FERROELECTRIC AND PIEZOELECTRIC PROPERTIES OF LEAD–FREE BIFEO$_3$– LINBO$_3$–BATIO$_3$ CERAMICS

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Abstract- Lead-free ternary (1–x)($Bi_{1.05}FeO_3$)–0.02$LiNbO_3$–x$BaTiO_3$ (BFLNBT, with x = 0.34–0.40) system were synthesized by conventional solid-state reaction method. The influence of BT-content on the crystal symmetry, dielectric properties, ferroelectric properties and field induced response of BFLNBT was investigated. The crystal symmetry were studied by X-ray diffractometer, which showed that all BFLNBT compositions possessed single phase perovskite structure with pseudocubic symmetry at room temperature. The ferroelectric behavior of BFLNBT system were successfully measured with fully and slim saturated polarization vs electric field (P–E) loops, under an applied field of 70 kV/cm. The maximum polarization (P_{max}) and remnant polarization (P_r) of BFLN–0.34BT were 32 μC/cm^2 and 19 μC/cm^2, respectively. At applied electric field of 7 kV/mm, the optimum (x = 0.34) ceramic composition show large normalized strain (d^*_{33}= S_{max}/E_{max} =) of 322 pm/V.

Keywords- Lead-Free, Dielectric, Ferroelectric, Field Induced Strain Properties

I. INTRODUCTION

Piezoelectric materials, which have high electrical properties, are extensively used in modern electronic devices for example sensors and actuators [1, 2]. Lead-based piezoceramics (i.e. $PbZrO_3$-$PbTiO_3$, PZT)) and its ternary systems possess outstanding ferroelectric and piezoelectric properties and therefore commonly used in many electrical devices. However, PZT-based piezoelectric materials are poisonous for human body and environment. Thus, considerable investigation have been focused on substituting the lead-based piezoelectric ceramics with their eco-friendly counterpart [1, 3].

Bismuth ferrite ($BiFeO_3$, BFO) is one of the most important single phase multiferroic materials having a rhombohedrally (with space group of R3c) distorted perovskite (ABO_3) structure at room temperature [4–8]. BF ceramics shows both ferroelectric polarization (Curie temperature, T_C ~ 830 ^oC) and anti-ferromagnetic ordering (Neel Temperature, T_N ~ 370 ^oC) [9–13]. Therefore, as a result of multi-functional characteristics of BF not only give opportunities to investigate the fundamental physics but also supports to explain the potential applications such as actuators, sensors, spintronics photovoltaic and energy storage devices [14]. However, pure BF ceramics generally exhibits poor ferroelectric and piezoelectric properties. Literature survey reveals that modification of BF with other ABO_3-type perovskites can enhanced the electrical properties. BF-based, BF-$BaTiO_3$ system has been widely investigated [4, 7, 8, 15, 16]. Kumar et al. proposed the phase diagram of BF–BT solid solution and reported rhombohedral ($0.00 \leq x \geq 0.33$), pseudo-cubic ($0.33 \leq x \geq 0.92$), and tetragonal ($0.92 \leq x \geq 1.00$) ABO_3 crystal symmetry in (1–x)BF–xBT binary system [17].

Recently, Lee et al. systematically investigated the BF-BT system and suggested morphotropic phase boundary (MPB) composition for 33–35 mol.% BT-content (BF-33BT) with relatively improved piezoelectric properties [4]. However, the overall performance of these ceramics is still inferior in comparison to PZT.

In this study, a lead free (1–x)($Bi_{1.05}FeO_3$)–0.02$LiNbO_3$–x$BaTiO_3$ (BFLNBT, with x = 0.34–0.40) ceramics were prepared by conventional mixed oxide route and their dielectric, ferroelectric and piezoelectric properties were investigated.

II. DETAILS EXPERIMENTAL

2.1. Materials and Procedures

(1–x)($Bi_{1.05}FeO_3$)–0.02$LiNbO_3$–x$BaTiO_3$ (BFLNBT, x = 0.34, 0.35, 0.36, 0.38, and 0.40) ceramics were prepared by a solid state-reaction method (followed by quenching process). The bulk ceramics were synthesized from raw powders of Bi_2O_3, Fe_2O_3, TiO_2, $BaCO_3$, Li_2CO_3, and Nb_2O_5 (99.9% Sigma Aldrich Co. St. Louis, MO). Starting materials were weighed according to stoichiometric ratio and then ball-milled for 20 h in ethanol with zirconia balls. The dried slurries were calcined at 800 ^oC for 5 h and re-milled for 6h. Then calcined BFLNBT powders were subsequently pressed into green pellets and sintered at 1000 ^oC for 3h.

The crystal structures of the polished samples were characterized by X-ray diffractometer (XRD, X'pert MPD 3040, Philips) in the range of 2θ from 10^o to 80^o. The temperature dependent dielectric constants and losses were measured by an impedance analyzer (HP4192A) at frequency of 10 kHz. Polarization-electric field (P–E) loops were examined at 20 Hz in a silicone oil bath with a ferroelectric test system

(Precision LC, Radian Technologies Inc., Albuquerque, NM). The bipolar/unipolar loops (S_{max}/E_{max}) ratio was used to evaluate the electromechanical response by using a contact type displacement sensor (Millitron; Model 140).

III. RESULTS AND DISCUSSION

3.1. Crystal Structure

Fig. 1 shows representative, room temperature XRD patterns of BFLNBT (x = 0.34, 0.35, 0.36, 0.38, and 0.40) ceramics in the 2θ range of 10°–80°. It showed well crystallized pseudocubic perovskite structures for all BFLNBT compositions, and no extra phases were noticed.

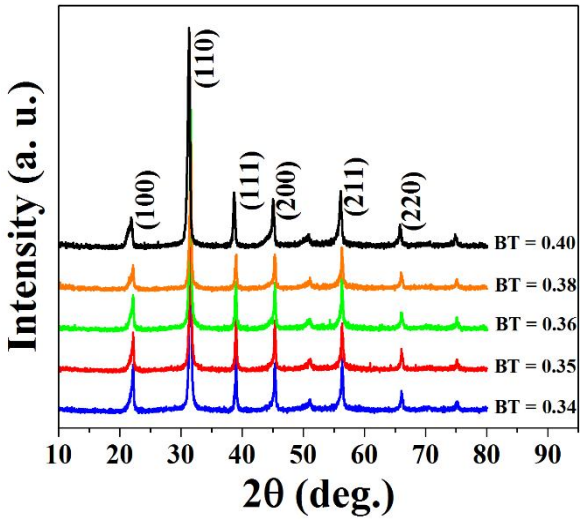


Fig.1. Room temperature, X-ray diffraction patterns of BFLNBT (x = 0.34–0.40) ceramics in 2θ ranges 10°–80°.

3.2. Dielectric Properties

The temperature dependent dielectric constants and dielectric losses at 10 kHz in the temperature range 20–500 °C are displayed in Fig. 2. The T_C is observed to be approximately > 360 ◦C for all investigated compositions which is comparable to PZT-based systems or even higher than the reported T_C values of KNN-based ceramics [18–21]. The dielectric constant gradually dropped and dielectric curve became broader by increasing BT-content in BFLNBT ceramics. The observed diffuseness in the dielectric curves probably originated by the co-occupancy of different ions, which resulted in the enhancement of the local random electric fields and lead to gradual increase in the dynamics of polar nano-regions. This apparent diffusion and increase/decrease in dielectric constant value with increasing BT-content can be due to some A/B-sites cations replacement by Ba^{+2}/Ti^{+4} and the disordered distribution in A/B-sites cations of BF/LN. Gradually, the ferroelectric long-ranged order is disturbed, the polar nano-regions are formed, and diffuse phase transition occurred. The diffuseness in the curves suggested that BFLNBT ceramics exhibited relaxor like behavior with increasing BT-content. The dielectric loss of BFLNBT ceramics was observed to be same at 10 kHz for all composition.

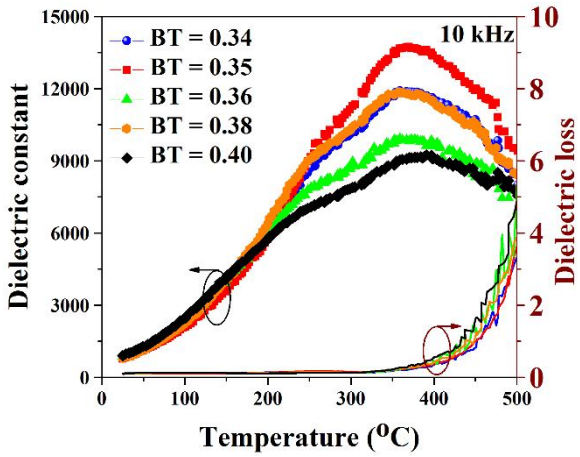


Fig.4. Temperature-dependent dielectric properties of BFLNBT ceramics

3.3. Ferroelectric Properties

The polarization hysteresis loops (P–E) also showed a significant change as a function of the BT concentration in BFLNBT ceramics, as shown in Fig. 3. All the samples showed well-saturated loops under applied electric field of 70 kV/cm. The P–E loops of the BFLN-0.34BT composition strongly resembles the behavior of a typical ferroelectric material with a relatively large maximum polarization (P_{max}) and remnant polarization (P_r) of 32 μC/cm^2 and 19 μC/cm^2, respectively. With increasing BT-content, the P_{max}, P_r, and E_c gradually decreased. This result indicates that excessive BT-content considerably weakens the ferroelectricity of the ceramics and the transformation from ferroelectric to relaxor state was occurred, evident by diffused dielectric curves (Fig. 2).

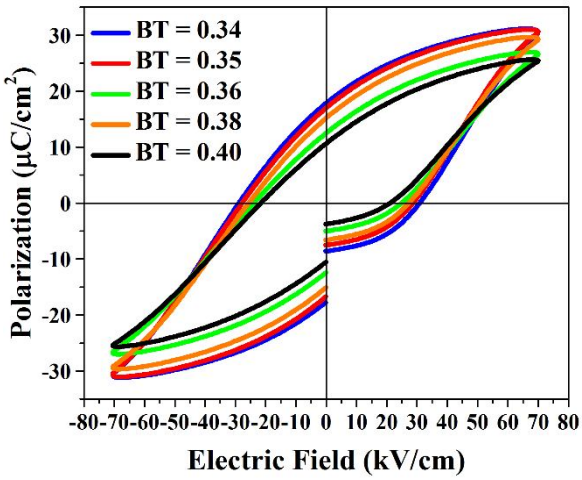


Fig.3. P–E hysteresis loops obtained at room temperature of BFLNBT ceramics (x = 0.34, 0.35, 0.36, 0.38, and 0.40).

3.4. Field Induced Strain Properties

Bipolar strain loops for the BFLNBT (x = 0.34, 0.35, 0.36, 0.38, and 0.40) ceramics were presented in Fig. 4. The BFLN–0.34BT composition shows the characteristic butterfly bipolar curve of a ferroelectric material with a maximum strain (S_{max}) of 0.225% and a negative strain (S_{neg}) of 0.04%. However, further increase in BT-content gradually reduces the S_{max} and

S_{neg}, may be due to the conversion of ferroelectric domains into dynamically active nano-domains of relaxor state. This behavior could be also related to the normal ferroelectric and diffuse and/or relaxor-ferroelectric, which consequently describe from both dielectric curves and P–E loops (Fig. 2 and Fig. 3, respectively).

Fig. 5 shows the unipolar field-induced strain curves of BFLNBT ceramics with x = 0.34–0.40 at an applied electric field of 7 kV/mm. The field induced strain increased significantly with increasing BT-content at x = 0.34, but then decreased with further increasing BT concentration. At BFLN–0.34BT composition, the abruptly highest value is 0.225% at an applied field of 7 kV/mm. However, the maximum strain vs maximum electric field (S_{max}/E_{max}) decreases with further addition of BT-content. The variation in S_{max}, and normalized strain (d^*_{33}) with BT-content is summarized in Fig. 5(b). The maximum d^*_{33} value obtained for the BFLN–0.34BT ceramic was 322 pm/V and relatively higher than previously reported BF-based ceramics [22–24]. Probably, this large strain response in BFLNBT system may be due to a reversible phase transition between a 'nonpolar' phase at zero fields and a field-induced ferroelectric phase [29].

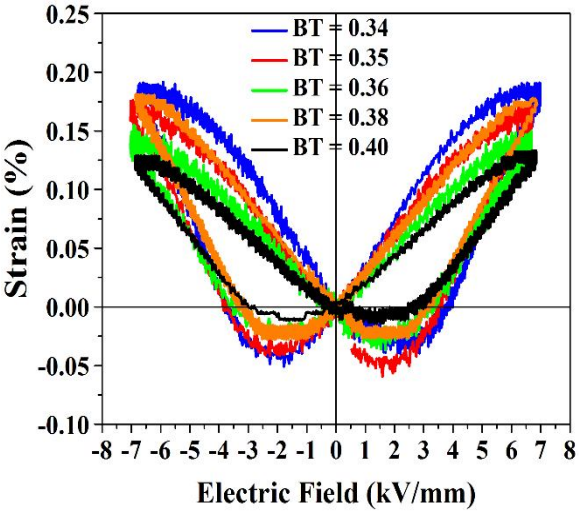
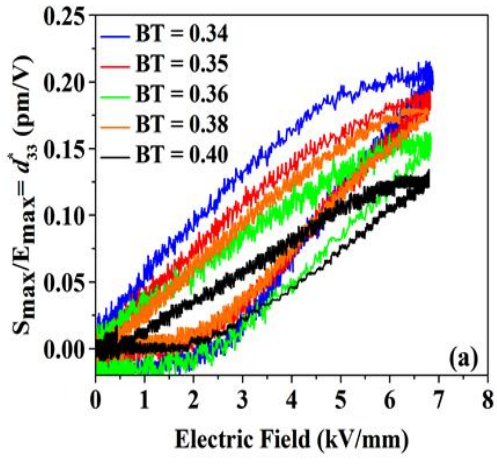


Fig.4. Bipolar strain (S–E) curves for the BFLNBT ceramics.



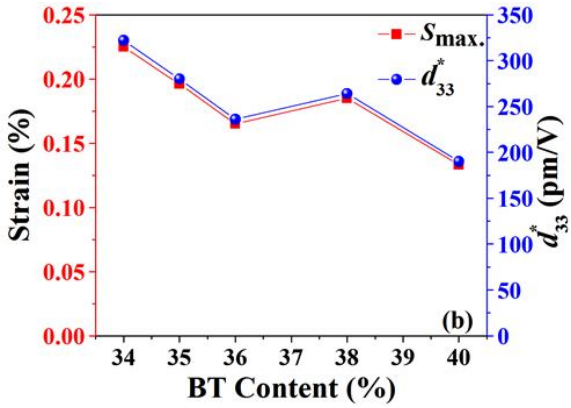


Fig.5. (a) Unipolar strain (S–E) curves of BFLNBT ceramics at an applied field of 7 kV/mm. (b) Maximum strain response (S_{max}) and dynamic piezoelectric constant (d^*_{33}) as a function of BT-content in BFLNBT ternary system.

CONCLUSIONS

Lead-free solid solution system of $(1–x)(Bi_{1.05}FeO_3)–0.02LiNbO_3– xBaTiO_3$ (BFLNBT, with x = 0.34–0.40) with large electromechanical response were fabricated by solid-state reaction route. Based on the measured results, we can conclude that a diffuse phase transition from ferroelectric to relaxor state occurred in BFLNBT ceramics. At BFLN–0.34BT sample, the field-induced strain (S–E) response was enhanced up to 0.225%, with corresponding dynamic piezoelectric constant of $d^*_{33}= S_{max}/E_{max}$ = 322 pm/V, under an applied electric field of 7 kV/mm.

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