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Room temperature ferromagnetism in Fe doped CuO nanorods

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ABSTRACT

One dimensional CuO and Fe doped CuO nanorods have been synthesized by template free solution phase hydrothermal methods. The typical diameter and the length of the $Cu_{1-x}Fe_xO$ nanorods ($x=0$, 0.02, 0.05, 0.10) are 20–25 and 300–400 nm. Pure CuO nanorods show weak ferromagnetism and the introduction of Fe within CuO lattice improves significantly the ferromagnetic property with the Curie temperature far above room temperature. The shape anisotropy is the key point to understand ferromagnetism in Fe doped CuO nanorods.

1. Introduction

The potential of exploiting the spin of the electron (in addition to its charge) in novel new electronic devices and the associated opportunities for new science have led to extensive search for viable magnetic semiconductors with room temperature ferromagnetism [1,2]. Some success for ferromagnetism has been reported in dilute magnetic semiconductors (DMS) and dilute magnetic oxides (DMO) containing a few percent of transition metal ions such as (Ga,Mn)As [3,4], (Zn,M)O [5,6], and (Ti,M)O_2 [7,8] with M=V, Cr, Mn, Co, Ni, and Cu. Most of the earlier works were concentrated on transition metal doped non-magnetic semiconductors. Nevertheless much more detailed investigations are required to understand the origin of ferromagnetism and possible applications in spintronic devices.

Transition metal monoxides MO, M=Mn, Co. Ni and Cu reveal complicated magnetic as well as electronic structure. Ferromagnetic property was observed in nanosized MO and 3d metals doped MO by modifying the original magnetic order. Among transition metal monoxides,Cupric oxide CuO is a strongly correlated electron system which exhibits Mott insulating behavior and anti ferromagnetic (AFM) with two magnetic transitions near 215 and 230 K [9], possesses complicated monoclinic tenorite structure. The magnetic structure of CuO consists of Cu–O parallel sheet of plane in which oxygen atom is located at the center of a copper distorted tetrahedron in $(1\,1\,0)$ plane. The exchange in the Cu–O–Cu chains along the $(1\,0\,\bar{1})$ direction is strongly and completely antiferromagnetic. Recently Zheng and his co workers [10,11], observed dramatic suppression of AFM coupling in Li doped CuO and CuO nanoparticles. Punnose et al. [12,13] explained the particle size dependence exchange bias and large coercivity in CuO nanoparticles on the basis of uncompensated surface spin of the nanocrystal. Li et al. [14] observed ferromagnetism in Mn doped bulk CuO and ferromagnetism enhanced by the co-doping of Al ion with low Curie temperature (below 100 K). Anomalous ferromagnetic behavior have observed in CuO nanorods [15]. Nanorods also have a number of advantages over thin films or nanoparticles with respect to studying ferromagnetism in DMSs. Specifically, they offer thermodynamically stable features and are typically single-crystalline and defect free. They can thus safely exclude the effect of defects and nonuniform distribution of dopants that are typically observed in DMSs prepared by nonequilibrium processing (e.g., molecular beam epitaxial process). All spin rotations in the nanorods could be limited to a single axis. Possible tetragonal distortion and shape anisotropy in the nanorods could also be helpful for the evolution of ferromagnetism [16,17]. Nanorods themselves are attractive building blocks for electronic devices. So nanorods could further fuel the development of ferromagnetism in DMSs.

In this article, we report the room temperature Ferromagnetic properties of Fe doped CuO nanorods. It was observed that the ferromagnetic coupling interaction increases with Fe concentration. The effect of Fe doping is discussed and relevant mechanism is proposed.

2. Experimental

Pure CuO and Fe doped CuO nanorods were synthesized by hydrothermal method. For the hydrothermal synthesis of the CuO nanorods, a closed cylindrical teflon linked autoclave with 23 ml

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capacity was used. In a typical preparation, 0.01 M cupric acetate $Cu(CH_3COO)_2 \cdot 6H_2O$, 1.25 mM NaOH and the required amount of ferric nitrate $[Fe(NO_3)_3 \cdot 9H_2O]$ were dissolved in deionised water to form an alkali solution. The mixture was stirred for 45–50 min and then it was transferred to an autoclave. The hydrothermal synthesis was conducted in an electric oven at 140 °C for 12 h. After the reaction was over, black crystalline products were harvested by centrifugation and through washing with deionised water and ethanol for several times. Finally the samples were dried at 60 °C for 24 h.

X-ray diffraction patterns of the samples were recorded by high resolution X'Pert PRO PANalytical X-ray diffractometer in the range 30−90° using Cu K_α radiation. Microstructure and crystal structures of the nanorods were obtained using transmission electron microscope (TEM) and high-resolution TEM (HRTEM, JEOL 2010) studies. The metal contents in the nanorods were determined by an inductively coupled plasma atomic emission spectrometer (ICP-AES), (Perkin Elmer). Doped samples were characterized by X-ray photoelectron spectroscopy (5400 ESCA). DC Conductivity was measured by high resistance electrometer (Keithley 6517A) in two probe configuration. Magnetization measurements were carried out by SQUID magnetometer, quantum design, MPMS XL (evercool).

3. Results and discussion

Fig. 1(a) shows the XRD patterns of the $Cu_{1-x}Fe_xO$ samples. It can be seen that all the samples contain a single CuO monoclinic phase. Because the radius difference between Cu^{2+} ion 0.73 Å and Fe^{3+} ion 0.64 Å or Fe^{2+} 0.74 Å is not remarkable, Cu^{2+} ions in lattice structure can be replaced by Fe ions. Here we have adopted modified Rietveld refinement procedure to obtain the refined values of structural and microstructural parameters. The whole pattern fitting has been done with the help of the software MAUD [18]. Initial simulation of the diffraction pattern was carried out with the CuO phase having space group C2/*c*. Then the Cu atom is accordingly substituted with the Fe atom for the doped samples. Fig. 1(b) shows the variation of unit cell volume as a function of dopant concentration. Clearly, the unit cell volume contraction by very small amount confirm the incorporation of Fe ion in CuO host lattice.

The atomic compositions of constituent elements in $Cu_{1-x}Fe_xO$ were determined from ICP-AES spectra with instrument resolution of 1 ppm. The concentration of Fe in pure CuO nanorods is about 100 ppm. The atomic ratio of Fe to Cu was quantitatively determined as 0.016 for CuO:2% Fe 0.041 for CuO:5%Fe and 0.098 for CuO:10%Fe nanorods.

Morphology of as synthesized samples was obtained using high-resolution transmission electron microscope studies. TEM and HRTEM images of the 10% Fe doped CuO nanorods are presented in Fig. 2. Inset shows a single nanorod grown along (1 1 0) direction. The average diameters of the nanorods vary between 20 and 25 nm. Length of nanorods are in the range 300–800 nm. The aspect ratio of the nanorods lies between 15 and 40. The high resolution TEM image is shown in Fig. 2(b) which exhibits clear lattice fringes. Homogeneous and parallel lattice fringes imply the single crystalline behavior of prepared samples. The interval between two adjacent lattice fringes is distinctly shown by arrows in Fig. 2b is 2.749 Å which corresponds to the (1 1 0) plane of the monoclinic structure of CuO. The oriented (1 1 0) nanorods are formed from dehydration of $Cu(OH)_2$ in solution medium by oxolation process [19].

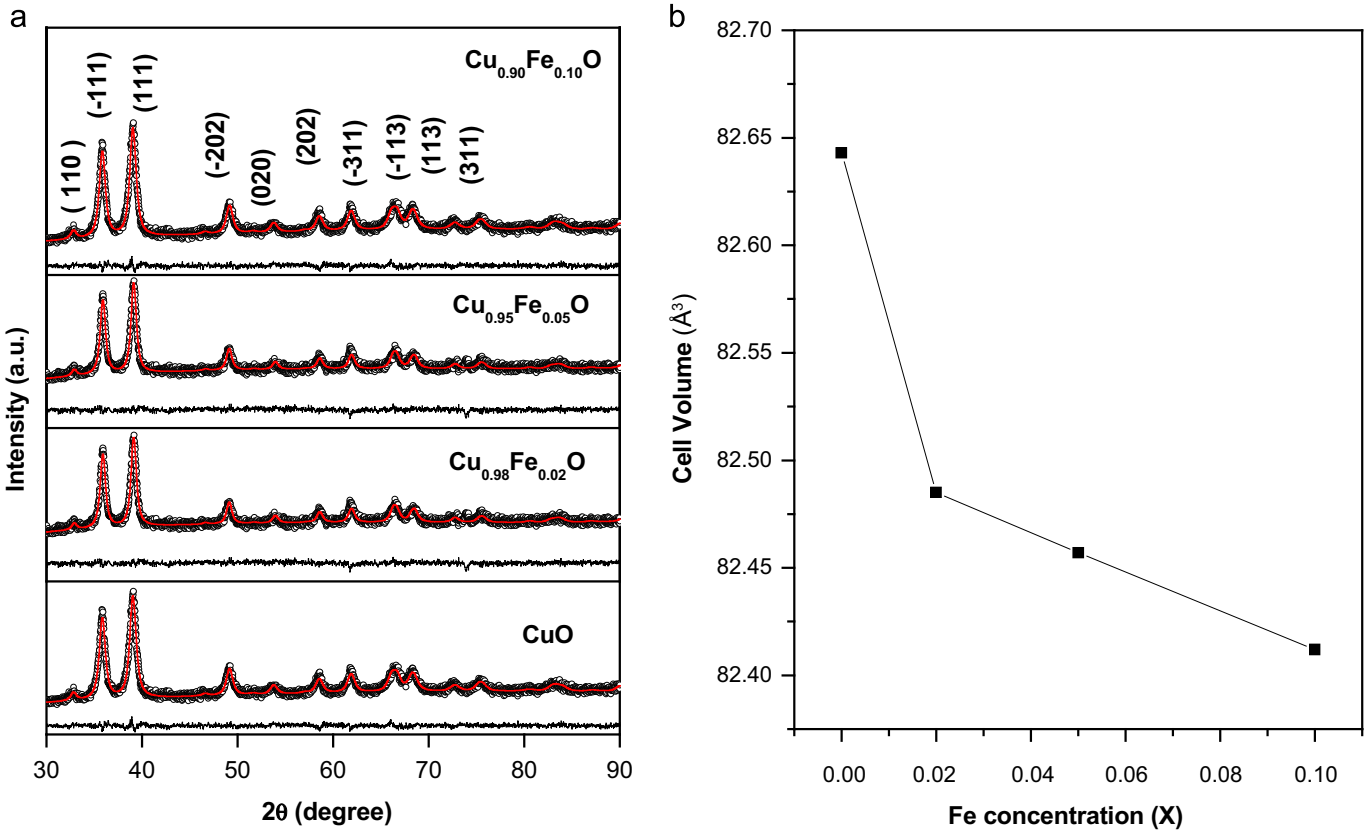

Fig. 1. (a) XRD patterns of the $Cu_{1-x}Fe_xO$ [x=0, 0.02, 0.05, 0.10] at room temperature. The calculated and observed diffraction profiles are shown at the top with the color solid line and open circle, respectively. The lower trace is a plot of the difference between calculated and observed intensities. (b) Fe Concentration dependence of unit-cell volume. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)