Preparation and characterization of $(CuAlSe_2)_{1-x}$ $(TaSe)_x$ alloy system ($0 \leq x \leq 0.5$).

**by**

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## Abstract

Polycrystalline samples of $(CuAlSe_2)_{1-x}$ $(TaSe)_x$ alloy system were prepared by the usual melt and anneal technique in the composition range $0 < x \leq 0.5$. The obtained ingots (1 gr) were characterized by x-ray powder diffraction and differential thermal analysis techniques. Güinier photographs shows the presence of two phases in the entire composition range studied; for $0 \leq x \leq 0.3$ the main phase indexes as tetragonal with unit cell parameters very close to the ternary $CuAlSe_2$ whereas the secondary phase appears as a trace. For $0.3 < x \leq 0.5$ the two phase are present in approximately the same proportion.

## Resumen

Las muestras policristalinas del sistema de aleaciones $(CuAlSe_2)_{1-x}$ $(TaSe)_x$, fueron preparadas por la técnica usual de fusión y recocido en el rango de composición $0 < x \leq 0.5$. Los lingotes obtenidos (1gr) fueron caracterizados por las técnicas de difracción de rayos-x y análisis térmico diferencial. Las fotografías de Güinier muestran la presencia de dos fases

en todo el rango de composición estudiado; para $0 \leq x \leq 0.3$ la fase principal indexa como tetragonal con parámetros de celda unidad muy cercano al ternario $CuAlSe_2$, mientras que la segunda fase aparece en trazas. Para $0.3 < x \leq 0.5$, las dos fases están presentes en aproximadamente la misma proporción.

## I. Introduction

This work is part of a systematic investigation on $(I\text{-}III\text{-}VI_2)_{1-x}(MT\text{-}VI)_x$ alloys, where $I\text{-}III\text{-}VI_2$ (I: Cu, Ag; III: Al, Ga, In; VI: S, Se, Te) are the well known family of chalcopyrite compounds (space group, I-42*d*) [2] 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 Tc. 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 [8-10]. Recently, the electronic and magnetic properties of MT doping at either cation sites in the class of $I\text{-}III\text{-}VI_2$ chalcopyrites are studied by first -principle calculations [6-7]. In the past, we reported the preparation and characterization of $(CuIn\text{-}VI_2)_{1-x}(Ta\text{-}VI)_x$ (VI: Se, Te), $(I\text{-}InSe_2)_{1-x}(VSe)_x$ (I: Cu and Ag) [1-5] alloys; in this work we reported for the first time the alloy system $(CuAlSe_2)_{1-x}(TaSe)_x$.

## II. Experimental Procedure

**1. Preparation of the samples**. Starting materials (Cu, Al, Ta, and Se) with a nominal purity of (at less) 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 chemical reaction of the elements with quartz. Polycrystalline ingots of about 1 g were prepared by the usual melt and anneal technique.

**2. X-ray powder diffraction**. X-ray powder diffraction photographs were recorded at 295(1)K using a Güinier-Wolf transmission camera (Enraf Nonious FR 552), equipped with a Johansson monochromator (CuKα radiation : λ = 1.54059 Å), $Pb(NO_3)_2$ was used as an external calibration standard. KODAK DEF 392 film was used for the Güinier photographs.

**3. Differential Thermal Analysis (DTA)**. 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. Transition temperatures were manually obtained from the ΔT 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 usually. The maximum error committed in the determination of transition temperatures by this method was estimated as ± 10 K.

**III. Experimental Results and Discussion**

**1. X-ray powder diffraction:** In Fig. I, Güinier photographs of the compositions studied are shown. The unit cell parameters for all composition studied were calculated from Güinier photographs using the available software for these cases and the results are shown in Fig. II. The x-ray powder diffraction showed the presence of two phases in the entire composition range studied, for the interval of $0 \leq x \leq 0.3$ the main phase indexes as tetragonal with lattice parameters very close to the ternary $CuAlSe_2$ whereas the secondary phase appears as a trace, has not yet been indexed.

**2. Differential Thermal Analysis:** In Figs. III and IV, the DTA heating and cooling cycle, respectively, are presented. The DTA analysis shows that the area under the peaks for $CuInSe_2$ are much bigger than for the other compositions; similar behavior has been observed in other quaternary compounds previously studied in other alloys systems; In the heating cycle for $CuAlSe_2$, there are only one thermal transitions, the melting, but in the

interval of $0.2 < x < 0.5$ almost two thermal transitions are clearly observed. Analogous behavior occurs in the cooling cycle.

## IV. Conclusions

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 abrupt change in the parameter between the compositions $0.2 < x < 0.3$, is indicative of an exchange phase. The melting point in the single phase region decreases with the composition, indicating instability of the host chalcopyrite structure in the composition range $0 < x < 0.2$.

## Acknowledgments

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**Figure I**

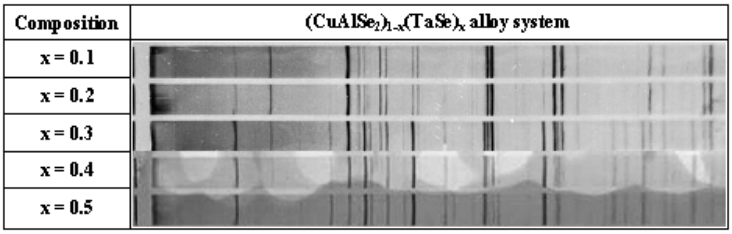



**Figure II**

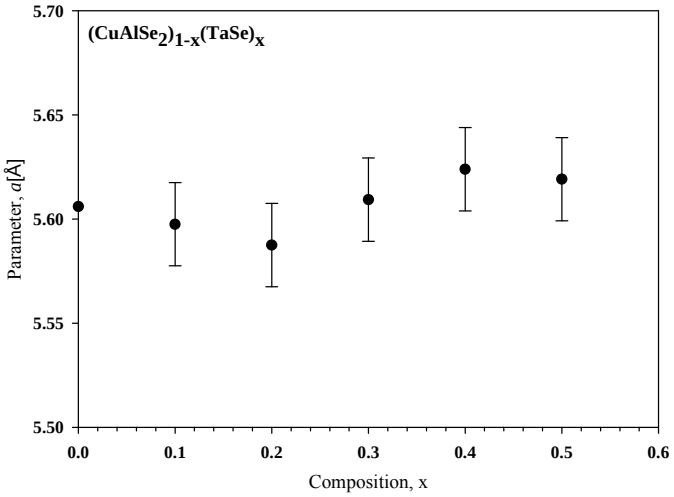



**Figure III**

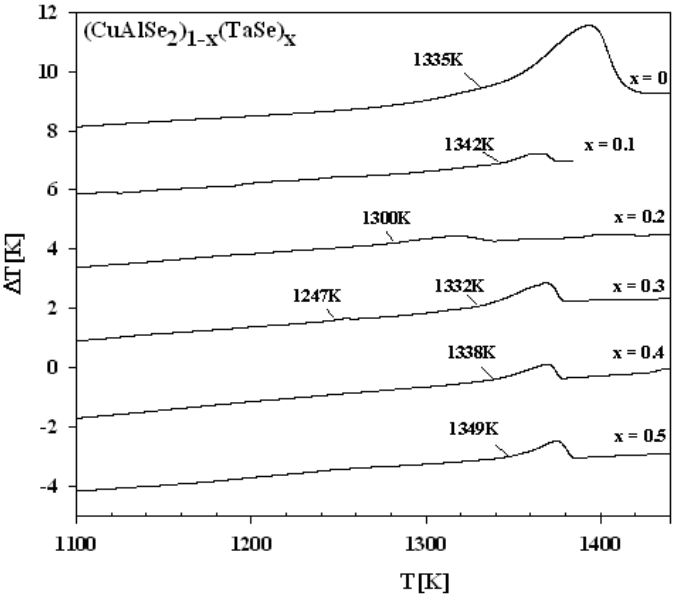
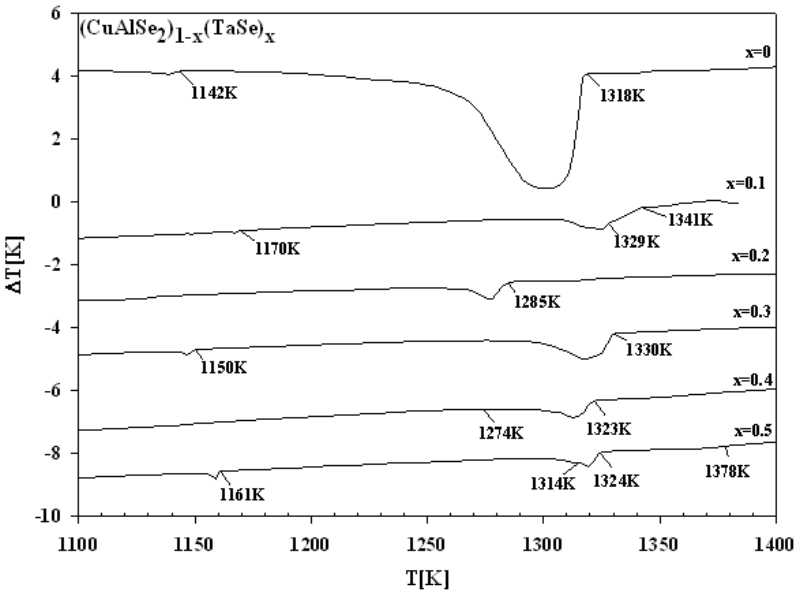



**Figure IV**




## Figure Captions

**Figure I.** X-ray powder diffraction photographs for the $(CuAlSe_2)_{1-x}$ $(TaSe)_x$ alloys system.

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

**Figure III.** DTA Heating.

**Figure IV.** DTA Cooling.