Effects of Tin and Sulfur Chemical Substitution on the Structural and Electrical Properties of CuCr$_2$Se$_4$ Selenospinel

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1. Introduction

The magnetic and transport properties of AB$_2$X$_4$ chalcogenide spinels are strongly influenced by the distribution of the metal ions in the structure. Because the cationic and anionic distribution can change when substitution occurs, the physical properties of the spinel material may differ significantly from those of the parent spinels. An interesting property of spinels containing Cr is magnetoresistance, which refers to the change in the electrical resistance of materials in the presence of a magnetic field [1]. This has been the focus of many studies because of its potential for use in new data storage devices with reduced energy consumption [2,3]. Therefore, solid solutions of seleno- and thiospinels have been well studied because of their extraordinary electrical and magnetic properties, which can differ significantly by substitution [4–11]. For example, replacing metal ions in the octahedral or tetrahedral position with diamagnetic ions can alter the magnetic properties of CuCr$_2$S$_4$ and CuCr$_2$Se$_4$. In (Cu)$_{1-x}$[Cr$_{2-x}$Ti$_x$]$_{1-x}$Se$_4$ spinels, the substitutions of Cr by M (M = Zr, Sn) have indicated that M is present as a $4^+$ ion, and Cu as a diamagnetic Cu$^+$ ion [3,12]. For CuCr$_2$S$_4$, its physical properties can be understood if its charge distribution is assumed to be Cu$^{+}$Cr$^{3+}$Cr$^{4+}$S$_4^{−}$; thus, metallic conduction and ferromagnetism are ascribed to the double exchange between Cr$^{3+}$ and Cr$^{4+}$ [13,14]. Looking at the magnetic phase diagram of (Cu)$_{1-x}$[Cr$_{2-x}$Ti$_x$]$_{1-x}$S$_4$, which results from the substitution of Cr by Ti, the magnetic frustration generated changes the ferromagnetic properties to a spin-glass
regime. Regarding (Cu)$_{\text{tet}}$(Cr$_2$$_x$Sn$_{4-x}$)$_{\text{oct}}$Se$_4$, where Sn replaced Cr, ferromagnetic interaction at $x = 0.3$ was noticeable, and for $x = 0.7$, ferromagnetic character was predominantly present in the antiferromagnetic (AF) behavior [6]. The degree of Se, Cu, or Cr substitution can modify the magnetic and electrical properties of chalcospinels. For example, CuCr$_2$$_x$Sn$_{3-x}$S$_2$Se$_2$ samples with $x = 0.2$ and 0.4 showed ferromagnetic interaction, whereas high transition temperature (AF) behavior occurred in $x = 0.6, 0.8$, and 1.0 samples [13].

In another case, the electrical conduction dependence on Cu$_{1-x}$Co$_x$Cr$_2$Se$_4$ exhibited metallic-type conductivity within the chemical 0.1 $\leq x \leq$ 0.5 range [16,17]. The substitution of Li by Cu in the CuCr$_2$Se$_4$ end-member caused a change from metallic to insulating behavior, which was ascribed to the suppression of holes in the ligand non-bonding $p$ orbitals of the selenium atoms resulting from the substitution [18]. Similarly, changes occurred when chalcogen was substituted, as in CuIr$_2$(S$_{1-y}$Se$_y$)$_4$, with $y \leq 0.15$, as metal-insulated transition occurred along with a structural modification from a cubic to tetragonal structure.

In CuCr$_2$$_x$Se$_{3-x}$, semiconduction appeared when CuCr$_2$S$_4$ and CuCr$_2$Se$_4$ spinels were mixed with metallic conduction [19,20]. Nagata et al. reported the magnetoresistance of CuCrZrS$_4$. This solid solution exhibited variable range hopping (VHR) behavior and decreasing resistivity with increasing magnetic field [21]. For other compounds, there was a progressive change in the electrical properties. Co$_{0.1}$Fe$_{0.9}$Cr$_2$S$_4$ showed a temperature dependence from metallic behavior (140–178 K) to semiconducting behavior at $T > 178$ K [22]. In addition, this material showed a linear decrease in electrical resistance as the applied external magnetic field increased. Chemical substitutions of Cr by Sn, such as in CuCr$_2$$_x$Sn$_{3-x}$S$_4$ ($x = 0.1$ and 0.2), resulted in $p$-type conduction with electrical conductivity ($\sigma$) values of approximately $1 \times 10^3$ S/m at room temperature (RT), revealing that CuCrSnS$_4$ exhibited semiconducting behavior with a band gap of approximately 0.9 eV [23]. In the case replacing Cr with Hf, CuCr$_2$Hf$_x$Se$_4$ exhibited metallic conduction, and the $\sigma$ value increased by two orders of magnitude from $x = 0.06$ to $x = 0.14$ [24]. From the crystallographic and chemical information obtained from a single crystal sample of CuCr$_1$$_x$Sn$_{0.9}$S$_2$Se$_{1.7}$, a rational synthesis of a family of compounds with a chemical formula of CuCr$_2$$_x$Sn$_{3-x}$S$_4$Se$_{1.7}$ and CuCr$_2$$_x$Se$_{1.7}$S$_2$Sn$_{0.3}$S$_2$Se$_{1.7}$ ($x = 0.4$, 0.6, and 1.0) was carried out to study the effect of the chemical replacement of Cr by Sn and Se by S on the physical properties. The present work describes the solid-state synthesis, crystallographic and electrical properties, and density functional theory (DFT) calculations to determine the influence of the chemical substitution of tin and chalcogen on the structure and physical properties of these compounds.

2. Materials and Methods

Powder samples of CuCr$_2$$_x$Sn$_{3-x}$S$_2$Se$_{1.7}$ and CuCr$_2$$_x$Sn$_{1.7}$S$_2$Se$_{2.3}$ were prepared by directly combining high-purity elemental powders (99.99%, Aldrich) in stoichiometric amounts (~0.5 g of the compound). Firstly, powders were mixed manually in hexane with ~5wt% excess of S and Se in an agate mortar and pestle. Hexane was selected to prepare a more homogenous mixture. Then, mixed powders were pressed into disc pellets at ~10 kPa, sealed in evacuated quartz ampoules, and placed in a horizontal tubular programmable furnace. All processes were carried out in an Ar atmosphere. The ampoules were slowly heated from RT to 500 °C at a rate of 150 °C/h and maintained at this temperature for 2 h, then were heated to 850 °C at a rate of 60 °C/h and kept for 10 days. Finally, the ampoules were gradually cooled to RT at a rate of 60 °C/h. The resulting powder was annealed and pressed into a pellet, then heated at 850 °C for 7 days with a 60 °C/min heating and cooling rate to RT. A similar procedure and stoichiometric amount (~300 mg of the compound) with ~5 wt% excess of Se was used to obtain single-crystal. The ampoules were gradually cooled at 10 °C/h until RT.

Single-crystal X-ray diffraction (XRD) data for CuCr$_1$$_x$Sn$_{0.9}$S$_2$Se$_{1.7}$ were accumulated at 293 K with a D8 Venture Bruker AXS diffractometer equipped with Mo Kα radiation ($\lambda = 0.71073$ Å). Data were accumulated using the Bruker SMART software package [25]. Structural refinement was performed using the SHELXL [26] and Olex2 [27] programs. Powder XRD (PXRD) patterns were collected at RT in the range of 5° < 2θ < 80° using a Bruker
D8 Advance powder diffractometer (Bruker, Billerica, MA, USA) with Cu Kα radiation (λ = 1.54178 Å). The XRD patterns were indexed using the CHEKCELL software [28]. The data were analyzed using Rietveld refinements performed in the MAUD program [29]. A LaB₆ powder standard was used to determine the instrumental profile. Chemical composition determination and mapping analyses of the samples were performed by energy dispersive spectroscopy (EDS) and scanning electron microscopy (SEM) using a Tescan Vega 3 scanning electron microscope equipped with a Quantax 400 EDS microanalyzer. Cylindrical pellets (6 mm in diameter and ~2 mm thick) were uniaxially pressed at approximately 5 × 10⁸ Pa. These samples were then mounted on double-sided carbon tape and adhered to an Al specimen holder for analysis. A Perkin–Elmer Lambda 20 UV/Vis spectrophotometer equipped with a Labsphere RSA-PE-20 diffuse reflectance accessory was used to measure the diffuse reflectance. Raman scattering measurements were conducted on a WITec alpha300 System using 532 nm wavelength excitation. The spectrometer was calibrated with a reference single-crystal Si sample (Raman peak at 520.7 cm⁻¹). The spectral data were collected at room temperature in a backscattering configuration in the spectral range of 100–450 cm⁻¹, with a laser spot of ~1 μm and laser power of 2 mW. The thermal analyses were performed using a Netzsch STA 449 F3 Jupiter apparatus with a heating rate of 10 K·min⁻¹. Hall-effect measurements were performed using an ECOPIA HMS 2000 system. The pellets for electrical measurements were uniaxially pressed at approximately 2.5 tons, resulting in cylindrical pellets with a 9.00 mm diameter and thicknesses ranging from 0.93 to 1.30 mm. The Hall coefficient, ±0.556 T, was obtained from the linear fit of the Hall resistivity. The electrical conductivity was measured using the van der Pauw method at RT. The density (ρ) was determined using the dimensions and mass of the sample, corresponding to an average pellet density of approximately 92% (experimental density/crystallographic density). Silver paint and/or InSb alloy were used as electrical contact. Electronic structure calculations were performed in the DFT framework using the Fritz Haber Institute ab initio molecular simulations (FHI-aims) package [30]. Geometry optimizations considered periodic boundary conditions with variable lattice parameters. The starting geometry was the crystallographic structure for CuCr₁₋₀₂Sn₀₉₈S₂₁₁Se₁₈⁹. stoichiometry was adjusted to be close to the different systems under study. Structural relaxations considered dispersion interactions by the Tkatchenko–Scheffler approximation [31] in conjunction with the PBE density functional [32] and the ‘light’ all-electron basis set. Band structure calculations included a larger basis set (‘tight’ in FHI-aims nomenclature) and a k-grid of 2x2x2 in the Self-Consistent Field step. Larger supercells (up to 8x8x8) were tested but provided similar band structures to smaller 2x2x2 calculations. This was expected since the unit cell was already large. Once the electron density was converged, band dispersion was plotted following the path L → G → X → W → K using 50 points for each step.

3. Results and Discussion
3.1. Crystal Structure Analysis, PXRD Patterns, and SEM-EDS Analyses

The motivation for this work was to analyze how changes in the Cr/Sn and S/Se chemical substitutions influence the structure and physical properties of the CuCr₂Se₄ end-member. The crystallographic data and atomic positions of cubic CuCr₁₋₀₂Sn₀₉₈S₂₁₁Se₁₈⁹ are given in Table 1 and Table S1 (see Supplementary Materials), respectively. The refinements were carried out in the Fd₃m space group. The method we applied to solve the crystal structure was that of a model Cu atom occupying the tetrahedral (A) sites, and Cr and Sn cations occupying the octahedral [B] sites. This model was based on linear functions constraining the Sn, Cu, and Cr atoms at the 16d and 8a sites. The sum of the site occupation factor (SOF) was forced to equal 1 (fully occupied) for 16d = (2 − x)Cr + xSn. Furthermore, for the chalcogenide site, the sum of the SOF was forced to equal 1 (fully occupied) for 32e = (4 − y)S + ySe, and the Sn/Cr and S/Se atoms were also constrained to have equivalent atomic displacement parameters (ADPs).
The CuCr$_{1-2x}$Sn$_{0.9-3x}$S$_2$3Se$_{1-7}$ compound crystallized in a normal spinel-type structure and cell parameter $a$ had an intermediate value between those of CuCrSnS$_4$ (10.175 Å) [33] and CuCrSnSe$_4$ (10.672 Å) [34], similar to the values reported for mixed spinels (Cu)$_{n-2x}$[Cr$_2x$Sn$_{1-2x}$]octS$_{3-2x}$Se$_y$ [13]. The Cu–X (X = Se/S) distance in CuCr$_{1-2x}$Sn$_{0.9-3x}$S$_2$3Se$_{1-7}$ was 2.3294(8) Å, which is intermediate between the Cu–Se bond length in (Cu)$_2$Se (2.2583–2.2737 Å) [5] and the Cu–S bond length in thiospinels (Cu)$_2$S (2.3832–2.3947 Å) and the Cu–S bond length in chalcospinels (Cu)$_2$S$_3$(S/Se) (2.5403(5) Å) [13]. The Cu–X distance was near to the tetrahedral covalent radii evaluated by Pyykkö [24] for Cu–S (2.313 Å). The CuCr$_{1-2x}$Sn$_{0.9-3x}$S$_2$3Se$_{1-7}$ tetrahedron was ideal with an angle of 109.5°. The [Cr$_{n}$]$_{oct}$–X bond distance was 2.5403(5) Å, which is comparable to the [Cr/Sn]–Se bond length in (Cu)$_{n-2x}$[Cr$_2x$Sn$_{1-2x}$]octSe$_4$ [13]. The other important structural parameters (bond distances and angles) were as expected and were in acceptable concordance with those of other thio- and selenospinels compounds. The degree of distortion in the octahedral sites was evaluated using distortion indices published by Baur et al. [35]. The [Cr$_{n}$]$_{oct}$X$_6$ octahedron showed a ~2.0% degree of distortion, which agrees with the octahedral distortions in chalcospinels already reported in our previous research [5,6,13]. The single positional u parameter of the chalcogen atoms (u, u, u), Wyckoff position 32e, of CuCr$_{1-2x}$Sn$_{0.9-3x}$S$_2$3Se$_{1-7}$, was 0.25484(4), which is comparable to the values found in cubic CuCr$_{1-2x}$Sn$_{0.9-3x}$Se$_4$ and CuCr$_{1-2x}$Sn$_{0.9-3x}$Se$_4$: u = 0.25663(4) and u = 0.256323(3), respectively [6].

From the single-crystal analysis, rational synthesis of CuCr$_{2-x}$Sn$_x$S$_2$3Se$_{1-7}$ and CuCr$_{2-x}$Sn$_x$S$_{1-7}$Se$_2$3 ($x = 0.4, 0.6,$ and 1.0) powder samples were performed. The SEM backscattered electron images (mapping) and EDS measurements revealed that the chemical compositions of all the powder samples were uniform throughout the scanned region (Figure 1). For example, the experimental results determined a Cu/Cr/Sn/S/Se ratio of approximately 1.1/1.0/0.8/1.8/2.2. No secondary phases or impurity peaks were revealed within the detection limits of this technique.
Figure 1. SEM analysis: Representative EDS mapping images (powder sample) and backscattered electron image of Cu$_{1.0}$Cr$_{1.0}$Sn$_{1.0}$S$_{1.7}$Se$_{2.3}$ (20 kV, 670×).

Figure 2. Representative powder XRD patterns at RT of (a) CuCr$_{1.4}$Sn$_{0.6}$S$_{2.3}$Se$_{1.7}$, (b) CuCr$_{1.6}$Sn$_{0.4}$S$_{2.5}$Se$_{1.7}$, (c) CuCr$_{1.4}$Sn$_{0.6}$S$_{1.7}$Se$_{2.3}$, and (d) CuCr$_{1.6}$Sn$_{0.4}$S$_{1.7}$Se$_{2.3}$ phases showing the corresponding hkl Miller indices.

Rietveld refinements were performed using the PXRD data collected at RT temperature (Figure S1—see Supplementary Materials). The structural model obtained was in good concordance with the model based on the single-crystal XRD data. The R-indices were
refined to reasonable values (Table 2). The Rietveld analysis refinement performed in the CuCr$_{1-x}$Sn$_{0.5}$S$_{2-x}$Se$_{1.7}$ sample indicated the presence of minor phase impurities. The cell lattice parameters gradually increased with increasing Sn concentration (x), which concords with Vegard’s law (Figure S2). The chemical composition of the Rietveld analysis was in accordance with the nominal compositions. As expected, CuCr$_{2-x}$Sn$_x$S$_{2-x}$Se$_{1.7}$ and CuCr$_{2-x}$Sn$_x$S$_{1.7}$Se$_{2-x}$ cell parameter phases expanded owing to the substitution of Cr $[\text{Cr}^{3+}/\text{Cr}^{4+}]$ by the larger Sn$^{4+}$ cation. The effective octahedral ionic radii of the Cr$^{3+}$, Cr$^{4+}$, and Sn$^{4+}$ cations published by Shannon are 0.62 Å, 0.55 Å, and 0.69 Å, respectively. The cell parameter of CuCr$_{1-x}$Sn$_{1.0}$S$_{2-x}$Se$_{1.7}$ was larger than that of CuCr$_{1-x}$Sn$_{1.0}$S$_{1.7}$Se$_{1.7}$ because of the substitution of S by the larger Se anions.

### Table 2. Cell $a$ parameters and $R$-indices obtained from Rietveld refinement of PXRD patterns of CuCr$_{2-x}$Sn$_x$S$_{1.7}$ and CuCr$_{2-x}$Sn$_x$S$_{1.7}$Se$_{2-x}$ ($x = 0.4, 0.6, \text{and} 1.0$).

| Sample                  | $a$ (Å)  | $R_p$    | $R_{exp}$ |
|-------------------------|----------|----------|-----------|
| CuCr$_{1.0}$Sn$_{0.5}$S$_{1.7}$ | 10.370 (2)| 0.0616   | 0.0284    |
| CuCr$_{1.4}$Sn$_{0.6}$S$_{1.7}$ | 10.240 (2)| 0.0808   | 0.0285    |
| CuCr$_{1.6}$Sn$_{0.4}$S$_{1.7}$ | 10.180 (3)| 0.1254   | 0.0471    |
| CuCr$_{1.0}$Sn$_{1.0}$S$_{1.7}$ | 10.447 (2)| 0.1040   | 0.0283    |
| CuCr$_{1.4}$Sn$_{0.6}$S$_{1.7}$ | 10.322 (1)| 0.0755   | 0.0266    |
| CuCr$_{1.6}$Sn$_{0.4}$S$_{1.7}$ | 10.250 (1)| 0.0691   | 0.0261    |

### 3.2. Electrical and Optical Properties, Raman Scattering and DFT Calculations

The conductivity, mobility, magnetoresistance, and carrier concentrations were measured using the van der Pauw method. Room-temperature Hall-effect measurements were conducted with a magnetic field intensity of 0.556 T and a current of 0.5 mA. The measured conductivity, mobility, carrier concentration, and magnetoresistance values are listed in Table 3.

### Table 3. Transport properties obtained from Hall-effect measurements of CuCr$_{2-x}$Sn$_x$S$_{1.7}$ and CuCr$_{2-x}$Sn$_x$S$_{1.7}$Se$_{2-x}$.

| Sample                  | Conductivity (S/cm) | Carrier Concentration (cm$^{-3}$) | Mobility (cm$^2$/V/s) | Magneto-Resistance (Ω) |
|-------------------------|---------------------|---------------------------------|------------------------|------------------------|
| CuCr$_{1.0}$Sn$_{1.0}$S$_{1.7}$ | 1.11 $\times 10^{-4}$ | +1.58 $\times 10^{20}$ | 9.13 $\times 10^{-3}$ | 6.70 $\times 10^{-3}$ |
| CuCr$_{1.4}$Sn$_{0.6}$S$_{1.7}$ | 23.9               | +1.90 $\times 10^{20}$ | 7.86 $\times 10^{-1}$ | 3.89 $\times 10^{-4}$ |
| CuCr$_{1.6}$Sn$_{0.4}$S$_{1.7}$ | 10.7               | +5.30 $\times 10^{19}$ | 1.89                   | 5.45 $\times 10^{-4}$ |
| CuCr$_{1.4}$Sn$_{0.6}$S$_{1.7}$ | 9.04               | +3.48 $\times 10^{20}$ | 2.53 $\times 10^{-1}$ | 4.11 $\times 10^{-4}$ |
| CuCr$_{1.6}$Sn$_{0.4}$S$_{1.7}$ | 17.2               | +6.11 $\times 10^{20}$ | 2.18 $\times 10^{-1}$ | 3.69 $\times 10^{-4}$ |

All the CuCr$_{2-x}$Sn$_x$S$_{2-x}$Se$_{1.7}$ and CuCr$_{2-x}$Sn$_x$S$_{1.7}$Se$_{2-x}$ ($x = 0.4, 0.6, \text{and} 1.0$) samples showed p-type conductivity, which was consistent with the results reported for CuCr$_{2-x}$Sn$_x$S$_4$ and CuCr$_{2-x}$Sb$_x$Se$_4$ [23,36]. The temperature dependence electrical conductivity for CuCr$_{1.4}$Sn$_{0.6}$S$_{1.7}$Se$_{2-x}$ and CuCr$_{1.4}$Sn$_{0.6}$S$_{1.7}$Se$_{2-x}$ is shown in Figure S3. The electrical conductivity ($\sigma$) increased almost exponentially with increasing temperature, revealing semiconductor behavior for the sample, followed by a temperature dependence of $\sigma \sim T^n$. The Hall coefficients were positive at RT, which is indicative of p-type behavior. The hole concentrations were similar at all studied phases, with a carrier concentration of approximately $10^{20}$ cm$^{-3}$. Khan et al. reported values of approximately $2.41 \times 10^{21}$ cm$^{-3}$ for CuCr$_{1.5}$Sb$_{0.5}$S$_4$, which showed typical degenerate semiconductor behavior. Electrical mobility is an important property for evaluating electrical behavior. The electrical hole mobilities of CuCr$_{2-x}$Sn$_x$S$_{2-x}$Se$_{1.7}$ and CuCr$_{2-x}$Sn$_x$S$_{1.7}$Se$_{2-x}$ (~0.10 cm$^2$/V/s) were smaller than the value reported for CuCr$_{1.5}$Sb$_{0.5}$S$_4$ (4.06 cm$^2$/V/s). The chalcogen S/Se substitution thus led to low mobility. The electrical conductivities, $\sigma$, of the CuCr$_{1.0}$Sn$_{1.0}$S$_{2-x}$, CuCr$_{2-x}$Sn$_x$S$_{2-x}$Se$_{1.7}$, and CuCr$_{2-x}$Sn$_x$S$_{2-x}$Se$_{2-x}$ phases were lower than those of the CuCr$_2$S$_4$ (667 S/cm) and CuCr$_2$Se$_4$ (1110 S/cm) end-members. This
indicates that $\sigma$ is quite sensitive to the Sn content. The electrical conductivity $\sigma$ showed chromium-content dependence, and it increased in all cases with decreasing $x$ values. The only exception was the CuCr$_{1-x}$Sn$_{0.7}$S$_{2-x}$Se$_{1.7}$ sample, which had the lowest $\sigma$ value. This sample showed a complex chemical composition related to chromium content; the Rietveld analysis refinement performed for this sample indicated the presence of minor phase impurities. Therefore, such as inhomogeneity could be responsible for the exceptional conductivity values. On the other hand, the $\sigma$ value for CuCr$_{1-x}$Sn$_{0.7}$S$_{2-x}$Se$_{1.7}$ was approximately 2 times larger than the value obtained for CuCr$_{1-x}$Sn$_{0.4}$S$_{2-x}$Se$_{2.3}$ and approximately 80 times larger than that of CuCr$_{1-x}$Sn$_{1.0}$S$_{2-x}$Se$_{2.0}$. This suggests that the chromium content is the main reason for the increased conductivity in these systems. Similar results have been observed for CuCr$_{1-x}$Sn$_{0.8}$S$_{4}$ (~40 S/cm) thiospinels [23]. Nagata et al. reported large magnetoresistance in CuCrZrS ($\sim$2.0 eV) [37,38].

The greater weight of Sn than Cr leads to a shift towards lower energies. In this phase, the chromium site was partially substituted by a diamagnetic metal. Therefore, such as inhomogeneity could be responsible for the exceptional conductivity values. On the other hand, the $\sigma$ value for CuCr$_{1-x}$Sn$_{0.7}$S$_{2-x}$Se$_{1.7}$ was approximately 2 times larger than the value obtained for CuCr$_{1-x}$Sn$_{0.4}$S$_{2-x}$Se$_{2.3}$ and approximately 80 times larger than that of CuCr$_{1-x}$Sn$_{1.0}$S$_{2-x}$Se$_{2.0}$. This suggests that the chromium content is the main reason for the increased conductivity in these systems. Similar results have been observed for CuCr$_{1-x}$Sn$_{0.8}$S$_{4}$ (~40 S/cm) thiospinels [23]. Nagata et al. reported large magnetoresistance in CuCrZrS$_{4}$. In this phase, the chromium site was partially substituted by a diamagnetic metal. This solid solution exhibited VRH behavior and resistivity that decreased with an increasing magnetic field [21]. In our systems, very low magnetoresistance was observed at an applied magnetic field of 0.556 T (see Table 3). This suggests that the electronic transport properties of CuCrMX$_{4}$ thio- and selenospinels are highly sensitive to chemical substitution.

These materials showed behavior typical of semiconductors, and the band gaps were measured using UV-vis-IR NIR diffuse reflectance spectroscopy (Figure 3). The observed band gaps of CuCr$_{2-x}$Sn$_{x}$S$_{2}$Se$_{1.7}$ and CuCr$_{2-x}$Sn$_{x}$S$_{1.7}$Se$_{2.3}$ ranged from ~1.6 to 1.9 eV. These values are comparable to those observed for CoCr$_{2}$S$_{4}$ nanocrystals (1.7 eV) and CuCr$_{2}$Se$_{4}$ (~2.0 eV) [37,38].

![Figure 3](image_url)

**Figure 3.** (a) Representative plot of diffuse reflectance against photon energy ($E_\text{ph}$) for CuCr$_{1.0}$Sn$_{0.7}$S$_{2.3}$Se$_{1.7}$ sample. Red line is included to show the baseline, and linear extrapolation used to determine the band gap. (b) Representative Raman spectral of CuCr$_{1-x}$Sn$_{0.4}$S$_{2.3}$Se$_{1.7}$ powder sample with the different contributions deduced from the fitting of the different peaks with Lorentzian curves (green lines).

Raman spectra of the CuCr$_{2-x}$Sn$_{x}$S$_{2.3}$Se$_{1.7}$ and CuCr$_{2-x}$Sn$_{x}$S$_{1.7}$Se$_{2.3}$ materials were compiled inside the 100 to 450 cm$^{-1}$ range (Figure 3). The spectra present five signals at approximately $\sim$124, 203, 265, 295, and 350 cm$^{-1}$. These signals are equivalent to the (Cu)$_{tet}$[Cr$_2$xSn$_x$]$_{tet}$S$_2$Se$_2$ (0.2 $\leq x \leq$ 1.0) spinels, where a partial substitution of Cr by Sn occurs [12]. The frequencies and vibrational assignment of Raman bands with respect to the CuCrSnS$_4$ and (Cu)$_{tet}$[Cr$_2$xSn$_x$]$_{tet}$S$_2$Se$_2$ is shown in Table S2 (see Supplementary Materials). The signals at $\sim$350 cm$^{-1}$ and $\sim$270 cm$^{-1}$ have been assigned to the A$_{1g}$ and F$_{2g}$ (2) modes which are associated with symmetrical and asymmetrical stretching of the chalcogen bond in the tetrahedral metal, respectively. We observed a significant shift at lower frequencies for peaks at $\sim$350 cm$^{-1}$, 295 cm$^{-1}$, and $\sim$265 cm$^{-1}$. The displacement of the signal is attributed to the incorporation of Sn atoms in an octahedral position. The greater weight of Sn than Cr leads to a shift towards lower energies. On the
other hand, as Sn–chalcogen interactions influence the environment, this results in a
change in the polarities of the bonds inducing variations in the intensity and position
of the signals.

To rationalize the physical measurements, DFT calculations were carried out on com-
ounds with different elemental compositions. To reach the stoichiometry of the current
compounds under discussion, the structure of the CuCr$_2$Se$_4$ spinel was modified to ac-
count for the different Cr/Sn and S/Se ratios. Ions were placed randomly, and geometric
optimization was repeated for three different ion arrangements for each case. To avoid
the optimization of large supercells, model stoichiometries were chosen to be close to the
studied systems while maintaining a single unit cell. Optimized cell parameters agreed
with the experimental data (less than 2% deviation in cell length) and are presented in
Table 4. Deviation between repetitions of the same stoichiometry ($\sigma$) was low, indicating
that the results were robust.

Table 4. Experimental and calculated cell parameters for different CuCr$_{2-x}$Sn$_x$S$_{4-y}$Se$_y$ compounds. The standard deviation was calculated from three optimizations with the same stichometry but
different ion arrangements.

| Model Stoichiometry | Reference Formula | $a$ Exp (Å) | $a$ Calc (Å) | $\sigma$ |
|---------------------|-------------------|-------------|--------------|---------|
| Cu$_8$Cr$_8$Sn$_8$S$_{16}$Se$_{16}$ | Cu$_1$Cr$_1$Sn$_{1.5}$S$_{2.5}$Se$_{1.5}$ | 10.398 § | 10.521 | 0.0197 |
| Cu$_8$Cr$_8$Sn$_{19}$Se$_{13}$ | Cu$_1$Cr$_1$Sn$_{1.7}$S$_{2.3}$Se$_{1.7}$ | 10.370 | 10.465 | 0.0195 |
| Cu$_8$Cr$_{11}$Sn$_{13}$Se$_{19}$ | Cu$_1$Cr$_1$Sn$_{1.9}$S$_{2.1}$Se$_{2.1}$ | 10.322 | 10.413 | 0.0170 |
| Cu$_9$Cr$_{11}$Sn$_{10}$Se$_{13}$ | Cu$_1$Cr$_1$Sn$_{1.9}$S$_{2.3}$Se$_{1.7}$ | 10.24 | 10.307 | 0.0155 |
| Cu$_8$Cr$_{13}$Sn$_{13}$Se$_{19}$ | Cu$_1$Cr$_1$Sn$_{1.9}$S$_{2.3}$Se$_{2.3}$ | 10.25 | 10.277 | 0.0499 |
| Cu$_8$Cr$_{13}$Sn$_{10}$Se$_{13}$ | Cu$_1$Cr$_1$Sn$_{1.9}$S$_{2.3}$Se$_{1.7}$ | 10.18 | 10.197 | 0.0100 |

§ cell $a$ parameter obtained from single-crystal analysis of CuCr$_{1.0}$Sn$_{1.0}$S$_{2.1}$Se$_{1.9}$ was 10.398(2) Å [12].

Regarding the electronic structure of the different spinels, the Cr centers concentrated
most of the spin density; Mulliken spin populations were always around 3.2–3.3 electrons.
A smaller spin polarization featuring the opposite spin was observed for S/Se atoms. Cu
ions showed small spin polarization, suggesting a monovalent state for this ion. The
different models showed minor changes, as the electronic configuration did not change
qualitatively when the elemental composition was modified. The calculated magnetic
moment was consistent with the presence of monovalent Cu ions and Cr$^{3+}$ ($S = 3/2$) centers
coupled antiferromagnetically with a delocalized electron with relevant spin density at the
S/Se atoms. This picture is in line with neutron diffraction measurements of CuCr$_2$Se$_4$
performed by Colominas [38]. Band structures for all models were consistent with the
observed semiconductor behavior and presented noticeable spin polarization (Figure S4).
The density of states clearly reflected the spin configuration of the systems. Figure 4
present the element and spin-resolved DOS for Cu$_8$Cr$_8$Sn$_{16}$Se$_{16}$. The unpaired electrons
associated with the Cr$^{3+}$ ion appear as a large contribution in the upper part of the valence
band between $-6$ and $-7$ eV. Unoccupied beta d-orbitals appear as a broad peak ranging
from $-5.5$ eV to $-2.5$ eV. The unpaired electron from S/Se is connected with the larger
contribution of these ions in the occupied part of the beta density of states. Other models
feature similar DOS plots (shown as Figure S5 in SI).
Figure 4. Element and spin-resolved density of states for the model CuCrSnS₂Se₂. Remaining systems are presented in Figure S5.

4. Conclusions

Single-crystal CuCr₁.₁Sn₀.₉S₂.₃Se₁.₇ and powder samples of CuCr₂ₓSnₓS₂.₃Se₁.₇ (x = 0.4, 0.6, and 1.0) were obtained via to using conventional solid-state synthesis. Their crystal structures, as determined by single-crystal XRD, corresponded to normal spinel-type structures. For all the samples, the vibrational analysis and optical properties were in good agreement with the selenospinel phases. The electrical measurements showed a p-type semiconductor behavior and electrical conductivities lower than those of the seleno- and sulfospinel CuCr₂X₄. DFT calculations suggested copper ions are monovalent and hence, diamagnetic. The spin density concentrated in the Cr₃⁺ ions (S = 3/2), while a more delocalized contribution was associated with S/Se. The theoretical DFT and experimental measurements clearly demonstrated that the conductivity is quite sensitive to the Sn content. However, the non-stoichiometry in the chalcogen, in this case, selenium and sulfur, had a weak influence on the electrical properties.

Supplementary Materials: The following materials are available online at https://www.mdpi.com/article/10.3390/app12031586/s1. Table S1: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters; Figure S1: Representative powder XRD data for CuCr₁.₁Sn₀.₉S₂.₃Se₁.₇; Figure S2: Vegard’s Law; Figure S3: Electrical conductivity against temperature of CuCr₂ₓSnₓS₂.₃Se₁.₇; Figure S4. Band structures for calculated models. Alpha bands are depicted in black, and beta bands are presented in green; Figure S5: Element and spin-resolved density of states for all calculated systems.

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