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Materials Letters 61 (2007) 2089 – 2092
materials letters
www.elsevier.com/locate/matlet

Synthesis of nanocrystalline xCuFe$_2$O$_4$–(1 − x)BiFeO$_3$ magnetoelectric composite by chemical method

Manoj Kumar, K.L. Yadav *

Smart Material Research Laboratory, Department of Physics Indian Institute of Technology Roorkee, Roorkee, 247667, India

Received 20 June 2006; accepted 8 August 2006
Available online 28 August 2006

Abstract

xCuFe$_2$O$_4$–(1 − x)BiFeO$_3$ spinel–perovskite nanocomposites with x = 0.1, 0.2, 0.3 and 0.4 were prepared using citrate precursor method. X-ray diffraction (XRD) analysis showed phase formation of xCuFe$_2$O$_4$–(1 − x)BiFeO$_3$ calcined at 500 °C. Transmission electron microscopy (TEM) shows formation of nanocrystallites of xCuFe$_2$O$_4$–(1 − x)BiFeO$_3$ with an average particle size of 40 nm. Variation of dielectric constant and dielectric loss with frequency showed dispersion in the low frequency range. Coercivity, saturation magnetization and squareness have been found to vary with concentration of ferrite phase and annealing temperature due to the increase in crystallite size. Squareness and coercivity increased with an increase in annealing temperature up to 500 °C and then decreased with a further increase in temperature to 600 °C. Magnetoelectric effect of the nanocomposites was found to be strongly depending on the magnetic bias and magnetic field frequency.

Keywords: Nanocomposites; Transmission electron microscopy; Magnetization; Coercivity; Magnetoelectric effect

1. Introduction

Magnetoelectric (ME) effect is a coupled, two-field effect in which the application of an electric field (E) induces magnetization and, conversely, a magnetic field (H) induces an electric polarization [1]. Magnetoelectric materials have the potential for applications as sensors, waveguides, switches, and modulators, but the realizable response ($\mathrm{d}E/\mathrm{d}H$) of currently known magnetoelectric compounds or solid solutions is too small for practical application [2,3]. A much larger $\mathrm{d}E/\mathrm{d}H$ can be obtained in composites of a ferroelectric phase and a ferrite phase [4,5], due to the coupling of piezoelectricity and magnetostriction. Therefore, a large piezoelectric response from the ferroelectric phase and a large magnetostrictive response from the ferrimagnetic (or ferromagnetic) phase are desirable.

Previous studies showed that BiFeO$_3$ had ferroelectric ordering (T_C = 850 °C) and antiferromagnetic ordering (T_N = 370–380 °C) with a cycloidal spin arrangement [6]. Copper ferrite, CuFe$_2$O$_4$, has a cubic close-packed arrangement of the oxygen ions with Cu^{2-} and Fe^{3-} ions at two different crystallographic sites [7]. This material can have tetragonal unit symmetry if cooled slowly from high temperature [8], although most spinel ferrites are cubic. Being a Jahn–Teller ion, Cu leads to improve the lattice distortion which is expected to produce a large strain in the piezomagnetic phase, thereby expecting to improve the ME effect in these composites. Since no work has been done on CuFe$_2$O$_4$–BiFeO$_3$ spinel–perovskite nanocomposite, therefore the aim of this paper is to prepare nanocomposites of xCuFe$_2$O$_4$–(1 − x)BiFeO$_3$ with x = 0.1, 0.2, 0.3, 0.4 from water soluble inorganic salts and characterize them for device application.

2. Experimental

Spinel–perovskite nanocomposites of xCuFe$_2$O$_4$–(1 − x) BiFeO$_3$ with x = 0.1, 0.2, 0.3 and 0.4 were prepared using water soluble inorganic salts. All chemicals used in the experiments were of analytical grade. Ferric nitrate Fe(NO$_3$)$_3$·9H$_2$O, copper nitrate Cu(NO$_3$)$_2$·3H$_2$O and bismuth nitrate Bi(NO$_3$)$_3$·5H$_2$O, citric acid and ethylene glycol were used as starting materials. Appropriate molar proportion of metal nitrates was fixed at Cu:Bi:Fe ratio of 1:9:11, 1:4:6, 3:7:13 and

* Corresponding author. Tel.: +91 1332 285744.
E-mail address: klalyfph@iitr.ernet.in (K.L. Yadav).

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doi:10.1016/j.matlet.2006.08.020

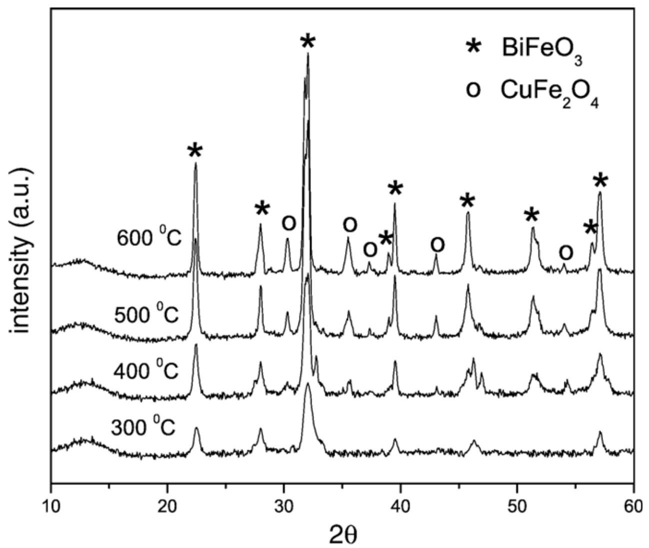

Fig. 1. XRD of $0.2CuFe_2O_4$–$0.8BiFeO_3$ powder annealed at different temperatures.

1:1.5:3.5. An aqueous solution of citric acid was prepared in distilled water. Then ferric nitrate, copper nitrate and bismuth nitrate were added in turn with constant stirring at 50–60 °C to avoid precipitation and obtain a homogeneous mixture. The brown-colored citrate mixture thus obtained was a clear solution with no precipitation. Now ethylene glycol was added into the solution with a proportion of citric acid/ethylene glycol ratio of 70:30. On heating at 100 °C on a hot plate a gel was formed after evaporation of water. Subsequently, the gel was decomposed at various temperatures ranging from 300 to 600 °C. The gel initially started to swell and filled the beaker producing a foamy precursor. This foam consists of very light and homogeneous flakes of very small particle size. Structural characterization of the powders was carried out using X-ray powder diffraction (XRD) with a monochromatic Cu K_α radiation. Transmission electron microscopy (TEM) was used to observe

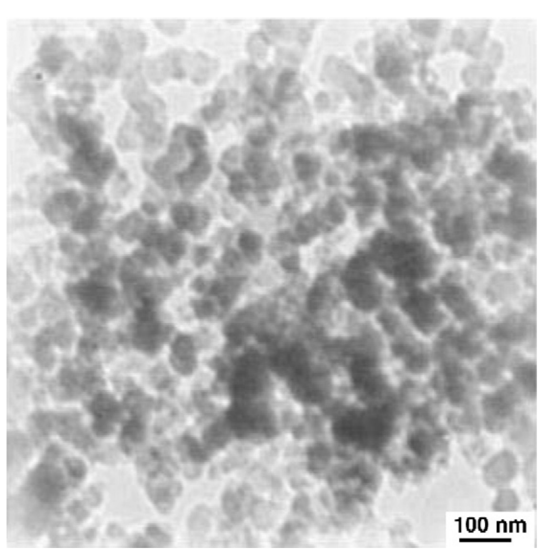

Fig. 2. TEM of $0.3CuFe_2O_4$–$0.7BiFeO_3$ powder annealed at 500 °C.

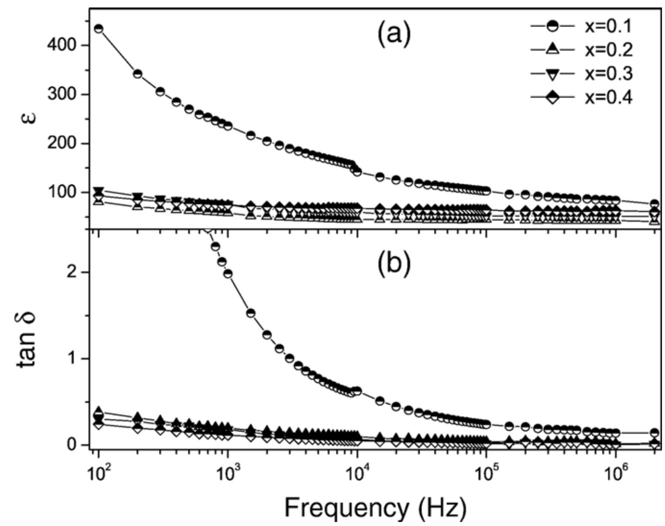

Fig. 3. Variation of the dielectric constant and the dielectric loss with frequency.

particle morphology and average particle size. Magnetic measurements were carried out at room temperature using a vibrating sample magnetometer (VSM) with a maximum magnetic field of 10 kOe. The dielectric measurements were done on silver coated pellets using HIKOI 3532-50LCR Hi-Tester. ME effect, which is characterized by the magnetoelectric voltage coefficient $\alpha_E = dE/dH$ induced by H and H_{bias} was measured using a lock-in-amplifier. A small alternating magnetic field H (10 Oe) was generated by a solenoid that was superimposed onto a magnetic bias up to 6 kOe.

3. Results and discussion

Fig. 1 shows the XRD pattern of $0.2CuFe_2O_4$–$0.8BiFeO_3$ powder annealed at different temperatures for 2 h which shows that composite consisting of $CuFe_2O_4$ and $BiFeO_3$ has formed after being annealed at 500 °C. On further increasing the annealing temperature to 600 °C, the

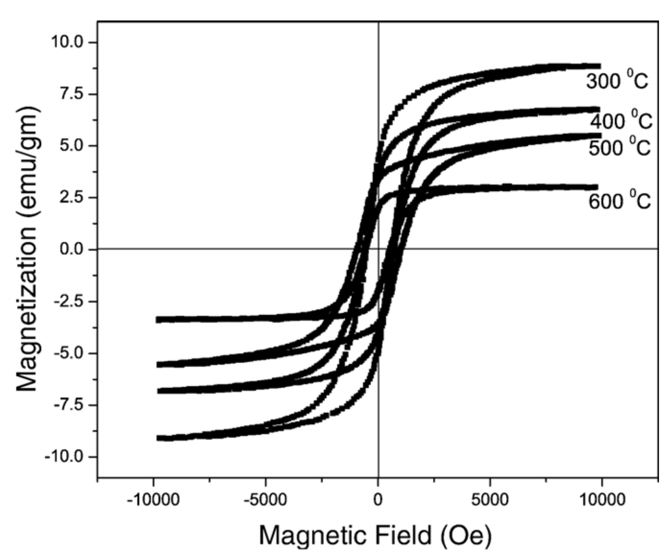

Fig. 4. Hysteresis loop of $0.2CuFe_2O_4$–$0.8BiFeO_3$ sample annealed at different temperatures.