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Effect of $Na_{0.5}Bi_{0.5}TiO_3$ on dielectric properties of $BaTiO_3$ based ceramics

Yue Sun [a,b], Hanxing Liu [a,b,*], Hua Hao [a,b], Shujun Zhang [c], Liling Guo [b], Zhiyong Yu [b]

[a] State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, 430070, PR China
[b] School of Materials Science and Engineering, Wuhan University of Technology, 430070, PR China
[c] Materials Research Institute, Pennsylvania State University, University Park, PA 16802, USA

Abstract

In this work, $Na_{0.5}Bi_{0.5}TiO_3$ (NBT) was used to improve the high temperature dielectric properties of Nb, Co-doped $BaTiO_3$ (BT). Different x was selected ($x = 0$, 0.02, 0.04, 0.06, 0.08, 0.1, 0.2, 0.3, 0.4) to optimize the ratio of BT to NBT in $(1-x)$ BT–xNBT solid solution. The dielectric constant of the original X7R material is about 4900 at room temperature, decreasing to 2500 with NBT addition ($x = 0.2$). Of important is that the temperature stability was improved with dielectric constant variation being less than ±15% up to 160 °C.

Keywords: C. Dielectric properties; D. $BaTiO_3$ and titanates; D. Perovskites; Multilayer ceramic capacitors

1. Introduction

The $BaTiO_3$–Nb_2O_5–Co_3O_4 ternary system has been used for commercial multilayer ceramic capacitors (MLCCs) in last few years [1]. The typical core–shell structure can easily results in a flattened TC (temperature vs. capacitance) curve with high dielectric constant [2,3]. However, the sharply change in dielectric constant at the Curie temperature of $BaTiO_3$ (~125 °C), has limited its application to a relatively narrow using temperature range. Therefore, the goal of this study is to modify this system to enhance the high temperature stability, with flattened TC curve above 125 °C.

In this study, $Na_{0.5}Bi_{0.5}TiO_3$ (NBT) was chosen as a secondary end member to solve the problem. NBT–BT has been widely studied as a piezoelectric material, where NBT is the matrix and BT is the dopant, which shows a good piezoelectric property [4,5]. However, in the study of MLCCs, the roles were inversed. NBT was used as Curie shifter, locally shift the T_c of $BaTiO_3$ and depress/diffuse the Curie peak. For example, Yuan et al. [6] successfully increased the Curie point of $BaTiO_3$ to 140 °C with 1 mol% NBT addition. Li et al. [7] reported that the dielectric constant peak at T_c is suppressed evidently. The most attractive property of NBT is the dielectric constant, which was found to increase monotonously from 125 °C to 200 °C, thus can be used as the dielectric compensator of the $BaTiO_3$ based ceramics. All these indicate that NBT can effectively enhance the high temperature stability of the $BaTiO_3$ based ceramics. So it is the purpose of this research to investigate NBT effects on Nb, Co-doped $BaTiO_3$ ceramic, as a dielectric compensator above Curie point of $BaTiO_3$.

2. Experimental procedures

$(1-x)(BaTiO_3 + Nb_2O_5 + Co_3O_4) - xNa_{0.5}Bi_{0.5}TiO_3$ ($x =$ 0, 0.02, 0.04, 0.06, 0.08, 0.1, 0.2, 0.3, 0.4) ceramic samples were prepared by the conventional solid state method. $BaTiO_3$ based material and NBT were pre-synthesized separately. $BaTiO_3$, Nb_2O_5, Co_3O_4 were mixed in ethanol, and then ball milled with zirconium media for 24 h. After drying, the powder mixture was calcined in air for 6 h at 1200 °C, while Na_2CO_3, Bi_2O_3 and TiO_2 powder were calcined at 850 °C for 2 h to pre-synthesize NBT. To improve the homogeneity, the mixed Nb, Co-doped $BaTiO_3$ and NBT were ball milled again. Then dried, added 3 wt.% polyvinyl alcohol (PVA) binder, pressed into pellet (~12 mm diameter, ~1 mm thick), subsequently sintered at 1170–1280 °C for 2 h. The specific sintering temperatures for each sample were listed in Table 1.

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* Corresponding author at: State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, 430070, PR China. Tel.: +86 27 87642079; fax: +86 27 87651779.
E-mail address: lhxhp@whut.edu.cn (H. Liu).

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Table 1
Sintering temperatures for each composition.

Sample	Composition		Temperature (°C)	Bulk density (g/cm^3)
	$(1-x)$(BT + Nb + Co)	xNBT		
1	1	0	1310	5.84
2	0.98	0.02	1280	5.83
3	0.96	0.04	1280	5.75
4	0.94	0.06	1280	5.83
5	0.92	0.08	1270	5.85
6	0.90	0.10	1260	5.75
7	0.80	0.20	1200	5.71
8	0.70	0.30	1200	5.80
9	0.60	0.40	1170	5.79
10	0	1	1160	5.77

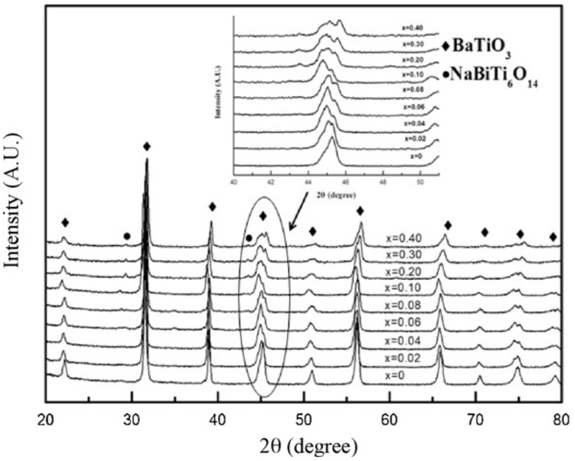

Fig. 1. XRD patterns for Nb, Co doped BaTiO$_3$ with different NBT contents.

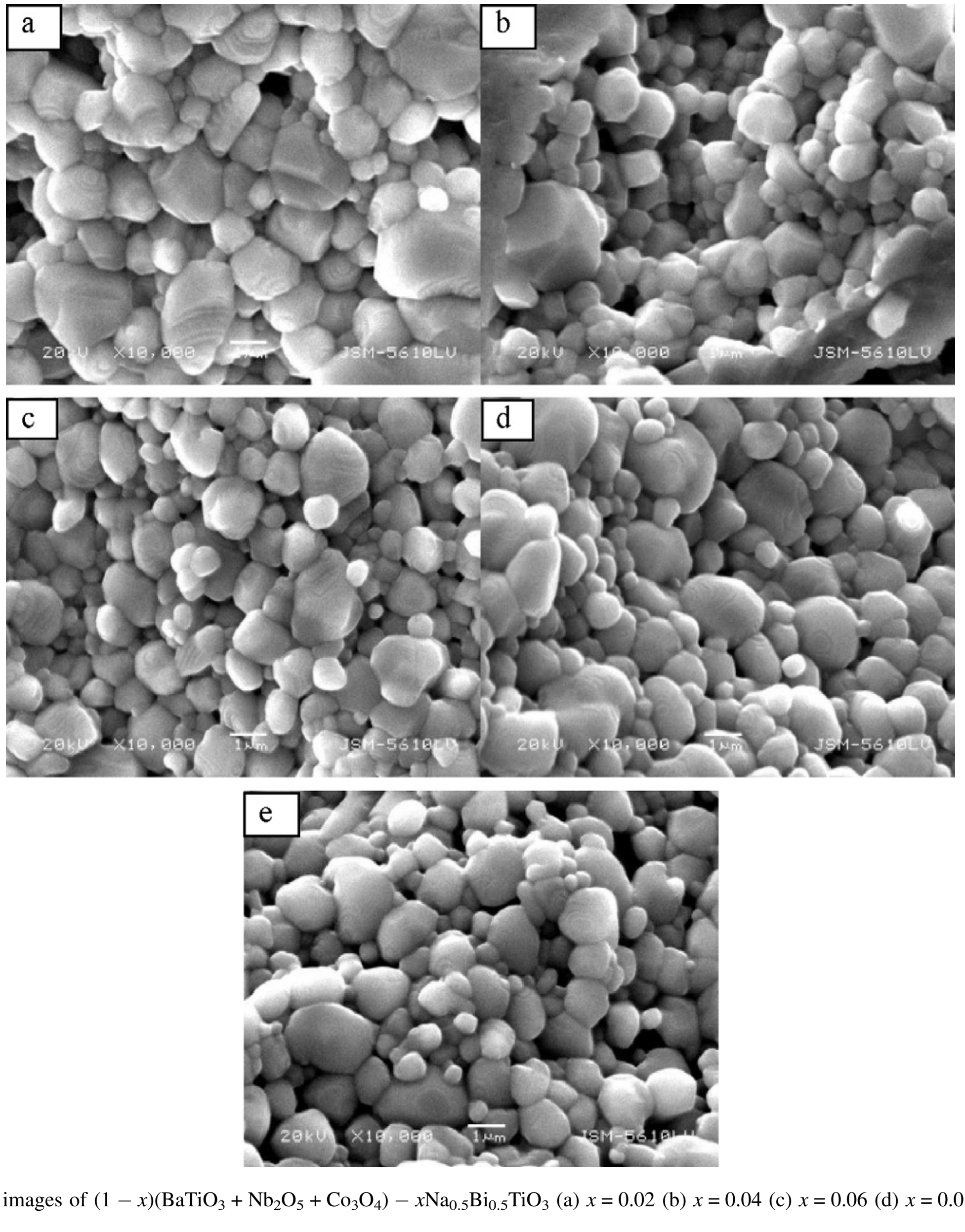

Fig. 2. SEM images of $(1-x)(BaTiO_3 + Nb_2O_5 + Co_3O_4) - xNa_{0.5}Bi_{0.5}TiO_3$ (a) $x = 0.02$ (b) $x = 0.04$ (c) $x = 0.06$ (d) $x = 0.08$ (e) $x = 0.1$.

Archimedes' method was used to measure the density of the samples and the densities were summarized in Table 1. XRD analysis was performed on the sintered pellets using Cu Kα radiation (X'Pert PRO, PANalytical, Holland). Microstructure was studied by scanning electron microscope (JSM-5610LV, JEOL, Japan). All samples are electrode using fire-on silver paste at 500 °C, the dielectric constant and loss were determined using Capacitance Meter (E4980A, Agilent, USA) at 1 kHz, in the temperature range of −55–180 °C.

3. Results and discussion

3.1. Phase characterization

Fig. 1 shows the XRD patterns for sintered $(1-x)$BT–xNBT samples with $x = 0, 0.02, 0.04, 0.06, 0.08, 0.1, 0.2, 0.3, 0.4$. It can be seen that $BaTiO_3$–Nb_2O_5–Co_3O_4 materials with NBT addition maintain the perovskite structure and an undesired phase (identified as $NaBiTi_6O_{14}$) was shown up when $x = 0.06$, which indicating the solid solution limitation is about $x = 0.06$. The undesired phase is becoming more evident at $x \geq 0.1$. For $x < 0.1$, the splitting becomes more evident is originate from the enhancement of tetragonality, which might be caused by the differences between the ionic radii of Ba^{2+} and (Na^+, Bi^{3+}). For $x \geq 0.1$, the amount of the new/second phase $NaBiTi_6O_{14}$ is increased. That might result in the change of phase structure (the Nb, Co-modified BT is in tetragonal phase, change to orthorhombic phase with increasing NBT). Especially, because the pure $NaBiTi_6O_{14}$ phase has two diffraction peaks in 45–46° and the one of the two peaks which near 45° is relatively strong. So the splitted peak around 45° might be the combination of $NaBiTi_6O_{14}$ and $BaTiO_3$. However, that is only a speculation; further studies are needed to confirm this explanation. The shift of the peak indicates the interplanar distance was affected by the NBT addition. This can be explained by the ionic radii of Bi^{3+} (1.14 Å) [8] and Na^+ (0.94 Å) [8] are smaller than that of Ba^{2+}(1.34 Å) [9], inducing lattice deformation when they entered into the lattice and replaced Ba^{2+}.

3.2. Microstructure

Fig. 2(a)–(e) shows the SEM images of $(1-x)$ ($BaTiO_3 + Nb_2O_5 + Co_3O_4$) − $x Na_{0.5}Bi_{0.5}TiO_3$, ($x = 0.02, 0.04, 0.06, 0.08, 0.1$). As seen in this figure, the grain size distribution was becoming narrower with increasing NBT. In Fig. 2(a), the grain size is distributed from 0.3 μm to 3 μm (calculated by *Image J*). But in Fig. 2(e), the grain size is distributed from 0.5 μm to 2 μm. That indicates the addition of NBT can make the grain size distributed more homogeneous. It can be also seen that the grain boundary was becoming clearer as the NBT content increasing. NBT has a relatively low melting point (1290 °C [10]) when compared to $BaTiO_3$, therefore, NBT will acted as a sintering aid and expedite the BT grain growth and it truly did.

3.3. Dielectric properties

Fig. 3 shows the TC curves of the original $BaTiO_3$ system, NBT, and the mixed $(1-x)$ ($BaTiO_3 + Nb_2O_5 + Co_3O_4$) − x-$Na_{0.5}Bi_{0.5}TiO_3$ ($x = 0, 0.02, 0.04, 0.06, 0.08, 0.1, 0.2, 0.3, 0.4$). It can be seen that BT–NBT materials show a compromising dielectric property. As expected, the curves of BT–NBT materials become more flat when compared to BT and NBT ceramics, with dielectric constant values being in between of BT and NBT, when $x < 0.1$. When $x < 0.1$, the TC curves still have the similar shape with the original curve of Nb, Co-doped $BaTiO_3$, as shown in Fig. 3(a). At first, the low temperature peaks shift to higher temperature range with increasing NBT, however, when $x \geq 0.06$ (it seems to be a turning point with the appearance of $NaBiTi_6O_{14}$), the low temperature peaks shift to lower temperature range. The high temperature peaks, namely the Curie peaks, however, were found to be depressed, diffused and move to higher temperature with increasing NBT (from $x = 0.02$ to 0.4). Because the Na^+, Bi^{3+} are might not homogeneously distributed in the solid solution, it might cause micro-region of compositional fluctuations, which induced the diffused T_c peaks. As Wang et al. [11] explained in his work of adding PST into $BaTiO_3$, in our work it can be explained in the same way. The melting point of NBT was as low as 1290 °C

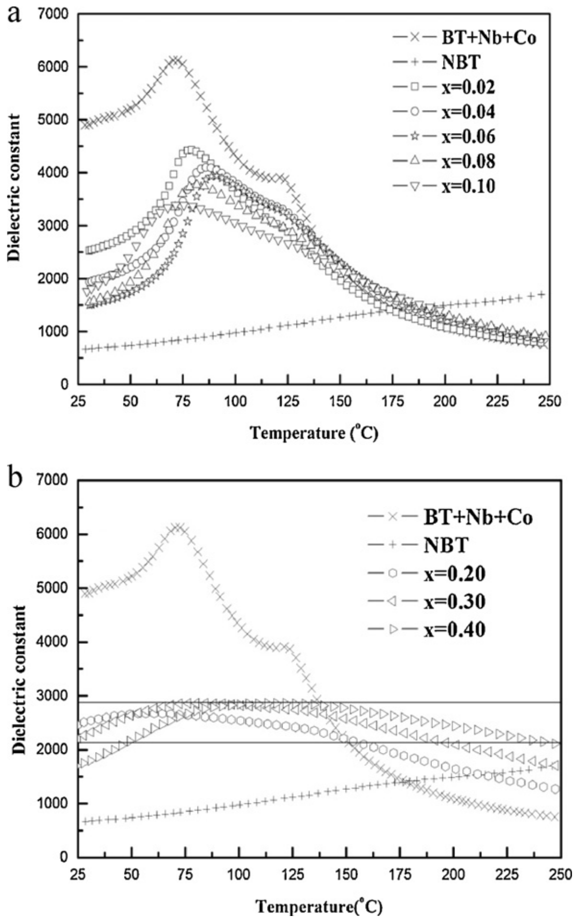

Fig. 3. Temperature dependence of the dielectric constant of Nb, Co-doped $BaTiO_3$, NBT and the mixed $(1-x)$ ($BaTiO_3 + Nb_2O_5 + Co_3O_4$) − $x Na_{0.5}Bi_{0.5}$-$Bi_{0.5}TiO_3$, (a) $x = 0.02, 0.04, 0.06, 0.08, 0.10$ (b) $x = 0.20, 0.30, 0.40$.

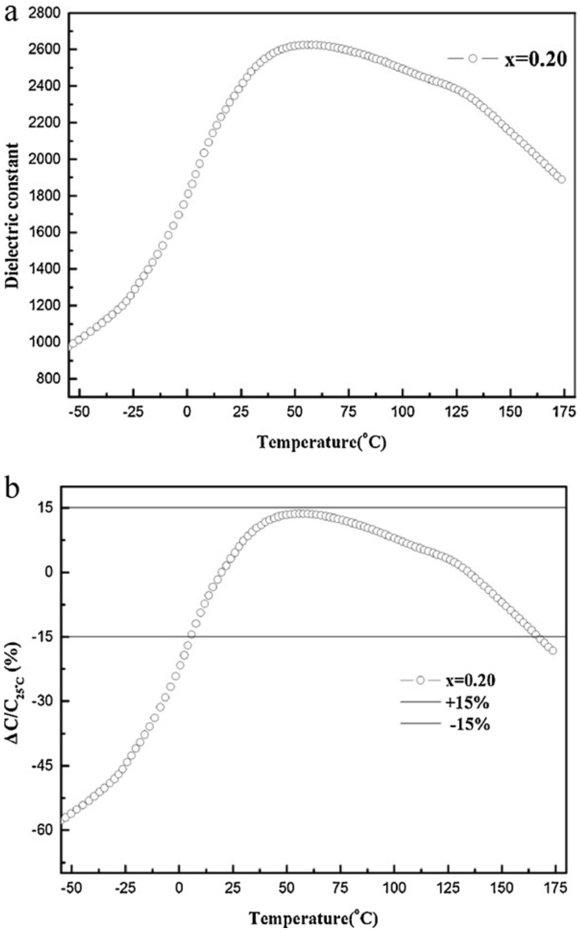

Fig. 4. Temperature dependence of (a) dielectric constant (b) $\Delta C/C_{25\ ^{\circ}\mathrm{C}}$ of sample $x = 0.20$.

[10], so the Na–O and Bi–O was weaker than Ba–O bonds, which strengthen Ti–O bonds after NBT added. Therefore, it needs a higher temperature to provide the energy for Ti^{4+} to resume its seat, leading to increased T_c. Of particular interest is that when $x > 0.1$, the two peaks are almost disappeared. Showing a very broad and diffused dielectric anomaly, giving rise to a flattened characteristics of the TC curves, as shown in Fig. 3(b). At $x = 0.2$, the dielectric constant was found to be ~2500 at room temperature and maintain similar values up to 160 °C, with $\Delta C/C_{25\ ^{\circ}\mathrm{C}}$ being on the order of $<\pm 15\%$ (in Fig. 3(b), the two straight lines are indicating the domain of ±15% variation of dielectric constant at $x = 0.2$), demonstrating much improved temperature stability of dielectric behavior (in high temperature range), when compared to the sample without NBT additions.

Fig. 3 shows that NBT can really raise up the decreasing TC curve as a dielectric compensator. However, when comes to the low temperature range, as shown in Fig. 4, the temperature coefficient of capacitance (sample $x = 0.20$) cannot satisfy the criterion of X8R from −55 °C to 5 °C. Therefore, future studies should be focused on the low temperature range.

4. Conclusion

The high temperature usage range of BT–Nb–Co system was successfully broadened by NBT addition. BT and NBT form partial solid solution with the limitation of $x = 0.06$ and exhibited improved dielectric property as expected. At $x = 0.20$, the material shows a high dielectric constant of 2500 at room temperature (1 kHz), with the temperature coefficient of capacitance (TCC) less than ±15% up to 160 °C. However, the low temperature range (from −55 °C to 5 °C) cannot satisfied the X8R criterion. Therefore, further studies should be focused on how to improve the low temperature stability of this system.

Acknowledgements

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