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Centro de Estudios de Semiconductores, Departamento de Física, Facultad de Ciencias, Universidad de Los Andes, Mérida [1])

$T(z)$ Phase Diagram of the $CuIn(Se_zTe_{1-z})_2$ Alloys

By

M. QUINTERO, R. TOVAR, E. GUERRERO, F. SÁNCHEZ, and J. C. WOOLLEY [2])

The $T(z)$ phase diagram of the system $CuIn(Se_zTe_{1-z})_2$ is obtained from X-ray diffraction and differential thermal analysis (DTA) measurements. DTA measurements are carried out on each sample and the transition temperatures are plotted as a function of alloy composition. Values of lattice parameter are determined in all the cases. Values of the optical energy gap at 300 and 70 K are obtained from optical absorption measurements.

Mittels Röntgenbeugungsmessungen und Differentialthermoanalyse (DTA) wird das $T(z)$-Phasendiagramm des Systems $CuIn(Se_zTe_{1-z})_2$ erhalten. DTA-Messungen werden an jeder Probe durchgeführt, und die Übergangstemperatur wird als Funktion der Legierungszusammensetzung aufgetragen. In allen Fällen werden die Werte der Gitterparameter bestimmt. Die Werte der optischen Energielücke bei 300 und 70 K werden aus optischen Absorptionsmessungen bestimmt.

1. Introduction

Considerable interest has been shown in the chalcopyrite I–III-VI_2 compounds and alloys because of their potential applications in optoelectronic and nonlinear optical devices [1]. Although many studies have been carried out on the growth, crystal structure, and electrical and optical properties of these materials, information related to the phase diagram and thermodynamical properties is scarce, especially in alloys involving a combination of selenium and tellurium. The pseudobinary alloys $CuIn(Se_zTe_{1-z})_2$ form the section $x = 0$ of the general diagram $CuIn(S_xSe_yTe_{1-x-y})_2$ which was studied by Quintero and Woolley [2], who determined the ranges of single phase solid solutions and lattice parameter values over the complete composition range. More recently, the phase diagram of the section $y = 0$, i.e. $CuIn(S_xTe_{1-x})_2$, was reported [3], but experimental data on the phase transition temperatures of the section $x = 0$ are not available in the literature. In the present work, the phase diagram of the $CuIn(Se_zTe_{1-z})_2$ system has been studied by means of X-ray diffraction and differential thermal analysis (DTA).

2. Sample Preparation and Experimental Investigations

Alloy samples of different compositions were prepared by the standard melt and anneal technique [2]. The components of each 1.0 g sample were sealed under vacuum in a quartz capsule, melted together at 1150 °C and then annealed to equilibrium at 600 °C, this temperature being chosen from a consideration of the known transition temperatures for $CuInTe_2$ [4] and $CuInSe_2$ [5]. X-ray photographs, either Debye-Scherrer or Guinier, were

[1]) Merida 5101, Venezuela.

[2]) Permanent address: Physics Department, University of Ottawa, Ottawa, Ontario K1N 6N5, Canada.

used to check the conditions of each sample. It was found that annealing times of one month were sufficient to give equilibrium conditions in each sample. In each case, a single phase of chalcopyrite structure was found and lattice parameter values were determined as a function of the composition variable.

Transition temperatures were obtained from DTA measurements with silver or gold used as reference materials. The charge was of powdered alloy of typical weight 50 to 100 mg. The temperature of the sample and that of the reference were determined with chromel–alumel thermocouples, the difference signal between sample and reference and the temperature signal being simultaneously continuously recorded. For each peak in the difference signal, a phase transition temperature was determined from the baseline intercept of the tangent to the peak [6]. Both heating and cooling runs were made, the average rates of heating and cooling being approximately 15 K/min.

Slices of each sample were cut and thinned down to give specimens for optical absorption measurements by the usual method [2]. These measurements were carried out at 300 and 70 K. Values of $\ln (I_0/I_t)$ were determined as a function of photon energy hv and corrected by subtracting a background value to give the absorption coefficient α. The relation $(\alpha hv)^2 = C(E_0 - hv)$, applicable to direct gap transitions, was then used to obtain a value for the optical energy gap E_0.

3. X-Ray Results

In all cases, the X-ray photographs showed each sample to be single phase with chalcopyrite structure and lattice parameter ratio $c/a = 2$. Values of the lattice parameter a were determined in all cases and these values are shown as a function of z in Fig. 1. The probable error in a is estimated to be ± 0.0005 nm which is the value shown by the circles in Fig. 1. It is seen from Fig. 1 that the value of a decreases from 0.6201 nm for $z = 0$, i.e. $CuInTe_2$, to 0.5781 nm for $z = 1.0$, i.e. $CuInSe_2$, and that, within the limits of experimental error, the variation of a with z follows a linear Vegard behavior over the whole composition range.

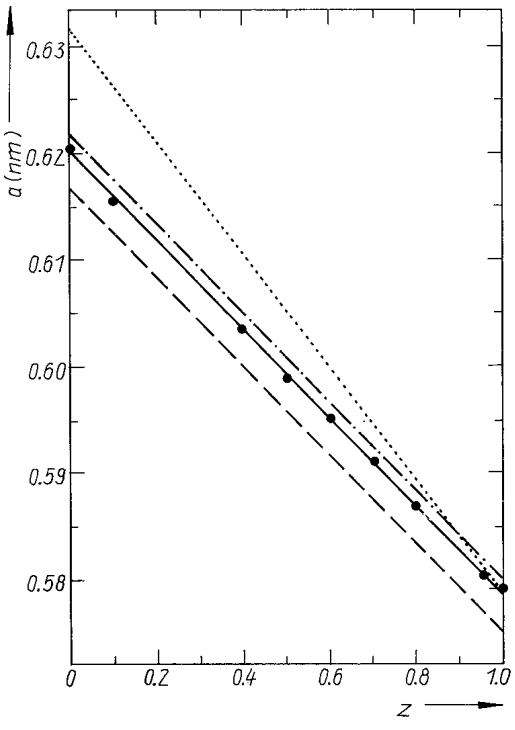

Fig. 1. Variation of lattice parameter a with z for the $CuIn(Se_zTe_{1-z})_2$ alloys. Solid line fitted curve, dashed line predicted values using Phillips radii, dash-dotted line predicted values using Pauling radii, dotted line predicted values using Shannon-Prewitt radii

For interpolation purposes, the variation of a versus z was fitted to a linear equation in z, giving

$$a = 0.6202 - 0.04196z \text{ (nm)}$$

with a standard deviation of the fitted points of 0.0006 nm.

4. DTA Results

DTA measurements were made on each sample as indicated above and the resulting variation of the transition temperatures with composition z is shown in Fig. 2. In this figure, the average relative accuracy in the points is estimated to be ± 10 K. It is observed that for $z = 0$ phase transitions occur at 660 and 780 °C. These values are in good agreement with those reported earlier by Palatnik and Rogacheva [4], and are attributed to the chalcopyrite α to zincblende β and to the β to liquid L transitions, respectively. In the case of $z = 1.0$ the values are in good agreement with the results of Manca and Garbato [5], being 810 and 982 °C for α to β and β to L transitions, respectively.

With regard to the alloys, it is seen from Fig. 2 that both α and β phase fields extend across the complete composition range and are separated by relatively wide (α + β) two-phase field. The β-phase field is wider at the terminal edges of the composition diagram. At temperatures above the limits of the β-phase, there is a wide (L + β) two-phase field. This field achieves a maximum width of ≈ 80 K at $z \approx 0.5$.

5. Energy Gap Results

Optical absorption measurements were made on each sample at 300 and 70 K and values of E_0 were determined as indicated above. The resulting variations of the fundamental energy gap E_0 versus z for 300 and 70 K are shown in Fig. 3. The relative accuracy of the E_0 values is approximately ± 0.005 eV. It is seen from Fig. 3 that the present values of E_0 for each temperature can, within the limits of experimental error, be fitted to a parabolic form $E_0 = A + Bz + Cz^2$ giving

$$E_0 = 0.949 - 0.419z + 0.429z^2 \text{ (eV)} \quad \text{for} \quad 300 \text{ K},$$
$$E_0 = 1.002 - 0.412z + 0.420z^2 \text{ (eV)} \quad \text{for} \quad 70 \text{ K}$$

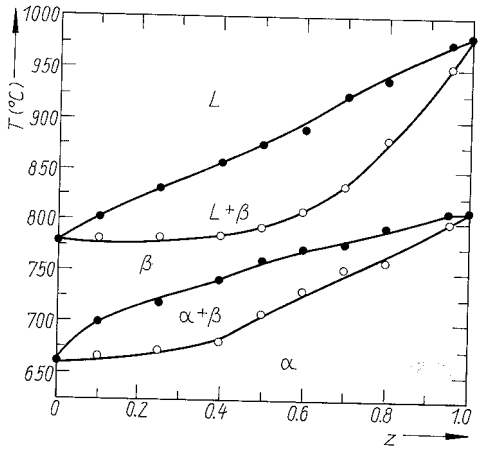

Fig. 2. $T(z)$ diagram for the $CuIn(Se_zTe_{1-z})_2$ alloys. α is the chalcopyrite and β the zincblende structure. ○ Heating run, ● cooling run

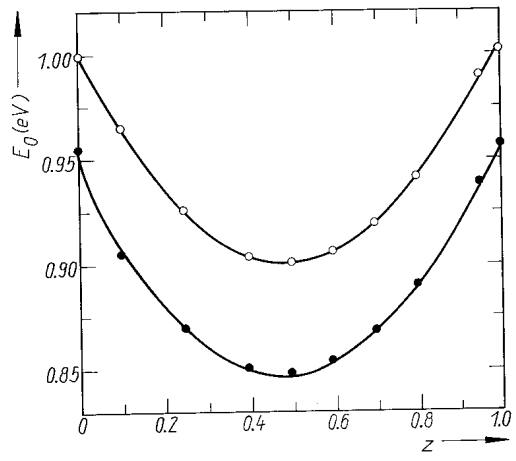

Fig. 3. Variation of optical energy gap E_0 for $CuIn(Se_zTe_{1-z})_2$ alloys. ● 300 K, ○ 70 K, solid lines curves fitted to $E_0 = A + Bz + Cz^2$

with standard deviation of the fitted points of 0.0035 and 0.0012 eV for 300 and 70 K, respectively.

6. Discussion

Jaffe and Zunger [7] have proposed a method for determining the values of lattice parameters a and c without using ternary compound data, the various crystallographic parameters being related to the atomic radii of the constituent elements. In terms of the appropriate radii r_A, r_B, and r_C, Jaffe and Zunger give the following relations:

$$a^2 = \frac{12\alpha^2}{2\beta + \alpha - |(2\beta + \alpha)^2 - 18\alpha^2|^{1/2}}, \tag{1}$$

$$n^2 = \frac{8(\beta - \alpha)}{3a^2}, \tag{2}$$

$$u = \frac{1}{2} - \frac{1}{4|2n^2 - 1|}, \tag{3}$$

$$\alpha = (r_A + r_C)^2 - (r_B + r_C)^2, \tag{4}$$

$$\beta = (r_A + r_C)^2 + (r_B + r_C)^2, \tag{5}$$

and $n = c/2a$. These equations can be solved to give values of lattice parameters a, c and the anion displacement u, and these values can then be compared with experimental data. Attempts were made in the present work to determine from the X-ray data values of the anion displacement u (from the ideal position 1/4). However, because the number of lines available in the powder technique was small and intensities could not be determined with high accuracy, it was not possible to obtain any reasonable experimental estimate of the parameter u.

In alloys of the present type, it was suggested [7] that r_A, r_B, and r_C can be taken as the weighted mean of the appropriate atoms, i.e.

$$r_A = r_{Cu}, \qquad r_B = r_{In}, \qquad r_C = z r_{Se} + (1 - z) r_{Te}.$$

Equations (1) to (5) have been solved for three different sets of atomic radii, viz. those of Pauling [8], Phillips [9], and Shannon and Prewitt [10] and these values are given in Table 1.

Table 1
Values of tetrahedral radii used in the analysis

	Pauling	Phillips	Shannon-Prewitt
r_{Cu} (nm)	0.135	0.1225	0.0635
r_{In} (nm)	0.144	0.1405	0.0765
r_{Se} (nm)	0.114	0.1225	0.1840
r_{Te} (nm)	0.132	0.1405	0.2070

The resulting predicted values of a are shown in Fig. 1. It is seen from this figure that the values predicted using the Pauling radii are in good agreement with the experimental values, while those from Phillips radii are poorer and those from Shannon and Prewitt are poorer still. A similar analysis was made for the $AgGa(Se_{z-1}Te_z)_2$ system [11], but in that case the best fit to the measured values of a was obtained using the Phillips radii.

On the assumption that the present diagram is pseudobinary, attempts were made to analyze the results by using the standard theory of solution proposed by Vieland [13], as used previously, for example, to analyze the HgSe–HgTe phase diagram data [14]. This involves the use of known thermodynamic parameters for the compounds. However, as the interaction parameters of the liquid and solid phases are not known for the present system, it was not possible to obtain a good fit to the experimental data. Hence, work is being carried out to determine these parameters and this will be discussed elsewhere.

With regard to the optical energy gap values, it is seen that the bowing parameter $C = 0.42$ is independent of temperature. This bowing of the E_0 versus composition curve was discussed for the alloys of zincblende compounds by Van Vechten and Bergstresser [12] and Jaffe and Zunger [7] extended this analysis to alloys of the related chalcopyrite compounds. They suggested that the bowing will be appreciable when the cations are varied, but small when anions are varied as in the present case. In recent work [11] and [15], optical absorption measurements were made to determine values of E_0 for several other similar $I–III–VI_2$ chalcopyrite alloys. It was found that for the cases of mixed cations the bowing parameter C was less than 0.05, while for the case of mixed anions the bowing parameter was found to be about 0.36. From these values of C and the value found here, it appears that the suggestion of Jaffe and Zunger does not apply for this type of alloy.

7. Conclusion

The X-ray experimental data confirm that single-phase solid solution of chalcopyrite structure occurs across the complete composition range. The parameter a varies linearly with z, with the ratio $c/a = 2$ across the whole composition range. When the theoretical predictions of Jaffe and Zunger are considered, it is found that the use of Pauling radii gives good agreement between the calculated values of a and the experimental data. Use of Phillips or Shannon-Prewitt radii worsens the agreement between predicted and experimental values in all cases.

The DTA results show that there are only four fields involving solid phases, viz. a single solid phase β zincblende field bounded by $(L + \beta)$ and $(\alpha + \beta)$ fields and a single solid phase field of α chalcopyrite structure.

The values of optical energy gap E_0 can be fitted to a second-order equation in z giving a bowing parameter of 0.41. Comparison with similar alloy systems indicates that the variation of E_0 with composition shows bowing of this type for mixed anions, while for the case of mixed cations the variation is close to linear.

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