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Letter

Phase study of the system $Cu_{1-x}Li_xInSe_2$

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Both constituent compounds of the alloy system under investigation belong to the large family of ternary chalcogenides that form lattices with tetrahedral coordination of the atoms. At ambient conditions $CuInSe_2$ crystallizes in the chalcopyrite structure which is a superstructure of the sphalerite lattice; undergoes with heating a polymorphous phase transition from the chalcopyrite to the sphalerite structure at 810 °C; and melts congruently at 986 °C [1]. Structure and differential thermoanalysis (DTA) studies of $LiInSe_2$ [2, 3] have shown that this compound crystallizes in the orthorhombic β-$NaFeO_2$ structure which represents a distorted superstructure of the wurtzite lattice. The melting temperature is 904 °C, and in contrast to $CuInSe_2$ no phase transitions of solid $LiInSe_2$ were observed between room temperature and the melting point. It was the aim of the present work to study the phase diagram of the quasi-binary alloy system $Cu_{1-x}Li_xInSe_2$ in order to define the region of solubility; to establish the stability ranges of the closely related but different structures of the alloy constituents; and to look for other ordered phases as they have been found, for instance, in some alloys of ternary chalcopyrite-structure chalcogenides with binary wurtzite or sphalerite-structure chalcogenides [4–6].

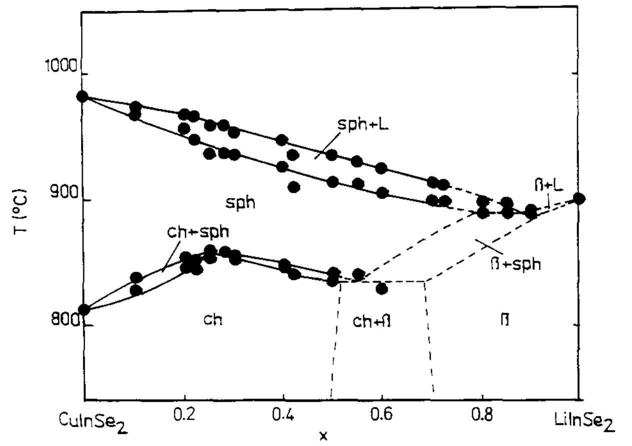

Fig. 1. Phase diagram of the system $Cu_{1-x}Li_xInSe_2$ (L–liquid, sph–sphalerite, ch–chalcopyrite, β–β-$NaFeO_2$ structure).

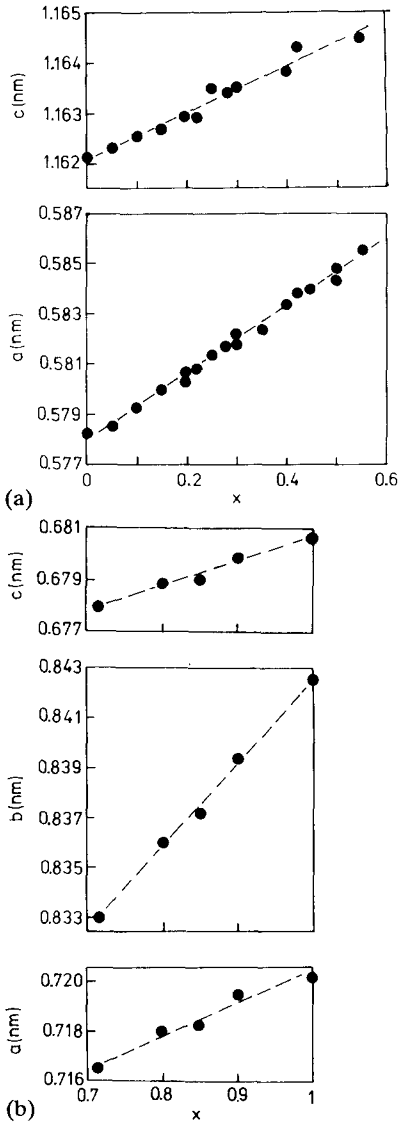

Fig. 2. Lattice parameters at room temperature of $Cu_{1-x}Li_xInSe_2$ alloys in the composition ranges with (a) chalcopyrite structure and (b) β-$NaFeO_2$ structure.

Alloy samples of the desired compositions were prepared by solid state reaction of corresponding mixtures of the constituent compounds. The constituent compounds themselves were synthesized by vacuum fusion

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of stoichiometric amounts of the high-purity elements (99.99% Li, 99.999% Cu, 99.9999% In and Se) using standard procedures as they have been described elsewhere for both $CuInSe_2$ [7, 8] and $LiInSe_2$ [2, 9]. These ternary starting materials were crushed to powder, taken in the desired proportions, thoroughly mixed for homogenization and sealed in quartz ampoules evacuated to a residual gas pressure of 10^{-2}–10^{-3} Pa. The charges were then annealed at 650, 780 and 800 °C for 72 days and at 900 °C for 30 days and afterwards quenched to liquid nitrogen or room temperature. For each of the annealing regimes a complete set of samples for the whole composition range was prepared in order to control the state of the reaction process. We found that annealing at 650 °C for 72 days and equally well annealing at 900 °C for 30 days ensures complete reaction of the constituents to a homogeneous alloy.

DTA measurements were made by means of a Setaram microthermoanalyser in the temperature range $T=300$–1050 °C ($\Delta T=\pm 5$ K) at a heating rate of 3 K $\min^{-1}$. In constructing the phase diagram we followed the same procedure as described in ref. 6. X-ray powder diffraction using filtered CuK_α radiation and silicon as the internal standard was used to identify the structure and to determine the lattice parameters of the samples, in all cases with an accuracy of ± 0.0004 nm or better.

The resulting phase diagram of the system $Cu_{1-x}Li_xInSe_2$ is shown in Fig. 1. At temperatures below 800 °C including room temperature the samples always have the chalcopyrite structure in the mole fraction range $0 \leqq x \leqq 0.5$ and the orthorhombic β-$NaFeO_2$ structure for $0.7 \leqq x \leqq 1.0$. At mole fractions of $0.5 < x < 0.7$ reflections from both phases could be identified in the diffraction diagrams. Obviously, this result indicates the presence of a miscibility gap in this composition range of the alloys. Finally, in none of the samples were any traces of an admixture of a sphalerite phase found at temperatures below about 800 °C. Consequently, it can be argued that alloy formation results in a random distribution of Cu and Li atoms on sites of the Group I cation sublattice on both the $CuInSe_2$ and $LiInSe_2$-rich sides of the system, while the indium sublattice remains unaffected.

The presence of a polymorphous phase transition was detected in all samples having compositions in the range $0 \leqq x \leqq 0.6$ (Fig. 1). It is interesting to note that at a mole fraction close to $x=0.25$ the phase transition temperature goes through a maximum which, in principle, could give rise to an ordered phase with the formula $Cu_3LiIn_4Se_8$. However, even very careful examination of the X-ray diffraction diagrams recorded on samples of this composition range did not give any hints to the presence of an additional ordered phase. At compositions $x > 0.6$ the DTA curves did not show any thermal response due to a polymorphous phase transition. Finally, it follows from Fig. 1 that the melting temperature decreases continuously with increasing Li content of the alloys, from 986 °C for $CuInSe_2$ to 904 °C for $LiInSe_2$ with, maybe, a weakly pronounced minimum in the melting temperature curve at a composition close to $x=0.9$.

The lattice parameters measured at room temperature are depicted in Fig. 2. In both the chalcopyrite and β-$NaFeO_2$ structure ranges the lattice parameters increase with increasing Li content of the alloys and all the lattice parameters change with composition according to Vegards rule.

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