

Investigation of transport behavior in Ba doped BiFeO₃

A.R. Makhdoom^a, M.J. Akhtar^b, M.A. Rafiq^{a,*}, M.M. Hassan^a

^a Department of Metallurgy and Materials Engineering, PIEAS Nilore, Islamabad, Pakistan

^b Physics Division, PINSTECH, P.O. Nilore, Islamabad, Pakistan

Received 28 September 2011; received in revised form 23 December 2011; accepted 12 January 2012

Available online 21 January 2012

Abstract

Bi_{1-x}Ba_xFeO₃ ($x = 0.00$ – 0.25) samples were prepared by conventional solid state reaction method. X-ray diffraction revealed the rhombohedrally distorted perovskite structure for undoped BiFeO₃ with a phase transition from rhombohedral to pseudo cubic on Ba substitution. The leakage current density of 10% Ba substituted sample is found to be four orders of magnitude less than that of the pure BiFeO₃. Grain boundary limited conduction and space charge limited conduction mechanisms are involved in low and high electric field regions respectively for all the samples except 10% Ba doped BiFeO₃ which obeys grain boundary limited conduction mechanism in whole of the electric field range. Dielectric measurements showed that the dielectric constant and dielectric loss attained their minimum values at 10% Ba substitution. Thus 10% Ba is found to be optimum concentration to have better multiferroic properties. Undoped BiFeO₃ and 5% Ba doped samples have very large values of dielectric constants and leakage current densities which can be attributed to a large number of oxygen vacancies in these samples, indicating an extrinsic response of these compositions.

© 2012 Elsevier Ltd and Techna Group S.r.l. All rights reserved.

Keywords: B. Grain size; B. Porosity; Multiferroics; Leakage current density

1. Introduction

Ferroelectric, ferromagnetic and ferroelastic behaviors of the materials are very useful from application point of view. The materials exhibiting at least two out of the above three behaviors simultaneously are known as multiferroics [1–3]. Among the various types of multiferroics, BiFeO₃ has attracted much attention of researchers due to its promising potential applications in the fields of electromagnetic coupling, spintronics, sensors and data storage devices [4–7]. In BiFeO₃, ferroelectric and anti-ferromagnetic ordering coexist in a single phase at room temperature, that is, dielectric properties can be controlled by applied magnetic field and magnetization can be controlled by varying electric field [8]. BiFeO₃ has rhombohedrally distorted ABO₃ type perovskite structure with space group R3c [9]. It has high ferroelectric Curie temperature $T_C \sim 1103$ K and G-type anti-ferromagnetic Néel temperature $T_N \sim 643$ K [10]. Ferroelectricity appears in pure BiFeO₃ due to off centered distortion of Fe³⁺ ions, caused by 6 s² lone

pair of Bi³⁺ ions in its noncentrosymmetric rhombohedral structure [11]. BiFeO₃ has canted spins structure that generates localized antiferromagnetism which is suppressed by the spiral spin structure at macroscopic level [12].

Large number of oxygen vacancies produced due to highly volatile nature of Bi and the multiple oxidation states of Fe (Fe²⁺ and Fe³⁺) cause a high leakage current in the material that degrades its ferroelectric properties. On the other hand, the localized ferromagnetism produced by the canting of spins in BiFeO₃ vanishes at macroscopic level due the spiral spin structure of the magnetic domains with a wavelength ~ 620 Å. Due to these limitations BiFeO₃ has restricted applications. Several researchers have worked to overcome these limitations by synthesizing nanostructures or thin films of BiFeO₃ using appropriate synthesis technique and/or by doping rare earth metals/lanthanides at A site and/or transition elements at B site. Kawae et al. [13] codoped BiFeO₃ with Mn and Ti and found greatly reduced leakage current and high remnant polarization of 75 $\mu\text{C}/\text{cm}^2$ when they applied an electric field of 2100 kV/cm. Qian et al. [14] found a large magneto-dielectric coefficient of 4.7% in as-prepared BiFeO₃ nanoparticles. Yang et al. [15] found a great enhancement in magnetization with Co²⁺ substitution for Fe³⁺ ions. Wang et al. [16] studied the

* Corresponding author. Tel.: +92 51 2208014; fax: +92 51 2208070.

E-mail address: fac221@pieas.edu.pk (M.A. Rafiq).

magnetic and ferroelectric properties of Ba doped BiFeO₃. In the present work, we replaced Bi³⁺ ions with Ba²⁺ to modify the structure and transport properties of BiFeO₃. We observed anomalous variations in leakage current density and dielectric properties with increasing Ba concentration and discussed their origin.

2. Experimental

Pure and Ba doped BiFeO₃ polycrystalline samples of the type Bi_{1-x}Ba_xFeO₃ ($x = 0.00, 0.05, 0.10, 0.15, 0.20, 0.25$) were synthesized by conventional solid state reaction method. Stoichiometric amounts of Bi₂O₃, Fe₂O₃ and BaCO₃ having 99.9% purity were thoroughly mixed and ground in a pestle and mortar for 30 min for each composition. The calcinations of the ground powders were carried out at temperatures of 750 °C and 800 °C for the time duration of 20 h, with an intermediate grinding for 30 min. Then the powders were ground and pressed into pellets having diameter ~9 mm and thickness ~1 mm and sintered at 825 °C.

In order to confirm the phase purity of the synthesized samples, XRD data was collected using D8 Discoverer HR-XRD BRUKER (Germany) with CuK_α radiations ($\lambda = 1.5418 \text{ \AA}$). The XRD data was collected in $15^\circ \leq 2\theta \leq 70^\circ$ range with a step size of 0.02° and count rate of 2 s/step. Scanning electron microscopy (SEM) was carried out to observe the microstructure of the synthesized samples. For electrical measurements the opposite flat faces of the pellets were coated with silver paste to make them a parallel plate capacitor and cured at 150 °C for 1 h. Room temperature dielectric measurements were carried out using Agilent E4980A LCR meter in the frequency range from 20 Hz to 2 MHz. The response of the current density, J , to applied electric field, E , was analyzed using Keithley 2400 Source Meter.

3. Results and discussions

Fig. 1(a) shows the XRD patterns of Bi_{1-x}Ba_xFeO₃ ($x = 0.00–0.25$) samples recorded at room temperature. All the diffraction peak positions for BiFeO₃ polycrystalline match well with those of the rhombohedral R3c structure [17,18] with no impurity peak. The diffraction peak positions for Ba doped BiFeO₃ show gradual variations in peaks when compared with parent BiFeO₃. Doubly split peaks near 32°; (1 0 4) and (1 1 0), near 37°; (0 0 6) and (2 0 2) and near 52°; (1 1 6) and (1 1 2) merge gradually. This shows a structural phase transition from distorted rhombohedral to pseudo cubic symmetry. This behavior has also been reported for Pb substitution at Bi site in BiFeO₃ [19]. Fig. 1(b) shows the enlarged portion between 2θ of 31° and 33°, where murgence of (1 0 4) and (1 1 0) peaks is evident. All diffraction peaks shift slightly towards low angle indicating an increase in lattice parameters [20] caused by substitution of Ba atoms with larger ionic radius (1.42 Å) in place of Bi atoms having smaller ionic radius (1.17 Å).

In Fig. 2, SEM images demonstrate the effects of Ba concentration in BiFeO₃ on the grain size and porosity of the samples. It is clear from Fig. 2 that the average grain size is

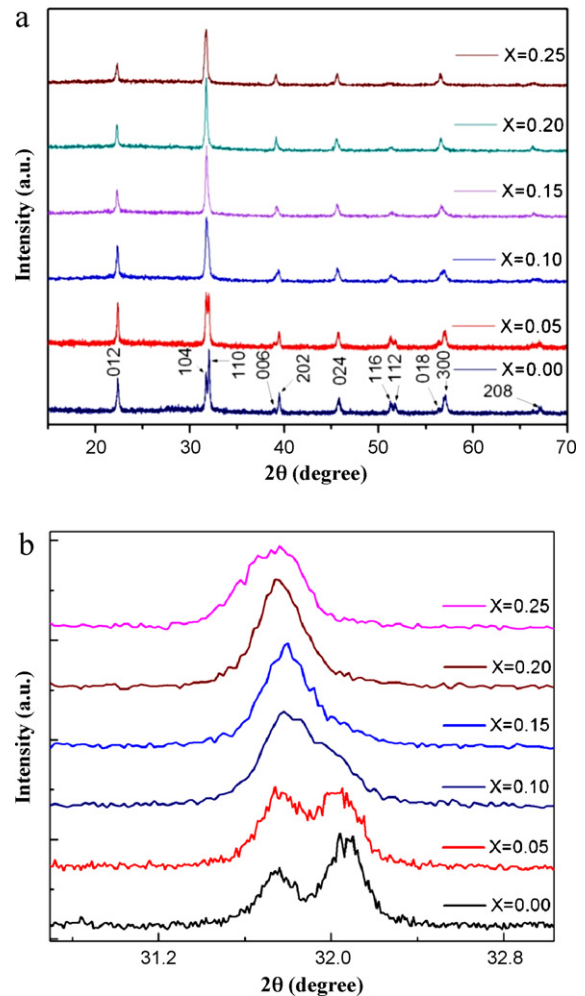


Fig. 1. (a) XRD pattern of the samples Bi_{1-x}Ba_xFeO₃ ($x = 0.00–0.25$), (b) Enlarged view of the diffraction peaks (1 0 4) and (1 1 0) near diffraction angle $2\theta = 32^\circ$.

greatly reduced from 5 μm to 100 nm with increasing Ba concentration. However for 15% Ba, the grain size is slightly increased. This may be due to the structure phase transition from rhombohedral to pseudo cubic structure as confirmed by the XRD pattern. It has been suggested that the grain growth depends upon the concentration of oxygen vacancies [21] and diffusion rate of the ions. Due to highly volatile nature of Bi, its evaporation generates large number of oxygen vacancies in pure BiFeO₃. This makes it easy for the ions to diffuse, resulting in a very large grain size as compared to the Ba doped BiFeO₃ samples. This phenomenon may be suppressed by the occupation of certain probable evaporated Bi sites by Ba ions at low doping level. Although, on further Ba doping oxygen vacancies are generated for charge neutralization, but grain growth is limited due to substitution of Ba atoms with larger ionic radius in place of Bi atoms having smaller ionic radius.

To investigate the leaky behavior of the Bi_{1-x}Ba_xFeO₃ ($x = 0.00–0.25$) system, these materials were subjected to the electric field up to 400 V/cm at room temperature and leakage current densities were measured against varying electric field. In Fig. 3, it is demonstrated that current density increases with

Download English Version:

<https://daneshyari.com/en/article/1462656>

Download Persian Version:

<https://daneshyari.com/article/1462656>

[Daneshyari.com](https://daneshyari.com)