DTA) та порошкової рентгенівської дифракції (PXRD), вперше побудовано фазову діаграму системи MnTe-Sb$_2$Te$_3$ у всьому діапазоні сполук. Система містить дві потрійні шаруваті сполуки ван дер Ваальса (vdW). Окрім відомої MnSb$_2$Te$_4$, в системі знайдено нову сполуку MnSb$_4$Te$_7$, яка є структурним аналогом відомої MnBi$_4$Te$_7$. Параметри кристалічної структури обох сполук визначали уточненим методом Рітвельда, використовуючи підхід до фундаментальних параметрів. Встановлено, що обидві сполуки розкладаються в результаті перитектичних реакцій і мають значні діапазони однорідності. Назва системи також характеризується існуванням широкого кола твердого розчину на основі вихідного Sb$_2$Te$_3$. Отримані результати можуть бути корисними для росту монокристалів обох сполук з рідкої фази шляхом визначення площ первинної кристалізації.

Ключові слова: система MnTe-Sb$_2$Te$_3$; марганець сурмі телуріди; магнітно-топологічні ізолятори; дифракція рентгенівських променів; фазова діаграма.