Phase Equilibria in PbTe/CdTe Alloys

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The Pb/Cd/Te phase diagram in the range $Pb_{1-x}Cd_xTe_{1+y}$ where $0 \leqslant x \leqslant 0.15$ and $y \leqslant \pm 0.05$ was examined by differential thermal analysis. The congruent melting point for PbTe was found to be unique. Annealing of alloys in Te-rich and deficient atmospheres showed that the phase width of the system increased and moved more towards the n-side with increasing cadmium content. The energy of formation of a divacancy for a 3 mole % CdTe alloy was found to be 0.16 eV less than that in PbTe.

1. Introduction

The frequent treatment of a ternary system as pseudobinary is quite satisfactory where gross features such as the formation of new phases or compounds are of interest, but fails where detailed knowledge is required. The need for a full treatment becomes especially apparent in a semiconductor ternary system with lattice vacancies of donor or acceptor type. Thus a small deviation from the pseudobinary plane may have a very large effect on the electrical properties of the material: the alloys of PbTe/CdTe are such a system.

Rosenberg *et al* [1] have investigated the lattice constants, solubility limits, and electronic states of PbTe/CdTe alloys; Nikolic [2] has determined the variation of optical energy gap with composition. However, these investigations have been performed without regard to the nonstoichiometry of the system, i.e. the system has been treated as a pseudobinary alloy. Both PbTe [3] and CdTe [4] have phase widths ($\leqslant \pm 0.1$ mole %) and it would be expected that their alloys should also have an extended range of composition. The extent of this range is considered in the present paper.

In order to grow large crystals of good quality from the melt it is desirable to avoid constitutional supercooling by having the melt and the solid of the same composition. This requires the existence of a congruent melting point, which exists for the PbTe system at a composition $Pb_1Te_{1.00004}$ [5]. In order to see if this congruent melting point extended into the three-component system, a differential thermal analysis (DTA)

was performed for the composition range $Pb_{1-x}Cd_xTe_{1+y}$ where $0 \leqslant x \leqslant 0.15$, $-0.05 \leqslant y \leqslant +0.05$.

2. Experimental

Ingots of alloys of compositions $Pb_{1-x}Cd_xTe_1$ where $0 \leqslant x \leqslant 0.15$ were made by the Bridgman method. The higher Cd concentration ingots contained inter- and intra-granular second phase and Widmanstätten precipitates, fig. 1. The precipitated CdTe, near a grain-boundary, diffused to it to produce a filled grain-boundary surrounded by a region clear of precipitates. The electrical resistance of some of the larger areas of second phase was determined, *in situ*, by probing the surface of a polished specimen. It was found to be extremely high, similar to that of the primary phase of a $Pb_{0.15}Cd_{0.85}Te$ alloy and a pure CdTe sample. X-ray diffraction of the two-phase material indicated the presence of PbTe/CdTe alloy solid solution and CdTe only. These results suggested that for $Pb_{1-x}Cd_xTe$ alloys for $x \leqslant 0.15$ the second phase, either as precipitates or as agglomerates is CdTe. The Seebeck coefficient varied along the length of the ingots indicating that Cd segregation had occurred. This was confirmed by chemical analysis, fig. 2.

In order to have material suitable for determining the phase-width of the alloys, single-crystal bars were cut from the as-grown ingots. These bars were small enough ($2 \times 2 \times 10$ mm) to contain negligible Cd concentration variations and minimal second phase. The bars were annealed at 800° C in evacuated quartz tubes in
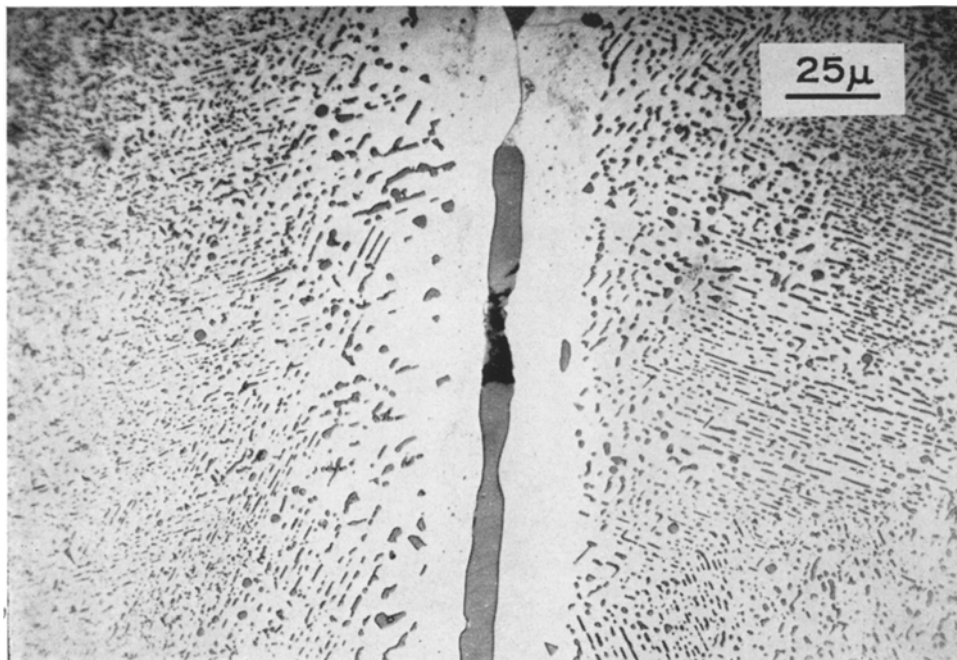
Figure 1 Grain-boundary and Widmanstätten precipitates in 85 mole % PbTe/15 mole % CdTe alloy.
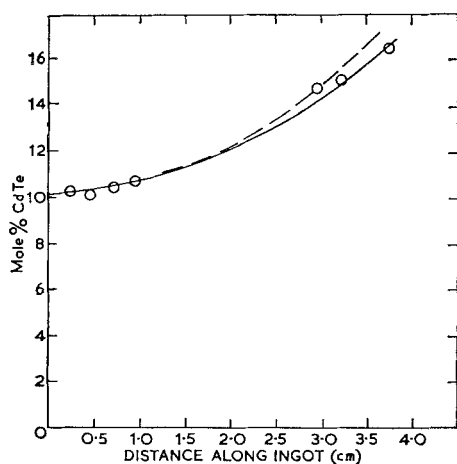

Figure 2 Variation of Cd content along the length of an ingot, showing segregation towards the last end to freeze. Dotted line = theoretical curve for normal freezing.

a Te- or Pb-rich atmosphere: the atmospheres were provided by melts of composition 40 at. % Pb/60 at. % Te or 70 at. % Pb/30 at. % Te [3]. The specimens were finally quenched in water.

The Seebeck coefficients of the specimens were determined at room temperature. One of these annealed specimens was then resealed in an evacuated quartz tube with little free space and annealed at 600° C. It was then quenched and

the Seebeck coefficient was remeasured. This was repeated for other 800° C annealed specimens at 400° C and 250° C. The specimens were chemically analysed for Cd and Pb after each annealing process. The carrier concentrations corresponding to the Seebeck coefficients were determined by comparison with the Hall data on larger samples [6] of single-phase material prepared in a similar way. Hall data could not be obtained on the quenched samples directly since they cracked on quenching and were too small. The number of carriers as a function of quench temperature and cadmium content is shown in fig. 3, where the solid line shows the extent of the single-phase material. The samples were also examined metallographically to check for the presence of a second phase.

The DTA of the system $Pb_{1-x}Cd_xTe_{1+y}$ where $0 \leqslant x \leqslant 0.15$ and $-0.05 \leqslant y \leqslant 0.05$ was determined by comparison of the temperature of a sample, enclosed in an evacuated, re-entrant sealed quartz tube, and an Al_2O_3 reference sample. Both the reference and measuring samples were placed in a large Ni block whose temperature was raised or lowered $\sim 1.6°$ C/min. Using samples weighing ~ 1 to 2 g, large deflections could be obtained from Pt/RhPt thermocouples on a 250 μV recorder.
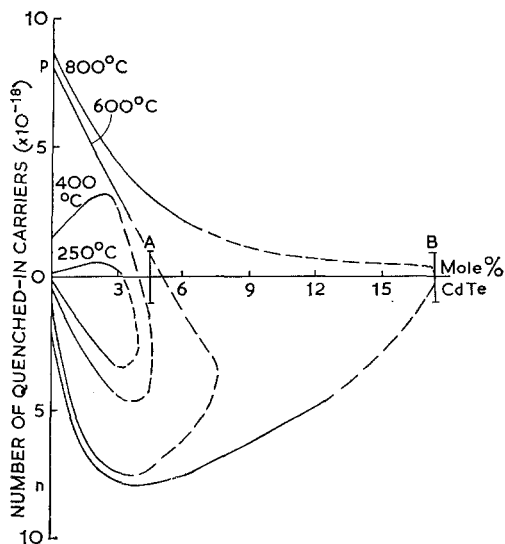
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Figure 3 The maximum range of carriers for specimens annealed at various temperatures. The dotted line is extrapolated and the vertical lines A and B are the solubility limits reported in [1].

By this method the freezing point of an alloy composition was found. The resultant solid was then remelted and the first deviation from the base line (FDBL) of the recorder, which indicates the onset of melting, was determined. This is shown in fig. 4.
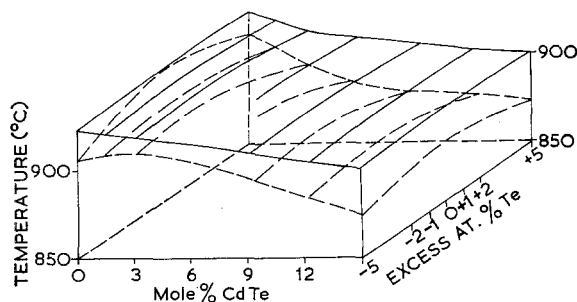

Figure 4 Part of the Pb/Cd/Te phase diagram. The solid lines are the range of freezing points and the dotted lines are the range of first deviation from the base line.

3. Discussion
3.1. DTA

The pseudobinary phase diagram of the PbTe/CdTe system has been previously determined [1], although no information is given on how accurately the cation-anion ratio was controlled. Such a diagram is only a cross-section of the three-component system and, as can be seen from fig. 4, is not very indicative of the system

as a whole. From the pseudobinary diagram, fig. 5, it is seen that the data obtained here agrees well with that of Rosenberg. It is interesting to note that although no attempt was made here to obtain a uniform solid, the solidus curve is very similar to that of Rosenberg et al [1]. This solidus curve cannot represent an equilibrium, since if it did one would expect to produce 4 mole % CdTe alloy solid from 15 mole % alloy melt. This has never been obtained,
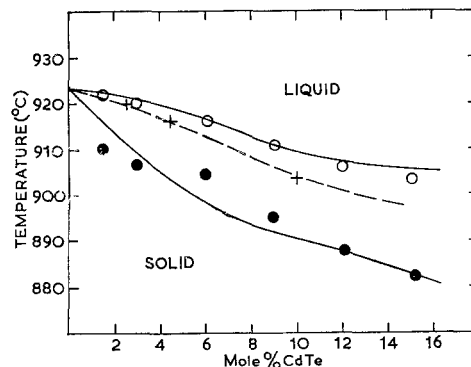

Figure 5 The pseudobinary cross-section of part of the Pb/Cd/Te phase diagram. Freezing point determinations 0, first deviation from base line ●, concentration of CdTe in first end to freeze of ingots +, solid lines from [1], dotted line suggested "true" solidus curve.

the lowest concentration solid formed from a 15 mole % alloy melt contains approximately 10 mole % CdTe. From a pseudobinary phase diagram one can measure the ratio $[CdTe_{liquid}]/[CdTe_{solid}]$ for a particular temperature. For an ideal solution the following equation should be obeyed [7]

$$\ln ([CdTe_{liquid}]/[CdTe_{solid}]) = \frac{(\Delta H_M)_{PbTe}}{R} \left[\frac{1}{T_M} - \frac{1}{T} \right]$$

where $(\Delta H_M)_{PbTe}$ is the heat of fusion of pure PbTe and T_M its melting point (923.9° C [5]). Using this equation and the data from fig. 5 for 910° C: $[CdTe_{liquid}] = 9.8$ mole %, $[CdTe_{solid}] = 2.9$ mole %, one obtains $\Delta H_M = 249$ kcal/ mole. This impossibly high figure confirms that the solidus line in fig. 5 is not the equilibrium line. Assuming Raoult's law is obeyed for the depression of the freezing point of PbTe [8]

$$-\Delta T = R T_M^2 [CdTe_{liquid}]/(\Delta H_M)_{PbTe}$$

where ΔT is the depression of the freezing point, one obtains, from the liquidus curve in fig. 5

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for 910° C, using the above data $\Delta H_M = 6$ kcal/ mole, which is of the right order of magnitude (cf $(\Delta H_M)_{PbS} \simeq 8$ kcal/mole [9]). The first end to freeze of crystals grown from 3, 6 and 15 mole % CdTe melts were chemically analysed and found to contain 2.7, 4.5, and 10 mole % CdTe respectively. These values give an indication of the concentrations of CdTe in solid and liquid phases in equilibrium and have been included in fig. 5. A suggested "true" solidus line is indicated.

The congruent melting point found for PbTe can be seen from fig. 4 to be unique and does not extend throughout the alloy system. This is apparent from the fact that at a congruent melting point all the solid should have the same composition as the melt. At least this is the ideal situation which requires rapid diffusion in the melt. In practice the majority of the solid will have a composition very near that of the melt. Hence on melting the solid the first deviation from the base line (FDBL), which corresponds to the melting of a considerable percentage of the solid, will be at the same temperature as the freezing point. However, where there is a difference in composition between the liquid and solid phases in equilibrium at a particular temperature, there will be, for a particular sample on freezing, a rapid enrichment of one component in the last end to freeze. On melting, the FDBL will correspond to the melting point of this last end to freeze, if it is in a large enough quantity, and will be below the freezing point of the sample. Hence, for a particular sample, the larger the separation between the FDBL and the freezing point, the larger will be the separation between the solidus and liquidus boundaries for the mean composition of the sample. As can be seen from fig. 4, the separation between the FDBL and the freezing point is only zero for PbTe and increases with increasing Cd content; i.e. only for PbTe is there a congruent melting point.

This lack of congruent melting point means that, irrespective of the alloy composition, a melt will always freeze to produce a solid poorer in Cd, e.g. a melt of $Pb_{0.85}Cd_{0.15}Te_1$ was found to be in equilibrium with the solid $Pb_{0.90}Cd_{0.10}Te_1$ (see above), and considerable segregation occurs along the length of the ingot, fig. 2. This means that constitutional supercooling will occur easily unless great care is taken to produce large thermal gradients.

The broken line in fig. 2 is a theoretical curve

[10] for the segregation of a component from a melt solidifying by normal freezing

$$C = C_0 k (1 - g)^{k-1}$$

where C is the concentration in the solid at the point where a fraction g of the original liquid has frozen, C_0 is the mean concentration, and k is the segregation coefficient (C_{solid}/C_{liquid}) which is taken to be 0.67 in this case (i.e. 10/15, the experimentally determined value). It is seen that quite good agreement is obtained. The distance along the ingot is not a linear function of the fraction solidified, because the ingot had a non-uniform diameter.

One very noticeable feature of the system (fig. 4) is that the liquidus for the higher Cd alloys becomes almost isothermal with varying Te content. The maximum in the FDBL moves towards the Te-deficient side of the stoichiometric line with increasing Cd content. This is reflected in the phase width where, as shown below, the n-side is larger for Cd alloys than for pure PbTe.

3.2. Phase Width

In determining the phase width with respect to Te, the retrograde solubility of Cd played a predominant part, since the phase width could only be determined for the higher alloys at high temperatures. On annealing at lower temperatures Widmanstätten precipitates were formed by the CdTe coming out of solution, in agreement with the retrograde solubility reported by Rosenberg et al [1].

The electrical properties of the 15 mole % CdTe alloys, annealed at 250° C, were very similar to those of the 3 mole % alloys, suggesting that the maximum solubility was 3 mole % and that the second phase contributed negligibly to the conduction process, i.e. had a high resistance. This was proved by making an ingot of composition $Pb_{0.15}Cd_{0.85}Te_1$ whose primary phase was found to be insulating and whose secondary phase was found to conduct and have a Seebeck coefficient similar to the 3 mole % alloy.

The tellurium-rich side of the phase diagram had less Widmanstätten precipitates than the metal-rich side. This suggests that the solubility limit, which is a line in the pseudobinary diagram and only a section of a three-dimensional surface, may extend to higher cadmium concentrations for higher tellurium concentrations.

The maximum range of carrier concentrations

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for single-phase material is shown in fig. 3 where it can be seen that adding CdTe (i) increases the phase width and (ii) enlarges the n-side and reduces the p-side of the stoichiometric line. It was probably this ease of producing n-type material that made Nikolic [2] think that alloys containing more than 2 mole % CdTe were all n-type, whereas it can be n- or p-type depending on the Te content.

The properties of 3 mole % CdTe ingots grown from Te or metal-rich melts ($Pb_{0.97}Cd_{0.03}Te_{1+y}$ where $y = \pm 0.01$) were very similar to those of the vapour-annealed specimens. The Seebeck coefficients of the ingot material, annealed at different temperatures, were the same as those of the vapour-annealed specimens for the same temperature. This suggests that equilibrium occurs between excess Te in the solid and Te precipitated in dislocations, as is the case for PbTe [3].

It is not known if these hole concentrations for p-type alloys are due to lead or cadmium vacancies. This increase in the n-side of the phase width suggested that the congruent melting point might have shifted towards the cation-rich side but, as has been shown, no congruent melting point was found although the maximum in the FDBL is on the anion side for the alloys.

Equation 6 in the appendix can be written

$$\ln\left(\frac{k_s'_{PbTe}}{k_s'_{alloy}}\right) = C - \frac{1}{kT}(E_{PbTe} - E_{alloy})$$

where k_s' is the Schottky constant, E_{PbTe} and E_{alloy} are the energy of formation of a divacancy for PbTe and alloy respectively, and C is a constant. From fig. 6, using the above equation, it is found that for 3 mole % CdTe alloys, $E_{PbTe} - E_{alloy} = 0.16$ eV, i.e. the energy of formation of a divacancy is less for the alloy than for PbTe. This is surprising, since on adding CdTe to PbTe the optical energy gap increases rapidly and this is often associated with an increase in bond strength. It would have been thought that an increase in bond strength resulted in a larger formation energy for a divacancy, However, PbTe has a lattice parameter, $a_0 = 6.459$ Å, whereas for a hypothetical crystal of CdTe in a rock salt structure a_0 has been estimated to be 6.159 Å at atmospheric pressure [1]. Hence there is considerable lattice relaxation around a Cd atom in a PbTe lattice. This relaxation energy is gained on removing a Pb atom from PbTe but would not be gained if Cd is removed from

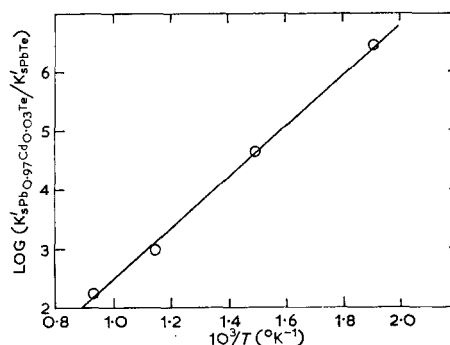PbTe. This loss of relaxation energy may be the cause of E_{alloy} being less than E_{PbTe}.

Figure 6 Variation of the ratio of Schottky constants of $Pb_{0.97}Cd_{0.03}Te_1$ and PbTe with temperature.

4. Conclusion

The DTA of the PbTe/CdTe alloy system showed that the congruent melting point found for the PbTe system does not extend into the alloy compositions. The consequent segregation causes an increase in Cd concentration to the last end to freeze. This increase was found to obey approximately the theoretical curve for normal freezing.

The phase-width of this ternary system was found to increase with increasing Cd content, and to shift to the n-side, i.e. the maximum hole concentration decreases and the maximum electron concentration increases with increasing Cd content. This increase in phase width showed that the energy of formation of a divacancy for $Pb_{0.97}Cd_{0.3}Te$ alloy was 0.16 eV less than that in PbTe.

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Appendix
Comparison of Schottky constants for PbTe and $Pb_{0.97}Cd_{0.03}Te$

The following equilibrium exists for both alloy and PbTe [11] using the notation of Kroger [12]

$$Te_D \text{ (or } \tfrac{1}{2} Te_{2gas}) \rightleftharpoons Te_{Te}^x + V_{Pb}' + h$$
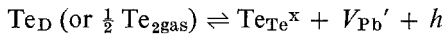
and hence

$$p[V_{Pb}'] = k[Te_D] , \qquad (1)$$

where Te_D represents Te precipitated in dislocations.

For the neutrality condition $p = [V_{Pb}']$ which exists for high $[Te_D]$ or tellurium pressures (P_{Te_2}) [12], equation 1 becomes

$$p^2 = k[Te_D] \qquad (2)$$

Equation 1 may be rewritten

$$(k_i/n) (k_s'/[V_{Te}^\cdot] = k[Te_D] \qquad (3)$$

where $k_i = np$, and the Schottky constant $k_s' = [V_{Te}^\cdot] [V_{Pb}']$.

For the neutrality condition, $n = [V_{Te}^\cdot]$,

which exists for low $[Te_D]$ or $[P_{Te_2}]$, equation 3 yields

$$n^2 = \{k_i k_s'/k\} [Te_D]^{-1} \qquad (4)$$

For constant $[Te_D]$ or P_{Te_2} at the p and n extremes of the phase width, equations 3 and 4 yield for two materials (1) and (2) $p_1^2/p_2^2 = k_1/k_2$ on the p extreme of the phase width and $(n_1^2/n_2^2) = (k_{i1}/k_{i2}) (k_s'_1/k_s'_2) (k_2/k_1)$ for the n extreme of the phase width. Hence $(k_s'_1/k_s'_2) = (n_1 p_1/n_2 p_2)^2 k_{i2}/k_{i1}$. It must be remembered that the n and p here refer to the electron and hole concentrations of two different samples of the same composition equilibrated under a Te-deficient or Te-rich atmosphere respectively.

Using effective masses for $Pb_{0.97}Cd_{0.03}Te$ [6] of $m_h^* = 0.5 \ m_0$ and $m_e^* = 0.3 \ m_0$ and $E_g = 0.4$ eV, and for PbTe $m_h^* = 0.35 \ m_0$ and $m_e^* = 0.25 \ m_0$ and $E_g = 0.3$ eV one can calculate $k_{i_{PbTe}}/k_{i_{alloy}} = 20.25$.

$$\text{Hence } \left(\frac{n_1 p_1}{n_2 p_2}\right)^2 = \frac{1}{20.25} \frac{k_s'_1}{k_s'_2} \qquad (5)$$

From fig. 3 the left hand side of equation 5 can can be determined as a function of temperature as can therefore $k_s'_1/k_s'_2$.

The Schottky constant has been shown [13] to be equal to

$$k_s' = A \exp - E/kT$$

where A is a constant involving vibration frequencies and total lattice sites, and E is the energy of formation of a vacancy pair. Hence

$$\frac{k_s'_1}{k_s'_2} = \frac{A_1}{A_2} \exp [-(E_1 - E_2)/kT] \qquad (6)$$

Thus knowing $k_s'_1/k_s'_2$ as a function of temperature, $E_1 - E_2$ can be determined.