Journal of Magnetism and Magnetic Materials 353 (2014) 57–64

Contents lists available at ScienceDirect

Journal of Magnetism and Magnetic Materials

journal homepage: www.elsevier.com/locate/jmmm

Study of structural, ferromagnetic and ferroelectric properties of nanostructured barium doped Bismuth Ferrite

A. Chaudhuri [a,b,*], K. Mandal [a,b,*]

[a] Department of Applied Science, Haldia Institute of Technology, Dist.- Purba Medinipur, Haldia- 721657, West Bengal, India
[b] Department of Condensed Matter Physics and Material Science, S.N. Bose National Center for Basic Sciences, Block JD, Salt Lake, Kolkata 700098, India

ARTICLE INFO

Article history:
Received 9 March 2013
Received in revised form
15 September 2013
Available online 11 October 2013

Keywords:
Hydrothermal synthesis
Multiferroic
Bismuth ferrite
Nanostructure
Doping

ABSTRACT

Nanostructured multiferroic $Bi_{(1-x)}Ba_xFeO_3$ $x=0.0$, 0.1, 0.2 were prepared by hydrothermal technique. All samples belonged to the rhombohedrally distorted perovskite structure. The morphology of the particles changed with the doping of barium. Effect of barium doping on the dielectric constant was studied over a wide frequency range of 1000 Hz–1 MHz. The activation energy due to relaxation and due to conduction was measured from the Cole Cole plot and the AC conductivity versus frequency plot respectively. The activation energy estimated from both the studies was close to each other. The activation energy also enhanced with the increase in the barium content. The magnetization at the highest available field (~ 1.6 T) increased from 0.05 emu/g for the sample with $x=0.0$–12 emu/g for the sample with $x=0.2$. The magnetic measurements show a significant increase in magnetization around 400 °C. Remnant polarization for $x=0.0$ was negligible and it increased to 0.06 $\mu C/cm^2$ for $x=0.2$.

1. Introduction

Bismuth Ferrite (BFO) is a single phase potential multiferroic material which shows antiferromagnetism and ferroelectricity simultaneously. Because of these properties it has tremendous possibility to be used in many commercial applications such as in ferroelectric memories, sensors, actuators and many spintronics devices [1–4]. It has an antiferromagnetic Neel temperature of $T_N \sim 370$ °C and a ferroelectric Curie temperature of $T_C \sim 830$ °C. It also has a rhombohedrally distorted perovskite structure with space group R3c. Superimposed on the antiferromagnetic ordering is a spiral spin structure in which the antiferromagnetic axis rotates through the crystal with an incommensurate long-wavelength period of 620 Å [5]. This spiral spin structure leads to a cancellation of the macroscopic magnetization and also inhibits the observation of the linear ME effect.

Bismuth is highly volatile because of the presence of lone pair of electrons. Hence there is a problem of non-stoichiometry and impurities in $BiFeO_3$. Moreover there is a problem of oxygen vacancies which makes $BiFeO_3$ conducting. Hence these deficiencies in $BiFeO_3$ restrict its commercial applications. There are various ways to overcome these deficiencies. One of the ways is to prepare nanostructured materials which will result in breakage of the spin cycloid provided the dimension of the particles be comparable to the size of the spin cycloid thereby enhancing the magnetization. Doping of various elements like rare earth, alkaline earth metal and transition metal in the A or B site of Bismuth Ferrite is also a way to improve its magnetoelectric properties [6–8].

We prepared nanostructures of barium doped bismuth ferrite $Bi_{(1-x)}Ba_xFeO_3$ ($x=0.0$, 0.1 and 0.2) by the hydrothermal technique. The motivation for synthesis of Barium doped BFO nanoparticles comes from the interesting magnetic behavior exhibited by $BaFeO_3$ [6]. Valency of Bismuth is 3+ whereas that of Barium is 2+. Hence incorporating Barium in the Bismuth site will require charge compensation. This may result in the formation of Fe^{4+} or oxygen vacancies; the former may distribute statistically with Fe^{3+} in the octahedron in Barium doped BFO (BBFO) and lead to a net magnetization and ferromagnetism [7–9]. By preparing nanostructured BBFO, magnetic properties can be improved further due to the breakage of spin cycloid. With this goal we prepared and studied nanostructured Barium doped Bismuth ferrite.

2. Experimental

The chemicals used in the synthesis were bismuth nitrate [$Bi(NO_3)_3$, $5H_2O$], iron nitrate [$Fe(NO_3)_3$, $9H_2O$] and barium nitrate [$Ba(NO_3)_2$] which were mixed in stoichiometric ratios in distilled water. All the chemicals were of analytical grade (99.99%) obtained from Sigma Aldrich. A 5 M 10 ml solution of NaOH was added drop by drop to the mixture to adjust the pH of the solution to more than 12 so that the reaction takes place in a basic medium. The

---

* Corresponding authors. Tel.: +91 33 2335 5706; fax: +91 33 2335 3477.
E-mail address: arkac123@gmail.com (A. Chaudhuri).

http://dx.doi.org/10.1016/j.jmmm.2013.09.049

resulting solution was then poured in an autoclave. The autoclave was kept in a furnace for 12 h at a temperature of 240 °C. It was then cooled naturally to room temperature [10]. The as obtained powder was washed with distilled water. We have prepared three sets of samples of $Bi_{(1-x)}Ba_xFeO_3$ (x=0.0, 0.1, 0.2).

X-ray diffraction was performed using a PAnalytical X-ray diffractometer with high intensity Cu K_α radiation. The lattice parameters and the crystal structure were refined using the Rietica package (Vision 1.7.7), based on the XRD results. The morphology of the particles was studied with the help of a Field Emission Scanning Electron Microscope (FEI). The magnetization M as a function of applied field H was measured using a Lake Shore Cryotronics Vibrating Sample Magnetometer. For the ferroelectric and dielectric measurements the powder samples were at first pressed into cylindrical pellets of 10 mm diameter and 1 mm thickness at a pressure of 60 MPa in a hydraulic press with Polyvinyl Alcohol as a binder. The pellets were sintered at a temperature of 500 °C for 3 h for densification. Secondly the pellets were carefully polished and subsequently pasted with Ag paste on both sides as electrodes. The frequency dependence of dielectric constant and dissipation factor was measured with the help of a Precision Impedance Analyzer (Agilent 4294A) over the frequency range from 1000 Hz to 1 MHz at room temperature as well as temperatures above room temperature and at applied ac voltage 500 mV. The polarization vs. electric field (*P*–*E*) hysteresis loops were measured at room temperature by the modified Sawyer-Tower circuit (Automatic *P*–*E* loop tracer system, Marine India Pvt. Ltd.). The pellets were poled at an applied field of 10 kV for 12 h for the PE loop measurements.

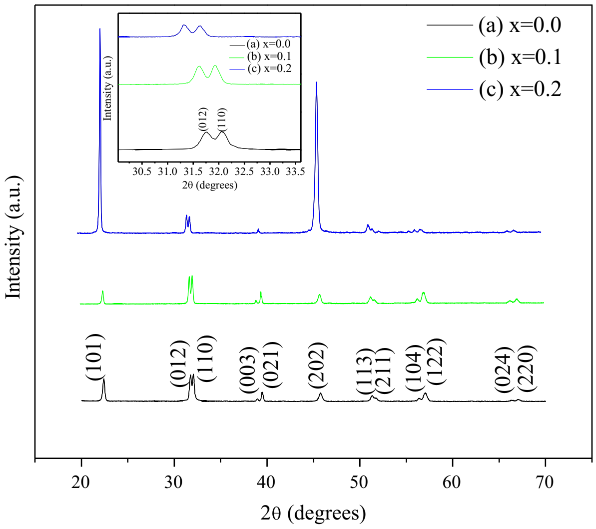

Fig. 1. X-ray diffraction of samples (a) x=0.0, (b) x=0.1 and (c) x=0.2. Inset: A comparison of the (012) and (110) diffraction pattern showing the peak shift.

Table 1
Compares the refined least squares lattice constants of BFO and BFOL with their estimated standard deviations in parenthesis.

Samples	*a* (Å)	*b* (Å)	*c* (Å)	Fe3O(1) (Å)	Fe3O(2) (Å)	*t* (tolerance factor)
$BiFeO_3$	5.58 (3)	5.58 (3)	13.87 (9)	195 (9)	2.12 (7)	0.891
$Bi_{0.9}Ba_{0.1}FeO_3$	5.59 (9)	5.59 (9)	13.92 (3)	2.00 (5)	2.24 (8)	0.879
$Bi_{0.8}Ba_{0.2}FeO_3$	5.71 (8)	5.71 (8)	14.12 (1)	1.94 (9)	2.20 (1)	0.845

3. Results and discussions

X-ray diffraction patterns of the samples are shown in Fig. 1. All the observed peaks of x=0.0, x=0.1 and x=0.2 confirmed the formation of $BiFeO_3$ which has a rhombohedrally distorted perovskite structure belonging to R3c space group. With doping a shift in the peaks was observed towards lower angles. In case of x=0.2 the maximum intensity peaks are that of the (101) and (202) planes instead of the (012) and (110) planes which is the

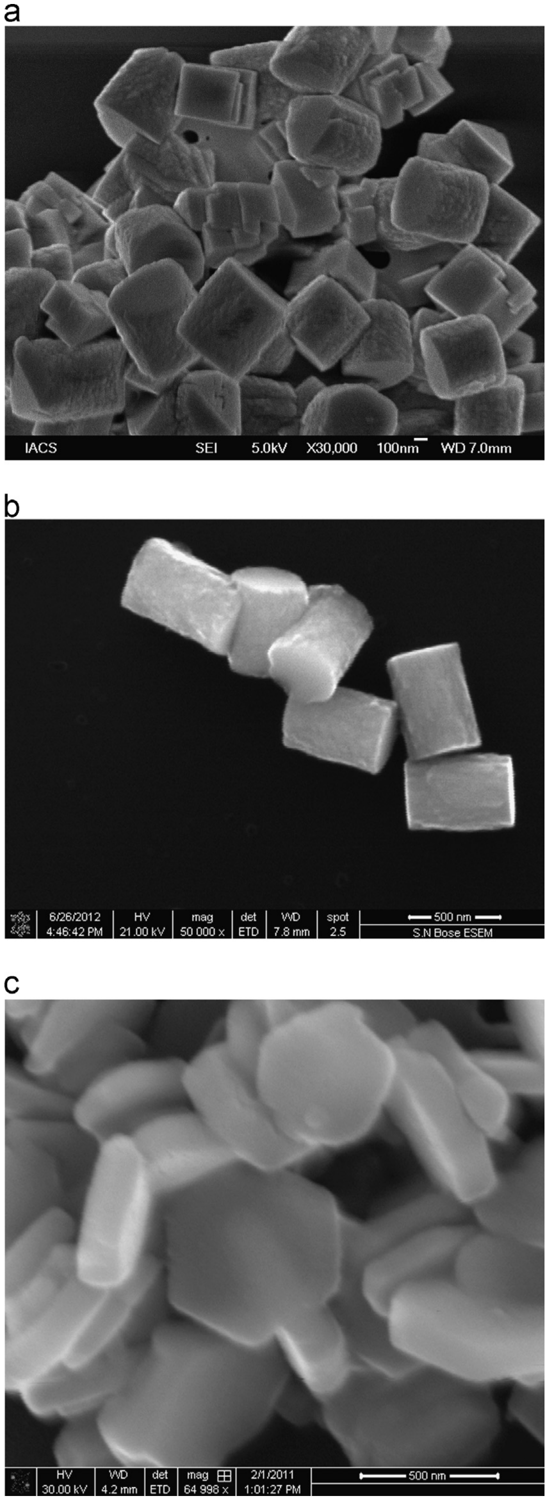

Fig. 2. Field Emmission Scanning Electron Micrographs of samples (a) x=0.0, (b) x=0.1 and (c) x=0.2.