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Preparation and investigation of the quaternary alloy $CuTaInSe_3$

P. Grima-Gallardo [a,*], M. Muñoz [a], S. Durán [a], G.E. Delgado [b], M. Quintero [a], J. Ruiz [a]

[a] *Centro de Estudios en Semiconductores (CES), Dpto. Física, Facultad de Ciencias, La Hechicera, Mérida, Venezuela*
[b] *Laboratorio de Cristalografía, Dpto. Química, Facultad de Ciencias, Universidad de Los Andes, Mérida 5101, Venezuela*

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Abstract

Polycrystalline samples of the quaternary alloy $CuTaInSe_3$ were prepared by the usual melt and anneal technique. The analysis of the diffraction pattern indicates a single phase which indexes as a tetragonal chalcopyrite-like structure with lattice parameters $a = 5.7837 \pm 0.0002$ Å; $c = 11.6208 \pm 0.0007$ Å and $V = 389 \pm 1$ Å^3. Differential thermal analysis shows that the melting transition of $CuTaInSe_3$ is incongruent with large liquid + solids regions.

Keywords: A. Alloys; A. Inorganic compounds; B. Chemical synthesis; C. X-ray diffraction; D. Crystal structure; D. Thermodynamic properties

1. Introduction

Tantalum chalcogenides with low dimensional structures frequently display interesting physical properties such as superconductivity, charge density waves and metal-insulator transition. Therefore, their properties and structural chemistry have attracted considerable interest [1].

The study of chalcopyrite-based diluted magnetic semiconductors (ChDMSs) was a part of earlier investigation of binary II–VI and III–V diluted magnetic semiconductors (DMSs) [2–5]. Recent works on ChDMSs reported room temperature ferromagnetism and high solubility of the metal atom indicating a promissory research field [6–16].

In the past, we have reported the preparation and characterization of some ChDMSs alloys: $(Cu–III–Se_2)_{1-x}(FeSe)_x$ (III: Al, Ga and In) [17,18], $(CuInSe_2)_{1-x}(CoSe)_x$ [19], $(I–InSe_2)_{1-x}(VSe)_x$ (I: Cu and Ag) [20,21], which represent part of a systematic investigation on $(A^{I}B^{III}X^{VI}_2)_{1-x}(MT–X^{VI})_x$ alloy systems where MT is a metal transition atom. In this work, the quaternary alloy $CuTaInSe_3$ which belongs to the alloys family $(CuInSe_2)_{1-x}(TaSe)_x$ with $x = 0.5$ (or $x = 1/3$ in the alternative nomenclature $(CuInSe_2)_{1-x}2(TaSe)_{x)}$ was prepared and investigated.

2. Experimental procedure

2.1. Preparation of the samples

Starting materials 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

* Corresponding author. Tel.: +58 2742401332; fax: +58 2742401286.
E-mail address: peg@ula.ve (P. Grima-Gallardo).

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the elements with the quartz. Polycrystalline ingots of about 1 g were prepared by the melt and anneal technique: the ampoule was heated slowly to 450 °C and held there for 48 h; then the temperature was raised slowly to 1150 °C and maintained there for 24 h. Mechanical shaking of the ampoule was used during the entire heating process. After that, the ampoule was cooled to room temperature at a very low rate for 1 week. Then, the ampoule was introduced again into a furnace kept at 650 °C for one moth. Finally, the furnace was switched off and the ampoule cooled at room temperature.

2.2. Measurements

2.2.1. X-ray powder diffraction

X-ray powder diffraction data were collected by means of a diffractometer (Bruker D5005) equipped with a graphite monochromator (Cu Kα, λ = 1.54059 Å) at 40 kV and 20 mA. Silicon powder was used as an external standard. The samples were scanned from 5–100° 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.

2.2.2. Differential thermal analysis

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 20 K/h. Transition temperatures were manually obtained from the ΔT versus T graph with the criteria that the transition occurs at the intersection of the base line with the slope of the thermal transition peak. The maximum error in the determination of transition temperatures by this method was estimated as ±10 K. The measurements were carried out until 1450 K which is the operational limit of our DTA system.

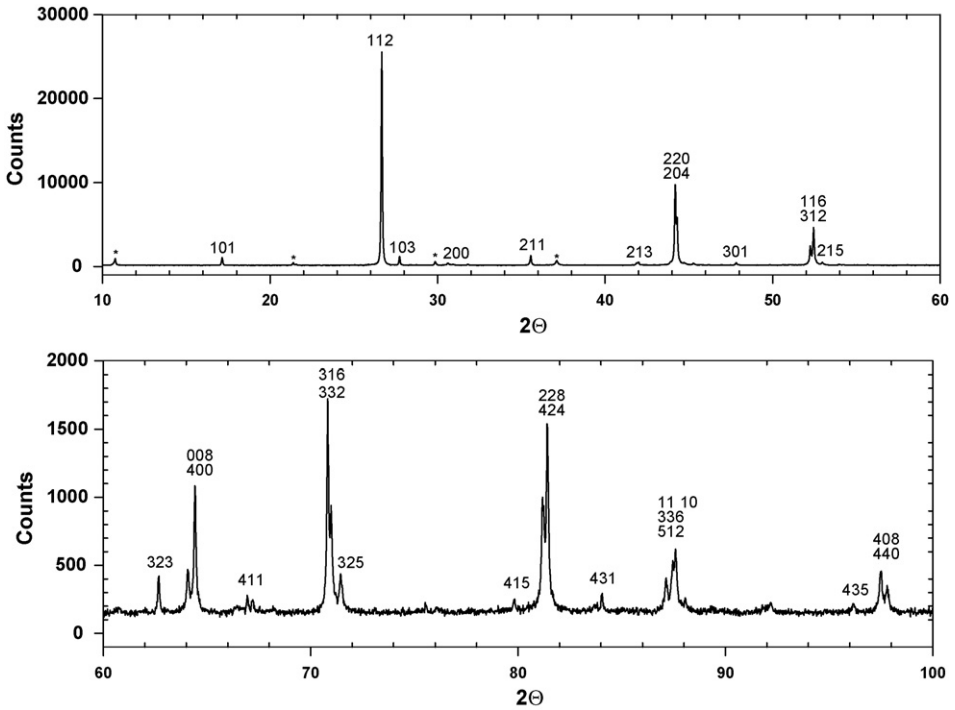

Fig. 1. X-ray powder diffraction pattern of the alloy $CuTaInSe_3$. The *h k l*-Miller indices used for indexation are showed. Some additional peaks were denoted by asterisks.