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Dielectric, optical, piezoelectric and ferroelectric studies of NBT–BT ceramics near MPB

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Abstract

Solid solutions of the lead free $(1-x)Na_{0.5}Bi_{0.5}TiO_3$–$xBaTiO_3$/NBT–*x*BT (where $x=0.05$, 0.06, 0.07, and 0.08) ferroelectric ceramics were synthesized in single perovskite phase by solid state reaction route. Higher values of remnant polarization (P_r) $\sim$31.71 μC/cm^2, dielectric constant (ε_r) $\sim$5067, piezoelectric coefficient (d_{33}) $\sim$105 pC/N, electromechanical coupling coefficient (k_p) $\sim$21.17 and maximum induced strain% of $\sim$0.45 were obtained in the $x=0.07$ NBT–*x*BT composition. The bipolar fatigue behavior of the NBT–*x*BT ($x=0.05$, 0.06, 0.07, and 0.08) ceramics was carried out by the remnant polarization vs. number of cycles (up to 10^9) study. Optical band gap of all the NBT–*x*BT ceramics was found to be $\sim$3 eV. Excellent dielectric, piezoelectric and ferroelectric properties suggested that the $x=0.07$ is the actual MPB composition of the NBT–*x*BT system.

Keywords: A. Sintering; C. Optical properties; Ferroelectrics; Dielectric response; X-ray diffraction

1. Introduction

Ferroelectric (FE) materials are widely utilized in the electronic devices such as capacitors, non-volatile random access memory (NVRAM), actuators, transducers, filters, sensors etc. Although, lead-containing perovskite ceramics are dominating the markets of both the piezoelectric and the ferroelectric devices, the toxicity of lead has raised serious environmental issues. Therefore, since last decade, many effective lead-free ferroelectric materials have been developed and among them $(Na_{0.5}Bi_{0.5})TiO_3$ (NBT), $(Bi_{0.5}K_{0.5})TiO_3$(BKT) and $(K_{0.5}Na_{0.5})NbO_3$ (KNN) are receiving greater attention [1]. NBT is considered as one of the good candidates among the lead-free piezoelectric ceramics because of possessing high Curie temperature (T_c) $\sim$320 °C and large remnant polarization (P_r) ($\sim$38 μC/cm^2) at room temperature (RT). However, the large coercive field, (E_c) $\sim$73 kV/cm, high conductivity during poling and the low de-poling temperature have hindered its use from wide-spread applications [2,3]. To overcome these disadvantages and improve the piezoelectric properties of the NBT system, many modifications, such as solid-solutions with $SrTiO_3$/ST, $NaNbO_3$/NN, $BaTiO_3$/BT, BT–KNN, BKT etc. systems [4–11] have been developed and studied.

The solid solution of the NBT–*x*BT system exhibits a morphotropic phase boundary (MPB), which lies within the compositional range of $0.06 \le x \le 0.07$. The NBT–*x*BT system shows promising dielectric, ferroelectric and piezoelectric properties near this MPB [12–14]. Below x=0.06 composition, the structure is rhombohedral with space group R3c and above x=0.08 composition, the structure is tetragonal with space group P4bm [15]. The structure of this system around this MPB region has little distinction from the cubic symmetry [16]. Despite promising ferroelectric properties for memory applications, still it remains a challenge to use the NBT–*x*BT system in various devices and applications. Major barrier to the introduction of ferroelectric devices in the market is the limited reliability due to their electrical fatigue nature. Fatigue in ferroelectric ceramics is defined as the gradual change of

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material properties with cyclic loading. In the literature, there is hardly any study related to the ferroelectric fatigue behavior of the NBT–*x*BT system near the MPB.

In the present work, solid solutions of the lead free NBT–*x*BT ferroelectric ceramics near MPB region are synthesized in single perovskite phase by solid state reaction route. The dielectric, piezoelectric, ferroelectric (along with bipolar ferroelectric fatigue) and optical properties of the NBT–*x*BT system were studied in detail.

2. Experimental description

Polycrystalline NBT–*x*BT ceramics were synthesized using a conventional solid state reaction method. Na_2CO_3 (Merck), Bi_2O_3 (Alfa Aesar), TiO_2 (Merck), $BaCO_3$ (Merck) (of purity $\geq 99\%$) were used as the raw precursors. The stoichiometric amounts of the raw precursors were weighed and ball-milled for 12 h with zirconia balls using acetone as the grinding media. The mixed powders were dried and calcined at 1000 °C for 4 h. The single perovskite phase formation of all the compositions was investigated using XRD (Rigaku Ultima-IV). The ultraviolet visible (UV–vis) diffuse reflectance spectra (DRS) of the calcined powders was recorded using a UV–vis spectrophotometer (Perkin-Elmer, Lambda 35 UV–vis spectrometer) in the 200–800 nm range and the $BaSO_4$ was used as the reflectance standard material. The calcined powders were mixed with 3 wt% polyvinyl alcohol (PVA) and uniaxially pressed using hydraulic press into disks of diameter ~10 mm and a thickness ~1 mm under ~70 MPa pressure. The green pellets were sintered at 1150 °C for 4 h in a covered alumina crucible with a heating rate of 5 °C/min. The sintered microstructures were observed using a JEOL T-330 scanning electron microscope (SEM). The bulk densities of the sintered ceramics were calculated by using the Archimedes principle where kerosene oil was used as the liquid medium. Silver paste was applied on both sides of the sintered pellets followed by heat treatment at 300 °C for 15 min to deposit the conducting electrodes for electrical measurements. Dielectric constant (ε_r) and dielectric loss (tan δ) at different frequencies of the NBT–*x*BT ceramics were measured as a function of temperature using a computer interfaced HIOKI 3532-50 LCR-HiTESTER. Polarizations vs. electric field (*P*–*E*) measurements were performed using precision premier II, a standard ferroelectric testing machine (Radiant Technology). The bipolar fatigue behaviors (standard cycling-and-PUND procedure) of the NBT–*x*BT ceramic samples were measured under a triangular wave of 10^5 Hz frequency with an applied electric field of ~50 kV/cm. The NBT–*x*BT ceramic samples were poled by corona poling unit by applying a dc electric field of ~55 kV/cm for 30 min at RT. The d_{33} values of the NBT–*x*BT samples were measured by a Piezo meter (YE2730A d_{33} 57 Meter, APC International Ltd.). The k_p values of the NBT–*x*BT ceramic samples were measured by a resonance and anti-resonance method using HIOKI 3532-50 LCR-HiTESTER. The bipolar strain vs. electric field (*S*–*E*) measurements of the NBT–*x*BT ceramic samples were performed by using an MTI-2100 fotonic sensor (Mech. Tech. Inc) attached with Precision Premier II, Radiant Technology.

3. Results and discussion

3.1. XRD studies

The XRD patterns of the calcined NBT–*x*BT ceramic samples near MPB ($0.05 \leq x \leq 0.08$) are shown in Fig. 1. The XRD patterns reveal the single perovskite phase formation without any trace of secondary phase peaks, which confirm the complete solid solution formation of the BT system with the NBT system [14]. A close inspection of each diffraction peak shows that there is no splitting or broadening in the 2θ between 40° and 46° range for all the compositions, which indicates that all these compositions have pseudo-cubic distortion [16]. Similar type of behavior is also reported earlier in the NBT–BT system [16]. The lattice parameters of rhombohedral NBT–*x*BT ($0.05 \leq x \leq 0.08$) ceramic samples are refined in hexagonal setting by using the standard computer program 'POWD' [17]. The transformation expressions used for rhombohedral (rh) (pseudo-cubic) to hexagonal (hex) symmetry are taken from the earlier report by the Picht et al. on the NBT–BT system [9]. The rhombohedral (pseudo-cubic) unit cell parameters of the NBT–*x*BT ($0.05 \leq x \leq 0.08$) ceramic samples are given in Table 1.

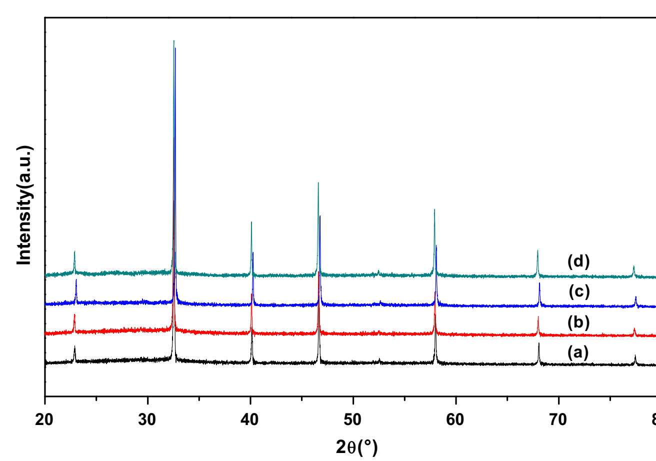

Fig. 1. XRD patterns of the calcined NBT–*x*BT ceramic samples with *x*=(a) 0.05, (b) 0.06, (c) 0.07, and (d) 0.08.

Table 1
Room temperature lattice parameters of the $(1-x)Na_{0.5}Bi_{0.5}TiO_3$–$xBaTiO_3$ ($0.05 \leq x \leq 0.08$) ceramics.

BT content	a_{hex}	c_{hex}	a_{rh}	α_{rh}
x=0.05	5.5062(4)	13.4615(2)	3.8909(2)	90.07(3)
x=0.06	5.5105(8)	13.4724(6)	3.8940(1)	90.07(5)
x=0.07	5.5019(3)	13.4173(5)	3.8847(4)	90.17(2)
x=0.08	5.5143(6)	13.4724(9)	3.8823(4)	90.09(6)