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# Enhanced dielectric properties in (In, Nb) co-doped BaTiO<sub>3</sub> ceramics



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### 1. Introduction

BaTiO<sub>3</sub> (BT) is an invaluable material for multilayer ceramic capacitors (MLCCs) due to its superior dielectric properties of high dielectric constant and low dielectric loss [1]. However, these properties can only be achieved over a narrow temperature range around the ferroelectric phase transition. To overcome this shortcoming, doping with alien element(s) at Ba, Ti, or both sites [2,3] has been widely employed to develop BT-based materials for more reliable MLCCs. Recently, remarkable improvement of dielectric properties behavior was reported in trivalent-element (In<sup>3+</sup>) and pentavalent-element (Nb<sup>5+</sup>) co-doped rutile TiO<sub>2</sub> [4]. Since TiO<sub>2</sub> is a constituent raw material in BT, it implies that dual doping of In<sup>3+</sup> and Nb<sup>5+</sup> ions at Ti-site might have positive influence on the dielectric properties of BT. Actually, dual doping of Ga<sup>3+</sup>and Nb<sup>5+</sup> ions at Ti-site of BT revealed better dielectric properties [5]. Therefore, it will be interesting to see whether the (In, Nb) co-doping can improve the dielectric properties of BT ceramics as well. Our results showed that the doping leads to great enhancement of the dielectric properties. The mechanism of the enhancement was also discussed.

## 2. Experimental

The samples were synthesized by a solid-state reaction method using the starting materials of BaCO<sub>3</sub> ( $\geq$ 99.0%), TiO<sub>2</sub> ( $\geq$ 99.99%), Nb<sub>2</sub>O<sub>5</sub> ( $\geq$ 99.99%), and In<sub>2</sub>O<sub>3</sub> ( $\geq$ 99.99%). The powders were weighed according to the stoichiometry of BaTi<sub>(1-x)</sub>(In<sub>0.5</sub>Nb<sub>0.5</sub>)<sub>x</sub>O<sub>3</sub> (BINT;

## ABSTRACT

BaTi<sub>1-x</sub>(In<sub>0.5</sub>Nb<sub>0.5</sub>)<sub>x</sub>O<sub>3</sub> (x = 0, 0.01, and 0.03) ceramic samples were prepared using the conventional solid-state reaction method. The dielectric properties of these samples were investigated as a function of temperature (300 K  $\leq T \leq$  700 K) and frequency (10<sup>2</sup> Hz  $\leq f \leq$  10<sup>6</sup> Hz). Great enhancement of dielectric constant in the dual doped samples was found. Defect diploles of [Nb<sup>5+</sup><sub>Ti</sub> – Ti<sup>3+</sup>] and [Nb<sup>5+</sup><sub>Ti</sub> – In<sup>3+</sup><sub>Ti</sub>] were suggest to account for the enhancement of dielectric constant.

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x = 0, 0.01, and 0.03) and thoroughly mixed for 2 h using a mortar and then calcined in air at 1423 K for 4 h. The resultant powder was re-milled for 2 h and then pressed into pellets with a size of 14 mm in diameter and 1-2 mm in thickness. All pellets were sintered at 1623 K in air for 6 h. Phase purity of the sintered pellets was characterized by X-ray diffraction (XRD) on a Rigaku SmartLab diffractometer (Rigaku Smartlab Beijing Co, Beijing, China) with Cu Ka radiation. Microstructure and element mapping were studied by a field-emission scanning electric microscope (SEM, Model S-4800, Hitachi Co., Tokyo, Japan). X-ray photoelectron spectroscopy (XPS, Thermo-Fisher ESCALAB 250Xi) was used to analyze the valence state of O element. Dielectric properties were measured using a Wayne Kerr 6500B precise impedance analyzer (Wayne Kerr Electronic Instrument Co., Shenzhen, China) with the sample mounted in a holder placed inside a PST-2000HL dielectric measuring system (Partulab Co., Wuhan, China).

## 3. Results and discussion

Fig. 1(a) shows the XRD patterns of BINT ceramics. The pattern peaks for all samples can be indexed based on a perovskite structure with *P*4 mm space group, consisted with pure BT (JCPDS file No. 74-2491) without any unindexable peaks confirming the pure phase of the compounds. Compared to the pure BT, the reflections from BINT ceramics shift to lower 20 scales, as clearly seen from the expanded view of (111) peak shown in Fig. 1(b). This fact indicates that partial of the smaller Ti<sup>4+</sup> ions (0.64 Å) were replaced by larger In<sup>3+</sup> ions (0.80 Å), leading to the increasement in lattice constant. As a result, the splitting of peaks was getting closer with increasing doping level.







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Fig. 1. (a) XRD patterns of BINT ceramics and (b) the expanded view of (111) peak.

In order to characterize the distribution of In<sup>3+</sup> and Nb<sup>5+</sup> in the matrix, elemental mapping of all samples were performed. Fig. 2 shows, as an emblematic case, the SEM image and elemental mapping of 3%BINT. Similar to those found in (In, Nb) co-doped TiO<sub>2</sub> [6], our results reveal that the In and Nb ions homogeneously distribute in the grains and grain boundaries. The temperature (T)dependence of the dielectric constant  $(\varepsilon')$  and dielectric loss tangent  $(\tan \delta)$  for BINT ceramics recorded at 100 Hz are shown in Fig. 3(a) and (b), respectively. Compared to BT ceramics, significant enhancement in dielectric constant was found in BINT. Meanwhile, the Curie temperature  $(T_c)$  decreases with increasing doping level. A clear cut correlation between the Curie temperature and the doping level is seen [inset of Fig 3(a)]. The reduction of  $T_c$  may related to the screening effect of electrons in the semiconducting BINT and can usually be rationalized on the basis of ion-size tolerance factor effects [7]. Moreover, with the increase of doping amount, the dielectric peak is obviously broadened; indicating that lowering the value of  $T_{C}$  is beneficial for improving the temperature stability of dielectric constant. The loss tangent of the pure sample shows a plateau-like behavior indicative of intrinsic behavior in the temperature range below ~500 K. Beyond this range, a pronounced peak occurs. Detailed investigations reveal that the peak is related to a thermally activated dielectric relaxation caused by oxygen vacancies [results not shown]. Dual doping increases the loss tangent values in the intrinsic range and decreases the values in the relaxation range. The frequency dependence of the dielectric constant and dielectric loss tangent (inset) for BINT ceramics recorded at room temperature are shown in Fig. 3(c). Compared to pure BT ( $\varepsilon' \sim 10^3$ ), 1%BINT shows colossal dielectric constant (CDC) ( $\varepsilon' > 10^4$ ) with faint frequency dependence in a wide frequency range of  $10^2 \sim 10^6$  Hz. Although 3%BINT also shows CDC behavior, a rapid low-frequency increase in dielectric constant and loss tangent is observed, indicating that the Maxwell–Wagner relaxation has contribution to the CDC behavior.

In order to obtain further information about (In, Nb) co-doping, we performed impedance and XPS measurements. For brevity, the following discussion mainly focus on 1%BINT sample. Fig. 4 (a) shows the complex impedance plots recorded at different temperatures. The plots display semicircular arcs, which can be well fitted by two *R*-CPE (R = resistor, CPE = constant phase element) circuits connected in series (lower inset) with one for the grain and the other for the grain boundary. The fitting results (solid curves) were also shown in the figure. It is seen that perfect fittings were achieved. The resulting resistances of grain and grain boundary were found to obey the Arrhenius law:

$$R = R_0 \exp(-E_a/k_B T) \tag{1}$$

where  $R_0$  is a constant,  $E_a$  is activation energy, and  $k_B$  is Boltzmann constant. The upper inset of Fig. 4 (a) displays the Arrhenius plots for grain and grain boundary. Linear fittings yield the values of  $E_a$  for the grain and grain boundary were listed in Table 1. The activation energy of both grain and grain boundary decreases with increasing the doping concentration.

Fig. 4 (b) shows the XPS spectra and corresponding fitting results of O 1s for 1% BINT sample, The spectra can be fitted with two Gaussian peaks denoted as A1 and A2 peaks at 530.6 and 529.18 eV corresponding to vacancy and lattice oxygen, respectively [8]. The area ratio of A1/A2 for all samples was given in



Fig. 2. SEM image of 3%BINT (a) and corresponding element mapping image of overall (b), In (c), and Nb (d). The bar is 50 µm.



Fig. 3. Temperature dependence of dielectric permittivity (a), loss tangent (b), and relationship of Curie temperature with doping concentration (inset) for BINT ceramics. (c) Frequency dependence of the dielectric permittivity and loss tangent (inset) for BINT ceramics measured at room temperature.



**Fig. 4.** (a) Complex impedance plots and corresponding fitting results (solid curves) of 1%BINT. The lower inset is the equivalent circuits for fittings and the upper inst is the Arrhenius plots for grain and grain boundary resistances deduced from the fittings. (b) XPS and corresponding fitting (solid curves) results of 0 1 s for 1% BINT.

**Table 1** The parameters of  $E_a$  and A1/A2 of BINT samples.

Doping level ( <i>x</i> )	$E_{\rm a}$ (eV) for grain	$E_{\rm a}$ (eV) for grain boundary	A1/A2
0 0.01 0.03	0.77 0.29	1.02 0.52	0.988
0.05	0.11	0.57	0.050

Table 1. It is clearly seen that the ratio notably decreases with increasing doping initially and trends to a saturated value with further increasing the doping level. This fact indicates that Nb<sup>5+</sup> ions substitute for the Ti<sup>4+</sup> ions acting as donors that effectively inhibit the formation of oxygen vacancies. Therefore, the donor doping can suppress the relaxation and reduce the loss tangent values in the relaxation range. On the other hand, the In<sup>3+</sup> ions doping on the Ti-site server as acceptors, which is beneficial for the formation of oxygen vacancies. The competition of the two opposite effects leads to the saturated concentration of oxygen vacancies. Besides, the donor doping leads to high conductivity due to Nb<sup>5+</sup> gives an electron to Ti<sup>4+</sup>, which in turn, changes to Ti<sup>3+</sup>. Since the conductivity ity also has contribution to dielectric loss, this is the reason why the doped samples show relatively high dielectric loss in the intrinsic range.

Based on the above results, the mechanism of enhanced dielectric properties in (In, Nb) co-doped samples can be reasonably explained. When Nb<sup>5+</sup> ions enter into the Ti site, they will be surrounded by six Ti<sup>4+</sup> ions [9]. One of them changes to Ti<sup>3+</sup> ion due to charge compensation, yielding the defect dipoles of  $[Nb_{Ti}^{5+} - Ti^{3+}]$  [9]. Meanwhile, the acceptor doping of In<sup>3+</sup> creates another defect dipoles of  $[Nb_{Ti}^{5+} - In_{Ti}^{3+}]$  [10]. Both kinds of dipoles lead to the enhancement of dielectric properties in (In, Nb) co-doped samples.

## 4. Conclusions

The effects of (In, Nb) co-doping on the dielectric properties of BaTiO<sub>3</sub> were investigated in temperature range of 300–700 K and frequency range of  $10^2-10^6$  Hz. The dual doping leads to (1) lower Curie temperature, (2) improved dielectric constant, (3) higher conductivity, and (4) reduced concentration of oxygen vacancies. The first effect can be understood based on the ion-size tolerance factor mechanism. The second effect is due to the formation of defect dipoles of  $[Nb_{Ti}^{5+} - Ti^{3+}]$  and  $[Nb_{Ti}^{5+} - In_{Ti}^{3+}]$ . The third and fourth effects are caused by the donor doping of Nb<sup>5+</sup> ions.

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## References

- [1] S. Krohns, P. Lunkenheimer, S. Meissner, et al., The route to resource-efficient novel materials, Nat. Mater. 10 (2011) 899–901.
- [2] W. Cai, C.L. Fu, Z.B. Lin, X.L. Deng, Vanadium doping effects on microstructure and dielectric properties of barium titanate ceramics, Ceram. Int. 37 (2011) 3643–3650.
- [3] D.Y. Lu, S.Z. Cui, Q.L. Liu, X.Y. Sun, Dielectric properties and defect chemistry of barium titanate ceramics co-doped R and Dy ions (R=Eu, Gd, Tb), Ceram. Int. 42 (2016) 14364–14373, and references therein.
- [4] W.B. Hu, Y. Liu, R.L. Withers, et al., Electron-pinned defect-dipoles for highperformance colossal permittivity materials, Nat. Mater. 12 (2013) 821–826.
- [5] Y. Wu, J.Y. Miao, Z.F. Liu, Y.X. Li, Colossal permittivity and dielectric relaxations in BaTi<sub>0.99</sub>(Nb<sub>0.5</sub>Ga <sub>0.5</sub>)<sub>0.02</sub>O<sub>3</sub> ceramics, Ceram. Int. 41 (2015) S846–S850.

- [6] J.L. Li, F. Li, Y.Y. Zhuang, et al., Microstructure and dielectric properties of (Nb + In) co-doped rutile TiO<sub>2</sub> ceramics, J. Appl. Phys. 116 (2014) 074105.
- [7] L.B. Ben, D.C. Sinclair, Anomalous Curie temperature behavior of A-site Gddoped BaTiO<sub>3</sub> ceramics: The influence of strain, Appl. Phys. Lett. 98 (2011) 092907.
- [8] X.J. Xi, S.Y. Wang, W.F. Liu, et al., Enhanced magnetic and conductive properties of Ba and Co co-doped BiFeO<sub>3</sub> ceramics, J. Magn. Mater. 355 (2014) 259–264.
- [9] V.V. Lemanov, A.V. Sotnikov, E.P. Smirnova, M. Weihnacht, Giant dielectric relaxation in SrTiO<sub>3</sub>-SrMg<sub>1/3</sub>Nb<sub>2/3</sub>O<sub>3</sub> and SrTiO<sub>3</sub>-SrSc<sub>1/2</sub>Ta<sub>1/2</sub>O<sub>3</sub> solid solutions, Phys. Solid State 44 (2002) 2039–2049.
- [10] Z.C. Cai, Z.X. Cheng, X.L. Wang, et al., A colossal dielectric constant of an amorphous TiO<sub>2</sub>:(Nb, In) film with low loss fabrication at room temperature, J. Mater. Chem. C. 2 (2014) 6790–6795.