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Some physical properties of the systems $Pb_{1-x}Mg_xSe$ and $Pb_{1-x}Cd_xSe$

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The solubilities of MgSe and CdSe in PbSe and the phase widths of the systems $Pb_{1-x}Mg_xSe$ and $Pb_{1-x}Cd_xSe$ have been determined in the temperature range 400 to 800°C. The solubilities are retrograde, the solubility of CdSe being greater and more temperature dependent than that of MgSe.

1. Introduction

The lead chalcogenides can exist in single phase form over an extended range of composition, the lattice incorporating either excess lead or chalcogen to give n-type or p-type electrical conductivity respectively. The extent of single phase material, called the phase width or existence range, is a function of temperature. By controlling the temperature and the partial pressure of lead or chalcogen, varying degrees of non-stoichiometry may be obtained within the phase width and consequently produce varying values of electrical conductivity since every excess lead atom (or chalcogen atom) gives rise to an electron (or hole). Previous work has shown that the alloy systems PbTe-MgTe [1], PbTe-CdTe [2] and PbTe-ZnTe [3] appreciably alter the phase width of PbTe together with many of the electrical properties. It was also found that the solubilities of CdTe and ZnTe in PbTe are retrograde but that of MgTe is not very dependent on temperature. Hence the allied systems PbSe-MgSe and PbSe-CdSe have been investigated in order to measure the solubilities of MgSe and CdSe in PbSe, to estimate the phase widths and to observe any changes in physical properties compared with PbSe.

2. Preparation of materials and measurement techniques

Single crystal ingots were grown by the Bridgman method and contained up to 6 mol % MgSe or 15 mol % CdSe. The pure elements (99.999 %) were reacted in an evacuated quartz crucible at least 50°C above the freezing point of the compound. For the PbSe-CdSe alloys the freezing point data of Wald and Rosenberg [4] was used. However, for the PbSe-MgSe alloys, the freezing point of PbSe was used as a guide. The molten charge was shaken several times to ensure the formation of a homogeneous melt before lowering through the temperature gradient of the furnace. The rate of lowering was usually 4 to 8 mm h^{-1} through a temperature gradient of 10 to 20°C cm^{-1} at the freezing point.

The magnesium and cadmium contents were measured along the length of the as-grown ingots using a Unicam SP90 atomic absorption spectrometer. The magnesium results were not very reproducible because the magnesium and selenium apparently interfered with one another. However, the probable error in magnesium content is less than 10 %. Any large error in alloy content due, for example, to a non-uniformity along the length of a Hall bar is shown as error bars in Figs. 1 and 5. The segregation coefficient was calculated from the variation of the MgSe and CdSe content along the length of the ingots.

The lattice parameters were measured as a function of MgSe and CdSe content by X-ray diffractometry and Debye Scherrer techniques, the experimental values corresponding to samples annealed at temperatures between 400 and 750°C and subsequently quenched to room temperature.

The solubility and phase width studies were carried out on single crystal specimens (approximately $2 \times 2 \times 10\ mm^3$) cut from the as-grown ingots. The method was identical to that de-

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scribed previously [1, 2]. However, the lead rich (giving n-type conduction) and selenium rich (p-type conduction) annealing atmospheres were provided by material of composition 60 at. % Pb-40 at. % Se and 60 at. % Se-40 at. % Pb respectively, having assumed these compositions were sufficient to bring the samples to the phase boundary. For small specimens the resistivity and Hall coefficient were measured using the van der Pauw method [5], and good agreement was obtained when some specimens were also measured using the more conventional technique. Consequently most measurements were carried out, immediately after annealing, using the simpler and faster van der Pauw method bearing in mind that it is less sensitive and accurate than the latter method. The optical direct energy gap was calculated from the infrared transmission spectrum of thin polished specimens using a Grubb Parsons M2 I.R. Spectrometer. The concentrations of MgSe and CdSe in each specimen after annealing and measurement was determined using a Unicam SP90 atomic absorption spectrometer.

TABLE I Segregation coefficients for $Pb_{1-x}Cd_xSe$ and $Pb_{1-x}Mg_xSe$

Alloy content (%)	Segregation coefficient, *k*	
	C_s/C_0* (FETF)	*k* variable-mean value along ingot
6 (CdSe)	0.80	—
6 (CdSe)	0.76	0.68 ± 0.11
10 (CdSe)	0.82	0.81 ± 0.04
3 (MgSe)	0.99	1.0
6 (MgSe)	0.7	—

*C_S is the concentration at FETF, C_0, the concentration in ingot.

3. Results and discussion

3.1. Segregation coefficients

From the variations of MgSe and CdSe content along the lengths of the ingots, values of the segregation coefficient were calculated assuming a concentration dependent segregation coefficient [1, 6], (Fig. 1). A value was also obtained by relating the concentration at the first end to freeze (FETF) to the average concentration in the ingots (Table I). Because of an uncertainty in the loss of MgSe to the crucible and in the measurement of the concentration (Section 2) the values of k(MgSe) are not very reliable.

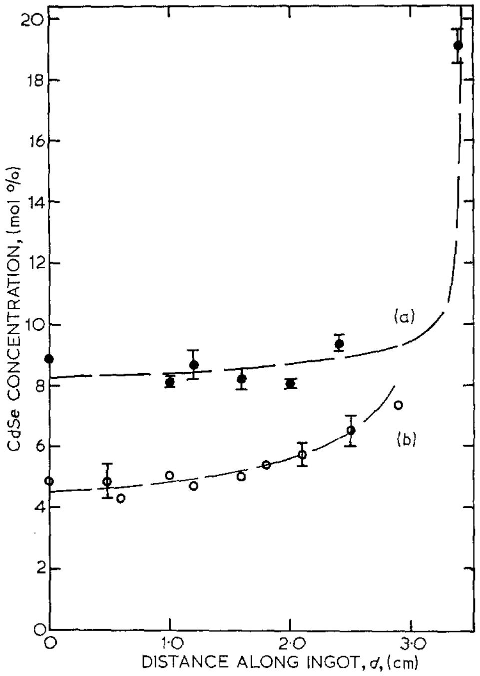

Figure 1 CdSe content as a function of distance along ingot for nominal CdSe concentrations (a) 10 mol %, (b) 6 mol %.

The segregation coefficient of the MgSe alloys appears to be less than unity suggesting that the freezing point decreases with increasing MgSe content in contrast to the MgTe-PbTe system, where the freezing point is raised with MgTe addition [1]. This result must be very tentative. The results for PbSe-CdSe alloys are consistent with the DTA work of Wald and Rosenberg [4] and are similar to those for the PbTe-CdTe system [2].

3.2. Variation of lattice parameter of $Pb_{1-x}Mg_xSe$ and $Pb_{1-x}Cd_xSe$ with x

The lattice parameters of samples annealed at various temperatures between 400 and 750°C were measured by X-ray diffraction techniques and are shown as a function of alloy content in Fig. 2, the estimated error being ± 0.001 Å. Straight lines can be drawn from zero alloy content (where $a_0 = 6.128 \pm 0.001$ Å for PbSe) and it is seen that 5 mol % MgSe is equivalent to about 4 mol % CdSe. The equations for the two lines are:

(i) $a_0\,(\mathrm{Cd}) = 6.128 - 0.38\,x$
(ii) $a_0\,(\mathrm{Mg}) = 6.128 - 0.31\,x$

Wald and Rosenberg [4] found the slope for the

$Pb_{1-x}Cd_xSe$ alloys to be 0.42 which is some 10% higher than this investigation. Reported lattice constants for PbSe are many and vary between 6.110 and 6.152Å, the most recent accurate value being 6.1265 ± 0.0003Å [7].

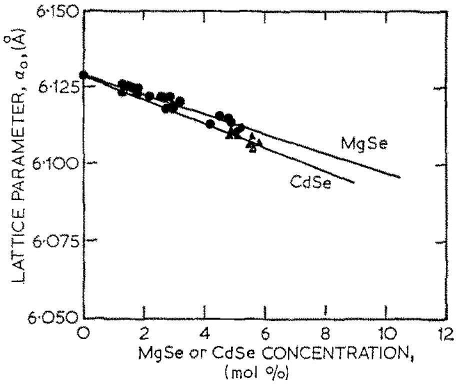

Figure 2 Lattice parameter versus alloy content for $Pb_{1-x}Cd_xSe$ (▲) and $Pb_{1-x}Mg_xSe$ (●).

3.3. Phase equilibria

The phase widths of the alloys $Pb_{1-x}Cd_xSe$ and $Pb_{1-x}Mg_xSe$ are both large, similar in magnitude to PbSe (see Figs. 3 and 4) and decrease with decreasing temperature. The alloys containing 1 to 3 mol% MgSe have very similar phase widths and cannot easily be separated on a $\log(n_{295}$ or $p_{295})$ versus $1/T$ K plot (Fig. 4b). The phase widths of the $Pb_{1-x}Cd_xSe$ alloys are more dependent on the CdSe content (see Figs. 3a and 4a). Both alloys have a retrograde solubility, the solubility of CdSe being 12 mol% at 800°C [4] and is estimated as 6 mol% at 400°C since two phase material is produced when samples containing 6 mol% CdSe are annealed at this temperature. The solubility of MgSe estimated from annealing experiments is less than CdSe and is about 6 mol% at 800°C and about 3.5 mol% at 400°C. This situation is similar to that of PbTe where CdTe is more soluble and more retrograde in nature than is MgTe. Because of the retrograde solubility in the selenide alloys, the low temperature annealing experiments are accompanied by the precipitation of second phase material similar in appearance to a rod eutectic [1]. Some precipitates are aligned along particular crystallographic directions and could be of the Widmanstätten type.

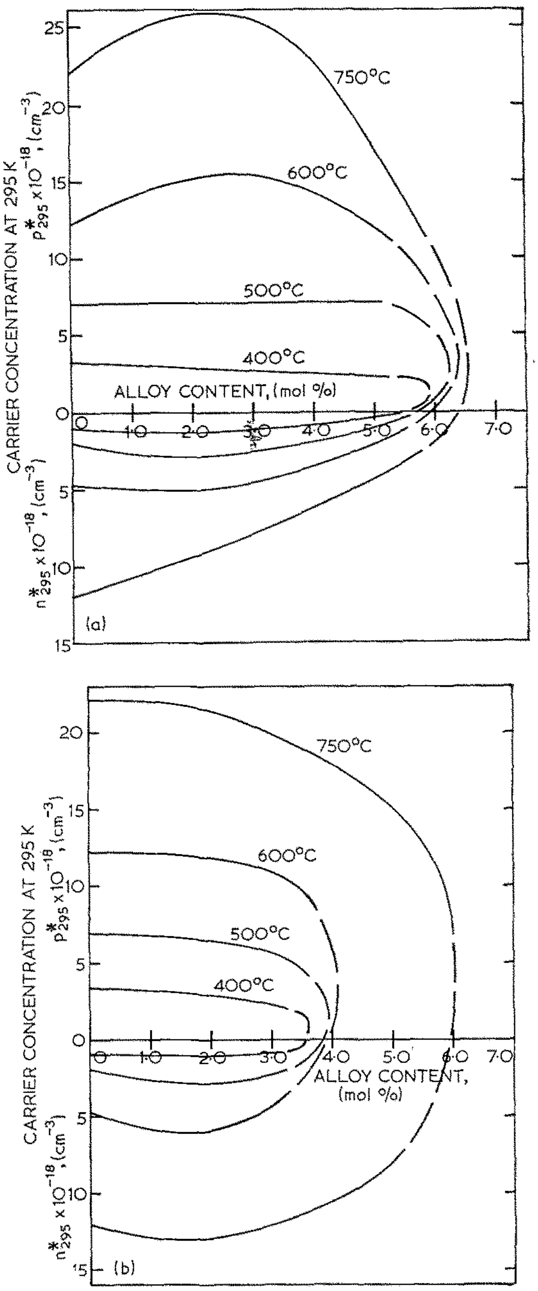

Figure 3 (a) Isotherms of alloy content versus carrier concentration for $Pb_{1-x}Cd_xSe$. (b) Isotherms of alloy content versus carrier concentration for $Pb_{1-x}Mg_xSe$.

The linear portions of the log(n or p) versus $1/T$ K (Figs. 4a and b) obey the equation $n \propto \exp(-E_n/k_0T)$ where E_n is an activation energy, k_0 is Boltzmann's constant and T is the annealing temperature in degrees Kelvin. For p-type material $p \propto \exp(-E_p/k_0T)$. E_n and E_p have been estimated as 0.45 and 0.38 eV for the MgSe alloy and 0.36 and 0.51 eV for the

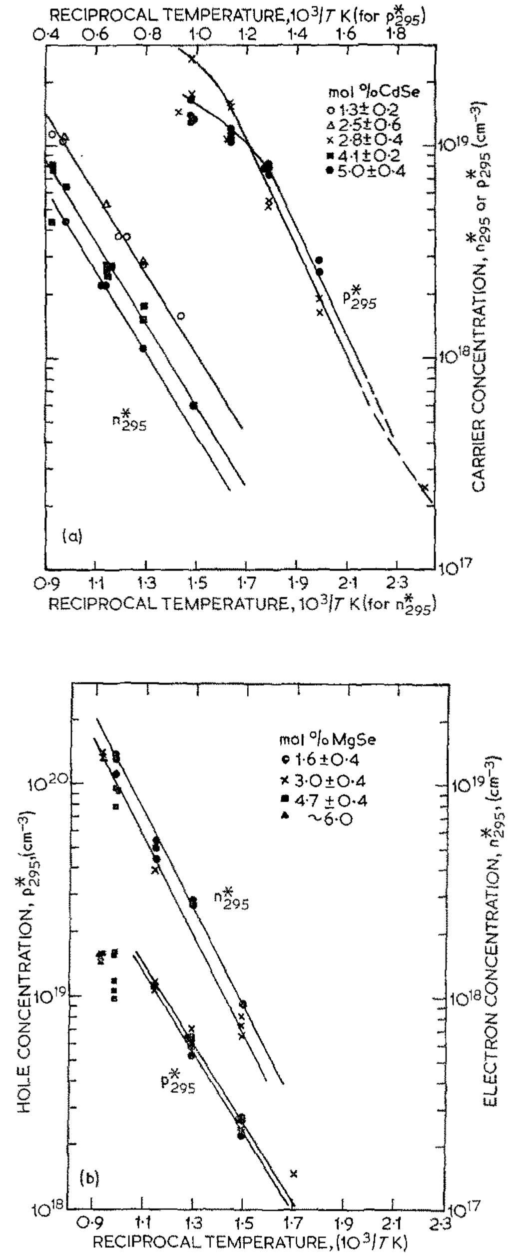

Figure 4 (a) Room temperature carrier concentration versus reciprocal temperature for $Pb_{1-x}Cd_xSe$. (b) Room temperature carrier concentration versus reciprocal temperature for $Pb_{1-x}Mg_xSe$.

CdSe alloy. The computation of reaction constants, such as Schottky constant, and reaction enthalpies from the values of E_n and E_p is possible and will be reported in a future paper.

3.4. Effective masses and mobility as a function of alloy content

The Seebeck coefficient and the Hall coefficient of all samples were measured and used to calculate the density of states effective masses from the equation:

$$n_{295}, p_{295} = \frac{4}{\sqrt{\pi}}\left(\frac{2\pi\, m_0\, k_0 T}{h^2}\right)^{3/2}\left(\frac{m^*}{m_0}\right)^{3/2} F_{1/2}(\eta)$$

where $F_{1/2}(\eta)$ is the Fermi-Dirac integral of the reduced Fermi energy, η, the latter quantity being related to the Seebeck coefficient [8]. The other symbols have their usual meanings. Assuming acoustical phonon scattering, the calculated values of m^*/m_0 increase with increasing alloy content (Fig. 5), the values for $Pb_{1-x}Cd_xSe$ being in agreement with other work [9]. A comparison of m^*/m_0 for the CdSe and MgSe containing alloys shows that 5 mol % MgSe is approximately equivalent to 3.5 mol % CdSe in PbSe.

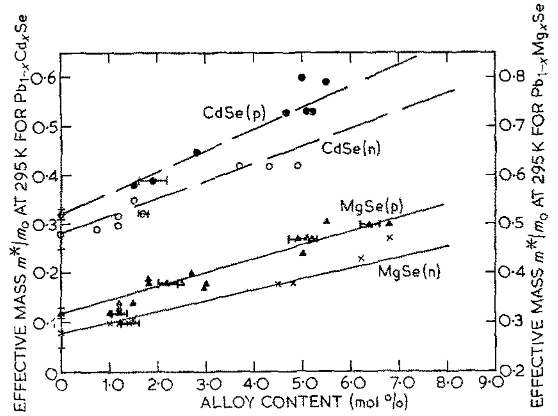

Figure 5 Density of states effective mass versus alloy content for $Pb_{1-x}Cd_xSe$ and $Pb_{1-x}Mg_xSe$.

Although there is large scatter in the Hall mobility data, especially for the n-type materials (Fig. 6), the results suggest that 5 mol % MgSe is equivalent to 3.5 mol % CdSe in PbSe in agreement with the m^*/m_0 results.

3.5. Optical energy gap

Samples were polished to a thickness of about 50 to 100 μm and their infra-red transmission spectra obtained in the region of the direct energy gap. In most cases an "effective" energy gap E_g* was determined from the intercept of the graph of the intensity I versus photon energy and is shown plotted as a function of alloy content in

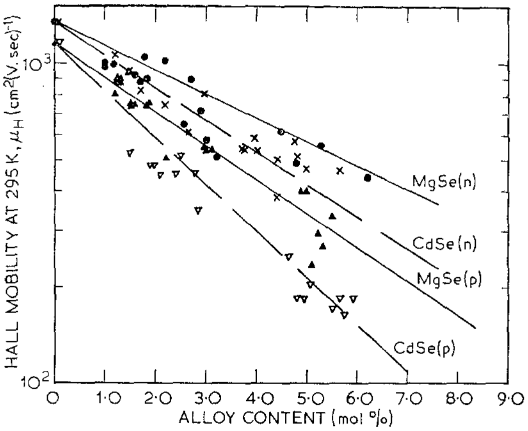

Figure 6 Hall mobility at 295 K versus alloy content for $Pb_{1-x}Cd_xSe$ (×, ▽) and $Pb_{1-x}Mg_xSe$ (●, ▲).

Fig. 7. The "effective" energy gap has been shown experimentally to lie close (~ ± 0.1 eV) to the direct energy gap and was found to be a useful parameter when comparing the effects of CdSe and MgSe on PbSe. Several direct energy gaps were calculated from the intercept of the square of the absorption coefficient (α^2) versus photon energy and indicated the "effective" energy gap to be generally a little higher than the true direct gap (Fig. 7). The absorption coefficient was calculated from the equation:

$$\alpha = \frac{2.3}{t} [2 \log_{10} (1 - R) - \log_{10} (I/I_0)]$$

where t is the specimen thickness, R is the reflection coefficient and I/I_0 the relative intensity of the transmitted infra-red radiation. The reflection coefficient, R, was assumed to be constant and equal to 45% for the small range of photon energy under consideration [9].

In agreement with electrical properties mentioned above the optical energy gap as a function of alloy content (Fig. 7) suggests that 5 mol % MgSe is equivalent to 3.5 to 4.0 mol % CdSe in PbSe.

Some of the PbSe-MgSe results in Fig. 7 do not lie on the straight line and contain precipitates (bracketed points), thus the measured MgSe content is beyond the solubility limit. This factor together with the electrical properties has enabled the approximate MgSe content of some two phase samples to be obtained so that extra points may be plotted on the phase diagram of Fig. 3b.

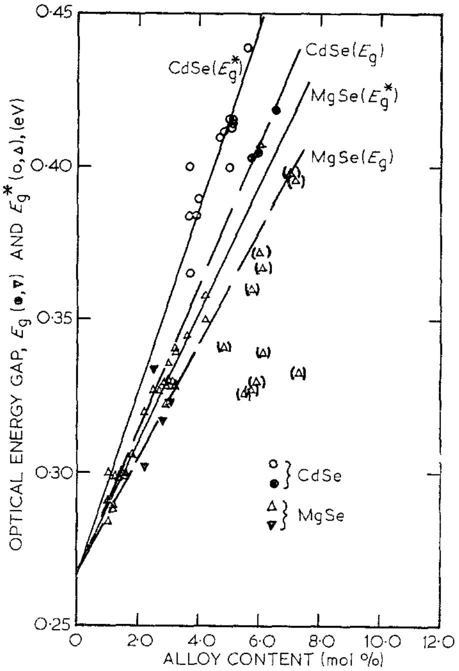

Figure 7 Optical energy gap versus alloy content at 295 K for $Pb_{1-x}Cd_xSe$ and $Pb_{1-x}Mg_xSe$. (Values in brackets are for two phase material.)

4. Conclusions

The segregation coefficients, k, for both PbSe-CdSe and PbTe-CdTe are less than unity indicating a decrease in freezing point on alloying. The magnesium containing alloys are different, the PbTe-MgTe system having $k \gtrsim 1$ and the PbSe-MgSe $k \lesssim 1$ (for 5 mol % MgTe or MgSe). However, there are no freezing point data to confirm the latter result.

The lattice parameters, effective masses, Hall mobilities and optical energy gaps have been determined as a function of alloy content and suggest that 5 mol % MgSe is equivalent to 3.5 mol % CdSe in PbSe, in contrast to the PbTe alloy systems where 6 mol % CdTe is equivalent to 5 mol % MgTe.

The solubility of both MgSe and CdSe in PbSe is retrograde, the CdSe alloys being more sensitive to temperature than the MgSe. The maximum solubility of MgSe at 800°C is about 6 mol % which is about 50% less than that of CdSe at the same temperature. The phase widths of the $Pb_{1-x}Cd_xSe$ and $Pb_{1-x}Mg_xSe$ systems are large and for $0 < x \lesssim 0.03$ are similar in magnitude to that of PbSe.

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