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Dielectric behaviors of Nb_2O_5–Co_2O_3 doped $BaTiO_3$–$Bi(Mg_{1/2}Ti_{1/2})O_3$ ceramics

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Abstract

Nb_2O_5 and Nb–Co doped $0.85BaTiO_3$–$0.15Bi(Mg_{1/2}Ti_{1/2})O_3$ (0.85BT–0.15BMT) ceramics were investigated. From XRD patterns, undesired phase was observed when the (Nb_2O_5/Nb-Co) doping levels exceed 3 wt.%/2 wt.%, giving rise to the deteriorate dielectric constant. The 0.85BT–0.15BMT ceramics doped with 2 wt.%Nb_2O_5 was found to possess a moderate dielectric constant ($\varepsilon \sim 1000$) and low dielectric loss ($\tan \delta = 0.9\%$) at room temperature and 1 kHz, showing flat dielectric behavior over the temperature range from −55 to 155 °C. It was found that the formation of core–shell structure in the BT based ceramics is controlled by the doping sequence of Nb- and Bi-oxides.

Keywords: B. Defects; C. Dielectric properties; E. Capacitors; Core–shell structure

1. Introduction

Recently, ferroelectric materials based on the $BiScO_3$–$BaTiO_3$ binary system were reported to show good dielectric behavior and temperature stability [1,2]. Similar to this system, another Bi-based perovskite, $Bi(Mg_{1/2}Ti_{1/2})O_3$ (BMT), in solid solutions with $BaTiO_3$(BT) end member, was expected to exhibit relaxor behavior and low temperature coefficient of dielectric constant, demonstrate the potential usage in the multilayer ceramic capacitor applications (MLCC) [3,4].

Based on our preliminary results, the solubility of BMT in the BT matrix was found to be only about 7%. The dielectric frequency behavior suggested that the solid solution $(1-x)$BT–xBMT behave like a normal ferroelectric with $x = 0-0.05$, while it exhibited relaxor-like behavior with further increasing of BMT, where the temperature stability was enhanced, with dielectric maxima temperature T_m shifted downward and became diffused. On the other hand, when doped level exceeded the solid solubility limit, undesired second phase was found to appear, which deteriorate the dielectric constant and slightly increase the T_m.

When BT was doped by Nb_2O_5 oxide, the Nb^{5+} will diffuse into the crystal lattice and form the chemically inhomogeneous structure called ‘‘core–shell’’, and increase the inner stress of the ‘‘shell’’ region to achieve good dielectric properties [5–9]. Meanwhile, Nb, Co dopants are usually applied to BT system as donor and acceptor dopants to improve temperature stability of dielectric constant. In addition, 0.85BT–0.15BMT showed high dielectric permittivity (∼2000) at room temperature and a relatively flat temperature coefficient above Curie point, as shown in Fig. 1, which can serve as a matrix for further modification studies. In this work, the effects of Nb_2O_5/Nb–Co dopants on the microstructure and dielectric properties of 0.85BT–0.15BMT were studied, the core–shell microstructure collapse mechanism was discussed.

2. Experimental procedures

Ceramic powders of 0.85BT–0.15BMT were prepared using a conventional solid-state method. Bi_2O_3 (99.99%), MgO (98.5%), $BaTiO_3$ (99.0%), TiO_2 (98.5%) were batched stoichiometrically based on the nominal compositions. The materials were ball milled in alcohol solution for 24 h and dried. After the calcination

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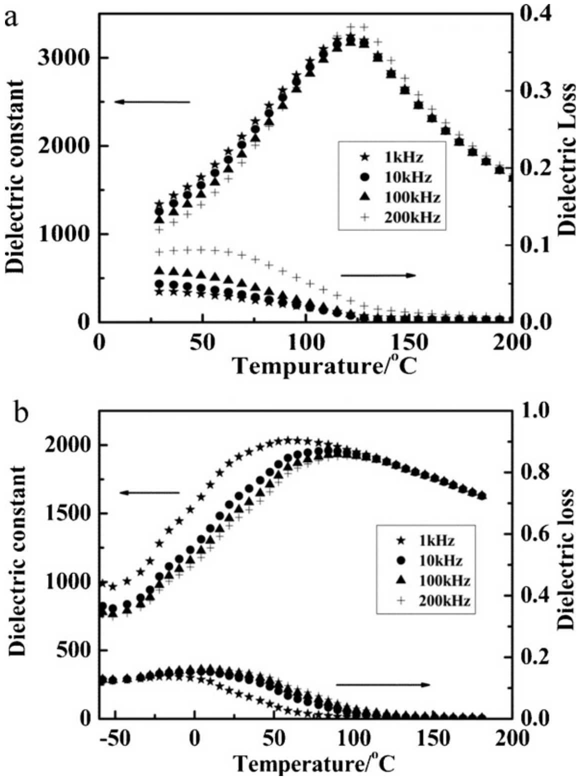

Fig. 1. Dielectric constant and dielectric loss as a function of temperature measured at frequencies from 1 kHz to 200 kHz for $(1-x)$BT–xBMT ceramics: (a) $x = 0.03$, (b) $x = 0.15$.

at 1000 °C for 2 h, Nb_2O_5–Co_2O_3 complex oxide (66.7 wt.% Nb_2O_5 and 33.3 wt.% Co_2O_3 calcined at 750 °C for 2 h) with different doped levels (0.5 wt.% $< x <$ 3 wt.%) were added in the matrix powder using ball milling for 12 h. Subsequently, the powders were pressed into pellets and sintered at temperatures between 1150 and 1200 °C for 2 h. As a comparative experiments (recorded as Approach B), $BaTiO_3$, Bi_2O_3, MgO and Nb_2O_5 were mixed stoichiometrically without pre-synthesis of 0.85BT–0.15BMT compound.

Phase purity was determined using X-ray powder diffraction (XRD) (Cu Kα radiation, PANalytical X'Pert PRO). Dielectric measurements were performed in a customer designed furnaces connected a precision LCR meter (E4980A, Agilent) and computerized control and data collection systems. The heating rate was 1 °C/min. The frequencies used for the measurement were from 1 kHz to 1 MHz, with an oscillating voltage of 1.0 V.

3. Results and discussion

Fig. 2 shows X-ray diffraction patterns of 0.85BT–0.15BMT ceramics with different wt.% Nb_2O_5/Nb–Co. Undesired second phases are detected when the Nb_2O_5/Nb–Co doped levels exceed 3 wt.%/2 wt.%, which is considered to be the titanium-rich phase [10–12].

An electronic compensation regime appears for low Nb_2O_5 concentrations in BT matrix [7,10,11]:

$$Nb_2O_5 \rightarrow 2Nb^{\bullet}_{Ti} + 2TiO_2 + O_0 + 2e' \quad (1)$$

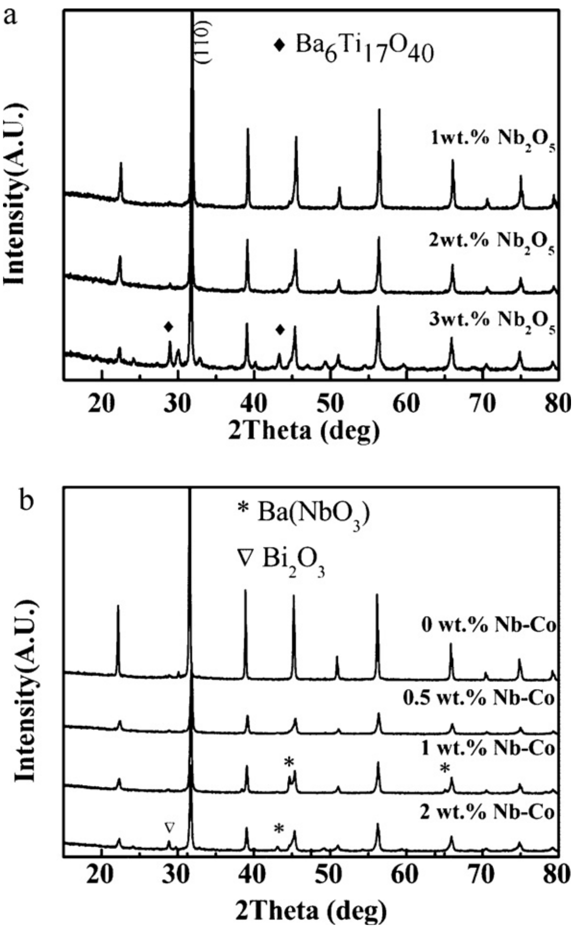

Fig. 2. X-ray diffraction pattern on 0.85BT–0.15BMT ceramics with different wt.% Nb_2O_5/Nb–Co.

With the increasing of donor concentration, the electronic compensation changes into vacancy compensation. V''_{Ba} or V''''_{Ti} will be formed, making the crystal lattice distorted and producing inner stress, as shown in the following equations:

$$Nb_2O_5 \rightarrow 2Nb^{\bullet}_{Ti} + 2TiO_2 + BaO + V''_{Ba} \quad (2)$$

or

$$2Nb_2O_5 \rightarrow 4Nb^{\bullet}_{Ti} + 5TiO_2 + V''''_{Ti} \quad (3)$$

Another possible mechanism for the ionic compensation regime is the substitution of Ti by Co, when Nb–Co was doped into BT–BMT:

$$\frac{1}{2}O_2 + Co_2O_3 + V''_{Ba} \rightarrow 2Co'_{Ti} + TiO_2 \quad (4)$$

or

$$2Co_2O_3 + V''''_{Ti} \rightarrow 4Co'_{Ti} + 3TiO_2 \quad (5)$$

It will affect the dielectric properties by reducing the number of vacancies and releasing stress by the formation of $[Nb^{5+}{}_{1/2}Co^{3+}{}_{1/2}]^{4+}$ [7,8,12].

Obviously, Nb or Co substitution on Ti site in the $BaTiO_3$ lattice will leave the excess Ti out of the grains, which is responsible for the titanium-rich phase formation at the grain boundary.

As shown in Fig. 2, the <1 1 0> peaks were found to shift toward lower angle with the Nb_2O_5/Nb–Co content increasing, indicate more Nb^{5+}/$[Nb^{5+}{}_{1/2}Co^{3+}{}_{1/2}]^{4+}$ with larger radius was introduced into the lattice.

It was reported that the charge neutrality condition of Nb-doped $BaTiO_3$ was controlled by the Ba/Ti ratio. Specifically, the Ba vacancies dominate when Ba/Ti < 1 while Ti vacancies dominate when Ba/Ti > 1 [11,13]. For BT–BMT system, the same phenomenon was expected, like Ba/Ti < 1. Ba vacancies are dominant when Nb ion substituted into BT–MT, which release more space to Ti^{4+} and enhance the spontaneous polarization, leading to the increased dielectric constant. For 0.85BT–0.15BMT ceramics with different wt.% Nb_2O_5/Nb–Co dopants, however, the results are contrary to the above explanation, as shown in Fig. 3. Among them, the 0.85BT–0.15BMT ceramics doped with 2 wt.%Nb_2O_5 achieved the best dielectric properties, with a moderate dielectric constant ($\varepsilon \sim 1000$) and low dielectric loss ($\tan\delta = 0.9\%$) at room temperature and 1 kHz, and capacitance change being on the order of ±15% over the temperature range from −55 to 155 °C. The dielectric properties of 0.85BT–0.15BMT ceramics are strongly correlated with Nb_2O_5/Nb–Co contents, where the dielectric constant and dielectric loss decreased significantly as doped level increased, due to the Ti-rich second phases formation in Nb-rich region [10]. Meanwhile, the T_m dropped owing to the formation of Ba(Ti, Nb)O_3, which has much lower T_C [14].

The formation of core–shell structure in Nb-doped BT system is attributed to the chemical inhomogeneity of Nb ion in BT grain, where the Nb ion mainly concentrated in the shell region, while the core is pure BT. The double peaks in ε–T curve can usually be observed in the ceramics with core–shell structure [7–9]. However, this phenomenon is not found in Fig. 3; while, it appears in samples prepared by approach B, as shown in Fig. 4. As mentioned, the solid solution limit of $(1-x)$BT–xBMT is about $x = 0.07$ and the perovskite structure of the BMT is unstable due to the low tolerance factor. Excess raw oxides, such as Bi_2O_3 and MgO, will segregate at the boundary of the BT grains in 0.85BT–0.15BMT ceramics and low melting compound including Bi_2O_3 and Ba(Ti, Nb)O_3 formed liquid phases, which would make BT–BMT grains dissolve more easily [8,12]. Hence, Nb (or Nb, Co) ion was much easier to diffuse and distributed uniformly over whole grain and the core–shell structure collapsed in the former system. This is another reason why the dielectric properties of 0.85BT–0.15BMT were deteriorated by doping Nb_2O_5/Nb–Co. For approach B, however, all the dopant oxides tend to accumulate at the grain boundary and diffuse simultaneously into BT grain. The liquid phases contain Nb and Bi, where the diffusion of Bi ions was weakened due to the slow diffusion of Nb liquid compounds during the sintering process, thus the core–shell structure survived. Bi_2O_3, MgO and TiO_2 mainly stayed in the shell region, thus the composition of core was pure BT which is responsible for the dielectric peak at ~130 °C, as shown in Fig. 4 [1,6].

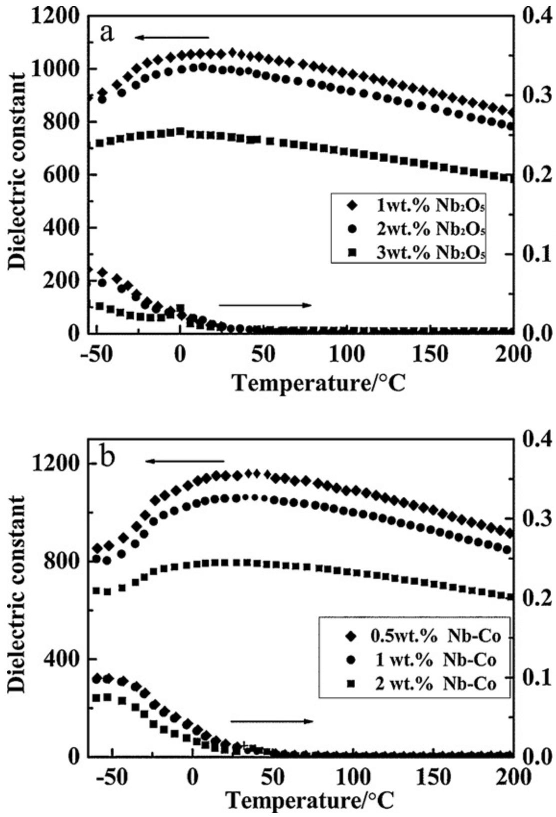

Fig. 3. Dielectric constant and dielectric loss as a function of temperature measured at 1 kHz for 0.85BT–0.15BMT ceramics with different wt.% Nb_2O_5/Nb–Co.

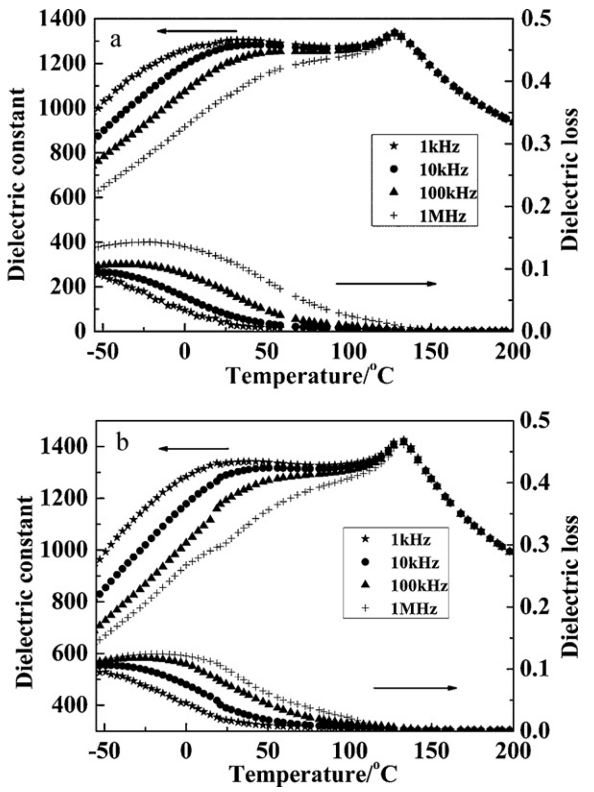

Fig. 4. Dielectric constant and dielectric loss as a function of temperature measured at frequencies from 1 kHz to 1 MHz for 0.85BT–0.15BMT −1 wt.%Nb_2O_5/Nb–Co ceramics prepared by approach B: (a) 1 wt.%Nb_2O_5, (b) 1 wt.%Nb–Co.

4. Conclusions

For 0.85BT–0.15BMT system, increasing Nb_2O_5/Nb–Co doping led to a lower dielectric loss and a more flat ε–T curve, but with reduced dielectric constant. Double peaks in ε–T curve of Nb-doped BT–BMT can be found in the samples prepared by approach B, indicating that chemical inhomogeneity of core–shell structure depends on the adding sequence of Nb and Bi oxide, etc. to BT-base ceramics. The excellent temperature stability of Nb doped BT–BMT make these materials promising candidates for MLCC applications.

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