

$T(z)$ diagram of the $\text{Mn}_{3z}\text{In}_{2(1-z)}\text{Te}_3$ system in the range $0 < z < 0.7$

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The $T(z)$ phase diagram of the system $\text{Mn}_{3z}\text{In}_{2(1-z)}\text{Te}_3$ was determined in the composition range $0 < z < 0.75$ from differential thermal analysis and X-ray diffraction measurements. It was shown that a single-phase solid solution with the adamantine structure occurs in the composition range $0 < z < 0.26$, but that for the rest of the composition range investigated two phase conditions apply. In the single-phase range, at higher temperature the structure is zinc-blende, with Mn atoms, In atoms and lattice vacancies arranged at random on the cation sublattice. Below $\sim 620^\circ\text{C}$, two separate ordered structures occur, one with $0 < z < \sim 0.03$, corresponding to the orthorhombic ordered structure of In_2Te_3 , and the other with $\sim 0.09 < z < 0.26$, corresponding to the tetragonal ordered structure of MnIn_2Te_4 .

1. Introduction

Semiconductor materials containing manganese have received considerable attention recently, because of the way that the magnetic properties associated with the manganese can modify and complement the semiconductor behaviour [1,2]. It has been found that adamantine compounds with tetrahedral coordination can accept large amounts of manganese in cation-substitution solid solution. Well-known examples of such materials are the semimagnetic semiconductor alloys based on II-VI compounds, e.g. $\text{Cd}_{1-z}\text{Mn}_z\text{Te}$, etc. [1]. In alloys of this type, a single-phase solid solution is obtained with ranges of z up to 0.85. Similar materials can be obtained by introducing manganese into the equivalent

ternary compounds, the tetrahedrally coordinated I-III-VI₂ chalcopyrites, e.g. $(\text{CuIn})_{1-z}\text{Mn}_{2z}\text{Te}_2$, for which ranges of single-phase solid solution up to $z_{\text{I}} = 0.65$ are found [3]. In these alloys, it has been shown that, depending upon the heat-treatment, a given material can have the manganese either ordered or disordered on the cation sublattice, and two different magnetic properties and band-gap behaviour in the alloys [3,4]. Another set of compounds which show the tetrahedrally bonded form are some of the III₂VI₃ compounds, e.g. In_2Te_3 , Ga_2Te_3 , Ga_2Se_3 , etc. Very little information is available on the substitutional solid solubility of manganese in these compounds. The compound In_2Te_3 has a defect zinc-blende structure, every third cation site being vacant. At high temperatures, the lattice vacancies are arranged at random on the cation sublattice, but below 615°C ordering occurs and the equilibrium condition is with the vacancies ordered on the

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cation sublattice, to give an orthorhombic symmetry [5]. Thus the symmetry of the structure changes from $F\bar{4}3m$ above 615°C to $Imm2$ below that temperature. No information has previously been given on the range of solid solubility of $MnTe$ in In_2Te_3 , i.e. in the alloy system $Mn_{1-z}In_{2(1-z)}Te_3$. However, one interesting composition in this system is $z = 0.25$ which gives the compound $MnIn_3Te_4$. The crystallography and optical energy gap behaviour of this compound were investigated previously [6] and the crystal structure is reported to be tetragonal with $a = 0.6191$ nm, $c/a = 2.00$ and $z = 2$. In this case, the lattice vacancies are ordered on the cation sublattice, but the Mn and In atoms are distributed randomly over the occupied cation sites.

In the present work, the $T(z)$ diagram, phase conditions and lattice parameter values for the $Mn_{1-z}In_{2(1-z)}Te_3$ system have been determined in the composition range $0 < z < 0.75$ from differential thermal analysis (DTA) measurements and powder X-ray diffraction photographs.

2. Preparation of samples and methods of measurements

All of the alloys used were prepared by the melt and anneal technique. The components of 1.5 g sample each were sealed under vacuum in small quartz ampoules which had previously been carbonized to prevent interaction of the alloy with the quartz. The components were melted together at 1150°C , annealed to equilibrium at 600°C and then slowly cooled to room temperature by leaving the ampoules in the switched-off

furnace. Previous experience indicates that for this type of alloy, this procedure gives samples showing conditions corresponding to equilibrium in the temperature range $200\text{--}300^\circ\text{C}$.

Standard closed-tube DTA measurements [7] were made in the temperature range from room temperature to 1100°C , on small samples of each of the compositions prepared, with silver being used as the reference material. The charge was in powder form and of approximately 100 mg weight. This was sealed under vacuum in a small quartz ampoule which had a re-entrant thermocouple well at the bottom. The temperatures of the sample and the reference were measured with chromel–alumel thermocouples, the difference signal between sample and reference and the temperature signal being continuously recorded. Each phase transition temperature was determined from the base-line intercept of the tangent to the leading edge of the peak in the difference signal. Both heating and cooling runs were made for each sample.

Guinier X-ray photographs were used to check the phase conditions of each sample and to determine values of lattice parameters as a function of the composition z , germanium being used as an internal standard.

3. Results and discussion

In the range $0 < z < 0.25$, all of the X-ray photographs appeared to show the cubic zincblende form, but with the presence of faint ordering lines. In the case of the $z = 0.075$ sample, two apparent cubic phases were observed with slightly

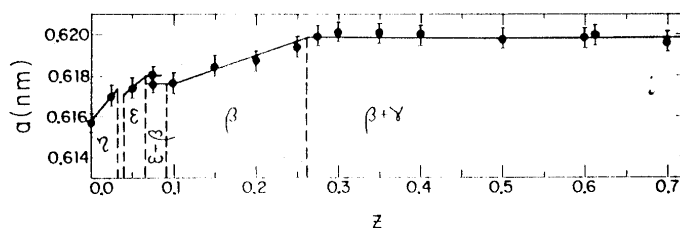


Fig. 1. Variation of lattice parameter a with z for $Mn_{1-z}In_{2(1-z)}Te_3$ alloys.

differing lattice parameters. The effective values of a obtained from these photographs are shown as a function of z in fig. 1. These a values indicate the presence of the various phase fields as shown and this was confirmed by a study of the ordering lines present in the various cases. Thus the η field in fig. 1 represents the ordered orthorhombic phase previously reported for In_2Te_3 ($z=0$), while the ϵ phase is the disordered zinc-blende phase. None of the samples investigated showed a two-phase $\eta + \epsilon$ condition, indicating that such a field must be very narrow in composition, and this is shown as a rough estimate only in fig. 1. Above $z \sim 0.09$, the β phase shows the form seen for $MnIn_2Te_4$ ($z=0.25$) being tetragonal with $c/a = 2.00$, and this β field extends to $z \sim 0.26$. Thus the two-phase sample at $z = 0.075$ lies in a two-phase $\epsilon + \beta$ field as shown. All samples with $z > 0.26$ (up to the limit of investigation of $z = 0.75$) were found to be two-phase, with lines corresponding to the NiAs structure of $MnTe$ (γ) in addition to the pseudocubic β phase. In this range, the values of the parameter a for

the pseudo-cubic phase were found, within the limits of experimental error, to be independent of z , as shown in fig. 1, indicating that the tie-lines of this field probably lie in the plane of the section being investigated.

The data from the DTA measurements are shown in fig. 2, where it is seen that no DTA transitions were observed below 550°C . The fields above 550°C can be clearly established from these DTA points, while below 550°C the absence of DTA transitions indicates that the phase boundaries are very steep and so can be drawn to be consistent with the X-ray data. The resulting $T(z)$ diagram is thus as shown in fig. 2. The low temperature phase fields have been labelled to be consistent with the X-ray data shown in fig. 1. At higher temperatures, a labelling of the fields which is consistent with the rest of the diagram is proposed, but these suggested field compositions have not been checked by any experimental measurements. With the narrow $L + \epsilon + \gamma$ three phase field as shown, the section cannot be pseudobinary, despite the tie-line conditions in the β - γ field mentioned above.

From the point of view of magnetic semiconductors, discussed in the Introduction, the region of interest in the present diagram is in the composition range $0 < z < 0.26$ and at temperatures below the solidus boundary between the $L + \epsilon$ and ϵ fields, i.e. the region in which single phase adamantite solid solution occurs at all points, except for the narrow $\eta + \epsilon$ and $\epsilon + \beta$ two-phase fields. At higher temperatures, the cation-disordered zinc-blende form (ϵ) occurs across the whole of this range, but below about 620°C two different ordered structures appear, one (η) corresponding to the ordered In_2Te_3 ($z=0$) form and the other (β) to the $MnIn_2Te_4$ ($z=0.25$) form. In each case, the ordering is of the lattice vacancies on the cation sublattice [5,6], and the presence of two different ordered structures can be attributed to the change in the lattice vacancy concentration, which falls from one in every three cations at $z=0$ to one in every four cations at $z=0.25$. The width of the η field is relatively small, $0 < z < 0.03$, indicating that even a small change in the vacancy concentration prevents the ordered η form occurring. However, the range of

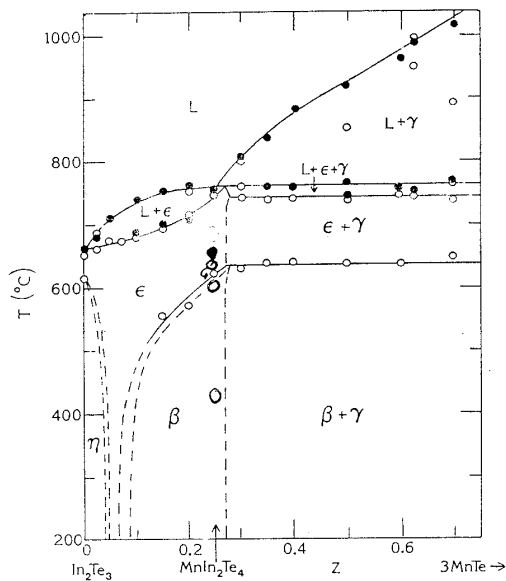


Fig. 2. $T(z)$ phase diagram for $Mn_{3z}In_{2(1-z)}Te_3$ alloys: (○) DTA heating run; (●) DTA cooling run.

the ordered β structure is considerably larger and is mainly on the low z side of $MnIn_2Te_4$ ($z = 0.25$), covering the composition range of $\sim 0.09 < z < 0.26$, the latter figure being the limit of single-phase solid solution. Thus when the lattice vacancy concentration falls below one cation in four, the single-phase structure soon becomes unstable. The exact behaviour of the lattice vacancies in the β field at values of z less than 0.25 has not as yet been investigated, but it is planned to carry out single crystal diffraction work for various concentrations in the β field.

4. Conclusions

In the $Mn_{3z}In_{2(1-z)}Te_3$ system, single-phase solid solution in a tetrahedrally coordinated adamantine structure is limited to the composition range $0 < z < 0.26$. In this composition range, above $\sim 620^\circ\text{C}$, the structure is zinc-blende, with the Mn and In atoms and lattice vacancies at random on the cation sublattice across the complete range of single-phase behaviour. Below 620°C , two ordered structures appear, corresponding to the ordering previously reported for In_2Te_3 ($z = 0$) and $MnIn_2Te_4$ ($z = 0.25$). In both cases, the ordering appears to be of the lattice vacancies, with the In and Mn atoms at random on the occupied sites of the cation sublattice.

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