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Phase Diagram and Lattice Parameter Values for the $Hg_{2x}(AgIn)_{1-x}Te_2$ Alloys

By

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Polycrystalline samples of $Hg_{2x}(AgIn)_{1-x}Te_2$ alloys are prepared by the melt and anneal technique. Differential thermal analysis (DTA) measurements are carried out on the alloys and the $T(x)$ diagram determined. Guinier X-ray powder photographs are used to show the equilibrium conditions and to give lattice parameter values. Only two single phase solid fields, the zincblende and chalcopyrite fields are found to exist in the diagram. The form of the solidus curve bounding a wide two-phase liquid plus solid field shows that the section is not pseudobinary. Microscopic and DTA data show the presence of the dissociated phase in the grain boundaries of the zinc-blende phase at temperatures below 400 °C.

Polykristalline Proben von $Hg_{2x}(AgIn)_{1-x}Te_2$-Legierungen werden mittels Schmelz- und Temperungstechnik präpariert. Thermische Differentialanalyse (DTA) wird an den Legierungen durchgeführt und das $T(x)$-Diagramm bestimmt. Guinier-Röntgen-Pulverphotographien werden benutzt, um die Gleichgewichtsbedingungen zu zeigen und Gitterparameterwerte anzugeben. Es wird gefunden, daß nur zwei Ein-Phasen-Festkörperfelder, die Zinkblende- und Chalkopyrit-Felder in dem Diagramm existieren. Die Form der Soliduskurve, die ein weites Zweiphasen-Flüssigkeits- und Festkörperfeld begrenzt, zeigt, daß der Abschnitt nicht pseudobinär ist. Mikroskopische und DTA-Werte zeigen die Anwesenheit der dissoziierten Phase in den Korngrenzen der Zinkblendephase bei Temperaturen unterhalb 400 °C.

1. Introduction

There is considerable interest in the II–VI and I–III–VI_2 compounds and their alloys, because of their potential use in technological applications such as solar-energy conversion, infrared radiation detectors, etc. [1]. Alloys of pairs of II–VI compounds have been investigated in some detail [2, 3], also mixed alloys of I–III–VI_2 compounds have received attention [4, 5]. Work on the pseudobinary I–III–VI_2–2(II–VI) has been carried out for a number of systems, e.g. $Cd_{2x}(CuIn)_{1-x}Te_2$ [6, 7], $Cd_{2x}(AgIn)_{1-x}Te_2$ [8], $Cd_{2x}(CuIn)_{1-x}Se_2$ [9], and $Zn_{2x}(CuGa)_{1-x}Te_2$ [10], but little work has been done on materials involving Hg.

The HgTe compound and its alloys are of interest as materials for infrared detectors and improvements in performance can be obtained with the addition of $AgInTe_2$. For this application, knowledge of the range of solid solubility and crystallography values of the system $Hg_{2x}(AgIn)_{1-x}Te_2$ is required. In the present work, lattice parameter values have been determined and DTA measurements have been made to give the $T(x)$ phase diagram of the system.

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2. Experimental Method

All of the alloys used were produced by the usual melt and anneal technique [11]. The components of each 1.5 g sample were sealed under vacuum in a quartz capsule and melted together at 1150 °C. As in all such multicomponent alloys, the suitable temperature of anneal is not easily determined until the $T(x)$ diagram is known for each section. In the present case, the samples were firstly annealed at approximately 500 °C in order to homogenize the material and then slowly cooled in the furnace to room temperature. These samples were used in the initial DTA measurements to give a good estimate of the $T(x)$ diagram. This indicated that a more suitable annealing temperature to obtain single phase samples was ≈ 400 °C. Samples annealed at this temperature and then cooled to room temperature were investigated by Guinier X-ray powder photographs. These allowed the equilibrium conditions of each sample to be determined. It was found that for the 400 °C anneal, annealing times of from 20 to 30 d gave samples showing good sharp X-ray diffraction lines. DTA runs on these samples confirmed the data obtained on the slowly cooled samples. Values of lattice parameters were determined as a function of the composition variables, germanium being used as an internal standard in the Guinier photographs.

The DTA measurements were made over a temperature range of 20 to 1000 °C using small quartz tubes provided with the usual re-entrant thermocouple position. The charge was approximately 100 mg for each sample and silver (melting point 961 °C) was used as the reference material.

3. DTA and X-Ray Results

Samples were prepared to cover the complete composition range in steps of approximately 0.1 in x. DTA measurements were made on all of the samples and values of the various transition temperatures for each sample were determined. The resulting $T(x)$ diagram is shown in Fig. 1 where boundaries found from DTA data only are shown as solid lines. As the DTA measurements do not give information about the various crystal structures that occur in the $T(x)$ diagram, crystallographic, and micrographic studies were carried out on the materials. The Guinier X-ray photographs showed that just two single phase solid fields occur in the composition diagram, namely the zincblence corresponding to HgTe and the chalcopyrite field corresponding to $AgInTe_2$. In the latter case, the structure was identified by line splitting which occurs because

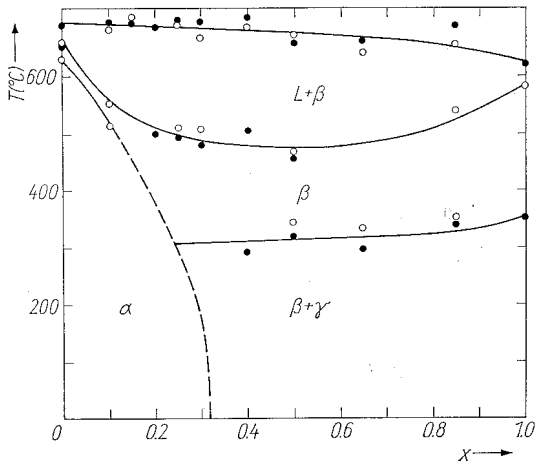

Fig. 1. $T(x)$ diagram for the $Hg_{2x}(AgIn)_{1-x}Te_2$ system. α is the chalcopyrite, β the zincblende, and γ a Hg-rich phase (see text); ○ heating run; ● cooling run

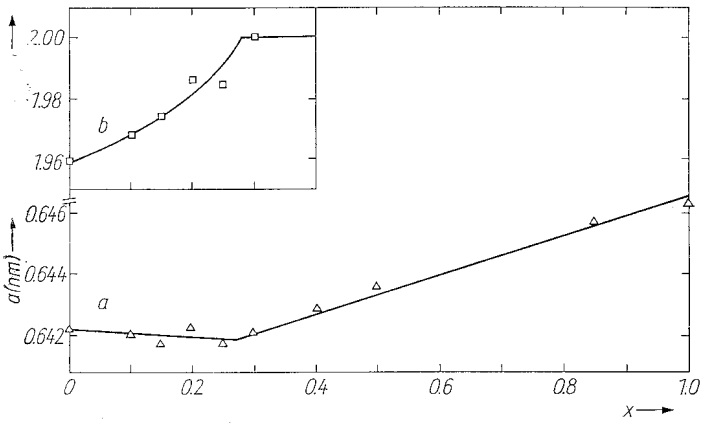

Fig. 2. a) Variation of lattice parameter a with x, b) variation of lattice parameter ratio c/a with x

$c/a \neq 2$. Appropriate lattice parameter values were determined in each case, and the variation of the parameter a with the composition x is shown in Fig. 2. It is seen that the a versus x data falls into two parts and that, within the limits of experimental error, the variation of a with x is linear in each part, the two lines intersecting at $x = 0.28$. This gives an estimate of the boundary between the zincblende and chalcopyrite fields.

In the case of materials with $x < 0.3$, i.e. close to $AgInTe_2$, it was found that the value of c/a increases toward 2 as the composition is moved away from $x = 0$, Fig. 2. It has been assumed that the composition at which c/a reaches 2 is the boundary between the zincblende and chalcopyrite fields. This second estimate, together with that obtained above from Fig. 2, has been taken as the boundary of the chalcopyrite field.

Previous experience has indicated that in these types of materials the conditions of slowly cooled samples represent the equilibrium conditions applicable for the temperatures 200 to 300 °C. Thus the above estimate has been taken as the boundary of the chalcopyrite field in this temperature range. Only two points on this field boundary were obtained from DTA data and so an estimate of the position of the boundary is shown as a dashed line in Fig. 1.

It is seen from Fig. 1 that the chalcopyrite α-phase appears for $x = 0$ at 635 °C. This is in reasonable agreement with the results of Chiang et al. [12] who found for $AgInTe_2$ a transition from zincblende β to chalcopyrite α structure at 649 °C. The composition width of the α field increases as the temperature is lowered and reaches a value of 0.28 at 250 °C. Close to $AgInTe_2$ the width of the zincblende β field is narrow, being bounded by the two phases (liquid L + β) field. However, as x is increased the β field widens and for $x < 0.3$, the phase β occurs at all temperatures below the solidus.

A two phase liquid + solid field is found in the temperature range 460 °C $< T <$ $<$ 700 °C, (Fig. 1). The presence of the liquid phase was confirmed by using a transparent quartz container which was heated to an appropriate temperature in the range 200 to 800 °C and left at that temperature for several hours. For various points in the (L + β) field of Fig. 1, the liquid phase was clearly observed. The associated solid phase is taken to be the zincblende β-phase, which occurs throughout the whole composition range.

It is clear from the form of the solidus boundary of the (L + β) field that the tie lines for this field cannot lie in the plane of the diagram, i.e. the section cannot be pseudobinary.

For values of $x > 0.325$, the DTA measurements indicated an additional solid–solid transition at about 340 °C. For samples annealed at 200, 300, 350, and 400 °C for 10 d, powder X-ray photographs showed in each case only the lines of the zincblende structure. However, microscopic examination for the lower-temperature cases showed segregation of a second phase γ at the grain boundaries. This result is similar to those in earlier work carried out on the compounds. In the case of HgTe, Delves et al. [13] observed a HgTe–Te eutectic transformation at a temperature of about 400 °C, while for $AgInTe_2$, Woolley and Williams [8] observed the appearance of a second phase for samples annealed at 400 °C, which could be associated with segregation of tellurium.

Thermal probe measurements were made on various samples to give an approximate estimate of the carrier sign and concentration as a function of composition. It was found that samples with $x < 0.4$ were n-type, while for the rest of the composition range, the behaviour was found to be p-type with the effective value of p increasing as x was increased. Such an increase in p-type conductivity has been observed in materials involving Hg and it has been attributed to Hg vacancies [14]. Hence, in the present case, for samples with $x > 0.3$, the β-phase should be slightly richer in Te and deficient in Hg as compared with the stoichiometric value. The second phase observed at the grain boundaries, as described above, could therefore be associated with the Hg lost from the main phase. An investigation of the dependence of this second phase behaviour on annealing temperature and time of anneal has not as yet been completed. Again, in this ($\beta + \gamma$) two phase field, it is clear that the tie lines cannot lie in the plane of the diagram i.e. pseudobinary behaviour is not obtained.

4. Conclusion

The X-ray experimental results show that there are only two single phase solid fields, viz. the zincblende β and the chalcopyrite α fields. The variation of the lattice parameter a with x is linear for both fields, but the lines show different slopes in the two fields.

Over the whole composition range the β field is bounded by a two phase (L + β) field. However, the tie lines of this field do not lie in the plane of the section, i.e. the section is not pseudobinary.

For samples with $x > 0.3$ segregation of a second phase was observed under the microscope, but was not detected in the X-ray diffraction photographs. This second phase was associated with the solid–solid transition observed in the DTA measurements at about 340 °C, which may be due to segregation of a phase rich in mercury.

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