

Preparation of $\text{GaAs}_{1-x}\text{P}_x$ compounds from the melt under controlled vapour pressures*

by

KOZO OSAMURA** and YOTARO MURAKAMI**

(Received September 29, 1971)

Abstracts

Crystalline solid solutions between GaAs and GaP compounds were prepared from the melt under controlled vapour pressures. The experimental results were found to agree with the theoretical formulae derived in order to calculate the pseudo-equilibrium in a heterogeneous system consisting of two parts with different temperatures. It was assumed that all condensed phases would be regular or sub-regular and that the gas phase is ideal. In addition some of the thermodynamic properties of the Ga-As-P ternary system were discussed. It was confirmed that one can apply the concept of the pseudo-equilibrium to preparation of crystalline solid solutions of III-V compounds containing two volatile components.

I. Introduction

III-V compounds have been grown from the melt, from gaseous phases, and from liquid metal solutions. These compounds are of considerable interest in the semiconductor field because of their electrical characteristics. Crystalline solid solutions of III-V compounds which contain As and P are of particular interest because their energy gaps are large and change continuously with concentration of As or P. The direct preparation from the melt of the crystalline solid solutions $\text{A}^{\text{III}}\text{As}_{1-x}\text{P}_x$ containing Al, Ga and In as a third group element has not been studied to any great extent. The main reason is that As and P have high equilibrium vapor pressures at the high temperatures required for preparation. The previous reports concerning the preparation of $\text{InAs}_{1-x}\text{P}_x$ ⁽¹⁾⁻⁽³⁾ and $\text{GaAs}_{1-x}\text{P}_x$ ^{(4),(5)} are not the ones which are considered as the conditions for controlling the vapour pressures.

The authors established a concept of pseudo-equilibrium in a heterogeneous system containing two different temperatures. Then, a method has been developed for preparation of the crystalline solid solutions in the entire range between GaAs

* This work was published originally in Japanese in the Journal of the Japan Institute of Metals, Vol. 35 (1971), 639-646.

** Department of Metallurgy

and GaP from the melt under controlled vapour pressures by using the quasi-binary phase diagram of GaAs–GaP compounds determined by the present authors. It was also shown that this method could be used as a general method of preparing $\text{A}^{\text{III}}\text{B}_{1-x}\text{C}_x^{\text{V}}$ compounds from the melt by controlling vapour pressures, if a quasi-binary phase diagram of $\text{A}^{\text{III}}\text{B}^{\text{V}}\text{--A}^{\text{III}}\text{C}^{\text{V}}$ compounds is established.

II. Experiments and Results

When crystalline solid solutions of $\text{GaAs}_{1-x}\text{P}_x$ are to be grown from the quasi-binary melt under controlled pressures of As and P, it must be considered that the total pressure at the melting point reaches from 1 atm⁽⁶⁾ to a maximum of about 25 atm⁽⁷⁾ as will be discussed later in section IV. This high pressure requires modifications in the usual techniques of preparing GaAs crystals. The usual apparatus was modified to permit operation at a pressure of less than about 10 atm. The modified apparatus that was used is shown in Fig. 1. It consists of (A) an electric furnace for permitting the control of pressure, (B) a RF induction coil with a 10 kw generator tuned to about 30 kHz, and (C) a subsidiary electric furnace. The reaction

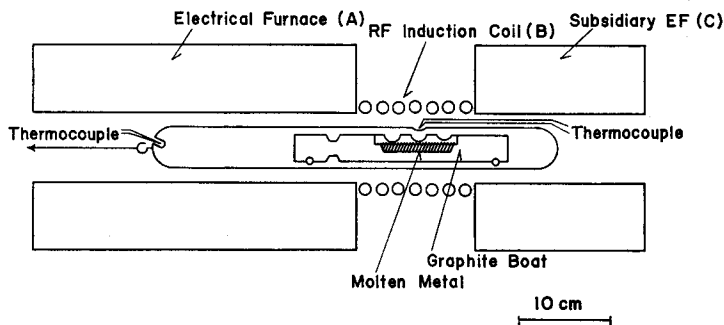


Fig. 1. Apparatus for the preparation of $\text{GaAs}_{1-x}\text{P}_x$ compound.

vessel for preparing the compound is located within the furnace as shown in Fig. 1. It consists of a 40 cm long fused silica tube with an internal diameter of 35 mm. This length is sufficient to keep a part of the tube in one of the lower temperature zones throughout the preparation of the ingot. The highest temperature which the fused silica reaches is 1000°C or less. The reaction vessel, containing Ga (in a high-purity graphite boat), As and P was evacuated. With the reaction vessel in place, the middle furnace (B) was slowly heated to the reaction temperature T_h and then an electric furnace (A) was heated to the temperature T_c required to hold the pressure calculated in the following section. The temperature of the subsidiary

furnace (C) was held at the intermediate temperature between T_h and T_c . After sufficient time passes, there will be As-P solid solution with vapour at the part T_c , and ternary liquid of Ga, As and P with vapour at the part T_h . When the pseudo-equilibrium in the system was sufficiently established, a silica tube with the sample boat was then moved through the RF coil at the constant rate as described later. The crystallization progresses from one end and solid ingots may be formed.

The effect of variables such as temperatures, T_c and T_h , the amounts of Ga, As and P, and travelling rate had been investigated to develop a suitable technique for producing uniform ingots of the crystalline solid solution of $\text{GaAs}_{1-x}\text{P}_x$.

The matter of primary importance in the crystal growth of crystalline solid solution is the metallographic knowledge with the equilibrium diagram between ternary liquid and solid solution. In the case of $\text{GaAs}_{1-x}\text{P}_x$, we can restrict the composition range of Ga, As and P to the quasi-binary section⁽⁶⁾ of GaAs-GaP, because the binding energy between the III and V atoms is very strong and two kinds of atoms form a stoichiometric compound, and additively in the quasi-binary system of these III-V compounds the atoms of V group element can be only substituted for the same group of atoms, that is, the quasi-binary compounds, $\text{GaAs}_{1-x}\text{P}_x$, are stoichiometrically formed. The quasi-binary phase diagram between GaAs and GaP was investigated, and the liquidus and solidus curves were determined by the authors.⁽⁸⁾ The relationship between liquid and solid phases can be treated as a quasi-binary equilibrium, if the composition of the melt is restricted so as to exist on the quasi-binary section of GaAs-GaP compounds by controlling the composition of a ternary liquid phase according to this method. Therefore, it is easy to find the composition and temperature of the melt from the quasi-binary phase diagram, for the crystalline solid solutions may be separated from the liquid phase on the quasi-binary section.

The best control over the composition of the grown crystals can be obtained when the amounts of Ga, As and P in the vessel correspond rigorously to the proportion calculated later by the concept of the pseudo-equilibrium. When the negligible small amount of the crystalline solid solution is formed, the necessary numericals to be determined are as follows: at the T_h part, molar quantities of N_{As}^{lh} , N_P^{lh} , N_{Ga}^{lh} , and at the T_c part, similar quantities of N_{As}^{sc} , N_P^{sc} , X_{As}^{sc} , and upper subscripts sh, lh and sc refer to the ternary solid and liquid with the compositions on the quasi-binary section and the solid solution of As and P respectively. Before solidification starts, total molar quantities of Ga, As, and P are $N_{Ga} = N_{Ga}^{lh}$, $N_{As} = N_{As}^{lh} + N_{As}^{sc}$ and $N_P = N_P^{lh} + N_P^{sc}$. The relative amounts of Ga, As and P were determined in conjunction with Eqs. (14) and (16) in order to obtain the mole fraction X_P^{sh} for $\text{GaAs}_{1-x}\text{P}_x$ compound. Then the value of X_P^{sc} in the left side of the

apparatus shown in Fig. 1 for the values of X_P^{lh} , X_P^{sh} and T_h in the right side can be calculated. After N_{Ga} and N_{As} moles of Ga and As were weighed out, the total amount N_P of P required was determined from the following equation which is reduced from the above definition,

$$N_P = 2N_{Ga} X_P^{lh} + [N_{As} - N_{Ga} (1 - 2X_P^{lh})] X_P^{sc} / (1 - X_P^{sc}). \quad (1)$$

The amounts of each element were initially weighed to correspond to the mole fractions, X_P^{sc} and $2X_P^{lh}$ listed in Table 1.

Table 1. Conditions for Preparation

| Sample number | Starting material | | | | Theoretical values | | | | | Experimental values | | |
|---------------|----------------------|----------|--------|----------------|--------------------|-------------|-------------|---------------------|---------------------|------------------------|---------------------|---------------------|
| | N_{Ga} | N_{As} | N_P | $N_{As} + N_P$ | X_P^{sc} | $2X_P^{lh}$ | $2X_P^{sh}$ | T_h^{cal} (°K) | T_c^{cal} (°K) | $2X_P^{sh}$ (ingot) | T_h^{exp} (°K) | T_c^{exp} (°K) |
| | ($\times 10^3$ mol) | | | N_{Ga} | | | | | | | | |
| 1 | 80.00 | 120.00 | — | 1.50 | 0.0 | 0.0 | 0.0 | 1518 | 885 | 0 | 1530 | 888 |
| 2 | 73.12 | 138.69 | 5.09 | 1.97 | 0.040 | 0.040 | 0.114 | 1535 | 877 | 0.110 | 1540 | 888 |
| 3 | 105.88 | 105.88 | 6.16 | 1.06 | 0.051 | 0.054 | 0.152 | 1541 | 875 | 0.150 | 1553 | 878 |
| 4 | 119.52 | 121.50 | 6.78 | 1.07 | 0.051 | 0.054 | 0.152 | 1541 | 875 | 0.042 | 1553 | 883 |
| 5 | 112.36 | 198.11 | 22.47 | 1.96 | 0.087 | 0.082 | 0.220 | 1552 | 873 | 0.324 | 1563 | 868 |
| 6 | 77.84 | 135.83 | 10.85 | 1.88 | 0.083 | 0.082 | 0.220 | 1552 | 873 | 0.130 | 1563 | 878 |
| 7 | 73.61 | 121.00 | 16.47 | 1.87 | 0.102 | 0.138 | 0.340 | 1572 | 859 | 0.390 | 1593 | 853 |
| 8 | 92.53 | 173.90 | 45.34 | 2.37 | 0.181 | 0.242 | 0.500 | 1603 | 847 | 0.506 | 1623 | 833 |
| 9 | 75.35 | 74.38 | 25.17 | 1.32 | 0.205 | 0.270 | 0.532 | 1610 | 848 | 0.500 | 1623 | 843 |
| 10 | 81.95 | 67.62 | 34.88 | 1.25 | 0.318 | 0.248 | 0.618 | 1629 | 837 | 0.660 | 1653 | 813 |
| 11 | 77.25 | 57.29 | 48.05 | 1.36 | 0.482 | 0.448 | 0.706 | 1650 | 836 | 0.720 | 1673 | 808 |
| 12 | 86.14 | 31.08 | 61.11 | 1.07 | 0.787 | 0.654 | 0.840 | 1688 | 858 | 0.900 | 1713 | 723 |
| 13 | 113.33 | 24.46 | 219.99 | 2.16 | 0.908 | 0.876 | 0.950 | 1722 | 868 | 0.954 | 1723 | 723 |
| 14 | 80.00 | — | 120.00 | 1.50 | 1.0 | — | — | 1738 | 873 | 1.00 | 1723 | 723 |

Next the temperatures of T_h and T_c must be determined. The solidus temperature, T_h corresponding to the desired compound is known from the quasi-binary diagram of GaAs-GaP. The temperature T_c which corresponds to T_h can be calculated together with X_P^{sc} from the condition of pseudo-equilibrium described later in section III. These calculated values are shown in Table 1.

The heating, holding and cooling of the furnaces were controlled by temperature regulators. The measurements of T_h and T_c were carried out as follows. T_h was measured preliminarily for the vessel without molten metal by both thermocouple and optical pyrometries. When the effect of RF heating on molten metal is neglected because of the large heat capacity of a graphite boat, the true temperature of molten metal will be considered to be very near the temperature measured preliminarily. The temperature profile of T_h over the molten metal seemed to have a small temperature gradient while the temperature profile of T_c was verified to be sufficiently uniform over the length of about 30 cm. The temperatures T_h^{exp} shown in the last column in Table 1 correspond to the temperatures of a carbon boat, and T_c^{exp} are the ones measured by the thermocouple which is shown on the left hand side in Fig. 1. When the vapor pressure increases over the order of several atmospheres

for the compounds with more than 60 mol% of GaP as shown in Fig. 7, the temperature of T_c had to be regulated for safety to be slightly lower than that ones which correspond to the theoretical value shown as a solid line in Fig. 5. The thermocouple which was inserted into the RF coil (see Fig. 1) was used only as a monitor. The travelling rate of the boat was kept about 1.0 cm/hr throughout the procedure.

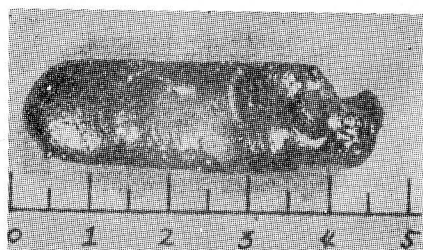


Photo. 1 An appearance of the prepared ingot. In this case, $2X_{P^{sh}}$ (ingot) is $0.506 (\times 1.6 \times 2/3)$

One of the ingots obtained in the present experiments is shown in Photo. 1. All ingots consisted of small crystals of grain size 5 mm or less. The ingot was cut into pieces of about 5 mm in length. The average composition of each piece was determined by a powder X -ray method assuming that the lattice constant changes linearly with composition.⁽⁹⁾ The composition was also estimated in another way. The intensity of the K_{α} - X -ray emission lines of P and As has been measured by using the electron-probe X -ray microanalyzer. Analysis of these emission lines provides a suitable method for determining a change in composition from one grain to another. In spite of the fact that the ingot cross section contains many small grains it was found that in all ingots with any initial composition the change of composition in the cross section perpendicular to the growth direction was very small in comparison with the change of composition in the growth direction.

The average composition of typical samples as a function of the position in the growth direction of the ingot is shown in Fig. 2. The composition of the crystalline solid solution was taken as the composition of the initially solidified part of the ingot. These compositions, written as $X_{P^{sh}}$ (ingot), are determined by the intercept of the mol% GaP curves with the vertical axis and are summarized in Table 1. Compare sample number 3 with 4, or 5 with 6. The composition of $X_{P^{sh}}$ of an ingot is largely dependent on the temperature T_c^{exp} , even when the relative molar amounts of Ga, As and P are weighed out to get the certain composition of an ingot. It is found that the lower value of T_c^{exp} than the calculated one results in a higher value of P concentration and, on the contrary, the higher value of T_c^{exp} produces a higher value of As concentration. The degree of composition change along an ingot varies as shown

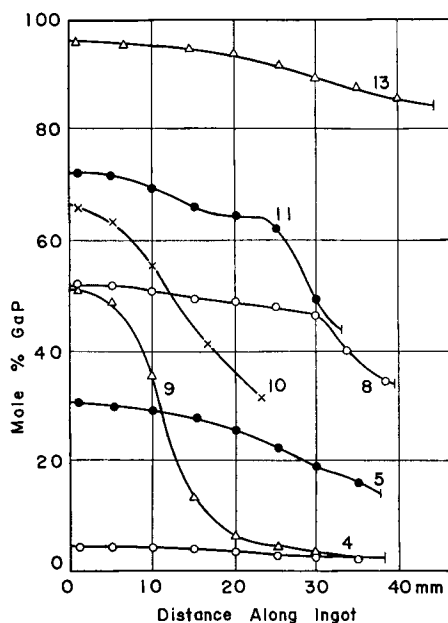


Fig. 2. Distribution of the $GaAs_{1-x}P_x$ alloy composition along the ingot.

in Fig. 2. The reason why such a difference takes place may not be a simple one, because various experimental conditions will interact with each other. It was generally found that the degree of composition variation was relatively small, when the ratio $(N_{As} + N_P)/N_{Ga}$ is large, as shown in sample number 5, 8 and 13. The reason will be described later. It was also observed that both the grown quasi-binary compound and the solid solution with a quenched microstructure exist in a carbon boat after the experiment was finished. (It is evident from trace lines on an ingot that it was grown from left to right as shown in Photo. 1. A narrow neck part in the right side was caused by rapid solidification.) It was observed that a large part of component elements concentrated in the lowest temperature part T_c and a very small quantity of the volatile components condensed in the middle temperature part. The substance condensed in T_c part was confirmed to be a homogeneous solid solution of As and P containing a trace of Ga by using the electron-probe X-ray microanalyzer. Thus the quantity of Ga which is transported to T_c part during the period of the experiment (about 30 hrs) is negligibly small. From these observations, the distribution of the substances in the closed system can be fixed and it is reasonably defined that quasi-binary liquid and solid phases in carbon boat exist together with binary solid in T_c part. The values of $X_P^{T_c}$ can not be determined from experiments, and so they were assumed as shown in Table 1.

III. Conditions for Pseudo-Equilibrium

Fig. 3 is a schematic diagram of the apparatus used in preparing $\text{GaAs}_{1-x}\text{P}_x$. Known quantities of As and P placed in the left side of the apparatus are maintained at a temperature T_c . T_c is always lower than T_h , the temperature of the right side of the apparatus. The phases present in the left side are known from the phase diagram of As-P system reported by Krebs⁽¹⁰⁾ which shows that two solid solution

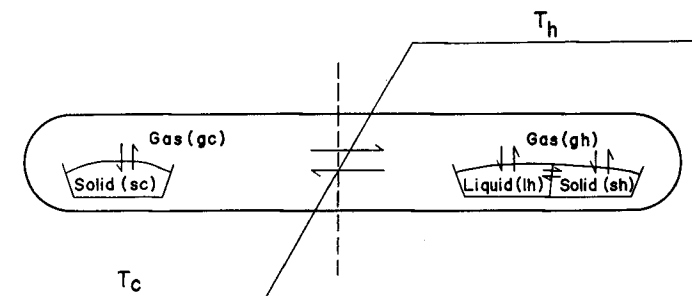


Fig. 3. Schematic representation of the present procedure. The closed system includes four phases as shown in the figure: (sc) Binary solid solution of As and P, (gc) and (gh) Gas phase, (lh) Ternary solution of Ga, As and P, (sh) crystalline solid solution of $\text{GaAs}_{1-x}\text{P}_x$

exist except in the two phases region in a range between 13 and 26% P. The thermodynamic parameters for As and P are determined by assuming that the solid solutions of As and P are regular as will be described further below. Then, the following condition can be considered. In the right side of the apparatus, a quasi-binary liquid consisting of the three components, As, P, and Ga is in equilibrium with an infinitely small quantity of a quasi-binary solid solution crystalline under the vapour phase filled in a closed apparatus. The partial pressure of Ga is assumed to be negligible compared with those of As and P because of a very low vapour pressure of Ga, i.e., about 4.2×10^{-4} atm, at 1538 °K.

In applying the phase rule to the system it is found that there are two degrees of freedom for each side of the apparatus considered independently. Hence, the equation of state for each phase can be determined if the temperature and pressure are fixed. The relation between the mass density and partial pressure of vapour phase species, assuming ideal gas conditions, is given by,

$$n = MP / RT, \quad (2)$$

where n and M are mass density and molecular weight respectively. It is reasonable

to consider the mass density rather than the corresponding partial pressure of each element in the gas phase at the constant temperature.

The components in the gas phase, assumed to be As and P, can exist as various molecular species. The possible stable molecular species in the temperature range from 600°K to 1800°K appear to include As_2 , As_4 , P_2 , P_4 , AsP and four atom molecules formed by various combination of As and P.

In the experiment mentioned above, when each furnace reaches the constant temperatures and is held for enough time, a steady state will be set up. The condition for balance at the steady state can be considered as follows. The mean free path of gaseous species at pressures in the range of 0.2–20 atm total pressure is about 10^{-4} – 10^{-6} cm and fairly small in comparison with the dimension of the apparatus. Therefore the gas phase is set up at thermal equilibrium in each part of the apparatus. Consider the hypothetical interface at the boundary between the T_c and T_h . Then the total mass flux passing through its interface from the T_c part is represented by the term, $[\sum_{i\lambda} n_{i\lambda} v_{i\lambda}]_{T_c}$, where $n_{i\lambda}$ and $v_{i\lambda}$ are mass density of molecular species $i\lambda$ and the mean molecular speed respectively. These quantities are assumed to be prescribed by the thermal condition of the T_c part of the apparatus. Similarly the total mass flux passing through the interface from the T_h part is indicated by the similar term, $[\sum_{i\lambda} n_{i\lambda} v_{i\lambda}]_{T_h}$. The condition that there is no net flow of atoms in either direction between T_c and T_h parts is related to the fact that the total mass flux from the T_c part is equal to that from the T_h at the interface. In the present case, we restrict As_2 , As_4 , P_2 and P_4 as molecular species in the gas phase, where the reactions between As_2 and As_4 , or P_2 and P_4 should be considered at the thermal equilibrium. Using equation (2), the mass flux of each individual species is rewritten as $n_{i\lambda} v_{i\lambda} = S_{i\lambda} P_{i\lambda}$. We could consider that the tube has a "pumping speed" $S_{i\lambda}$, which is a function of molecular weight $M_{i\lambda}$. From a simple kinetic theory of gases, the mean molecular speed is given by $\sqrt{8RT/\pi M}$. Accordingly the pumping speed defined as $S = Mv/RT$ is represented by $\sqrt{8M_{i\lambda}/\pi RT}$. Neglecting thermal diffusion, the condition for balance at steady state where no net atom flow occurs is represented by the following equation.

$$\sum_{\lambda} (S_{i\lambda h} P_{i\lambda h} - S_{i\lambda c} P_{i\lambda c}) = 0, \quad i = As, P \quad (3)$$

where λ refers to number of atoms of each species, and i to the kind of species. The temperature in the transition region between both parts of the apparatus may gradually change from T_h to T_c , but for simplicity, the transition region is assumed to be very narrow.

The system described in the previous paragraphs is in a state which might be

described as a sort of pseudo-equilibrium. If the pseudo-equilibrium is realized between the left side and the right side of the apparatus, the conditions for equilibrium can be thermodynamically developed. Here it is assumed that the binary solution of As and P is regular, that the liquid and solid solution of Ga, As and P is regular or sub-regular, and that the gas phase is ideal. The theory of regular solution is now applied to the present system.

Consider the thermodynamic properties of As and P located in the left hand side of the apparatus shown in Fig. 3. The integral molar free energy of mixing of the solid solution ΔG_M containing the two components may be expressed⁽¹¹⁾ by

$$\begin{aligned} \Delta G_M(\text{As} - \text{P Binary}) &= RT_c \sum_i \ln a_i^{sc} \\ &= X_{As}^{sc} X_P^{sc} \mathcal{Q}_{AsP^s} + RT(X_{As}^{sc} \ln X_{As}^{sc} + X_P^{sc} \ln X_P^{sc}), \end{aligned} \quad (4)$$

where X and a are the mole fraction and activity of the component respectively, \mathcal{Q}_{AsP^s} is the quasi-chemical interchange energy per gr-atom between As and P in the solid phase, R is the gas constant, and T is the absolute temperature. By applying the Duhems differential relation to Eq. (4), the activities a_{As}^{sc} and a_P^{sc} may be expressed by

$$\ln a_{As}^{sc} = \ln X_{As}^{sc} + (1 - X_{As}^{sc})^2 \mathcal{Q}_{AsP^s}/RT, \quad (5\text{-a})$$

$$\ln a_P^{sc} = \ln X_P^{sc} + (1 - X_P^{sc})^2 \mathcal{Q}_{AsP^s}/RT, \quad (5\text{-b})$$

where the upper subscripts sc and gc refer to the condensed phase and the gas phase respectively in the left side.

When the gas and solid phases coexist in equilibrium at temperature T_c , the congruent chemical potential of each component may be expressed as follows:

$$\mu_i^{sc}(\text{As} - \text{P Binary}, T_c) = \mu_i^{gc}(\text{Gas}, T_c), \quad i = \text{As}, \text{P} \quad (6)$$

Then activities of each component in the solid solution can be represented in terms of the corresponding partial pressure of some molecular species in the gas phase.

$$a_{As}^{sc} = [P_{As4}(T_c)/P_{As4}^0(T_c)]^{1/4} = [P_{As2}(T_c)/P_{As2}^0(T_c)]^{1/2}, \quad (7\text{-a})$$

$$a_P^{sc} = [P_{P4}(T_c)/P_{P4}^0(T_c)]^{1/4} = [P_{P2}(T_c)/P_{P2}^0(T_c)]^{1/2}, \quad (7\text{-b})$$

where P_i is the partial pressure above the saturated solution and P^0 is the pressure above pure substance.

In a similar way, the thermodynamic properties of the components located in the right side of the apparatus (Fig. 3) may be derived by assuming that chemical equilibrium among the three phases is established. It follows that the ternary integral

molar energy of mixing may be given as

$$\Delta G_M(\text{Ternary Liquid}) = X_{Ga}^{lh} X_{As}^{lh} \mathcal{Q}_{GaAs}^l + X_{Ga}^{lh} X_P^{lh} \mathcal{Q}_{GaP}^l + X_{As}^{lh} X_P^{lh} \mathcal{Q}_{AsP}^l \\ + RT_h (X_{Ga}^{lh} \ln X_{Ga}^{lh} + X_{As}^{lh} \ln X_{As}^{lh} + X_P^{lh} \ln X_P^{lh}). \quad (8)$$

The activities a_{Ga}^{lh} , a_{As}^{lh} , and a_P^{lh} may be analytically expressed as follows.⁽¹¹⁾

$$\ln a_{Ga}^{lh} = \ln X_{Ga}^{lh} + [(\mathcal{Q}_{GaAs}^l X_{As}^{lh} + \mathcal{Q}_{GaP}^l X_P^{lh}) \\ (X_{As}^{lh} + X_P^{lh}) - \mathcal{Q}_{AsP}^l X_{As}^{lh} X_P^{lh}] / RT_h, \quad (9-a)$$

$$\ln a_{As}^{lh} = \ln X_{As}^{lh} + [(\mathcal{Q}_{GaAs}^l X_{Ga}^{lh} + \mathcal{Q}_{AsP}^l X_P^{lh}) \\ (X_{Ga}^{lh} + X_P^{lh}) - \mathcal{Q}_{GaP}^l X_{Ga}^{lh} X_P^{lh}] / RT_h, \quad (9-b)$$

$$\ln a_P^{lh} = \ln X_P^{lh} + [(\mathcal{Q}_{GaP}^l X_{Ga}^{lh} + \mathcal{Q}_{AsP}^l X_{As}^{lh}) \\ (X_{Ga}^{lh} + X_{As}^{lh}) - \mathcal{Q}_{GaAs}^l X_{Ga}^{lh} X_{As}^{lh}] / RT_h. \quad (9-c)$$

The condition for the chemical equilibrium between liquid and gas phase is found to be

$$\mu_i^{lh}(\text{Ternary Liquid}, T_h) = \mu_i^{gh}(G_{as}, T_h), \quad i = Ga, As, P. \quad (10)$$

Neglecting the partial pressure of Ga, the partial pressures of As_4 , As_2 , P_2 and P_4 are related to the activities of As and P by

$$a_{As}^{lh} = [P_{As4}(T_h)/P_{As4}^0(T_h)]^{1/4} = [P_{As2}(T_h)/P_{As2}^0(T_h)]^{1/2}, \quad (11-a)$$

$$a_P^{lh} = [P_{P4}(T_h)/P_{P4}^0(T_h)]^{1/4} = [P_{P2}(T_h)/P_{P2}^0(T_h)]^{1/2}. \quad (11-b)$$

Stringfellow et al.⁽¹³⁾ show that the chemical potentials for III-V compounds, for example, $GaAs_{1-x}P_x$ are expressed as follows,

$$\mu_{GaAs}^{sh} = \mu_{GaAs}^{sh0} + RT_h \ln a_{GaAs}^{sh}, \quad (12-a)$$

$$\mu_{GaP}^{sh} = \mu_{GaP}^{sh0} + RT_h \ln a_{GaP}^{sh}, \quad (12-b)$$

Assuming that the quasi-binary solution between the component GaAs and GaP is regular, activity of GaAs is expressed as $\ln a_{GaAs}^{sh} = X^2 \mathcal{Q}_s / RT_h + \ln(1-X)$, and that of GaP as $\ln a_{GaP}^{sh} = (1-X)^2 \mathcal{Q}_s / RT_h + \ln X$, where \mathcal{Q}_s is interaction energy parameter between GaAs and GaP.

The conditions for the chemical equilibrium between such solid and liquid phases are represented as follows,

$$\mu_{GaAs}^{sh} = \mu_{Ga}^{lh} + \mu_{As}^{lh} \quad (13-a)$$

$$\mu_{GaP}^{sh} = \mu_{Ga}^{lh} + \mu_P^{lh}. \quad (13-b)$$

There are such relationships in a section of quasi-binary system that $x_{Ga}^{lh} = 0.5$,

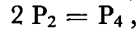
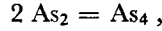
$x_{As}^{lh} + x_P^{lh} = 0.5$, and then substituting Equation (9) and (12) into (13),

$$\ln(1 - X) + X^2 \Omega_s / RT_h = \ln(1 - 2X_P^{lh}) + (2X_P^{lh})^2 \Omega_{AsP} / 2RT_h + \Delta G_{fGaAs} / RT_h \quad (14-a)$$

$$\ln X + (1 - X)^2 \Omega_s / RT_h = \ln(2X_P^{lh}) + (1 - 2X_P^{lh})^2 \Omega_{AsP} / 2RT_h + \Delta G_{fGaP} / RT_h \quad (14-b)$$

in the quasi-binary section. Therefore we can find numerically the equilibrium condition between ternary liquid and solid phase, when these parameters in the equations above are known.

On the other hand, for the reactions in the gas phase,



then, the equilibrium constants, K_{As} and K_P may be defined as

$$K_{As} = P_{As4} / [P_{As2}]^2, \quad (15-a)$$

$$K_P = P_{P4} / [P_{P2}]^2, \quad (15-b)$$

where the total pressures of As and P, P_{AsT} and P_{PT} , are expressed as

$$P_{AsT} = P_{As2} + P_{As4},$$

$$P_{PT} = P_{P2} + P_{P4}.$$

Upon substituting Eqs. (7) and (11) into Eq. (3), one obtains

$$\ln \frac{P_{AsT}^0(T_c)}{P_{AsT}^0(T_h)} + 4 \ln \frac{a_{As}^{sc}}{a_{As}^{lh}} + \ln \frac{S_{As4}(T_c) w(\text{As, sc}, T_c)}{S_{As4}(T_h) w(\text{As, lh}, T_h)} = 0, \quad (16-a)$$

$$\ln \frac{P_{PT}^0(T_c)}{P_{PT}^0(T_h)} + 4 \ln \frac{a_P^{sc}}{a_P^{lh}} + \ln \frac{S_{P4}(T_c) w(\text{P, sc}, T_c)}{S_{P4}(T_h) w(\text{P, lh}, T_h)} = 0, \quad (16-b)$$

where

$$w(i, m, T) = 1 + \frac{P_{i2}^0(T)}{P_{iT}^0(T)} \frac{S_{i2}(T) - S_{i4}(T) \{a_i^m(T)\}^2}{S_{i4}(T) \{a_i^m(T)\}^2}$$

Eqs. (16-a) and (16-b) represent the fundamental relations of equation (3) for the pseudo-equilibrium between the binary solid phase at the T_c part and the ternary liquid phase at the T_h part.

In order to crystallize out the quasi-binary compound with a composition of X_P^{sh} at the higher temperature part T_h , the composition X_P^{lh} of a quasi-binary liquid which is in equilibrium with the compound must be firstly determined from equation

(14) or Fig. 4, and then the composition $X_p^{s,c}$ and temperature T_c for the condensed phase have also to be calculated using the condition for pseudoequilibrium shown by equation (16). These numericals are calculated in the following paragraph.

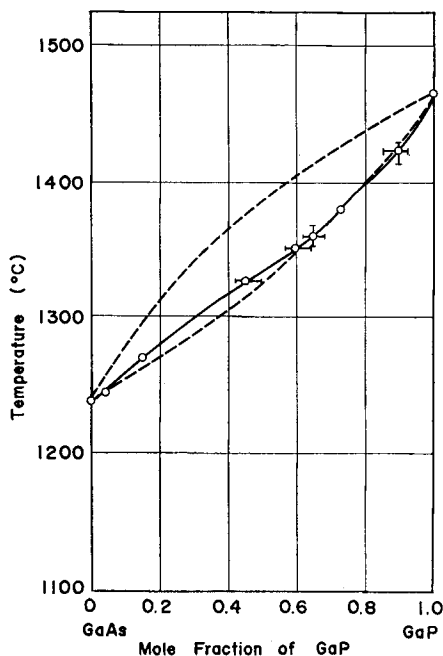


Fig. 4. Phase diagram of GaAs-GaP quasi-binary system⁶. Solid and dotted lines show the experimental data and theoretical curves, respectively.

Here, the process for preparation of the crystalline solid solutions by the experiment may be summarized as follows. When each furnace reaches each constant temperature and is held for an enough time, a quasi-binary liquid phase, an infinitely small quantity of a quasi-binary solid solution crystalline and gaseous phase will coexist in the T_h part, while a binary solid solution and gaseous phase will exist in the T_c part. Under these conditions any net atom flow does not occur, because a steady state would be set up as described already in detail. When the sample boat was then moved, solidification of a quasi-binary solid solution will start from the top part probably at the temperature of 1 or 2 °C lower than T_h , because of the relatively slower temperature gradient in the top part. When a compound is crystallized out, the composition of a quasi-binary liquid will change, and so a balance for distribution of substance in the system will break for a moment, and then, at the next instance, the pseudo-equilibrium will return to be set up, because the growth rate of an ingot

is slow enough to maintain the pseudo-equilibrium in the system. It is possible to produce a homogeneous ingot along the growth direction by controlling the experimental conditions. This will be discussed in detail later.

IV. Numerical Analysis

In order to analyze numerically the above pseudo-equilibrium, it is necessary to know their parameters. The data on the vapour pressure over the pure elements of Table 2 is used to analyze the pseudo-equilibrium state. The molecular species of the pure elements listed in Table 2 are thought to consist of four atoms as studied by various authors in the low temperature measurements.

Table 2. Vapour Pressures and Equilibrium Constants for Arsenic and Phosphor.

| | Log P_i (atm) | | Log K_i |
|----------|--------------------------|----------------------------|-------------------------|
| | Solid | Liquid | |
| Arsenic | $-7357/T + 8.279^{(14)}$ | $-2450/T + 3.800^{(14)}$ | $15360/T - 8.29^{(16)}$ |
| Phosphor | $-6322/T + 8.958^{(15)}$ | $-2757.5/T + 5.073^{(14)}$ | $7518/T - 4.938^{(14)}$ |

In general, an interaction energy parameter Ω is independent of composition and temperature in a regular solid solution. However, in real binary liquids such as Ga-As and Ga-P, it is found to depend on temperature, and in such solutions Ω is expressed as $\Omega = \alpha - \beta T$. We call these solutions sub-regular ones, because it could be treated similarly as a regular solution within the limits of the present experimental conditions. The following values given by Thurmond⁽¹⁸⁾ were used.

$$\Omega_{GaAs}^l = 9969 - 11.15 T \quad (17-a)$$

$$\Omega_{GaP}^l = 7900 - 7.00 T \quad (17-b)$$

The dimension of Ω is cal/g mol. The parameter of the binary solid solution was calculated as

$$\Omega_{AsP}^s = 2000. \quad (18)$$

On the other hand, it was assumed that the value of Ω_{As-P}^l is zero at a higher temperature than 1500°K.

The dotted curves in Fig. 4 indicate the ideal solidus and liquidus lines calculated on the assumption of the molecular-like model of Ga-As or Ga-P atomic pairs. In this diagram, the experimental values indicated by open circles are in good agreement with the calculated solidus line. In addition, it is well known that the change of lattice parameter vs. composition for the GaAs-GaP system obeys Vegard's law.

Thus it is reasonable to consider that the solid solution behaves like an ideal one. Therefore, Ω_s can be taken to be approximately zero.

The free energy change* due to fusion for GaAs and GaP are expressed in the following:

$$\Delta G_{fGaAs} = 23380 - 15.47 T \quad (19-a)$$

$$\Delta G_{fGaP} = 28242 - 16.25 T \quad (19-b)$$

where the dimension of ΔG is cal/mol.

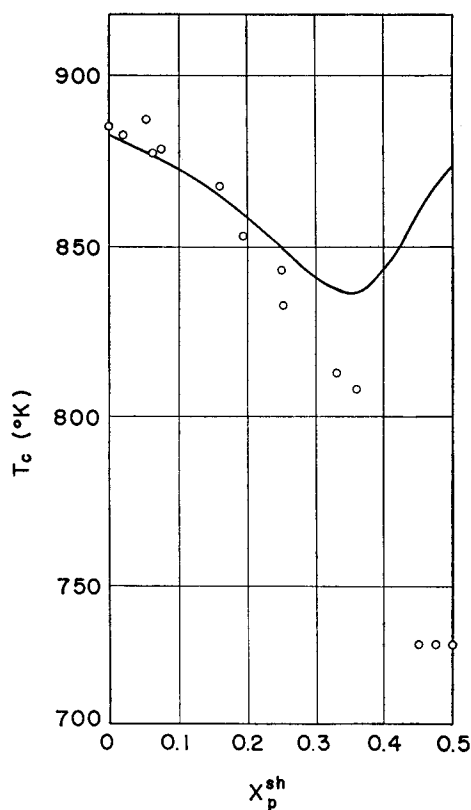


Fig. 5. Temperature in the T_c part required to obtain the crystalline solid solution of mole fraction X_p^{sh} . The solid line shows the theoretical curves. Open circles are the values obtained experimentally.

* The change in the free energy due to fusion is expressed as $\Delta G_f = \Delta H_f - T\Delta S_f$. Taking that the melting temperature for a compound is T_m , that is $\Delta H_f = T_m\Delta S_f$. Then, ΔS_f was computed as 15.47 and 16.25 e.u. for GaAs and GaP respectively, taking entropy of fusion for Ga and Si as a standard state.

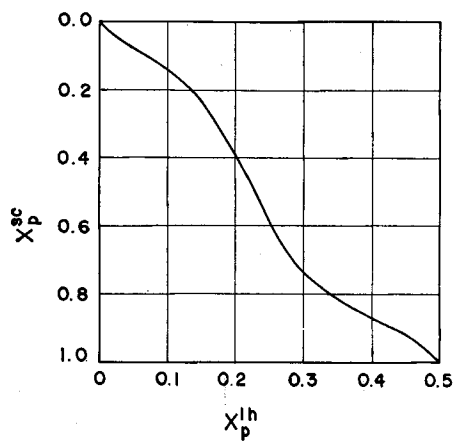


Fig. 6. Distribution of P in two phases (sc) and (lh) necessary to hold the pseudo-equilibrium.

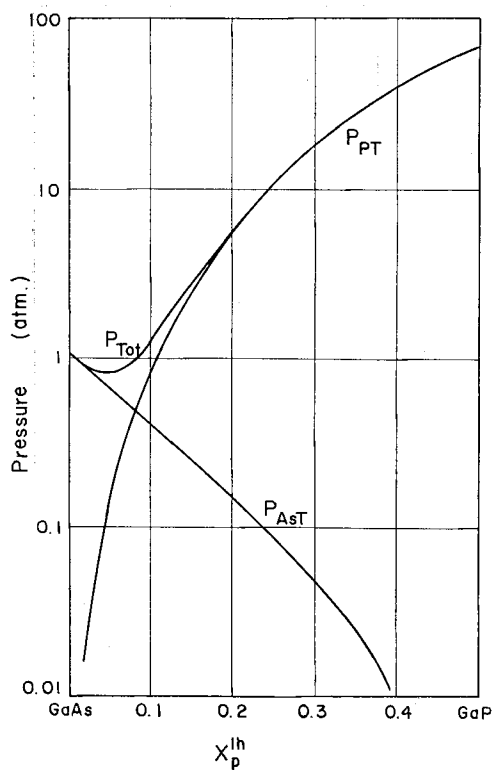


Fig. 7. Theoretical equilibrium partial and total pressures of As and P along the liquidus curve.

Using various values discussed above, the composition of crystalline solid solution equilibrated with the corresponding ternary liquid can be found from equation (14). Then, various thermodynamic parameters of the system in pseudo-equilibrium can be computed from equation (16). Fig. 5 shows the temperature T_c , which corresponds to the temperature in the lower temperature part, which is required to get the composition X_P^{sh} . The solid line shows the theoretical curve and open circles are the values obtained experimentally. Fig. 6 shows the composition X_P^{sc} as a function of composition X_P^{sh} . These theoretical values are given compared with the experimental conditions in Table 1. Fig. 7 indicates the equilibrium partial and total pressures of As and P on the liquidus line in the quasibinary section.

V. Discussion

In the present work, the method for preparation of the crystalline solid solution of $GaAs_{1-x}P_x$ in the whole composition range between GaAs and GaP from the melt has been developed by controlling vapour pressures of As and P. The crystal structure and lattice parameters of the ingot which are polycrystalline were examined by means of powder X-ray method. Compounds thus obtained were confirmed to have the zinc-blende type crystal structure and exhibit a high degree of homogeneity perpendicular to the growth direction. From the experimental results of optical properties by using these compounds, the composition dependence of the absorption edge of the compounds were found to be in good agreement with the results reported by other authors. This could be strong evidence for their having a stoichiometric composition. The homogeneity of the compounds was also confirmed by the experiments⁽¹⁹⁾ of electronic transitions between different energy bands. As shown in Fig. 2, the composition along the growth direction remains constant or changes gradually depending upon the preparation conditions. Several important points used to obtain a homogeneous ingot with the desired composition by the present technique will now be discussed as follows.

It is found that, between $2X_P^{sh}$ (ingot) and T_c^{exp} , there is a definite tendency that the higher values of T_c^{exp} produces the lower values of $2X_P^{sh}$ and vice versa. When comparing sample No. 3 with No. 4, the conditions of an experiment is nearly the same except for T_c^{exp} . Temperature dependence of vapour pressures of As and P are expressed by

$$d \ln P_{AsT}/dT \cong (16940 - 4000 X_P^{sc})/T^2 \quad (20-a)$$

$$d \ln P_{PT}/dT \cong (1050 + 4000 X_P^{sc})/T^2 \quad (20-b)$$

From these equations, it is clear that the vapour pressure of As is larger than that of

P in the range of smaller X_P^{sc} . The value of T_c^{exp} for sample No. 4 is higher than that for No.3, and therefore this results in higher concentration of As in gaseous phase, which would produce higher concentration of As in the quasi-binary solid solution through an effect upon the quasi-binary liquid at T_h part.

Moreover, comparing sample No. 5 with No. 6 whose experimental condition is similar to No. 5, values of N_{Ga} , N_{As} and N_P are different, while values of X_P^{sc} , $2X_P^{lh}$, $2X_P^{sh}$ and T_h^{exp} are the same. The difference between No. 5 and 6 is about 10°K and its average is 873°K , and the average value of $2X_P^{sh}(\text{ingot})$ is 0.227, which is in good agreement with the calculated value. Such a slight change near by $T_c^{cal}=873^\circ\text{K}$ which is calculated theoretically affects $2X_P^{sh}(\text{ingot})$, and these effects could be explained qualitatively in terms of temperature dependence of vapour pressures. Experiments were carried out along the calculated values in the range of lower values of X_P^{sh} , while lower temperatures were intentionally adopted in the case of higher values of X_P^{sh} to decrease vapour pressures. Let us consider the X_P^{sh} dependence of the temperatures T_c^{cal} calculated theoretically. The data on the vapour pressures over the pure elements would affect directly the results of numerical analysis. The value of As vapour pressure has been adopted from the paper reported by Thurmond. Then the condition for the direct growth of GaAs from the melt was calculated as $T_c=882^\circ\text{K}$ and the vapour pressure over the GaAs melt is 1.04 atm. The values are the very same as the data reported by the other authors. On the other hand, the values were calculated to be $T_c=873^\circ\text{K}$ and $P_{GaP}=58.3$ atm. Frosch et al. reported that the total pressure at the melting point of GaP is about 25 atm. Since the value of P vapour pressure employed in the present analysis was adopted from the data determined at the lower temperature by various authors, the numerical results would contain a systematic error. The value of interaction energy parameter was adopted from the data reported by Thurmond, showing that plots of \mathcal{Q} versus T are largely scattered and therefore, the value of \mathcal{Q}_{GaP}^1 could not be an exact one. From these considerations, the equilibrium partial and total vapour pressures would be the lower ones. Therefore, the value of T_c corresponding to the composition X_P^{sh} seems to be lower in GaP side. It might be suggested that the temperatures T_c^{exp} which are given for No. 12, 13 and 14, are much lower than the expected ones, and that the composition of the ternary liquid could deviate from the quasi-binary section. However, judging from the fact that the compositions of ingots are very close to the calculated ones, the molar fraction of Ga in a ternary liquid phase seems to correspond to about 0.5.

Fig. 8 shows the relation between $X_P^{sh}(\text{ingot})$ and X_P^{sh} which was initially determined, where the solid line means a coincidence of the theoretical consideration with the experiments. Relatively large deviation of the experimental points is

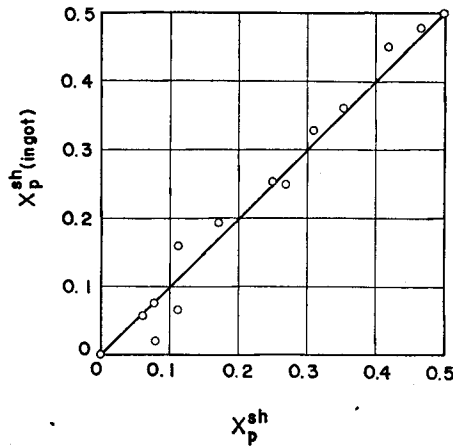


Fig. 8. Coincidence between the theoretical consideration and experiments, where $X_{P^{sh}}(\text{ingot})$ is the composition of ingot determined by the powder X -ray method and $X_{P^{sh}}$ is the initially determined composition in conjunction with the concept of the pseudo-equilibrium.

observed in the neighbourhood of $X_{P^{sh}}=0.1$, and the direction of the deviation could be explained qualitatively in terms of temperature variation in T_c part. As shown clearly in Fig. 4, since the composition change of $dX_{P^{sh}}/dX_{P^{lh}}$, becomes large in the case of small $X_{P^{sh}}$, and consequently relatively large deviation of the composition of the solid phase will be induced by the small change of compositions in the quasi-binary liquid phase in GaAs side, the apparent degree of deviation is observed to become large when $X_{P^{sh}}$ is small. The fact that the experimental data are located around the solid line in Fig. 5 will prove that the composition of the ternary liquid which is in equilibrium with the quasi-binary compound at the higher temperature part exists in or very near the quasi-binary section. Therefore, it would be reasonable to consider that the pseudo-equilibrium is set up between the ternary Ga-As-P system and the binary As-P system.

The change of composition along the direction of growth will be considered in the following. As solidification proceeds, the liquid composition shifts generally along the liquidus surface, and not necessarily along the liquidus line of the quasi-binary section. However, since mass transfer occurs from the As-P binary solid solution according to the condition of the pseudo-equilibrium in the present case, it is possible to control the growth of a compound with homogeneity by compensating variation of the composition of the melt in higher temperature part, provided that sufficiently large amounts of As and P are put in T_c part. For example, the experiments for sample No. 5, 8 and 10 show a tendency to satisfy such a condition.

The moving rate of the boat would be controlled as slow as possible in order to solidify under a condition of the pseudo-equilibrium, but it was concluded that the moving rate of 1 cm/hr is sufficient to obtain a sound and homogeneous compound.

VI. Summary

A method has been developed for a preparation of $\text{GaAs}_{1-x}\text{P}_x$ compounds. As shown in Table I, $\text{GaAs}_{1-x}\text{P}_x$ compounds in the whole range between GaAs and GaP were obtained from the melt in the present work. The compounds are confirmed to have exact stoichiometric compositions of a zinc-blende type, and to exhibit a high degree of homogeneity perpendicular to the growth direction. It is also possible to obtain an ingot with homogeneous composition along the growth direction under suitable conditions.

The theoretical formulae were derived in order to calculate the pseudo-equilibrium in a heterogeneous system consisting of two parts with different temperatures, which was based on an assumption that there is no net flow of atoms in either direction between T_c and T_h parts. The equilibrium has been concluded to exist between the Ga-As-P ternary system and the As-P binary system under suitable conditions.

The authors wish to express their hearty appreciation to Prof. T. Senoo, University of Tokyo, and Prof. K. Igaki, Tohoku University for their valuable discussion.

References

- 1) O. G. Folberth: *Z. Naturforsch.*, 10 (1955), 502.
- 2) W. Koster and W. Ulrich: *Z. Metallk.*, 49 (1958), 365.
- 3) O. V. Bogorodskii, A. Yanashel'skii and V. Z. Ostrovskaya: *Sov. Phys. Cryst.*, 6 (1961), 95.
- 4) M. B. Panish: *J. Phys. Chem. Solids*, 30 (1969), 1083.
- 5) G. A. Antypas: *J. Electrochem. Soc.*, 117 (1970), 700.
- 6) D. Richman: *J. Phys. Chem. Solids*, 24 (1963), 1131.
- 7) C. J. Frosch and L. Derick: *J. Electrochem. Soc.*, 108 (1961), 251.
- 8) K. Osamura and Y. Murakami: *Japan. J. Appl. Phys.*, 8 (1969), 967.
- 9) M. E. Straumains, J-P. Krumme and M. Rubenstein: *J. Electrochem. Soc.*, 114 (1967), 640.
- 10) H. Krebs, W. Holz and K. W. Worms: *Chem. Ber.*, 90 (1958), 1031.
- 11) R. A. Swalin: *Thermodynamics of Solids*, John Wiley and Sons, New York, (1963).
- 12) Y. Furukawa and C. D. Thurmond: *J. Phys. Chem. Solids*, 26 (1965), 1535.
- 13) G. B. Stringfellow and P. E. Greene: *J. Phys. Chem. Solids*, 30 (1969), 1779.
- 14) A. N. Nesmeyanov: *Vapor Pressure of the Chemical Elements*, Elsevier Publishing Company, (1963).
- 15) R. E. Honig: *RCA Review*, (1962), 567.
- 16) J. Drowart and P. Goldfinger: *J. chem. phys.*, 55 (1958), 721.
- 17) C. D. Thurmond: *J. Phys. Chem. Solid*, 26 (1965), 785.
- 18) J. R. Arthur: *J. Phys. Chem. Solids*, 28 (1967), 2257.
- 19) K. Osamura and Y. Murakami: *J. Phys. Soc. Japan*, 26 (1969), 1063.