X-ray diffraction of \((\text{CuInTe}_2)_{1-x}(\text{TaTe})_x\) alloy system \((0 \leq x \leq 1)\)

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**Keywords:** CuInTe\(_2\), TaTe; solid solution; phase transition; X-ray diffraction; differential thermal analysis.

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La estructura cristalina del sistema de aleaciones \((\text{CuInTe}_2)_{1-x}(\text{TaTe})_x\) \((0 \leq x \leq 1)\) fueron preparados por la técnica usual de fusión y recocido. Éstas han sido estudiadas por las técnicas de difracción de rayos-X y los parámetros de la celda unidad fueron obtenidos. Un comportamiento monofásico fue observado en el rango de composición \(0 < x < 2/3\). Esta fase simple fue indexada como una estructura parecida a la calcopirita. Para \(2/3 < x < 3/4\) otra fase desconocida se observa junto con la calcopirita. Esta nueva fase se observa claramente en las muestras \(x = 5/6\) y \(6/7\), pero no puede ser indexadas debido a su comportamiento multifásico. Para valores más altos de \(x\) el patrón de difracción es característica de muestras no cristalinas.

**Keywords:** CuInTe\(_2\), TaTe; solid solution; phase transition; X-ray diffraction; differential thermal analysis.

**Descriptores:** CuInTe\(_2\), TaTe; solución sólida; transición de fase; difracción de rayos-X; análisis térmico diferencial.

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1. **Introduction**

Chalcopyrite-based diluted magnetic semiconductors (DMSs) have industrial applications because of their property of room temperature ferromagnetism. The first reports on chalcopyrite DMS were Mn: CdGeP\(_2\) and Mn: ZnGeP\(_2\) [1-2] for which, in addition to room temperature ferromagnetism, a high Mn solubility was observed.

Analogous to the III-V and II-VI semiconductor-based DMSs, the ferromagnetism of chalcopyrite DMS is induced by 3d carriers. This is because the magnetic state is mainly determined by the competition between the double-exchange and super-exchange interactions [3-4]. In chalcopyrite \(A^I\,B^{II\,I\,X^{V\,I\,2}}\) DMSs, the metal transition (MT) atom would substitute any of the two metal sites A or B. The site preference of MT doping in CuB\(^{II\,I\,I\,X^{V\,I\,2}}\) is crucial because it releases different type of carriers: electrons for the substitution on the Cu sites, and holes for the substitution on the M\(^{II\,I}\) sites. Using first principle calculations, it is found that Mn doping at the III site provides holes and stabilizes the ferromagnetic interaction between neutral Mn defects. The neutral Mn\(^{II}\)Cu also stabilizes the ferromagnetism, although it provides electrons to the conduction band, instead of holes [5-6]. It was also found that ferromagnetism was stable in V- and Cr-doped chalcopyrite DMSs, whereas for Fe- and Co-doping the spinglass-like state is realized; on the hand, in the cases of Mn doped \(A^I\,B^{II\,I\,X^{V\,I\,2}}\) and \(A^{II\,I}\,B^{IV\,X^{V\,2}}\) type DMS, the ground state was ferromagnetic and spinglass-like, respectively [7-8].

The present work is part of a systematic investigation on \((A^I\,B^{II\,I\,X^{V\,I\,2}})_{1-x}(MT-X^{V\,I})_x\) alloy systems. Recently, we have reported the preparation and characterization of \((\text{Cu-III-Se})_{1-x}(\text{FeSe})_x\) (III: Al, Ga and In) [8-9], \((\text{CuInSe}_2)_{1-x}(\text{CoSe})_x\) [10], (I-InSe\(_2\))\(_{1-x}(\text{VSe})_x\) (I: Cu and Ag) [11-12] alloys. Now, we report the \((\text{CuInTe}_2)_{1-x}(\text{TaTe})_x\) alloys system.

2. **Experimental procedure**

Starting materials (Cu, In, Ta, and Te) with a nominal purity of (at least) 99.99 wt\% were mixed together in the stoichiometric ratio in an evacuated and sealed quartz tube with the inner walls previously carbonized in order to prevent a chemical reaction of the elements with the 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 an 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 Kα lines were used. The accelerating voltage was 15KV. The samples were tilted 35°. 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 data were collected for some compositions by means of a diffractometer (Bruker D5005) equipped with a graphite monochromator (CuKα, λ = 1.54059 Å) at 40kV and 20mA. Silicon powder was used as an external standard. The samples were scanned from 10-100° 2θ, 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 α1 component and to strip mathematically the α2 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 an internal standard. The heating and cooling rates were controlled to 20K/h. Transition temperatures were manually obtained from the T vs. T 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 ±10K.

3. Analysis and discussion

In figures 1a and 1b the diffraction patterns of samples in the composition range $0 < x < 7/8$ are presented.

The diffraction pattern of CuInTe$_2$ was calculated using Power Cell package software with lattice parameters $a = 6.1944 \, \text{Å}$ and $c = 12.4157 \, \text{Å}$ and shown for comparison. At first view, it can clearly be observed that good crystalline samples exist only for $0 < x < 2/3$. The mean phase was indexed as a chalcopyrite-like structure, and lattice parameters $a$, $c$ and $c/a$ are given in figures 2a, 2b and 2c, respectively.

A secondary phase can be observed for samples $x = 1/8$, $x = 1/7$ and $x = 1/6$, whereas for the rest of the samples, in the composition range $0 < x < 2/3$, the behavior is of a single phase structure with traces (if any) of a secondary phase.

It is worth observing how the intensity of some peaks increases (or decreases) due to the random substitution of Cu or In-atoms by Ta which have a mass attenuation coefficient for CuKα ($\text{cm}^2/\text{g}$) of 52.9, 243 and 166, respectively. Substitution of Cu by Ta must reduce, whereas substitution of In by Ta must increase the intensity of the respective peak. If we observe the diffraction patterns of samples $x = 1/8$, $x = 1/7$ and $x = 1/6$, the intensity of the (400,008) peak increases very fast and reduces again for sample $x = 1/5$. In sample $x = 1/5$, the intensity of the (220,204) peak is bigger that (112). These variations suggest a high disorder of the cation sublattice.

Analysis of the lattice parameters confirms the former observation. Although parameter a does not have an appreciable variation, the scattering around $x = 0.2$ suggests some kind of disorder. Lattice parameter c shows a local minimum at around this value ($x = 0.2$), also reflected in the c/a parameter, giving indication of this disorder.

The large solubility of Ta in the chalcopyrite host is not unexpected since the covalent ratio of Ta (1.37 Å) is very close to the average between Cu (1.17Å) and In (1.50 Å).
Magnetic measurements in these alloys are in progress and will be the object of a future article.

4. Conclusions

A large solid solubility of Ta in the chalcopyrite was observed for \((\text{CuInTe}_2)_{1-x}(\text{TaTe})_x\) alloys, although traces of a secondary phase were also observed for some compositions. The lattice parameters do not have appreciable variation in the entire composition range.