Solid solubility of Mg and enhanced electrical conduction in the C-axis orientation of CuCr$_{1-x}$Mg$_x$O$_2$ polycrystals

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**ABSTRACT**

The c-axis orientation of CuCr$_{1-x}$Mg$_x$O$_2$ (0 ≤ x ≤ 0.08) ceramics was prepared through solid-state reactions. The effects of a Mg solid solution in CuCrO$_2$ have been investigated in terms of electrical conductivity, thermopower, and microstructure. While x = 0–0.03, the polycrystalline grains in a single-phase delafossite grew along the ab-plane with increasing (001) Lotgering factors of up to 0.53. It exhibited semiconducting electrical transport. The room temperature conductivity increased by 3–4 orders of magnitude, even up to 12.03 S·cm$^{-1}$, because of a reduction in Arrhenius activation energy. The Seebeck coefficient decreased from 828 to 257.8 μV·K$^{-1}$ at 330 K. For the doped samples, due to the contribution of the phonon drag thermopower overmatching the variation of the carrier concentration to the thermopower, it increased with increasing temperature, which was the opposite to that observed in the undoped samples. While x = 0.04–0.08, the second-phase MgCr$_2$O$_4$ spinel appeared and the properties and microstructure hardly changed. The layered structure of the c-axis orientation led to dominant electrical transport along the ab-plane and reduced the grain boundary, leading to weakened defect scattering, which caused an enhancement in conductivity.

1. Introduction

As a p-type transparent conductive oxide (TCO), the delafossite structure oxide, CuCrO$_2$, with a wide band gap (3.2 eV) has broad application prospects in thermoelectricity, optoelectronics, and catalysis [1–7]. Poienar M et al. [1] studied the single crystal’s intrinsic electrical transport properties and a large resistivity anisotropy ($\rho_{c(300K)} / \rho_{ab(300K)} = 35$), indicating that the [Cu$^+$] or [CrO$_6$] layer is a much better conductive path than the c-axis (Cr-O-Cu). Due to the strong localization effect of oxygen at the valence band edge, the attraction to holes was so great that its conductivity was 3–4 orders of magnitude lower than the n-type TCO, which limits its device application. However, acceptor doping can effectively improve the electrical conductivity of the material. Huang et al. studied the acceptor doping of calcium, nickel, aluminum, and magnesium [2–6,8–11]. The Mg-doping modulates the thermal, electrical, and magnetic transport properties of CuCrO$_2$ oxide [6,7,12–15]. Triputri S. Tripathi et al. [12] showed that CuCr$_{0.9}$Mg$_{0.1}$O$_2$ film has a maximum conductivity of 217 S·cm$^{-1}$, which is 10–200 times higher than undoped film and has the highest conductivity of all the available film. However, thin film preparation is complicated and costly, and high-quality polycrystalline ceramics are an issue for thin films. Up until now, research on Mg-doping CuCrO$_2$ has focused on the properties of optoelectronics and catalysis of thin films [6,7,12–15], rather than on the structure and properties of polycrystalline [16–21], including conductivity, thermopower, and magnetic properties [16–18]. A report by T. Okuda et al. showed that the maximum electrical conductivity was 15 S·cm$^{-1}$, which is nearly 4000 times greater than the undoped polycrystalline [16]. Ismail et al. compared Mg-doped and Fe-doped CuCrO$_2$ nanocrystals prepared by hydrothermal synthesis and found that the properties of the Mg-doped CuCrO$_2$ were superior to those of Fe-doped CuCrO$_2$ [21]. We determined the solid solubility of Mg in CuCrO$_2$ polycrystalline and discussed the physical mechanism of Mg-doping effects on the structure, morphology, and thermoelectric transport properties of CuCrO$_2$.

2. Experiment

CuCr$_{1-x}$Mg$_x$O$_2$ (x = 0, 0.005, 0.01, 0.02, 0.03, 0.04, 0.05, 0.08) polycrystalline samples were prepared through solid-state reactions in air. Cu$_2$O (99.9%), Cr$_2$O$_3$ (99.95%), and MgO (99.99%) were weighed according to the stoichiometric ratio. The raw materials were mixed well and ground, and the subsequent fine powders were pressed into pellets and pre-sintered at 1100°C for 12 h. Finally, the pellets were ground and pressed into pellets again, sintered at 1100°C for 12 h, and cooled to room temperature.

The phase structure of the obtained polycrystalline samples were characterized by BDX3200 X-ray
diffraction. The microstructure and morphology were observed by XL30E SEM. The resistivity–temperature (p-T) curves were tested by the four-probe method between 77 K and 330 K. The Seebeck coefficient–temperature (S-T) curves were measured by the Linseis-LSR3 Seebeck coefficient test system between 300 K and 1000 K.

3. Results and discussion

3.1. Phase structure and orientation characterization

Figure 1 shows the XRD patterns of CuCr$_{1-x}$Mg$_x$O$_2$ (0 ≤ x ≤ 0.08) polycrystals. In contrast to the CuCrO$_2$ (PDF 89–0539) standard spectrum, the main phase of all samples was the 3 R delafossite structure. When x ≤ 0.03, the polycrystals were single phase. While x ≥ 0.04, small diffraction peaks of the second phase appeared, which were assumed to be the Mg(Cu)Cr$_2$O$_4$ spinel phase. Due to the CuCr$_2$O$_4$ phase being transformed into the CuCrO$_2$ phase over 800°C, the spinal phase was confirmed as MgCr$_2$O$_4$ [13,18]. The (006) diffraction peak of our samples was the strongest peak, which was different from the strongest (012) peak of the isotropic standard powder diffraction spectrum and was especially stronger with an increase in the Mg-doping amount (x). All samples showed highly (00 l) preferred orientation, which is in agreement with the literature [14–16].

We further characterized the degree of (00 l) preferential orientation with the Lotgering orientation factor $F = \frac{P_l - P_0}{P_l + P_0}$ [22,23], where $P_l$ and $P_0$ are the p-values of the preferred orientation samples and the standard diffraction spectrum, respectively, and $P = \sum_{hkl} I_{hkl} / \sum_{hkl} I_{00l}$, with $I_{hkl}$ the relative intensities of the (00 l) plane group diffraction peaks and $I_{00l}$ plane group orientation diffraction peaks, respectively. The results of the orientation factors of the samples are shown in Table 1, which indicate that Mg-doping enhanced the c-axis preferential orientation at x = 0–0.03, and the (00 l) Lotgering factor increased from 0.39 to 0.53.

The lattice constants and measured sample densities are shown in Table 1. At x = 0–0.03, the increase in a and the decrease in c from the XRD results are owed to Mg$^{2+}$ ions (radius of 0.86 Å) and substituted Cr$^{3+}$ ions (radius of 0.76 Å). Correspondingly, the Cr$_2$O$_3$ layer expanded and the Cu-O-Cu bond length was compressed, which is consistent with previous reports [16–18]. Bulk density measured by the drainage method increased significantly with increasing Mg-doping amount at x = 0–0.03. When x = 0.04–0.08, the lattice constants and the bulk density of the samples were almost unchanged, which owed to the Mg substitution in the CuCrO$_2$ lattice reaching the point of saturation (x ~ 0.03).

3.2. Vertical section morphology observation

The cross-sectional morphologies of the samples are shown in Figure 2. At x = 0–0.03, the small grains grew sharply and were distributed homogeneously and loosely. The increasing grain size grew sufficiently in the ab-plane and reduced boundaries and pores of the layered polycrystalline significantly as the doping amount increased, resulting in increased bulk densities. When x ≥ 0.04, the second-phase particles began to emerge at the grain boundaries, which was due to Mg$^{2+}$ cations no longer being substituted by Cr$^{3+}$ cations, forming spinel phase MgCr$_2$O$_4$ and segregating at the grain boundaries, as can be observed in Figure 2(f).

The growth and compactness of the grains can be explained by the crystal growth kinetics formula [24–26]:

| Sample | Lotgering | Lattice constants | Bulk density | Conductivity | Activation energy | Seebeck coefficient |
|--------|-----------|------------------|--------------|--------------|------------------|-------------------|
| x = 0  | 0.39      | 2.974            | 17.11        | 3.58         | 2.17 × 10⁻¹      | 0.273             | 828              |
| x = 0.005 | 0.49      | 2.979            | 17.05        | 3.45         | 0.019            | 0.188             | /                |
| x = 0.01 | 0.49      | 2.975            | 17.04        | 3.58         | 0.062            | 0.110             | /                |
| x = 0.02 | 0.52      | 2.978            | 17.03        | 3.82         | 2.96             | 0.047             | 260              |
| x = 0.03 | 0.53      | 2.979            | 17.01        | 4.35         | 12.03            | 0.031             | 257.8            |
| x = 0.04 | 0.31      | 2.980            | 17.01        | 4.28         | 11.64            | 0.032             | 254.5            |
| x = 0.05 | 0.29      | 2.980            | 17.01        | 4.28         | 11.61            | 0.035             | 252.5            |
| x = 0.08 | 0.30      | 2.980            | 17.01        | 4.53         | 11.61            | 0.035             | 251              |

Figure 1. XRD patterns of CuCr$_{1-x}$Mg$_x$O$_2$ (0 ≤ x ≤ 0.08) polycrystals.

Table 1. Summary of the microstructure and properties of CuCr$_{1-x}$Mg$_x$O$_2$ (0 ≤ x ≤ 0.08) polycrystals.
\[ G^n - G_0^n = A \exp\left(\frac{Q}{RT}\right) \] (1)

where \( G \) is the average grain size at time, \( t \); \( G_0 \) is the initial grain size; \( n \) is the kinetics grain growth exponent; \( A \) is the constant; \( Q \) is the apparent activation energy; \( R \) is the gas constant; and \( T \) is the absolute temperature. According to the analysis, at the same \( T \) and \( t \), Mg-doping may increase the kinetics of the grain growth exponent and decrease the apparent activation energy, promoting grain growth.

### 3.3. Thermoelectric transport properties

The resistivity–temperature curves (\( \rho-T \)) and fitting curves (\( \ln(1/\rho)-1000/T \)) are shown in Figure 3. All samples exhibited semiconducting electrical transport behavior as observed in Figure 3(a). At \( x = 0-0.03 \), the polycrystal resistivities decreased significantly with increasing \( x \). The room temperature conductivity was up to 12.03 S·cm\(^{-1}\) at \( x = 0.03 \); it was nearly 6000 times that of the undoped samples and only an order of magnitude from the conductivity of \( \text{CuCr}_{1-x}\text{Mg}_x\text{O}_2 \) film [6,20,25], whereas the resistivity increased slightly at \( x = 0.04-0.08 \). This is

![Figure 2](image1.png)

![Figure 3](image2.png)
consistent with the change in crystal cross-sectional morphology. As the grains grew, the boundary decreased and the conductivity increased. The fitting results in Figure 3(b) show that the linear relationship between \( \ln(1/\rho) \) and \( 1000/T \) adheres to formula (2) in the range of 200–300 K, which proved that the CuCr\(_{1-x}\)Mg\(_x\)O\(_2\) polycrystals were in agreement with Arrhenius thermal activation at room temperature.

\[
\sigma = \sigma_0 \exp(-\frac{E_a}{k_B T})
\]

where \( \sigma_0 \) is the constant related to the carrier concentration, \( T \) is the absolute temperature, \( E_a \) is the thermal activation energy, and \( k_B \) is the Boltzmann constant.

At \( x = 0.03 \), the thermal activation energy as shown in Table 1 gradually decreased from 0.273 eV to 0.031 eV and then remained unchanged at \( x = 0.04–0.08 \). The change occurred at \( x = 0.03 \). The low \( E_a \) values were much less than the forbidden band width (3.2 eV), indicating that the conduction mode holes in the valence band became the carriers, and the holes were generated when electrons were excited from the valence band to the acceptor energy level.

Figure 4 shows the Seebeck coefficient–temperature curves at 300–860 K. The positive Seebeck coefficients indicate that the holes were the main carriers. The thermopower of the doped samples decreased markedly at \( x = 0.03 \) and hardly changed at \( x = 0.04–0.08 \). Combined with the variation characteristics of morphologies and electrical conductivity, the solubility of Mg in CuCr\(_{1-x}\)Mg\(_x\)O\(_2\) polycrystals was approximately 0.03. The thermopower of the undoped samples \( (x = 0) \) decreased with increasing temperature. These samples showed typical intrinsic semiconductor behavior. However, the lowered thermopower of the doped samples \( (x = 0.02–0.08) \) increased slowly with increasing temperatures. This is due to the contribution of the phonon drag. The increasing thermopower induced by the intensified lattice vibration overmatched the decreasing intrinsic excitation and Mg-doping thermopower with rising temperatures.

### 3.4. Mg-doping mechanism

Due to low formation energy, the acceptor defect Cu vacancies \( V_{\text{Cu}} \) and interstitial oxygen \( O_i \) were formed spontaneously and generated hole conduction by the low-migration energy \( V_{\text{Cu}} \) [14], which induces \( p \)-type conduction of the intrinsic CuCrO\(_2\). The acceptor doping caused by the substitution of Mg\(^{2+}\) for Cr\(^{3+}\) brought in many low-localization hole carriers, which was crucial for the enhancement in conductivity. Also, Mg-doping led to a strong preference for c-axis orientation, \( \rho_{[100]} / \rho_{[001]} \approx 35 \) [1]. The transport component in the \( ab \)-plane increased, and the resistivity decreased significantly. In addition, the weakened grain boundaries and carrier scattering enhanced carrier mobility.

From the energy band view, the measured thermal activation \( E_a (x = 0–0.03) \) values were 0.273, 0.118, 0.110, 0.047, and 0.031 eV, respectively, and were much narrower than the forbidden band width (3.2 eV). It was speculated that the acceptor energy level formed by Mg\(^{2+}\) appeared near the valence band top after Mg-doping. With increasing \( x \), the broadened second-phase energy level moved toward the valence band top, and the Fermi level moved toward the valence band edge, which caused electrons to easily jump from the valence band to the acceptor level. Accordingly, the carrier concentration increased, which led to a decline in resistivity and thermopower. According to the state density calculation results of Arnold et al. [27], the occupied states near the valence band top were Cu 3d and Cr 3d, and Cu\(^+\) ions were found in XPS, indicating that the low-localization holes in the \( ab \)-plane were concentrated in the [Cu\(^+\)] or [CrO\(_2\)] layer. Therefore, a small number of insulated phases did not hinder the main conductive path and had little effect on thermoelectric transport.

### 4. Conclusions

P-type TCO CuCr\(_{1-x}\)Mg\(_x\)O\(_2\) \( (0 \leq x \leq 0.08) \) polycrystalline was prepared using a solid-state reaction method, and the (001) Lotgering factor was 0.53 at \( x = 0.03 \). When \( x = 0.03–0.08 \), with increasing \( x \), the layered grains grew significantly in the \( ab \)-plane, the density increased, the conductivity increased by 3–4 orders of magnitude, the acceptor energy level was introduced, the thermal activation energy and thermopower decreased, and the maximum room temperature conductivity was 12.03 S-cm\(^{-1}\) at \( x = 0.03 \). When \( x = 0.04–0.08 \), the second-phase MgCr\(_2\)O\(_4\) spinel appeared and did not change transport properties. The
experimental and analysis results repeatedly showed that the maximum solid solubility of Mg-doping was approximately 0.03. The polycrystalline samples in the c-axis orientation could be obtained through Mg-doping in the range of solid solubility, enhanced the transport component in the ab-plane, and significantly increased the hole carrier’s concentration, which improved electrical conductivity. In addition, fewer grain boundaries and pores weakened the scattering of carriers and reduced resistivity.

**Disclosure statement**

No potential conflict of interest was reported by the authors.

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