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Review

Synthesis, structural and magnetic studies of the $CuCr_{1-x}Co_xO_2$ delafossite oxide

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ABSTRACT

We modulate the spin chirality and the magnetization in $CuCrO_2$, by doping at Cr^{3+} sites with magnetic ions of slightly different size. Structure and magnetic properties of delafossite oxide $CuCr_{1-x}Co_xO_2$ ($0 \leq x \leq 0.06$) have been investigated. With the substitution of magnetic Co^{3+} for Cr^{3+} ($S=3/2$), the antiferromagnetic (AF) transition becomes broader and the transition temperature increases. However, at low temperature, the magnetic data for $CuCr_{1-x}Co_xO_2$ shows evidence for weak ferromagnetism. Comparing the substitution effect of Co^{3+} to those of other magnetic metal transition, magnetization around the AF transition does not seem to correlate with randomness and lattice parameter.

1. Introduction

Much attention has been focused on diluted magnetic semiconductors (DMSs) with Curie temperature (TC) at or above room temperature (RT), since both the charge and spin of the carriers can be controlled in the same material simultaneously [1,2]. Particularly, oxide-based DMSs such as ZnO [3,4], SnO_2 [5,6], In_2O_3 [7,8], and TiO_2 [9,10] doped with different transition metals (TMs) have been widely studied following the theoretical prediction by Dietl et al. of RT ferromagnetism in Mn-doped ZnO and GaN [11].

Although there is wholly a new class of semiconductors, most experimental and theoretical efforts so far have mainly focused on n-type oxide semiconductors, ignoring the existence of p-type oxide-based DMSs. Recently, attention has turned to copper chromite, $CuCrO_2$, which reportedly has a bandgap of 3.1 eV [12] and the highest p-type conductivity among the delafossites, 220 S/cm when doped with 5% Mg [13]. The $CuCrO_2$ shows paramagnetic (PM) to antiferromagnetic (AFM) transition at $T\sim 23$ K, consistent with earlier report [14–16]. Moreover, $CuCrO_2$ is also reported to exhibit ferroelectric property [14]. The magnetic structure and the mechanism responsible for the ferroelectricity are still under investigation. This finding suggests that the delafossite $CuCrO_2$ phase has the advantage of possessing two cation sites, Cu^{1+} and Cr^{3+}, for possible magnetic ion substitution. Subsequently, magnetic properties of Mn-doped transparent $CuCrO_2$ semiconductors have been discussed [17]. In addition, theoretical first-principles calculations based on $CuAlO_2$ show that the ferromagnetic states of $Cu(AlCo)O_2$ are highly stable, which makes them candidates for ferromagnetic DMSs [18]. According to Monte Carlo Simulations (MCS) it is found that the value of the Curie temperature (TC) exceeds 80 K in $(Cu(FeAl)O_2$ and $Cu(AlCo)O_2$ [19]. Recently, $Cu(AlCo)O_2$ thin film was synthesized [20], they observed ferromagnetism for Co-doped $CuAlO_2$ at room temperature. To our knowledge, there is still a lack of experimental data available on the Co-doped $CuCrO_2$ semiconductor, which motivates further studies. Theoretical and experimental exploring the magnetic behavior in Co-doped $CuCrO_2$ semiconductor will facilitate its potential applications such as spin-based light emitting diodes, spin–valve transistors, nonvolatile memory and detectors in spintronic devices. In this work, we synthesize Co-doped $CuCrO_2$ by solid-state reaction. We systematically study the influence of Co composition on the magnetic properties of $CuCr_{1-x}Co_xO_2$ with varying x prepared via the same method.

2. Experimental section

The polycrystalline $CuCr_{1-x}Co_xO_2$ ($x=0$, 0.02, 0.04, 0.05, and 0.06), was synthesized by using a procedure for a standard solid-state reaction. We weighed, mixed, and ground into a powder of Cu_2O, Cr_2O_3 and CoO with purities of 99.99%. The resulting polycrystalline powder was pressed into a pellet and then calcined in air at 1000 °C for 12 h in an alumina crucible. The obtained mixture was ground and calcined several times in air at 1100 °C for about 100 h with a grinding procedure repeated at regular intervals. To characterize the samples, we conducted powder X-ray diffraction (XRD) measurements. The lattice parameters were obtained by Rietveld refinement of the collected XRD patterns. Raman spectroscopy measurement was conducted on

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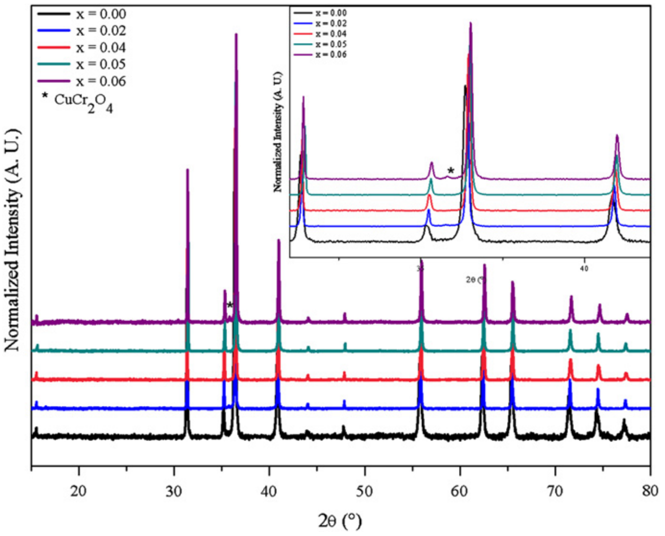

Fig. 1. XRD pattern evolution with contentment for $CuCr_{1-x}Co_xO_2$ ($0 \le x \le 0.06$).

a laser Raman spectrometer (Spectra Physics krypton ion laser) Magnetization dependence on temperature was measured in a quantum design superconducting quantum interference device (SQUID) magnetometer while warming from 2 to 300 K at 0.1 T (zero-field cooling ZFC).

3. Results and discussion

3.1. Microstructure and crystal structure

The XRD patterns of the $CuCr_{1-x}Co_xO_2$, are shown in Fig. 1, provide convincing evidence that the samples are all single-phase delafossite (space group: R-3 m), while some tiny impurity peaks was observed in $CuCr_{1-x}Co_xO_2$ for $x=0.06$ (Fig. 1). This indicates that the Co-substitution is limited to 5%. The impurity was identified to be the spinel-type $CoCr_2O_4$. The lattice parameters a and c of the $CuCr_{1-x}Co_xO_2$ samples are shown in Table 1. The in-plane and out-of-plane lattice parameters (a and c) deduced by the Rietveld refinement monotonically decrease with an increase of Co content, as shown in Fig. 2.

The decrease of the in-plane lattice parameter indicate that the valence of Co ions was not Co^{2+} (HS) or Co^{3+} (H.S) according to the data of the ionic radius of six fold coordinated Co and Cr (Co^{2+} (HS): 0.745 Å, Co^{3+} (HS): 0.61 Å, Co^{3+} (LS): 0.545 Å and Cr^{3+}: 0.615 Å) [21] as well as lattice expansion. The lattice parameters a and c would increase if the valence state of the Co ions is 2+ (HS) in Co-doped $CuCrO_2$ semiconductors because the ionic radii of Co^{2+} are larger than that of Cr^{3+}. However it would remain constant if the Co ions is 3+ (HS). Moreover the changes in the lattice parameters a and c due Co-dopping are very small. Therefore, the valence state of the Co ions presented in the samples should be 3+ since the ionic radius of Co^{3+}(LS) is smaller than that of Cr^{3+}, whereas the valence state of Co ions cannot be totally confirmed by the changes in the lattice parameters.

It is expected to introduce mainly atomic disorder in $CuCr_{1-x}Co_xO_2$ in the Cr network, since Co^{3+} (LS) and Cr^{3+} have the same oxidation state, M^{3+}. The change is rather anisotropic as it is mainly due to the shrinking of the a parameter whereas the c parameter remains more or less constant (Table 1). As the Cu–O distance does not very much in delafossite, this tendency reflects a flattening of the MO_6 octahedra. A nice geometric account of this evolution is given in [13] where the authors suggest that the strong repulsion between M^{3+} ions across the octahedron shared edges reduces the O–O distance to the contact distance. Therefore the increase of the size of M cation leads to an increase of the octahedron distortion and in turn of the M–M distance that corresponds to the a parameter. We may recall that in $CuMO_2$, as M changes from Al^{3+} to La^{3+}, the a parameter undergoes a huge increase from 2.8 to 3.8 Å. This general trend is also observed at a smaller scale in the investigated samples.

Table 1
The lattice parameters a and c of the $CuCr_{1-x}Co_xO_2$ ($0 \le x \le 0.06$).

Samples	a (Å)	c (Å)
$CuCrO_2$	2.973 (4)	17.112(1)
$CuCr_{0.98}Co_{0.02}O_2$	2.972(5)	17.109(1)
$CuCr_{0.96}$ $Co_{0.04}O_2$	2.970(1)	17.105(1)
$CuCr_{0.95}$ $Co_{0.05}O_2$	2.968(3)	17.102(8)
$CuCr_{0.94}$ $Co_{0.06}O_2$	2.967(9)	17.101(4)

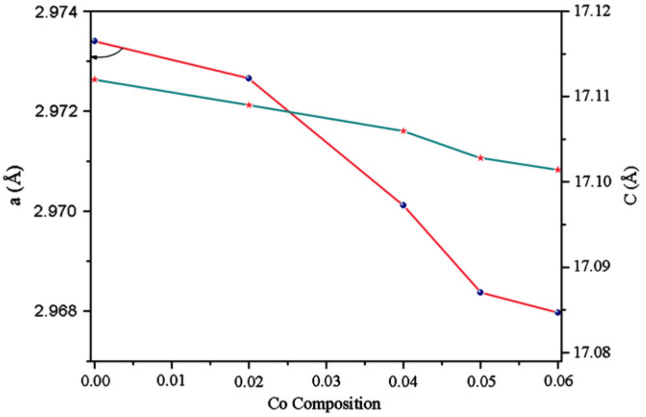

Fig. 2. Composition dependences of the lattice constants for $CuCr_{1-x}Co_xO_2$ ($0 \le x \le 0.06$).

3.2. Raman spectra at room temperature

Delafossite compounds (space group R-3 m) such as $CuCrO_2$ have one formula unit per unit cell with a total of 12 possible vibrational modes. Among these modes only two are Raman active with E_g and A_{1g} symmetry. The A_{1g} mode corresponds to vibrations of the Cu–O bonds along the c-axis while the E_g mode represents vibrations in the triangular lattice perpendicular to the c-axis.

Fig. 3 shows the Raman spectra of $CuCr_{1-x}Co_xO_2$ for different doped samples using a 514.5 nm laser wavelength excitation. The frequencies shift to shorter wave numbers, indicating the increase of the lattice distortion with Co^{3+}(LS) doping. This lattice distortion may be mainly caused by the difference of ionic radii. The intensity decrease of Co-doped Raman peaks (Fig. 3) as it is reported by Zheng et al. [22], supporting the valence +3 for the M. The A_{1g} mode, in particular, is more sensitive to M^{3+} substitution; its frequency is thus very sensitive to M-site atom–oxygen bonding characteristics. As mentioned earlier, $CuCrO_2$ should only have two Raman modes. However, Co-doped compounds show additional features (Fig. 3) similar to those observed in other delafossite compounds such as $CuAlO_2$ [23] and $CuGaO_2$ [24]. In agreement with *ab initio* calculations, these additional modes in $CuAlO_2$ are attributed to non-zero wave vector phonons which are normally forbidden by Raman selection rules [23]. As suggested, the selection rules are possibly relaxed by defects such as Cu vacancies, or interstitial oxygen [23]. Thus, the additional features observed in Co-doped $CuCrO_2$ could have an origin similar to that observed in