Journal of Molecular Structure 1108 (2016) 54–59

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: http://www.elsevier.com/locate/molstruc

Crystal structure refinement and magnetic properties of $Bi_{0.8}Ba_{0.2}FeO_3$ substituted $Na_{0.5}Bi_{0.5}TiO_3$ ceramics

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ARTICLE INFO

Article history:
Received 14 August 2015
Received in revised form
26 November 2015
Accepted 26 November 2015
Available online 2 December 2015

Keywords:
X-ray crystallography
Crystal structure
Multiferroics
Magnetic properties

ABSTRACT

In this study, $Bi_{0.8}Ba_{0.2}FeO_3$ modified $Na_{0.5}Bi_{0.5}TiO_3$ ceramics having composition $(1-x)(Na_{0.5}Bi_{0.5}TiO_3) - x(Bi_{0.8}Ba_{0.2}FeO_3)$ with $0 \le x \le 0.40$ are fabricated by conventional solid state reaction technique. Rietveld analysis of X-ray diffraction pattern of the prepared ceramics revealed that all the samples crystallized into single phase with rhombohedral symmetry (R3c space group). Magnetic measurements were performed at room temperature up to a field of 6 kOe. The magnetic hysteresis loops for samples $x \le 0.10$ show linear magnetic field dependence of magnetization with narrow hysteresis loop, indicating the typical antiferromagnetic nature (AFM) with canted spins. For samples $0.20 \le x \le 0.40$, an appreciable increase in the values of remnant magnetization and coercive field are observed. Thus, the addition of BBFO content gives rise to significant increase in magnetization.

1. Introduction

Ferroelectric materials have become the most important smart material in various microelectronic and micro electromechanical devices, due to their dielectric, ferroelectric, piezoelectric performances [1]. Lead based ferroelectric materials with perovskite structure have variety of applications in sensors, actuators, transducers and other electronic devices due to their excellent piezoelectric properties. The high toxicity of lead oxide limits the use of lead-based ceramics which causes serious environmental pollution. Therefore, lead - free piezoelectric materials such as $Na_{0.5}Bi_{0.5}TiO_3$ - based oxides, bismuth layer structure oxides and tungsten bronze - type oxides have received a considerable attention owing to their device applications [2,3]. Sodium bismuth titanate (NBT), is a kind of perovskite (ABO_3 - type) ferroelectric discovered by Smolenskii et al. in 1960 [4]. $Na_{0.5}Bi_{0.5}TiO_3$ (NBT) exhibits a rhombohedral symmetry at room temperature. It undergoes a series of phase transitions: (i) ferroelectric rhombohedral to antiferroelectric tetragonal around 230 °C, (ii) antiferroelectric tetragonal to non-polar tetragonal around 320 °C, (iii) non-polar tetragonal to cubic around 520 °C [5]. NBT is considered as one of the good candidates for lead-free piezoelectric ceramics due to its large remnant polarization ($P_r = 38\ \mu C\ cm^{-2}$) at room temperature and high Curie temperature ($T_c = 320\ ^\circ C$). But the major problems associated with NBT system are high (i) dielectric loss, (ii) leakage current, and (iii) coercive field ($E_c = 73\ kV\ cm^{-1}$). Its high coercive field causes the poling of the ceramic difficult. In order to overcome these drawbacks and to improve piezoelectric properties, NBT based ceramics can be modified in two ways. Firstly, solid solution of NBT with other components have been formed and investigated by various researchers such asNBT-$(Ba,Sr)TiO_3$ [6], NBT-$BiFeO_3$ [7–9], NBT-$NaNbO_3$ [10], NBT-$BiCrO_3$ [11], $BiFeO_3$–$PbTiO_3$ [12], $BaZr_{0.025}Ti_{0.975}O_3$–$BiFeO_3$ [13], $(BiFeO_3)$-$(BaTiO_3)$ [14]. Secondly, suitable modification of NBT at A and/or B site have been studied by various researchers [15–17]. However, the formation of solid solutions can be an effective way to improve piezoelectric properties. In order to further enhance the properties of NBT - related ceramics and meet the requirement for practical uses, it is necessary to develop new NBT based ceramics. In NBT, the large ferroelectricity is attributed to $(Bi_{0.5}Na_{0.5})^{2+}$ ions, especially the Bi^{3+} ions, on the A-site of ABO_3 perovskite structure [18]. So, the addition of Bi - based ferroelectrics will play an important role in modified NBT - based ceramics. Among Bi - based ferroelectrics, bismuth ferrite $BiFeO_3$ (BFO) has keen of interest due to its simple perovskite structure with rhombohedral symmetry (R3c space group) same as that of NBT. As NBT does not have any magnetic properties, so the solid solutions of NBT and BFO will show interesting intrinsic multiferroic behavior. BFO possesses a magnetic ordering and a ferroelectric polarization

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http://dx.doi.org/10.1016/j.molstruc.2015.11.075

above room temperature [19,20]. The Neel temperature is about 367 °C, and the ferroelectric Curie temperature is about 827 °C. Though these properties are very promising in terms of practical applications, but BFO has some inherent problems such as preparation of the phase pure compound, a high leakage current, lower magnetoelectric coupling coefficients and wide difference in ferroic transition temperatures [21]. The magnetic ordering in BFO is of antiferromagnetic type, having a spatially modulated spin structure, which does not allow net magnetization and also inhibits the observation of the linear magnetoelectric effect. In order to overcome these problems, many attempts have been made recently among which doping at A- and B- site is quite effective [22–30]. Khomchenko et al. [24] reported the enhancement of magnetization by divalent ion substitution at A-site of BFO. Das et al. [31] also studied the effect of Ba^{2+} doping on magnetic properties of BFO and reported the enhanced magnetization in Ba^{2+} substituted BFO (BBFO ceramics). There are several reports on solid solutions of NBT with BFO ceramics [7–9] but none about the solid solutions of NBT with BBFO ceramics. Therefore, the aim of the present work is to synthesize BBFO modified NBT ceramics. In this work, the structure and magnetic properties of $(1-x)(Na_{0.5}Bi_{0.5}TiO_3) - x(Bi_{0.8}Ba_{0.2}FeO_3)$ ceramics with $0 \le x \le 0.40$ have been studied.

2. Experimental details

Solid solutions of NBT and BBFO ceramics, $(1-x)(Na_{0.5}Bi_{0.5}TiO_3) - x(Bi_{0.8}Ba_{0.2}FeO_3)$ with $x = 0.0$, 0.10, 0.20, 0.30, 0.40 were synthesized by solid state reaction method using high purity powders of Bi_2O_3, Na_2CO_3, TiO_2, $BaCO_3$, Fe_2O_3 (purity >99% Sigma-Aldrich) as starting materials. The stoichiometric amount of these chemicals were weighed and ground in an agate mortar until a homogeneous mixture is formed. The calcination of the above mixture was carried out at an optimized temperature of 600 °C for 5 h at the rate of 5 °C/min and then reground for half an hour. Final sintering was carried out at 900 °C for 2 h.The sintered power was again reground for 20 min. The structural characterization of the sintered ceramics was carried out by X-ray diffraction (XRD). The XRD pattern was recorded at room temperature using a Rigaku Miniflex-II diffractometer with Cu K_α radiation in the 2θ range (10° - 80°) at the scanning rate of 2° per minute. The XRD data was further analyzed by the Rietveld refinement performed by Full-Prof programme. Magnetic measurements were carried out at room temperature using Vibrating Sample Magnetometer up to a maximum field of 6 KOe.

3. Results and discussions

3.1. Structural analysis

Fig. 1 shows the X-ray diffraction patterns of $(1-x)(Na_{0.5}Bi_{0.5}TiO_3) - x(Bi_{0.8}Ba_{0.2}FeO_3)$ ($x = 0.0$, 0.10, 0.20, 0.30, and 0.40) samples recorded at room temperature. The presence of sharp and well defined diffraction peaks indicates the polycrystalline behavior with good crystallinity. The XRD patterns of the sintered ceramics indicate that all the samples crystallized into a single phase perovskite structure and the absence of impurity phase implies that Bi^{3+}, Ba^{2+}, Fe^{3+} cations diffused into NBT lattices to form a solid solution. $Na_{0.5}Bi_{0.5}TiO_3$ crystallized in rhombohedral symmetry (space group R3c) as reported by Rao et al. [5]. It is also well known that at room temperature, NBT and BBFO both are distorted rhombohedral perovskite with R3c space group. Symmetry does not change with the addition of BBFO in NBT lattice, and remains same as that of parent NBT lattice. The magnified patterns in the vicinity of 2θ ~32° are shown in the Fig. 1b which clearly depicts that with the increase of BBFO content, the main peak shifts towards lower diffraction angle, indicating increment in the dimension of unit cell. This is due to larger ionic radii of Ba^{2+}/Bi^{3+} and Fe^{3+} ions as compared to Bi^{3+}/Na^{+} and Ti^{4+} ions, respectively. XRD data was further analyzed by Rietveld refinement performed by Full-prof programme. The Rietveld refinement technique requires a structural model that has an approximation for actual structure. Rietveld refinement of the XRD pattern for all the prepared samples was performed using space group R3c and structural model allowed reproducing all the observed peaks. For hexagonal setting of rhombohedral perovskite with space group R3c, the fractional coordinates can be written in terms of s, t, e, and d parameters developed by Megaw and Darlington [32]. According to their convention, positional parameters for A-site ions $Na^{+}/Bi^{3+}/Ba^{2+}$ are (0, 0, s + 0.25); B - site ions Ti^{4+}/Fe^{3+} are (0, 0, t) and O^{2-} ions are (1/6 - 2e - 2d, 1/3 - 4d, 1/12) where parameters s and t describe the fractional shift of A- and B- site cations along [111] axis, parameter d gives the distortion of oxygen octahedra BO_6 and e parameter is related to octahedra tilt about [111] axis. The tilting angle ω is given by $\tan \omega = 4\sqrt{3}e$. These positional parameters were used as starting parameters to perform the refinement of the prepared samples. Full prof programme refine the parameters includes peak shape parameter (e.g. FWHM, asymmetry parameter), scale factor, cell parameters, background parameters, positional parameters, overall B - factor, isotropic thermal parameters, instrumental parameters, B_{iso} parameters etc. In Rietveld refinement, we need to minimize the function Δ, given as

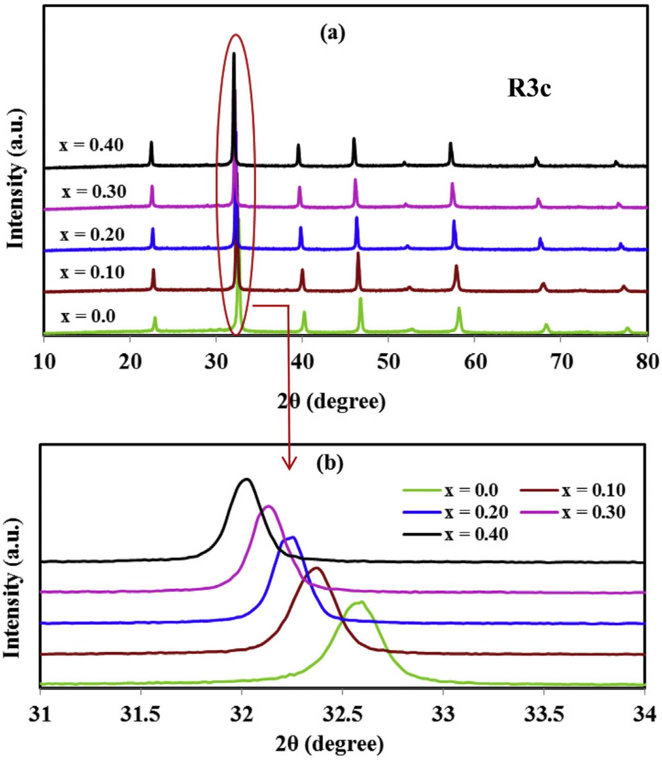

Fig. 1. (a) XRD patterns of $(1-x)(Na_{0.5}Bi_{0.5}TiO_3)-x(Bi_{0.8}Ba_{0.2}FeO_3)$; $x = 0.0$, 0.10, 0.20, 0.30 and 0.40 samples at room temperature (b) the magnified pattern in the vicinity of 2θ ~ 32°.

$$\Delta = \sum_i w_i \left(y_{c,i} - y_{o,i}\right)^2 \tag{1}$$

Where $w_i = 1/\sigma^2[y_{o,i}]$, σ_i being standard deviation associated with intensity at each $2\theta_i$ value, $y_{o,i}$ and $y_{c,i}$ are observed and calculated intensities for diffraction angle $2\theta_i$. The residual factors R_p, R_{wp} can