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Phase Relations in the System In-CuInS$_2$

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By DTA and x-ray diffraction the phase relations in the pseudobinary system In-CuInS$_2$ have been investigated. CuInS$_2$ hs a melting point of 1090° C and within this system there is a broad region of liquid immiscibility. A four phase invariant reaction exists at 633° C which is of the form: $L_2 = L_1 + CuInS_2 + InS$.

Key words: CuInS$_2$, phase relations, solar cells

INTRODUCTION

The chalcopyrite CuInS$_2$ is of interest as a possible alternative photovoltaic base material. It possesses a room temperature band gap of 1.5 eV which is the optimum for a single junction photovoltaic device.[1] To date the highest reported solar cell efficiency is over 9%,[2] for a liquid junction solar cell using a CuInS$_2$ single crystal. A thin film device has been developed with an efficiency of 7.3%.[3] One reason for the slow development of the melt grown material can be found in the phase relations regarding the chalcopyrite phase. Binsma *et al.* evaluated the phase relations in the system Cu$_2$S-In$_2$S$_3$[4] and found two solid state phase transformations. With regard to crystal growth from the melt these transformations would severcly restrict the growth of large, crack-free single crystals. One way to circumvent this problem would be to grow this material from the vapor or from high temperature solutions, thus allowing growth to occur at temperatures below these sub-solidus transformations.

CuInS$_2$ has been grown by CVT, but these materials are intrinsic and incorporate the transport agent.[5] CuInS$_2$ has also been produced by single, two[6,7] and three[8] source evaporation methods. For better quality films one must resort to growth from high temperature solutions. One obvious choice of solvent would be indium and recently there have been a number of publications concerning solution growth of CuInS$_2$ from indium and copper/indium solutions. Takenoshita *et al.*[9] grew CuInS$_2$ films from indium solutions onto ZnSe substrates, Hsu *et al.*[10] used the traveling heater method to grow CuInS$_2$ single crystals using an indium zone, Hwang *et al.*[11] produced CuInS$_2$ films by LPE onto GaP substrates, and by the flux method Fleming *et al.*[12] grew CuInS$_2$ single crysals from Cu/In melts.

With the increased interest in the growth of CuInS$_2$ from In-solution, it was felt that a better understanding of the phase relations in the In-rich corner of the Cu-In-S system would greatly facilitate research in this direction. Previously, the binary boundaries Cu-S,[13] In-S,[14] and Cu-In,[15] have been established. Binsma *et al.*[4] have investigated the Cu$_2$S-In$_2$S$_3$ quasibinary, and Thiel[16] has determined the liquidus for the CuInS$_2$-Cu$_{0.5}$In$_{0.5}$ pseudobinary (see figure 1). In the present study the pseudobinary system CuInS$_2$-In has been investigated using DTA. Room temperature x-ray powder diffraction was used to aid in the identification of the phases present.

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EXPERIMENTAL

CuInS$_2$ powder, obtained from material synthesized by the two-zone gradient freeze method,[17] and 5N In were used for the DTA studies. The CuInS$_2$ starting material was analysed by room temperature x-ray diffraction, DTA and electron probe microanalysis to establish its homogeneity and stoichiometry and was found to represent the desired material with little variation of the composition.

Samples of predetermined amounts of In and CuInS$_2$ were sealed under vacuum in 5 mm o.d. quartz tubes and placed into platinum crucibles to ensure a uniform temperature. The temperature programming and data acquisition were performed by use of a Netzsch Simultaneous Thermal Analyser 409. Heating and cooling curves were ran at rates from 2 to 10° C/min with the rate 5° C/min chosen for the present study.

Powder diffractograms were measured in the usual 0–20-coupled geometry with a SIEMENS D500, using a Cu-anode with 45 kV and 30 mA. A secondary graphite monochromator was used to avoid K_β-reflexions and to reduce fluorescent scattering ($\lambda(CuK_\alpha) = 1.5418$Å). All measurements were done in a step scan mode ($x°/y$ sec).

RESULTS AND DISCUSSION

The pseudobinary CuS$_2$-In is shown in Fig. 2. Our results for the transitions of stoichiometric CuInS$_2$, Fig. 3, agree reasonably well with those of Binsma *et al.*[4] CuInS$_2$ was found to melt at 1090° C (1090° C) with solid stte phase transformations occurring at 1047° C (1045° C) and 975° C (980° C). The wurzite and zinc blend high temperature modifications, ζ and δ, were not stabilized with respect to the chalco-

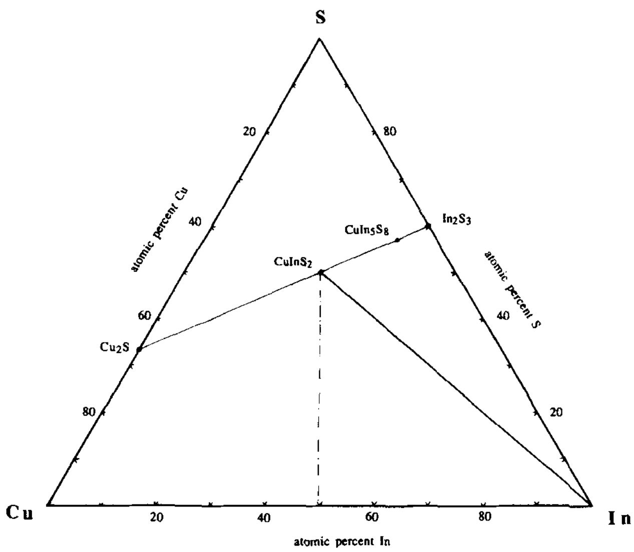

Fig. 1 — The ternary system Cu-In-S.

pyrite, γ-phase with excess In. Nor was there appreciable solubility of In in $CuInS_2$. The peritectic decomposition of the ζ-phase occurs at 1048° C and that of the δ-phase at 978° C. The two liquid region extends from $X_{In} = 0.43$ to approximately $X_{In} = 0.93$ and has a critical temperature along this pseudobinary at approximately 845° C. Due to undercooling of the melt, (Fig. 4), the formation of InS, as well as the formation of γ (but less severely), occurs at lower temperatures and the metastable invariant reaction was found to take place at around 580° C. This phenomenon was also encountered in the study of the In_xS_{1-x} system,[14] therefore the heating curves were used to define the reaction temperatures within this two liquid region. X-ray powder diffraction analysis of the resulting DTA samples containing a

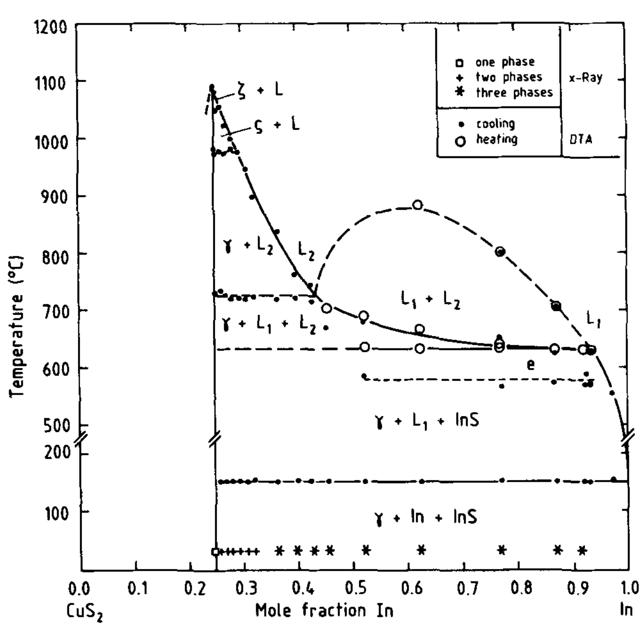

Fig. 2 — The CuS_2-In pseudobinary diagram.

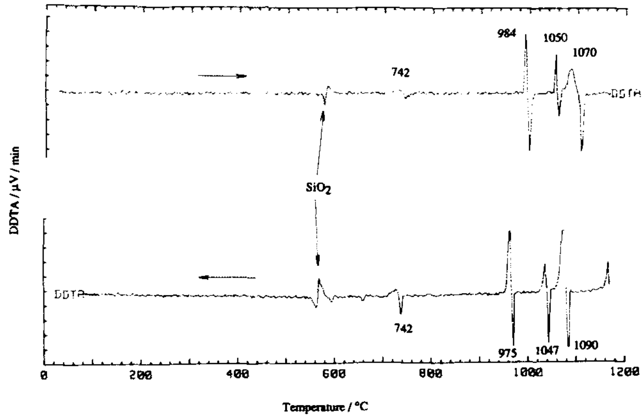

Fig. 3 — Heating and cooling curves for stoichiometric $CuInS_2$.

large In excess clearly showed the presence of red InS crystals. This would indicate an interrupton of a eutectic curve by the two liquid region where the eutectic separates two three-phase fields exhibiting the following reactions: $L_2 = L_1 + \gamma$ and $L_2 = L_1 +$ InS, with the monotectic reaction reaching a minimum at the invariant rection temperature of 633° C. The reaction at this eutectic would therefore be: $L_2 = L_1 + \gamma +$ InS with the eutectic crossing this pseudobinary between $X_{In} = 0.85$ to 0.90 In, or *e* in Fig. 2. We were not able to resolve the location of this eutectic due to the close proximity of the isotherm and the monotectic on the In-rich side. The liquidus beyond the monotectic ends at a degenerate eutectic near the indium corner at a temperature of 153° C.

The low temperature phase relations were difficult to establish due to the lower sensitivity of the thermal analyser at these temperatures. The positions of these phase boundaries are further complicated by the γ-L_1-InS Gibbs triangle, of which the L_1 vertex lies on the Cu side of the $CuInS_2$-In pseudobinary cut.[12] This region between the invariant reaction and the degenerate eutectic has simply been indicated as: $\gamma + L_1 +$ InS. It is evident from room temperature x-ray analysis that the $CuInS_2$-In two phase field extends from $CuInS_2$ towards In to be-

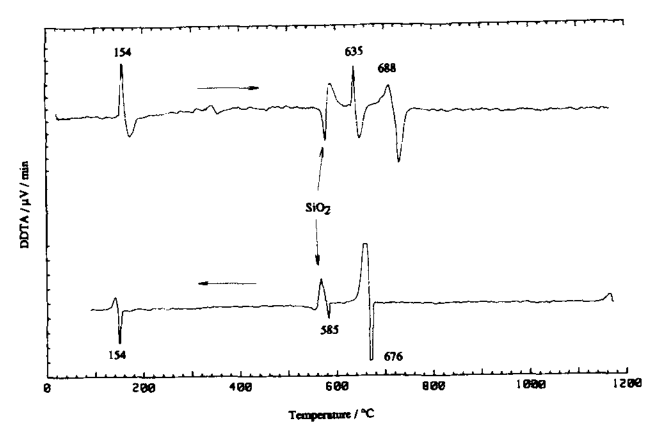

Fig. 4 — Heating and cooling curves showing undercooling of the two liquids with respect to InS formation for $X_{In} = 0.525$.

tween 32 and 36 mole-% In, Fig. 2. From there one enters the three phase field, and the three phases co-exist at least as far as $X_{In} = 0.93$.

CONCLUSION

In conclusion, the phase relations for the $CuInS_2$-In have been established by DTA and x-ray diffraction. The liquidus from the 1090° C melting point descends rapidly to the two liquid region, which dominates a large composition range. The two high temperature phases, ζ and δ, are not stabilized with respect to chalcopyrite by the addition of In nor was there appreciable solubility of In in $CuInS_2$. Furthermore, at 633° C, a temperature invariant reaction was encountered with the form: $L_2 = L_1 + \gamma + InS$.

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