PREPARATION AND SEMICONDUCTING PROPERTIES OF PSEUDOBINARY SOLID SOLUTIONS Zn_3As_2—Zn_3P_2

By W. Żdanowicz

Department of Solid State Physics, Research Center, Polish Academy of Sciences, Zabrze*

F. Królicki

Institute of Inorganic Chemistry and Metallurgy of Rare Elements, Technical University, Wrocław**

And P. Plenkiewicz

Institute of Technical Physics, Technical University, Wrocław***

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The results of studies concerning the preparation and measurements of some electric and galvanomagnetic properties of pseudobinary three-component solid solutions of $Zn_3As_2-Zn_3P_2$ in the system Zn-As-P are presented. It has been shown that both Zn_3As_2 and Zn_3P_2 semiconductors form continuous series of solid solutions. The results were examined by *X*-ray analysis and dilatometric measurements. Hall coefficient and resistivity measurements were carried out between 300 and 800°K.

1. Introduction

The following pseudobinary three- and four-component solid solutions of II–V group were obtained and studied in recent years, $Cd_3As_2-Zn_3As_2$ [1, 2], $Cd_3As_2-Cd_3P_2$ [3], $Cd_3P_2-Zn_3P_2$ [4] and $Cd_3As_2-Zn_3P_2$ [5]. Zn_3As_2 is always a *p*-type semiconductor. At 300°K, at a hole concentration $p \simeq 7.3 \times 10^{17}$ cm^{-3}, the Hall mobility equals (μ_H) 17 cm^2/Vs and conductivity (σ) is in the range 0.1–0.2 $(\Omega \cdot \text{cm})^{-1}$. The width of the forbid-

* Address: Zakład Fizyki Ciała Stałego, Centrum Badań Naukowych PAN, Kawalca 3, 41-800 Zabrze, Poland.

** Address: Instytut Chemii Nieorganicznej i Metalurgii Pierwiastków Rzadkich, Politechnika Wrocławska, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland.

*** Address: Instytut Fizyki Technicznej, Politechnika Wrocławska, Wybrzeże Wyspiańskiego 27, 50–370 Wrocław, Poland.

den band obtained from electrical measurements ΔE_0 is 0.86 eV [6]. Zn_3P_2 is also a p-type semiconductor. At 300°K its conductivity (σ) is around 10^{-5} $(\Omega \cdot \text{cm})^{-1}$ and ΔE_0 equals 1. 2 eV. As yet the data concerning hole concentration and mobility are uncertain.

From different electrical and optical properties of these two compounds it may be concluded that their solid solutions would also exhibit interesting semiconducting properties.

2. Preparation

Both isomorphic compounds (Zn_3As_2 and Zn_3P_2) were prepared by direct synthesis of the highly purified elements Zn-99.999%, As-99.9% and P-99.99% in sealed, carbonized silica ampoules. The compounds obtained were additionally purified by threefold sublimation in vacuum. The solid solutions of $Zn_3As_{2-x}P_x$ were prepared by the melting together of stoichiometric proportions of Zn_3As_2 and Zn_3P_2 at 1500°K, in carbonized and evacuated silica ampoules. The alloys obtained were cooled a few degrees below the melting point and then annealed at this temperature within a period of two to three weeks.

3. X-ray and dilatometric measurements

In order to carry out the X-ray analysis, the samples were pulverised and mixed with NaCl (a = 5.6392 Å) internal standard. The X-ray diagrams were obtained with a Guinier focussing camera and CuK_α radiation. The lattice constants were calculated with an accuracy of 0.1%. The calculations were performed on an Elliot 803 digital computer[1]. In Fig. 1 we have shown the X-ray photometric diagrams for $5° < \theta < 35°$. The shifts of fundamental reflections and their monotonic changes of intensity at the transition from Zn_3As_2 to Zn_3P_2 are observed. The solid solutions are formed mainly on the base of the structure of Zn_3P_2. Fig. 2 represents the variation of the tetragonal lattice constants of the solid solutions of $Zn_3As_{2-x}P_x$ on their molar composition. As it may be seen, the lattice constants vary almost in accordance with Vegard's law from Zn_3As_2 (a = 8.316 Å, c = 11.76 Å) to Zn_3P_2 (a = 8.097 Å, c = 11.45 Å) [10]. Additional data on the $Zn_3As_2-Zn_3P_2$ system ware obtained by the dilatometric method. The measurements were performed of the Leitz-Wetzlar type dilatometer with optical recording. Cylindrical samples 3.5–4.5 cm long were obtained by cooling the needed alloys in a graphite tube sealed in a silica ampoule filled with argon. Dilatations Δl were measured with respect to chronine used as a standard. Temperature was determined by a Pt–PtPd thermocouple. Dilatometric measurements of $Zn_3As_{2-x}P_x$ alloys were carried out for nine different compositions with the molar contents of Zn_3P_2 increased in 10 per cent steps. (Fig. 3). The results of dilatometric measurements for Zn_3As_2 are reported in [11]. For Zn_3P_2 the measurements were performed in temperature interval 20–920°C. Over 920°C, under normal pressure the sample of Zn_3P_2 dissociates thermally. In the whole range of temperatures 20–920°C

[1] The authors wish to express their thanks to Professor K. Łukaszewicz for his help in programming and computing.

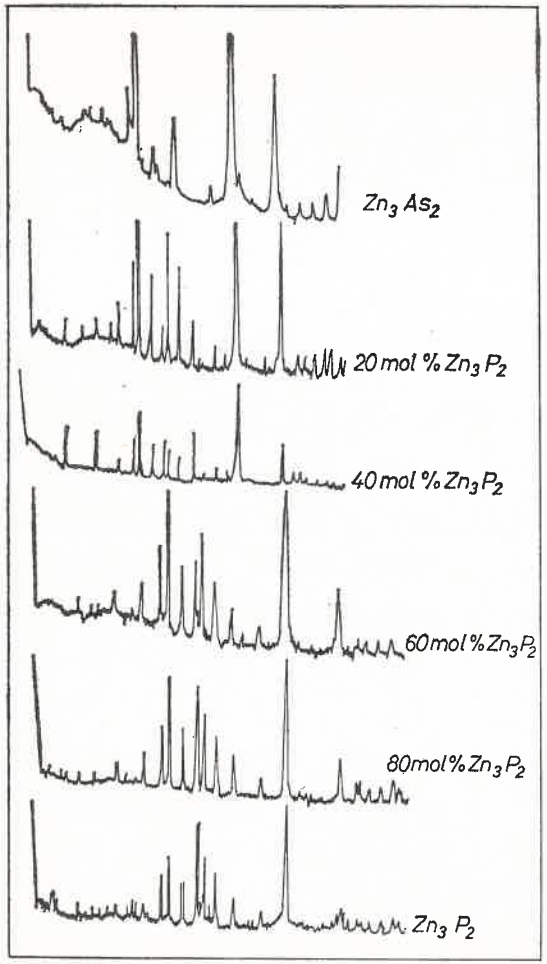

Fig. 1. *X*-ray photometric diagram of Zn_3P_2, Zn_3As_2 and some of their solid solutions

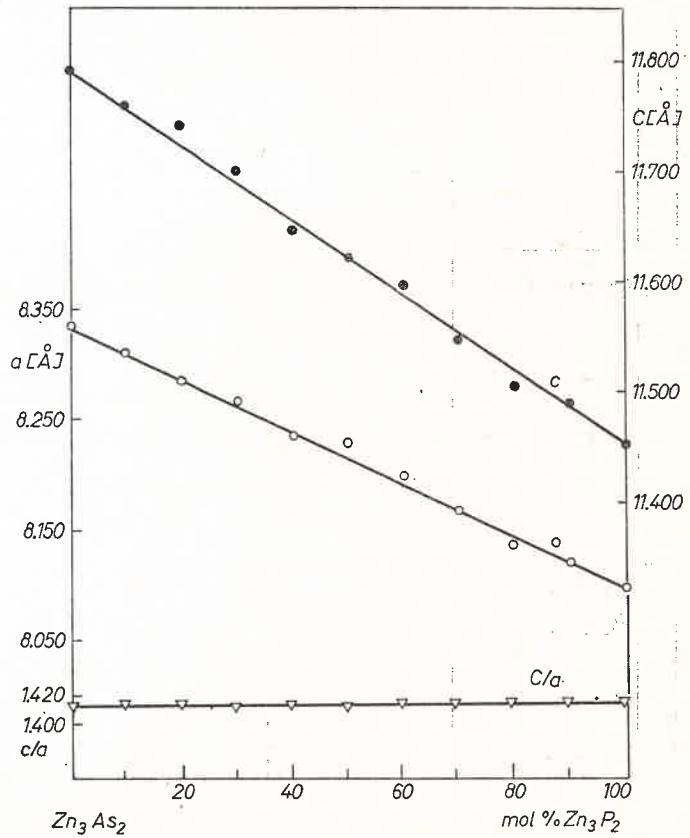

Fig. 2. Dependence of the tetragonal lattice constants of solid solutions of $Zn_3As_{2-x}P_x$ on their molar composition

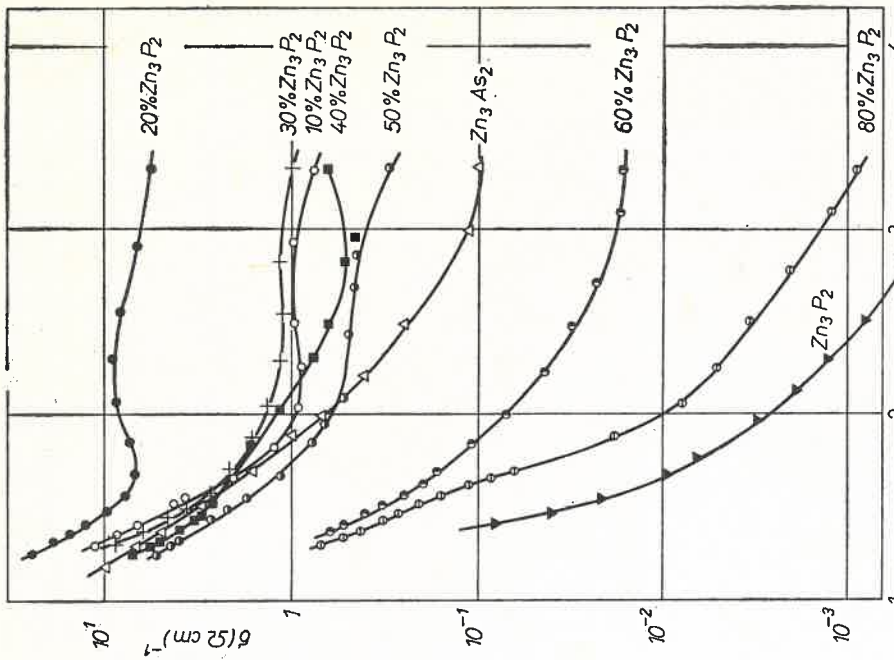

Fig. 4. Temperature dependence of the conductivity of different samples of solid solutions of $Zn_3As_{2-x}P_x$

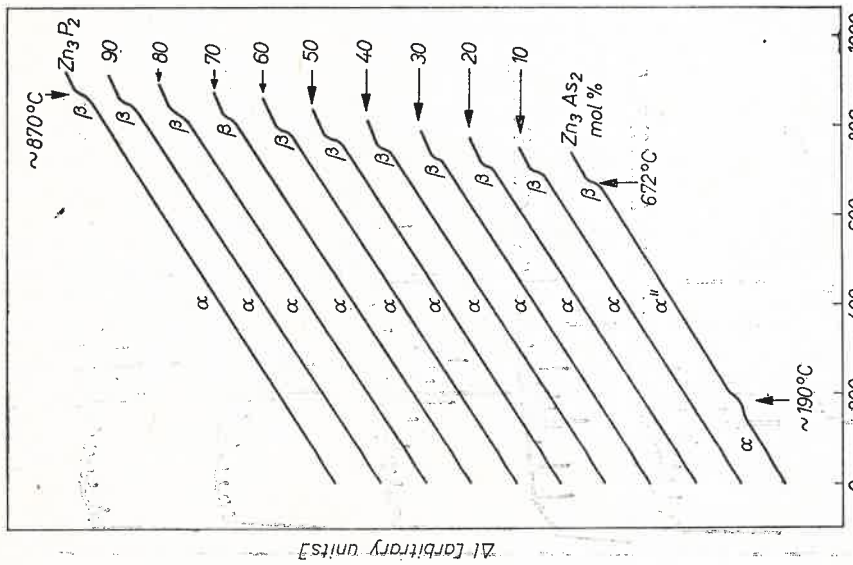

Fig. 3. Dilatometric curves of Zn_3P_2, Zn_3As_2 and their solid solutions

and concentrations of investigated solid solutions only one high temperature reversible phase transition $\alpha \rightarrow \beta(\alpha/\beta - Zn_3As_2 - 672°C$ and $\alpha/\beta - Zn_3P_2 - 870°C)$ is observed. (Fig. 3). The linear expansion coefficients calculated from the data obtained are equal, for $\alpha - Zn_3P_2, -9.1 \times 10^{-6}$ deg.$^{-1}$ for $\beta - Zn_3P_2, -13.7 \times 10^{-6}$ deg.$^{-1}$.

4. Electrical measurements

The resistivity and the Hall coefficient measurements of prepared samples polished to the size of about $1.5 \times 4 \times 10$ mm^3 were carried out by means of a d. c. potentiometer method in a temperature interval 300°–800° K. The samples before measurements were

TABLE I

Some semiconducting properties of $Zn_3As_2 - Zn_3P_2$ type solid solutions

Mol % of Zn_3As_2 / Properties at 300°K	100%	90%	80%	70%	60%	50%	40%	20%	Zn_3P_2
Conductivity σ $(\Omega \cdot cm)^{-1}$	0.10	0.75	5.5	2.0	0.5	0.25	$1.6 \cdot 10^{-2}$	$8.7 \cdot 10^{-4}$	10^{-5}
Mobility μ_H(cm^2/V.s)	17	9.7	85	11	11	11	—	—	—
Concentration p (cm^{-3})	$7.3 \cdot 10^{17}$	$4.7 \cdot 10^{17}$	$1.0 \cdot 10^{18}$	$1.2 \cdot 10^{18}$	$3.9 \cdot 10^{17}$	$1.2 \cdot 10^{17}$	—	—	—
Forbidden band ΔE_0 obtained from $\sigma = f(T)$ and $R_H = f(T)$ (eV)	0.86 0.86	0.72 0.77	0.75 0.78	— 0.82	0.96 0.87	0.91	0.96	1.10	1.20
Energy of ionisation of acceptor level (from σ and R_H measur.) (eV)	—	0.32	0.33	0.32	0.32	0.32	0.27	0.29	0.49

annealed at 700° K during several days. The results of electrical measurements and some semiconducting properties of investigated solid solutions as functions of the molar composition are presented in Table I.

Fig. 4 shows the temperature dependence of the conductivity of investigated samples (always p-type). The conductivity of the investigated samples at $T = 300°$K varies from 10^1 $(\Omega \cdot cm)^{-1}$ for 20% Zn_3P_2 to 10^4 $(\Omega \cdot cm)^{-1}$ for Zn_3P_2. It should be noted that the

conductivity value of the investigated solutions at 300°K, containing less than 50% of Zn_3P_2, is higher than for pure Zn_3As_2. The data and the curves of temperature dependences for pure Zn_3As_2 and Zn_3P_2 are quoted from the work in [6] and [8].

Fig. 5 shows the results of the temperature dependence measurements of the Hall coefficients of investigated samples. It should be mentioned that because of a lack of stability and reproducibility of results it was impossible to measure the temperature dependence

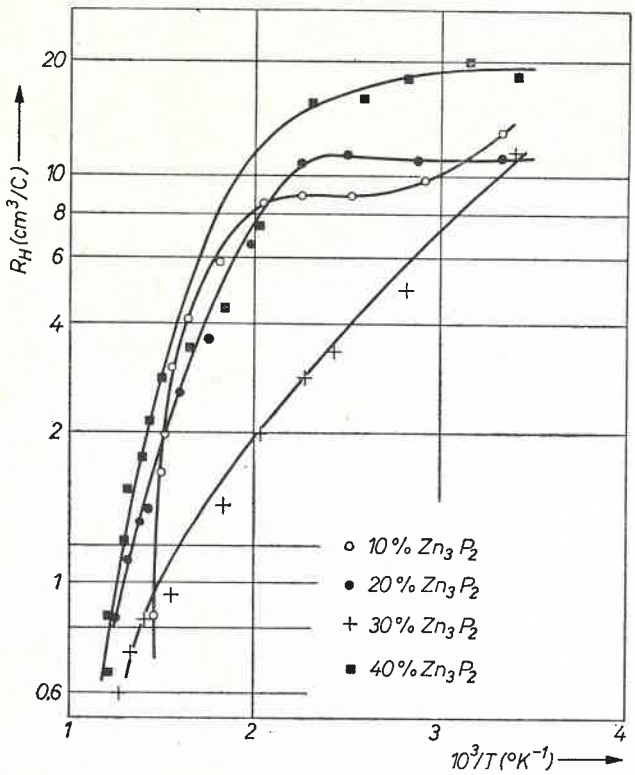

Fig. 5. Temperature dependence of the Hall coefficient

of the very small Hall coefficient for samples containing more than 50% of Zn_3P_2. All investigated samples were always p-type. Basing on the relation $R_H = \frac{1}{pe}$ and assuming that $p \gg n$, the concentration of holes p was calculated at $T = 300°K$ (Table I). Fig. 6 shows the temperature dependence of the Hall mobility $\mu_H = R_H \cdot \sigma$ of investigated samples. Above room temperature, the mobility is determined by scattering from lattice vibrations ($\mu_H \sim T^{-3/2}$). The width of the forbidden band (ΔE_0) of some samples of the investigated solid solutions (to 50% of Zn_3P_2) has been calculated from the temperature dependence of R_H and σ in the intrinsic range. The ionisation energy of acceptors from the extrinsic range of the conductivity also has been calculated.

5. *Discussion*

The phase transition $\alpha \rightarrow \beta$ observed in Fig. 3 determines the region of the existence of solid solutions based on the structure of the α—Zn_3P_2 and β—Zn_3P_2-type. The stabilization of the structure of Zn_3P_2 in high as well as in room temperature occurs even at small amounts of Zn_3P_2. The sample of 10 mol percent of Zn_3P_2 is completely monophase one, and the stabilization of Zn_3As_2 structure [11, 12] is not observed. This results from the

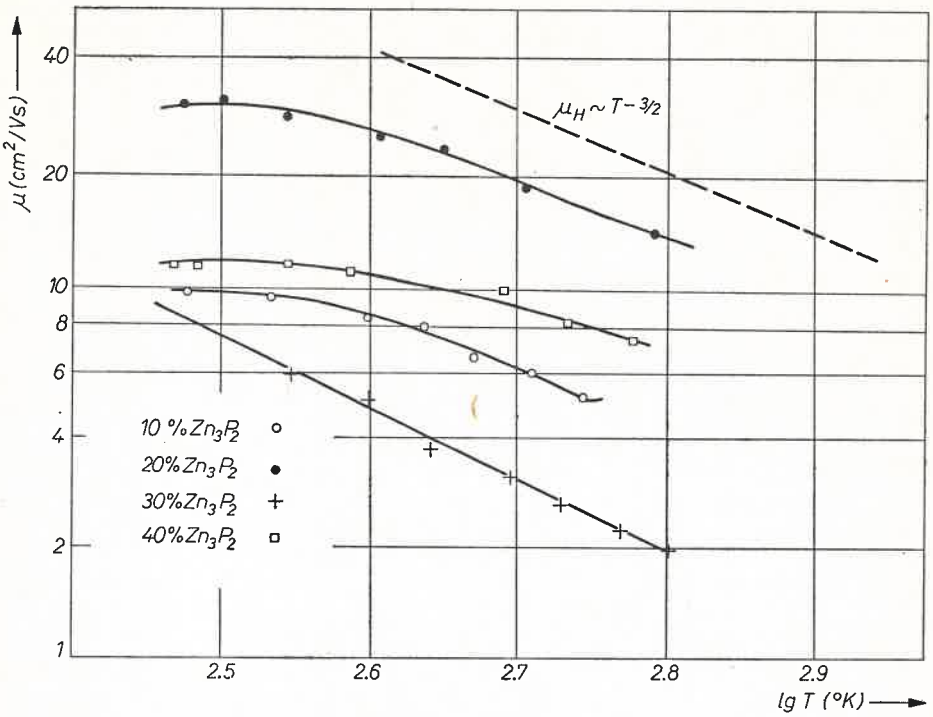

Fig. 6

fact, that the formation of solid solutions based upon the structure of Zn_3P_2 is more probable because of the symmetry and of the structure of the unit cell in Zn_3P_2. From the temperature dependence of the conductivity and the Hall coefficient follows the possibility of existence of an acceptor band with energy activation 0.29–0.32 eV — depending on the composition. A similar band was found in Zn_3P_2 in [8] and [9].

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