



Fe concentration dependences of microstructure and magnetic properties for $\text{Cu}(\text{Cr}_{1-x}\text{Fe}_x)\text{O}_2$ ceramics



Cai Gao, Fangting Lin*, Xiaoshan Zhou, Wangzhou Shi, Aiyun Liu

Key Laboratory of Optoelectronic Material and Device, Department of Physics, Shanghai Normal University, Shanghai 200234, PR China

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ABSTRACT

The preferred *c*-oriented $\text{Cu}(\text{Cr}_{1-x}\text{Fe}_x)\text{O}_2$ ceramics ($0 \leq x \leq 15$ at.%) were prepared by solid-state reaction. The effects of Fe concentration on microstructure, morphology and magnetism were investigated. All the samples have a pure 3R- CuCrO_2 delafossite structure, with a stress-induced preferential orientation. The lattice expansion supports the Fe entrance into the Cr sublattice in the form of Fe^{3+} , which is further certified by the X-ray photoelectron spectra and the Mössbauer spectra. The Mössbauer study also reveals a preferential growth orientation and an increase of Fe–O bond lengths with the Fe addition, matching well with the X-ray diffraction analysis. Ferromagnetism is achieved in the Fe-doped samples with Curie temperatures higher than 246 K, which is expected to originate from the hole-mediated Fe^{3+} – Cr^{3+} superexchange interaction. The saturation magnetization of this CuMO_2 delafossite ($M = \text{Cr}, \text{Fe}$) is decreased almost linearly with the increasing Fe concentration, due to the combined influence of the number of the M – M pairs, the M – M distances and the hole concentration. The present work indicates that Fe-doped CuCrO_2 is a dilute magnetic semiconductor and Curie temperature can be remarkably enhanced to close to room temperature by Fe doping.

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1. Introduction

Oxide-based dilute magnetic semiconductors (DMSs) exhibit unique magnetic, magneto-optical, magneto-electric effects and high transparency in the visible region. Therefore they show potential applications in the fields of spintronic devices and transparent electron devices, such as spin-valve transistors, spin light-emitting diodes, nonvolatile logic devices, transparent electrodes in flat panel displays, and window layers in solar cells.

Theoretical predictions [1–3] pointed out that ferromagnetic coupling between magnetic ions could be formed more easily in p-type semiconductors. These reports substantially aroused the researchers' enthusiasm for p-type oxide-based DMSs. However, p-type doping is hard to achieve in most oxide semiconductors, which hinders the realization of high-Curie-temperature (T_C) ferromagnetism. At present, DMSs still face some critical problems such as low T_C , small magnetization, easy formation of ferromagnetic impurities and controversial origin of magnetism. Therefore it has been a hot issue to explore new matrix semiconductors to develop desired DMSs meeting the device requirements.

As one typical p-type transparent conducting oxide (TCO), the delafossite (ABO_2) structure has drawn an extensive attention in

recent years. It is a possible way to obtain high- T_C ferromagnetism through introducing 3d transition metals into delafossite oxides. In 2005, Kizaki et al. [4] predicted that high-spin ferromagnetic state was expected to be stable in p-type delafossite ($\text{Cu}_{1-x}\text{TM}_x\text{AlO}_2$ ($\text{TM} = \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}$)). However, there was no evidence for a ferromagnetic transition even at 2 K in delafossite-based $\text{Cu}(\text{Al}_{1-x}\text{Mn}_x)\text{O}_2$ bulks [5], which was probably associated with the Mn doping site. In 2009, Li et al. [6] reported that p-type CuCrO_2 polycrystalline semiconductor, synthesized by the sol–gel method, was antiferromagnetic below 25 K, while Mn doping could induce ferromagnetic order with $T_C \leq 120$ K. The ferromagnetism was considered to arise from the double-exchange interaction between Mn^{3+} and Cr^{3+} in $\text{Cu}(\text{Cr}_{1-x}\text{Mn}_x)\text{O}_2$.

In this article, CuCrO_2 delafossite was selected as a p-type matrix semiconductor, and ferromagnetism with enhanced T_C has been achieved through B-site Fe doping. There are three main reasons for our choice: (1) CuCrO_2 thin films have the highest p-type conductivity (220 S cm^{-1}) among all p-type TCOs [7]. This is beneficial to hole-mediated magnetic exchange interactions. (2) The introduction of Fe into CuCrO_2 may induce ferromagnetic couplings between Fe ions or between Fe and Cr ions. The coexistence of several magnetic exchange pathways will further facilitate the enhancement of magnetization and T_C . (3) The radius of Fe^{3+} is similar to that of Cr^{3+} [8] so that the substitution can be expected to realize more easily without the formation of impurity phases.

* Corresponding author. Tel.: +86 21 64322726; fax: +86 21 64328894.

E-mail address: nounou7@163.com (F. Lin).

2. Experimental

$\text{Cu}(\text{Cr}_{1-x}\text{Fe}_x)\text{O}_2$ ceramics ($x = 0, 1, 5, 10, 15$ at.%) were prepared using the solid-state reaction technique. High-purity (99.99%) CuO , Cr_2O_3 and $\alpha\text{-Fe}_2\text{O}_3$ powders based on the stoichiometric compositions were mixed, ground and calcined in air at 1050°C for 24 h. Subsequently, the powders were pressed into pellets and sintered in air at 1200°C for 48 h.

Crystal structure was analyzed using BRUKER D8-Focus X-ray diffractometer (XRD) with $\text{Cu K}\alpha$ radiation. Valence states of Cu, Cr and Fe ions were verified by X-ray photoelectron spectroscopy (XPS) on VG Escalab-MKII spectrometer with an $\text{Al K}\alpha$ excitation source. ^{57}Fe Mössbauer spectra were collected at room temperature in transmission geometry on constant acceleration spectrometer with a $^{57}\text{Co}(\text{Pd})$ source. The velocity was calibrated with pure $\alpha\text{-Fe}$ foil. Surface morphology was observed by FEI Sirion-200 field emission scanning electron microscope (FE-SEM). The magnetization vs. magnetic field (M-H) curves were measured on LAKESHORE 7407 vibrating sample magnetometer (VSM), and the magnetization vs. temperature (M-T) curves were recorded using Physical Property Measurement System (PPMS).

3. Results and analysis

3.1. Crystal structure

Fig. 1 gives the XRD patterns for $\text{Cu}(\text{Cr}_{1-x}\text{Fe}_x)\text{O}_2$ ceramics. There are no structural differences among five samples. All sharp diffraction peaks can be indexed to a pure CuCrO_2 delafossite phase (space group: R-3m (166)). No evidence for impurity phases such as Fe_2O_3 and Fe_3O_4 is found. Also, phase separation of CuCrO_2 and CuFeO_2 is not observed. First, almost all XRD peaks are of a symmetric shape. Second, the peaks located at 62.416° , 62.378° , 62.313° , 62.273° and 62.155° , respectively, for $x = 0, 1, 5, 10, 15$ at.% can be ascribed to CuCrO_2 (110) peak (at 62.412° , JCPDS No. 89-0539) instead of CuFeO_2 (110) peak (at 61.006° , JCPDS No. 75-2146). It is clearly indicated that all the samples possess a single CuCrO_2 delafossite structure with Fe incorporated into host lattice.

As shown in Fig. 1, the relative strength of XRD peaks is different from the standard data. Especially, the third strongest line (006) dominates over the strongest (012), suggesting that $\text{Cu}(\text{Cr}_{1-x}\text{Fe}_x)\text{O}_2$ ceramics grow preferentially along the c axis. This can be attributed to the stress produced during the ceramic preparation process, which has been confirmed by the following experiment. The $x = 0$ sample was ground for 1 h, and the obtained powder was examined by XRD as presented in Fig. 2. It is seen that

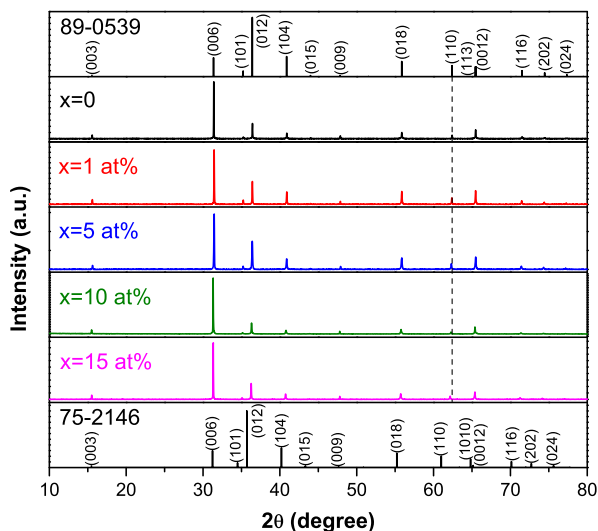


Fig. 1. XRD patterns of $\text{Cu}(\text{Cr}_{1-x}\text{Fe}_x)\text{O}_2$ ceramics and the standard data for CuCrO_2 (JCPDS No. 89-0539) and CuFeO_2 (JCPDS No. 75-2146). The dashed line is a guide for eyes.

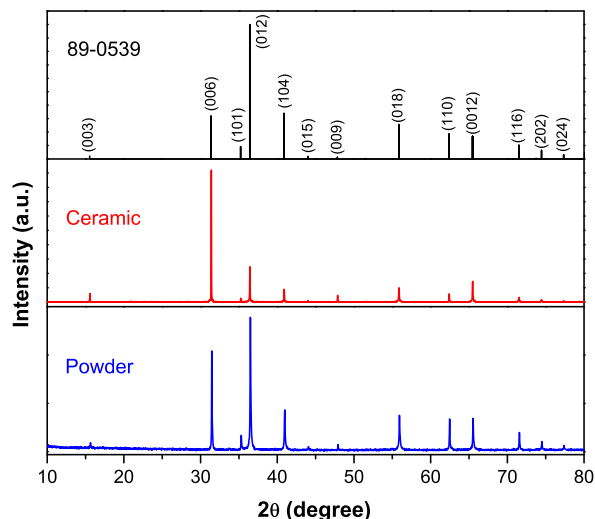


Fig. 2. XRD patterns of CuCrO_2 ceramic and powder, and the standard data (JCPDS No. 89-0539).

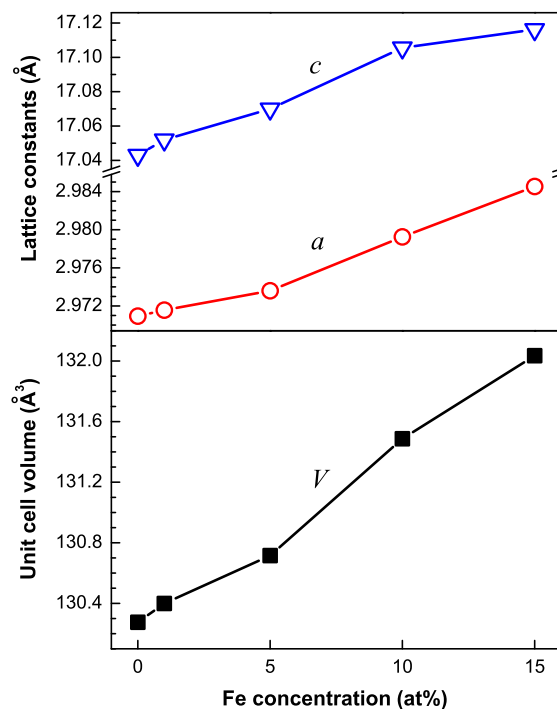


Fig. 3. Composition dependences of lattice constants (a and c) and unit cell volume (V) for $\text{Cu}(\text{Cr}_{1-x}\text{Fe}_x)\text{O}_2$ ceramics.

the preferential growth orientation disappears and the (012) peak regains its dominant role after grinding due to the stress relief.

The calculated lattice constants (a and c) and unit cell volume (V) of $\text{Cu}(\text{Cr}_{1-x}\text{Fe}_x)\text{O}_2$ ceramics are plotted in Fig. 3, in good agreement with CuCrO_2 (JCPDS No. 89-0539, $a = b = 2.973$ Å, $c = 17.10$ Å, $V = 130.93$ Å³) rather than CuFeO_2 (JCPDS No. 75-2146, $a = b = 3.035$ Å, $c = 17.16$ Å, $V = 136.94$ Å³). The a , c and V values are all increased almost linearly with the Fe concentration. The Fe ions are thus deduced to have occupied the B site in the trivalent state, due to the same valence and a little larger size (0.645 Å) of Fe^{3+} compared with Cr^{3+} (0.615 Å) [8]. If the Fe valence were 2+, the variations in a , c and V would be great owing to the much larger size of Fe^{2+} (0.780 Å) than that of Cr^{3+} [8]. These results are further

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