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High permittivity neodymium-doped barium titanate sintered in pure nitrogen

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Abstract

This paper investigated the resistivity and dielectric properties of neodymium-doped $BaTiO_3$. The influence of variable doping concentration and Ba/Ti ratio on densification, microstructure, resistivity and dielectric properties was studied profoundly. A new dielectric with high permittivity of 3,00,000 and low dissipation factor of 0.05 measured at 1 kHz, meeting the EIA X8R temperature characteristic was obtained in this study. Resistivity of the material was $10^9\ \Omega$ cm orders of magnitude. The starting material was hydrothermally synthesized $BaTiO_3$, the sintering atmosphere was pure nitrogen. When Ba/Ti ratio was identical, with neodymium concentration increasing, the apparent density decreased, sintering shrinkage of ceramic becomes smaller and ceramic is less dense, resistivity decreased, dielectric constant decreased and dielectric loss increased. Whereas when doping concentration was fixed, with Ba/Ti ratio increasing, the grain size of ceramic becomes smaller and ceramic was denser, resistivity decreased, dielectric constant increased and dissipation factor decreased.

Keywords: C. Dielectric properties; D. Barium titanate; Resistivity; Neodymium; Pure nitrogen

1. Introduction

There are many papers presenting the doping mechanism and doping effects of barium titanate. With the development of base metal inner electrode multilayer ceramic capacitor (BME-MLCCs), defect chemistry of barium titanate was studied profoundly [1–5]. During the investigation on anti-reduction ceramic dielectric of barium titanate, Ba/Ti ratio, doping ion radius and valence and oxygen partial pressure are the three key factors to influence the doping mechanism and defect structure of barium titanate [6–9].

The ionic radius of neodymium is 0.0983 nm, almost exactly at midway between those of Ti (0.0605 nm) and Ba (0.135 nm) [10]. Nd appears to substitute equally at both Ba and Ti sites. Shaikh and Vest [11] reported that neodymium occupies barium sites and charge compensation takes place by creation of titanium vacancies, and the Curie temperature (T_c) of $BaTiO_3$ decreased drastically with addition of Nd_2O_3. Whereas Hirose et al. [12] reported a double substitution mechanism: Ba + Ti $\Rightarrow$ 2Nd, and the sharp permittivity maximum at $\sim$127 °C in stoichiometric $BaTiO_3$ broadens very rapidly with doping amount of Nd_2O_3 and gradually moves to lower temperatures.

In this paper, with control of Ba/Ti $\geq$ 1, we hope that neodymium occupies Ti sites as an acceptor. The influence of variable doping concentration and Ba/Ti ratio on densification, microstructure, resistivity and dielectric properties for neodymium-doped $BaTiO_3$ were studied.

2. Experimental procedure

The formulations of samples were prepared according to Table 1.

Sample preparation was performed by conventional powder processing method, including ball milling, drying, uniaxially pressing and sintering in pure nitrogen. The starting materials were hydrothermally synthesized $BaTiO_3$ and highly pure oxides (reagent grade), Nd_2O_3, $Ba(COOH)_2$. Before mixing with the dopants, the hydrothermal $BaTiO_3$ was calcinated at 1000 °C to remove water and defects within it. The doped oxides and calcinated hydrothermal $BaTiO_3$ were mixed by wet ball milling using deionized water and ZrO_2 balls (ϕ = 3 mm), then fired at 950 °C for 2 h to promote the diffusion of dopants. The calcined powder was

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Table 1
Compositions, densities and resitivities of samples

Sample	Composition	Density (g/cm^3)	Resistivity (Ω cm)
BTNd1	$Ba_{1.005}(Ti_{0.99}Nd_{0.01})O_{2.995}$	5.674	6.33×10^9
BTNd2	$Ba_{1.01}(Ti_{0.99}Nd_{0.01})O_3$	5.808	4.78×10^9
BTNd3	$Ba_{1.005}(Ti_{0.98}Nd_{0.02})O_{2.985}$	5.621	3.93×10^9
BTNd4	$Ba_{1.01}(Ti_{0.98}Nd_{0.02})O_{2.99}$	5.542	3.56×10^9

then uniaxially pressed into disks with 10 mm in diameter and about 1 mm in thickness. And then the disks were fired in pure nitrogen at various temperatures after the binder was burned out in air. After sintering, silver electrode was coated on both sides of specimens for electrical measurements. Then, the samples with silver electrode were calcined at 520 °C in air. Microstructures of ceramics were studied on the as-fired surfaces of the sintered ceramics using SEM (JEOL 5510LV) with an accelerating voltage of 10 kV.

Dielectric properties of sintered disk were measured from −60 to 160 °C with an impedance analyzer LCR (HP 4284A) at frequency of 1 kHz and oscillation level of 1 V rms. The heating rate was 2 °C/min and the accuracy was 0.1 °C.

After sintering, apparent densities of samples were determined by the Archimedes method. Insulation resistivity was investigated by means of a high resistance meter (Keithley 6517A) using alternating polarity resistance test method. The alternating polarity resistance was designed to improve high resistance measurements and it was possible to eliminate the effects of the background currents. The test voltage was 100 V.

3. Results and discussion

3.1. Sintering density

Densities of neodymium-doped $BaTiO_3$ fired in pure nitrogen were showed in Table 1. As can be seen from Table 1, when Ba/Ti ratio was fixed, the apparent density decreased with neodymium concentration increasing. Samples with Ba/Ti ratio 1.01 and doping concentration 1 at.% had the highest density, and samples with Ba/Ti ratio 1.01 and doping concentration 2 at.% had the lowest density.

3.2. Microstructure development

Fig. 1 illustrates the SEM morphology of as-fired ceramics sintered at 1250 °C with a soak time 2 h in pure nitrogen. As can be seen from Fig. 1, with doping concentration increasing, the sintering shrinkage of ceramic becomes smaller and ceramic is less dense. When doping concentration was equal to 1 at.%, with Ba/Ti ratio increasing, the grain size of ceramic becomes smaller and ceramic was denser. Samples with Ba/Ti ratio 1.005 and doping concentration 1 at.% had abnormal grain growth. This agrees well with the apparent density measurement.

3.3. Resistivity properties of as-fired ceramics

Resistivities of four compositions were listed in Table 1, the sintering atmosphere was nitrogen and sintering temperature was 1250 °C with a hold time 2 h. As can be seen from Table 1, when Ba/Ti ratio was fixed, resistivity decreased

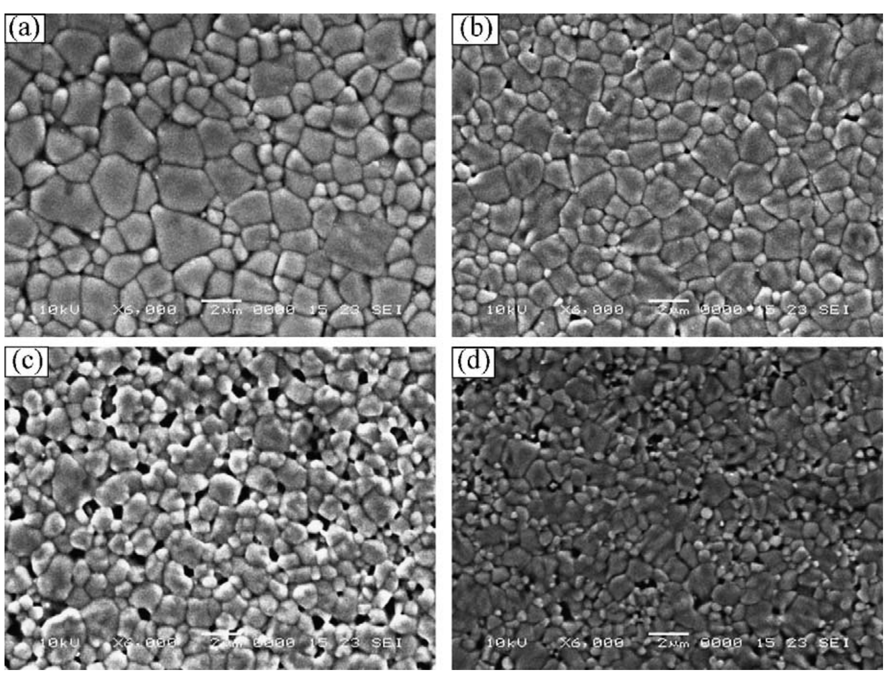

Fig. 1. SEM morphology of as-fired ceramics sintered at 1250 °C with a soak time of 2 h in pure nitrogen: (a) BTNd1, (b) BTNd2, (c) BTNd3 and (d) BTNd4.

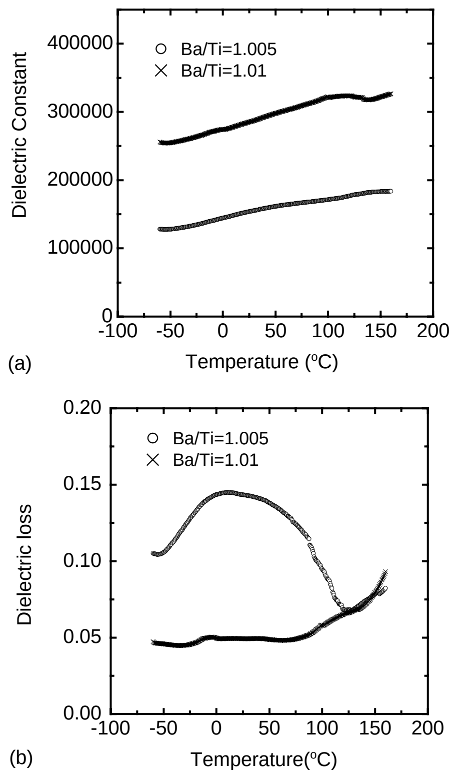

Fig. 2. Influence of Ba/Ti ratio on the dielectric properties for samples Nd (1 at.%) in Ti site (test frequency is 1 kHz).

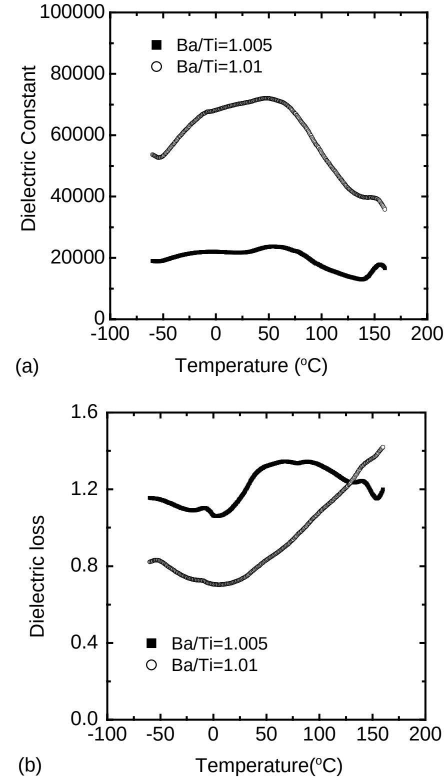

Fig. 3. Influence of Ba/Ti ratio on the dielectric properties for samples Nd (2 at.%) in Ti site (test frequency is 1 kHz).

with doping concentration increasing, and when doping concentration was identical, resistivity decreased with Ba/Ti ratio increasing. But all compositions had resistivities of 10^9 orders of magnitude.

3.4. Dielectric properties of as-fired ceramics

Fig. 2 shows the influence of Ba/Ti ratio on the dielectric properties for samples Nd (1 at.%) in Ti site. As can be seen from Fig. 2, with Ba/Ti ratio increasing, dielectric constant increased and dissipation factor decreased. When Ba/Ti ratio was equal to 1.005, the dielectric constant was about 1,50,000 and the dissipation factor was 0.15. Whereas, when Ba/Ti ratio was equal to 1.01, the dielectric constant was up to 3,00,000 and the dissipation factor was 0.05. It can be found that Ba/Ti ratio has an important influence on the dielectric properties of neodymium-doped $BaTiO_3$.

Fig. 3 illustrates that the influence of Ba/Ti ratio on the dielectric properties for samples Nd (2 at.%) in Ti site. As can be seen from Fig. 3, just like samples Nd (1 at.%) in Ti site, with Ba/Ti ratio increasing, dielectric constant increased and dissipation factor decreased. When Ba/Ti ratio was equal to 1.005, the dielectric constant was about 20,000 and the dissipation factor was 1.2. Whereas, when Ba/Ti ratio was equal to 1.01, the dielectric constant was up to 70,000 and the dissipation factor was 0.8.

Compare Fig. 2 with Fig. 3, it can be found that doping concentration had a crucial effect on the dielectric properties. With doping concentration increasing, the dielectric constant decreased drastically and dielectric loss increased a lot simultaneously.

Fig. 4 shows temperature coefficient of capacitance for samples Nd-doped $BaTiO_3$ sintered in pure nitrogen. All the four compositions had good capacitance–temperature coefficient: BTNd1, BTNd2, BTNd3 and BTNd4 satisfy X7R, X8R, X5R and Y5V specifications of EIA, respectively. Especially, composition BTNd2 had high dielectric constant,

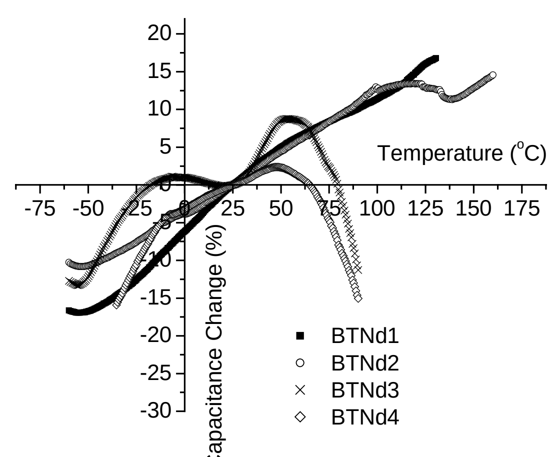

Fig. 4. Temperature coefficient of capacitance for samples Nd-doped $BaTiO_3$ sintered in pure nitrogen (test frequency is 1 kHz).

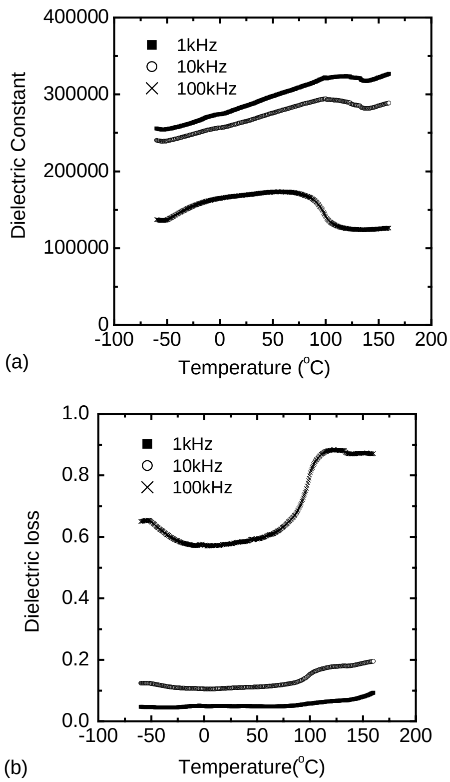

Fig. 5. Temperature dependence of the dielectric constant and dielectric loss in disk specimen (BTNd2) sintered in pure nitrogen.

3,00,000 and low dissipation factor, 0.05. And its temperature coefficient of capacitance satisfies X8R specification of EIA. The permittivity of BTNd2 dispersed with frequency, as can be seen from Fig. 5.

4. Conclusions

A new dielectric with high permittivity of 3,00,000 and low dissipation factor of 0.05, meeting EIA X8R temperature characteristic was obtained in this study. And its resistivity was 10^9 orders of magnitude. The starting material was hydrothermally synthesized $BaTiO_3$ powder and the sintering atmosphere was pure nitrogen.

When Ba/Ti ratio was identical, with neodymium concentration increasing, the apparent density decreased, sintering shrinkage of ceramic becomes smaller and ceramic is less dense, resistivity decreased, dielectric constant decreased and dielectric loss increased. Whereas, when doping concentration was fixed, with Ba/Ti ratio increasing, the grain size of ceramic becomes smaller and ceramic was denser, resistivity decreased, dielectric constant increased and dissipation factor decreased.

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References

[1] J. Daniels, K.H. Härdtl, D. Hennings, R. Wernicke, Defect chemistry and electrical conductivity of doped barium titanate ceramics, Philips Res. Rep. 31 (6) (1976) 487–559.
[2] Y.H. Han, J.B. Appleby, D.M. Smyth, Calcium as an acceptor impurity in $BaTiO_3$, J. Am. Ceram. Soc. 70 (2) (1987) 96–100.
[3] X.W. Zhang, Y.H. Han, M. Lal, D.M. Smyth, Defect chemistry of $BaTiO_3$ with additions of $CaTiO_3$, J. Am. Ceram. Soc. 70 (2) (1987) 100–103.
[4] V. Bheemineni, E.K. Chang, M. Cal, M.P. Harmer, D.M. Smyth, Suppression of acceptor solubilities in $BaTiO_3$ densified in highly reducing atmosphere, J. Am. Ceram. Soc. 77 (12) (1994) 3173–3176.
[5] Y. Tsur, T.D. Dunbar, C.A. Randall, Crystal and defect chemistry of rare earth cations in $BaTiO_3$, J. Electroceram. 7 (2001) 25–34.
[6] D.F.K. Hennings, H. Schreinemacher, Ca-acceptors in dielectric ceramics sintered in reductive atmosphere, J. Eur. Ceram. Soc. 15 (1995) 795–800.
[7] Y. Okino, H. Shizuno, S. Kusumi, H. Kishi, Dielectric properties of rare-earth-oxide-doped $BaTiO_3$ ceramics fired in reducing atmosphere, Jpn. J. Appl. Phys. 33 (1994) 5393–5396.
[8] W.H. Lee, T.Y. Tseng, D. Hennings, Effects of A/B cation ratio on the microstructure and lifetime of $(Ba_{1-x}Ca_x)_z(Ti_{0.99-y}Zr_yMn_{0.01})O_3$ (BCTZM) sintered in reducing atmosphere, J. Mater. Sci. Mater. Electron. 11 (2000) 157–162.
[9] M.T. Buscaglia, M. Viviani, V. Buscaglia, C. Bottino, P. Nanni, Incorporation of Er^{3+} into $BaTiO_3$, J. Am. Ceram. Soc. 85 (6) (2002) 1569–1575.
[10] R.D. Shannon, Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides, Acta Cryst. A32 (1976) 751–761.
[11] A.S. Shaikh, R.W. Vest, Defect structure and dielectric properties of Nd_2O_3-modified $BaTiO_3$, J. Am. Ceram. Soc. 69 (9) (1986) 689–694.
[12] N. Hirose, J.M.S. Skakle, A.R. West, Doping mechanism and permittivity correlations in Nd-doped $BaTiO_3$, J. Electroceram. 3:3 (1999) 233–238.