Structural and electromechanical properties of Na\textsubscript{0.5}Bi\textsubscript{0.5}TiO\textsubscript{3} ceramics produced by different synthesis routes

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Abstract. Sodium bismuth titanate, Na\textsubscript{0.5}Bi\textsubscript{0.5}TiO\textsubscript{3} (NBT) ceramics were produced by three different methods; conventional mixed-oxide (CMO) route, molten salt synthesis (MSS) and topochemical microcrystal conversion (TMC) and then sintered at 1150 °C for 2 h in air atmosphere. The crystal structure, dielectric, ferroelectric and field-induced strain properties were investigated for all samples. All samples showed a single phase perovskite structure without any evidences of unwanted secondary phases. The NBT ceramics synthesized by the TMC method show slightly better dielectric, ferroelectric and field induced strain response as compared with CMO and MSS synthesized ceramics. The room temperature dielectric constant measured at 1 kHz increased from 218 for NBT ceramics synthesized by MSS method to 271 and 330 for CMO and TMC synthesized ceramics, respectively. Similarly, the dynamic piezoelectric coefficient (\(d_{33}\)) enhanced from 91 pm/V for CMO synthesized to 97 pm/V and 107 pm/V for MSS and TMC synthesized ceramics, respectively.

1. Introduction
Oxide piezoelectric ceramics are used in numerous devices such as sensors, actuators, filters, resonators, multilayer capacitor, transducers, micro electromechanical systems (MEMS) and memory devices [1-3]. Most of these devices are fabricated from the lead-based ceramics such as lead zirconate titanate (PZT) and its solid solutions because of their high performance [4]. Nevertheless, the pollution of lethal lead during the synthesis and waste products cause serious environmental problems. Therefore, there is an increasing demand for the development of lead-free piezoelectric ceramics to minimize pollution produced by lead-based materials [5].

Sodium bismuth titanate, Na\textsubscript{0.5}Bi\textsubscript{0.5}TiO\textsubscript{3}(NBT) is considered a promising substitute for PZT because of its high Currie temperature (T\textsubscript{c}) and large polarization [6]. Moreover, it is well established that the covalency of unoccupied states of the Pb\textsuperscript{6+} in the perovskite structure and oxygen p-states favor ferroelectric ground states [7]. Pb\textsuperscript{2+}, Bi\textsuperscript{3+} ions are in an isoelectronic state which show a longer pair effect that stimulate research on NBT as an alternative to PZT ceramics. In lead-based ceramics, Pb\textsuperscript{2+} is responsible for high polarization due to its long pair effect of 6s valence shell electron. It may be pointed out that Bi\textsuperscript{3+} in NBT has similar electronic configuration to that of lead in PZT which motivates the piezoelectric community to consider the NBT system as replacement of PZT. NBT has a perovskite structure and shows a sequence of phase transitions as a function of temperature. There are
numerous research reports from different research groups about the structural phases, types of electric ordering and its relaxor behavior of NBT that exits at different temperatures [8-12].

Beside all these, little efforts have been concentrated on the development and comparison of electromechanical properties of NBT ceramics produced by different routes. In this work, an effort has been made to prepare NBT ceramics by three different routes CMO, MSS and TMC followed by investigation and comparison of their crystal structural, dielectric, ferroelectric and field-induced strain properties to get insight into their structure and properties relationship.

2. Experimental method

Na$_2$CO$_3$ (99.95%), Bi$_2$O$_3$ (99.95%) and TiO$_2$ (99.99%) were used as starting raw materials for preparation of NBT ceramics by CMO and MSS methods. First, the starting raw materials were weighed using a physical balance according to stoichiometric formula of Na$_{0.5}$Bi$_{0.5}$TiO$_3$. For synthesis of NBT by MSS process, NaCl (99.95%) was added to oxide powder in the weight ratio of 1.5:1. Both batches were separately ball-milled in ethanol with yettria stabilized zirconia balls as a medium for 24 h and then dried. The dried slurries were placed in a tightly covered alumina crucibles and heated for 4 h at 950 °C. After heat treatment, the MSS synthesized NBT ceramics were thoroughly washed with hot de-ionized water to eliminate residual salt and then dried at 80 °C.

Aurivillius type bismuth layered structure ferroelectric, Na$_{0.5}$Bi$_{4.5}$Ti$_4$O$_{15}$ (NBT4) was used as precursor material for the synthesis of simple NBT ceramics by TMC method. Reagent grade Na$_2$CO$_3$, Bi$_2$O$_3$ and TiO$_2$ powders of purity more than (99.90%) were initially mixed following the stoichiometry of Na$_{0.5}$Bi$_{4.5}$Ti$_4$O$_{15}$ (NBT4) and then NaCl (99.95%) was added to NBT4 mixture in weight ratio (1.5:1). Detail procedure for the preparation of the NBT ceramics by TMC method can found in reports [13-14]. All powder produced by CMO, MSS and TMC methods were pressed into green disks of diameter of 10 mm and thicknesses of 2 mm. The green disks were embedded in the same compositional powder to minimize the evaporation of the volatile elements (Bi, Na) and then sintered at 1150 °C for 2 h in air atmosphere.

The crystalline phase and purity information of the NBT ceramics synthesized by different routes were checked by X-ray diffraction machine (XRD, RAD III, Rigaku, Japan) using CuKα radiation (λ = 1.541 Å) at room temperature. The upper and the lower extensive surfaces of the samples were polished and coated with a silver-palladium paste to form electrodes for electrical properties measurements. The dielectric constant and loss response were measured through an impedance analyzer (HP4194A, Agilent Technologies, Palo Alto, CA). The ferroelectric hysteresis loops were measured using a Precision Premier II device (Radiant Technology, Inc.) at 50 Hz. Field-induced strain response was measured using a contact-type displacement sensor (Model 1240; Mahr GmbH, Göttingen, Germany) at 50 mHz.

3. Results and discussion

Figure 1 shows the XRD pattern of sintered NBT ceramics synthesized by different routes (CMO, MSS and TMC). All samples crystallized into a single-phase perovskite structure, which is consistent with JCPDS card No. 36-0340 of the Na$_{0.5}$Bi$_{0.5}$TiO$_3$ ceramics. Neglecting a small rhombohedral distortion, all diffraction peaks were indexed on the basis of pseudocubic perovskite unit cell. The NBT ceramics synthesized by CMO and MSS methods have similar diffraction pattern to that of TMC, however, different heights of the intensity peaks evident from the (110) and (200) peaks. NBT ceramics synthesized by CMO and MSS have strong (110) peaks, suggesting random orientation while that synthesized by TMC method have (100) and (200) intense peaks indicating (h00) preferred orientation. The dissimilarity of NBT ceramics synthesized by TMC can be attributed to the difference in its synthesis routes.

The variation of dielectric constant and loss of NBT ceramics synthesized by different routes as a function of temperature at different frequencies (1, 10 and 100 kHz) are shown in Figure 2. It can be observed from the dielectric constant vs temperature graph that dielectric constant increases with increase in temperature up to certain point and shows two broad dielectric maximum at specific
temperature, commonly referred as depolarization temperature \( T_d \) and maximum permittivity temperature \( T_m \). The dielectric constant decreases slowly when temperature is raised above \( T_m \). This variation of dielectric constant as a function of temperature is consistent with previously published reports [15-17]. The dielectric loss curves show high dispersion for the CMO sample as compared with MSS and TMC synthesized samples. This high loss at higher temperature may be due to transport of ions with higher thermal energy. The broad transition peaks and frequency dependent response confirm the relaxor-like characteristics of the samples. However, probably due to difference in fabrication processes, the depolarization temperature \( T_d \) and \( T_m \) appears at different temperatures. It can be seen in Table 1 that \( T_d \) and \( T_m \) values of MSS and TMC synthesized NBT ceramics are slightly higher than TMC synthesized ceramics. The frequency dispersion at \( T_m \) is quite high for the CMO synthesized ceramics as compared with the MSS and TMC processed ceramics. This is probably due to the elements Na\(^+\) and Bi\(^{3+}\), which are randomly distributed in the 12-fold coordination sites of NBT, resulting in the disordering of \( A \)-site cations and the compositional fluctuation [17]. So, the observed diffused phase transition at \( T_m \) is attributing to inhomogeneous distribution of \( A \)-site cations, which appears to be responsible for relaxor behavior. All the samples show the typical character of a ferroelectric relaxor because of diffused phase transition. The dielectric constant has high frequency dependence especially at low frequency and high temperature, which is called as low frequency dielectric dispersion. This may be due to increase in dielectric loss at low frequency and high temperature.

Figure 1. XRD pattern of NBT ceramics synthesized by different routes

Figure 2. Dielectric constant and loss of NBT synthesized by different routes

Figure 3 shows the room temperature P-E hysteresis loops at room temperature of NBT ceramics synthesized by different routes. It can be clearly observed that all the samples exhibit saturated hysteresis loops under an applied electric field of 90 kV/cm at 100 Hz. There is no significant difference among the polarization curves. However, NBT ceramics synthesized by TMC have slightly better ferroelectric response (higher polarization and low coercive field) than CMO and MSS synthesized samples. As TMC synthesized ceramics exhibit single crystal type nature and for single crystal it is known that their coercive field is usually lower than that of random ceramics of the same composition [18]. Detailed values of the Remnant polarization \( P_r \), and coercive \( E_c \) of these samples are given in Table 1.

| Technique | \( T_d \) (°C) | \( \varepsilon_r \) | \( P_r \) (pC/N) | \( E_c \) (kV/mm) | \( S_{\text{max}} \) (%) | \( d_{33} \) (pm/V) |
|-----------|----------------|-----------------|----------------|----------------|----------------|-----------------|
| CMO       | 233            | 271             | 30.88          | 57.80          | 0.068          | 97              |
| MSS       | 218            | 290             | 30.01          | 61.02          | 0.072          | 102             |
| TMC       | 195            | 330             | 31.50          | 55.44          | 0.075          | 107             |

Table 1. Dielectric, ferroelectric and field-induced strain response of NBT synthesized by different routes
Figure 3 shows the room temperature P-E hysteresis loops at room temperature of NBT ceramics synthesized by different routes. It can be clearly observed that all the samples exhibit saturated-hysteresis loops under an applied electric field of 90 kV/cm at 100 Hz. There is no significant difference among the polarization curves. However, NBT ceramics synthesized by TMC have slightly better ferroelectric response (higher polarization and low coercive field) than CMO and MSS synthesized samples. As TMC synthesized ceramics exhibit single crystal type nature and for single crystal it is known that their coercive field is usually lower than that of random ceramics of the same composition [18]. Detailed values of the Remnant polarization ($P_r$), and coercive ($E_c$) of these samples are given in Table 1.

The electric field-induced bipolar and unipolar strain curves of NBT ceramics synthesized by different routes are shown in Figure 4. The bipolar strain curves (Figure 4a) present that all samples have negative strain ($S_{neg}$, which is associated with domain back switching, i.e., the difference between zero field and lowest strain) as well as maximum strain ($S_{max}$, which is the difference between positive and negative maximum strain) similar to that of the typical for ferroelectric materials. The variation in the bipolar curves is consistent with the observed P-E hysteresis loops response shown in Figure 3. The grain oriented NBT ceramics synthesized by TMC results in better ferroelectric and field-induced strain response as compared with randomly oriented CMO and MSS synthesized samples. The unipolar field-induced strain response of the NBT ceramics synthesized by different routes were measured at 7 kV/mm and is shown in Figure 4b. The room temperature unipolar field induced-strain increased from 0.068 for CMO synthesized sample to 0.075 for TMC synthesized sample. Detail information of field-induced strain response along with their corresponding dynamic piezoelectric coefficient ($d''_{33} = S_{max}/E_{max}$) values obtained for these specimens provided in Table 1. The better ferroelectric and field induced strain response of the NBT ceramics synthesized by the TMC method can be attributed to their single crystal type nature.

4. Conclusions
NBT ceramics were successfully synthesized by three different routes and their electromechanical properties were investigated. All sample have same crystal structure, however different grain orientations. NBT ceramics synthesized by TMC show (100) strong intensity peaks indicating (100) grain orientation, while those by CMO and MSS exhibit strong (110) peak signifying random orientation. At measuring frequency of 100 kHz, room temperature dielectric constant increase from 271 for CMO sample to 290 and 330 for MSS and TMC samples. Enhancement in unipolar strain from
0.068% for CMO synthesized sample to 0.072% and 0.075% were observed for MSS and TMC synthesized samples.

5. Acknowledgements
This work is supported by the National Research Foundation of Korea (NRF) grant funded by the Korean government (MOE) (2013R1A1A2058345) and Basic Research program through the National Research Foundation of Korea (NRF) funded by Ministry, Science and Technology (MEST) (2011-0030058).

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