Synthesis, Microstructure, Optical and Magnetic Properties of Ge-doped CuFeO$_2$ Delafossite Oxide

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Abstract

Delafossite CuFe$_{1-x}$Ge$_x$O$_2$ (0.0 $\leq$ x $\leq$ 0.1) semiconductors were synthesized by solid state reaction. The effects of Ge concentration on microstructure, optical and magnetic properties were investigated. The XRD results reveal the formation of delafossite structure. The optical properties at room temperature exhibited the transparent in the visible region with direct optical band energy gap of 3.43 eV. The magnetic hysteresis loops measurements at 50 K show that the Ge-doped CuFeO$_2$ samples have the ferromagnetic behavior. The curie temperature suggests that the ferromagnetism originating from the CuFe$_{1-x}$Ge$_x$O$_2$ matrices.

1. Introduction

In the past decade, materials with delafossite-type structure have attracted interest because of their optoelectric, electric and thermoelectric properties. Among them, Cu based materials is a widely studied for transparent conducting oxides (TCOs) and thermoelectric applications. The magnetic property of the delafossite oxide have also gained attention due to their great application potential for diluted magnetic semiconductors (DMSs), especially, applications for spintronic devices and transparent electron devices. Recently, CuFeO$_2$ have caught considerable attention due to its multiferroic phase, where the antiferromagnetism and ferroelectricity coexist, under an applying magnetic field or substituting Fe$^{3+}$ with nonmagnetic trivalent ions. For instance, Mn-substituted CuFeO$_2$ was reported to generate ferroelectric property [1]. In this work, CuFe$_{1-x}$Ge$_x$O$_2$ has been synthesized by conventional solid-state reaction. The influences of Ge composition on the microstructural, electrical, optical and magnetic properties of CuFe$_{1-x}$Ge$_x$O$_2$ were systematically investigated. We examine whether the partial Ge substitution would yield the multiferroic phase.

2. Experiments

Experimental details

In this work the polycrystalline CuFe$_{1-x}$Ge$_x$O$_2$ (x = 0.01, 0.03, 0.05, and 0.10) specimens were synthesized by conventional solid state reaction. Phase and the crystal structure of the synthesized specimens were characterized by x-ray diffraction (XRD). The optical transmission spectra were recorded on powder sample by using a UV-VIS-NIR scanning spectrophotometer in the range of 200 to 800 nm. The magnetizations vs. magnetic field curves were conducted using in Quantum Desing VersaLab3 Tesla Cryogen-free equipped with a vibrating sample magnetometer (VSM) at 50 K. The magnetization dependence on temperature was measured in the zero-field cooled (ZFC) from 50 to 350 K at 0.15 T.

Fig. 1 The XRD patterns of the CuFeO$_2$ and CuFe$_{1-x}$Ge$_x$O$_2$ (x = 0.01, 0.03, 0.05, and 0.10) specimens with Ge content of x = 0.00, 0.01, 0.03, 0.05 and 0.10.
Optical properties

Fig. 2 shows the optical absorption spectra of CuFe$_{1-x}$Ge$_x$O$_2$ samples. The results clearly show that all samples have a high absorption coefficient ($\alpha$) in the UV light region (250-300 nm) and a low absorbability in the visible light and near IR regions (300-800 nm). The direct optical band gap of CuFe$_{1-x}$Ge$_x$O$_2$ samples was estimated to be 3.43 eV. This value corresponds to those reported for bulk CuFeO$_2$ crystal (3.35 eV) [2].

Magnetic properties

The magnetic properties of CuFe$_{1-x}$Ge$_x$O$_2$ samples were determined by VSM at 50 K, as shown in Fig. 3(a). It is observed that the Ge-doped CuFeO$_2$ samples exhibit weak ferromagnetic behavior according to well defined hysteresis loops. The saturation magnetization ($M_s$) is greatly increased with the increase of the Ge content $x$ up to 0.01. However, the Ge content above 0.01 minimizes $M_s$ values. In order to investigate the effect of the Ge substitution upon the magnetic transition of CuFeO$_2$, temperature dependence of ZFC susceptibility ($\chi$) curves have been collected between 50 to 350 K in magnetic field ($H$) of 0.15 T, as presented in Fig. 3(b). This behavior can be attributed as a cascade magnetic transition. The magnetic transition temperature for these samples is 116 K. Similar behavior is observed for CuFe$_{1-x}$Mn$_x$O$_2$ [3], which corresponds to the magnetic transition from the paramagnetic to spin-liquid phases [4]. The temperature ($T_c$) was extracted from the temperature dependence susceptibility curve. The typical curve of $x = 0.01$ sample is given as an example, as seen in Fig. 6(c). The estimated $T_c$ is 163.5, 233.7 and 264.5 for $x = 0.01$, 0.03 and 0.05, respectively. These $T_c$ values are much higher than those of CuCr$_{1-x}$Mn$_x$O$_2$ ceramics ($T_c \leq 120$ K) [5] and Monte carlo Simulations for Cu(FeAl)O$_2$ and Cu(AlCo)O$_2$ ($T_c$ exceeds 80 K) [6]. In addition, the values of the $T_c$ are close to room temperature. It indicates that CuFe$_{1-x}$Ge$_x$O$_2$ delafossite can also be used as the oxide-based DMSs materials.

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References