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Growth of Bulk Single Crystals of $Cd_xZn_yMn_zTe$ Alloys

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Single-crystal samples of the $Cd_xZn_yMn_zTe$ pseudo-ternary alloys were grown by the Bridgman technique. Comparison of the initial growth material composition with the initial melt composition indicates that the liquidus and solidus sheets must have a temperature separation of less than 5°C. The single-crystal sample compositions were determined by measuring the lattice parameter and the spin glass transition temperature. © 1988 Academic Press, Inc.

One of the more convenient and simple methods of growing single-crystal samples of compounds is by the Bridgman technique. This is particularly suitable for line compounds of medium range and congruent melting point. However, when alloys showing a range of solid solution are considered, other problems arise. Thus, if at the composition of interest the temperature difference ΔT between liquidus and solidus curves is appreciable, the first solid to freeze has a different composition from the liquid phase and so as freezing continues, composition of liquid and hence freezing solid changes. The resulting grown ingot shows a composition variation along its length. Thus, reasonably uniform crystals or ingots can be grown only when the temperature difference ΔT is small.

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For the $Cd_xZn_yMn_zTe$ pseudo-ternary alloys, no information is available about liquidus–solidus temperatures in the general composition range, but data are known for the boundary pseudo-binary edges of the diagram. For the $Cd_{1-z}Mn_zTe$ system, the phase diagram (*1*) shows that in the range $0 < z < 0.7$, the value of ΔT is always less than 5°C, and this is reflected in the relative ease of growth of single crystals of these alloys. The phase diagram for the $Cd_{1-y}Zn_yTe$ alloys (*2*) shows single-phase solution through the composition range and a simple liquidus–solidus form. The maximum value of ΔT, in the vicinity of $y = 0.6$, is approximately 35°C. This is an appreciable value for ΔT and means that the difference in y between equilibrium liquid and solid phases can be as large as 0.2. Finally for the $Zn_{1-z}Mn_zTe$ alloys, no phase diagram seems to be available but data by Furdyna *et al.* (*3*) on Bridgman grown single crystals gives approximate information in this case. Their

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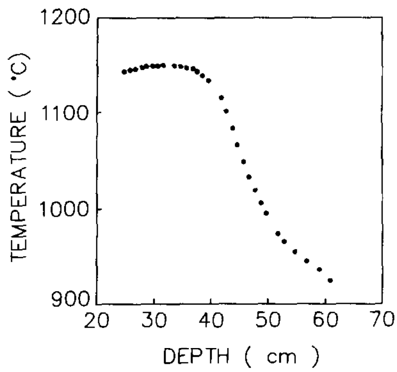

FIG. 1. Typical temperature profile in the two-zone Bridgman furnace.

composition of starting material and of grown crystal are consistent with a diagram having a maximum ΔT of approximately 15°C. In the present work, Bridgman growth of pseudo-ternary alloys of the $Cd_xZn_yMn_zTe$ was carried out and the composition of the first part of the grown material gives further information on the general phase diagram.

Samples of the required compositions were weighed out from the elements and contained in a carbon crucible which was then sealed under vacuum in quartz tubing. This arrangement prevented interaction of the charge with the quartz at high temperatures. The samples were melted in the high-temperature region of the growth furnace. The resulting ingots were roughly cylindrical but tapered to a point at the lower end to initiate single-crystal growth. Each ingot was approximately 2 cm in total length with a maximum diameter of 6 mm. The furnace initially used for the growth was a two-zone furnace used previously for horizontal Bridgman production of polycrystalline III–V alloys (*4*). This consisted of two zones with a water-cooled copper disk between them to help obtain a steep temperature gradient. The choice of temperature to be used in each case was guided by the $Cd_{1-z}Mn_zTe$ values (*1*). The sample ingot was lowered through the temperature gradient at a rate of 5 mm/hr. The ingots grown in this way appeared to be polycrystalline

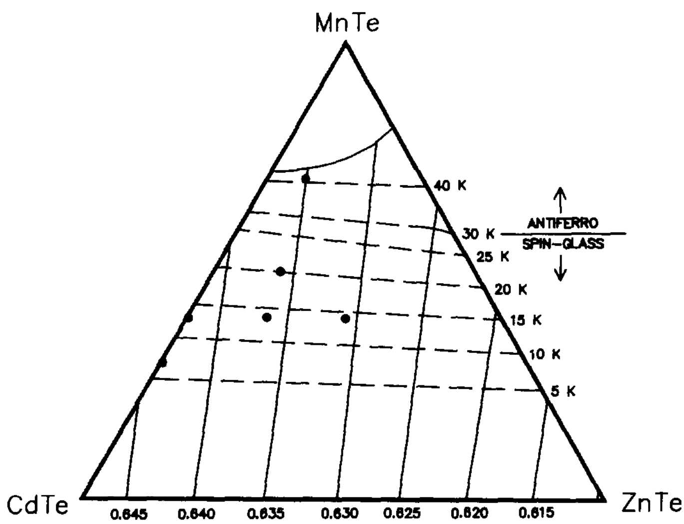

FIG. 2. Phase diagram for the $Cd_xZn_yMn_zTe$ pseudo-ternary alloys, showing lines of constant lattice parameter (continuous lines) and constant T_g (dashed lines) and nominal composition of ingots investigated in detail (circles).

TABLE I

VALUES OF LATTICE PARAMETER a AND MAGNETIC TRANSITION TEMPERATURE T_g FOR STARTING INGOT AND FIRST SOLID TO FREEZE

Nominal composition			Starting ingot		First to freeze	
x	y	z	a (nm) ± 0.0003	T_g (K)	a (nm) ± 0.0003	T_g (K)
0.225	0.075	0.7	0.6349	39 ± 1	0.6341	40 ± 2
0.7	0	0.3	0.6438	7.1 ± 0.5	0.6341	9 ± 0.5
0.6	0	0.4	0.6422	12 ± 0.5	0.6422	13 ± 1
0.3	0.3	0.4	0.6306	13.2 ± 0.5	0.6306	13.7 ± 0.5
0.45	0.15	0.4	0.6365	14.7 ± 1.0	0.6368	16.0 ± 0.5
0.375	0.125	0.5	0.6359	20.7 ± 1.0	0.6357	20.7 ± 0.5

but with single-crystal grains of up to 3 × 3 × 1-mm^3 dimensions. This was confirmed by Laue X-ray photographs.

To improve growth conditions, a new furnace was constructed and care was taken to obtain good temperature stability, steep temperature gradient, etc. The copper disk was replaced with a thin platinum sheet placed between the zones to act as a heat reflector. To further control the temperature gradient at the zone junction, a small auxiliary heating coil was added to the second zone close to the platinum sheet. A typical temperature profile, as used in the growth, is shown in Fig. 1. With this system, all but one of the ingots grown were single crystal.

Small specimens cut from the first region to freeze were used for Debye–Scherrer X-ray analysis to obtain the values of the lattice parameter. These in all cases were found to be close to the value expected for the initial melt composition. However, for pseudo-ternary alloys a second parameter is required to allow the composition of the grown sample to be determined. Since the samples were being grown for magnetic measurements, the chosen second parameter was the spin glass transition temperature T_g. This was a suitable choice since the contours of constant a (*5*) and those of constant T_g (*6*) intersect at an angle approaching 90°, as shown in Fig. 2, giving a good composition estimate. In Table I, data are given for six alloys investigated in detail, with values of a and T_g for the initial melt composition and the grown crystal. It is seen that in all cases the composition of the grown sample is very close to that of the initial growth material. Two of the samples are from the $Cd_{1-z}Mn_z$ edge and indicate the deviations that may occur in the data. The other four are for general pseudo-ternary samples, three on the $x = 3y$ line with $x = 0.4$, 0.5, and 0.7, respectively, and the other on the $x = y$ line with $z = 0.4$. The data for these cases indicate that in the range of composition covered, the liquidus and solidus sheets must have a temperature separation of less than 5°C.

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