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Characterization of transparent superconductivity Fe-doped $CuCrO_2$ delafossite oxide

Chutirat Taddee[a], Teerasak Kamwanna[b,c,d,*], Vittaya Amornkitbamrung[b,c,d]

[a] Materials Science and Nanotechnology Program, Faculty of Science, Khon Kaen University, Khon Kaen 40002, Thailand
[b] Department of Physics, Faculty of Science, Khon Kaen University, Khon Kaen 40002, Thailand
[c] Nanotec-KKU Center of Excellence on Advanced Nanomaterials for Energy Production and Storage, Khon Kaen 40002, Thailand
[d] Integrated Nanotechnology Research Center (INRC), Khon Kaen University, Khon Kaen 40002, Thailand

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ABSTRACT

Delafossite $CuCr_{1-x}Fe_xO_2$ ($0.0 \leq x \leq 0.15$) semiconductors were synthesized using a self-combustion urea nitrate process. The effects of Fe concentration on its microstructural, optical, magnetic, and electrical properties were investigated. X-ray diffraction (XRD) analysis results revealed the delafossite structure in all the samples. The lattice spacing of $CuCr_{1-x}Fe_xO_2$ slightly increased with increasing substitution of Fe at the Cr sites. The optical properties measured at room temperature using UV–visible spectroscopy showed a weak absorbability in the visible light and near IR regions. The corresponding direct optical band gap was about 3.61 eV, exhibiting transparency in the visible region. The magnetic hysteresis loop measurements showed that the Fe-doped $CuCrO_2$ samples exhibited ferromagnetic behavior at room temperature. This indicated that the substitution of Fe^{3+} for Cr^{3+} produced a mixed effect on the magnetic properties of $CuCrO_2$ delafossite oxide. The temperature dependent resistivity measurements clearly revealed the presence of superconductivity in the $CuCr_{1-x}Fe_xO_2$ with a superconducting transition up to 118 K.

1. Introduction

In the past decade, materials with a delafossite-type structure have attracted interest due to their optoelectric, electric and thermoelectric properties [1–6]. Delafossites are p-type wide-bandgap oxide semiconductors. Among them, Cu-based materials are widely studied for transparent conducting oxide (TCOs) applications due to their unique combination of electrical conductivity and optical transparency [2]. Examples of p-type transparent conducting oxides are $CuFe_{1-x}Sn_xO_2$ [7], $CuNdO_2$ [8], $CuFe_{1-x}Cr_xO_2$ [9], and $CuGaO_2$ [10]. $CuCrO_2$ has been given considerable attention as a p-type Cu-based delafossite oxide for optoelectronic device applications [11,12], since they contain no precious elements. $CuCrO_2$ reportedly has a bandgap of 3.1 eV and the highest p-type conductivity [13].

The magnetic properties of delafossite oxide have gained attention due to their great potential for applications in diluted magnetic semiconductors (DMSs) [10,14,15], especially applications for spintronic devices and transparent electronic devices. However, there have been few studies of DMS materials. $CuCrO_2$ shows a paramagnetic to antiferromagnetic transition at ~23 K. Moreover, $CuCrO_2$ is reported to exhibit ferromagnetic properties [16]. Recently, low-temperature ferromagnetism was realized in $Cu(Cr_{1-x}M_x)O_2$ (M = Mn [17,18], Ni [19,20], Al [21], Rh [22], and Co [14]) ceramics. Furthermore, $Cu(Cr_{1-x}Mn_x)O_2$ thin films that exhibited room-temperature ferromagnetism were successfully fabricated [23]. The magnetic structure and the mechanisms responsible for their ferromagnetic properties are still under investigation.

Recently, Nakanishi and Katayama-Yoshida suggested a new application of the delafossite structure of $CuAlO_2$ for transparent superconductivity [24]. They calculated the superconducting critical temperature (T_c) of hole-doped delafossite $CuAlO_2$ based on first-principles calculations. They found that the T_c goes up to about 50 K due to a strong electron–phonon interaction and high phonon frequency caused by the two dimensional flat band at the top of the valence band. This suggests that delafossite oxide may be a promising material for fabricating new superconducting materials. Moreover, no systematic studies of the superconductivity of $CuCrO_2$ have been reported in the literature. Therefore, we systematically investigated the effects of Fe content on superconductivity

* Corresponding author at: Department of Physics, Faculty of Science, Khon Kaen University, Khon Kaen 40002, Thailand. Tel.: +66 846109597.
E-mail addresses: teekam@kku.ac.th, k.teerasak@hotmail.com (T. Kamwanna).

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in $CuCrO_2$. In this work, $CuCr_{1-x}Fe_xO_2$ was synthesized using a self-combustion urea nitrate process. The influences of Fe content on the microstructural, optical, magnetic, and electrical properties of $CuCr_{1-x}Fe_xO_2$ were systematically investigated.

2. Experiments

2.1. Sample preparations

In this work, polycrystalline $CuCr_{1-x}Fe_xO_2$ (x = 0.01, 0.03, 0.05, 0.10 and 0.15) powders were synthesized using a self-combustion urea nitrate process (UNP). Copper nitrate [$Cu(NO_3)_2{\cdot}3H_2O$, Kanto, purity 99.9%], chromium nitrate [$Cr(NO_3)_3{\cdot}9H_2O$, Kanto, purity 99.9%], iron nitrate [$Fe(NO_3)_3\ 9H_2O$, Kanto, purity 99.9%], and urea were used as precursor materials. The self-combustion process has been described in detail [25,26]. Briefly, the desired amounts of precursor materials were dissolved in deionize water to form a mixed solution. Urea to nitrate molar ratios of 0.67:1 (UN0.67) and 1:1 (UN1) were used. After continuous stirring at 363 K for 1 h, the precursor solution was heated to 473 K to evaporate water. A highly viscous transparent moisture-sensitive glassy material was obtained. This material was then heated in a crucible on a hot plate at 573 K. The material spontaneously ignited, resulting in a dark green mass. The resulting powder was calcined at 1053 K for 3 h in a N_2 atmosphere. The calcined powders were ground and pressed into pellets of 9.5 mm diameter and ~1 mm thickness by uniaxial compression under a pressure of 250 MPa and then sintered in air at 1273 K for 3 h.

2.2. Characterization

The phase and crystal structure of the synthesized $CuCr_{1-x}Fe_xO_2$ powders were characterized using x-ray diffraction (XRD). This was done using a Philips PW3040 diffractometer with Cu K_α radiation (λ = 0.15406 nm). The X-ray data were collected using grazing incidence in a diffraction range of 20–80° (2θ) with step width of 0.02°. Scanning electron microscope (SEM) images were recorded using a SNE-4500 M SEM, South Korea. Absorption spectroscopy of the calcined powders was obtained for the dry-pressed with the sample holder using a UV-VIS-NIR scanning spectrophotometer (UV-3101PC, Shimadzu) over the range of 200–800 nm at room temperature. Magnetization vs. magnetic field (M–H) curves was developed using a Quantum Design VersaLab 3 Tesla Cryogen-free equipped with a vibrating sample magnetometer (VSM) at room temperature. Temperature dependence of electrical resistivity was measured at temperatures as low as 50 K using the conventional van der Pauw configuration on a Quantum Design VersaLab 3 Tesla Cryogen-free equipment.

3. Results and discussion

3.1. Structural characterization

X-ray diffraction measurements were first used to characterize the structure of $CuCr_{1-x}Fe_xO_2$. Fig. 1 shows the XRD patterns for calcined powders at room temperature with nominal compositions, where x = 0.01, 0.03, 0.05, 0.10 and 0.15. The standard JCPDS card (No. 89-0539) of $CuCrO_2$ is also shown for comparison. When comparing the measured diffraction peaks of the $CuCr_{1-x}Fe_xO_2$ with standards, excellent agreement was observed, thus demonstrating that all $CuCr_{1-x}Fe_xO_2$ samples formed a pure polycrystalline phase having the delafossite structure within the $R\bar{3}m$ space group. A secondary phase of CuO was also observed. Furthermore, the relative strength of XRD peaks was different from the standard. It was observed that the polycrystalline grains in the samples with low Fe

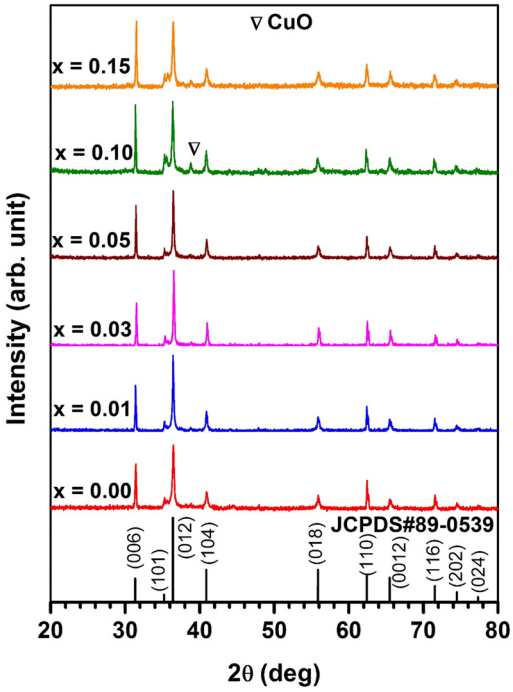

Fig. 1. XRD patterns of calcined $CuCrO_2$ and $CuCr_{1-x}Fe_xO_2$ powders with Fe contents of x = 0.01, 0.03, 0.05, 0.10 and 0.15.

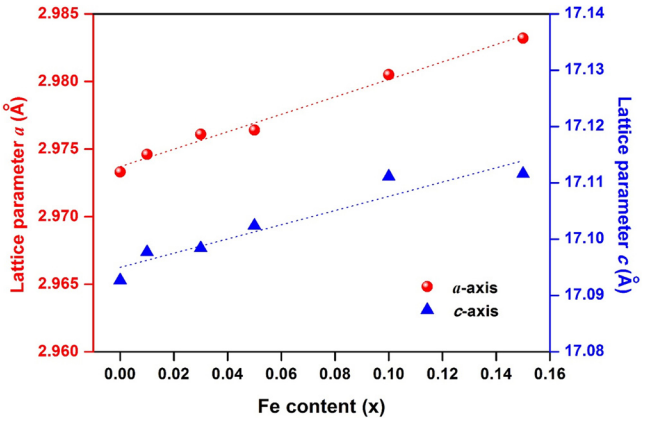

Fig. 2. Lattice parameters of calcined $CuCr_{1-x}Fe_xO_2$ (x = 0.00, 0.01, 0.03, 0.05, 0.10, and 0.15) powders as a function of Fe content.

content, $x \leq 0.05$, exhibited a strong preferential alignment along the hexagonal (0 1 2) axis. When the Fe content, x, was ≈0.15, the polycrystalline grains were more aligned on the (0 0 6) axis. This suggested that $CuCr_{1-x}Fe_xO_2$ grew preferentially along the c-axis.

The value of lattice parameters of the delafossite phase of $CuCr_{1-x}Fe_xO_2$ were calculated using Cohen's least mean square method and are illustrated in Fig. 2 as a function of Fe content. It was found that the lattice parameters of the calcined powders slightly depended on their Fe content. The extracted lattice parameters a and c increased slightly with Fe substitution. They varied slightly from the standard file of JCPDS (a = 2.973 Å, c = 17.100 Å). Moreover, the lattice parameter, c, increased more rapidly than for the a-axis (from a = 2.973 Å, c = 17.093 Å for x = 0.00 to a = 2.983 Å, c = 17.112 Å for x = 0.15). This behavior suggested that the ionic radius for a six-fold coordination of Cr^{3+} was partial substituted by the slightly larger Fe^{3+} $\left(r_{Fe^{+3}} = 0.645\ Å\ ;\ r_{Cr^{3+}} = 0.615\ Å\right)$ [27]. The results indicated that the larger ionic radius of Fe^{3+} increased the number of O–Cu–O dumbbells found parallel to the c-axis. It