

T(z) Diagram and Optical Energy Gap Values of Cd_{1-z}Mn_zGa₂Se₄ Alloys

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The T(z) diagram of the system Cd_{1-z}Mn_zGa₂Se₄ was obtained from x-ray diffraction and differential thermal analysis measurements. It was found that at lower temperatures, a single phase solid solution occurs across the whole compositional range and values of lattice parameters were determined as a function of z. At higher temperatures, an order-disorder transition occurs, in the range 0 < z < 0.6 to a partially ordered tetragonal structure and for 0.6 < z < 1.0 to a disordered defect zinc-blende structure. In the T(z) diagram, both the ordering boundary and the solidus curve appear to show discontinuities at z = 0.6, corresponding to the change in the disordered phase. It is suggested that the symmetries of the terminal compounds are different one from the other. Optical absorption measurements were made at 300 K to show the variation of the direct optical energy gap E_g with z, and again the values appear to divide into two parts below the above z = 0.6.

Key words: Group II-III₂-VI₄ alloys, lattice parameters, optical energy gaps, phase diagram

INTRODUCTION

Semiconductor materials containing manganese have received considerable attention recently, because of the manner in which the magnetic behavior associated with the manganese can modify and complement the semiconductor properties.^{1,2} It has been found that adamantine compounds with tetrahedral coordination can accept a large amount of manganese in cation substitutional solid solutions. Well-known examples of such materials are the semimagnetic semiconductor alloys formed from the II-VI compounds; e.g. Cd_{1-z}Mn_zTe, etc.¹ In alloys of this type, single phase solid solution is obtained with ranges of z up to 0.85. Similar alloys can be obtained by introducing manganese into the equivalent ternary

compounds, the tetrahedrally coordinated I-III-VI₂ chalcopyrites; e.g. (CuIn)_{1-z}MnTe, etc. for which ranges of single phase solid solution up to z = 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 hence can show two different sets of magnetic and band-gap behavior in the alloy.^{3,4} Another group of compounds that show the tetrahedrally bonded form (or adamantine structure) are some of the II-III₂-VI₄ compounds; e.g. CdGa₂Se₄, CdIn₂Te₄, etc. Very little information is available on the substitutional solid solubility of manganese in these compounds.

The compounds CdGa₂Se₄ and MnGa₂Se₄ both have a defect tetragonal structure. Both have been reported to have 14 symmetry with the lattice vacancies, the gallium atoms, and the cadmium or manganese atoms ordered on the cation sublattice.^{5,6} In the present work, the T(z) diagram, lattice param-

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eter and optical energy gap values for the $\text{Cd}_{1-z}\text{Mn}_z\text{Ga}_2\text{Se}_4$ system have been determined from differential thermal analysis, powder x-ray diffraction photographs, and optical absorption measurements.

SAMPLE PREPARATION AND MEASUREMENTS

Alloys samples of $\text{Cd}_{1-z}\text{Mn}_z\text{Ga}_2\text{Se}_4$ with various values of z were prepared by the standard melt and annealing technique.⁷ The components of each 1.0 g sample were sealed under vacuum in a quartz capsule, melted together at 1150°C and then annealed to equilibrium at 500°C, this temperature being chosen from a consideration of the known transition temperature for CdGa_2Se_4 .⁵ Guinier x-ray photographs were used to check the condition of each sample, and it was found that annealing times of one month gave good equilibrium conditions for each sample.

Transition temperatures were determined from differential thermal analysis (DTA) measurements with silver or gold used as reference materials. The charge was of powdered alloy of typical weight 50–100 mg. The temperature of the sample and that of the reference were determined with chromel-alumel ther-

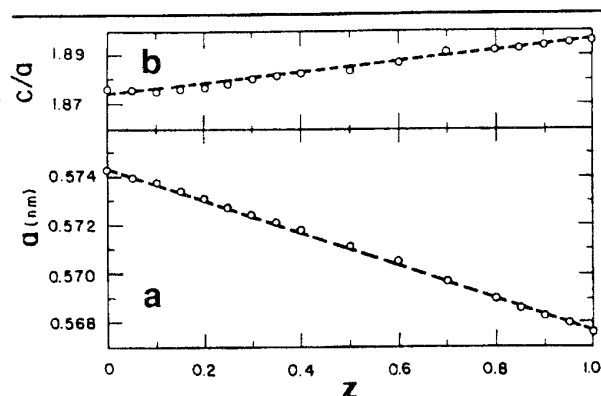


Fig. 1. Variation of (a) lattice parameter a and (b) parameter ratio c/a with z for $\text{Cd}_{1-z}\text{Mn}_z\text{Ga}_2\text{Se}_4$ alloys. (○) experimental values; — lines fitted to linear equations.

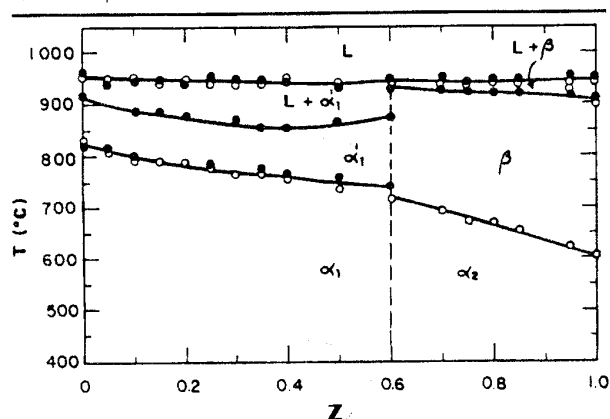


Fig. 2. $T(z)$ diagram for $\text{Cd}_{1-z}\text{Mn}_z\text{Ga}_2\text{Se}_4$ alloys. (○) DTA heating run; (●) DTA cooling run; α_1 , ordered tetragonal structure $\overline{14}$; α_2 , ordered tetragonal structure $\overline{14}2m$; α_1' , partially disordered tetragonal structure; β , disordered defect zinc-blende structure.

mocouples, the difference signal between sample and reference and the temperature signal being simultaneously continuously recorded. For each peak in the difference signal, a phase transition temperature was determined from the baseline intercept of the tangent to the leading edge of peak.⁸ Both heating and cooling runs were made, the average rates of heating and cooling being approximately 15 K/min.

Slices of each sample were cut and thinned down to give specimens for optical absorption measurements by the usual method.⁹ Values of $\ln(I_0/I)$ were determined as a function of photon energy $h\nu$ and corrected by subtracting a background value to give the absorption coefficient α . The relation $(\alpha h\nu)^n = C(h\nu - E_g)$, where $n = 2$ and $1/2$ for a direct or indirect optical transitions, respectively, was then used to obtain a value for the optical energy gap E_g .

X-RAY RESULTS AND ANALYSIS

In all cases, the x-ray photographs showed single samples with tetragonal structure and lattice parameter ratio $c/a < 2$, in agreement with earlier results obtained for the compounds.^{5,6} The ordering lines observed were consistent with the previously reported space group of 14 for both compounds. However, it is to be noted that the space group $\overline{14}2m$ would give the same ordering lines. Values of lattice parameters were determined in all cases; and in Figs. 1a and b, the resulting variations of a and c/a with z are shown. The probable error in the lattice parameter values is estimated to be ± 0.0003 nm, which is the value shown by the circles.

It is seen from these figures that the values of a decrease while those of c/a increase slightly as z is increased; i.e. as cadmium is replaced by manganese. As indicated by the dash lines in Fig. 1, the variation of these parameters with z appears to show a linear behavior over the whole composition range, within the estimated limits of experimental error. However, this is discussed in more detail below.

For interpolation purposes, the variation of each of these parameters with z was fitted to a linear equation in z , giving

$$a = 0.5744 - 0.0067z \text{ (nm)}$$

$$c/a = 1.874 + 0.022z$$

with standard deviations of the fitted points of 0.0008 nm and 0.0009 for a and c/a , respectively.

DTA RESULTS AND ANALYSIS

Differential thermal analysis measurements were made on each sample as indicated above and the resulting $T(z)$ diagram is shown in Fig. 2. From this figure, the estimated average accuracy in the points shown is $\pm 15^\circ\text{C}$. It is observed that for $z = 0$ (i.e. CdGa_2Se_4) phase transitions occur at 825, 920, and 955°C. These values are in agreement with those reported earlier by Loireau-Lozac'h et al.⁵ for the CdGa_2Se_4 point in the Ga_2Se_3 -CdSe diagram. They proposed that the observed transitions were, in order

of increasing temperature, as follows: (i) at 830°C from a thiogallate structure α to a partially disordered tetragonal structure α' in which the lattice vacancies remain ordered but the cadmium and gallium atoms are disordered on the occupied cation sites, (ii) at 940°C from α' to a two phase liquid-plus-solid field (labeled in the present work $L + \alpha'$), and (iii) at 965°C from $L + \alpha'$ to L . For $z = 1.0$; i.e. MnGa_2Se_4 , the phase transitions occur at 605 , 910 , and 950°C . In this case, no information on the Ga_2Se_3 - MnSe T(z) phase diagram is at present available in the literature. However, work on this diagram by the present authors (to be published) shows that these transitions can be attributed to α to β , β to $(L + \beta)$ and $(L + \beta)$ to L , respectively, where α is an ordered tetragonal structure and β a defect zinc-blende structure with lattice vacancies, manganese and gallium atoms at random on the cation sublattice.

With regard to the alloys, it is seen from Fig. 2 that the ordered tetragonal α field appears to extend across the complete composition range and is bounded by an order-disorder transition for which the temperature varies almost linearly with z . However, this also is discussed in more detail below. Above this temperature, there is the partially disordered tetragonal structure α' at low z values and the disordered defect zinc-blende β structure at high z values. The composition at which the transition from α' to β occurs is determined from the behavior of the upper boundary of this region, i.e. the $\alpha' \rightarrow L + \alpha'$ and $\beta \rightarrow L + \beta$ transitions. As is seen from Fig. 2, there is a discontinuity in this boundary at approximately $z = 0.6$ and indeed the $z = 0.6$ sample shows DTA points corresponding to both transitions, indicating that in this region this sample is essentially two phase $\alpha' + \beta$. Further information is given by the shapes of the DTA peaks for the $z = 0.5, 0.6$, and 0.7 samples shown in Fig. 3. It is seen that while the $L + \beta \rightarrow \beta$ peaks have large amplitude and are relatively narrow in temperature the $L + \alpha' \rightarrow \alpha'$ peaks have a much smaller amplitude and extend over a larger temperature range, indicating that the two are different transitions. Since further detailed study was not carried out in this range, in Fig. 2, a single dashed line is drawn at $z = 0.6$ to indicate the approximate position of the boundary between the α' and β fields.

In light of the above results, further consideration of the ordering line seems to be needed, and it appears that there could be a similar discontinuity at $z = 0.6$ in this line, as is shown by the full line in Fig. 2. However, in this case the difference is comparable with the experimental error in the DTA points and so this proposed discontinuity is not clearly defined. However, it should be noted that for $z < 0.6$, peaks corresponding to the $\alpha_1 \rightarrow \beta'$ transition can be observed on both the heating and cooling runs, while for $z > 0.6$ the corresponding $\alpha \rightarrow \beta$ peak is observed only in the heating runs, indicating a different transition in the two cases.

A very similar behavior to that described above, is shown by the $\text{Cd}_{1-z}\text{Mn}_z\text{In}_2\text{Te}_4$ alloys,¹⁰ where similar

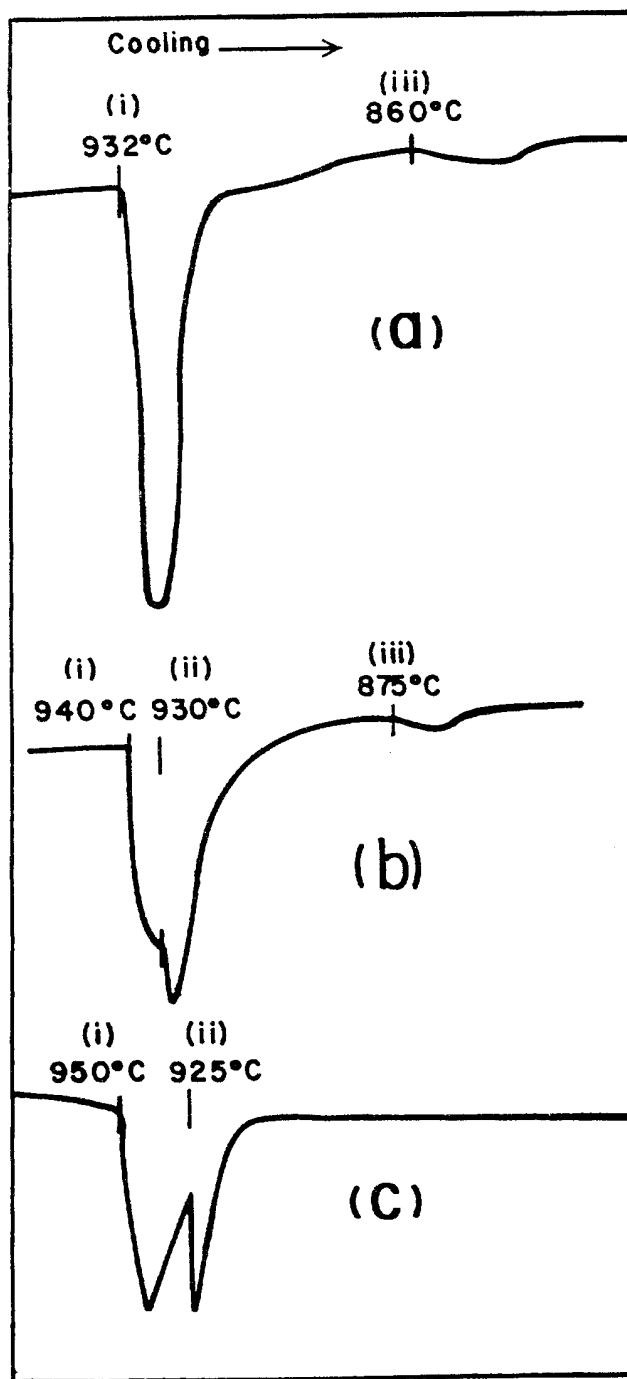


Fig. 3. Cooling DTA line shapes for (a) $z = 0.5$, (b) $z = 0.6$ and (c) $z = 0.7$: (i) $L \rightarrow L + \beta$ and/or $L \rightarrow L + \alpha'$; (ii) $L + \beta \rightarrow \beta$; (iii) $L + \alpha' \rightarrow \alpha'$.

discontinuities at $z = 0.5$ are attributed to a change in symmetry of the order tetragonal phase from 14 (α_1) of CdIn_2Te_4 to 142 (α_2) of MnIn_2Te_4 . On the basis of these previous results plus the present experimental data, it is proposed that the symmetry of InGa_2Se_4 is in fact 142 m and not 14 as previously reported. The difficulty in distinguishing between these two symmetry groups is illustrated by various disagreements in the literature (e.g. Refs. 11, 12). Thus, in Fig. 2, the ordered tetragonal field is divided, and is labelled α_1 for $0 < z < 0.6$ and α_2 for $0.6 < z < 1$. (For consistency,

the previous α' is labelled α_1' .) With regard to the variation of a and c/a with z shown in Fig. 1, it is seen that there could be a small discontinuity at $z = 0.6$ in both of these lines.

ENERGY GAP RESULTS AND ANALYSIS

Optical absorption measurements were made on each sample at 300 K and the relation $(\alpha hv)^n$ vs hv was plotted for both $n = 2$ and $1/2$. It was found that the case $n = 2$, the value for a direct interband transition, gave the best fit to the experimental points. The values of the direct energy gap E_0 were then determined by extrapolation of the $(\alpha hv)^2$ line to $\alpha = 0$, and the resulting variation of E_0 with z is shown in Fig. 4. The relative accuracy of the E_0 values is approximately ± 0.01 eV.

Previous room temperature optical absorption measurements on CdGa_2Se_4 ¹³⁻¹⁷ gave values of the direct energy gap E_0 in the range 1.9 to 2.32 eV. Bacewicz et al.¹⁸ suggested that this variation is due to the sensitivity of the absorption edge to crystal purity and surface treatment. This latter group made measurements of both optical absorption and thermorefectance on single crystals of CdGa_2Se_4 . Their optical absorption data gave a value of energy gap comparable with those quoted above, but the thermal modulation value at room temperature was 2.57 eV. The present value of $E_0 = 2.20$ eV for $z = 0$; i.e. CdGa_2Se_4 , is thus in good agreement with the previous value obtained by absorption measurements. The value of E_0 at $z = 1$, (i.e. MnGa_2Se_4) is 2.33 eV, but in this case, there are no previous values quoted in the literature.

With regard to the variation of E_0 with z , for a wide range of alloys it has been shown that E_0 varies in a parabolic form with z ¹⁹ (i.e. $E_0 = A + Bz + Cz^2$). However, in applying this form here, it is necessary to keep in mind the symmetry change occurring at $z = 0.6$. Thus, for the present data, the values for $0 < z < 0.6$ have been fitted separately from the values for $0.6 < z < 1$. In the $z < 0.6$ range, the E_0 data are reasonably well fitted by the relation $E_0 = 2.218 + 1.399z - 1.645z^2$ and the fitted curve in this range is shown by the full line in Fig. 4. For the $z > 0.6$ range, because of fewer points and the experimental scatter, the fit is more approximate, but a reasonable form is given by $E_0 = 1.46 + 2.96z - 2.08z^2$ and this is shown by the dashed line in Fig. 4. Thus, in both cases, the bowing param-

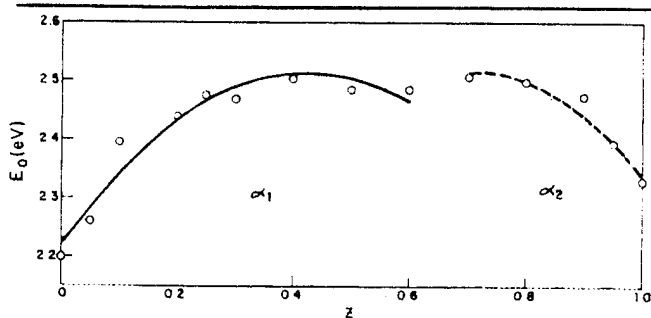


Fig. 4. Variation of optical absorption band gap E_0 with z for the $\text{Cd}_{1-z}\text{Mn}_z\text{Ga}_2\text{Se}_4$ alloys; \circ experimental values; — parabolic fit to α_1 samples; - - - parabolic fit to α_2 samples.

eter C has a negative value. In the majority of alloy systems investigated previously, C has a positive value, but cases with C negative appear to be possible (e.g. Refs. 19, 20).

CONCLUSIONS

In the $T(z)$ diagram determined here, it is found that in the lower temperature range an ordered tetragonal α phase appears to extend across the complete solid solution range and to show a linear variation for both a and c/a values with z . At higher temperatures, there is an order-disorder transition, the temperature of which varies almost linearly with composition, but appears to show a small discontinuity at $z = 0.6$. Because of the form of the various phase boundaries, it is proposed that the α field actually consists of two parts, labelled α_1 for $0 < z < 0.6$ and α_2 for $0.6 < z < 1$. For the α_1 range, the order-disorder transition is to a partially ordered tetragonal structure α_1' while for the α_2 range, it is to a disordered zincblende structure β . The value of the composition at which the boundary between these α_1' and β fields occurs is given by the higher temperature transitions $L + \alpha_1' \rightarrow \alpha_1'$ and $L + \beta \rightarrow \beta$, where a discontinuity in the temperature values and DTA peak shapes indicate that the boundary is close to $z = 0.6$, at which composition there may be a narrow two-phase ($\alpha_1' + \beta$) field. The observed discontinuities at $z = 0.6$ are attributed to a change from 14 symmetry for α_1 to $142m$ symmetry for α_2 .

With regard to the room temperature E_0 values, the present value of 2.20 eV for CdGa_2Se_4 is in good agreement with previous absorption measurements¹³⁻¹⁷ but is considerably lower than the thermorefectance value for CdGa_2Se_4 .¹⁶ The values of E_0 in the two ranges, α_1 and α_2 , have been fitted to a parabolic form and in each range a negative bowing parameter C was obtained.

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