Journal of Sensor Science and Technology
Vol. 29, No. 1 (2020) pp. 7-13
http://dx.doi.org/10.5369/JSST.2019.29.1.7
pISSN 1225-5475/eISSN 2093-7563

Suppression of Dielectric Loss at High Temperature in $(Bi_{1/2}Na_{1/2})TiO_3$ Ceramic by Controlling A-site Cation Deficiency and Heat Treatment

Ju-Hyeon Lee[1], Geon-Ju Lee[1], Thuy-Linh Pham[2], Jong-Sook Lee[2], and Wook Jo[1+]

Abstract

Dielectric capacitors are integral components in electronic devices that protect the electric circuit by providing modulated steady voltage. Explosive growth of the electric automobile market has resulted in an increasing demand for dielectric capacitors that can operate at temperatures as high as 400 °C. To surpass the operation temperature limit of currently available commercial capacitors that operate in temperatures up to 125 °C, $Bi_{1/2}Na_{1/2}TiO_3$ (BNT), which has a large temperature-insensitive dielectric response with a maximum dielectric permittivity temperature of 300 °C, was selected. By introducing an intentional A-site cation deficiency and post-heat treatment, we successfully manage to control the dielectric properties of BNT to use it for high-temperature applications. The key feature of this new BNT is remarkable reduction in dielectric loss (0.36 to 0.018) at high temperature (300 °C). Structural, dielectric, and electrical properties of this newly developed BNT were systematically investigated to understand the underlying mechanism.

Keywords: High-temperature dielectrics, Relaxor ferroelectrics, BNT, dielectric loss

1. INTRODUCTION

Every electronic device with an electric circuit employs a dielectric capacitor, which is an integral component in devices as it provides modulated steady voltage to the circuit. Nowadays, the importance of improving the functional properties of electric components such as the capacitor has been acknowledged, and it has received considerable research attention owing to the explosive growth of the electric automobile market [1]. As the electronic parts in an automobile increase and the power semiconductors that emit more heat using higher voltages for power are adopted, electric circuits will continue to be operated under higher temperature [2-3]. This has led to an increase in the demand for dielectric capacitors that can operate even at temperatures as high as 400 °C.

The currently market dominating $BaTiO_3$ (BT) based multilayer ceramic capacitors (MLCC), called X7R according to the electronic industries alliance (EIA) class-II dielectric nomenclature, can only cover a temperature range from −55 °C to 125 °C. Therefore, there is an increasing need for developing non-BT based high-temperature dielectric materials that can replace X7R and operate at temperatures at least over 200 °C [4-5]. Yet, appropriate high-temperature dielectric materials, which have a stable relative permittivity (ε_r), i.e., $100\Delta\varepsilon/\varepsilon_{RT} = \pm 15\%$(ε: dielectric permittivity RT: room temperature), and a low dielectric loss of tan δ < 0.02 over a broad temperature range have not been developed even after both extensive and intensive efforts by many researchers. Although some dielectric materials satisfy a thermally stable dielectric permittivity, they are difficult to commercialize because they contain rare earth elements or have a fairly high dielectric loss at high temperatures [6-7].

$Bi_{1/2}Na_{1/2}TiO_3$ (BNT) is a candidate material for replacing BT in high-temperature dielectric applications as it has a high maximum dielectric temperature (T_m) of ~300 °C, and it has a broad dielectric permittivity maxima as a relaxor ferroelectric [8] in contrast to the general ferroelectrics that have a sharp peak at the phase transition temperature (i.e., Curie temperature, T_c). In the case of ferroelectric BT, it has its T_c at about 120 °C that sets the upper temperature limit for the operation of the commercial capacitors. In this sense, BNT is a highly potential candidate for developing a high-temperature dielectric that can replace the current commercial capacitors, as long as its electrical properties

[1]School of Materials Science and Engineering & Julich-UNIST Joint Leading Institute for Advanced Energy Research, Ulsan National Institute of Science and Technology, Ulsan 44919, Korea
[2]School of Materials Science and Engineering, Chonnam National Universitiy, Gwangju 500-757, Korea
[+]Corresponding author: wookjo@unist.ac.kr
(Received : Jan. 14. 2020, Revised : Jan. 30, 2020, Accepted : Jan. 30, 2020)

are properly adjusted. In particular, BNT suffers from a large variation between $\varepsilon_{r,\max}$ (ε_r at the maximum dielectric temperature) and ε_{RT}, and an excessively high dielectric loss at high temperatures above 200 °C. As indicated by early work [9], the dielectric permittivity flattens and the exponentially increasing dielectric loss can be notably suppressed in the presence of Na deficiency with little change in the maximum dielectric permittivity temperature. This implies that the defect chemistry may be key to modifying the high-temperature dielectric properties of BNT ceramics.

To explore this possibility, we prepared a series of Na-deficient BNT ceramics with different deficiency levels, and then, we thermally annealed these ceramics at different temperatures for extended times, expecting to tune the defect configuration. We show the presence of a critical annealing temperature that influences dielectric property in BNT. The conduction mechanism of Na deficiency and the effect of post-heat treatment will be discussed with supporting experimental data.

2. EXPERIMENTAL

The conventional solid solution method was used to prepare BNT ceramics samples. Dried raw powders, Bi_2O_3 (99.9%, Sigma Aldrich), Na_2CO_3 (99%, Sigma Aldrich), and TiO_2 (99%, Sigma Aldrich) were mixed by ball-milling for 24 h in ethanol according to the formula of $Bi_{1/2}Na_{1/2-x}TiO_3$ (x = 0, 0.02, 0.04, 0.06; BNTa, a = 100x, representing the level of deficiency, e.g., BNT4 for $Bi_{1/2}Na_{1/2-0.04}TiO_3$). The mixed powders were calcined at 850 °C for 2 h in an alumina crucible. The calcined powder underwent a second ball-milling. Then, the powder was mixed with polyvinyl alcohol (PVA) as a binder with 5 wt%, sieved with a 150 μm mesh before being pressed into pellets of 12 mm in the diameter under 180 MPa. These samples were heat-treated at 550 °C for 2 h for a binder burnout and then sintered in air at 1150 °C for 2 h, as samples were covered with the same composition powder to minimize the volatilization of bismuth. After sintering, BNTa samples were thermally annealed at 500, 600, and 700 °C for 24 h (BNTa-tA, t: annealing temperature, e.g., BNT4-700A for BNT4 annealed at 700 °C) and then furnace cooled.

Room temperature X-ray powder diffraction data were collected using a powder X-ray diffractometer (D8 ADVANCE, Bruker AXS, Billerica, Massachusetts, USA) using Cu-Kα radiation, on the samples sintered, crushed, and thermally annealed at 400 °C for excluding the strain effect. For the microstructure observation, scanning electron microscopy (SEM, Quanta 200 FEG, FEI company, Hillsboro, USA) was used on thermally etched and polished samples with Pt sputtering. The temperature- and frequency-dependent dielectric permittivity, dielectric loss, and impedance were measured on disk-shaped, poled samples covered with Ag paste as an electrode after a burn-in treatment at 600 °C for 30 min, using an impedance analyzer (HP 4192A, Hewlett-Packard Company, Palo Alto, CA) in conjunction with a customized sample holder. Poling was carried out at room temperature in silicone oil by applying unipolar electric field cycle at 6 kV/mm three times on samples of 1 mm thickness. Electric-field-induced properties such as polarization field (P–E), strain field (S–E) hysteresis loops, and the associated switching current (I–V) behavior were measured with a piezoelectric measurement system (aixACCT aixPES, Aachen, Germany).

3. RESULTS AND DISCUSSIONS

Fig. 1 displays the XRD profiles which reveal that all compositions except for BNT6 are phase-pure within the resolution limit of the XRD apparatus employed. The presence of a superlattice reflection ½(311) and the splitting of $(111)_{pc}$ (the subscripts "pc" denotes a pseudo-cubic index) suggests that BNT0 conforms well with the known R3c rhombohedral structure [10]. With an increasing deficiency level, the intensity of the ½(311) superlattice reflection tends to be weakened with the splitting of $(111)_{pc}$ disappearing. This implies that the coherence length of rhombohedral distortion tends to be smaller with the increasing deficiency level. The crystallinity is observed to increase as indicated by the decrease in the full width at half maximum (FWHM) of $(200)_{pc}$ reflection from 0.16 at BNT0 to 0.14 at BNT4. Meanwhile, the increasing deficiency level shifts the

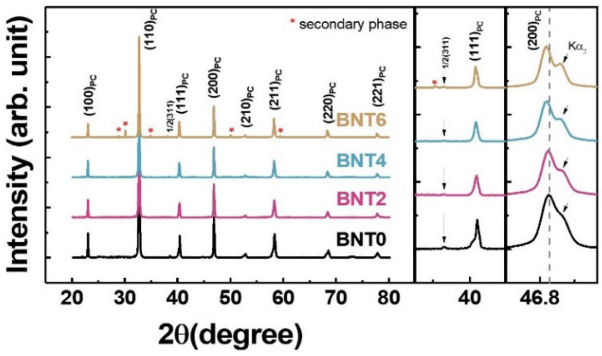

Fig. 1. X-ray diffraction data of BNT as a function of deficiency level.

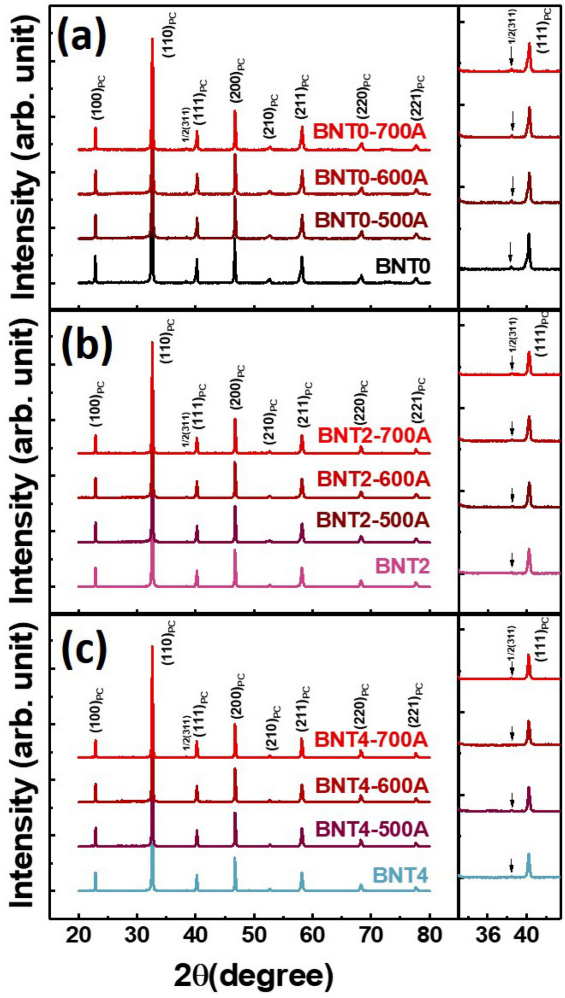

Fig. 2. X-ray diffraction data of (a)BNT0, (b)BNT2, and (c)BNT4 as function of annealing temperature

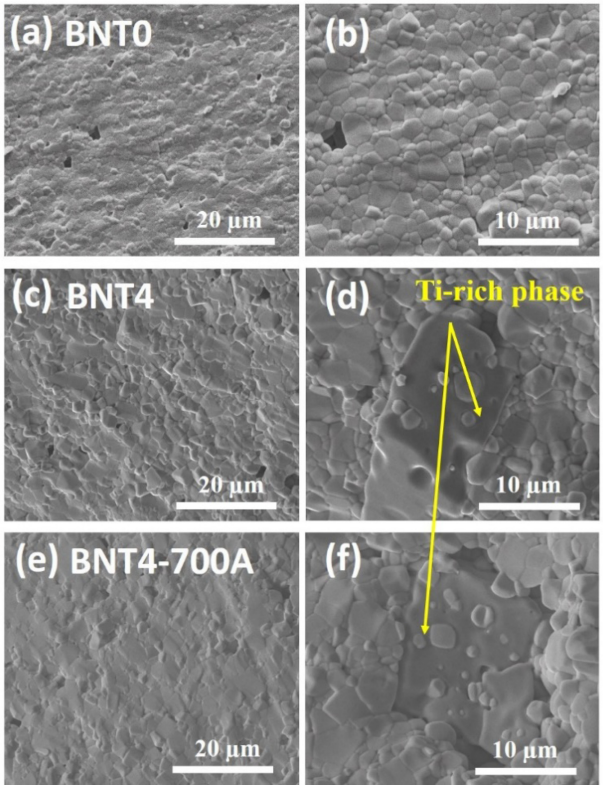

Fig. 3. Scanning electron microscopy images of (a) & (b) BNT0, (c) & (d) BNT4, and (e) & (f) BNT4-700A.

$(200)_{pc}$ peak gradually towards lower angles, reflecting the fact that the intentionally introduced deficiency is correlated with the formation of vacancies.

Fig. 2 represents the XRD data of the BNTa system as a function of annealing temperature from 500-700 °C. There is no significant difference between BNT0 and BNT0-700A, whereas, the FWHM of $(200)_{pc}$ slightly decreases from 0.14 at BNT4 to 0.12 at BNT4-700A. All compositions annealed at both 500 °C and 600 °C have no difference from the non-annealed BNTa. This means that annealing at temperatures below 700 °C does not influence the structure and crystallinity of BNTa.

The microstructures of BNT0, BNT4, and BNT4-700A presented in Fig. 3(a)-(f) revealed that the average grain sizes of BNT0, BNT4, and BNT4-700A are 1.2 μm, 1.4 μm, and 1.5 μm, respectively. It is noted that the enforced introduction of Na deficiency results in the formation of a Ti-rich secondary phase as consistent with the previous report [11], although it was not detected in the XRD analysis. On the other hand, there is no noticeable difference between BNT4 and BNT4-700A, which implies the post-heat treatment does not affect the microstructure of the BNTa system even after annealing at 700 °C. Nevertheless, the post-heat treatment at 700 °C influences the dielectric properties in the BNTa system significantly, as depicted in Fig. 4.

As noted, BNT is a non-ergodic relaxor ferroelectric material that remains at the induced ferroelectric state after being converted into a ferroelectric state by the application of the electric field, i.e., an irreversible electric field-induced phase transformation [12]. The induced ferroelectric state returns to the initial relaxor state with the induced long-range ferroelectric domains breaking down into polar nanoregions (PNRs) at and above the ferroelectric-to-relaxor phase transition temperature (T_{F-R}), which is located at ~200 °C in the case of BNT. Above the T_{F-R} appear the relaxor properties, representatively, the strong frequency-dependent dispersion in dielectric permittivity, and the dielectric loss. BNT has the maximum dielectric permittivity temperature (T_m) at ~330 °C, which is unusually high among the well-known relaxor ferroelectrics, e.g., $Pb(Mg_{1/3}Nb_{2/3})O_3$, the T_m for which is below 0 °C. Such high T_m inherent to BNT is highly advantageous for high-temperature dielectric applications owing to the broad and

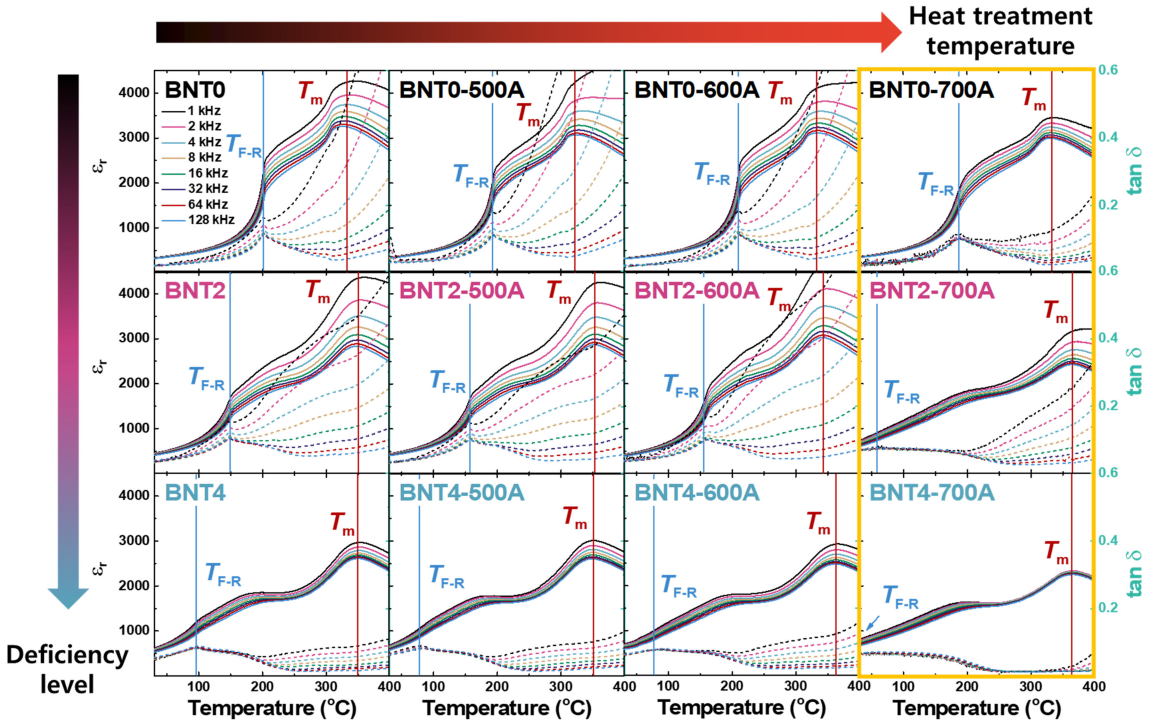

Fig. 4. Temperature dependent dielectric permittivity and dielectric loss of all poled compositions as function of heat treatment temperature. Note that the solid and the broken line refer to the dielectric permittivity and the loss, respectively.

relatively flat dielectric response about T_m. With these advantages, the dielectric properties of BNT still need to be enhanced further to meet the requirements for high-temperature dielectric applications as the disparity between the dielectric permittivity at room temperature and that at the maximum dielectric permittivity is still too large, and the dielectric loss increases exponentially at about 200 °C.

To improve the dielectric properties in BNT, we first utilized a defect chemistry through Na deficiency based on our earlier work [9], and we then applied the post-heat treatment expecting to stabilize the temperature dependence of dielectric properties. A significant influence of non-stoichiometry in BNT has been recognized as a new family of ion conductors and high-temperature dielectrics [13]. In particular, the Na deficiency makes the dielectric permittivity temperature-insensitive, i.e., thermally stable, and the dielectric loss suppressed with increasing resistivity [11]. The tendency that dielectric permittivity is stabilized over a broad temperature range as the deficiency level increases is depicted in Fig. 4. The temperature regime between T_{F-R} and T_m stretches by increasing the deficiency level as T_{F-R} shifts to lower temperatures, e.g., from 200 °C for BNT0 to 95 °C for BNT4. In addition, the problematic dielectric loss is suppressed from ~0.36 for BNT0 to ~0.1 for BNT4, although the dielectric loss is still high in BNT4 even with the maximum Na deficiency level. It is commonly claimed that the dielectric loss at such high temperature is correlated with oxygen vacancies as the major charge carrier [14-16]. Therefore, we applied thermal annealing at various temperatures to reduce oxygen vacancies by re-oxidation. Fig. 4 presents the critical annealing temperature that can influence the dielectric properties of BNT dramatically. The thermally stable dielectric permittivity and considerably lower dielectric loss compared to that of pristine BNT appears from BNTa-700A, whereas both BNTa-500A and BNTa-600A show little difference from BNTa. Annealing at 700 °C for 24 h is effective in making BNT achieve high-temperature dielectric properties with a similar tendency but a better outcome in comparison to the effect of Na deficiency. In particular, the suppression of the dielectric loss is evident in BNTa-700A. Further, BNT4-700A with the maximum Na deficiency and post-heat treated at the critical temperature has the best high-temperature dielectric properties with highly suppressed dielectric loss up to ~0.018 at 300 °C and 1 kHz.

The influences of deficiency and annealing are best observed in the temperature-dependent dielectric properties of un-poled samples (Fig. 5). There is an abnormal dielectric relaxation (ADR) in dielectric loss in the temperature range between 200-300 °C denoted by the black arrow in Fig. 5. Given that the dielectric properties in BNT are sensitive to the oxidizing atmosphere or

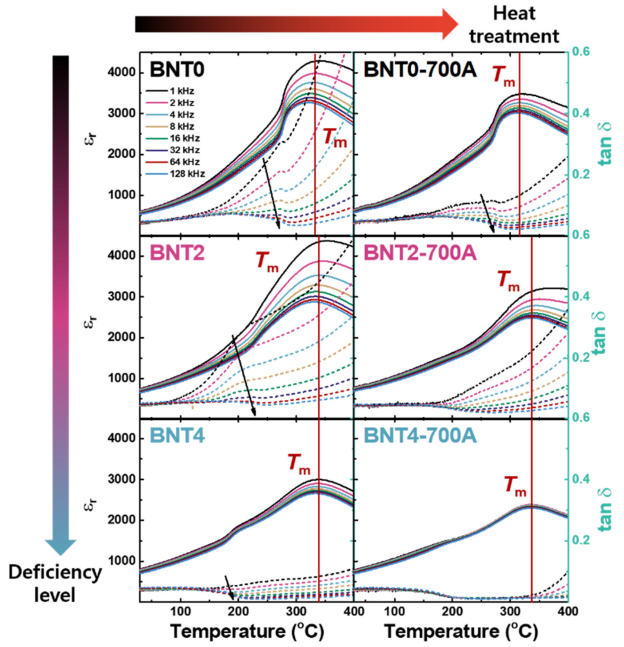

Fig. 5. Temperature-dependent dielectric permittivity and dielectric loss of unpoled BNTa and BNTa-700A. The blue lines are tangent lines of dielectric loss at 1 kHz, 350°C. Note that the solid and the broken line refer to the dielectric permittivity and the loss, respectively.

reducing atmosphere during sintering, the ADR is related to oxygen vacancies ($V_O^{\bullet\bullet}$)[17]. The temperature, where ADR relaxation appears, is shifted to lower temperatures and the peak of ADR is broadened as the deficiency level increases. In this case, the Na deficiency suppressed this relaxation by making immobile defect complexes made of V'_{Na} and $V_O^{\bullet\bullet}$ such as $V'_{Na}-V_O^{\bullet\bullet}-V'_{Na}$, as shown below.

$$2Na_{Na}^{\times}+O_O^{\times} \leftrightarrow 2V'_{Na}+V_O^{\bullet\bullet}+Na_2O \quad (1)$$

In other words, Na deficiency reduces the concentration of mobile ($V_O^{\bullet\bullet}$)[18]. Interestingly, ADR is almost reduced by annealing. The intensity of ADR in BNT0-700A is weaker than that in BNT0 and it becomes so broadened that the ADR peak disappears in BNT2-700A. The composition which has the maximum deficiency level and post-heat treatment, i.e., BNT4-700A, has the best dielectric property. Not only is the problematic dielectric loss at the high-temperature region eliminated, but the degree of frequency dispersion in the dielectric permittivity is also decreased. Thus, post-heat treatment tends to be similar with the Na deficiency effect, but it more effectively influences dielectric properties.

To investigate the mechanism of suppressing the ADR in the temperature range between 200 °C and 300 °C, we focused on the

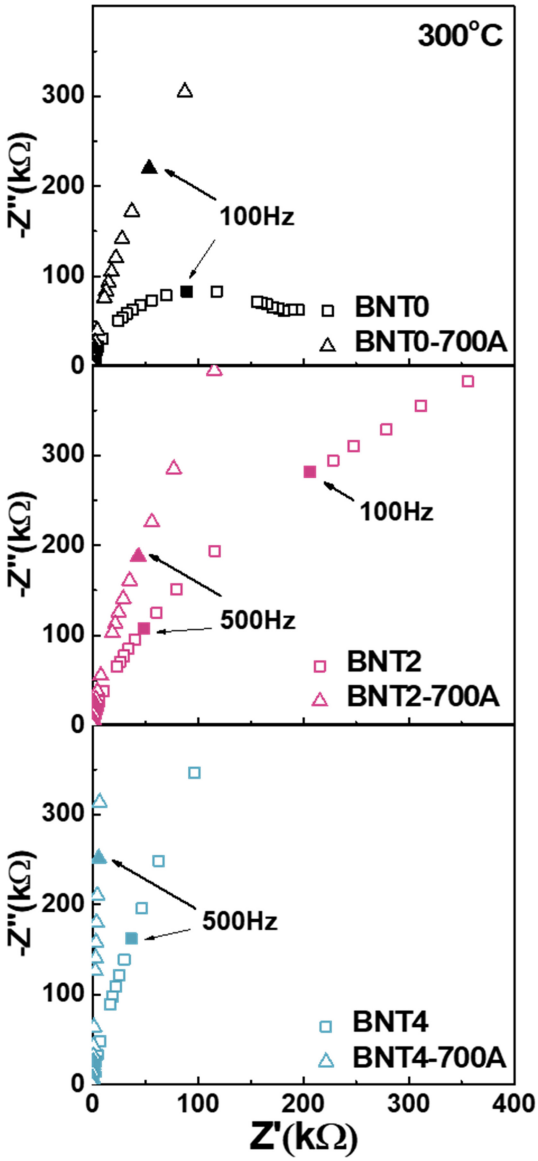

Fig. 6. Z^* plots of BNTa and BNTa-700A at 300°C, frequency range is 10Hz ~ 10MHz. filled symbols indicate particular frequencies.

impedance spectra obtained at 300 °C (Fig. 6). The increase in the Na deficiency level results in an exponential increase in the representing bulk resistivity (ρ_b) in BNTa. The increasing resistivity in the presence of Na deficiency supports the effect of defect complexes as they make oxygen vacancies immobile.

The post-heat treatment also insulates BNT, as all compositions of BNTa-700A have a larger semicircle than BNTa. There are several estimated mechanisms that increases ρ_b by annealing, e.g., making $V_O^{\bullet\bullet}$ immobile by the rearrangement of vacancies or reducing $V_O^{\bullet\bullet}$ concentration by the re-oxidation of vacancies. Further investigations are required to gain a better understanding of the mechanism behind increasing ρ_b by annealing.

4. CONCLUSIONS

We investigated the influences of Na deficiency and post heat treatment at various temperatures on the dielectric properties of $Bi_{1/2}Na_{1/2}TiO_3$ (BNT). As the Na cation deficiency increases up to 4 mol%, good high-temperature dielectric properties are observed with a plateau dielectric permittivity and low dielectric loss by rising a bulk resistivity in BNT. Post-heat treatment at 700 °C for 24 h influences the dielectric properties significantly whereas the other annealing conditions below the 700 °C do not change any properties. BNT4-700A had the best high-temperature dielectric property with a thermally stable dielectric permittivity that reduces $100\Delta\varepsilon/\varepsilon_{RT}$ from 590% to 200%. Moreover, the problematic dielectric loss factor at high temperature was suppressed to ~0.018 at 300 °C, 1 kHz, while pristine BNT had a high dielectric loss ~0.36 in same temperature range and frequency.

These two methods improve the high-temperature dielectric properties by suppressing the abnormal dielectric relaxation (ADR), which is related to oxygen vacancy; however, the exact mechanism of annealing is unclear. In conclusion, the combination of Na deficiency and post-heat treatment creates synergetic effects for the improvement of the high-temperature dielectric property with thermally stable dielectric permittivity and suppressed dielectric loss at high temperature. Yet, the high temperature dielectric properties of deficient and annealed BNT are not suitable for replacing a commercial dielectric capacitor, and the effects of deficiency and heat treatment provide opportunities for controlling dielectric properties in a direction suitable for high temperature dielectric applications. Further investigations are in progress to develop new high-temperature dielectric materials and determine the suppressing ADR mechanism of annealing.

ACKNOWLEDGMENT

This research was supported by the Leading Foreign Research Institute Recruitment Program (2017K1A4A3015437) and by the Engineering Research Center of Excellence Program (2018R1A5A1025224) through the National Research Foundation of Korea (NRF) funded by the Ministry of Science and ICT (MSIP).

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