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Stabilization of the relaxor phase by adding CuO in lead-free $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3\text{-SrTiO}_3\text{-BiFeO}_3$ ceramics

Chang-Heon Lee^a, Hyung-Su Han^{a,*}, Trang An Duong^a, Thi Hinh Dinh^a, Chang Won Ahn^b, Jae-Shin Lee^a

^a School of Materials Science and Engineering, University of Ulsan, 93, Daehak-ro, Nam-gu, Ulsan, Republic of Korea

^b Department of Physics, University of Ulsan, 93, Daehak-ro, Nam-gu, Ulsan, Republic of Korea

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ABSTRACT

We investigated microstructures, crystal structures, and electrical properties of high temperature sintered $(1-x)\text{BiNaTiO}_3\text{-}x\text{SrTiO}_3\text{-}2\text{BiFeO}_3$ (BNST100x-2BF, $x = 0.20$ and 0.22) ceramics without added CuO and compared these results with low temperature sintered BNST100x-2BF ceramics with 1 mol% of added CuO. The sintering temperature and average grain size of BNST100x-2BF ceramics decreased after addition of CuO. We found that changes in the stabilized relaxor phase with decreasing sintering temperature resulted in changes in the temperature dependent dielectric properties and provided the enhanced electromechanical strain properties in BNST100x-2BF ceramics. Therefore, we suggest that the nonergodicity to ergodicity transition is able to induce by changes in sintering temperature with added CuO and this result is important to tailor the electrical properties of BNT-based lead-free ceramics in proceeding with practical application.

1. Introduction

Lead zirconate titanate $\text{Pb}(\text{Zr,Ti})\text{O}_3$ (PZT) ceramics are a conventional piezoelectric materials that contain more than 60 wt% lead (Pb), which is harmful and toxic to humans and presents environmental risks [1,2]. Therefore, many studies have focused on lead-free piezoelectric materials to replace lead-based ceramics [1–5]. Among them, $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ (BNT)-based relaxor materials [6] as incipient piezoceramics have attracted attention due to their excellent electromechanical strain properties [7–10], which are suitable for using it to the high-stroke actuators, esp., on-off type actuators, such as for fuel injectors, air valves for car seat adjustment, etc., where the highest possible $S_{\text{max}}/E_{\text{max}}$ is desired [2]. This incipient piezoelectricity with large electromechanical strain in BNT-based lead-free relaxor ceramics can be demonstrated as the consequence of a reduction in remanent strain (S_{rem}) [11] with the presence of a nonpolar phase as a relaxor [6,7] at ‘zero’ electric field. Moreover, this phenomenon is associated with a reversible electric-field-induced phase transition from a relaxor to a ferroelectric (FE) [6,11]. In fact, such a relaxor phase (more precisely an ER) can be stabilized by a small amount of chemical modifications or increasing temperature [7].

Multi-layered ceramic actuators (MLAs) are one of the most widely used actuator types, and they are fabricated by co-firing metal electrodes and ceramics [12–18]. Since the sintering temperature of

ceramics is high, expensive electrodes with a high melting point such as Ag/Pd alloys must be used to match this temperature requirement. This is one barrier that prevents BNT-based relaxor materials from being used in practical applications, because the manufacturing costs increase due to the need for expensive electrodes. Therefore, low temperature sintering on BNT-based materials needs to be investigated to overcome this problem. Low temperature sintering provides an additional advantage in BNT-based materials, because they normally contain highly volatile elements such as Na and Bi. In fact, KNN- and BNT-based materials have been successfully sintered at low temperature by adding CuO as a sintering aid [19–26]. It is well known that sintering aids form a liquid phase and improve densification during sintering [19].

However, beyond the lowering in sintering temperature, the addition of CuO also has a pronounced impact on defect structures due to the formation of defect dipoles that have acceptor doping effects, which influence the piezoelectric properties [27]. Typical acceptor dopants are K^+ or Na^+ on the A-site and Fe^{3+} or Mn^{2+} on the B-site in PZT, and these lead to the formation of charge-compensating oxygen vacancies, which subsequently pair with acceptor-type dopants to form defect dipoles. These defect dipoles align parallel to the polarization direction, leading to the formation of an internal bias field (E_{ib}), which influences the domain wall mobility [28–35]. It is often referred to as hard-type dopants. Therefore, hard-type piezoceramics have two different fea-

* Corresponding author.

E-mail address: hsejs@ulsan.ac.kr (H. Han).

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tures such as an asymmetric shape after poling and a constricted shape after aging in ferroelectric hysteresis [29–35] which results in changes of electrical properties in general such as degradation of coercive field (E_c), remanent polarization (P_r), dielectric constant (ϵ_r), electromechanical coupling factor (k^2), piezoelectric constant (d_{33}) and improvement of mechanical quality factor (Q_m), dielectric loss, elastic hardness as verified by high frequency constant (N_p) [23,35]. Acceptor doping with even donor doping have a profound effect on domain stability in PZT as mentioned above. However, their effect on lead-free materials has not been systematically studied in detail, especially in BNT-based materials. There are some reports that focused on how the acceptor doping effect influences the electrical properties of BNT-based materials [24,25,36–43]. However, most of these studies not were clearly able to support the acceptor doping effect on their electrical property changes. Moreover, there has been little report so far concerning the stabilization of relaxor phase with adding acceptor elements. In fact, this acceptor doping effect in lead-free piezoceramics does not seem to be obviously matched with the classical theory of PZT, which have been pointed out by Hong *et al.*, [2].

According to these backgrounds as low temperature and acceptor doping effect issues, this study investigated microstructures, crystal structures, and electrical properties of high temperature sintered $(1-x)\text{BiNaTiO}_3-x\text{SrTiO}_3-2\text{BiFeO}_3$ (BNST100x–2BF, $x = 0.20$ and 0.22) ceramics without adding CuO and compared the results with those of low temperature sintered BNST100x–2BF ceramics with 1 mol% added CuO.

2. Experimental procedure

$(0.98-x)(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3-x\text{SrTiO}_3-0.02\text{BiFeO}_3$ (BNST100x–2BF, $x = 0.20$ and 0.22) powders were prepared using a conventional solid-state reaction route. Bi_2O_3 , Na_2CO_3 , Fe_2O_3 , SrCO_3 , and TiO_2 (99.9%, High Purity Chemicals, Japan) powders were used as raw materials. Before the experiment, these raw materials were put in a drying oven at 100°C for 24 h to remove moisture. Then, the raw materials were weighed according to the stoichiometric formula. The powders were ball-milled in ethanol with zirconia balls for 48 h, dried at 100°C for 24 h, and then mixed powders were calcined at 850°C for 2 h in a covered alumina crucible. After calcination, to add a sintering aid, part of powders was ball-milled again with 1 mol% CuO (99.9%, High Purity Chemicals, Japan) and the rest was ball-milled again using the same conditions. Then, ball-milled powders were dried at 100°C for 24 h again. After that, we prepared BNST100x–2BF powders with CuO and without adding CuO. The powders were mixed with aqueous polyvinyl alcohol (PVA) as a binder. Then, the obtained powers of each composition were pressed into discs with a diameter of 12 mm under a uniaxial pressure of 180 MPa. These pellets of BNST100x–2BF samples without added CuO were sintered at 1175°C , while BNST100x–2BF samples with added CuO were sintered at 1000°C in a covered alumina crucible for 2 h in air. All sintered pellets were ground on both sides and lapped to a thickness of 1 mm. After that, all samples were printed with a silver paste and then fired at 700°C for 30 min. All samples were poled under a D.C field of 4 kV/mm for 30 min in a silicone oil bath at room temperature.

The density of the sintered samples was determined using the Archimedes method. The piezoelectric charge coefficient d_{33} was measured using a piezo d_{33}/d_{31} meter (ZJ-6B; Institute of Acoustics, Chinese Academy of Sciences, Beijing, China). The electromechanical coupling factor (k_p) was calculated by a resonance–antiresonance method using an impedance analyzer (HP4194A, Agilent Technologies, Santa Clara, CA, USA). Crystal structures in sintered samples were monitored by X-ray diffraction (XRD; Rigaku, D/MAX 2500–V/PC, Japan) using $\text{CuK}\alpha_1$ radiation at room temperature. The surfaces of all sintered samples were ground by lapping for microstructural analysis. After lapping, samples were polished and thermally etched at $850\text{--}900^\circ\text{C}$ for 30 min. Finally, field-emission scanning

Table 1

The shrinkage and relative densities of BNST100x–2BF ceramics with CuO and without added CuO.

Composition	Sintering temperature ($^\circ\text{C}$)	Shrinkage (%)	Relative density (%)	d_{33} (pC/N)	k_p (%)
BNST20–2BF without CuO	1175	14.6	97.7	157	27.3
	1000	6.8	–	–	–
BNST20–2BF with CuO	1000	15.2	98.4	55	20.7
BNST22–2BF without CuO	1175	15.1	97.0	112	17.3
	1000	6.1	–	–	–
BNST22–2BF with CuO	1000	15.3	98.7	38	16.4

electron microscopy and energy dispersive spectroscopy (FE-SEM/EDS; Carl Zeiss, Supra 40, Swiss) were used to examine the microstructure of the polished and thermally etched samples. The temperature dependence of dielectric permittivity was measured at 1, 10 and 100 kHz and in the temperature range of 25°C to 400°C at $2^\circ\text{C}/\text{min}$ using a high temperature electric prober system (LABSYS HTEP-8000, NEXTRON, Korea). The polarization hysteresis (P) and strain (S) on the electric field (E) were measured at 1 Hz and various temperatures using the aixPES (aixACCT Systems GmbH, Germany).

3. Result and discussion

The sintering behaviors of BNST100x–2BF ceramics without and with added CuO are compared at two different sintering temperatures in Table 1. In the case of BNST100x–2BF ceramics without added CuO, samples were well sintered at 1175°C because both shrinkage and relative densities reached values over 14% and 97%, respectively. In contrast, samples were not dense enough at 1000°C during low temperature sintering. It is well known that BNT-based lead-free ceramics have an optimal sintering temperature between 1150°C and 1200°C [8,9,44–46]. On the other hand, the sinterability of BNST100x–2BF ceramics with added CuO were much improved after sintering at 1000°C . The obtained shrinkage and relative densities were over 15% and 98%, respectively, which were higher than the values of sintered BNST100x–2BF ceramics without added CuO. These sintering behaviors assume that the liquid-phase sintering (LPS) [19,23] is responsible for the improved sinterability of BNST100x–2BF ceramics by CuO addition [25]. In addition, the values of the piezoelectric constant (d_{33}) and mechanical coupling factor (k_p) for BNST100x–2BF ceramics decreased with added CuO and decreasing sintering temperature. There are two approaches to explain these degradations. The first approach is the CuO/or acceptor element doping/or adding effect on the piezoelectric properties, which is often observed in normal ferroelectric ceramics [25]. In addition, the induced liquid-phase as secondary phase by adding the sintering aid might affect the degradation of electrical properties [22,47]. The second is relates to the induced nonergodicity to ergodicity transition behavior caused by impurity doping in BNT-based lead-free relaxor materials [2,7,8,44–46].

The thermally-etched surface images and EDS analysis results of BNST100x–2BF ceramics with and without added CuO are displayed in Fig. 1. All images revealed dense microstructures despite being sintered at two different temperatures. The average grain sizes (AGS) were $4.7\ \mu\text{m}$ and $3.9\ \mu\text{m}$ for the high temperature sintered (1175°C for 2 h) BNST20–2BF and BNST22–2BF ceramics without added CuO, respectively, while the AGS of low temperature sintered (1000°C for 2 h) samples with added CuO were $2.5\ \mu\text{m}$ and $2.3\ \mu\text{m}$. These results suggest that sintering at 1000°C might not be sufficient to grow grains

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