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ABSTRACT

The delafossite CuAlO$_2$ is a rare p-type semiconductor with potential applications as a thermoelectric and as a dilute magnetic semiconductor when doped with transition metal ions. Reported here are results from our investigations of CuAl$_{1-x}$Fe$_x$O$_2$ ($x = 0, 0.01, 0.05,$ and 0.1) with a focus on the x-dependence of structural and magnetic properties, and role of impurities. The samples prepared by the solid-state reaction at 1,100°C were characterized by X-ray diffraction (XRD), energy dispersive (X-ray) spectroscopy (EDS) and X-ray photoelectron spectroscopy (XPS). The magnetic results show that the Curie constant ($\chi$), low temperature magnetization ($M$) and the lattice constants scale with $x$. High resolution $M$-$H$ loop measurements at 300 K and 10 K show negligible coercivity $H_C$ at 10 K but $H_C \sim 100$ Oe at 300 K. These results suggest the presence of minute quantities of hematite ($\alpha$-Fe$_2$O$_3$) that are not detected in our XRD and XPS. The role of impurities on the published results in this system is discussed.

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I. INTRODUCTION

There has been considerable interest in the various properties of CuAlO$_2$-based materials for the following reasons: CuAlO$_2$ is a rare p-type semiconductor with indirect bandgap $E_g \sim 1.8$ eV and direct $E_g \sim 3.5$ eV$^{1,2}$ the concentration of holes can be controlled by Cu vacancies and interstitial oxygen, making it suitable for optical displays and thermoelectric energy conversion$^{3-7}$ and on doping with transition metal ions, it is predicted to become a dilute magnetic semiconductor suitable for spintronic applications.$^{8,9}$ In our recent paper,$^{10}$ we have reported our initial results on the magnetic properties of CuAl$_{1-x}$Fe$_x$O$_2$ ($x = 0.0, 0.01, 0.05,$ and 0.10). In these samples prepared by solid-state reaction, these studies showed that Fe substitutes for Al and its electronic state is Fe$^{3+}$. In addition, the concentration $x$ was determined from the analysis of the data on the temperature ($T$) and magnetic field ($H$) dependence of magnetization ($M$). This analysis yields $x$ very close to the nominal $x$ except for the $x = 0.10$ sample for which magnetic measurements yielded $x = 0.08$. In this paper, we present new results related to the question whether CuAl$_{1-x}$Fe$_x$O$_2$ is a room temperature ferromagnet as some recent papers have reported.$^{8,9}$ We also focus on how the measured magnetization and magnetic susceptibility vary with $x$. Major conclusions from these investigations reported here are that although $M$ and $\chi$ do vary nearly with $x$, minutes quantities of impurities such as the spinel phase CuAl$_2$O$_4$ and $\alpha$-Fe$_2$O$_3$ which are not easily detected in X-ray diffraction (XRD) studies of the samples, play important roles in the measured properties. The presence of $\alpha$-Fe$_2$O$_3$ which is a weak ferromagnet for $T > T_M = 260$ K but an antiferromagnet for $T < T_M = 111$ K is the likely source of observed hysteresis loops at room temperature. Details of these results are presented in the following pages.

II. EXPERIMENTAL PROCEDURES AND APPARATUS

The X-ray diffraction was done using a PANalytical X’Pert Pro X-ray Diffractometer (XRD) with a Cu-K$_\alpha$ source ($\lambda = 1.542$ Å). The magnetic measurements were done using a PPMS Evercool II system. The chemical and elemental characterization of the samples...
was performed using a PHI 5000 VersaProbe X-ray photoelectron spectroscopy system with a Mg conventional X-ray source and an EDAX system on a Hitachi S-4700 Scanning Electron Microscope, respectively.

As described in detail in our recent paper, the polycrystalline samples of CuAl\textsubscript{1-x}Fe\textsubscript{x}O\textsubscript{2} were prepared by the solid state method reacting stoichiometric amounts of CuO (99.99% purity), Al\textsubscript{2}O\textsubscript{3} (99.9% purity), and α-Fe\textsubscript{2}O\textsubscript{3} (99.9% purity) at 1,100 °C, using the optimum baking time of 144 hours. This optimum baking time was determined experimentally in an effort to eliminate the formation of the impurity spinel phase of CuAl\textsubscript{2}O\textsubscript{4}. Whereas CuAl\textsubscript{2}O\textsubscript{4} (delafossite) is expected to be diamagnetic with Cu\textsuperscript{+} and Al\textsuperscript{3+} as the electronic states, CuAl\textsubscript{2}O\textsubscript{4} is expected to be paramagnetic because of the electronic state of Cu\textsuperscript{2+} with spin $s = 1/2$. By Scherrer analysis the crystallite sizes are determined to be about 40 nm.

III. RESULTS AND DISCUSSIONS

A. Structural characterization

1. X-ray diffraction

The X-ray diffraction patterns of CuAl\textsubscript{1-x}Fe\textsubscript{x}O\textsubscript{2} samples with $x = 0, 0.01, 0.05$, and 0.10 are presented in an earlier paper. The samples have rhombohedral delafossite structure and there is a lattice expansion associated with replacing Al with Fe which shows up as the peaks shift to lower angles. The calculated $a$ and $c$ parameters are: $a = 2.86$ Å for $x = 0$ and $a = 2.88$ Å for $x = 0.10$ representing 0.70% increase in a lattice parameter. Likewise, $c$ lattice parameter increases from $c = 16.96$ Å for $x = 0$ to $c = 16.97$ Å for $x = 0.10$ showing 0.06% increase. Therefore, the increase in $a$ is more prominent than that in $c$. The conventional unit cell volume changes from $V = 120.1$ Å$^3$ for $x = 0$ to $V = 121.5$ Å$^3$ showing an expansion of 1.2%.

2. Energy dispersive spectroscopy

Secondary electron microscopy (SEM) and energy dispersive (X-ray) spectroscopy (EDS) was performed on all four CuAl\textsubscript{1-x}Fe\textsubscript{x}O\textsubscript{2} samples. An SEM image and EDS spectrum are shown for $x = 0.10$ (see Fig. 1 (a)). The SEM image shows a powder with a distribution of particle sizes, consistent with earlier Scherrer analysis. The image is taken at 15 kV accelerating voltage, 10 µA electron beam current and the EDS signal is collected from the whole region shown. From the usual elemental quantification (ZAF), concentration of C was about 15% for all samples, which is typical for an air exposed powder. The inset on the right shows the Fe Kα peak for $x = 0.0$. The inset on the right shows the Fe Kα peak for $x = 0.0$.
0.01, 0.05 and 0.10. This Fe peak monotonically increases with nominal x value. The center inset, is a plot showing EDS determined x values vs. nominal x values using several calculation methods. These methods include: ZAF analysis using the Cu and Fe K lines (open squares); ZAF using Cu and Fe L lines (open diamonds), and the ratio between the Fe and Cu K lines (corrected for the fluorescence differences between Fe and Cu) (open triangles), (dashed lines are visual guides, and the black solid line shows the expected value of x vs. nominal). The Fe to Cu ratio shows the expected linear relationship, with exaggerated measured x, which is probably the result of the Z dependence in the EDS process not considered. The K-line ZAF analysis shows the best quantitative agreement, with a small systematic exaggeration of the measured x. The L-line ZAF analysis gives poor agreement with saturated behavior. This poor agreement with standards. Certainly, the EDS measurements supports the nominal elemental Fe content for these samples.

3. X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) is done on all CuAl$_{1-x}$Fe$_x$O$_2$ powder samples. Figure 1 (b) shows the survey scan (step size 0.5 eV) for CuAl$_{0.90}$Fe$_{0.10}$O$_2$. Detailed scans (step size 0.1 eV) are shown as insets. Details of the peak fitting is indicated in these insets. The Cu 2p peaks (~285 eV) are fitted to an alkane (C-H), alcohol (C-OH), and acid/ester (O-C=O) peaks. The O 1s peak (~530 eV) is fitted to three lattice peaks associated with Al$^{3+}$, Cu$^{3+}$, and Cu$^{2+}$ along with organic and water peaks. The Cu 2p peaks (~935 eV) is fitted as Cu$^{2+}$ and Cu$^{2+}$ 2p peaks. Fe 2p peak (~711 eV) is fitted as Fe$^{3+}$. The Cu 3s/Al 2s combined peaks (~120 eV) are fitted as separate Cu 3s Al 2s peaks (where the area of Cu 3s is consistent with that from Cu 2p peaks). To determine the chemical makeup of our powder, we disregard the alkane C peak, but use the alcohol and acid/ester related peaks to determine their contribution to the Oxygen peak (peaks labeled in inset). For the Oxygen content we disregard the contribution of the organic O as well as the O in water. The size of the lattice peaks for Al$^{3+}$, Cu$^{3+}$, and Cu$^{2+}$ are consistent in area from the associated Al 2s and Cu 2p lines. Thus, we have a procedure to determine the Cu$^{3+}$, Cu$^{2+}$, Al, and O (lattice only) content for the powders. The table in the upper right contains the ratios for Fe$_{2p}^{2+}$ and Cu$_{2p}^{3+}$. The former is related to the experimentally determined x. The table shows this ratio monotonically increases with the nominal value of x, as expected, however, the ratio is much less than x and appears to saturate. The latter ratio measures the amount of the different copper valences of 1+ and 2+. This ratio indicates that within the surface layer probed by XPS (about 10 nm) there is a near even mixture of Cu$^{3+}$ and Cu$^{2+}$ with a systematic trend to lower Cu$^{3+}$ for higher Fe content. The delafossite has Cu$^{3+}$ (spinel Cu$^{2+}$) and it is not surprising that at the surface there is further oxidation leading to more Cu$^{3+}$. In fact, this may be where the small amount of the spinel phase, as measured using XRD, tends to be located. Moreover, this Cu$^{3+}$ may also contribute to the paramagnetism described in our recent paper.

B. Magnetic measurements

1. Variation of magnetic properties with change in Fe concentration

In our recent paper, we reported the temperature and magnetic field variation of the magnetization (and magnetic susceptibility) of the CuAl$_{1-x}$Fe$_x$O$_2$ (x = 0.0, 0.01, 0.05, and 0.10) samples for the temperature range of 2 to 300 K and magnetic fields H up to 90 kOe. The data of x vs. T in applied magnetic field H = 1 kOe shown in Fig. 2 (a) was fitted to the modified Curie-Weiss law:

$$\chi = \chi_0 + \frac{C}{(T - \theta)}$$

(1)

Here $\chi_0$ is the temperature independent component from diamagnetism of the ions and Van Vleck susceptibility, $\theta$ is the Curie-Weiss temperature indicative of any exchange coupling, C = $N\mu^2/3k_B$ is the Curie constant with N being the number of magnetic ions per gram and $k_B$ the Boltzmann constant. We have given detailed analysis of the magnitudes of C, $\theta$, $\chi_0$, and $\mu$ determined for each sample in the recent paper. The weak paramagnetism observed in the x = 0 sample is interpreted to result from 2.8% of the spinel phase CuAl$_{2}$O$_4$ present as an impurity; in CuAl$_{2}$O$_4$, Cu has the electronic state of Cu$^{2+}$ with spin $s=1/2$ leading to paramagnetism. For the Fe-doped samples of CuAl$_{1-x}$Fe$_x$O$_2$ with nominal x = 0.01, 0.05 and 0.10, the analysis of the x vs. T data using Eq. (1) yielded $x = 0.01$, 0.048 and 0.08 respectively using $g=2$, $s=5/2$ and $\mu = 5.916 \mu_B$ for Fe$^{3+}$. Later we argue that these lower values of x compared to nominal x is likely due to the presence of a-Fe$_2$O$_3$ as an impurity which is not detectable in the standard XRD analysis. Here, we focus on how C and $\chi$ vary with x. In Fig. 2 (a) and (b), we show the variation of C and $\chi$ with change in x wherein we show the data points for using both x = 0.08 and x = 0.1 for the nominal x = 0.10 sample. As stated previously, a better linearity is observed using x = 0.08 for the nominal x = 0.1 sample confirm the above analysis.

The M vs. H data at select T in the recent paper was fitted to the modified Brillouin function $B_s(y)$:

$$M = M_0B_s(y) = xNg\mu_BSB_s(y) = \frac{g\mu_BSH}{k_B(T - \theta)}$$

(2)

According to Eq. (2), the magnetization M should also scale with x. In Fig. 2 (c), we show the plot of M vs. H/(T-\theta) for the four samples at T = 2 K and in Fig. 3 (d) we show the plots of M vs. x at 2 K in H = 5, 10, 50, and 90 kOe. Approximate linearity of M vs. x is observed.

2. High resolution magnetic hysteresis loops

To address the question of room temperature ferromagnetism (RTFM) in the CuAl$_{1-x}$Fe$_x$O$_2$ samples, we recently carried out high resolution hysteresis loop measurements of M vs. H at 300 and 10 K. The plots of M vs. H at 300 and 10 K for the low-H region are shown in Fig. 2 (e) for x = 0.0 and 0.10 samples. The variation of coercivity $H_C$ vs. x measured at 300 and 10 K for all four samples is plotted in Fig. 2 (f). For the x = 0.0 sample, $H_C = 0$ at both 300 and 10 K. For the samples with x = 0.01 and 0.05, $H_C = 0$ at 10 K but significant $H_C \sim 100$ Oe is observed at 300 K. For the x = 0.10 sample, $H_C \sim 100$ Oe both at 10 and 300 K. These results suggest...
that the samples of CuAl$_{1-x}$Fe$_2$O$_4$ doped with Fe are ferromagnetic at 300 K as also reported by others.\(^9,10\) However, $H_C \sim 0$ at 10 K for the $x = 0.01$ and 0.05 samples suggest that these observations are very likely due to hematite ($\alpha$-Fe$_2$O$_3$) present in the samples as an impurity but not detected by XRD or XPS. This conclusion is based on the fact that $\alpha$-Fe$_2$O$_3$ is a weak ferromagnet above the Morin temperature $T_M \approx 260$ K but it transforms to an antiferromagnet for $T < T_M$.\(^13,14\) So $M$ vs. $H$ variation due to $\alpha$-Fe$_2$O$_3$ will show hysteresis loop at 300 K but $M$ vs. $H$ will be linear without hysteresis at 10 K. Based on the observed magnitude of the weak ferromagnetic moment of 0.001, 0.001, and 0.02 emu/g at 300 K for the nominal $x = 0.01, 0.05$ and 0.10 samples of CuAl$_{1-x}$Fe$_2$O$_4$ respectively as compared to $M_s = 0.45$ emu/g for bulk sample of $\alpha$-Fe$_2$O$_3$,\(^12,13\) the concentration of $\alpha$-Fe$_2$O$_3$ impurity in CuAl$_{1-x}$Fe$_2$O$_4$ samples is estimated to be about 0.2% in the $x = 0.01$ and 0.05 samples and about 4% in the $x = 0.10$ samples. The source of this impurity is some unreacted $\alpha$-Fe$_2$O$_3$ since $\alpha$-Fe$_2$O$_3$ is one of the precursors used in the synthesis of the CuAl$_{1-x}$Fe$_2$O$_4$ samples. This also explains why the concentration $x$ determined from the analysis of the magnetic data, particularly for the sample with nominal $x = 0.1$, is significantly smaller than the nominal value as noted above. Perhaps temperatures higher than 1,100 °C during the synthesis of the samples are needed to eliminate this impurity. Regarding the question of RTFM in the CuAl$_{1-x}$Fe$_2$O$_4$ samples, it is clear that the role of impurities needs to be considered carefully since as noted here, these impurities levels are not detectable in standard XRD analysis of the samples. From the results presented here, it is inferred that the pure samples of CuAl$_{1-x}$Fe$_2$O$_4$ without impurities are likely not ferromagnetic at room temperatures.

IV. CONCLUSIONS

The results presented here on the CuAl$_{1-x}$Fe$_2$O$_4$ samples for $x = 0.0, 0.01, 0.05$, and 0.10 show that magnetization and magnetic susceptibility scale with $x$. The hysteresis loops and weak ferromagnetism observed at 300 K for the Fe-doped samples is shown to be likely due to the presence of hematite as an impurity in the samples. This impurity likely results from some un-reacted hematite which is one of the precursors used in the solid-state synthesis of the CuAl$_{1-x}$Fe$_2$O$_4$ samples. Since the small level of this impurity is not detected in the standard XRD analysis of the samples, magnetic measurements as reported here are essential to detect this impurity. Because hematite is a weak ferromagnet at room temperature, the presence of RTFM in the impurity-free samples of CuAl$_{1-x}$Fe$_2$O$_4$ samples is highly unlikely.

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