CuCr\textsubscript{2-x}Sb\textsubscript{x}S\textsubscript{4} and Cu\textsubscript{1-y}Sb\textsubscript{y}Cr\textsubscript{2}S\textsubscript{4} Solid Solutions


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Abstract—CuCr\textsubscript{2-x}Sb\textsubscript{x}S\textsubscript{4} and Cu\textsubscript{1-y}Sb\textsubscript{y}Cr\textsubscript{2}S\textsubscript{4} solid solutions with the spinel structure were synthesized, and their magnetic and electrical properties were studied. The limits of solid solutions in these systems were found to be \( x = 0.5 \) and \( y = 0.22 \). Models of the cation distributions in the solid solutions are proposed. The CuCr\textsubscript{2-x}Sb\textsubscript{x}S\textsubscript{4} solid solutions with \( 0.10 < x < 0.15 \) are magnetic semiconductors with high ferromagnetic ordering temperatures.

The development of modern electronic technology stimulates interest in magnetic semiconductors—materials characterized by strong interaction between the electrical and magnetic systems, which gives rise to unique physical effects. A great deal of attention is paid to magnetic semiconductors based on the ACr\textsubscript{2}X\textsubscript{4} (A = Cu, Cd, Hg, Zn, Fe, Co; X = S, Se) chalcogenide spinels, whose properties can be varied over a wide range via cation and anion substitutions [1].

CuCr\textsubscript{2}S\textsubscript{4} stands out among the other chalcogenide spinels because of its high ferromagnetic ordering temperature \( T_c \) in combination with metallic conductivity. Isomorphous substitutions on both cation and anion sites of CuCr\textsubscript{2}S\textsubscript{4} are possible over wide concentration ranges [1]. The resulting substituted material may exhibit semiconducting behavior, retaining a fairly high ferromagnetic ordering temperature. One interesting and yet poorly studied substituent is antimony, which can be accommodated in both anion and cation sites of CuCr\textsubscript{2}S\textsubscript{4}.

Experimental evidence that Sb\textsuperscript{5+} ions occupy B sites in the structure of oxide spinels was first reported by Dulac and Durif [2] and Bayer [3], who obtained the Co\textsubscript{7/3}Sb\textsubscript{2/3}O\textsubscript{4} and Zn\textsubscript{7/3}Sb\textsubscript{2/3}O\textsubscript{4} spinels. In most published reports to date, antimony has been substituted at the B site of oxide spinels such as

\[ \text{Ni}_{1+x} \text{Fe}_{2-3x} \text{Sb}_3 \text{O}_4, \text{Mg}_{1+x} \text{Fe}_{2-3x} \text{Sb}_3 \text{O}_4, \]
\[ \text{Li}_{0.5+x} \text{Fe}_{2-2x} \text{Sb}_3 \text{O}_4, \text{Ni}_{5/3-s} \text{Zn}_{s} \text{Fe}_{1-s} \text{Sb}_3 \text{O}_4, \]
\[ \text{Co}_{1+x} \text{Fe}_{2-3x} \text{Sb}_3 \text{O}_4 [4], \]

and Mn\textsubscript{1+s}Cr\textsubscript{2-3s}Sb\textsubscript{s}S\textsubscript{4} (0.05 < s < 0.30) [5], where Sb also has a valence of 5+. In 1989, Kalinin et al. [6] identified a new mineral, florencovite, belonging to the family of chalcogenide spinels. Its composition was determined to be Cu\textsuperscript{+}Cr\textsuperscript{3+}Sb\textsuperscript{4+} \text{S}^{-2}\text{ZnCrS}_{4}.

The ability of antimony to substitute for the Cu site is evidenced by the formation of Cu\textsubscript{4-2x}Sb\textsubscript{x}Cr\textsubscript{8-2x}Se\textsubscript{16-3x} solid solutions in the CuCr\textsubscript{2}Se\textsubscript{4}–Cu\textsubscript{2}Sb\textsubscript{2}Cr\textsubscript{6}Se\textsubscript{13} system [7].

With the aim of preparing new CuCr\textsubscript{2}S\textsubscript{4}(Sb)-based materials, we studied two solid-solution systems in which antimony was expected to substitute for both Cu and Cr sites.

Solid solutions were synthesized from elemental mixtures of OSCh 11-4 copper powder (99.99+% purity), ERKh chromium powder (99.99+%), SU-000 antimony (99.999+%), and OSCh 16-5 sulfur (99.9999+%). Samples weighing 5 g were sealed in quartz tubes under a vacuum of 10\textsuperscript{-2} Pa. The temperature was raised stepwise. After holding at temperature, the samples were cooled to 400°C over a period of 1 day, followed by furnace-cooling. Next, the samples were reground and refired. The starting-mixture composition was expected to predetermine which sites in the spinel structure will be occupied by antimony ions.

The choice of the firing temperature (600°C) and elemental synthesis was dictated by earlier data [8], according to which increasing the synthesis temperature or the use of precursor compounds decelerates the formation of CuCr\textsubscript{2}S\textsubscript{4}.

The conditions for the preparation of CuCr\textsubscript{2-x}Sb\textsubscript{x}S\textsubscript{4} solid solutions were chosen in preliminary experiments by varying the firing time of the \( x = 0.1 \) and 0.4 mixtures (Table 1). The materials prepared by firing at 600°C for 4–7 days were mixed-phase. Only after annealing for an additional 14 days were single-phase samples obtained.

Based on these results, both CuCr\textsubscript{2-x}Sb\textsubscript{x}S\textsubscript{4} (0 < x < 0.60) and Cu\textsubscript{1-y}Sb\textsubscript{y}Cr\textsubscript{2}S\textsubscript{4} (0 < y < 0.375) materials were...
CuCr\(_{2-x}\)S\(_x\)S\(_4\) AND Cu\(_{1-y}\)S\(_y\)Cr\(_2\)S\(_4\) SOLID SOLUTIONS

Table 1. Conditions for CuCr\(_2\)S\(_4\)(Sb) synthesis

<table>
<thead>
<tr>
<th>System</th>
<th>(x, y)</th>
<th>(t_{\text{syn}}, ^\circ\text{C})</th>
<th>(t_{\text{syn}}, \text{days})</th>
<th>(t_{\text{ann}}, ^\circ\text{C})</th>
<th>(t_{\text{ann}}, \text{days})</th>
<th>Phase composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuCr(_{2-x})S(_x)S(_4)</td>
<td>0.1</td>
<td>610</td>
<td>4</td>
<td></td>
<td></td>
<td>Spinel + Cu(_2)S</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>600</td>
<td>7</td>
<td></td>
<td></td>
<td>Spinel + Cu(_2)S</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>600</td>
<td>7</td>
<td>600</td>
<td>14</td>
<td>Spinel</td>
</tr>
<tr>
<td></td>
<td>0.4</td>
<td>600</td>
<td>4</td>
<td>600</td>
<td>14</td>
<td>Spinel + Cu(_2)S</td>
</tr>
<tr>
<td></td>
<td>0.4</td>
<td>600</td>
<td>7</td>
<td>600</td>
<td>14</td>
<td>Spinel</td>
</tr>
<tr>
<td></td>
<td>0.4</td>
<td>600</td>
<td>9</td>
<td>600</td>
<td>14</td>
<td>Spinel</td>
</tr>
<tr>
<td></td>
<td>0.4</td>
<td>600</td>
<td>15</td>
<td>600</td>
<td>19</td>
<td>Spinel</td>
</tr>
<tr>
<td>Cu(_{1-y})S(_y)Cr(_2)S(_4)</td>
<td>0.02–0.16</td>
<td>600</td>
<td>(t_{\text{syn}})</td>
<td>600</td>
<td>14</td>
<td>Mixed-phase</td>
</tr>
<tr>
<td></td>
<td>0.20</td>
<td></td>
<td>7</td>
<td>600</td>
<td>15</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.28</td>
<td></td>
<td>8</td>
<td>600</td>
<td>15</td>
<td></td>
</tr>
</tbody>
</table>

synthesized by firing at 600–610\(^\circ\)C for 7 days, followed by annealing at 600\(^\circ\)C for 14 days.

Phase composition of the resultant polycrystalline materials was determined by x-ray diffraction (XRD) with DRON-1 and Rigaku diffractometers (Ni-filtered CuK\(_\alpha\) radiation, continuous scan rate of 1 deg/min, \(2\theta = 10^\circ–100^\circ\)). Diffraction patterns were indexed using earlier structural data for the Cu–Cr–Sb–S system and the JCPDS Powder Diffraction File. Lattice parameters were refined by least squares fitting.

According to XRD data, the Cu\(_{1-y}\)S\(_y\)Cr\(_2\)S\(_4\) materials were single-phase in the composition range \(y = 0–0.20\) and had the spinel structure. The \(y = 0.231\) sample contained trace levels of an impurity phase. The materials with \(y > 0.25\) were mixed-phase.

In the CuCr\(_{2-x}\)S\(_x\)S\(_4\) system, single-phase spinel materials were obtained up to \(x = 0.50\). At \(x > 0.50\), the samples contained the additional phase Cu\(_3\)Sb\(_2\)S\(_4\).

To accurately determine the limits of the solid solutions, we used the composition dependences of the lattice parameter (Fig. 1). In the CuCr\(_{2-x}\)S\(_x\)S\(_4\) system, the \(a\) vs. \(x\) data show a positive deviation from Vegard’s law (Fig. 1a). At \(x > 0.50\), the lattice parameter is constant. Therefore, Sb substitutes on Cr sites in the structure of CuCr\(_2\)S\(_4\) up to \(x = 0.50\).

In the Cu\(_{1-y}\)S\(_y\)Cr\(_2\)S\(_4\) system, the lattice parameter rises linearly with antimony content (Fig. 1b). The \(a\) vs. \(y\) data show a break at \(y = 0.22\), corresponding to the limit of the solid solution.

As shown in earlier studies [2–5], the antimony introduced into spinel oxides occupies octahedral sites and is in the oxidation state 5+. The oxidation state 3+ is characteristic of other, nonspinel phases with orthorhombic (FeSb\(_2\)S\(_4\) [9], SnSb\(_2\)S\(_4\) [10], EuSb\(_2\)S\(_4\) [11]) or hexagonal (PbSb\(_2\)S\(_4\) [10]) structures.

According to Shannon [12], the effective ionic radius of Sb\(^{5+}\) (0.60 \(\text{Å}\) at CN = 6) differs little from the tetrahedral radii of Cu\(^+\) (0.60 \(\text{Å}\)) and Cu\(^{2+}\) (0.57 \(\text{Å}\)) and octahedral radii of Cr\(^{3+}\) (0.615 \(\text{Å}\)) and Cr\(^{4+}\) (0.55 \(\text{Å}\)), which is favorable for the formation of broad solid-solution ranges. Electronegativity data [13], as well as Mössbauer and NMR studies [14–16], also provide evidence that the Sb substituent in the structure of CuCr\(_{2-x}\)S\(_x\)S\(_4\) and Cu\(_{1-y}\)S\(_y\)Cr\(_2\)S\(_4\) has a valence of 5+.

In terms of Lotgering’s model [17], the charge balance is retained if Sb\(^{5+}\) substitution is accompanied by Cr reduction, Cr\(^{4+}\) \(\rightarrow\) Cr\(^{3+}\), which would be expected to increase the lattice parameter. We propose the follow-