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Preparation and investigation of $(\text{CuInSe}_2)_{1-x}(\text{TaSe})_x$ solid solutions ($0 \leq x \leq 0.5$)

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Alloys of $(\text{CuInSe}_2)_{1-x}(\text{TaSe})_x$ ($0 \leq x \leq 0.5$) system have been synthesized by the usual melt and anneal method. For the first time, it was established by X-ray and DTA methods that a continuous row of solid solutions, with a chalcopyrite-like (α) structure, is formed in the system in the composition range $0 < x < 0.2$. For $0.2 < x < 0.5$, traces of a new (γ) phase appear together with the chalcopyrite structure.

Keywords: CuInSe₂; TaSe; solid solution; X-ray diffraction; differential thermal analysis.

El sistema de aleaciones $(\text{CuInSe}_2)_{1-x}(\text{TaSe})_x$ ($0 \leq x \leq 0.5$) han sido sintetizadas por el método usual de fusión y recocido. Por primera vez, podemos establecer por los métodos de rayos-X y ATD, que continúan una fila de soluciones sólidas con una estructura (α) parecida a la calcopirita, es formada en ese sistema en el rango de composición de $0 < x < 0.2$. Para $0.2 < x < 0.5$, trazas de una nueva fase (γ) aparece junto con la estructura calcopirita.

Descriptores: CuInSe₂; TaSe; solución sólida; difracción de rayos-X; análisis térmico diferencial.

PACS: 81.05.Bx; 81.40.Cd; 07.85.Nc; 81.70.Pg

1. Introduction

This work is part of a systematic investigation on $(\text{I-III-VI}_2)_{1-x}(\text{MT-VI})_x$ alloys, where I-III-VI₂ (I: Cu, Ag; III: Al, Ga, In; VI: S, Se, Te) are the well known family of chalcopyrite compounds (space group, $D_{2d}^{12}-I42d$) [1] and MT is a transition metal. This substitution gives place to a new family of chalcopyrite diluted magnetic semiconductors (DMSs). From the point of view of material design, this investigation aims at the discovery of new ferromagnetic DMSs with high T_c. Recently, the electronic and magnetic properties of MT doping at either cation sites in the class of I-III-VI₂ chalcopyrites are studied by first-principle calculations [2-6]. It is found that Mn doping at the III site provides holes and stabilizes the ferromagnetic interaction between neutral Mn defects whereas the neutral also stabilizes the ferromagnetism, although it provides electrons to the conduction band, instead of holes [2-4]. In the case of V- and Cr-doped the ferromagnetism was also stable, but for Fe and Co doping, the spinglass-like state was realized [4-6]. In the past, we reported the preparation and characterization of $(\text{Cu-III-Se}_2)_{1-x}(\text{FeSe})_x$ (III: Al, Ga and In) [7-8], $(\text{CuInSe}_2)_{1-x}(\text{CoSe})_x$ [9], $(\text{I-InSe}_2)_{1-x}(\text{VSe})_x$ (I: Cu and Ag) [10-11] alloys; in this work we reported for the first time the alloy system $(\text{CuInSe}_2)_{1-x}(\text{TaSe})_x$.

2. Experimental procedure

Starting materials (Cu, In, Ta, and Se) with a nominal purity of (at least) 99.99 wt% in the stoichiometric ratio were mixed together in an evacuated and sealed quartz tube with the inner walls previously carbonized in order to prevent a chemi-

cal reaction of the elements with quartz. Polycrystalline ingots of about 1 g were prepared by the usual melt and anneal technique. The stoichiometric relation of the samples was investigated by the scanning electron microscopy technique, using Hitachi S2500 equipment. The micro chemical composition was found by an energy-dispersive x-ray spectrometer (EDS) coupled with a computer-based multichannel analyzer (MCA), (Delta III analysis and Quantex software, KeveX). For the EDS analysis, K lines were used. Accelerating voltage was 15 kV. The samples were tilted 35 degrees. A standardless EDS analysis was made with a relative error of 5-10% and detection limits of the order of 0.3 wt%, where the k-ratios are based on theoretical standards. X-ray powder diffraction photographs for sample $x = 2/3$ were recorded at 295(1)K using a Ginier-Wolf transmission camera (Enraf Nonious FR 552) equipped with a Johansson monochromator (CuK_α radiation : $\lambda = 1.54059 \text{ \AA}$), $\text{Pb}(\text{NO}_3)_2$ was used as an external calibration standard. KODAK DEF 392 film was used for the Ginier photographs. More precise X-ray powder diffraction data for $x = 0.5$ was collected by means of a diffractometer (Bruker D5005) equipped with a graphite monochromator (CuK_α , $\lambda = 1.54059 \text{ \AA}$) at 40kV and 20mA. Silicon powder was used as an external standard. The samples were scanned from $10\text{-}100^\circ 2\theta$, with a step size of 0.02° and counting time of 20s. The Bruker analytical software was used to establish the positions of the peaks from the 1 component and to strip mathematically the α_2 components from each reflection. The peak positions were extracted by means of single-peak profile fitting carried out through the Bruker DIFFRACplus software. Each reflection was modeled by means of a pseudo-Voigt function. The differential Thermal Analysis (DTA) was carried out in a fully automatic Perkin-

Elmer apparatus with Pt/Pt-Rh thermocouples. Au was used as internal standard. The heating and cooling rates were controlled to 20K h^{-1} . Transition temperatures were manually obtained from the T vs. ΔT graph with the criteria that the transition occurs at the intersection of the base line with the slope of the thermal transition peak, as usual. The maximum error committed in the determination of transition temperatures by this method was estimated as $\pm 10\text{ K}$.

3. Analysis and discussion

As it is routine in our laboratory, stoichiometric relations of all the samples were checked out in several external parts of the experimental ingot, along the longitudinal axis and, after that, over a thin slide ($\sim 1\text{-}2\text{ mms}$ thick) cut off from the center of the ingot. The experimental results are in good agreement with the nominal stoichiometry, with differences below that of the experimental error, estimated as $\pm 5\%$. We did not observe any systematic as a function of the position in the ingot or in the slide. From Guinier photographs, the lattice parameter were calculated for all compositions and shown in Fig. 1.

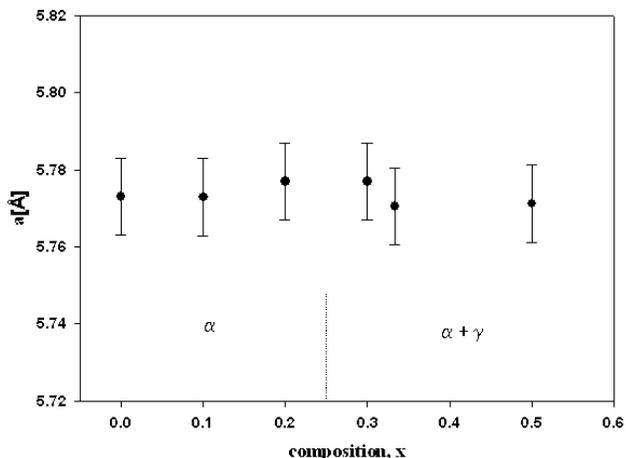


FIGURE 1. Lattice parameter a [Å] vs. Composition.

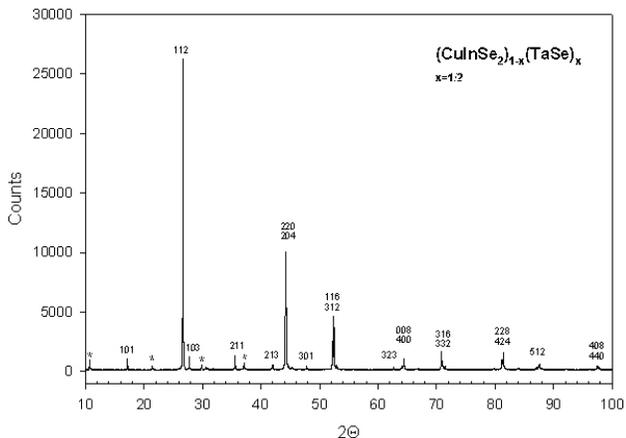


FIGURE 2. Diffraction pattern of sample $x=(1/2)$

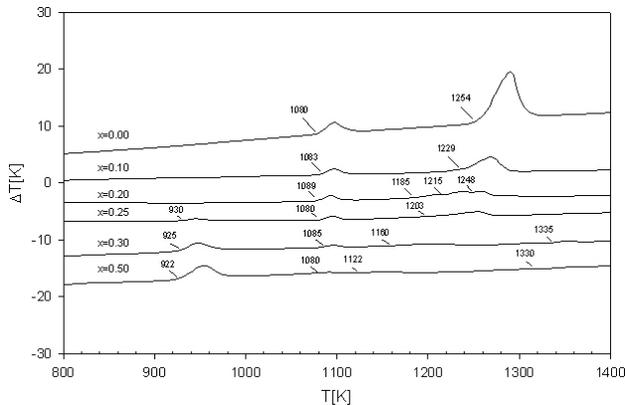


FIGURE 3. DTA Heating.

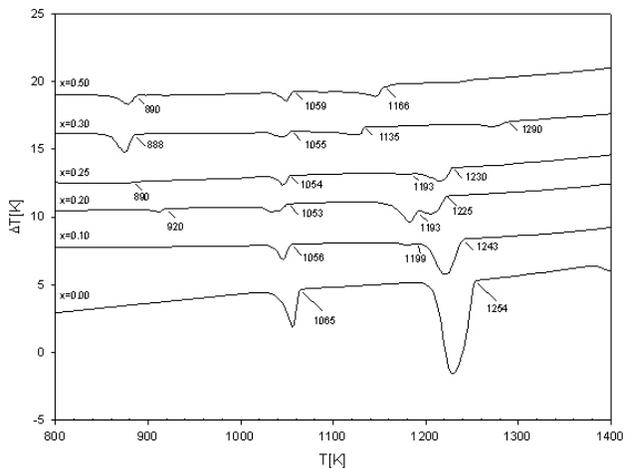


FIGURE 4. DTA Cooling.

Although some scattering is observed, the lattice parameter does not vary in the range studied. This result can be justified if the covalent radius of Ta is very close to the average (Cu + In). In Fig. 2, the diffraction pattern of sample $x = 0.5$ is shown.

It can be observed that together with the chalcopyrite structure, new sharp peaks appear (denoted with asterisks). We have interpreted these new peaks as the presence of traces of a new phase that becomes from Ta, and that we have denoted as γ -phase. Unfortunately, there are not enough peaks for indexation of this phase and, for the moment, it rests unknown. In Figs. 3 and 4, the DTA heating and cooling cycle, respectively, are presented.

In the heating cycle, one can observe how the melting peak decreases in intensity, indicating instability of the host chalcopyrite structure in the composition range $0 < x < 0.25$, whereas a new peak appears, increasing its intensity for $0.2 < x < 0.5$ at around 925K. The same behavior is observed in the cooling cycle.

4. Conclusion

From the analysis of x-ray and DTA measurements, it can be concluded that the solubility of hypothetical TaSe in the

chalcopyrite host is about 20%. The lattice parameter does not vary in the composition range studied in the limits of the experimental error.

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