

EFFECTS OF BiNbO₄ AND Nb₂O₅ ADDITIONS ON THE TEMPERATURE STABILITY OF MODIFIED BaTiO₃

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High-temperature capacitor materials were prepared in a BaTiO₃ (BT)-Bi_{0.5}Na_{0.5}TiO₃ (BNT)-BiNbO₄ (BN)-Nb₂O₅ system. The effects of BN and Nb₂O₅ on the dielectric properties and microstructure of 5 mol% BNT-doped BT ceramics were investigated. The dielectric constant peak at T_C was suppressed with the addition of BN, whereas an enhancement in the dielectric constant at lower temperatures was observed. In the case of 3 mol% BN addition, the temperature characteristic of capacitance satisfied the EIA X8R specification (-55 to 150°C, $\Delta C/C_{25^\circ\text{C}}$ less than $\pm 15\%$). Scanning electron microscope and X-ray diffraction analyses suggested that a small amount of secondary phases existed in all the samples and the proportion of the secondary phases decreased with the addition of BN. When Nb₂O₅ was added to BT-BNT-BN ceramics, the dielectric constant at higher temperatures was markedly enhanced with an increase in Nb₂O₅ content. Therefore, the high-temperature specification (-55 to 200°C, $\Delta C/C_{25^\circ\text{C}}$ less than $\pm 15\%$) is met when 3 mol% BN and 4 mol% Nb₂O₅ was added to 5 mol% BNT-doped BT ceramics, with a dielectric constant greater than 1200 and a dielectric loss lower than 1.5 %.

INTRODUCTION

Multilayer ceramic capacitors (MLCCs) have been widely used in automotive electronic parts, such as engine control unit (ECU), anti-lock brake system (ABS) and programmed fuel injection (PGMFI). MLCCs in these modules must keep their performance under high temperatures approximately above 130°C. Therefore, X8R capacitors have been developed rapidly (X8R: -55 to 150°C, $\Delta C/C_{25^\circ\text{C}}$ less than $\pm 15\%$) [1-3]. Recently, MLCCs have come into use at much higher temperatures, such as oil drilling and aerospace application. Therefore, there is in great need to develop high-temperature ceramic capacitors, which exhibit stable temperature characteristic (TC) over a wide temperature range.

Most conventional X8R capacitors are based on BaTiO₃ (BT) because of its high dielectric constant and environmental friendship. However, it is difficult to achieve high-temperature stability for BT, since the Curie temperature (T_C) of pure BT is close to 130°C and a rapid drop of capacitance happens above T_C . It has been proposed to shift T_C to higher temperatures to solve this problem, by adding Bi_{0.5}Na_{0.5}TiO₃ (BNT) [4], Bi_{0.5}K_{0.5}TiO₃ (BKT) [5], Bi₄Ti₃O₁₂ (BIT) [6] or rare earth elements with smaller ionic radii (e.g. Er, Yb, Lu) [1,

2]. BNT is an attractive lead-free piezoelectric material with a perovskite structure and a relatively high T_C of 320°C [7]. In our previous work, the Curie temperature of BT can be raised by doping BNT [4]. When 5 mol% BNT was added to BT (0.95BT-0.05BNT, abbreviated to BTBNT5), T_C was increased to 145°C. This change is favorable for us to improve the high-temperature stability of BT ceramics.

Bismuth-based dielectric ceramics are well known as low-fired materials and have been widely used as multilayer ceramic capacitors or piezoelectric materials [8, 9]. The microwave dielectric properties of BiNbO₄ (BN) ceramics were first reported by Kagata and his co-workers [10]. As a candidate for low-temperature sintering microwave materials, BN has been widely investigated. However, its application in the preparation of temperature-stable capacitors is seldom reported. A dielectric material satisfying the X8R specification was synthesized in BT-BNT system using BN as a modifier [3]. In the present work, high-temperature dielectrics have been developed based on BTBNT5 by adding BN and Nb₂O₅, which satisfies the high-temperature specification: -55 to 200°C, $\Delta C/C_{25^\circ\text{C}}$ less than $\pm 15\%$. The effects of BN and Nb₂O₅ dopants on the temperature characteristic and microstructure were discussed.

EXPERIMENTAL PROCEDURE

BNT and BN powders were individually synthesized by the conventional solid-state method from reagent-grade oxide powders: Bi_2O_3 , TiO_2 , Na_2CO_3 and Nb_2O_5 . The starting materials were mixed and ball-milled in ethylalcohol for 12 h with stabilized zirconia balls. Both mixtures were dried and calcined at 800°C for 2 h. Powders of hydrothermal BT ($\sim 0.4 \mu\text{m}$) and 5 mol% BNT were mixed in deionized water by ball milling and then calcined at 1150°C for 2 h. Samples with the following chemical compositions were prepared.

BTBNT5 + x mol% BiNbO_4 , [x = 0.5, 1.0, 2.0, 3.0].

BTBNT5 + 3 mol% BiNbO_4 + y mol% Nb_2O_5 , [y = 0.5, 1.0, 2.0, 4.0].

The powders of BTBNT5, BN and Nb_2O_5 were weighed and mixed in deionized water with stabilized zirconia balls by ball milling for 6 h. Then the mixture was dried and sieved. The prepared ceramic powders with 3 wt % PVA binder were pressed into pellets with dimensions of 10 mm in diameter and 1 mm in thickness. After debinding, the pellets were finally fired at 1150°C for 2 h in air.

The surface microstructure of sintered ceramics was observed with scanning electronic microscope (SEM). X-ray diffraction (XRD) analysis was carried out using a Philips X'pert diffractometer over the 2θ range of 20 to 80° with CuK_α radiation. After samples were fired at 700°C with silver paste on both sides, the dielectric properties were measured at 1 kHz with an LCR meter (HP 4192A) at temperatures ranging from -55 to 200°C .

RESULTS AND DISCUSSION

Figure 1 shows the temperature dependence of the dielectric constants of samples sintered at 1150°C for 2 h with the addition of 0.5–3 mol% BN. The

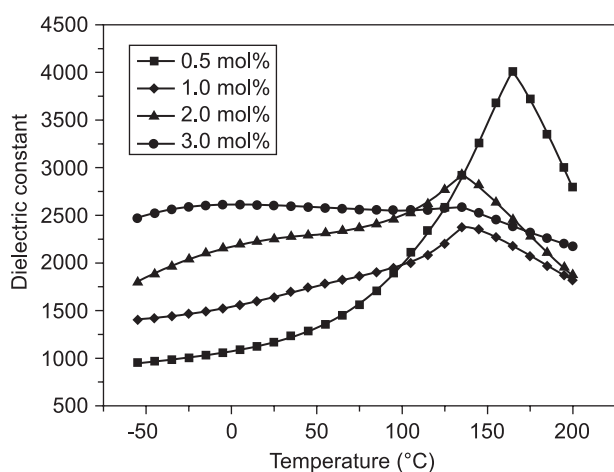


Figure 1. Temperature dependence of the dielectric constants of 0.95BT-0.05BT-xmol%BN ceramics as a function of BN content.

Curie temperature of BTBNT5 was raised to 165°C by adding 0.5 mol% BN, then decreased to 135°C with further additions. With 0.5 mol% BN addition, the sample shows the typical temperature dependence of dielectric constant at T_c as pure BT. As the amount of BN increased, the dielectric constant peak at T_c was suppressed. On the contrary, the dielectric constant was markedly enhanced at lower temperatures. D. Hennings has suggested that a core-shell structure with chemical inhomogeneity is formed by adding BN to BT, due to the low diffusion rate of Nb^{5+} [11]. The dielectric constant peak at T_c is correlated with the ferroelectric-paraelectric phase transition of the cores, and the broad dielectric constant at lower temperature is associated with the phase transition of the shells. The volume fraction of shells increased with increasing BN content so that a distinct enhancement in the dielectric constant at lower temperatures was observed. The ceramic doped with 3 mol% BN exhibits the highest dielectric constant at room temperature.

According to ionic radii [12], Bi^{3+} (1.32 \AA , 12 coordinate) could be dissolved in the Ba sites and Nb^{5+} (0.64 \AA , 6 coordinate) would occupy the Ti sites of BT. It should be noted that Bi^{3+} has a smaller ionic radius than Ba^{2+} (1.61 \AA , 12 coordinate), whereas Nb^{5+} has a larger ionic radius than Ti^{4+} (0.605 \AA , 6 coordinate). The substitution of small Bi^{3+} ions for large Ba^{2+} ions would decrease the cell size, leading to shrink of TiO_6 oxygen octahedral. Accordingly, it is more difficult for the center Ti^{4+} ions to move by introducing smaller ions to the Ba sites. It is well accepted that the ferroelectricity of BT originates from the uniform direction of Ti–O dipoles. Therefore, the ferroelectricity of local BT would be significantly weakened, even disappeared, when smaller ions occupy the Ba sites. In the same way, the replacement of large Nb^{5+} to Ti^{4+} ions also decreases the spontaneous polarization of BT. Accordingly, the dielectric constant at T_c was reduced by the addition of BN dopant.

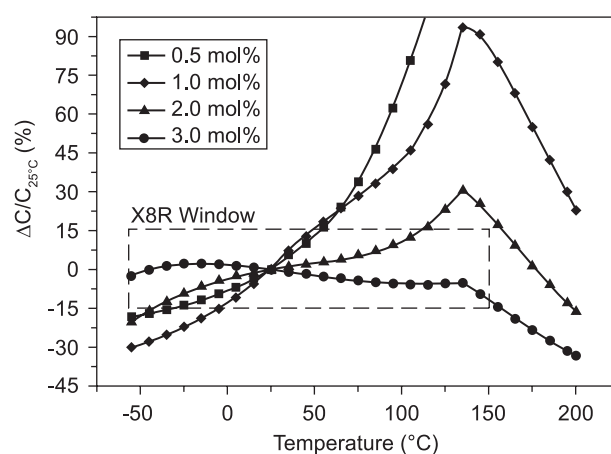


Figure 2. Temperature dependence of $\Delta C/C_{25^\circ\text{C}}$ for 0.95BT-0.05BT-xmol%BN ceramics as a function of BN content.

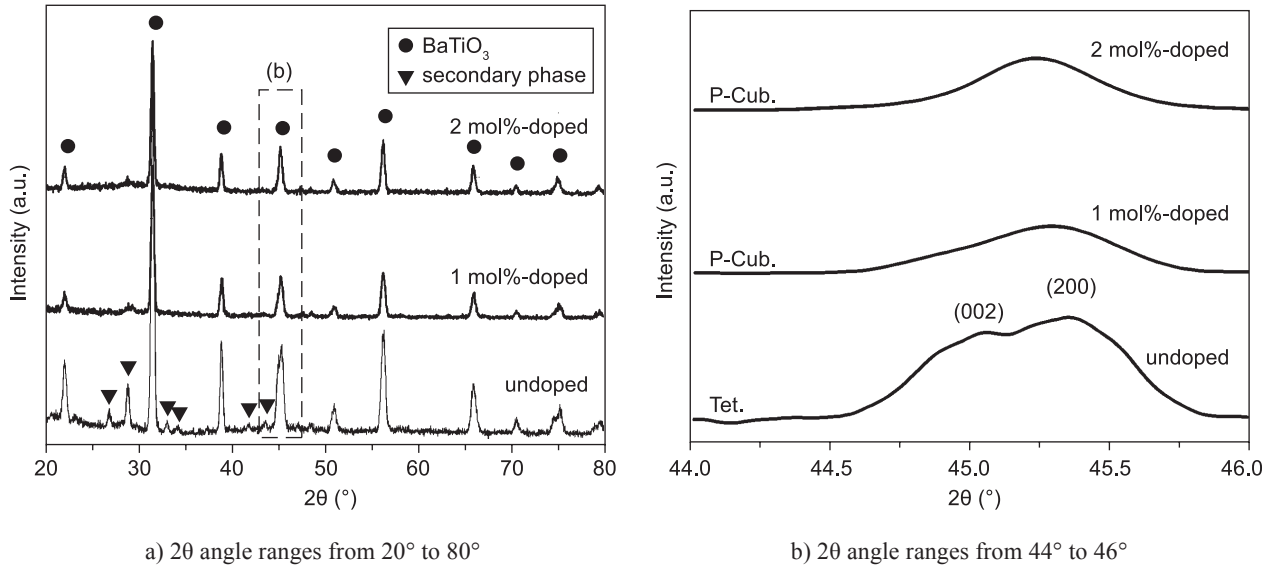
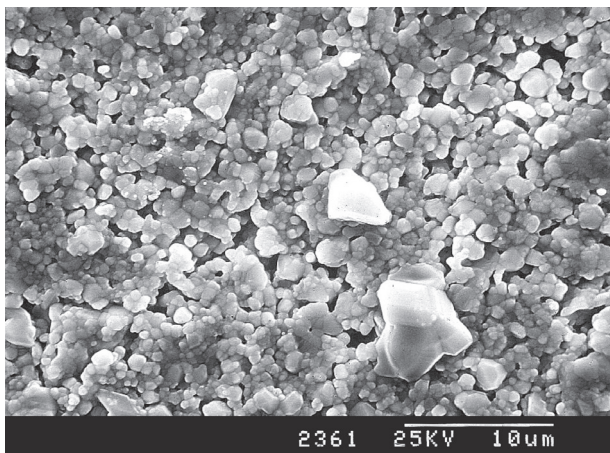
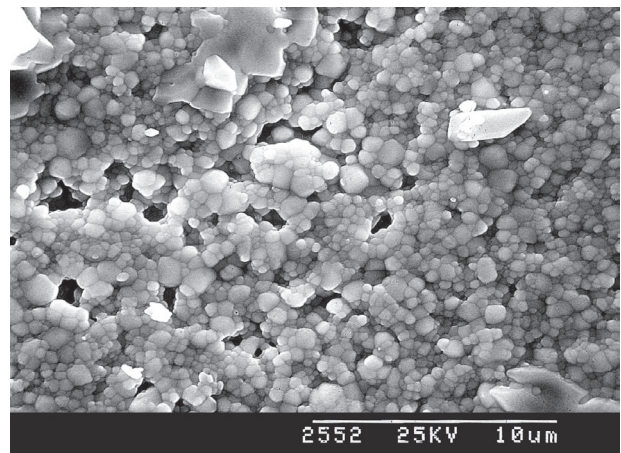


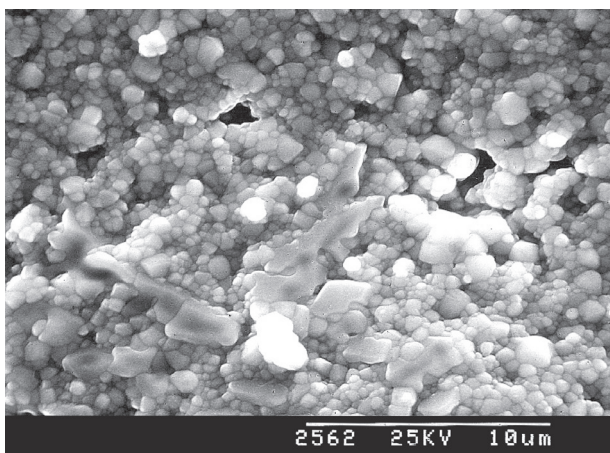
Figure 3. X-ray diffractograms of 0.95BT-0.05BNT-xmol%BN ceramics with various amounts of BN sintered at 1150°C for 2 h.



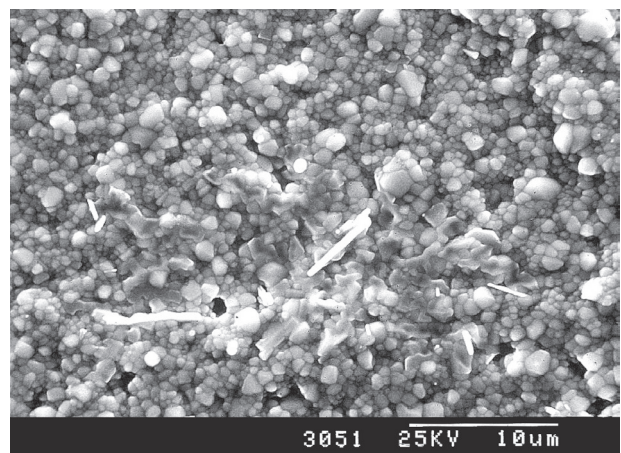
a) BN - 0.5 mol%



b) BN 1.0 mol%



c) 2.0 mol%



d) 3.0 mol%

Figure 4. SEM micrographs of 0.95BT-0.05BNT-xmol%BN ceramics with various amounts of BN.

Figure 2 shows the temperature coefficient of capacitance (TCC) curves for BN-doped ceramics sintered at 1150°C for 2 h. The variation of capacitance decreased with proper amounts of BN addition. The specimen doped with 3 mol % BN can satisfy the X8R specification, which is surrounded by a bold line of rectangular shape as shown in Figure 2. However, all the samples can not satisfy the high-temperature specification.

Figure 3 shows the dependence of XRD patterns for BTBNT5-BN system ceramics with an increase in BN content. Figure 3a revealed that all the samples were mainly composed of BT. Diffraction peaks that corresponded to some secondary phases were observed for the BTBNT5 ceramic without BN. However, the intensity of the diffraction peaks corresponding to these secondary phases decreased with the addition of BN. Moreover, a transformation in the crystal phase from tetragonal to pseudo-cubic was observed by adding BN, indicated by the combination of (002) and (200) diffraction peaks, as shown in Figure 3b.

SEM micrographs for the BTBNT5-BN system ceramics with various amounts of BN (0.5 ~ 3 mol%) sintered at 1150°C are revealed in Figure 4. Fine matrix grains and a small amount of secondary phase grains were observed for all the samples. It was also can be seen that pores were decreased as increasing BN content, due to the sintering aid of low-fired BN.

As shown in Figure 1, the dielectric constant at higher temperatures was depressed by adding BN dopant, whereas the dielectric constant at lower temperatures was raised remarkably. With 3 mol% BN addition, the TCC was improved greatly and the EIA X8R specification was met, as shown in Figure 2. However, the variation of the dielectric constant exceeded -15 % above 150°C . At 200°C , the variation of the dielectric constant was around -33 %. Therefore, this material must be modi-

fied before it can be used in stable high-temperature capacitors. As a grain-growth inhibitor, niobium oxide has been widely used in fabrication of dielectrics with stable TC over a wide temperature range, such as BT- Nb_2O_5 - Co_2O_3 [13] and BT- Nb_2O_5 -ZnO [14] system. Our research also indicated that Nb_2O_5 can effectively improve the TCC for BN-doped BTBNT5 ceramics.

Figure 5 shows the temperature dependence of the dielectric constants of 3 mol% BN-doped BTBNT5 ceramics with various Nb_2O_5 contents. As shown in Figure 5, all the samples exhibited a dielectric constant peak at T_c and a broad peak at lower temperatures. The dielectric constant within the temperature range from room temperature to 200°C was raised with an increase in Nb_2O_5 content. Moreover, the amount of Nb_2O_5 had little influence on the dielectric constant below room temperature. For the pure BTBNT5 ceramic, the dielectric loss was 2.8%. The dielectric loss was decreased to 1.5% when 3 mol% BN was added, and 1.3% by further adding 4 mol% Nb_2O_5 .

Figure 6 shows the TCC curves of 3 mol% BN-doped BTBNT5 ceramics with various Nb_2O_5 contents. The variation of capacitance at higher temperatures was decreased by the increase of Nb_2O_5 content. With an addition of 4 mol% Nb_2O_5 , the high-temperature specification (-55 to 200°C , $\Delta C/C_{25^\circ\text{C}}$ less than $\pm 15\%$) was satisfied, which is surrounded by a bold line of rectangular shape as shown in Figure 6.

CONCLUSION

In the present report, dielectric properties and microstructures of BT-BNT-BN- Nb_2O_5 system ceramics have been studied. The Curie temperature of BTBNT5 was increased to 165°C by adding 0.5 mol% BN, and then decreased to 135°C with further additions. The

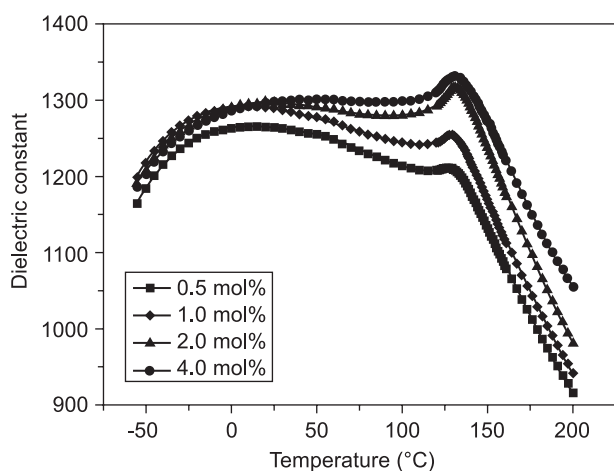


Figure 5. Temperature dependence of the dielectric constants of 0.95BT-0.05BNT-3mol%BN ceramics doped with various Nb_2O_5 contents.

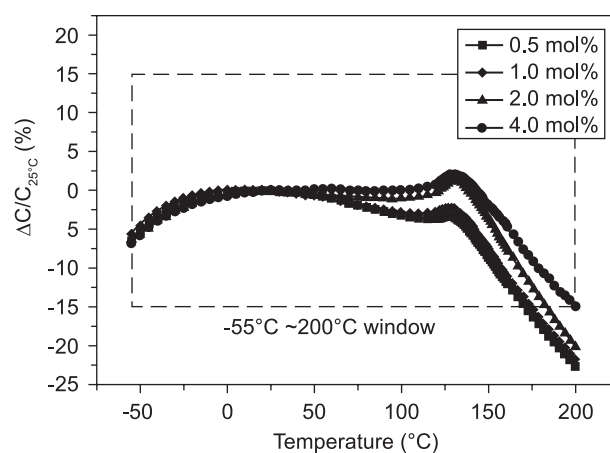


Figure 6. Temperature dependence of $\Delta C/C_{25^\circ\text{C}}$ of 0.95BT-0.05BNT-3mol%BN ceramics doped with various Nb_2O_5 contents.

addition of BN suppressed the dielectric constant at T_c and increased the dielectric constant at lower temperatures. The TCC curve satisfied the X8R requirements with 3 mol% BN. XRD and SEM analyses proved that a small amount of secondary phase grains occurred in all the samples. In addition, the fraction of the secondary phase was decreased by doping BN. Nb_2O_5 doping can greatly improve the TCC for BN-doped BTBNT5 ceramics. With 3 mol% BN and 4 mol% Nb_2O_5 , the sample exhibited a dielectric constant greater than 1200 and a dielectric loss lower than 1.5% with flat temperature coefficients of capacitance ($\Delta C/C_{25^\circ C} \leq \pm 15\%$) over the temperature range from $-55^\circ C$ to $200^\circ C$. Therefore, this novel system is a promising material for high-temperature capacitor applications.

References

1. Jung Y. S., Na E. S., Paik U.: *Mater. Res. Bull.* **37**, 1633 (2002).
2. Song Y.H., Han Y. H.: *Jpn. J. Appl. Phys.* **44**, 6143 (2005).
3. Yuan Y., Du M., Zhang S. R.: *J. Mater. Sci.: Mater. Electron.* **20**, 157 (2009).
4. Yuan Y., Zhang S. R., Zhou X. H.: *J. Electron. Mater.* **38**, 706 (2009).
5. Hiruma Y., Aoyagi R., Nagata H.: *Jpn. J. Appl. Phys.* **43**, 7556 (2004).
6. Jain T. A., Chen C. C., Fung K. Z.: *J. Eur. Ceram. Soc.* **29**, 2595 (2009).
7. Smolenskii G. A., Isupo V. A., Agranovskaya A. I.: *Sov. Phys. Solid State* **2**, 2651 (1961).
8. Liu D., Liu Y., Huang S. Q.: *J. Am. Ceram. Soc.* **76**, 2129 (1993).
9. Choy J. H., Han Y. S., Sohn J. H.: *J. Am. Ceram. Soc.* **78**, 1169 (1995).
10. Kagata H., Inoue Y., Kato J.: *Jpn. J. Appl. Phys.* **31**, 3152 (1992).
11. Hennings D., Rosenstein G.: *J. Am. Ceram. Soc.* **67**, 249 (1984).
12. Shannon R. D.: *Acta Crystallogr* **A32**, 751 (1976).
13. Chazono H., Kishi H.: *J. Am. Ceram. Soc.* **82**, 2689 (1999).
14. Du M., Li Y. R., Yuan Y.: *J. Electro. Mater.* **36**, 1389 (2007).