Available online at www.sciencedirect.com

ScienceDirect

Ceramics International 41 (2015) 10557–10564

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Relaxor behavior and piezoelectric properties of $Bi(Mg_{0.5}Ti_{0.5})O_3$-modified $Bi_{0.5}Na_{0.5}TiO_3$ lead-free ceramics

Aman Ullah[a,b], Muhammad Ishfaq[b], Chang Won Ahn[a], Amir Ullah[c], Saeed Ehsan Awan[d], Ill Won Kim[a,*]

[a]*Department of Physics and EHSRC, University of Ulsan, Ulsan 680-749, South Korea*
[b]*Department of Physics, University of Science and Technology, Bannu, Khyber Pakhtunkhwa, Pakistan*
[c]*Department of Physics, Islamia College University, Peshawar, Khyber Pakhtunkhwa, Pakistan*
[d]*Department of Electrical Engineering, COMSATS Institute of Information Technology, Attock Campus, Pakistan*

Received 26 February 2015; received in revised form 27 April 2015; accepted 27 April 2015
Available online 6 May 2015

Abstract

Lead-free $(1-x)Bi_{0.5}Na_{0.5}TiO_3-xBi(Mg_{0.5}Ti_{0.5})O_3$ (BNT–BMT) ($x=0.00-0.06$) solid solutions were synthesized via a solid state processing technique, and the effects of BMT on the structural, microstructural, dielectric, ferroelectric, and piezoelectric properties were investigated. The XRD analysis demonstrated that BMT has no pronounced effect on the crystal structure of BNT in the composition range studied, where all samples consisted of a pure perovskite phase with rhombohedral symmetry. The temperature and frequency dependences of the dielectric constant revealed that the studied compositions exhibited dielectric diffuse-to-relaxor type phase transformation. The degree of deviation from the Curie–Weiss law increased with increasing BMT concentration. The addition of BMT significantly decreased the coercive field of BNT and resulted in enhanced remnant polarization and piezoelectric constant of 38 $\mu C/cm^2$ and 108 pC/N, respectively at $x=0.04$. Polarization hysteresis was also measured at increased temperatures. These findings, along with the thermal hysteresis in the dielectric maximum, provide evidence for the observed diffuse-to-relaxor type phase transformation of these ceramics.

Keywords: C. Dielectric properties; C. Ferroelectric properties; C. Piezoelectric properties; Relaxor ferroelectrics

1. Introduction

Relaxor ferroelectrics (RFE) have been widely studied and have drawn much attention due to their various technological applications [1]. In particular, relaxor ferroelectrics belong to the family of lead-based materials such as $Pb(Mg_{1/3}Nb_{2/3})O_3$, $Pb(Sc_{1/3}Nb_{2/3})O_3$ and their derivatives, which are widely used as electromechanical sensors and actuators [2,3]. However, due to the growing awareness regarding lead oxide toxicity and the increasing demand for worldwide environmental protection, research concerning lead-free piezoelectric ceramics has greatly increased in recent years, with the aim of identifying suitable replacements for existing lead-based materials [4,5]. In this regard, some very promising lead-free materials have been proposed. However, no single lead-free ceramic has been developed to compete with PZT in all applications.

As a lead-free candidate material, bismuth sodium titanate, $Bi_{0.5}Na_{0.5}TiO_3$ (BNT), has attracted much attention and has been widely investigated during the past several years due to its strong ferroelectric properties. BNT has rhombohedral symmetry at room temperature and a relatively large remanent polarization of 38 $\mu C/cm^2$ and comparatively high Curie temperature [6,7]. However, BNT needs a large applied field to attain polarization due to its unsuitably large coercive field [3,4]. Thus, poling of BNT ceramics is challenging due to their high coercive fields. As a result, BNT shows poor piezoelectric properties in individual form, restricting it from device applications [7,8]. One possible way to reduce the large coercive field of BNT and enhance its overall electromechanical properties is

*Corresponding author.
E-mail address: kimiw@mail.ulsan.ac.kr (I. Won Kim).

http://dx.doi.org/10.1016/j.ceramint.2015.04.150
0272-8842/

the formation of solid solutions of BNT with other lead-free materials such as $BaTiO_3$ (BT) [9], $BiAlO_3$ (BA) [10], $Bi_{0.5}K_{0.5}TiO_3$ (BKT) [11,12], $SrTiO_3$ (ST) [13], and $KNbO_3$ (KN) [14].These solid solutions have been confirmed to be helpful in the poling process in order to improve piezoelectric properties [9–14].

Bi-based perovskites of $Bi(Me)O_3$ ceramics, where Me represents a single cation or a mixture with an average valence of $+3$, have received much consideration in recent years [15–17]. Solid solutions of $Bi(Me)O_3$ with $PbTiO_3$ have been widely investigated. However, there are few reports of $Bi(Me)O_3$ solid solutions with other lead-free perovskite end members [15–19]. Zhang et al. fabricated a BNT-$Bi(Zn_{0.5}Ti_{0.5})O_3$ (BZT) solid solution and observed promising piezoelectric properties [20]. A high remnant polarization ($P_r \sim 35$ μC/cm^2) was reported by Patterson and his coworkers in a similar solid solution of BNT–BZT. They found that, at a high BZT concentration, the dielectric curves displayed relaxor behavior characteristics [21]. Recently, we demonstrated that a small concentration of $Bi(Mg_{0.5}Ti_{0.5})O_3$ (BMT) can significantly improve the strain response of bismuth-based piezoelectrics at a low driving field [22]. The effects of (BMT) substitution on the crystal structure and electric properties of BNT were investigated by Wang et al., who observed an enhancement of d_{33} from 58 pC/N for BNT to 110 pC/N for 5 mol% BMT [23].

In the present study, $Bi(Mg_{0.5}Ti_{0.5})O_3$ was utilized as a chemical modifier, and the BNT–BMT solid solution system was investigated from the viewpoint of improving the piezoelectric properties and obtaining better understanding of relaxation behavior in the bismuth-based piezoelectric system.

2. Experiments

Solid solutions of $Bi_{0.5}Na_{0.5}TiO_3$–$Bi(Mg_{0.5}Ti_{0.5})O_3$ were synthesized through a solid state reaction method. Bi_2O_3, TiO_2, MgO (99.9%, High Purity Chemicals), and Na_2CO_3 (99.9%, Cerac Specialty Inorganics) were used as the starting materials. For each composition, the dried oxides and carbonates were weighed based on the desired stoichiometry and ball-milled for 24 h in ethanol. The material was dried at 80 °C, and the dried slurries were then ground and calcined at 800 °C for 2 h in a closed crucible. The powders were then ground again and ball milled for 24 h. The resulting powders were pulverized, mixed with an aqueous polyvinyl alcohol (PVA) solution, and pressed at 100 MPa into green disks with a diameter of 13 mm. Sintering was carried out at optimum sintering temperature ranging from 1150 °C to 1170 °C for 2 h in a covered alumina crucible. Crystal structure characterization of the ceramics was performed using an X-ray diffractometer (XRD, X'pert PRO MRD, Philips). For the microstructural evaluation, the as-sintered samples were thoroughly polished and then thermally etched at 1100 °C for 1 h, and FE-SEM (FE-SEM, Hitachi, S-4200, Japan) was used to study the morphology of the samples. Sintered pellets were polished to evaluate their electrical properties. Silver paste was electroded on both surfaces of the pellets, followed by firing at 700 °C for 30 min. The temperature dependence of the dielectric properties was measured using an impedance analyzer (HP4192A). Ferroelectric hysteresis loops were obtained using a Sawyer–Tower circuit. The piezoelectric constant, d_{33}, was measured using a piezo-d_{33} meter (ZJ-6B, China).

3. Results and discussion

Fig. 1 shows the XRD patterns of the $(1-x)$BNT–xBMT ceramics with $0 \le x \le 0.06$ in the 2θ range of 20–50°. In the studied composition range, all of the samples exhibited a pure perovskite structure, confirming the formation of a stable solid solution between BNT and BMT. The addition of BMT had no pronounced effect on the crystal symmetry of BNT, and all of the investigated compositions showed typical rhombohedral symmetry characterized by split (003)/(021) peaks at 40°. However, Wang and his coworkers observed lattice expansion upon the addition of BMT into the BNT lattice [23].

Fig. 2 shows FE-SEM images of the $(1-x)$BNT–xBMT samples ($x=0$, 0.02, 0.04, and 0.06). The micrographs validate that all of the samples possessed a good density. The morphology of the pure BNT ceramic consisted of irregular mixed grains, while the addition of BMT into the BNT matrix resulted in a pronounced change in grain size and shape. Firstly, the addition of BMT ceramics resulted in inhibition of grain growth, such that the BMT-substituted BNT micrographs had a more uniform size and shape. Secondly, the grain size was considerably reduced with increasing BMT concentration, which is consistent with the results obtained by Wang et al. [23].

The temperature dependence of the dielectric constant and dielectric loss of the poled BNT–BMT ceramics at different frequencies (1, 10, and 100 kHz) are displayed in Fig. 3. Two inflection points were observed in the dielectric curves of the ceramic with $x=0$, confirming the involvement of two phase transitions usually noticed in BNT-based ceramics [8,9,11–13,22]. Several features were noticed in the dielectric curves of the investigated samples: Firstly, the temperature at the dielectric maxima (T_m) increased slightly with increasing BMT content. Secondly, it is obvious that the studied compositions exhibited the dielectric diffuse-to-relaxor type phase transformation. Thirdly, the frequency dependence of T_m increased with increasing BMT

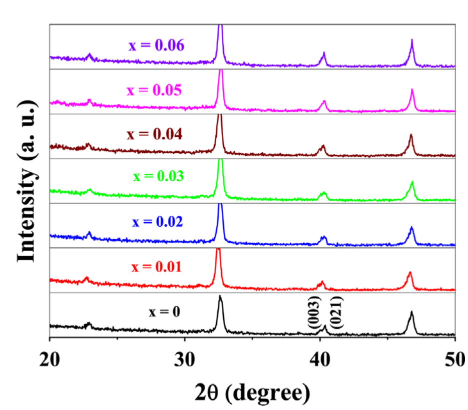

Fig. 1. X-ray diffraction patterns of the $(1-x)$BNT–xBMT ceramics ($x=0$–0.06) in the 2θ range of 20–50°.