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X-Ray Diffraction, Differential Thermal Analysis and Magnetic Susceptibility Measurements on Nominally $CuFeCrSe_3$

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X-ray powder diffraction, Differential Thermal Analysis (DTA) and magnetic susceptibility measurements were performed on polycrystalline samples of nominally $CuFeCrSe_3$ prepared by the usual melt and anneal technique. The X-ray diffraction pattern was analyzed to determine the crystalline structure and lattice parameter values. The results suggested that $CuFeCrSe_3$ has the ordered tetragonal stannite structure with $a = 5.512 \pm 0.003$ Å and $c/a \approx 2$, in coexistence with a secondary phase that have been identified as $CuCrSe_2$. The DTA spectra suggest a complicated process for melting throughout successive peritectic transformations as it was observed before in other CuFe-III-Se3 compounds; nevertheless, a solidification point of 1002 K can be clearly observed. Magnetic susceptibility measurements reveal paramagnetic Curie-Weiss behavior with $\theta_c \approx 280$ K. All the samples showed n-type conductivity.

Introduction I–II–III–VI_3 materials belong to $(I{-}III{-}VI_2)_{1-x}(II{-}VI)_x$ alloys with $x = 0.5$. They obey the Grimm-Sommerfeld rules [1], so it is to be expected that they crystallize in a tetrahedral structure, analogous to the chalcopyrite or zincblende, but disordered since the cationic sites are sharing by three different cations. Some of these alloys have been studied in the past [2 to 3] with Zn, Cd or Hg as group-II atom. Recently, studies of alloys with metal transition atoms (Mn, Fe) as group-II atom have been performed [4 to 9]. In particular, $CuFeGaSe_3$ and $CuFeInSe_3$, showed single phase tetragonal structures, with lattice parameters very close to the ternaries $CuGaSe_2$ and $CuInSe_2$, respectively [9].

In the present work, it is reported X-ray powder diffraction, Differential Thermal Analysis (DTA) and magnetic susceptibility measurements performed on polycrystalline samples of nominally $CuFeCrSe_3$ prepared by the usual melt and anneal technique. In our knowledge, it is the first time that this hypothetically compound is prepared.

Experimental Starting materials (Cu, Fe, Cr and Se) with nominal purity of 99.9999% in the stoichiometric ratio were mixed together in a evacuated and sealed quartz tube with inner walls previously carbonized in order to avoid reactions of the starting materials with the quartz ampoule. Polycrystalline ingots of about 1 g were prepared by the usual melt and anneal technique.

X-ray powder diffraction measurements were performed at 300 K on a KODAK DEF-392 film with a calibrated Guinier de Wolf camera (Enraf Nonious FR 552) and a diffractometer Siemens D5005 using, in both cases, CuKα (λ = 1.54059 Å) radiation. Phase transition temperatures were obtained from DTA measurements using Perkin Elmer DTA-7 equipment. Both, heating and cooling runs were carried out at rates varying between 10 and 50 K/h. Several runs taken were found to be alike. Magnetic susceptibility measurements were performed in a SQUID (Superconducting Quantum Interference Device) in the temperature range 2 to 300 K. At first, the $CuFeCrSe_3$ sample was cooled down to 2 K in the absence of externally applied magnetic field. The curves of the susceptibility $\chi(T)$ measured while heating up to room temperature are labeled ZFC (zero-field-cooling). Then the susceptibility was measured when the temperature goes down under the applied external field (FC). The applied magnetic field was 100 Gauss and the weight of the sample approximately 100 mg. Using Seebeck effect, the compound appeared to have n-type conductivity.

Results and Discussion

X-ray diffraction The resulting X-ray diffraction pattern is shown in Fig. 1. It can be seen from this figure that the diffraction lines are sharp indicating that the sample was in good thermal equilibrium. Indexation of the phases observed in the spectrum was made using the computer program DICVOL91 [10] with an absolute error of 0.03° (2 θ) in the calculations. The results suggested a tetragonal stannite structure with lattice parameter a = 5.512 ± 0.003 Å, very close to $CuFeSe_2$ (a = 5.53 Å [11, 12]). The secondary phase was identified as $CuCrSe_2$. The stronger diffraction line of the secondary phase is about 25% of the strongest line of the mean phase. In addition, weak diffraction lines, indicated with asterisks in Fig. 1, could not be fully identified. However, in

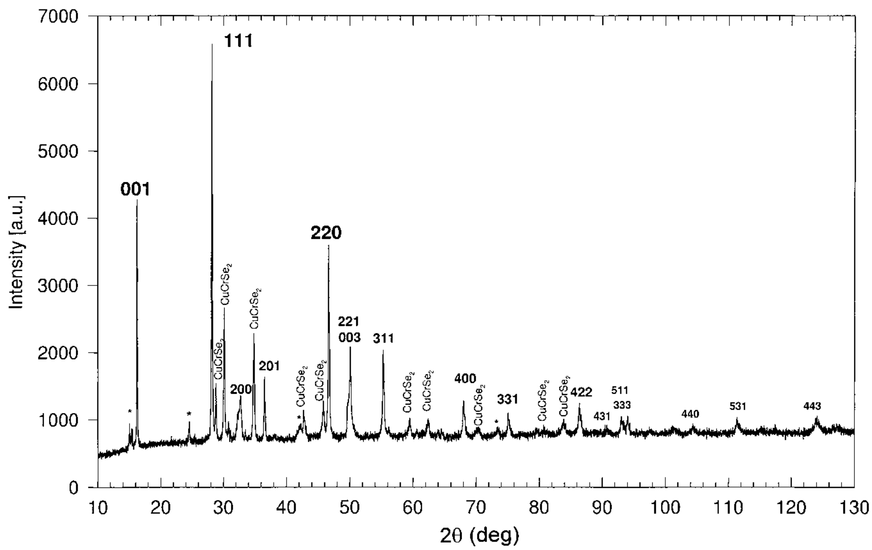

Fig. 1. X-ray diffraction pattern of $CuFeCrSe_3$. Numbers over the peaks are the *hkl* planes for the mean phase. The secondary phase ($CuCrSe_2$) is identified by his name. Asterisks denote not identified peaks

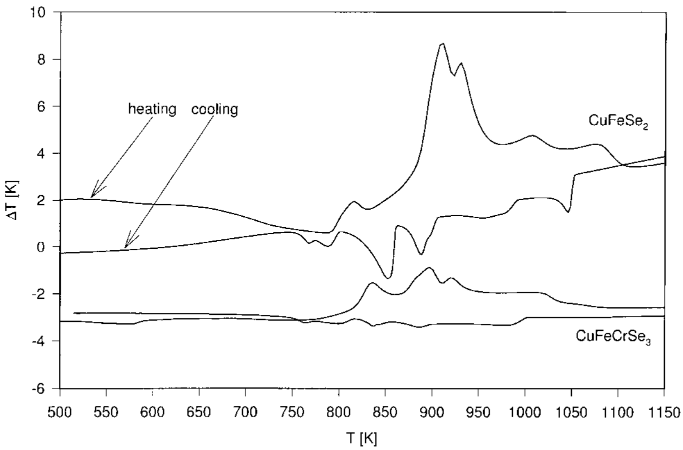

Fig. 2. DTA spectrum of $CuFeCrSe_3$ and, for comparison, that of $CuFeSe_2$. Heating and cooling curves are shown and identified in the figure

previous works, carried out in compounds involving Fe, it has been observed the presence of magnetite (Fe_3O_4) [13, 14].

Differential thermal analysis (DTA) In Fig. 2 it is shown the DTA spectra of nominally $CuFeCrSe_3$ and $CuFeSe_2$ for comparison. In both cases several transitions were observed, but the spectra of both phases are unambiguously different. It is probable that the reactions are of the peritectic type indicating a complicated form of the phase diagram. It is to be mentioned that peritectic behaviors have also been observed in the equilibrium diagrams for some Cr and/or Fe based ternary and quaternary compounds such as $CuCr_2Se_4$ [15], $CuFeGaSe_3$ [9], $CuFeInSe_3$ [9] and $CuZn_{0.5}InCrSe_4$ [16]. From the cooling curve, the melting temperature value of nominally $CuFeCrSe_3$ was estimated to be about 1002 K.

Magnetic susceptibility The obtained magnetic susceptibility χ versus T curve is shown in Fig. 3. It can be seen from this figure that the ZFC and FC curves split at about $T \approx 150$ K and the width increases with decreasing temperature, i.e. temperature hysteresis occurs. It is observed that the FC curve increases as the temperature is decreased, the

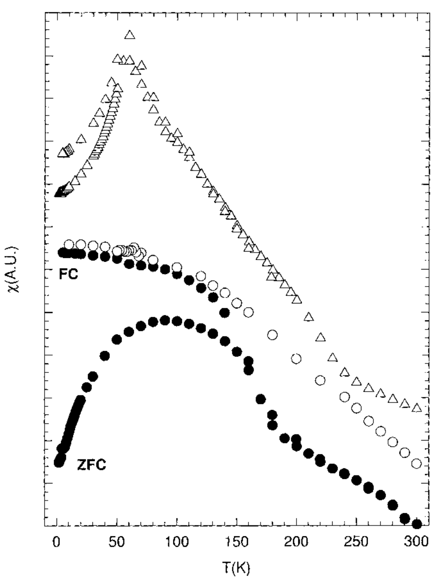

Fig. 3. Magnetic susceptibility of $CuFeCrSe_3$ (full circles) and for comparison those of $CuFeSe_2$ (empty circles) and $CuCrSe_2$ (empty triangles)

same variation was previously observed for the $FeGa_2O_4$ magnetic compound [17]. It was qualitatively suggested that this result could be due to a behavior close to a superparamagnetic one, where the increase of the FC curve should reflect a progressive blocking of residual clusters [17]. However, because the number of secondary phases observed in the present $CuFeCrSe_3$ sample, no conclusions on this behavior are given here. Only for comparison, magnetic susceptibility curves of $CuFeSe_2$ and $CuCrSe_2$ were also given.

Conclusions The X-ray results suggested that the $CuFeCrSe_3$ compound has the tetragonal stannite structure, with lattice parameter $a = 5.512 \pm 0.003$ Å, and ratio $c/a \approx 2$. A secondary phase, identified as $CuCrSe_2$ is in coexistence with the mean phase. DTA measurements showed several transitions, which probably could be peritectic reactions indicating a complicated form of the phase diagram for this compound. The solidification point was estimated to be about 1002 K. The magnetic results show a temperature hysteresis at about 150 K. Nevertheless, because of the number of secondary phases observed, in the present case a reliable analysis of the magnetic data could not given here. In order to obtain samples of $CuFeCrSe_3$ without secondary phases, anneal treatment and single crystal growth are in process.

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