Materials Science in Semiconductor Processing 27 (2014) 611–618

Contents lists available at ScienceDirect

Materials Science in Semiconductor Processing

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

Effect of particle size on multiferroism of barium-doped bismuth ferrite nanoparticles

Gitanjali Dhir*, Poonam Uniyal, N.K. Verma

Nano Research Lab, School of Physics and Materials Science, Thapar University, Patiala 147004, India

ARTICLE INFO

Available online 24 August 2014

Keywords:
Nanoparticles
Magnetic materials
Dielectric
Ferromagnetism
Size-dependent

ABSTRACT

Barium-doped bismuth ferrite ($Bi_{1-x}Ba_xFeO_3$ ($x=0$ and 0.15)) nanoparticles synthesized by a sol–gel method have been found to exhibit strong influence of size on structural, morphological, magnetic and dielectric properties. The size of Ba-doped $BiFeO_3$ nanoparticle has been tailored via variation of calcination temperature. Structural analysis reveals the stabilization of rhombohedral phase for $x=0.15$ Ba-substitution in $BiFeO_3$ lattice. Undoped $BiFeO_3$ nanoparticles have been found to possess saturation magnetization value of 2.535 emu/g. Ba-substitution, enhancing ferromagnetism by about 1.7 times, is ascribed to suppression of spin cycloidal by oxygen vacancies created due to divalent substitution at trivalent site. Further, this value decreases as the particle size of doped nanoparticles increases owing to the decreasing surface to volume ratio. The magnetic phase transition temperature value registers a decay of 0.86 times with Ba-doping in comparison to undoped $BiFeO_3$ nanoparticles. Also, the doped nanoparticles exhibit strong particle size dependence. Decreasing magnetic exchange interactions with reducing particle size leads to lowering of Nèel temperature. Ba-substitution has been found to result in decay of dielectric properties by about 0.85 times due to creation of oxygen vacancies. This property further decreases with increasing particle size of doped nanoparticles. These observations reveal strong correlation of size and multiferroism.

1. Introduction

Multiferroics classify materials possessing more than two ferroic orders [1–5]. These have been of immense significance for understanding fundamental aspects of physics involved in the unique phenomenon known as magnetoelectric (ME) coupling. This coupling also possesses huge potential for new device applications such as data storage, spintronics, sensors and multiple-state memories [1–5]. However, this class of materials is scarce owing to the contrary prerequisites essential for ferroelectricity and ferromagnetism [1]. Ferromagnetism requires partially filled 3d orbitals, whereas non-centrosymmetric system gives rise to spontaneous polarization, which happens when 3d orbit is empty. Amongst multiferroic materials of different structural families, the research interest in $BiFeO_3$ is due to its well above room temperature ferroelectric (Curie temperature ~1103 K) and G-type antiferromagnetic (Nèel temperature ~643 K) properties [2–5]. While this being a promising feature from application point of view, superimposed G-type antiferromagnetic ordering, superimposed on spiral spin structure, results in no net magnetization and no ME effect in bulk [2–5]. Also, in bulk form, it possesses low resistivity owing to defects and non-stoichiometric issues, which prohibit its complete polarization [3]. Studies aiming at enhancement of magnetism and dielectric properties reveal that reduction of size to nanoscale [6–8] and alkaline earth metal ion substitution [4,5] have been effectively found to overcome these problems. A large number of reports dealing with the influence of size on various properties of

* Corresponding author. Tel.: +91 175 2393343; fax: +91 175 2364498.
E-mail address: gitanjali.thaprian@gmail.com (G. Dhir).

http://dx.doi.org/10.1016/j.mssp.2014.07.041
1369-8001/

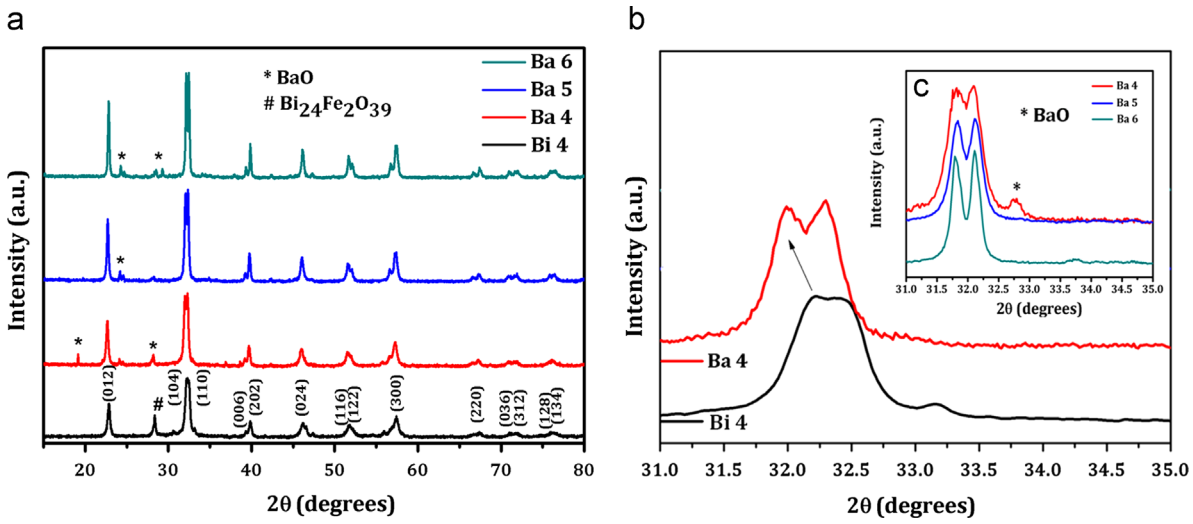

Fig. 1. (a) XRD patterns of Bi 4, Ba 4, Ba 5 and Ba 6 nanoparticles at room temperature, (b) enlarged view of XRD patterns at around $2\theta \sim 32^\circ$ for (b) Bi 4, Ba 4 and (c) Ba 4, Ba 5, Ba 6 nanoparticles.

$BiFeO_3$ are available [6–8]. It has been observed that size plays a key role in deciding the overall properties of the system. However, not much of the work has been done in the same direction for alkaline earth metal doped $BiFeO_3$ nanoparticles [4]. Therefore, being motivated from the said gap, a detailed study has been conducted in order to witness the influence of size on Ba-doped $BiFeO_3$ nanoparticles.

Present work reports the size influenced structural, morphological, magnetic, and dielectric properties of Ba-doped $BiFeO_3$ nanoparticles synthesized using a sol–gel method.

2. Experimental section

2.1. Materials

All the chemicals, bismuth (III) nitrate ($(Bi(NO_3)_3 \cdot 5H_2O$), ferric nitrate ($Fe(NO_3)_3 \cdot 9H_2O$), barium nitrate ($Ba(NO_3)_2$), tartaric acid and ethylene glycol of analytical grade were procured from Sigma Aldrich. Before use, they were not subjected to any further purification.

2.2. Synthesis

$Bi_{1-x}Ba_xFeO_3$ ($x=0$ and 0.15) nanoparticles were prepared by the sol–gel method [9]. A stoichiometric ratio of $Bi(NO_3)_3 \cdot 5H_2O$ to $Fe(NO_3)_3 \cdot 9H_2O$ was dissolved in ethylene glycol for the preparation of precursor solution. The precursor solution was stirred magnetically at 70 °C at a constant rpm. This was followed by the addition of tartaric acid in 1:1 M ratio with respect to precursors. The resulting solution was left for stirring until the gel was formed. The gel was dried at 100 °C and ground into powder. For the synthesis of 15% Ba-doped $BiFeO_3$ nanoparticles, Bi $(NO_3)_3 \cdot 5H_2O$, $Ba(NO_3)_2$ and $Fe(NO_3)_3 \cdot 9H_2O$ were dissolved in ethylene glycol in the ratio $1-x:x:1$ ($x=0.15$), keeping other reaction conditions constant. $BiFeO_3$ nanoparticles were acquired by calcining at 450 °C (Bi 4). 15% Ba-doped $BiFeO_3$ nanoparticles of different particle sizes were obtained by the calcination at different temperatures viz. 450 °C (Ba 4), 550 °C (Ba 5) and 650 °C (Ba 6) for 4 h.

2.3. Characterizations

The structural analysis was carried out using X-ray diffractometer (XRD: PANalytical X'Pert PRO MRD ML) having CuKα radiation ($\lambda=1.54060$ Å). The morphology and size of the synthesized nanoparticles were determined using transmission electron microscopy (TEM: Philips-CM200), and a field emission gun-scanning electron microscope (FEG-SEM: JSM-7600F) having resolution of 1.0 nm at 15 kV and magnification varying from 25 to 1,000,000 ×. 'AxioVision' software was used for the determination of particle size from TEM micrographs. Room temperature magnetic properties and saturation magnetization values were obtained using vibrating sample magnetometer (VSM: Princeton Applied Research Model 151/155). Nèel temperature (T_N) of the synthesized nanoparticles was determined by differential scanning calorimetry (DSC: Jupiter STA 449). In order to perform the dielectric measurements, pelletization of powder by uniaxial press at pressure of 10 t/cm^2 was done. The dielectric constant and loss measurements were carried out on an Ag-pellet-Ag capacitor using Agilent 4284A LCR meter.

3. Results and discussion

3.1. Structural and phase analyses

Fig. 1(a) shows XRD patterns of Bi 4, Ba 4, Ba 5 and Ba 6 nanoparticles. All the diffraction peaks characterize rhombohedral structure of undoped $BiFeO_3$ having R3c space group (JCPDS file no. 86-1518). Traces of impurities denoted by ∗ and # (Fig. 1(a)) correspond to $Bi_{24}Fe_2O_{39}$ (JCPDS file no. 42-0201) and BaO (JCPDS file no. 26-0177), respectively. Structural parameters, namely, crystallite size and lattice parameters are summarized in Table 1.