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LETTER TO THE EDITOR

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Abstract. The system $(MnTe)_{1-x}$–$(In_2Te_3)_x$ has been investigated by microscopic examinations and x-ray diffraction to determine the region of mutual solubility. It has been found that a miscibility gap exists up to about $x = 0.50$, while for $x \geq 0.50$ the two chalcogenides form a complete solid solution. At room temperature, the tetragonal symmetry is stable in the range $0.50 \leq x \leq 0.80$, while alloys with $x > 0.80$ exhibit a FCC cell (defect zincblende) with partial cation order. Structural data for the adamantine phase $MnIn_2Te_4$ are also reported.

The physics of diluted magnetic semiconductors (DMS), also known as semi-magnetic semiconductors, presents many interesting phenomena, such as giant Faraday rotation [1], large negative magnetoresistance [2] and spin-glass behaviour in the magnetic susceptibility [3, 4]. These materials are formally obtained by substitutional dilution of the cation sublattice of a binary or more complex diamagnetic semiconducting compound by a paramagnetic ion. Most of the experimental work in this field has been carried out on Mn-based alloys, such as pseudo-binary MnX^{VI}–$M^{II}X^{VI}$ ($M^{II} \equiv Zn, Cd, Hg$; $X^{VI} \equiv S$, Se, Te) [5–7] and pseudo-ternary $M^{II}X^{VI}$–MnX^{VI}–$N^{II}X^{VI}$ ($M^{II} \neq N^{II}$) [8–10] systems. Other DMS have been derived from ternary $M^{I}M^{III}X_2^{VI}$ ($M^{I} \equiv Cu, Ag$; $M^{III} \equiv Al, Ga, In$) chalcopyrites [11–13]. The condition for the occurrence of a tetrahedral bond [14, 15] is now that a pair of Mn^{2+} ions substitutes for a I–III pair. Many results indicate that ordering of manganese occurs in these quaternary alloys with significant influence on their magnetic properties [11, 13, 16].

Ternary semi-magnetic alloys can also be prepared by diluting a binary $M_2^{III}X_3^{VI}$ compound with a MnX^{VI} chalcogenide. As a result, cation-deficient phases are obtained and ordering of vacancies makes possible the formation of superstructures.

The equilibrium phase diagram of the section MnS–Ga$_2$S$_3$ has been investigated [17], and attention has been drawn to the possible existence of metastable phases due to off-equilibrium preparation conditions.

Here we present some results on the room temperature phase relationships in the semi-magnetic system MnTe–In$_2$Te$_3$. It is shown that a solid solution can be formed over a wide range of compositions. Our preliminary data also indicate that metastable ordered phases can be observed in this system as well.

Alloys of the general composition $Mn_{1-x}In_{2x}Te_{1+2x}$ were prepared by direct synthesis from 'specpure' elements (In 5N, Te 4N). Purification of electrolytic manganese was carried out as described elsewhere [11]. The step in x was fixed at 0.05 near the terminal

points and 0.10 for other compositions. Significant points in the range of the system ($x =$ 0.25; 0.33; 0.66; 0.75) were also examined. To minimise chemical reaction of manganese with the holder, the elements were introduced into alumina crucibles, sealed under vacuum (10^{-5} Torr) in quartz tubes. The ampoules were heated up to 1150 °C, kept at

Table 1. X-ray data for $MnIn_2Te_4$.

| d_{exp} (Å)	$\sin^2 \theta_{exp}$	$\sin^2 \theta_{calc}$	hkl	I/I_0
5.5446	0.0194	0.0193	101	0.7
4.3820	0.0311	0.0309	110	0.6
3.5760	0.0464	0.0464	112	68.4
3.4345	0.0503	0.0503	103	5.0
3.0985	0.0619	0.0618	200, 004	5.9
2.7705	0.0775	0.0773	202	3.9
2.7032	0.0812	0.0812	211	9.3
2.5286	0.0928	0.0928	114	2.0
2.3006	0.1121	0.1121	105, 213	4.1
2.1901	0.1239	0.1237	220, 204	100.0
2.0653	0.1392	0.1391	222	0.6
2.0370	0.1431	0.1430	301	3.4
1.9591	0.1548	0.1546	310	0.7
1.8677	0.1701	0.1701	312, 116	23.1
1.7885	0.1856	0.1855	224	1.0
1.7181	0.2009	0.2010	206	1.0
1.6559	0.2165	0.2164	314	0.7
1.5863	0.2360	0.2358	323, 305	1.9
1.5486	0.2477	0.2474	008, 400	5.6
1.5026	0.2628	0.2628	402, 226	1.2
1.4916	0.2667	0.2667	217, 411	2.0
1.4601	0.2782	0.2783	118, 330	0.9
1.4213	0.2938	0.2937	316, 332	11.1
1.4120	0.2978	0.2976	413, 325	5.6
1.3853	0.3092	0.3092	420, 404, 208	0.7
1.3518	0.3248	0.3247	422	0.9
1.2646	0.3710	0.3710	424, 228	11.8
1.2328	0.3906	0.3904	501, 327, 431	2.1
1.2149	0.4018	0.4020	318, 510	0.9
1.1923	0.4175	0.4174	512, 336	8.0
1.1867	0.4214	0.4213	433, 503	2.4
1.1504	0.4481	0.4483	426	0.8
1.1455	0.4522	0.4522	417, 521	2.5
1.1082	0.4832	0.4831	435, 505, 523	1.3
1.0952	0.4945	0.4947	408, 2016	5.6
1.0625	0.5257	0.5256	530, 338	0.6
1.0472	0.5409	0.5411	516, 532	2.6
1.0434	0.5450	0.5450	525	0.6
1.0150	0.5759	0.5759	437, 507, 611	2.0
0.9795	0.6183	0.6184	604, 620	3.1
0.9447	0.6643	0.6649	536	0.5

this temperature for 2 days and then lowered to room temperature by an average cooling rate of 1.5 °C min^{-1}. After preliminary metallographic and x-ray examination, the samples were annealed at 550 °C for 70 days in order to attain equilibrium conditions.
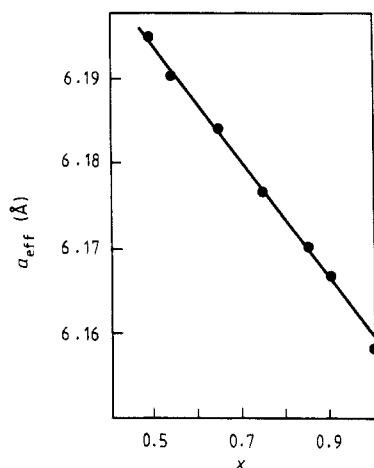
Figure 1. Variation of the effective cubic lattice constant $a_{\text{eff}} = (\frac{1}{2}a_0^2 c_0)^{1/3}$ with composition x in the homogeneous region of the system $(\text{MnTe})_{1-x}-(\text{In}_2\text{Te}_3)_x$.

Structural characterisation of samples was obtained using a powder x-ray diffractometer (Cu $K\alpha$ radiation) with graphite monochromator and rotating sample holder (step scan = 0.02 deg, measuring rate 0.25 deg s^{-1}. The background and $K\alpha_2$ component were subtracted before data analysis.

No differences in the solubility limits were observed before and after annealing. Analysis of the x-ray diffraction data showed that alloys in the composition range $0.05 \le x < 0.50$ were heterogeneous mixtures of tetragonal and hexagonal (NiAs-type) structures, often containing macroscopic precipitates of cubic (FeS$_2$-type) MnTe$_2$. This result indicates that the MnTe–In$_2$Te$_3$ system is not a true pseudo-binary section. Further confirmation of this comes from the fact that the lattice parameters of the tetragonal phase are also fairly composition-dependent in the heterogeneous region. Compositions with $x \ge 0.50$ were homogeneous. At room temperature the tetragonal symmetry was stable in the range $0.50 \le x \le 0.80$, while the In$_2$Te$_3$-rich region exhibited the FCC structure. In this latter region, however, some differences were observed in the x-ray powder patterns of slowly cooled and annealed samples. For example, the $x = 0.90$ composition, prepared by slow cooling, was indexed on a FCC cell ($a_0 = 6.167$ Å), with an exception for three faint additional lines indicative of the existence of a cubic superstructure with period $a_0 = 18.43$ Å. No foreign phases or precipitates were revealed

○ Anion

○ Mn

● In
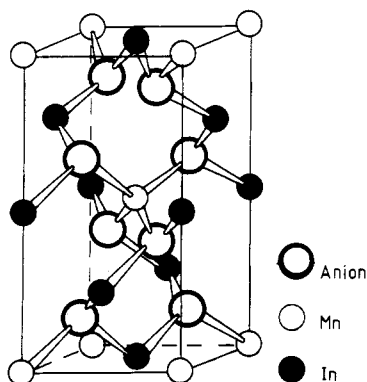
Figure 2. The crystal cell of thiogallate ($\overline{I4}$–S_4^2). Anions lie on the 8(g) sites. When complete order occurs in MnIn$_2$Te$_4$, the Mn atoms occupy the 2(a) sites, the In atoms occupy the 2(b) and 2(c) sites, respectively.

by microscopic examinations. The superstructure lines disappeared after annealing at 550 °C, this suggesting a completely randomised distribution of metal atoms and vacancies in the cationic sublattice. The structural behaviour of alloys in the cubic region ($x > 0.80$) is similar to the thermal polymorphism of In_2Te_3, which transforms to a completely disordered zincblende structure (β-In_2Te_3) over the temperature range 520–620 °C [18, 19]. The low-temperature modification (α-In_2Te_3) crystallises in a FCC supercell (space group F$\overline{4}$3m) due to ordering of vacancies [20–22]. In the case of the semi-magnetic system Mn–In–Te, however, only partial order is observed in the In_2Te_3-rich region under our experimental conditions, depending on the statistical likelihood of the diluted manganese occupying the vacant sites.

Figure 1 shows the composition dependence of the effective cubic lattice parameter $a_{eff} = (\frac{1}{2}a_0^2 c_0)^{1/3}$ of alloys in the single-phase region. The straight line $a_{eff}(x)$ can be extrapolated at the $x = 0$ composition to give the lattice constant of a hypothetical zincblende phase of MnTe. We obtain 2.70 Å for the tetrahedral Mn–Te bond length. This value is slightly smaller than those derived from the study of the MnTe–CdTe [6] and $CuInTe_2$–MnTe [11] systems, but it agrees very well with the value of 2.71 Å calculated in [23] and predicted by the Pauling set of tetrahedral radii [24].
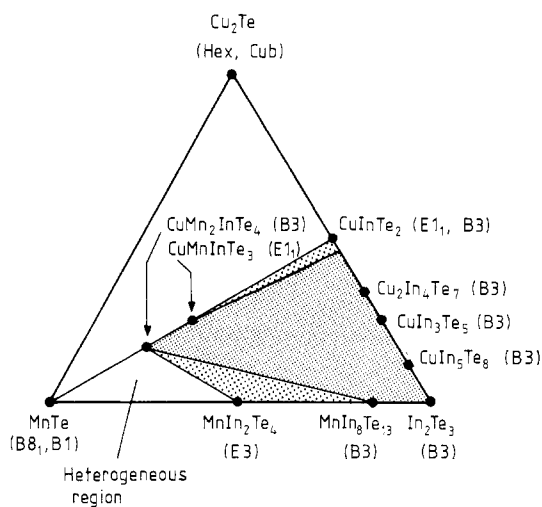
Figure 3. Composition triangle for the system Cu_2Te–In_2Te_3–MnTe. The structures follow the Strukturbericht notation: E3 = defect chalcopyrite; B3 = zincblende; E1$_1$ = normal chalcopyrite; B8$_1$ = nickel arsenide; B1 = sodium chloride. Lightly shaded areas indicate regions with tetragonal symmetry. The heavily shaded area refers to the homogeneous region with cubic symmetry.

Table 1 lists the observed peak sequence of the x-ray spectrum of the $x = 0.50$ composition and all the allowed indexes for the inner centred symmetry. $MnIn_2Te_4$ crystallises in a tetragonal deficient $CdGa_2S_4$-like structure, typical of most of the compounds of the adamantine $M^{II}M_2^{III}X_4^{VI}$ family (figure 2). The lattice parameters, refined by the least-squares method on 41 reflections, are $a_0 = 6.1951(4)$ Å and $c_0 = 12.390(2)$ Å, leading to a tetragonal deformation $\delta = 2 - c/a \simeq 0$. Assuming d(Mn–Te) = 2.71 Å and d(In–Te) = 2.76 Å as average values for the cation–anion distances, the anion coordinate should be just slightly shifted from the ideal position. The simultaneous absence of tetragonal and internal crystallographic distortion suggests for this compound a structural order–disorder behaviour at high temperature [25–27].

The present investigation, together with our previous results for the $CuInTe_2$–MnTe phase diagram [11] and those concerning the Cu_2Te–In_2Te_3 system [28–30] can be used to construct the composition triangle shown in figure 3.

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