$Hg_{2x}(AgIn)_{1-x}Se_2$ ALLOYS PHASE DIAGRAM AND LATTICE PARAMETER VALUES

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Abstract

Polycrystalline samples of $Hg_{2x}(AgIn)_{1-x}Se_2$ alloys were prepared by melt and anneal technique. Differential thermal analysis (DTA) measurements were carried out on the alloys and the T(x) diagram determined. Debye-Scherrer X-ray power photographs were used to determine equilibrium conditions and lattice parameter values. It is found that single phase solid solution occurs at all values of composition. The tetragonal chalcopyrite (α) phase extends in the range $0 \leq x \leq 0.28$, an ordered cubic probably stannite (β') phase in the range $0.28 \leq x \leq 0.6$ and a disordered cubic zincblende (β) phase for the rest of the diagram.

INTRODUCTION

There is considerable interest in the II-IV and I-III-VI_2 semiconductor compounds because of their potential use in technological applications such as lasers, solar-energy conversion, infrared radiation detectors, etc. [1, 2]. Work on II_{2x} $(I\text{-}III)_{1-x}$ VI_2 alloys have been carried out for several systems involving Zn and Cd, but little work has been done with Hg. $AgInSe_2$ is of interest as material for near-infrared light detector applications and improvements on its performance may be obtained with addition of HgSe; for that, knowledge of the range of solid solubility and crystallographic data on this system are required. In the present work, which forms a part of a systematic study of Hg_{2x} $(I\text{-}III)_{1-x}$ VI_2 alloy systems [3, 4, 5], lattice parameter values have been determined and DTA measurements have been made to give the T(x) phase diagram of the $Hg_{2x}(AgIn)_{1-x}Se_2$ alloy system.

SAMPLE PREPARATION AND EXPERIMENTAL MEASUREMENTS

The alloys used were produced by the usual melt and anneal techniques. Samples were prepared to cover the complete composition range in the steps of $dx = 0.1$ in composition. The components of each 2 g sample were sealed under vacuum in a quartz ampoule. The reaction of the elements was achieved by increasing the furnace temperature slowly (10 °C/h), in order to avoid explosion, from room temperature to 450°C and maintaining this temperature for 24 h. After that, the temperature was raised to 1150°C at a rate of 20°C/h and maintained for 2 h to ensure complete mixing of the elements. The ampoule was continuously shaken during all the heating process. The resulting alloy was then slowly cooled (10°C/h) in the furnace in about four days down to room temperature. As in all such multicomponents alloys, a suitable temperature of anneal is not easily determined until the T(x) diagram is known. However, the results for other Hg alloy systems like $Hg_{2x}(AgIn)_{1-x}Se_2$, $Hg_{2x}(CuIn)_{1-x}Te_2$ and $Hg_{2x}(CuIn)_{1-x}Se_2$ alloys previously investigated [3, 4, 5] indicate that an annealing temperature of 450°C should be satisfactory and this value was used here. Debye-Scherrer X-ray photographs were used to check the equilibrium conditions of each sample and to determine whether a single phase was obtained. It was found that annealing times of 30 days gave samples showing good sharp X-ray diffraction lines. Values of lattice parameters were determined as a function of the composition variables from the room temperature X-ray photographs. DTA measurements [6] were made over a temperature range from 20 to 1050°C using small quartz tubes sealed under vacuum with the thermocouple in the usual re-entrant position. The charge was approximately 100 mg for each sample, and silver and gold were used as the

reference materials. The temperature of the sample and reference were simultaneously measured with chromel-alumel thermocouples. The difference signal between sample and reference was recorded simultaneously with the furnace temperature. Each phase transition temperature was determined from the base-line intercept of the tangent to the leading edge of the peak in the difference signal. Both heating and cooling runs, were carried out on each sample. A simple mechanical system permitted adjust the heating rate at 10°C/min whereas the cooling rate was the natural cooling down rate of the furnace after switch off.

X- RAY DIFFRACTION RESULTS

The Debye-Scherrer photographs showed that only single phase structures occur in the entire composition diagram. Since c/a ≠ 2 for $AgInSe_2$ (1.919 in ref. 7) it is easy to observe the splitting of the lines corresponding to the chalcopyryte (α) structure and these were observed in the range $0 \leq x \leq 0.3$ as an indication of the boundary for the tetragonal chalcopyrite (α) phase field. For $0.3 \leq x \leq 0.6$ together with the usual cubic spectra, weak ordered lines were observed in samples x = 0.4, 0.5 and 0.6. These ordering lines are very weak for samples x = 0.4 and 0.6 little stronger for x = 0.5. Sample x = 0.3 not shows ordering lines. Attempts were made to index the ordering lines to a stannite structure with relative success because of the weakness of the lines that makes it difficult unambiguously. For $0.6 \leq x \leq 1$ only lines corresponding to the cubic (β) zincblende structure were observed. Appropriate lattice parameter values were determined in each case, and the variation of the lattice parameter a and c/a with composition x are shown in Figures 1a and 1b. The error in the lattice parameter values is estimated to be ± 0.005 Å that is approximately the value shown by the circles.

DTA RESULTS

DTA measurements were made on all the samples and values of the various transition temperatures for each sample were determined. The resulting T(x) phase diagram is shown in Figure 2. Previous experience has indicated that in this type of materials the conditions of slowly cooled 8 samples represent the equilibrium conditions applicable for temperatures between 200-300°C and for this reason the minimal temperature shown in the diagram is 200°C. For $AgInSe_2$, the first-order transition from the ordered (α) chalcopyrite to rhombohedral high temperature phase (α') was 705°C, in good agreement with previous results [8] that give a value of 695°C for this transition. The melting

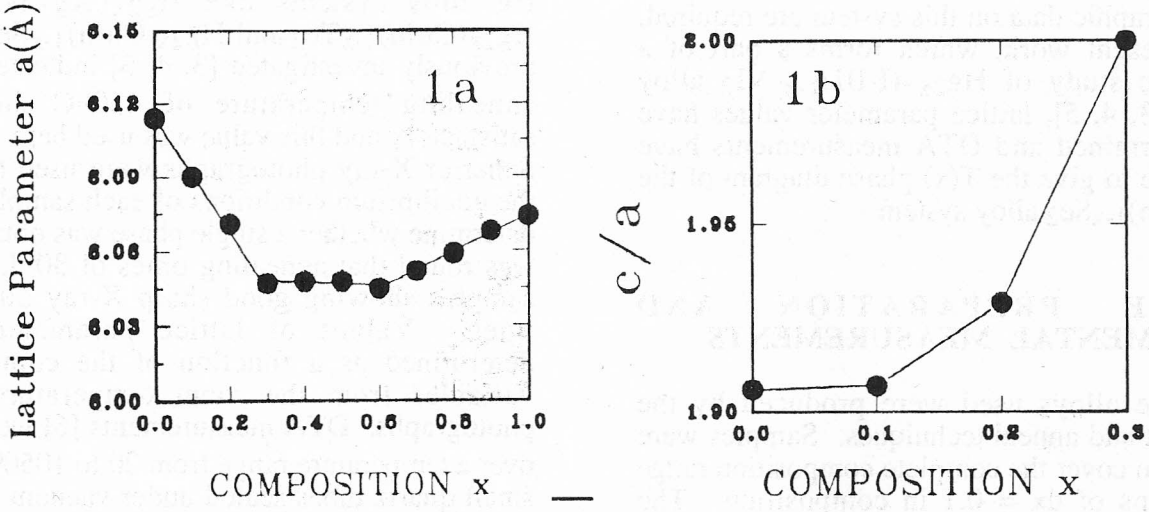

Figure 1. a) Variation of the lattice parameter a (Å) with composition x
b) Variation of c/a with composition x.

point was observed at 780°C according to the usual value of 778°C reported in literature [8]. The composition width of the chalcopyrite field increases as the temperature is lowered and by extrapolation reaches a value of x≈0.28 at 200°C in agreement with X-ray results. The single rhombohedral (α') phase domain has its maximum width at x=0 and disappears at x=0.4, the lower temperature limit remains approximately constant at 700°C but its upper limit decreases from the maximum temperature value, 778°C, at x=0 to 700°C for x=0.4. A two phase field (α' + β') seems to separate the rhombohedral (α') phase from the ordered (β') cubic phase field and attempts were made to quench samples in this temperature range, but only cubic or multiphase field (less than 100°C). For $0.28 \leq x \leq 0.6$ an ordered (β') cubic structure, probably stannite, exists with an upper temperature limit of 600°C. The cubic (β) zincblende phase exists in the rest of structures were retained due to the small temperature region of existence of this two phase the composition diagram, its upper limit is 700°C

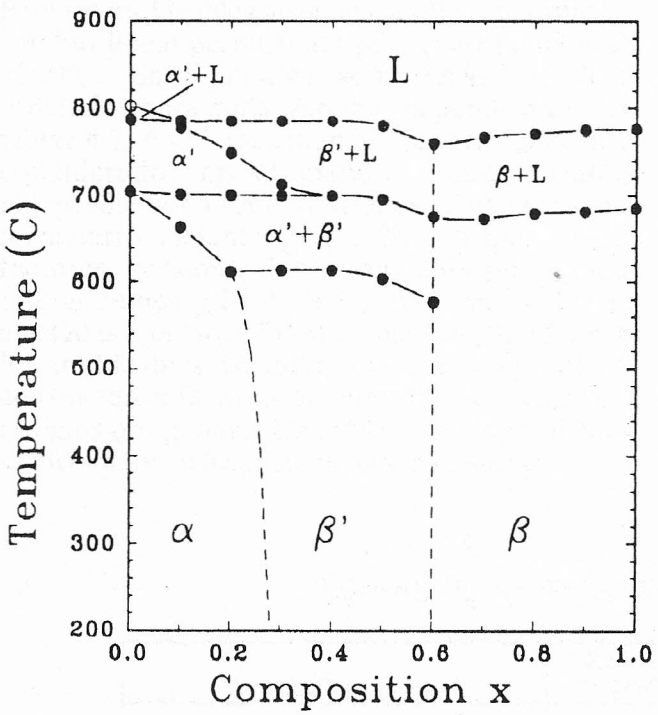

Figure 2. Phase Diagram
Simbols and solids lines: Experimental Values.
Dashed lnes: Estimated boundaries.

in temperature and $0.6 \leq x \leq 1$ in composition. The solid phases are separate of the liquid phase by three two phase (liquid + solid) regions. The first (α' + L) is a little one corresponding to the peritectic character of the melting point of $AgInSe_2$, it extends for $0 \leq x \leq 0.1$ and its maximum temperature width (≈20°C) is attained at x=0. The second one (β + L) exists in the range $0.1 \leq x \leq 0.6$ and its temperature width increases with composition attained a maximum value of ≈ 80°C at x=0.6. Finally, the third one (β + L) exists in the composition range of $0.6 \leq x \leq 1$ with a constant temperature width of ≈ 100°C. The estimated error in the temperature values is ± 10°C.

CONCLUSION

The X-ray experimental results show that, within the accuracy of the measurements, there are only single phase solid fields along all the composition diagram. The behavior of the lattice parameter a vs composition x and DTA result shows that the chalcopyrite field extends from x=0 to x≈0.28, whereas the cubic structure values. An intermediate ordered cubic structure that we have attributed to stannite was found in the range $0.28 \leq x \leq 0.6$ and a disordered cubic structure attributed to the zincblende phase to extends for the rest of the diagram. The result indicates complete solid miscibility in the $Hg_{2x}(AgIn)_{1-x}Se_2$ alloy system.

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