The study of Ca-doped BCTZ ceramics sintered in reducing atmosphere

**Lei Chen · Longtu Li · Xiaohui Wang ·
Zhibin Tian · Zhilun Gui**

Abstract Effects of Ca^{2+} doped into $(Ba_{1-x}Ca_x)(Ti_{1-y}Zr_y)O_3$ (BCTZ) ceramics on microstructure and insulation resistance have been investigated. It is found that the shift of Ca^{2+} from *A*-sites to *B*-sites greatly influences the unit cell volume and the Curie temperature of BCTZ ceramics. During the firing process in reducing atmosphere, the large amounts of additive Ca^{2+} dispense among the grain boundaries and lead to the restrain of the grain growth. Within the same volume, the specimen with smaller grain size provides more grain boundaries, which helps in providing an efficient diffusion pathway for oxygen during annealing step and results in the improvement of the insulation resistance of the samples.

Keywords BCTZ · MLCC · Calcium · Insulation resistance

1 Introduction

Barium titanate ($BaTiO_3$), due to its high relative dielectric constant and excellent electrical performance, had become the most important dielectric material for the fabrication of Ni-electrode multilayer ceramic capacitors [1, 2]. In order to avoid oxidation of the Ni electrodes, the capacitors should be sintered in a reducing atmosphere and then annealed to reoxidize the ceramics [3]. Much effort has been expended to improve the dielectric properties by way of controlling grain growth and designing the microstruc-

L. Chen (✉) · L. Li · X. Wang · Z. Tian · Z. Gui
State Key Laboratory of New Ceramics and Fine Processing,
Department of Materials Science and Engineering,
Tsinghua University,
Beijing 100084, People's Republic of China
e-mail: chenlei98@mails.tsinghua.edu.cn

X. Wang
e-mail: wxh@tsinghua.edu.cn

ture. The substitution of the divalent Ca^{2+} at *A*-sites and the isovalent Zr^{4+} at *B*-sites of perovskite structure forms a solid solution with $BaTiO_3$ and alters the lattice parameters, leading to the shift of phase transition temperature and broadening the peak of dielectric constant maximum [4, 5].

High-permittivity dielectrics showing EIA Y5V specification are usually prepared from ceramic mixed crystals of the $(Ba_{1-x}Ca_x)(Ti_{1-y}Zr_y)O_3$ (BCTZ) system [6]. The position and function of divalent Ca^{2+} in the ABO_3 type perovskite structure have already been investiged by many literatures [7–9]. In BCTZ Ca^{2+} strongly prefer the *A*-sites of the perovskite lattice [10]. The radius of Ca^{2+} (1.06 Å) is between those of *A*-sites Ba^{2+} (1.43 Å) and *B*-sites Ti^{4+} (0.64 Å)/Zr^{4+} (0.87 Å). When doping into BCTZ, Ca^{2+} can enter both *A*-sites and *B*-sites. It was reported that at 1300°C a maximum solubility is about 20% $\left[Ca^{2+}_{(A)}\right]$ in $BaTiO_3$ [11]. Incorporation of Ba^{2+} on the *A*-sites can make the primary *A*-sites Ca^{2+} shift to *B*-sites which greatly changes the unit cell volume and Curie temperature [12, 13]. In our investigation, the experiment was divided into to two series called *A* and *B*, respectively. In *Serie A* $BaCO_3$ was added to BCTZ so that the primary Ca^{2+} in *A*-sites was forced to enter *B*-sites, while in *Serie B* $CaCO_3$ and TiO_2 with the mole ratio 1:1 were added to BCTZ so that the doped Ca^{2+} entered *A*-sites and Ti^{4+} entered *B*-sites.

2 Experimental

The host material was BCTZ powders prepared by hydrothermal method with the composition of $(Ba_{0.95}Ca_{0.05})(Ti_{0.85}Zr_{0.15})O_3$, of which the average grain size was about 200 nm. The additives to BCTZ were $CaCO_3$, $BaCO_3$ and TiO_2. The samples were prepared according to the formulations shown in Table 1. The additives were finely distributed

Table 1 Doping content of the additives and relative densities of sintered samples.

Sample	BaCO₃ mol%	CaCO₃ mol%	TiO₂ mol%	Relative density (%)
A1	0.2			98.7
A2	0.5			98.2
A3	0.8			98.4
A4	1.0			98.5
A5	1.5			98.6
A6	2.0			99.3
A7	2.5			98.2
A8	3.0			99.8
A9	4.0			98.7
A10	6.0			98.5
B1		1	1	98.5
B2		3	3	98.4
B3		5	5	97.4
B4		10	10	96.6
B5		16	16	95.1
B6		18	18	93.8

over BCTZ by wet milling in an enclosed polyurethane pot with $\Phi3$ mm ZrO₂ balls. The doped powders were pressed into disks with 10 mm in diameter and about 1 mm in thickness. After that the disks were sintered at 1400°C for 2 h in a N₂–H₂ reducing atmosphere and then annealed at 950°C for 3 h. During the sintering step P_{O_2} was adjusted to the range between 10^{-13} and 10^{-9} MPa, and the annealing step P_{O_2} was adjusted to the range between 10^{-9} and 10^{-6} MPa.
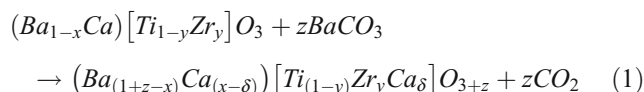
After sintering, apparent densities of samples were determined by the Archimedes method. The lattice parameters of the measured samples were calculated by the X-ray diffraction results. HP 4240B was employed to measure the insulation resistance (IR). And HP4192A LF impendence analyzer with an automatic temperature controller was utilized to measure the temperature dependence of the dielectric constant and dielectric loss of the samples. The microstructure of the samples was observed by JSM 6301F scanning electronic microscope experiments.

3 Results and discussion

As shown in Table 1, BCTZ doped with BaO which forced A-sites Ca²⁺ to B-sites resulted in dense ceramics with the relative density over 98%, while the addition of Ca²⁺ can lead to a gradual reduction of sintered density from 98.5% to 93.2%.

Figures 1 and 2 show the change of the unit cell volume with the *Serie A* and *Serie B*, respectively. The change of the unit cell volume caused by the incorporation of BaCO₃ in BCTZ was denoted by the following equation:

$$(Ba_{1-x}Ca)\left[Ti_{1-y}Zr_y\right]O_3 + zBaCO_3$$
$$\rightarrow \left(Ba_{(1+z-x)}Ca_{(x-\delta)}\right)\left[Ti_{(1-y)}Zr_yCa_\delta\right]O_{3+z} + zCO_2 \quad (1)$$

It can be found from Fig. 1 that the unit cell volume increased almost linearly up to BaCO₃ additions of z=0.03. With the incorporation of Ba²⁺ in A-sites, the A-sites Ca²⁺ was forced to enter B-sites, which can also indicated by Eq. 1. The position transformation of Ca²⁺ resulted in the increase of unit cell volume. When the doping Ba content reached 3%, the maximum unit cell volume was obtained and began to fell down with the increase of Ba content over 3%. So by the curve in Fig. 1 a maximum solubility of z=0.03 BaO in A-sites of BCTZ was derived. With the sequential addition of BaCO₃, the Ba²⁺ didn't enter A-sites any more but entered the lattice and led to the decrease of the unit cell volume.

When the additive CaCO₃ and TiO₂ were imported to BCTZ, the Ca²⁺ entered A-sites and the same amount of Ti⁴⁺
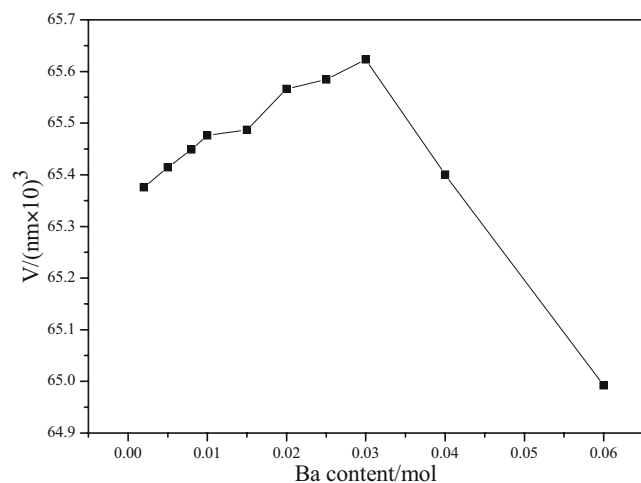
Fig. 1 Result of the unit cell volume with the *Serie A* addition
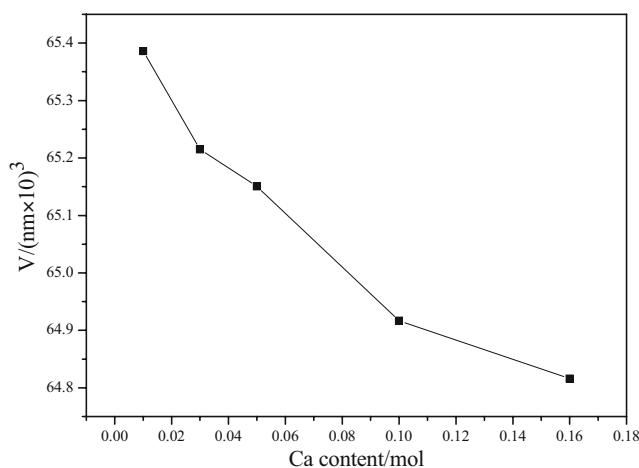
Fig. 2 Result of the unit cell volume with the *Serie B* addition
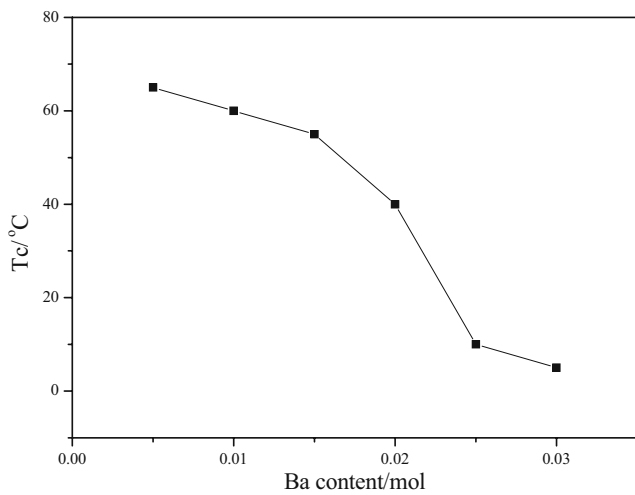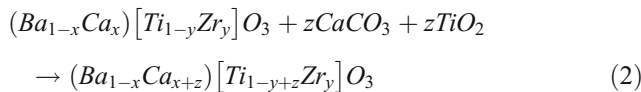
Fig. 3 Curie temperature with different doping content of *Serie A*

Fig. 5 IR with different doping content of *Serie B*

entered *B*-sites, respectively. The change of the unit cell volume caused by the incorporation of $CaCO_3$ in BCTZ was denoted by the following equation:

$$(Ba_{1-x}Ca_x)[Ti_{1-y}Zr_y]O_3 + zCaCO_3 + zTiO_2$$
$$\rightarrow (Ba_{1-x}Ca_{x+z})[Ti_{1-y+z}Zr_y]O_3 \qquad (2)$$

It can be seen in Fig. 2 that the unit cell volume decrease all along with the increase of the additive Ca content up to z=16%. During this course, the change of the unit cell volume was caused mostly by the apparent radius difference between Ca^{2+} and Ba^{2+}. The result indicated that the Ca^{2+} entered *A*-sites more easily than *B*-sites. It can also be inferred that in ABO_3 type perovskite structure the *A*-sites accommodation of Ca^{2+} is largely greater than that of *B*-sites.

The Curie temperature Tc with different doping contents of *Serie A* and *Serie B* are shown in Figs. 3 and 4. The Tc of BCTZ ceramic without any dopant is 70°C. From Fig. 3 it can be seen that the incorporation of Ba to *A*-sites shifted the Tc of the samples towards lower temperatures. The re-
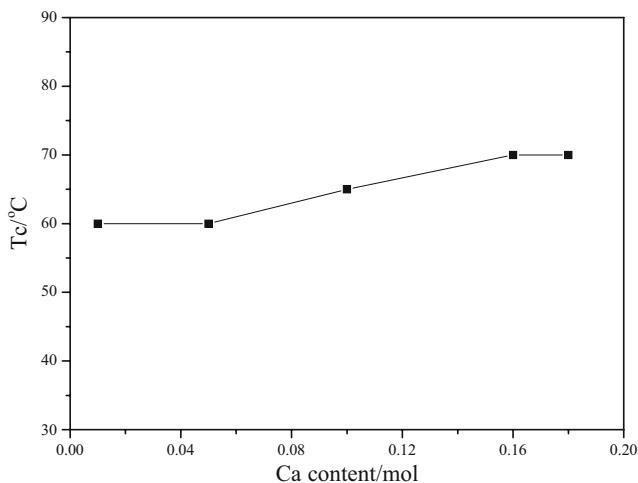
duction of Tc was caused by the transformation of the Ca^{2+}. In an embodiment, the Ca^{2+} entered *B*-sites from the primary *A*-sites by the incorporation of BaO and then changed the lattice parameter and unit cell volume, which greatly affected the polarization degree of the ferroelectric domains in sintered BCTZ grains. This effect led to the shift of Tc in macroscopic view. However, the result of *Serie B* shown in Fig. 4 was quite different with that of *Serie A*. Only a very small change of the Tc from 60 to 70°C occurred with the increase of doped Ca content from 1 to 18%. This result exhibited that the *A*-sites solution of Ca^{2+} can hardly affect the dielectric properties of BCTZ ceramics.

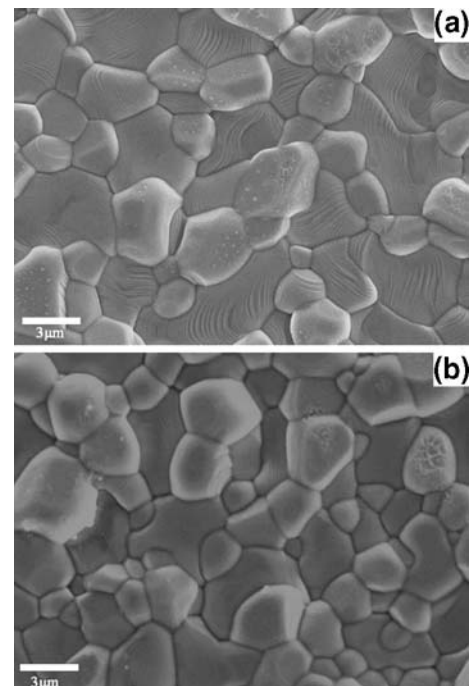Fig. 4 Curie temperature with different doping content of *Serie B*

Fig. 6 SEM images with different doping Ca contents: (a) Ca=1%; (b) Ca=5%

The measured IR result of *Serie B* is shown in Fig. 5. It is quite clear in *Serie B* that the IR increases apparently with the increase of the Ca doped content. All of the IR results were over 10^{10} $\Omega\cdot$cm, and reached 10^{11} $\Omega\cdot$cm when the Ca content was above 10%. The reason of IR increase caused by Ca additive can be explained as followed. The additive Ca^{2+} dispense among the grain boundaries so that the grain growth through sintering was restrained. The SEM images of samples with different Ca^{2+} doped contents were shown in Fig. 6. It can also be considered that the addition of Ca^{2+} led to the appearance of more grain boundaries. It is well known that after sintering in a reducing atmosphere an annealing process in a lower temperature was needed to decrease the large amount of oxygen vacancies formed in the reducing atmosphere sintering in order to improve the IR and the reliability of the samples. At the same annealing process the smaller grain size provided more grain boundaries which act as diffusion pathways of oxygen, and was effective to improve the IR of the samples.

4 Conclusion

In our study *Serie A* and *Serie B* were named to investigate in BCTZ ceramics the effects of Ca^{2+} in different sites of perovskite structure. The position transformation of Ca^{2+} from *A*-sites to *B*-sites resulted in the increase of unit cell volume and the shift to lower temperature of Curie temperature. When the doping Ba content reached 3%, the maximum unit cell volume was obtained. However, the result of *Serie B* was quite different that only a very small change of the Tc occurred, which exhibited that the *A*-sites solution

of Ca^{2+} can hardly affect the dielectric properties of BCTZ ceramics. In *Serie B*, the large amount of additive Ca^{2+} dispense among the grain boundaries which lead to the restrain of the grain growth, and improve the IR of the samples.

References

1. J.M. Herbert, *Ceramic Dielectrics and Capacitors* (Gordon and Breach, London, 1985), pp. 150–168
2. H. Kishi, Y. Mizuno, H. Chazono, Jpn. J. Appl. Phys. **42**, 1 (2003)
3. D.M. Smyth, *Applications of Ferroelectrics* (ISAF, Southampton, 2000)
4. S.M. Neirman, J. Mater. Sci. **23**, 3973 (1988)
5. D. Hennings, A. Schnell, G. Simon, J. Am. Ceram. Soc. **65**(11), 539 (1982)
6. P. Hansen, D. Hennings, H. Schreinemacher, J. Electroceram. **2**(2), 85 (1998)
7. X.W. Zhang, Y.H. Han, D.M. Smyth, J. Am. Ceram. Soc. **70**(2), 100 (1987)
8. W.H. Lee, T.Y. Tseng, J. Mater. Sci. Mater. Electron. **11**, 157 (2000)
9. J. Lee, S. Lee, V.A. Hackley, J. Am. Ceram. Soc. **86**(6), 1034 (2003)
10. B. Jaffe, W.R. Cook, H. Jaffe, *Piezoelectric Ceramics: In Non-Metallic Solids* (Academic, London, 1971), p. 91
11. D. Hennings, H. Schreinemacher, Mater. Res. Bull. **12**, 1221 (1977)
12. D. Hennings, H. Schreinemacher, J. Eur. Ceram. Soc. **15**, 795 (1995)
13. W. Lee, T.Y. Tseng, D. Hennings, J. Am. Ceram. Soc. **83**(6), 1402 (2000)