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A comparison of phase equilibria in some II-IV-VI compounds based on PbTe

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The solubilities of the group II elements Cd, Zn, Hg, Ca and Mg in PbTe are compared over the temperature range 250 to 800°C. Cd, Zn and Mg have retrograde solubilities whilst Hg and Ca are virtually insoluble in "as-grown" material. A consequence of these solubilities is a change in the properties of the alloys compared with PbTe. Thus the phase widths of the Cd/PbTe, Mg/PbTe and Zn/PbTe systems differ from that of PbTe. With the exception of the Zn/PbTe system, (where there is reasonable evidence to support the solubility of Zn in PbTe) there is a significant change in all measured electrical properties compared with PbTe.

1. Introduction

In general, binary compounds may contain a variety of imperfections which may or may not affect the measured physical properties. The main expected defects for a compound AB are, (i) phonons, (ii) electrons, e′, (iii) holes, h•, (iv) excitons, (v) vacancies, i.e. vacant lattice sites $V_A^\times$ or $V_B^\times$, (vi) interstitials, i.e. atoms occupying sites other than lattice sites, $A_i^\times$ or $B_i^\times$, (vii) foreign atoms, either interstial, M_i, or substitutional M_A or M_B, (viii) dislocations, (ix) grain boundaries and (x) external surfaces. For undoped bulk single crystal lead chalcogenides (ii), (iii), (v) and (vi) are the important defects which control electrical properties. Atomic defects may exist singly or in association and may be either charged or neutral with respect to the crystal lattice.

All binary compounds exhibit finite existence ranges, i.e. there is a range of compositions near $[A]/[B] = 1$ (where the square brackets indicate concentrations) for which a single phase material is obtained. In general, one finds that insulators and semiconductors have narrow existence ranges and metallic compounds wide ones [2].

The existence range is an important property of the lead chalcogenides because of its width and because it straddles the stoichiometric composition. By controlling the temperature and partial pressure of lead or chalcogen, varying degrees of non-stoichiometry may be achieved within the existence range. It is possible to relate such deviations from stoichiometry to lattice imperfections, such as vacancies or interstitials, which are assumed to have zero or very small ionization energy [3] and produce one charge carrier per defect [1]. Hence, either *n*-type or *p*-type conductivity may be obtained by changing the composition from lead rich to chalcogen rich respectively.

There is some evidence from diffusion data that the ionized Frenkel defect is predominant in lead rich material [4-8]. However, we have assumed Schottky disorder in the analysis presented here (Section 3).

Studies of the phase widths of PbTe [9-13] PbSe [13-16] and PbS [17] have been reported in some detail. However, more recently the properties of ternary alloys based on one or other of the lead chalcogenides have received increasing attention. Thus alloys of PbTe with CdTe [18], InTe [19], SnTe [16] and MgTe [20] have been studied. It was discovered that the phase widths of PbTe and PbSe can be modified by the addition of some group II elements [18, 20, 21] and that the solubility limit differs for each element. This paper compares the changes in phase widths, solubilities and some electrical parameters as a function of alloying PbTe with the group II elements, cadmium, zinc, mercury,

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calcium and magnesium. In order to make a comparison of measured properties it is assumed that the imperfections in the ternary system are identical to those in the host crystal and that the group II element substitutes for lead.

2. Preparation of materials and measurement techniques

Single crystals were grown by the Bridgman method from the pure elements (99.999 %) except for the Pb_{1-x} Hg_x Te alloys where HgTe was used instead of liquid mercury. The use of HgTe was found to be more controllable than the method employing liquid mercury but the resultant ingot was porous and not suitable for electrical or optical (infra-red) analysis. The ingots with more than 1 mol % ZnTe contained second phase in the form of large intergranular masses. Second phase was found in both the Pb_{1-x} Hg_x Te and Pb_{1-x} Ca_x Te systems where $x = 0.005 - 0.02$ for the former and $x = 0.01$ for the latter. No evidence of Widmanstätten precipitates or eutectic was found in any of the alloys in contrast to Pb_{1-x} Cd_x Te [18] and Pb_{1-x} Mg_x Te [20].

The systems PbTe-HgTe and PbTe-CaTe were not pursued in detail because of the difficulty in growing good PbTe-HgTe ingots and the apparent low solubility of HgTe and CaTe in PbTe (suggested by large amounts of second phase in the as-grown ingots and electrical properties identical to those of PbTe).

Following experiments to measure the phase width as a function of temperature (see [18] and [20] for experimental details) all samples were analysed for concentration of group II element using a Unicam SP90 atomic absorption spectrometer, the probable error being 5 to 10 %.

The lattice parameter of alloys containing 0.5, 1.0 and 1.5 mol % ZnTe was determined by X-ray diffractometry and the optical energy gap of a polished p-type specimen (~ 50 μm thickness) containing approximately 1.5 mol % ZnTe was measured at 300K using a Grubb Parsons M2 infra-red spectrometer. The resulting parameters were compared with the values for lead telluride and the other PbTe – group II alloy systems (see Table III).

3. Results and discussion

The variation of the phase width of Pb_{1-x} Zn_x Te with temperature and alloy content appears in Fig. 1, together with results for the $Pb_{1-x}Cd_x$ Te [18] and $Pb_{1-x}Mg_xTe$ [20] systems at 250 and 800°C. The solubilities of the alloys are seen to differ (Fig. 1 and Table I), those containing ZnTe, CdTe (and HgTe [22]) being retrograde in nature whilst the solubility of MgTe is not very dependent on temperature [20]. For an alloy containing 1 mol % ZnTe, CdTe, or MgTe, the phase widths on the n-side at 800°C increase in the order MgTe-CdTe-ZnTe. However, on the p-side they are similar but are all smaller than that of lead telluride [10, 13].

TABLE I Solubilities of some group II elements in PbTe

Temperature (°C)	Solubility (mol %)				
	MgTe*	CdTe†	ZnTe	HgTe‡	CaTe
800	6.5	18	1.5	5	~0
250	6	3	1.0	—	~0

*From [20].
†From [18].
‡From [22], solubility at 600°C.

The rate of change of phase width with temperature differs for the three alloy systems (i.e. MgTe, CdTe and ZnTe) and is shown in Figs. 2 and 3 as a plot of log (carrier concentra-

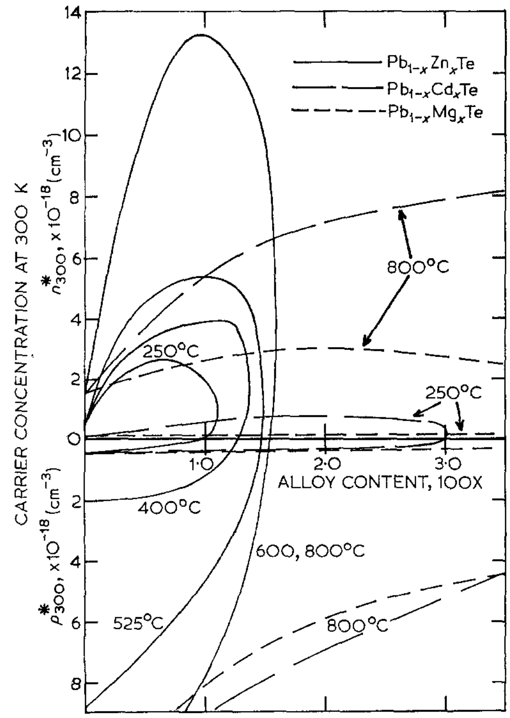

Figure 1 Isotherms of alloy content versus room temperature carrier concentration for the systems $Pb_{1-x}A_xTe$ (A ≡ Cd, Mg, Zn).

TABLE II Values of E_n, E_p and reaction enthalpies for PbTe and alloys ($500 \leqslant T \leqslant 800$K).

Enthalpy (eV)	Alloy			
	PbTe	Mg/PbTe	Zn/PbTe	Cd/PbTe
E_n	0.66*	0.29 ± 0.02†	0.20 ± 0.03	0.21 ± 0.02
E_p	0.52*	0.36 ± 0.04†	0.55 ± 0.03	0.45 ± 0.02
H_{PM}‡	1.9	1.55	1.37	1.10
H_{R}	−1.0	−1.3	−1.5	−1.5
H_{M}	—	−1.2	−1.0	−0.7
H_{Ox}§	0.53	0.2	0.6	0.4

*[10, 13].
†[20].
‡[26].
§Calculated using $H_{\mathrm{PM}} = 1.0$ eV for Te_2 gas [13].

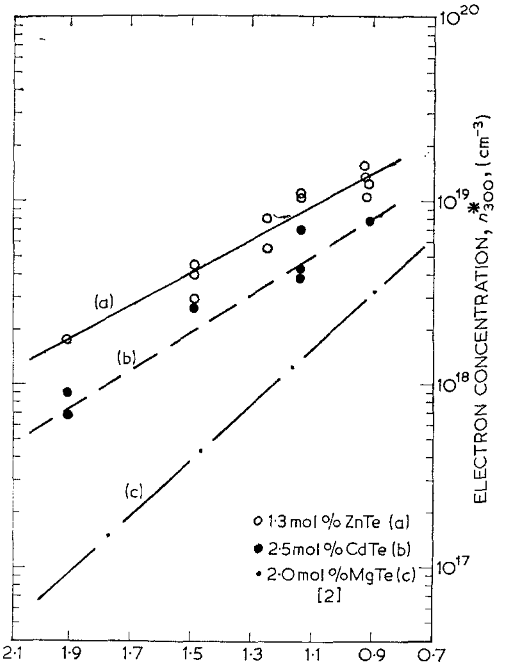

Figure 2 Room temperature electron concentration versus reciprocal temperature for the systems $Pb_{1-x}A_xTe$ (A ≡ Cd, Mg, Zn).

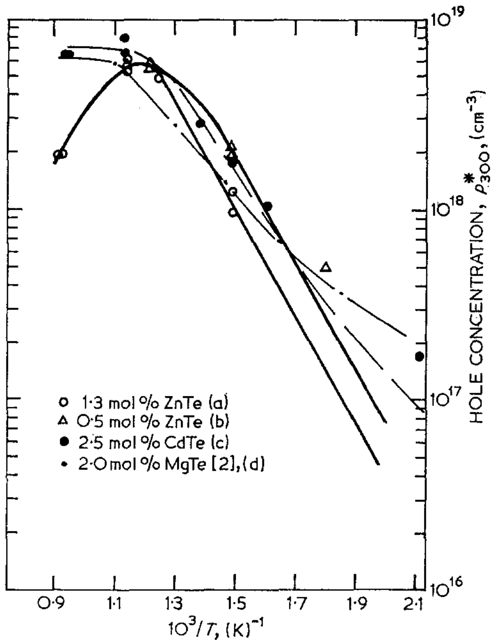

Figure 3 Room temperature hole concentration versus reciprocal temperature for the systems $Pb_{1-x}A_xTe$ (A ≡ Cd, Mg, Zn).

tion) versus reciprocal absolute temperature. The results for $Pb_{0.98}Mg_{0.02}Te$ are taken from [20] and the $Pb_{0.075}Cd_{0.025}Te$ have been redetermined here and agree with previously reported values [18].

Over the approximate temperature range 500 to 800K, activation energies (E_n for n-type and E_p for p-type material) may be calculated from the straight line portions of Figs. 2 and 3 and are compared for the different alloys in Table II. One notices a fairly large change in E_n for the alloys compared with PbTe which is difficult to explain definitively. However, a possible explanation is as follows. The soluble group II elements (Cd, Zn, Mg) do produce changes in all the properties of the host material with the exception of Zn where changes are very small. Thus the band structure (energy gap) is altered, and so is the lattice parameter and freezing point [18, 20], (see Table III), i.e. we essentially have a different semiconductor material from PbTe. The values of E_n are effectively measures of the enthalpy for defect formation in the material

TABLE III Comparison of some properties of PbTe and alloys at 300K (x = 1.3 mol%)

Property	PbTe	Zn/PbTe	Cd/PbTe	Mg/PbTe
Direct energy gap E_g (eV), (± 0.01)	0.29	0.30	0.32*	0.32*
Lattice parameter (Å, ± 0.001 Å)	6.464†	6.462	6.460†	6.458†
Hall mobility μ_e	1600‡	1400 ± 240	1400‡	1300†
cm^2 (Vsec)$^{-1}$ μ_h	850‡	800 ± 110	600‡	580†
Freezing point (°C)	924§	—	923‖	927†

*[23].
†[20].
‡[27].
§[28].
‖[18].

[1, 10, 13]. Thus one may under equilibrium conditions derive mass action equations for the probable reactions that take place between the gas phase and the solid (assuming Schottky disorder predominates) [1, 13] namely

$$\mathrm{Pb(g)} = \mathrm{Pb_{Pb}}^{\times} + \mathrm{V_{Te}}^{\bullet} + \mathrm{e}', \quad n^2 = K_{\mathrm{R}}P_{\mathrm{Pb}} \quad (1)$$

$$\mathrm{M(g)} = \mathrm{M_{Pb}}^{\times} + \mathrm{V_{Te}}^{\bullet} + \mathrm{e}', \quad n^2 = K_{\mathrm{M}}P_{\mathrm{M}} \quad (2)$$

$$\tfrac{1}{2}\mathrm{Te_2(g)} = \mathrm{Te_{Te}}^{\times} + \mathrm{V_{Pb}}' + \mathrm{h}^{\bullet}, \quad p^2 = K_{\mathrm{OX}}P_{\mathrm{Te_2}}{}^{\frac{1}{2}} \quad (3)$$

where the neutrality conditions $n = [\mathrm{V_{Te}}^{\bullet}]$ and $p = [\mathrm{V_{Pb}}']$ are assumed [13]. The notation used in the above equations is after Kröger [1], P_i denoting the partial pressure of the species i and the K's are reaction constants which are of the form, $K = K_0\exp(-H/kT)$. The assumption that Cd, Zn and Mg substitute for lead is implicit in Equation 2. Equations 1 and 2 represent two competing processes which link the electron concentration n, to the partial pressures of both lead and alloying element. Consequently, the activation energy E_n is linked to the heat of vaporization of lead and metal and to the reaction constants K_{R} and K_{M}.

Equations 1, 2 and 3 give rise to the following:

$$2E_n = H_{\mathrm{R}} + H_{P\mathrm{Pb}} \quad (1a)$$

$$2E_n = H_{\mathrm{M}} + H_{P\mathrm{M}} \quad (2a)$$

$$2E_p = H_{\mathrm{OX}} + H_{P\mathrm{Te_2}/2} \quad (3a)$$

where the heats of vaporization, $H_{P\mathrm{Pb}}$ and $H_{P\mathrm{M}}$ are the same as those over the pure elements (see Table II). Thus we may estimate values for the enthalpies H_{R}, H_{M} and H_{OX} using the experimental values of E_n and E_p. Notice that the trend in enthalpy values (Table II) follows the measured changes in E_n and E_p. We may now reverse the argument and say that as the incorporation of lead into PbTe is likely to differ from the incorporation into an alloy with slightly different properties, it is not surprising (considering Equations 1 and 2) that values of E_n for the alloys and PbTe are different. It is surprising, however, that E_n is similar for the Cd and Zn alloys because $H_{P\mathrm{M}}$ is appreciably different for these two elements.

The Seebeck coefficient of the $\mathrm{Pb}_{1-x}\mathrm{Zn}_x$ Te alloy (x = 0.013 ± 0.003) was measured as a function of electron and hole concentrations. From these results (Fig. 4) it was possible to estimate the value of the electron and hole density of states effective masses(m^*)by using the expression

$$n_{300}, p_{300} = (4/\sqrt{\pi})\,(2\pi m_0 kT/h^2)^{3/2}(m^*/m_0)^{3/2}F_{1/2}(\eta)$$

where η is the reduced Fermi energy (determined from the Seebeck coefficient), $F_{1/2}(\eta)$ is the Fermi Dirac integral and other symbols have their usual meanings. Hence the electron effective mass was found to be $m^*_e = 0.30 \pm 0.03\ m_0$ and the hole effective mass $m_{d1}^* = 0.33 \pm 0.03\ m_0$ and are equal to the values for PbTe (derived by a similar method) within experimental errors. The values of m_e^* and m_{d1}^* for the Cd [23] and Mg [20] alloys containing 1.3 mol % of the group II element are significantly different from those of PbTe.

The mobilities of n- and p-type $\mathrm{Pb}_{1-x}\mathrm{Zn}_x\mathrm{Te}$ alloys are indistinguishable from those of pure lead telluride, but for the Cd and Mg alloys there are significant changes (Table III). The large error quoted for the mobilities of the Zn alloy is partially explained by the fact that they are the mean result of samples having a variable zinc content, the average value of which is 1.3 ± 0.3 mol %. A further error which is difficult to ascertain may be owing to the method of

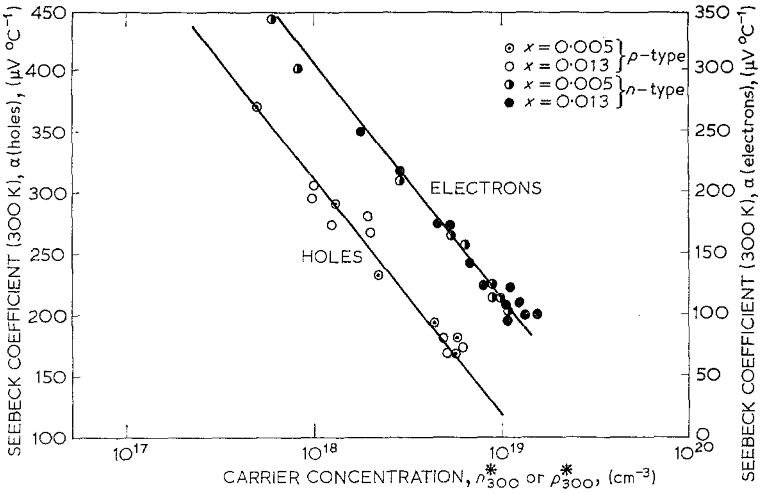

Figure 4 Plot of Seebeck coefficient versus room temperature carrier concentration for Pb$_{1-x}$Zn$_x$Te.

measurement (van der Pauw [24]) which can be less sensitive and accurate than the more conventional method. However, for the samples which were measured by both methods, good agreement was obtained.

The optical energy gap of a *p*-type specimen which had been annealed at 800° C, under tellurium rich concitions and contained ~ 1.5 mol % ZnTe was compared with that of a vapour-grown PbTe crystal polished to similar thickness (~ 50 μm). Assuming the reflectivity of both specimens to be identical (~ 45% [23]) the Pb$_{1-x}$Zn$_x$Te alloy had an energy gap equal to that of PbTe within experimental error.

There is a certain amount of evidence to confirm the solubility of ZnTe reported in Table I. Thus, (i) compositions containing up to 1.5 mol % ZnTe were found to be free of second phase as estimated metallographically, whilst those containing 3 mol % ZnTe had large lumps of second phase material, (ii) the phase width on the *n*-side is increased considerably compared with that for PbTe, (iii) it has been previously reported that ZnTe is partially soluble in PbTe [25].

Our results suggest that HgTe is not very soluble in PbTe but this may be owing to its retrograde solubility [22] and a consequence of the material produced being unsuitable for detailed annealing experiments to confirm the published work [22]. CaTe is virtually insoluble in PbTe and does not act as an acceptor or donor. Compared with Pb, Cd, Zn, Hg and Mg, Ca has a larger radius (covalent, ionic and atomic) which, because these elements are thought to substitute for lead, suggests that a reason for the insolubility of calcium in lead telluride is its large size. The other elements, Cd, Zn, Hg and Mg are all smaller than Pb.

In order for a meaningful comparison with the Zn/PbTe alloys to be made, those properties of the alloys which have been mentioned (Table III) are mainly for concentrations of the group II element $\lesssim$ 2 mol %. However, Cd and Mg have appreciable solubilities in PbTe (Table I) and all their properties, e.g. direct energy gap, lattice parameter, Hall mobility, density of states effective mass, change monotonically with increasing Cd or Mg concentrations. Thus for alloys containing $\geqslant$ 6 mol % CdTe or MgTe there are very large differences in properties compared with those of PbTe [20, 23]. One major difference in the Cd/PbTe and Mg/PbTe alloys is that addition of Mg causes an increase in the freezing point of PbTe [20] whereas the addition of Cd causes a decrease [18, 19].

4. Conclusion

The phase widths and solubilities of PbTe–ZnTe, PbTe–CdTe and PbTe–MgTe have been compared and are appreciably different from one another and from PbTe. Thus the addition of 1 mol % group II element decreases the phase width on the *p*-side and causes an increase on the *n*-side for $250 < T < 800$° C.

The electrical properties, lattice parameters and freezing points of the Cd/PbTe and Mg/PbTe alloys are significantly different from those of

PbTe. Similar properties measured for the Zn/PbTe alloys are indistinguishable from those of PbTe. That Zn is soluble in PbTe is supported by the lack of second phase, the marked change in phase width and a previous publication.

Calcium is insoluble in PbTe, whilst the HgTe alloys proved difficult to prepare and indicated a smaller solubility than previously reported.

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