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Synthesis, Microstructure, Optical and Magnetic Properties of Ge-doped $CuFeO_2$ Delafossite Oxide

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Abstract

Delafossite $CuFe_{1-x}Ge_xO_2$ ($0.0 \leq x \leq 0.1$) 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 $CuFe_{1-x}Ge_xO_2$ 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, $CuFe_{1-x}Ge_xO_2$ has been synthesized by conventional solid-state reaction. The influences of Ge composition on the microstructural, electrical, optical and magnetic properties of $CuFe_{1-x}Ge_xO_2$ were systematically investigated. We examine whether the partial Ge substitution would yield the multiferroic phase.

2. Experiments

Experimental details

In this work the polycrystalline $CuFe_{1-x}Ge_xO_2$ (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.

Structural characterizations

Fig. 1 shows the XRD patterns of sintered $CuFeO_2$ and $CuFe_{1-x}Ge_xO_2$. It is found that all of the $CuFeO_2$ and $CuFe_{1-x}Ge_xO_2$ diffraction peaks coincide well with that standard peaks. These results confirm that all $CuFe_{1-x}Ge_xO_2$ samples form a pure polycrystalline phase of the delafossite structure.

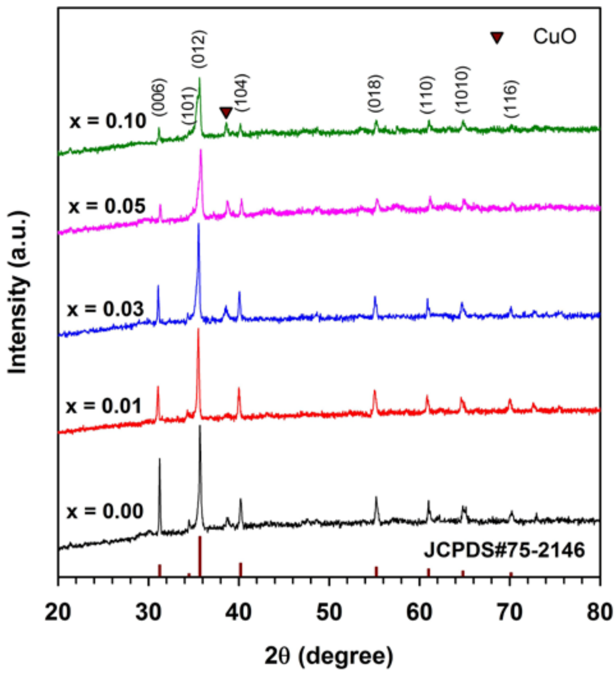

Fig. 1 The XRD patterns of the $CuFeO_2$ and the $CuFe_{1-x}Ge_xO_2$ specimens with Ge content of x = 0.01, 0.03, 0.05 and 0.10.

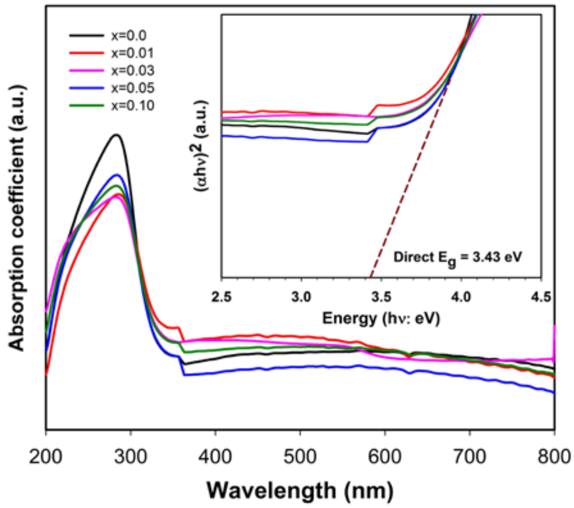

Fig. 2 The absorption spectra of the $CuFe_{1-x}Ge_xO_2$ samples at room temperature. The direct optical band energy gap is in the inset of figure.

Optical properties

Fig. 2 shows the optical absorption spectra of $CuFe_{1-x}Ge_xO_2$ samples. The results clearly show that all samples have a high absorption coefficient (α) in the UV light region (250-300 nm) and a low absorbability in the visible light and the near IR regions (300-800 nm). The direct optical band gap of $CuFe_{1-x}Ge_xO_2$ 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 $CuFe_{1-x}Ge_xO_2$ 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 (χ) 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 $CuFe_{1-x}Mn_xO_2$ [3], which corresponds to the magnetic transition from the paramagnetic to spin-liquid phases [4]. The curie 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 $CuCr_{1-x}Mn_xO_2$ ceramics ($T_C \leq 120$ K) [5] and Monte carlo Simulations for Cu(FeAl)O2 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 $CuFe_{1-x}Ge_xO_2$ delafossite can also be used as the oxide-based DMSs materials.

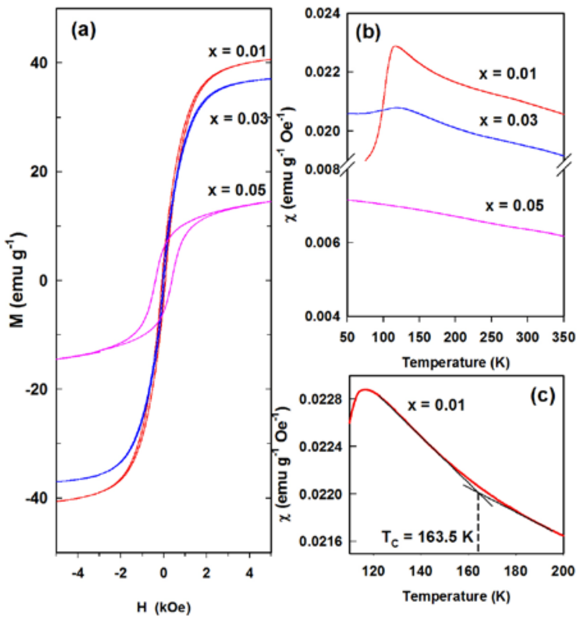

Fig. 3 (a) M-H curves of $CuFe_{1-x}Ge_xO_2$ samples measured at 50 K. (b) Temperature dependence of ZFC susceptibility of $CuFe_{1-x}Ge_xO_2$ samples at 0.15 T. (c) The extracted curie temperature for x = 0.01 sample.

3. Conclusions

The $CuFe_{1-x}Ge_xO_2$ samples have been successfully synthesized by the solid state reaction method. The XRD results imply the formation of delafossite structure. The optical band energy gap for the direct optical band transition was estimated to be 3.43 eV, exhibiting the transparency in the visible region. The magnetic measurements at 50 K for Ge-doped $CuFeO_2$ samples show a weak ferromagnetic. The Ge concentrations have strongly effects on magnetic properties. The temperature dependence of ZFC susceptibility measurements reveals the magnetic transition temperature at 116 K. The curie temperature suggests that the ferromagnetism originates from the $CuFe_{1-x}Ge_xO_2$ matrices.

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