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# Colossal permittivity in niobium doped BaTiO$_3$ ceramics annealed in N$_2$

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ABSTRACT

$Nb^{5+}$ and/or $In^{3+}$ doped BaTiO$_3$ ceramics were prepared by a conventional solid-state method, followed by annealing in N$_2$. At the room temperature and 1 kHz, permittivity of $Nb^{5+}$ doped BaTiO$_3$ (BTNb) is up to 80,888 and its dielectric loss is as low as 0.03. The origin of the colossal permittivity in BTNb is ascribed to the giant defect dipoles ($Ti^{4+} \cdot e' - V_O^{\bullet\bullet} - Ti^{4+} \cdot e'$). Besides, ($V_{Ba}'' - V_O^{\bullet\bullet}$) defect dipoles are also proved to be present in BTNb, which plays an important role on maintaining lower dielectric loss in a wide temperature region for BTNb.

Dielectric with high permittivity and low dielectric loss are of important applications in the field of microelectronics such as capacitors and energy-storage devices [1]. Up to now, several candidates have been reported. CaCu$_3$Ti$_4$O$_{12}$ (CCTO) has an abnormally high (~$10^5$) permittivity and good temperature stability, but the relatively high dielectric loss (~0.1) and rapid reduction of permittivity in high frequency have limited its practical applications [2]. Non-ferroelectric transition-metal oxides such as doped NiO [3], Fe-containing complex perovskites A (Fe$_{1/2}$B$_{1/2}$)O$_3$ (A = Ba, Sr, Ca and B = Nb, Ta,Sb) [4] and La$_{2x}$Sr$_x$NiO$_4$ ($x$ = 1/3 or 1/8) [5] also have high, temperature-independent permittivity (~$10^5$), their dielectric losses (over 0.1), however, are still relatively high. Recently, a new type of colossal permittivity (CP) material, (Nb + In) co-doped TiO$_2$ [6], has been reported, which exhibits a large temperature- and frequency-independent CP ($>10^4$) as well as a low dielectric loss (mostly $<0.05$) over a very broad temperature range from 80 to 450 K. Inspired by this work, other researchers also found similar CP behavior in (Nb + In) co-doped TiO$_2$ amorphous films [7] and (Ga, Bi, Zn) + Nb co-doped TiO$_2$ ceramics [8], although the origin of the CP behavior in donor and acceptor co-doped TiO$_2$ is still debated. Besides, Cao et al. reported that SrTiO$_3$ (ST) ceramics sintered in N$_2$ have a weak temperature- and frequency-dependent giant permittivity ($>10^4$) and a very low dielectric loss ($<0.02$) over a broad temperature range from −100 °C to 200 °C, which is due to giant defect dipoles generated by the $Ti^{3+}$ ions and fully ionized oxygen vacancies [9]. These research works give us an enlightenment that large permittivity might be obtained in titanate-based ceramics by controlling the defect dipoles.

BaTiO$_3$ (BT)-based ceramics have been widely used in multilayer ceramic capacitors (MLCC). Pure BT has a relatively large permittivity (~$10^3$) and medium dielectric loss (~0.02) at the ambient temperature. Unfortunately, its large permittivity is temperature-dependent and can only be achieved over a narrow temperature range close to a ferroelectric phase transition. Although temperature stability of permittivity in BT can be improved by doping other elements or compositing with other oxides [10], forming a compositionally homogeneously core-shell structure [11], its permittivity is still far from satisfactory. Therefore, it is a big challenge to improve its permittivity to a large extent and simultaneously maintain a lower dielectric loss, which will be very beneficial to its practical applications.

In the present paper, Nb and In doped BaTiO$_3$ ceramics were prepared by a conventional solid state method, followed by annealing in N$_2$ so as to create defect dipoles. Nb has a fixed 5+ oxidation state, and its ionic radius $r_{Nb}^{5+} = 78$ pm and In has a fixed 3+ oxidation state, and its ionic radius $r_{In}^{3+} = 94$ pm [12]. Therefore, both Nb and In are located at $Ti^{4+}$ site ($r_{Ti}^{4+} = 74.5$ pm) [12] site in the solid solutions since their ionic radius are similar to that of the $Ti^{4+}$. By using the Kröger-Vink notation, their defect reactions are as follows:

$$Nb_2O_5 \rightarrow 2Nb_{Ti}^{\bullet} + 2e' + 5O_O^{\times} \tag{1}$$

$$In_2O_3 \rightarrow 2In_{Ti}' + V_O^{\bullet\bullet} + 3O_O^{\times} \tag{2}$$

and oxygen vacancies are created when the samples are annealed in N$_2$:

$$O_O^{\times} \rightarrow V_O^{\bullet\bullet} + 2e' + 1/2O_2 \tag{3}$$

Accordingly, defect dipoles are created in Nb and/or In doped BaTiO$_3$ ceramics, leading to that a very large permittivity of 80,888 and a low

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dielectric loss of 0.03 were simultaneously observed in Nb doped BT ceramics, which are superior to most of CP materials [2–5]. And the correlation between dielectric properties and defect chemistry of Nb and/or In doped $BaTiO_3$ ceramics are studied.

$BaTi_{0.995}Nb_{0.005}O_3$ (BTNb), $BaTi_{0.995}In_{0.005}O_{0.9975}$ (BTIn) and $BaTi_{0.99}Nb_{0.005}In_{0.005}O_3$ (BTNbIn) ceramics were prepared by solid state reaction using $BaCO_3$ (99.9%), $Nb_2O_5$ (99.9%), $In_2O_3$ (99.9%) and $TiO_2$ (99.9%), which were dried prior to weighing at 180, 700 and 900 °C, respectively. The powders were mixed with ethanol and ball-milled for 12 h. The mixture was dried, calcined at 1100 °C for 6 h, then crushed and ball-milled for 12 h. The dried powders were sieved and then uniaxially pressed into green pellets at room temperature. The pellets were sintered at 1300 °C (BTNb and BTIn) and 1450 °C (BTNbIn) for 3 h in the air. Then, the samples were annealed in the atmosphere of $N_2$ at 1200 °C (BTNb and BTIn) and 1300 °C (BTNbIn) for 2 h (abbreviated as BTNb-$N_2$, BTIn-$N_2$ and BTNbIn-$N_2$). The present phases were analyzed by X-ray powder diffraction (XRD; D/Max2550VB+/PC, Rigaku, Tokyo, Japan) using Cu-K$\alpha_1$ radiation with linear position-sensitive detector. Microstructural properties such as grain size distribution and morphology were determined using field-emission scanning electron microscopy (SEM; JEOL-6700F, Japan Electron Co., Tokyo, Japan). Temperature decedent dielectric properties of the samples were studied by a precision LCR meter (E4980, Agilent, Santa Clara, CA, USA) associated with a temperature controller (TP94, Linkam, Surrey, U.K.) under the frequency from 100 Hz to 1 MHz at a signal level of 0.5 V/mm. Frequency dependent dielectric properties was measured using a impedance analyzer (E4294A, Agilent, Santa Clara, CA, USA) over the frequency range from 100 Hz to 1 MHz and under the applied *ac* measuring voltage of 0.5 V. X-ray photoelectron spectroscopy (XPS) measurements were performed with a spectrometer (PHI5400, Perkin Elmer, Waltham, USA) with Al K$\alpha$ ($E = 1486.6$ eV) radiation. Electron paramagnetic resonance (EPR) spectra were measured at room temperature using an X-band spectrometer (A300-10/12, Bruker, Karlsruhe, German) operating at 9.84 GHz.

XRD patterns of BTNb, BTIn and BTNbIn ceramics sintered at 1300 °C (BTNb and BTIn) and 1450 °C (BTNbIn) for 3 h in air are shown in Fig. S1. All the compositions are pure phase. These results suggest that Nb and In have completely solute in the $BaTiO_3$ lattice. Fig. S2(a–d) illustrates SEM images of BTNb, BTIn and BTNbIn ceramics sintered in air and annealed in $N_2$. All the ceramics have dense microstructure. The average grain size of BTIn, BTNb and BTNbIn ceramics is found to 5.75 μm, 1.02 μm and 13.41 μm. BTNb has dense microstructure and smaller grain size distribution, which is related to its high permittivity performance [13]. Annealing in $N_2$ has less impact on the microstructure of BTNb, BTIn and BTNbIn ceramics, because the annealing temperature in $N_2$ is lower than the sintering temperature in air.

Dielectric permittivity and loss tangent as a function of temperature are shown in Fig. 1. Two phase transitions, tetragonal-cubic and orthorhombic-tetragonal, are obviously observed in Fig. 1(a, e, i), corresponding to the temperature of $T_C$ and $T_{O-T}$, respectively. $T_C$ of BTIn, BTNb and BTNbIn are 117, 119 and 117 °C, respectively. $T_{O-T}$ of BTIn, BTNb and BTNbIn are 15, 25 and 19 °C, respectively. Compared to other two samples, $T_C$ peak of BTNb is a little broadened, illustrating the inhomogeneous nature of the microstructure. All the samples behave relatively lower dielectric loss (~0.02) at the room temperature, as shown in Fig. 1(b, f, j). After the sample is annealed in $N_2$, temperature dependent dielectric behavior of BTIn behaves nearly the same as the sample sintered in the air, as shown in Fig. 1(c, d). This is reasonable because for acceptor doped $BaTiO_3$, the defect reaction shown in Eq. (3) can hardly happen and quasi-free electron ($e'$) is not created after the sample is annealed in $N_2$. However, BTNb and BTNbIn show completely different behavior after annealed in $N_2$. As shown in Fig. 3(g, k), permittivity remarkably increases to a very high value and there is no distinct peak indicating $T_C$ and $T_{O-T}$. At the room temperature and 1 kHz, permittivity is up to 80,888 and 47,123 for BTNb and BTNbIn, respectively. The dielectric loss at the room temperature is 0.03 and 0.34 for BTNb and BTNbIn, respectively. Compared to other materials reported in literatures, dielectric properties of BTNb-$N_2$ has colossal permittivity and relatively lower dielectric loss, as well as good temperature stability in a broad temperature range, as shown in Table 1.

Fig. 2 shows permittivity and dielectric loss as a function of frequency for BTIn, BTNb and BTNbIn before and after annealed in $N_2$ at different temperatures. For BTIn, BTNb and BTNbIn, it is clear that two dielectric plateaus exist in the whole frequency ranges. With increasing the temperature, dielectric plateaus shift slightly to higher frequency region, revealing that the relaxation is related to the thermally activated process [9]. In general, the relaxation behavior at lower frequency can be attributed to the contribution from additional interfaces between electrode and sample, while the origin of the relaxation behavior at higher frequency can be attributed to the intrinsic contribution of the sample [20]. After annealed in $N_2$, BTNb-$N_2$ and BTNbIn-$N_2$ have a large increase in permittivity in the whole frequency region, which indicates that the CP behavior does not originate from an internal barrier layer capacitance (IBLC) effect which dominates in CCTO or NiO. A further important benefit which should be noticed is that a frequency-independent CP behavior can be achieved in BTNb-$N_2$ at the room temperature.

These results indicate that annealing in $N_2$ has a striking effect on the dielectric properties of donor ($Nb^{5+}$) and equivalent ($Nb^{5+}$ and $In^{3+}$) doped $BaTiO_3$. Since we have confirmed that annealing in $N_2$ has less impact on the microstructure of the samples, it is reasonable to predict that the main reason caused the large increase in permittivity of BTNb and BTNbIn after annealed in $N_2$ is ascribed to the defect dipoles. When BTNb and BTNbIn are annealed in $N_2$, oxygen vacancies are created and charge is balanced by the electronic compensation, as shown in defect reaction (3). Therefore, $(Ti^{4+}\cdot e' - V_O^{\bullet\bullet} - Ti^{4+}\cdot e')$ defect dipoles are formed, in which the electrons created by either $Nb^{5+}$ donor doping or electronic compensation due to oxygen loss, are in a quasi-free state and would be bound by $Ti^{4+}$ ions. Thus, some $Ti^{4+}$ ions could be reduced to $Ti^{3+}$ ions. Giant defect dipoles $(Ti^{4+}\cdot e' - V_O^{\bullet\bullet} - Ti^{4+}\cdot e')$ finally lead to the colossal permittivity in BTNb and BTNbIn, which have also been confirmed in literatures [6,9].

In order to evidence the proposed mechanism, XPS measurements were undertaken for BTNb annealed in $N_2$. All binding energies are referenced to the C 1 s neutral carbon peak, which is assigned the value of 284.6 eV to compensate for surface charge effects. The survey XPS spectrum of BTNb-$N_2$ is shown in Fig. 3(a), which indicates the samples contain Ba, Ti and Nb. Ti2p doublet with $2p_{3/2}$ and $2p_{1/2}$ binding energies of 457.6 eV and 463.3 eV, respectively, are clearly present in Fig. 3(b). The peak of Ti2$p_{3/2}$ can be fitted to a peak located at 457.5 eV and a shoulder located at 458.6 eV, which correspond to the characteristic peak of $Ti^{3+}$ [21] and $Ti^{4+}$ [22], respectively. As can be seen from Fig. 3, the intensity of $Ti^{3+}$ peak is larger than that of $Ti^{4+}$, indicating that $Ti^{3+}$ ions are formed easily when BTNb are sintered in $N_2$ at high temperatures. This phenomenon is also observed in $SrTiO_3$ after annealed in $N_2$ [9]. The O 1s profile is depicted in Fig. 3(c), which consists of a peak and a shoulder. The lower energy peak around 528.9 eV usually corresponds to the bulk Ti-O [23], while the shoulder appeared at 531.1 eV or even higher energies is assigned to the surface hydroxyl or oxygen vacancies [24]. This result indicates that oxygen loss is occurred when BTNb is annealed in $N_2$, as the Eq. (3).

To further explore the defect chemistry of Nb and In doped $BaTiO_3$, we measured EPR spectra of BTNb, BTIn, BTNbIn and BTNb-$N_2$ and compared their spectra, as seen in Fig. 4. In the spectra, the peak $g = 1.99$ can be assigned to oxygen vacancy ($V_O^{\bullet\bullet}$) [25] and the peak $g = 1.97$ can be assigned to barium vacancy ($V_{Ba}''$) [26]. It can be seen from Fig. 4 that oxygen vacancies are present in all the