DEFECT CHEMISTRY AND LOW-LOSS CHARACTERISTICS OF ND-DOPED BATiO₃ DIELECTRIC CERAMICS

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ABSTRACT

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(Ba_{1-x}Nd_x)Ti_{1-x/4}O₃ ($x = 0.03-0.06$) (BNT) ceramics with a single-phase perovskite structure were prepared using the mixed-oxides method. The structure, microstructure, point defects, defect chemistry, and dielectric properties of these ceramics were investigated using X-ray diffraction, scanning electron microscopy, electron paramagnetic resonance, and dielectric measurements. Except for BNT with $x = 0.04$, all BNT ceramics are semiconductors because of the strong doping effect from A-site Nd³⁺. The defect chemistry is given. The highest concentrations of Ti vacancies and the intense reduction from Mn³⁺ or Mn⁴⁺ to Mn²⁺ as well as a small amount of Ba vacancies in BNT with $x = 0.04$ are responsible for low dielectric loss (< 0.05) over the temperature range -50 to 150 °C.

KEYWORDS

Nd-doped BaTiO₃ ceramics, X-ray diffraction, dielectric properties, defect chemistry, electron paramagnetic resonance

1. INTRODUCTION

In the dielectric field, Neodymium (Nd) is an effective rare-earth dopant in BaTiO₃ ceramics. Nd-doped BaTiO₃ ceramics with single substitution and with double substitutions have been widely investigated [1-9]. It is generally considered that Nd³⁺ is predominantly substituted for the A-site, whereas a self-compensation model in (Ba_{1-x}Nd_x)(Ti_{1-x}Nd_x)O₃ with Ba/Ti = 1 and a slight amphoteric behavior of Nd³⁺ in (Ba_{1-x}Nd_x)(Ti_{1-x}Ho_x)O₃ were discovered [1-9]. It is obvious that Nd³⁺ favors the A-site over the B-site because of its larger B-site ionic size (Table 1) [10]. However, the defect chemistry of Nd-doped BaTiO₃ ceramics has never reported.

Table 1: Ionic radii as a function of coordinate number (CN) [11].

Ion	CN	r (Å)
Ba ²⁺	12	1.61
Ti ⁴⁺	6	0.605
Nd ³⁺	12	1.27
Nd ³⁺	6	0.983

In this work, (Ba_{1-x}Nd_x)Ti_{1-x/4}O₃ ceramics were prepared using a mixed-oxide method. The defect chemistry is studied. It was found that the dielectric loss was depressed at $x = 0.04$ in terms of the kinetic equilibrium of various defects.

2. EXPERIMENTAL

2.1 Sample Preparation

The initial materials were reagent-grade BaCO₃, TiO₂, and Nd₂O₃. BNT ceramics were prepared according to the nominal formula of (Ba_{1-x}Nd_x)Ti_{1-x/4}O₃ ($x = 0.03, 0.04, 0.05$, and 0.06) using a conventional mixed-oxide method. The well-mixed oxides were calcined at 1100 °C for 5 h. The mixtures with aqueous PVA were ground and pressed uniaxially at 200

MPa into disk-like pellets of 12 mm in diameter. The disks were heated at a rate of 100 °C/h and sintered at 1450 °C for 24 h in air to form ceramics, and then furnace-cooled to room temperature (RT).

2.2 Characterization

Powder X-ray diffraction (XRD) patterns were measured at RT using a DX-2700 X-ray diffractometer (Dandong Haoyuan). All XRD data were collected between $20^\circ \leq 2\theta \leq 85^\circ$ in steps of 0.02° and for 3 s per step. The lattice parameters and unit-cell volumes were calculated by a software package (Accelrys Inc.) using Cu K α_1 radiation ($\lambda = 1.540562$ Å). The microstructures were observed using a JSM-6330F scanning electron microscope (SEM, JEOL) operated at 15 kV. The average grain size (GS) was determined using Fullman's method [11]. The temperature dependences of the dielectric permittivity and the dielectric loss were measured at 1 kHz from -75 to 200 °C at a heating rate of 2 °C/min using a Concept 41 Dielectric/Impedance spectrometer (Novocontrol) with an applied voltage of 1 V. Electron paramagnetic resonance (EPR) spectra were measured at RT using an A300 electron-spin resonance spectrometer system (Bruker BioSpin GMBH) at an X-band frequency of 9.86 GHz. The gyromagnetic factor (g) was calculated by the relationship $h\nu_0 = g\beta H$, where h is the Planck constant ($h = 6.626 \times 10^{-34}$ J·s), ν_0 is the microwave frequency, β is the Bohr magneton ($\beta = 9.262 \times 10^{-24}$ J/T), and H is the magnetic field strength.

3. RESULTS AND DISCUSSION

Powder XRD patterns of BNT ceramics are shown in Figure 1. BNT exhibited a tetragonal perovskite structure at $x \leq 0.04$ and a pseudo-cubic perovskite structure at $x \geq 0.05$. The miller indexes corresponding to the diffraction peaks of the tetragonal and cubic structures are given in Figure 1 (a). The (002)/(200) peak splitting is characteristic of the tetragonal BaTiO₃ (JCPDS cards No. 5-626). With the increase of x , it can be seen from Figure 1 (b) that two separate (002) and (200) peaks of BNT shift towards each other from 0.03 to 0.04 , indicating a decrease in tetragonality. As x is increased to 0.05 , these two peaks are incorporated into a symmetric (200) peak characteristic of the cubic BaTiO₃ (JCPDS cards No. 31-174).

The variations in lattice parameters (a , c) and unit-cell volume (V_0) as functions of x for BNT are shown in Fig. 2. The V_0 decreases with increasing x , following Vegard's law in the region from $x = 0.03$ to 0.05. On the basis of a comparison in 12-CN ionic size between Ba^{2+} (1.61 Å) and Nd^{3+} (1.27 Å) and in 6-CN ionic size between Ti^{4+} (0.605 Å) and Nd^{3+} (0.983 Å), the

decrease in V_0 provides evidence for the main occupations of the A-sites by Nd^{3+} [10]. It is not easy for 6-CN Nd^{3+} (0.983 Å) to enter B-site because of its larger ionic size as compared to Ti^{4+} .

Figure 1: (a) Powder XRD patterns of $(\text{Ba}_{1-x}\text{Nd}_x)\text{Ti}_{1-x/4}\text{O}_3$ ($x = 0.03\text{--}0.06$) (BNT) ceramics sintered at $T_s = 1450^\circ\text{C}$. (b) Gaussian fitting to the peaks in the vicinity of 45° .

Figure 2: Variations in lattice parameters (a , c) and unit-cell volume (V_0) as functions of x for BNT

Figure 3: SEM images of the polished and thermally etched surfaces of BNT with $x =$ (a) 0.04, (b) 0.05, and (c) 0.06.

The SEM images of BNT are shown in Figure 3. BNT exhibits a non-uniform microstructure, with an average grain size of $\sim 3 \mu\text{m}$. This indicates that Nd doping in BaTiO_3 cannot greatly suppress grain growth. The lamellar domain structures characteristic of ferroelectric phase were observed to exist in all BNT samples, as clearly observed at $x = 0.04$. This fact reveals that the crystalline structure of BNT with $x \geq 0.05$ is pseudo-cubic.

The temperature dependences of the dielectric permittivity (ϵ') and the

dielectric loss ($\tan \delta$) for BPT are shown in Figure 4. The main dielectric peak corresponds to the tetragonal-cubic phase transition point. The dielectric-peak temperatures (T_m) are 66°C at $x = 0.03$ and 51°C at $x = 0.04$, indicating a T_m -shifting rate of $-15^\circ\text{C/at.}\%$ Nd. This rate is far lower than that reported by Shaikh and Vest ($-22^\circ\text{C/at.}\%$ Nd) [5]. This suggests that some Nd^{3+} ions entered the B-sites except for dominant A-site substitutions, because B-site occupations by Nd^{3+} will give rise to a much lower T_m -shifting rate [6].

Figure 4: Temperature dependences of (a) ϵ' and (b) $\tan \delta$ at 1 kHz for BNT with $x = 0.03, 0.04$, and 0.06 .

The T_2 corresponds to the orthorhombic-tetragonal phase transition point, indicating a decreased T_2 as compared to BaTiO_3 ($T_2 = 130^\circ\text{C}$) [12]. This peak vanishes at $x \geq 0.04$, implying incomplete occupations by A-site Nd^{3+} . BNT ceramics with $x = 0.03$ and $x \geq 0.05$ are semiconductors because of their high values of $\tan \delta > 0.15$. Their semi-conducting nature arises from the strong doping effect from A-site Nd^{3+} , which relates to a higher sintering temperature of 1400°C and long-term sintering for 24 h. The $x = 0.04$ sample exhibits a higher room-temperature permittivity of $\epsilon'_{\text{RT}} = 6955$ and a lower $\tan \delta (< 0.05)$ over the temperature range -50 to 150°C (Figure 5). The sample is not a semiconductor, rather than a common ferroelectric.

Figure 5: Enlarged ϵ' - T and $\tan \delta$ - T curves for BNT with $x = 0.04$.

To understand the origin of lower $\tan \delta$ of BNT with $x = 0.04$, the EPR spectra of all BNT samples was measured, as shown in Fig. 6. Three EPR signals were observed at $x = 0.03$. A sextet signal arises from Mn^{2+} impurities existing in ceramics. The second and third ones at $g = 2.004$ and 1.974 originates from ionized Ti-vacancy (V_{Ti}) and Ba-vacancy (V_{Ba}),

respectively [13–15]. As x is increased to 0.04 , the intensity of both V_{Ti} -related and Mn^{2+} signals evidently increases, whereas that of the V_{Ba} -related signal decreases and subsequently it disappears at $x \geq 0.05$; at the same time, both V_{Ti} -related and Mn^{2+} signals become very weak.

Figure 6: EPR spectra of BNT, measured at room temperature.

On the basis of nominal compositions $(\text{Ba}_{1-x}\text{Nd}_x)\text{Ti}_{1-x/4}\text{O}_3$, the persistent existence of V_{Ti} implies dominant occupations of the A-sites by Nd^{3+} in BNT, which can not only contribute to creation of V_{Ti} (Eq. (1)) but also to the unwelcome doping effect (Eq. (2)).

Defect notation proposed by Kröger and Vink are adopted [16].

In BaTiO_3 -based ceramics, Mn impurities generally exist in the high valence states of Mn^{3+} or Mn^{4+} . The reduction from Mn^{3+} or Mn^{4+} to Mn^{2+} induced by the Nd^{3+} doping plays an important role in trapping electrons created by the doping effect (Eq. (1)) and therefore can reduce the dielectric loss.

The existence of the V_{Ba} -related signal at $x \leq 0.04$ reveals that some Nd^{3+} ions transfer from A-sites to B-sites, in accordance with the dielectric behavior.

The point defects in BNT with $x = 0.04$ are A-site Nd^{3+} (Nd_{Ba}'), Ba vacancies (V_{Ba}''), B-site Nd^{3+} (Nd_{Ti}'), and Ti vacancies (V_{Ti}'''). This sample has the highest concentrations of Ti vacancies and Mn^{2+} as well as a small amount of Ba vacancies, which are responsible for its low dielectric loss.

4. CONCLUSIONS

The nominal $(Ba_{1-x}Nd_x)Ti_{1-x/4}O_3$ ($x = 0.03-0.06$) ceramics were prepared at $1450^\circ C$ for 24 h in air using the mixed-oxide method. BNT exhibited a tetragonal perovskite structure at $x \leq 0.04$ and a pseudo-cubic perovskite structure at $x \geq 0.05$. BNT with $x = 0.03$ and $x \geq 0.05$ are semiconductors because of the strong doping effect from A-site Nd^{3+} . The defect chemistry is given. BNT with $x = 0.04$ is a common ferroelectric, showing higher ϵ'_{RT} ($= 6955$) and lower $\tan \delta$ (< 0.05) over the temperature range -50 to $150^\circ C$; the highest concentrations of Ti vacancies and the intense reduction from Mn^{3+} or Mn^{4+} to Mn^{2+} as well as a small amount of Ba vacancies are responsible for low dielectric loss.

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REFERENCES

[1] Liu, Q., Liu, J., Lu, D., Zheng, W. 2018. Colossal dielectric behavior and relaxation in Nd-doped $BaTiO_3$ at low temperature. *Ceramics International*, 44 (6), 7251-7258.

[2] Jena, H., Mittal, V.K., Bera, S., Narasimhan, S.V., Govindan Kutty, K.V., Kutty T.R.N. 2008. X-ray photoelectron spectroscopic investigations on cubic $BaTiO_3$, $BaTi_{0.9}Fe_{0.1}O_3$ and $Ba_{0.9}Nd_{0.1}TiO_3$ systems. *Applied Surface Science*, 254 (21), 7074-7079.

[3] Yao, Z., Liu, H., Liu, Y., Wu, Z., Shen, Z., Liu, Y., Cao, M. 2008. Structure and dielectric behavior of Nd-doped $BaTiO_3$ perovskites. *Materials Chemistry and Physics*, 109 (2-3), 475-481.

[4] Kutty, T.R.N., Murugaraj, P. 1987. Phase relations and dielectric properties of $BaTiO_3$ ceramics heavily substituted with neodymium. *Journal of Materials Science*, 22, 3652-3664.

[5] Shaikh, A.S., Vest, R.W. 1986. Defect structure and dielectric properties Nd_2O_3 -modified $BaTiO_3$. *Journal of the American Ceramic Society*, 69 (9), 689-694.

[6] Hirose, N., Skakle, J.M.S., West, A.R. 1999. Doping mechanism and permittivity correlations in Nd-doped $BaTiO_3$. *Journal of Electron ceramics*, 3, 233-238.

[7] Ghosh, S.K., Ganguly, M., Rout, S.K., Chanda, S., Sinha, T.P. 2014. Structural, optical and dielectric relaxor properties of neodymium doped cubic perovskite $(Ba_{1-x}Nd_{2x/3})(Zr_{0.3}Ti_{0.7})O_3$. *Solid State Science*, 30, 68-77.

[8] Wei, M., Zhang, J., Wu, K., Chen, H., Yang, C. 2017. Effect of $BiMO_3$ ($M=Al, In, Y, Sm, Nd$, and La) doping on the dielectric properties of $BaTiO_3$ ceramics. *Ceramics International*, 43 (13), 9593-9599.

[9] Lu, D., Guan, D., Li, H. 2018. Multiplicity of photoluminescence in Raman spectroscopy and defect chemistry of $(Ba_{1-x}R_x)(Ti_{1-x}Ho_x)O_3$ ($R = La, Pr, Nd, Sm$) dielectric ceramics. *Ceramics International*, 44 (2), 1483-1492.

[10] Shannon, R.D. 1976. Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallogr. Sect A* 32, 751-767.

[11] Dieter, G.E. 1988. *Mechanical Metallurgy*. London, McGraw-Hill.

[12] Lu, D., Toda, M., Sugano, M. 2006. High-permittivity double rare-earth-doped barium titanate ceramics with diffuse phase transition. *Journal of the American Ceramic Society*, 89 (10), 3112-3123.

[13] Kolodiazny, T., Petric, A. 2003. Analysis of point defects in polycrystalline $BaTiO_3$ by electron paramagnetic resonance, *Journal of Physics and Chemistry of Solids*, 64, 953-960.

[14] Dunber, T.D., Warren, W.L., Tuttle, B.A., Randall, C.A., Tsur, T. 2004. Electron paramagnetic resonance investigation of lanthanide-doped barium titanate: dopant site occupancy. *The Journal of Physical Chemistry B*, 108, 908-917.

[15] Lu, D., Cui, S. 2014. Defects characterization of Dy-doped $BaTiO_3$ ceramics via electron paramagnetic resonance. *Journal of European Ceramic Society*, 34 (10), 2217-2227.

[16] Kröger, F.A., Vink, H.J. 1956. Relations between the Concentrations of Imperfections in Crystalline Solids. In Seitz, F. & Turnbull, D. (Eds.), *Solid State Physics* (p. 307). New York: Academic Press.