Solid Solubility of TaTe in the ternary $CuInTe_2$ chalcopyrite compound

by

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Resumen

Las muestras policristalinas del sistema de aleaciones $(CuInTe_2)_{1-x}(TaTe)_x$ $(0 \leq x \leq 1)$ han sido preparadas por la técnica usual de fusión y recocido y los parámetros de celda unidad fueron obtenidos por las técnicas de difracción de rayos-X. El análisis de los resultados de difracción de rayos-X, muestran un comportamiento de una fase en el rango de composición $0 < x < 2/3$ y fue indexada como una estructura calcopirita. Otra fase desconocida fue observada entre 2/3 y 3/4.

Abstract

Polycrystalline samples of $(CuInTe_2)_{1-x}(TaTe)_x(0 \leq x \leq 1)$ alloy system prepared by the usual melt and anneal technique have been studied by x-ray diffraction technique and lattice parameters were obtained. The analysis of the results using x-ray diffraction shows a single phase behavior in the composition range $0 \leq x \leq 2/3$ and was indexed as a chalcopyrite-like

structure. Another unknown phase is observed together with the chalcopyrite-like phase between 2/3 and 3/4.

Introduction

Chalcopyrite-based diluted magnetic semiconductors (DMSs) have industrial applications because of their property of room temperature ferromagnetism. In chalcopyrite $A^{I}B^{III}X^{VI}_{2}$ DMSs, the metal transition (MT) atom would substitute any of the two metal sites A or B. The site preference of MT doping in $CuB^{III}X^{VI}_{2}$ 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^{III} sites. 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 $A^{I}B^{III}X^{VI}_{2}$ and $A^{II}B^{IV}X^{V}_{2}$ type DMS, the ground state was ferromagnetic and spinglass-like, respectively [5-6].

The present work is part of a systematic investigation on $(A^{I}B^{III}X^{VI}_{2})_{1-x}$ $(MT\text{-}X^{VI})_{x}$ alloy systems. Recently, we have reported the preparation and characterization of $(Cu\text{-}III\text{-}VI_{2})_{1-x}$ $(VI\text{-}Se)_{x}$ (III: Al, Ga and In; VI: Fe, Co) [1-2, 6], $(I\text{-}InSe_{2})_{1-x}$ $(VSe)_{x}$ (I: Cu and Ag) [3-4] alloys. Now, we report the $(CuInTe_{2})_{1-x}$ $(TaTe)_{x}$ alloys system.

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 chemical reaction of the elements with the quartz. Polycrystalline ingots of about 1 g were prepared by the usual melt and anneal technique.

X-ray powder diffraction data were collected, for some compositions, by means of a diffractometer (Bruker D5005) equipped with a graphite monochromator (Cuk_{α}, $\lambda = 1.54059$ Å) at 40 kV and 20 mA. 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 20 s. The Bruker analytical software was used to establish the positions of the peaks from the α_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 DIFFRAC^{plus} software. Each reflection was modeled by means of a pseudo-Voigt function.

Analysis and discussion

In figures Ia and Ib 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 unit cell $\boldsymbol{a}$ = 6.1944 Å and $\boldsymbol{c}$ = 12.4157 Å and shown for comparison. A first view, it can clearly observed that good crystalline samples exist only for $0 < x < 2/3$. The mean phase was indexed as a chalcopyrite-like structure and unit cell $\boldsymbol{a}$, $\boldsymbol{c}$ and c/a are given in figures IIa, IIb and IIc, respectively. A secondary phase can be observed for samples $x = 1/2$ and $x = 1/3$, 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 to observe how the intensity of some peaks increase (or decrease) due to the random substitution of Cu or In-atoms by Ta which have a mass attenuation coefficient for CuK_α (cm^2/g) of 52.9, 243 and 166, respectively. Substitution of Cu by Ta must reduces whereas substitution of In by Ta must increases 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 the parameter a do not have an appreciable variation, the scattering around $x = 0.2$ suggest that some kind of disorder. The lattice parameter ***c*** shows a local minimum at around this value (x = 0.2) reflected also 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 (1.17 Å) and In (1.50 Å).

Conclusions

A large solid solubility of Ta in the chalcopyrite was observed for $(CuInTe_2)_{1-x}(TaTe)_x$ 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.

Acknowledgments

The authors want to thanks to FONACIT for financial support.

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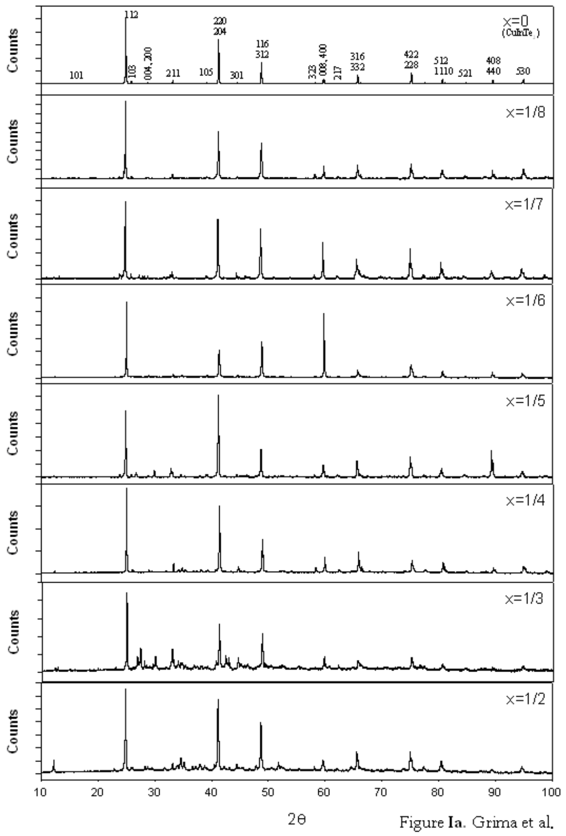

Figure Ia. Grima et al.

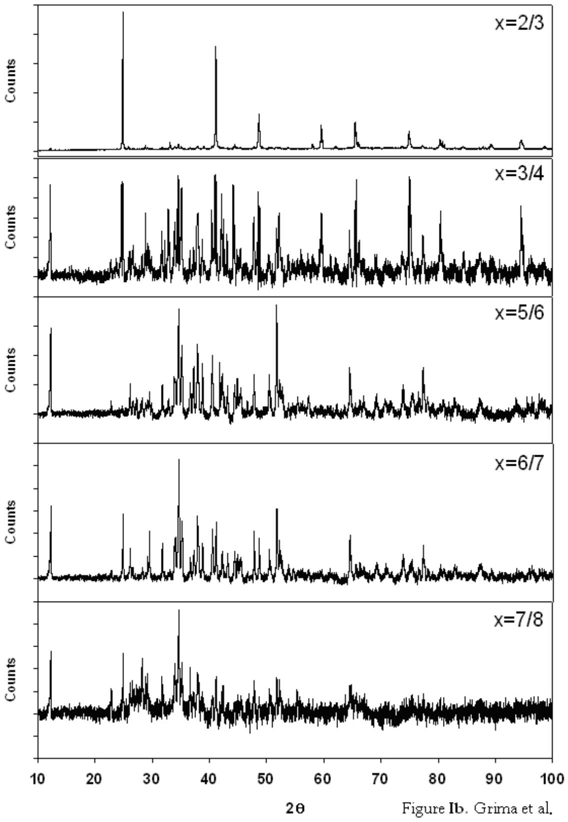

Figure Ib. Grima et al.

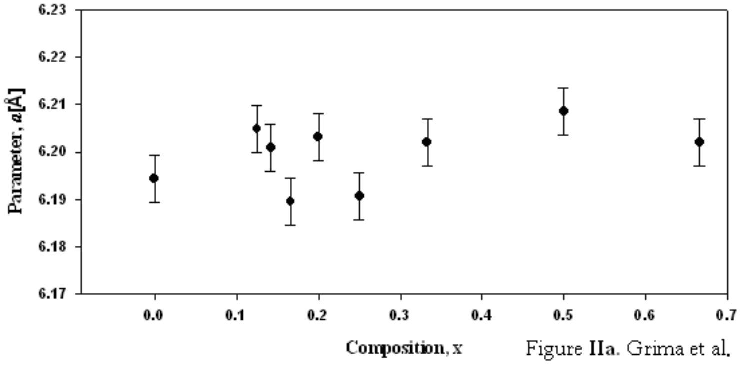

Figure IIa. Grima et al.

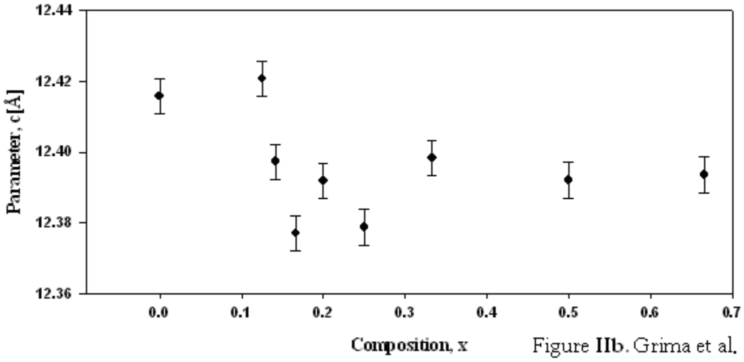

Figure IIb. Grima et al.

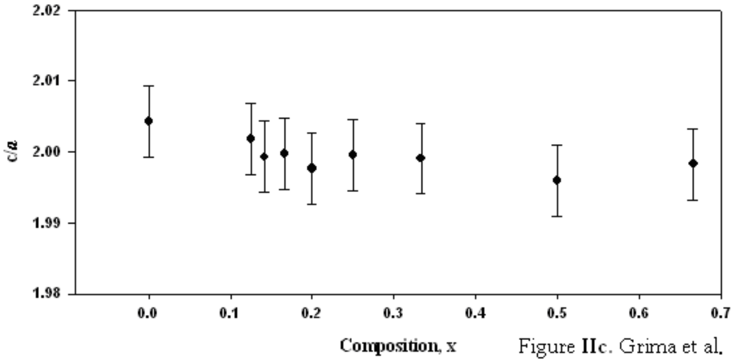

Figure IIc. Grima et al.

Figure Captions

Figure Ia. Diffraction patterns of samples in the composition range $0 \leq x \leq 1/2$.

Figure Ib. Diffraction patterns of samples in the composition range $2/3 \leq x \leq 7/8$.

Figure IIa. Unit cell parameter ***a***[Å] vs. Composition.

Figure IIb. Unit cell parameter ***c***[Å] vs. Composition.

Figure IIc. *c*/*a* vs. Composition**.**