Preparation of DC-bias-free (Ba, Sr)TiO₃-Bi(Mg, Ti)O₃-NaNbO₃ Ceramics with Reduced Temperature Dependent Dielectric Properties

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(1-2x)(Ba_{0.8}Sr_{0.2})TiO₃-x(Bi(Mg_{0.5}Ti_{0.5})O₃-NaNbO₃) (x = 0 - 0.33) ceramics were prepared by solid-state synthesis and the dielectric properties were investigated. At x = 0, the ceramics showed a ferroelectric behavior, and thus the dielectric properties were strongly dependent on electric field and temperature. With increasing x, the ferroelectric behavior became weak, and the electric field and temperature dependence became smaller. For the ceramics with x = 0.25 and 0.33, the dc bias and temperature dependence of the dielectric constant was small, that is, the dielectric constant was 310 – 573 under dc bias fields of 0 - 180 kV/cm and temperatures of 25 - 400 °C. Moreover, at x = 0.33, the grain size dependence was also small; the dielectric constant at 25 °C and no dc bias was 481 – 561 at grains sizes of 1.0 – 3.2 μm. These stable dielectric properties indicated that the ceramics could be candidate materials for high temperature, dc-bias-free capacitor applications.

Key words: DC-bias-free dielectrics, grain size, and dielectric property

1. INTRODUCTION

Multilayer ceramic capacitor (MLCC) is one of the important electronic parts. For many MLCCs, BaTiO₃ (BT) is the main component of the dielectric materials due to the large dielectric constant, which contributes to the miniaturization of MLCC. However, the dielectric constant of BT is strongly dependent on an electric field and temperature. This may become a problem when the MLCCs are, for example, used in automobile under a large dc electric field and high temperature.

Solid-solutions of BT and Bi-based perovskite oxides such as BiScO₃ [1, 2], Bi(Mg_{1/2}Ti_{1/2})O₃ (BMT) [3], Bi(Zn_{1/2}Ti_{1/2})O₃ [4], and Bi(Ni_{1/2}Ti_{1/2})O₃ [5] are candidate materials for capacitors operating at high electric field and high temperature. This is because polarization electric field loops were less hysteretic and rather linear and thus the dc bias dependence of the dielectric constant was reduced. On the temperature dependence of the dielectric constant, a characteristic broad peak was observed for the solid-solutions, which led a temperature-stable dielectric constant from 200-400 °C, although a strong dielectric dispersion was observed near room temperature. Recently, in the BT-Bi(Zn_{1/2}Ti_{1/2})O₃ system, this problem of the dielectric dispersion was circumvented by addition of NaNbO₃ (NN) to lower the temperature that the dielectric properties became strongly frequency dependent [6].

In this study, the ceramics of the (Ba_{0.8}Sr_{0.2})TiO₃ (BST)-BMT-NN ternary system with the focus of (1-2x)BST-x(BMT-NN) compositions were prepared, and the dielectric properties were investigated. Here, Ba was substituted with Sr to further stabilize the dielectric properties near room temperature by lowering the Curie temperature of BT. Effect of the grain size on the dielectric properties including the dielectric breakdown

strength (E_B), a measure of reliability, was also studied for a selected composition. This was because the dielectric properties were strongly dependent on grain size in BT and (Ba, Sr)TiO₃ based ceramics and the E_B value was influenced by grain size for some oxides [7].

2. EXPERIMENTAL PROCEDURES

(1-2x)(Ba_{0.8}Sr_{0.2})TiO₃-x(Bi(Mg_{1/2}Ti_{1/2})O₃-NaNbO₃) ceramics were prepared by a solid state synthesis. The compositions of the prepared samples are plotted in the chemical composition diagram shown in Fig. 1. Powders of Bi₂O₃ (99.9%, CIK NanoTec), BaCO₃ (99.9%, Nippon Chemical Industrial), TiO₂ (>95%, Showa Denko), MgO (>95%, Ube Materials), SrCO₃ (Ube Materials), Nb₂O₅ (>99.9%, Mitsui Kinzoku), Na₂CO₃ (99.9%, Rare Metallic) were weighted for the desired compositions, and ball-milled with zirconia balls and ethanol for 20 h. After drying at 80 °C, the dried masses were ground and calcined at 800 °C for 6 h in air. (For the grain size study, the calcination temperature was changed.) The calcinated agglomerate was ground and the powders were ball-milled for 20 h, followed by drying at 80 °C. The calcined powders were milled and mixed with polyvinyl butyral (PVB, 2wt%) as a binder, and again milled to a fine powder, and sieved through a 250 mesh screen. The powders were then pressed at 250 MPa to pellets. The binder was removed at 700 °C for 10 h, and the compacts were sintered at 1000-1400 °C for 2-8 h in air. The density of all the samples was evaluated by an Archimedes method. The crystal structures were examined by X-ray diffraction (XRD; UltimaIV, Rigaku). Microstructures of the samples were observed by scanning electron microscopy (SEM). Average grain size for each composition was determined by an intercept method using an SEM image of the microstructure (the intercept length was regarded as the

average grain size). For electric measurements, the samples were polished down to 0.2 mm in thickness and gold electrodes were sputtered on both sides. The samples were then cut into 2 mm × 2 mm × 0.2 mm. The dielectric constant and loss were measured using an impedance analyzer (Agilent Technologies Co., HP4294). Polarization-electric field (P-E) curves were measured in silicone oil at room temperature with a triangular wave of 100 Hz by ferroelectric characteristics evaluation systems. The dc bias dependence of the dielectric constant was estimated by differentiating P with E (dP/dE) of the P-E loop of the samples. To determine E_B value, P-E loops were measured with increasing electric field amplitude by 10 kV/cm until the sample was electrically broke down. The E_B values were defined as the average of the

electric fields just before the samples were broken down for three samples for each composition.

3. RESULTS AND DISCUSSION

Figure 2 shows XRD patterns of the ceramics with different compositions. A single perovskite phase was observed for all the samples. The crystal system could be assigned to be cubic (or pseudo-cubic). No clear shift of diffraction peaks due to the change in the compositions was observed.

The microstructures of the ceramics were observed by SEM, and the microstructure at $x = 0.05$ is shown in Fig. 3, as an example. Dense microstructures were observed for the ceramics, and the relative densities of the ceramics were higher than 95%. The grain size with

Fig. 1 The chemical compositions of the BST-BMT-NN ceramics prepared in this study.

Fig. 2 XRD patterns of the (1-2x)BST-x(BMT-NN) ceramics with x from 0 to 0.33.

Fig. 3 SEM images of the BST-BMT-NN ceramics with $x = 0.05$

Table I Chemical composition dependence of sintering temperature, relative density, grain size, E_B and dielectric constant for the BST-BMT-NN ceramics.

x	Sintering temperature [°C]	Relative density [%]	Grain size [μm]	E_B [kV/cm]	Dielectric constant
0	1400	95	11.7	120	1867
0.05	1225	98	0.4	130	1330
0.085	1225	98	0.6	180	880
0.1	1225	98	0.6	180	794
0.15	1175	99	0.9	190	652
0.25	1150	98	1.8	180	573
0.33	1100	97	2.2	200	561

Fig. 4 Temperature dependence of dielectric properties of the BST-BMT-NN ceramics with (a) $x = 0$, (c) $x = 0.33$ and 0.25, measured at 10 kHz, 100 kHz, and 1 MHz. The arrows indicate directions of increasing frequency. (b) The data measured at 1MHz for the ceramics with $x = 0.05 - 0.33$. Thick lines indicate dielectric constant while thin lines indicate $\tan\delta$.

their composition as well as sintering temperature and the relative density was summarized in Table I. At $x = 0$, the grain size was as large as $11.7 \mu\text{m}$. When BMT and NN were added, the sintering temperature that needed to densify the ceramics was reduced and therefore the grain size was reduced to $0.4 - 2.2 \mu\text{m}$.

Figure 4 (a) shows the temperature dependence of the dielectric properties measured at the frequencies of 10 kHz, 100 kHz, and 1 MHz at $x = 0$. A strong peak of the dielectric constant was observed near 50°C . When BMT and NN were added, the peak was suppressed and the peak temperature was lowered below room temperature. Therefore, the dielectric constant at room temperature was decreased and the temperature dependence of the dielectric properties above room temperature was flattened; the dielectric constants were found to be 520 – 320 at the temperature range of $25 - 400^\circ\text{C}$ (Fig. 4 (b)). For solid-solutions of BT – Bi-based perovskites, it was reported that there was a characteristic frequency-dependent dielectric constant near room temperature [1-5]. However, such a dispersion was not observed at $x = 0.25$ and 0.33 , as shown in Fig. 4 (c). Thus, the dielectric properties of these samples were less frequency-dependent. On the other hand, a dielectric relaxation was observed in the dielectric loss profile at temperatures between 200 and 300°C . This might be ascribed to some defects such as defect dipoles and space charges [8]. The dielectric relaxation can be suppressed by dopants such as Mn.

Figure 5 shows P-E loops of the samples. At $x = 0$, a ferroelectric P-E loop was observed. At $x = 0.05$, the remanent polarization was reduced and the P-E loop became less hysteretic. At $x = 0.085 - 0.33$, the P-E response became nearly hysteresis-free and the induced polarization decreased to $\sim 10 \mu\text{C}/\text{cm}^2$. The dc bias dependence of the dielectric constant, which was calculated from the P-E loop, is shown in Figs. 6. At $x = 0$, the dielectric constant was strongly dependent on the dc bias field. With increasing x , the dielectric constant at no bias decreased and the dc bias dependence of the dielectric constant was reduced. This was attributed to the suppression of the ferroelectricity of BST with increasing value of x . Note that the dielectric constant at $x = 0$ was larger than 10000, while the dielectric constant shown in Fig. 4 (a) was about 2000. The difference in the dielectric constant was caused by the

Fig. 5. P-E hysteresis loops of the $(1-2x)\text{BST}-x(\text{BMT-NN})$ ceramics with x from 0 to 0.33.

difference in the ac field amplitude applied to the sample to measure the dielectric constant. The dielectric constant shown in Fig. 4(a) was measured by applying a small ac field ($< 1 \text{ kV}/\text{cm}$) using the impedance analyzer, while that in Fig. 6 (a) was measured by applying the large ac field of $120 - 130 \text{ kV}/\text{cm}$ from the P-E loop. For ferroelectrics, it is known that contributions to the dielectric properties were largely associated with deformation of the lattice and motion of domain walls. The latter contribution was strongly increased by the ac field amplitude. Thus, the dielectric constant shown in Fig. 6(a) ($x=0$) was larger than that in Fig. 4(a), due to a larger domain wall contribution. For other compositions, the difference in the dielectric constants measured by the impedance analyzer and the P-E loop was small because of the reduced domain wall contributions.

The E_B values were measured through P-E loop measurements for the samples. The results are listed in Table I. As could be seen, the E_B value increased with increasing x . It was known that E_B value increased with decreasing dielectric constant [9]. Since the dielectric constant decreased with x in this study, the trend among the E_B , x , and the dielectric constant was consistent with previous study.

For the ceramics with $x = 0.33$, grain size effect on the dielectric properties were further investigated. The ceramics with grain sizes of $1.0 - 3.2 \mu\text{m}$ were prepared

Figs. 6 The dc bias dependence of dielectric constant of the ceramics with (a) $x = 0$, (b) $x = 0.05 - 0.33$. Dielectric constant was estimated by differentiating P with E (dP/dE) for the P-E loop of the ceramics.

with changing calcination and sintering temperatures and sintering time at sintering temperatures. Table II summarizes the firing conditions, relative density, grain size, dielectric constant, and E_B value. The ceramics with varied grain sizes had dense microstructures with the relative density higher than 93 %, as represented by the sample with the sintering temperature of 1100 °C, calcination temperature of 800 °C and the grain size of 2.2 μm (Fig. 7). It was found that the dielectric constant was less grain size dependent in the grain size range; the dielectric constant was 481 – 561, and $\tan\delta$ was almost unchanged. This could be attributed to the reduced ferroelectricity. It is interesting to note that the E_B values tended to increase with grain size. This trend was opposite to that observed for oxides such as TiO₂, MgO, and BaTiO₃ [7]. Further study is needed to elucidate the grain size effect on the E_B values for the ceramics.

The results obtained so far in this study showed that, at $x = 0.25$ and 0.33 , the dielectric constant at no dc bias field was 561 – 573 and the reduction in the dielectric constant with dc bias field was less than 18%. The E_B value was 180 kV/cm. Moreover, the change in the dielectric constant at temperatures between room temperature and 400 °C was less than 43% and the grain size dependence of the dielectric constant was small. These results suggested that the ceramics with $x = 0.25$ and 0.33 are strong candidates for the high temperature, dc-bias-free capacitor applications.

4. CONCLUSION

In this study, we prepared the $(1-2x)(\text{Ba}_{0.8}\text{Sr}_{0.2})\text{TiO}_3-x(\text{Bi}(\text{Mg}_{1/2}\text{Ti}_{1/2})\text{O}_3-\text{NaNbO}_3)$ ceramics and measured the dielectric properties. At $x = 0.25$ and 0.33 , the dielectric constant was 310 – 573 at dc bias fields of 0 – 180 kV/cm and temperatures of 25 –

Table II . Calcination, sintering temperatures, and sintering time dependences of the relative density, grain size, E_B , and dielectric constant of the ceramics with $x = 0.33$.

Sintering temperature [°C]	Sintering time [h]	Calcination temperature [°C]	Relative density [%]	Grain size [μm]	E_B [kV/cm]	Dielectric constant
1000	2	800	99	1.0	110	495
1000	2	1000	93	1.4	140	481
1000	8	800	98	1.7	170	497
1100	2	800	97	2.2	200	561
1100	2	1000	96	2.2	140	494
1100	8	800	96	3.2	170	552

Fig. 7 The SEM image of the ceramics with $x = 0.33$.

400 °C, and the dielectric constant at $x = 0.33$ was 481 – 561 at the grain sizes of 1.0 – 3.2 μm . The dielectric materials with the stable dielectric properties could be used for high temperature capacitor application under high a dc bias condition.

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(Received March 31, 2015; Accepted June 9, 2015)