High-temperature stable dielectrics in Mn-modified (1-x) $Bi_{0.5}Na_{0.5}TiO_3$-$xCaTiO_3$ ceramics

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Abstract In the current work, the bulk (1-x) $Bi_{0.5}Na_{0.5}TiO_3$-$xCaTiO_3$ [BNCT100x] system was synthesized via solid-state route. $CaTiO_3$ in solid solution with $Bi_{0.5}Na_{0.5}TiO_3$ was observed to decrease the dielectric constant at higher temperature and raise the dielectric constant at lower temperature. Polarization hysteresis measurements indicated that the ferroelectricity of $Bi_{0.5}Na_{0.5}TiO_3$ was weakened with an increase of $CaTiO_3$, resulted in the shift of the depolarization temperature (T_d) toward lower temperatures. X-ray diffraction analysis revealed that TiO_2 was produced as a secondary phase due to the losses of Bi and Na during milling and sintering processes. Moreover, the addition of Ca promoted the segregation of Ti out of BNT grains. Dielectric properties of BNCT12 ceramics with different dopant levels of Mn were characterized as a function of temperature for potential use of high-temperature capacitors. Modification of BNCT12 materials with Mn improved the temperature characteristic of capacitance ($-55°C$ to $250°C$, $\triangle C/C_{25°C} \leq \pm 15\%$). Finally, by doping 1.5 wt% Mn, the dielectric constant at room temperature could reach over 900, with a low dielectric loss below 1% and a high insulation resistivity about 10^{12} $\Omega \cdot cm$. Furthermore, a small amount of Mn influenced the microstructure in the way to inhibit the long grains and grain growth of BNCT solution ceramics. However, excess Mn caused abnormal grain growth, and therefore, rectangle grains appeared again.

Keywords Bismuth sodium titanate · Calcium titanate · Dielectric properties · Microstructure

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1 Introduction

In recently years, $Bi_{0.5}Na_{0.5}TiO_3$ (BNT) discovered by Smolenskii in 1960 has attracted considerable attention as the most important lead-free piezoelectric material [1]. BNT has strong ferroelectricity at room temperature (P_r= 38 $\mu C/cm^2$) and a high Curie temperature (T_c=320°C). BNT belongs to ABO_3-type perovskites with rhombohedral symmetry at room temperature. Many modifications on BNT have been performed before it can be practically used as piezoelectric devices, such as additions of $PbTiO_3$ (PT), $BaTiO_3$ (BT), $SrTiO_3$ (ST), $Bi_{0.5}K_{0.5}TiO_3$ (BKT), CeO_2, La_2O_3, Dy_2O_3, etc [2–9]. Among them, BNT-BT system has good piezoelectric properties because of the existence of a rhombohedral (F_α)-tetragonal (F_β) morphotropic phase boundary (MPB) [10].

While most research has been concentrating on the modification of BNT for piezoelectric application, this material is also considered to be a good candidate for a high-temperature relaxor. Our previous research has indicated that BNT-BT system is a typical relaxor ferroelectric and exhibits a diffuse phase transition within a wide temperature range. Moreover, a temperature-stable dielectric was developed based on BNT-BT system using $CaTiO_3$ (CT) as a modifier. Temperature-stable dielectric materials are widely used in high-temperature capacitors, which need to be operated in such harsh environments as automobile electronic control unit, anti-lock brakes, aircraft engine, and aerospace propulsion [11, 12]. These materials must withstand high temperature while maintain good electrical properties.

Most conventional X7R and X8R capacitors are based on BT because of its high dielectric constant and environmental friendliness (X7R: the capacitance within the temperature range from −55 to 125°C is within ±15% of
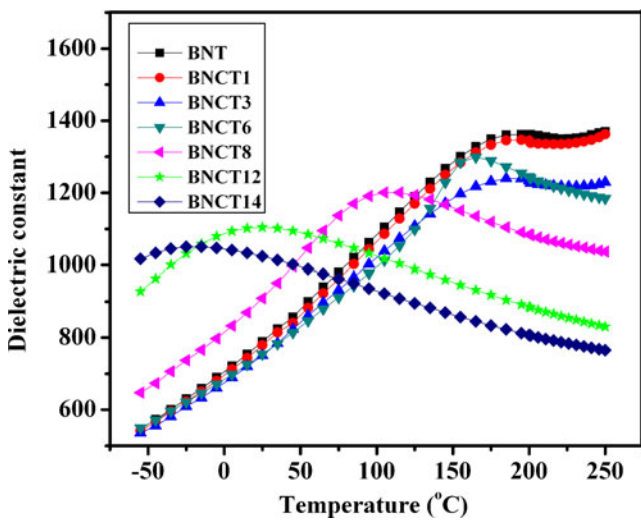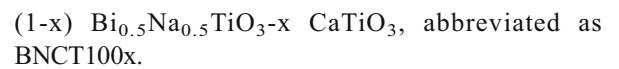
Fig. 1 Temperature dependence of the dielectric constants of BNT and BNCT100x (x=0.01~0.14) ceramics at 1 kHz

room temperature capacitance; X8R: the capacitance within the temperature range from −55 to 150°C is within ±15% of room temperature capacitance). However, it is difficult to achieve high-temperature stability in a dielectric ceramic composition consisting of BT as the main component,
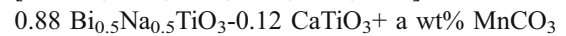
because the dielectric constant of BT will decrease rapidly above the Curie temperature ($T_C \approx 120$°C). In this study, the dielectric and ferroelectric properties of (1-x) BNT-xCT system were investigated. Furthermore, a novel temperature-stable dielectric was developed in this system using Mn as a modifier, which met the requirement: −55 to +250°C, $\triangle C/C_{25°C}$ less than ±15%.

2 Experimental procedures

As starting materials, Reagent-grade oxide or carbonate powders of Bi_2O_3, TiO_2, Na_2CO_3, $CaCO_3$ and $MnCO_3$ were used. Samples with the following chemical compositions were prepared.

(1-x) $Bi_{0.5}Na_{0.5}TiO_3$-x $CaTiO_3$, abbreviated as BNCT100x.
[x=0.01, 0.03, 0.06, 0.08, 0.12, 0.14]
0.88 $Bi_{0.5}Na_{0.5}TiO_3$-0.12 $CaTiO_3$+ a wt% $MnCO_3$
[a=0.3, 0.6, 0.9, 1.2, 1.5]

The weighed raw materials were mixed in deionized water with stabilized zirconia balls by ball milling for 6 h. Then the mixture was dried and calcined at 800°C for 2 h. The calcined
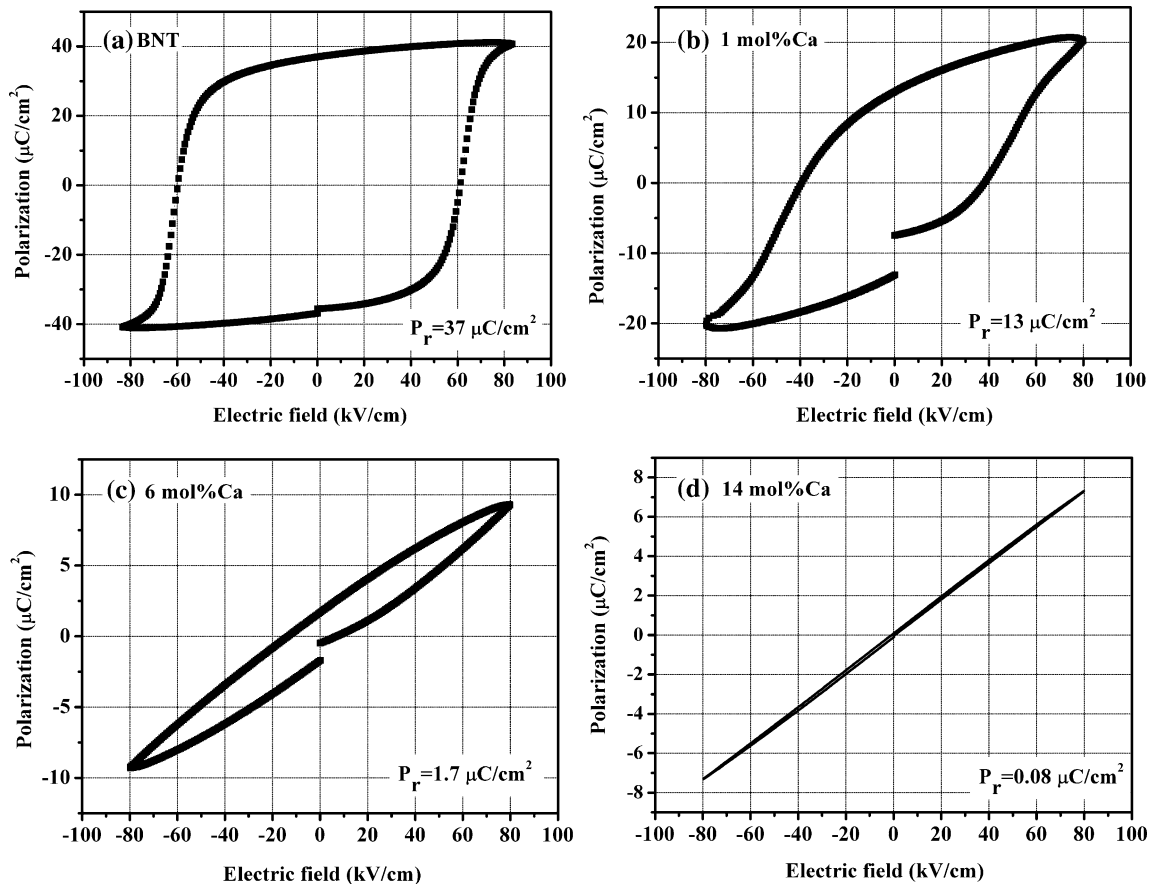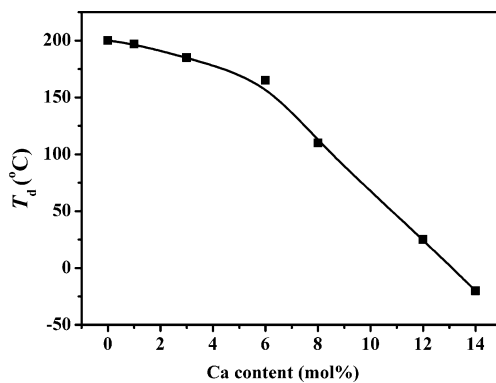

Fig. 2 P-E hysteresis loops of BNT and BNCT100x (x=0.01, 0.06, 0.14) ceramics
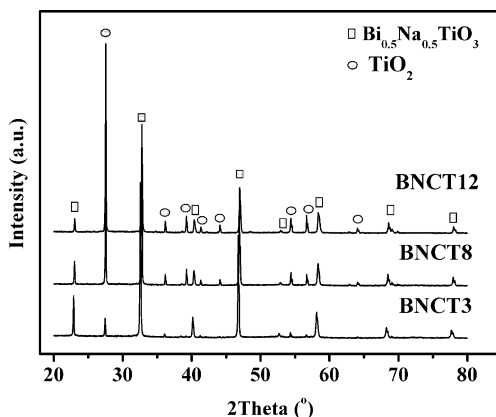
Fig. 3 Depolarization temperature of BNT and BNCT100x ceramics as a function of Ca content

powders were ground again by ball milling for 24 h and pressed into a disk form (~10 mm in diameter and ~1 mm thick) by mixing ceramic powders with 3 wt% PVA binders. After debindering, the disks were sintered at 1150°C for 2 h in air.

Ag was applied on both sides of the as-fired samples after firing to obtain contact electrodes. Dielectric measurements of the samples were performed using a LCR meter (HP 4192A) auto controlled by computer at 1 kHz and 1.0 V rms within a temperature range from −55°C to 250°C in air. The crystal structure of samples with various Ca contents was investigated by x-ray powder diffraction (XRD, model Philips X'Pert). Data collection was performed in the 2θ range of 20°–80° using CuKα radiation. The surface microstructure of sintered ceramics was observed by scanning electron microscope (SEM, model S-530).

3 Results and discussion

The temperature dependence of the dielectric constants of BNT and BNCT100x ceramics (x=0.01, 0.03, 0.06, 0.08, 0.12, 0.14) is illustrated in Fig. 1. As the amount of Ca

increased, the dielectric constant at higher temperatures was decreased markedly. On the contrary, the dielectric constant at lower temperatures was enhanced when Ca content exceeded 8 mol%. Furthermore, the dielectric constant peak was depressed and broadened with increasing Ca content. Here, the temperature correlated with the dielectric constant peak is called depolarization temperature T_d. For pure BNT, T_d is about 200°C in this study. There are several inconsistent explanations about T_d. Some reports indicated that T_d is related to the transition between ferroelectric (FE) and antiferroelectric (AFE) phases because double hysteresis loops were observed above T_d [3, 7]. However, Park [4] and Suchanicz [5] et al. found the intermediate phase as mixture of rhombohedral micro-polar regions and a tetragonal non-polar matrix. In this study, it can be seen that T_d moved towards lower temperatures as Ca content increased (Fig. 1). The decrease of T_d implied that the addition of $Ca^{2\pm}$ decreased the polarization of BNT, and therefore caused the weakening of ferroelectricity.

The ionic radii of Bi, Na, Ca, Ti and O are summarized as follows: A-site (12 coordinate): Bi^{3+} = 1.32 Å, Na^+ = 1.39 Å, Ca^{2+} = 1.34 Å; B-site (6 coordinate): Ti^{4+} = 0.605 Å, Ca^{2+} = 1.00 Å, O^{2-} = 1.40 Å. The ionic radius of Bi^{3+} in 12 coordinate is based on the relationship between coordination number and effective ionic radii after Shannon's table [13]. The ionic radius of Ca^{2+} ion is close to that of Bi^{3+} and Na^+.

Fig. 4 XRD patterns of samples with various Ca contents of x=3, 8, 12 mol% in BNCT100x
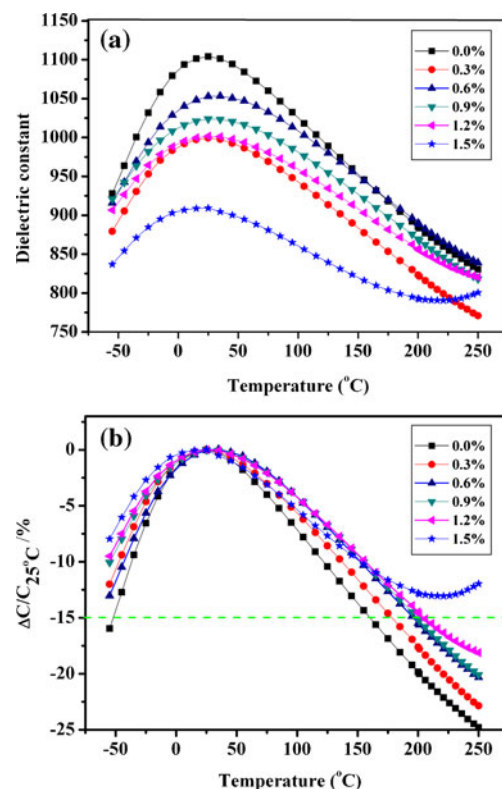
Fig. 5 Temperature dependence of (**a**) dielectric constant (**b**) $\Delta C/C_{25°C}$ of samples doped with various $MnCO_3$ contents

Therefore, Ca^{2+} prefers to dissolve in the A-sites of BNT. The substitution of Ca^{2+} for Bi^{3+} decreased the contribution of Bi^{3+} to polarization due to lower polarizability of Ca^{2+}.

To investigate the influence of Ca addition on the polarization behavior of BNT ceramics, the hysteresis loops of pure BNT and BNCT100x (x=0.01, 0.06, 0.14) ceramics were measured, as shown in Fig. 2.

As shown in Fig. 2(a), pure BNT is a typical normal ferroelectric with $P_r \approx 37$ μC/cm^2, which is in good agreement with previous reports. It can be seen that the remnant polarization P_r was decreased to 13 μC/cm^2 by adding 1 mol % Ca (Fig. 2(b)). That is to say that the addition of Ca lowered the ferroelectricity of BNT, which is consistent with the above discussion. As 14 mol% Ca was added, the hysteresis loop is similar to that of paraelectric with $P_r \approx$ 0 μC/cm^2 (Fig. 2(d)). In addition, no double hysteresis loop that indicates the existence of antiferroelectric phase was observed for all the samples.

Figure 3 shows the depolarization temperature T_d as a function of Ca content. It was found that T_d was shifted to

Fig. 6 SEM micrographs of (a) 0 (b) 0.3 (c) 0.6 (d) 0.9 (e) 1.2 (f) 1.5 wt% Mn-added BNCT12 ceramics
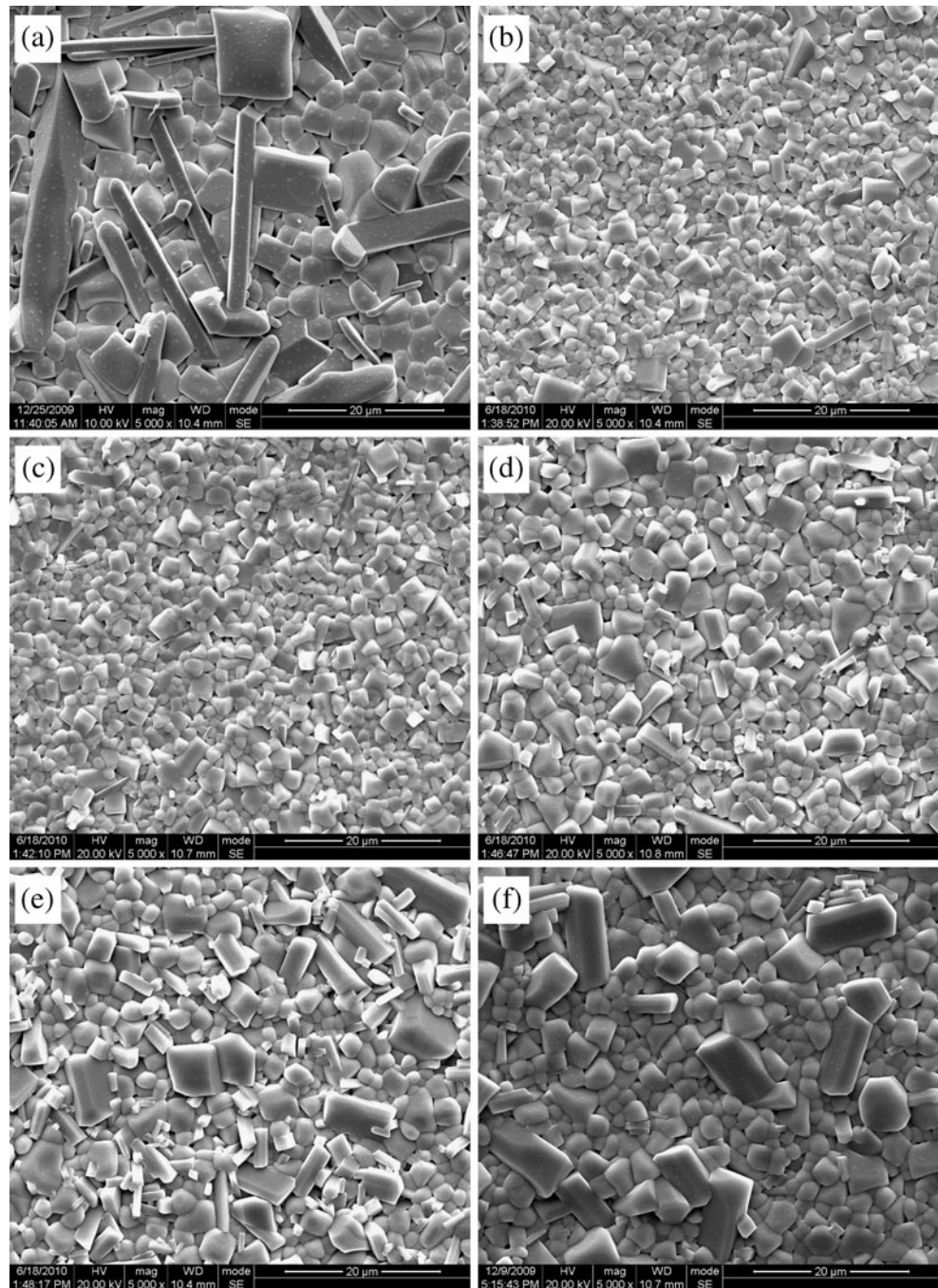
lower temperatures within the investigated Ca content range. When the amount of Ca was lower than about 5 mol%, T_d moved downwards slowly with an increase of Ca content (small slope). However, as the amount of Ca exceeded 5 mol%, T_d was decreased rapidly (large slope). This result might be due to the shift of Ca^{2+} from the A- to B-sites of BNT. Hennings et al. suggested that Ca^{2+} ions, which are well known as A-site substituents, may also enter the B-sites of BT [14]. When Ca^{2+} substituted to Ti^{4+}, the defect Ca_{Ti}'' was produced and extra negative charge could be compensated by $V_O^{\bullet\bullet}$, according to the reaction (1):

$$Ti_{Ti}^x + O_O^x + CaO \Rightarrow Ca_{Ti}'' + V_O^{\bullet\bullet} + TiO_2 \qquad (1)$$
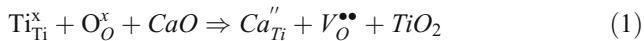
That is to say, for each Ca^{2+} on Ti-sites, one oxygen vacancy is formed. It is well accepted that the coupling of TiO_6 oxygen octahedral plays a crucial role in the stability of ferroelectric phase in the $ATiO_3$-type perovskite structure [15, 16]. The neighboring TiO_6 octahedra are linked by sharing the same oxygen ion. Therefore, the coupling between neighboring TiO_6 octahedra or the stability of ferroelectric phase would be significantly weakened by introducing oxygen vacancy. Moreover, the doping of $Ca^{2\pm}$ on Ti-sites reduced the number of TiO_6 octahedra per unit volume, which would lead to the decrease of polarizability. On the other hand, the adjacent TiO_6 octahedra was compressed due to the replacement of Ti^{4+} (6 coordinate, $r=0.605$ Å) by larger Ca^{2+} (6 coordinate, $r=1.0$ Å) ions. Therefore, it would be difficult for Ti^{4+} to depart from the center of TiO_6 octahedra, which resulted in the loss of spontaneous polarization of local areas. Accordingly, T_d was decreased sharply when Ca^{2+} entered into the Ti-sites of BNT. At the same time, the peak dielectric constant was decreased with increasing Ca content, caused by the weakening of ferroelectricity (Fig. 1). It also could be concluded that the shift of T_d was responsible for the increase of dielectric constant at lower temperatures as Ca content was higher than 6 mol%.

Figure 4 shows the dependence of XRD patterns of BNCT100x ceramics with an increase in CT content (x=0.03, 0.08, 0.12). It was confirmed that the matrix phase is BNT by the comparison between the XRD patterns with the respective Inorganic Crystal Structure Database (ICSD) no. 00-046-0001. It was also observed that a secondary phase of TiO_2 was formed in all samples. For BNCT3, excessive Ti segregated out of grains due to the loss of Bi and Na during milling and sintering process. However, according to the reaction (1), more TiO_2 would be produced if Ti^{4+} ions were replaced by Ca^{2+} ions. Therefore, the diffraction peak intensity of TiO_2 was obviously strengthened with increasing Ca, indicating an increase of the volume fraction of TiO_2. The lattice parameters decreased monotonically with increasing Ca, because the diffraction peaks shifted toward higher angle of 2θ.

As shown in Fig. 1, BNCT ceramic is a promising candidate for high-temperature relaxor because of the diffuse phase transition and broadening permittivity over a wide temperature range. However, BNCT must be modified before it can be used in stable high-temperature capacitors. Our research indicates that Mn can effectively improve the temperature characteristic of capacitance (TCC) for BNCT system.

Figure 5 shows the temperature dependence of the dielectric constants and capacitance changes ($\triangle C/C_{25°C}$) for BNCT12 doped with various $MnCO_3$ contents sintered at 1150°C for 2 h. As shown in Fig. 5(a), the dielectric constant of samples decreased with increasing Mn content. Especially, the dielectric constant at lower temperatures was effectively depressed. The addition of Mn had no influence on the depolarization temperature ($T_d=25°C$). It can be seen from Fig. 5(b) that the capacitance change at higher temperatures shifted towards positive direction as the amount of Mn increased. Therefore, the temperature characteristic of capacitance was obviously improved by the addition of Mn. For the pure BNCT12 ceramics, the dielectric loss was 1.35% and the resistivity at room temperature was 10^{10} $\Omega\bullet cm$. When 1.5 wt% Mn was added, the dielectric loss was decreased to 0.85%, whereas the resistivity was raised to 2×10^{12} $\Omega\bullet cm$. High-temperature stable dielectric was achieved when 1.5 wt% Mn was added, with a dielectric constant greater than 900 and satisfied the specification: −55 to 250°C, $\triangle C/C_{25°C} \leq \pm15\%$.

SEM micrographs for the pure BNCT12 and Mn-added BNCT12 ceramics with various Mn contents sintered at 1150°C for 2 h are revealed in Fig. 6. Some long grains are present in the surface of the pure BNCT12 ceramics, as shown in Fig. 6(a). An addition of a small amount of Mn (≤0.6 wt%) contributed to smaller grain size and elongated grains almost disappeared as illustrated in Fig. 6(b). This result indicated that doping with a small quantity of Mn was effective in suppressing the long grains and grain
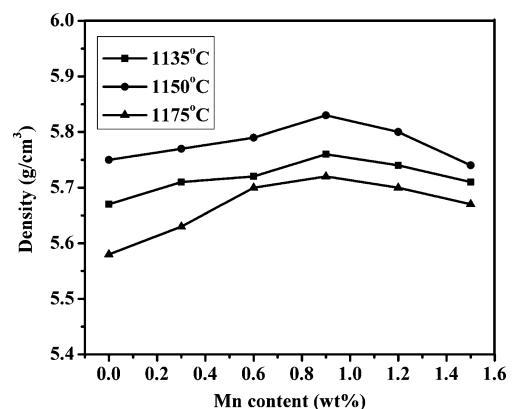
Fig. 7 Densities of samples sintered at 1135, 1150 and 1175°C as a function of Mn content

growth of BNCT12 ceramics. However, as Mn content increased further (≥0.9 wt%), abnormal grain growth happened, therefore, some large grains appeared. Especially, for 1.5 wt% Mn-doped BNCT12 ceramic, rectangle grains appeared again.

The resulting microstructures of these ceramics were in good agreement with their measured densities. The densities of BNCT12 ceramics doped with various amounts of Mn sintered at 1135°C, 1150°C and 1175°C, respectively, are illustrated in Fig. 7. As shown in Fig. 7, the undoped BNCT12 ceramics possessed a relatively lower density. As the amount of Mn increased, the densities were increased and the highest densities were achieved in 0.9 wt% Mn-doped BNCT12 ceramics regardless of their sintering temperature. Increasing the sintering temperature caused the samples to be better densified and therefore the samples sintered at 1150°C possessed higher densities. However, as the sintering temperature was raised to 1175°C, the densities were decreased, maybe due to the abnormal grain growth in these samples.

4 Conclusion

In the present report, dielectric, ferroelectric properties and microstructures of Mn-modified (1-x) BNT-xCT ceramics have been studied. The peak dielectric constant was depressed and broadened by adding Ca. The addition of Ca was observed to weaken the ferroelectricity of BNT and induce paraelectric behavior, which resulted in the shift of the depolarization temperature T_d to lower temperatures. When Ca^{2+} entered into the Ti-sites of BNT, the amount of the secondary phase TiO_2 was increased and a large quantity of long grains were observed in the surface of the pure BNCT12. The addition of ≤0.6 wt% Mn inhibited the grain growth and the elongated grains vanished. As Mn content increased further (≥0.9 wt%), abnormal grain growth happened and rectangle grains appeared again. The highest densities were obtained with the addition of 0.9 wt% Mn, independent of the sintering temperature. Furthermore, Mn doping greatly improved the temperature characteristic of capacitance for BNCT ceramics, with lower dielectric losses and higher resistivities compared with the unmodified BNCT. The BNCT12 ceramics with 1.5 wt% Mn exhibited a dielectric constant greater than 900 and a low dielectric loss below 1% at room temperature, with flat temperature coefficients of capacitance ($\triangle C/C_{25°C} \leq \pm15\%$) over the temperature range from −55°C to 250°C. Therefore, this novel system is a promising material for high temperature capacitor applications.

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