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Preparation and characterization of Zn_3P_2–Cd_3P_2 solid solutions

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Solid solutions of Zn_3P_2–Cd_3P_2 systems of the type $(Zn_xCd_{1-x})_3P_2$ have been prepared by direct reaction of the constituent elements (Zn, Cd, P) for values of x equal to 0.0, 0.2, 0.4, 0.5, 0.6, 0.8 and 1.0. X-ray diffraction data indicate that all the systems crystallize in tetragonal (α) phase only, exhibiting preferred orientation along the (2 2 0) and (2 2 4) directions. The lattice parameters, a and c, and the interplanar spacing, d, vary linearly with x, obeying Vegard's law. The systems show minimum conductivity at room temperature for composition corresponding to x values in the range 0.4–0.6. Electrical conductivity for all systems is measured in the temperature range 100–450 K. In view of the estimated (low) values of the activation energy the conduction process in the different temperature regions has been attributed to the presence of shallow trapping levels in the systems.

1. Introduction

In recent years, tri-zinc and tri-cadmium diphosphides (Zn_3P_2 and Cd_3P_2) belonging to A_3^{II}–B_2^{V} compound semiconductors, have opened up new prospects because of their interesting optoelectronic properties [1–3]. Zn_3P_2, an intrinsically p-type direct band gap ($\sim$ 1.5 eV) compound semiconductor, finds applications as a possible candidate for low-cost PV devices. While extensive studies have been made on the electrical and optical properties of Zn_3P_2 by several workers [4–7], similar investigations have not been carried out so extensively on Cd_3P_2, a degenerate n-type direct band gap ($\sim$ 0.5 eV) compound semiconductor, which finds applications in NIR sensors, solid state lasers, etc. The crystal structure of these compound semiconductors is tetragonal (D_{4h}^{15}) and they are found to form pseudobinary solid solutions for all the compositions [9]. For the specific applications of solid-state devices one can vary the optical band gap from 0.5–1.5 eV by making appropriate solid solutions of these two compounds. Juza *et al.* [8] prepared Zn_3P_2-rich ternaries by the sublimation of the mixture of the powders of both these compounds; while Masumoto *et al.* [9] prepared the same systems by sintering as well as by direct melting of the constituent elements. The plots of lattice parameters, a and c, and the interplanar spacing, d, for different ($h\,k\,l$) planes presented by Masumoto *et al.*, indicate values which do not tally with the values for Zn_3P_2 and Cd_3P_2 reported in the ASTM data file [10]; these values, however, seem to coincide with the Zn_3As_2–Cd_3As_2 systems.

Except for these two reports [8, 9], very little practical work has been done on the solid solutions of Zn_3P_2–Cd_3P_2 systems. In order to investigate systematically the structural, electrical and optical properties of thin films of these systems, homogeneous solid solutions of Zn_3P_2–Cd_3P_2 of the type $(Zn_xCd_{1-x})_3P_2$ have been prepared varying x from 0.0–1.0 by direct reaction of the constituent elements at relatively low temperatures. These pseudobinary compounds which will be used as source materials for the preparation of thin films, have been characterized and their structural and electrical properties are reported in this paper.

2. Materials synthesis

The ternary systems $(Zn_xCd_{1-x})_3P_2$ are prepared by direct reaction of the constituent elements, using stoichiometric quantities of Zn/Cd (99.999% purity) and red phosphorus (99.99% purity). A sealed (at 10^{-5} torr) quartz ampoule (80 mm length and 12 mm inner diameter) containing the specpure elements is heated in a single zone furnace adopting an optimized programme of heating. For all the compositions of the solid solutions, the temperature of the ampoule is raised slowly in the first instance up to 400 °C and then the ampoule was heated at a constant rate of 10 °C h^{-1} to a maximum temperature between 700 and 850 °C, depending upon the system. Basically the programme of temperatures profiling has been tried taking the guidelines from the phase diagram shown in Fig. 1. At the maximum temperature all the samples were well-agitated and annealed for 48 h for homogenization, and thereafter cooled to room temperature at a rate of 50 °C h^{-1}.

3. Characterization

3.1. X-ray diffraction

The materials synthesized in this way are found to crystallize in the α phase only, and X-ray diffraction (XRD) data (presented in Fig. 2) indicated prominent

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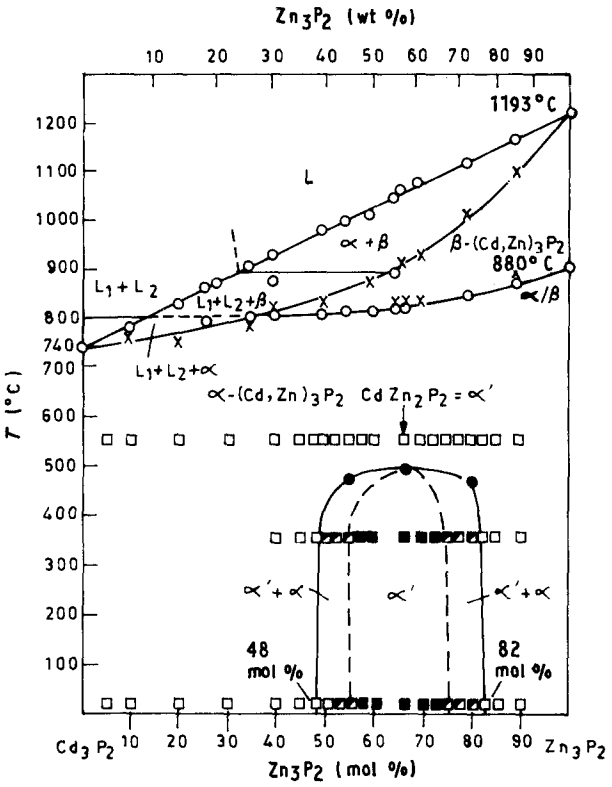

Figure 1 Phase diagram for the Zn_3P_2–Cd_3P_2 system [11].

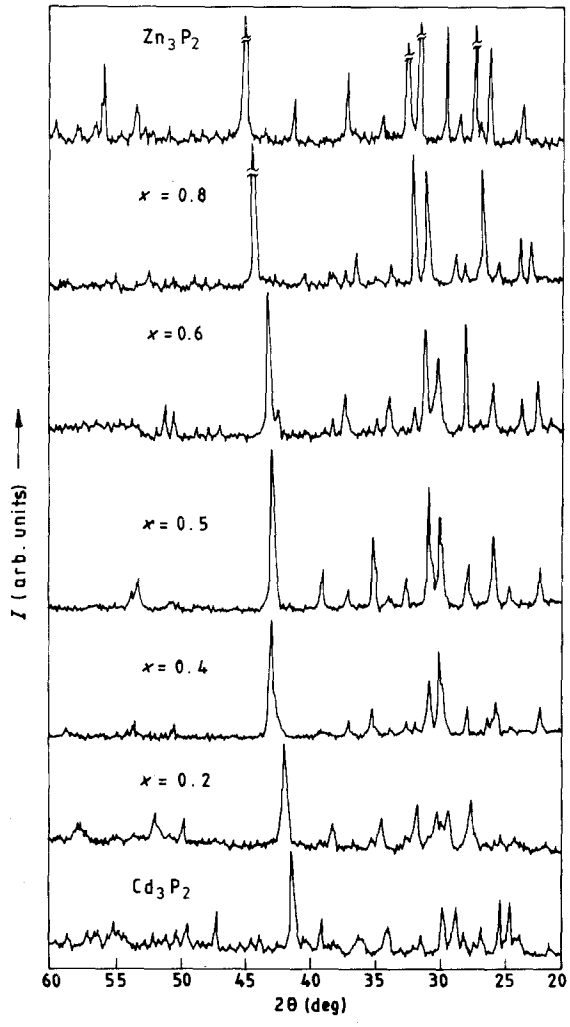

Figure 2 XRD of solid solutions of $(Zn_xCd_{1-x})_3P_2$ for different compositions, x.

lines showing preferential orientation along the (2 2 0) and (2 2 4) directions. The lattice parameters, a and c, and the interplanar distance, d, for all the systems, calculated using the formula (for tetragonal system)

$$\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2} \quad (1)$$

are presented in Tables I and II. It is found that all the above parameters (a, c and d) vary linearly with the composition, x, following Vegard's law in an excellent manner (Figs 3 and 4)

$$P_{(\text{ternary})} = xP_{(Zn_3P_2)} + (1 - x)P_{(Cd_3P_2)} \quad (2)$$

where P represents a, c or d. The c/a ratio for all the systems has been found to be $2^{1/2}$, indicating an excellent development of single phase, namely α phase, which is tetragonal. To date, no satisfactory ASTM data of these systems have been reported and the existing data for Cd_3P_2 seem to refer to cubic phase, but not the tetragonal phase.

3.2. Electrical measurements

Electrical conductivity, σ, of all the polycrystalline samples has been measured in the temperature range 100–450 K using pressed tablets of 8 mm diameter. Silver paint was applied and the coated tablets, annealed for 4 h at 250 °C, were found to develop good ohmic contacts. The I–V plots (Fig. 5) studied at room temperature for all the systems including Zn_3P_2 and Cd_3P_2, were found to be linear. While the value of resistivity (calculated from the slope of the above plots) for both the binary systems is of the order of 2–5 kΩ cm, the ternaries are observed to indicate higher values of resistivity in the range 20–35 kΩ cm for compositions corresponding to values of x in the range 0.4–0.6. The Arrhenius plots of σ versus $1/T$ (shown in Fig. 6) indicate nearly linear variation in the three regions of temperature, namely (i) 110–160 K, (ii) 170–240 K and (iii) 250–450 K; the corresponding activation energies, E, have been estimated using the relation

$$\sigma = \sigma_0 \exp(-E/KT) \quad (3)$$

and these values are 0.01–0.09 eV for Region (i), 0.03–0.15 eV for Region (ii), and 0.10–0.26 eV for Region (iii).

4. Conclusion

The solid solutions of Zn_3P_2–Cd_3P_2 systems prepared by direct reaction of their constituents show the

TABLE I Lattice constants, a and c, of $(Zn_xCd_{1-x})_3P_2$ solid solutions for different compositions, x

Composition (x)	a (nm)	c (nm)	c/a
Zn_3P_2	8.06	11.40	1.414
0.80	8.20	11.60	1.415
0.60	8.34	11.80	1.415
0.50	8.39	11.87	1.415
0.40	8.43	11.95	1.417
0.20	8.61	12.18	1.415
Cd_3P_2	8.72	12.34	1.415

TABLE II Interplanar distance, d, for different $(h\,k\,l)$ planes of $(Zn_xCd_{1-x})_3P_2$ solid solutions for different compositions, x

$h\,k\,l$	Zn_3P_2		x = 0.80		0.60		0.50		0.40		0.20		Cd_3P_2	
	d (nm)	I/I_0	d (nm)	I/I_0	d (nm)	I/I_0	d (nm)	I/I_0	d (nm)	I/I_0	d (nm)	I/I_0	d (nm)	I/I_0
201	0.380	10	0.387	15	0.393	35	0.395	22	0.397	25	0.408	12	0.411	12
202	0.330	35	0.335	23	0.340	35	0.343	42	0.345	30	0.352	15	0.362	50
212	0.305	22	0.309	10	0.316	75	0.318	25	0.319	25	0.322	80	0.330	23
220	0.285	50	0.289	23	0.295	55	0.296	55	0.298	70	0.304	40	0.310	45
203	0.277	28	0.281	27	0.286	70	0.288	72	0.290	46	0.295	32	0.299	45
224	0.201	100	0.205	100	0.208	100	0.209	100	0.211	100	0.215	100	0.218	100
242	0.174	5	0.175	23	0.180	15	–	–	0.181	10	0.183	26	0.192	40

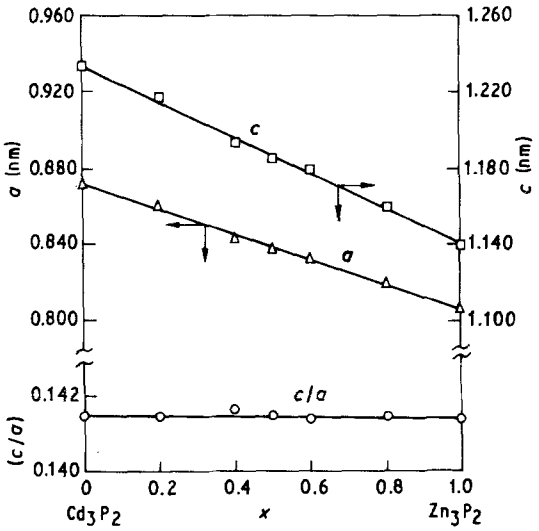

Figure 3 Dependence of the tetragonal lattice constants, a and c, of solid solutions of $(Zn_xCd_{1-x})_3P_2$ on composition, x.

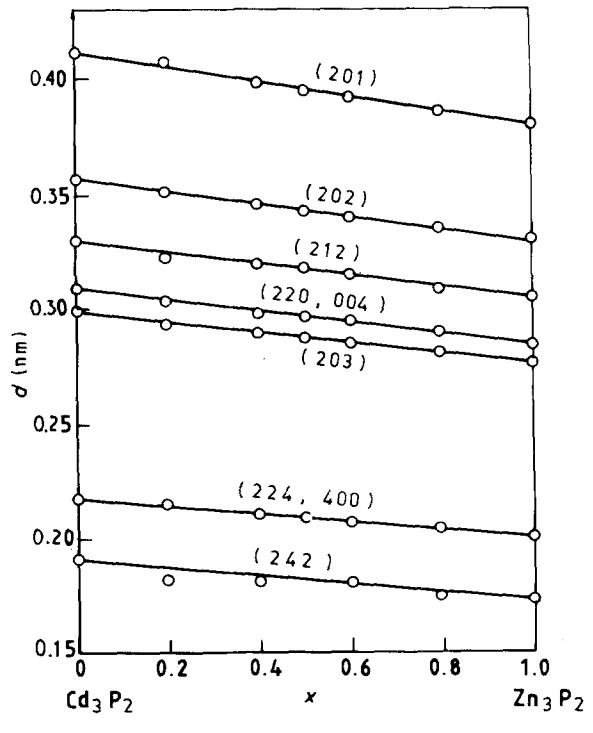

Figure 4 Dependence of the interplanar spacing, d, of solid solutions of $(Zn_xCd_{1-x})_3P_2$ on composition, x.

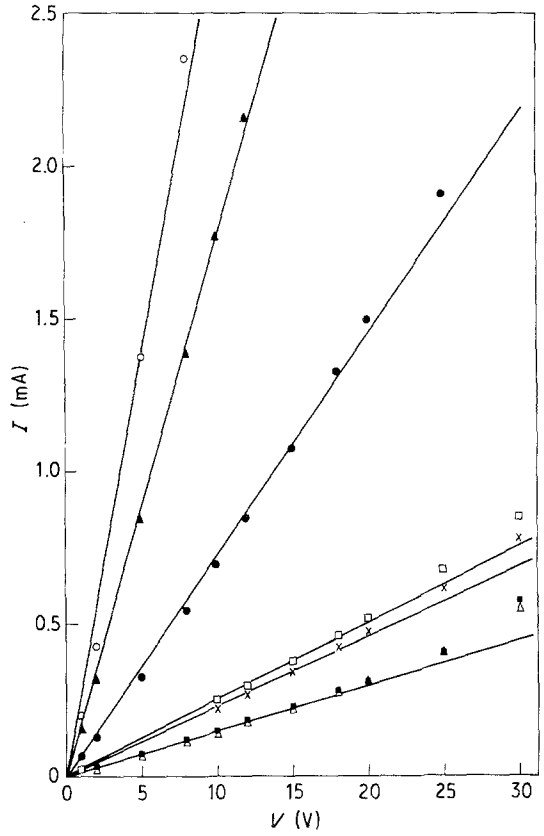

Figure 5 I–V curves at room temperature of solid solutions of $(Zn_xCd_{1-x})_3P_2$ for different compositions, x. (●) Zn_3P_2, (○) Cd_3P_2; x: (×) 0.8, (△) 0.6, (■) 0.5, (□) 0.4, (▲) 0.2.

α-phase of tetragonal crystal structure. The lattice parameters and the interplanar spacings are found to vary linearly with composition obeying Vegard's law. Electrical conductivity measurements on the pressed pellets of the solid solution depict a minimum value when equal proportions of both the compounds, namely Zn_3P_2 and Cd_3P_2, are mixed. Because it is already well established that Zn_3P_2 and Cd_3P_2 are p- and n-type semiconductors respectively, the observed minimum conductivity at room temperature for the composition corresponding to x in the range 0.4–0.6, suggests some compensation to occur leading to the nearly intrinsic behaviour of these systems of solid solutions. The low values of the activation energies may be attributed to the presence of shallow trapping levels. Further investigation is needed for

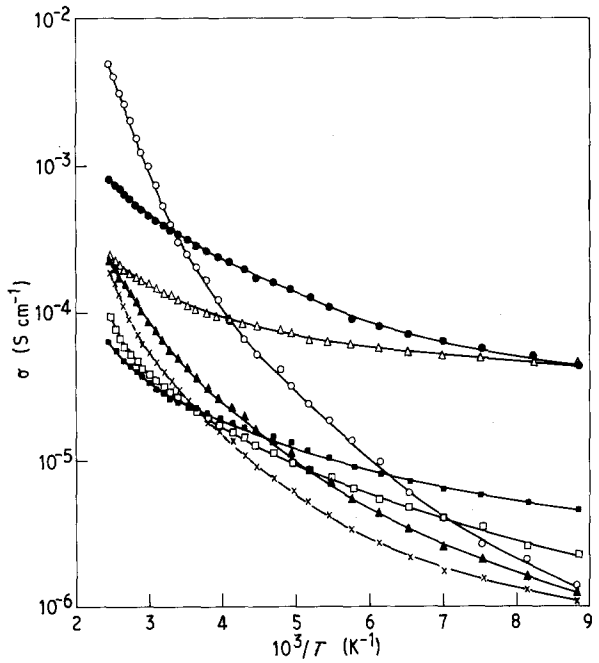

Figure 6 Temperature dependence of the electrical conductivity of solid solutions of $(Zn_xCd_{1-x})_3P_2$ pellets for different compositions, x. (△) Zn_3P_2, (○) Cd_3P_2; x: (×) 0.8, (■) 0.6, (□) 0.5, (▲) 0.4, (●) 0.2.

their identification and understanding of the involved electronic processes.

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