High piezoelectric properties and good temperature stabilities of CuO-modified Ba(Ti_{0.96}Sn_xZr_{0.04-x})O₃ ceramics

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In order to obtain both high piezoelectric property and good temperature stability in BaTiO₃-based ceramics in the common usage temperature range, Sn⁴⁺ and Zr⁴⁺ are co-doped into BaTiO₃ ceramics according to the formula of Ba(Ti_{0.96}Sn_xZr_{0.04-x})O₃ (BTSZ) ($x = 0.01-0.4$) with 1 mol% CuO being added as sintering-aid in this study. The CuO-modified BTSZ ceramics show both high piezoelectric properties and good temperature stability. Particularly, the CuO-modified Ba(Ti_{0.96}Sn_{0.01}Zr_{0.03})O₃ ceramic displays the high piezoelectric properties of $d_{33} = 350$ pC/N, $k_p = 49.5\%$ at room-temperature and a weak temperature dependence of k_p in the temperature range of -15°C and 60°C . Moreover, the CuO-modified Ba(Ti_{0.96}Sn_{0.01}Zr_{0.03})O₃ ceramic shows stable thermal aging behavior with the d_{33} being almost unchanged until the aging temperature of 100°C , which is even higher than its Curie temperature. The high piezoelectric properties of CuO-modified Ba(Ti_{0.96}Sn_{0.01}Zr_{0.03})O₃ ceramic were ascribed to the dense microstructure with small and uniform grain size distribution. The stable thermal aging behavior can be explained by the aging effect based on the defect dipolar model.

Keywords: Lead-free piezoelectric materials; BaTiO₃-based ceramics; high piezoelectric activity; temperature stabilities; defect dipolar.

1. Introduction

Piezoelectric materials have been widely used in actuators, resonators, transducers, and other electronic devices. Among all those piezoelectric materials, BaTiO₃ is the first material practically used to fabricate piezoelectric ceramics. However, for quite a long time, the d_{33} of BaTiO₃ ceramics had been reported to be only around 190 pC/N,^{1,2} which is much inferior to lead-based piezoelectric ceramics. Nevertheless, during recent years, a lot of progresses have been made on fabricating high-performance BaTiO₃ piezoelectric ceramics with different sintering methods.³⁻⁶ Particularly, our research group has succeeded in fabricating high-performance BaTiO₃ ceramics with d_{33} as high as 419 pC/N through traditional solid-state reaction route with ordinary BaCO₃ and TiO₂ powders.⁷ This progress brings great hope that the BaTiO₃ ceramics may become a popular type of lead-free piezoelectric materials.

However, due to the orthogonal-tetragonal phase transition around room-temperature, the piezoelectric properties of BaTiO₃ ceramics show large temperature dependence. This may be a big obstacle in the practical application of BaTiO₃ ceramics. In order to reduce the piezoelectric temperature dependence of BaTiO₃ ceramics, Ti⁴⁺ was partially substituted with Zr⁴⁺ or Sn⁴⁺ in our previous studies so that the relatively temperature-stable orthogonal phase could be shifted to the common usage temperature range.^{8,9} Moreover, due to the high sintering temperature and relatively low piezoelectric properties of Ba(Ti,Zr)O₃ and Ba(Ti,Sn)O₃ ceramics, CuO was added as sintering-aid in the sintering

process of the Ba(Ti,Zr)O₃ and Ba(Ti,Sn)O₃ ceramics.⁸⁻¹⁰ As a result, high d_{33} values and good temperature stabilities were obtained simultaneously. However, when making a comparison between the CuO-modified Ba(Ti,Sn)O₃ ceramics and the CuO-modified Ba(Ti,Zr)O₃ ceramics, it was found that the former ones have higher d_{33} values while lower Curie temperature, and the latter ones exhibit higher Curie temperature while lower d_{33} value. So, in order to obtain higher d_{33} values and better temperature stabilities simultaneously, Sn⁴⁺ and Zr⁴⁺ were co-doped with the formula Ba(Ti_{0.96}Sn_xZr_{0.04-x})O₃ (BTSZ) ceramics in this study. It was found that the CuO-modified BTSZ ceramics all show high piezoelectric properties (d_{33} values greater than 350 pC/N) and weak piezoelectric temperature dependence in the common usage temperature range. Moreover, all the CuO-modified BTSZ ceramics exhibit good thermal aging stabilities.

2. Experimental

CuO-modified BTSZ ($x = 0.01-0.04$) ceramics were prepared using commercial powders of BaCO₃ (purity $\geq 99.0\%$, Sinopharm Chemical Reagent Co. Ltd.), TiO₂ (purity $\geq 99.8\%$, Xiantao Zhongxing Electronic Material Co. Ltd.), SnO₂ (purity $\geq 99.8\%$, Sinopharm Chemical Reagent Co. Ltd.) and ZrO₂ (purity $\geq 99.8\%$, Sinopharm Chemical Reagent Co. Ltd.) as starting materials. The raw materials were weighed according to the stoichiometric ratio, ball-mixed for 12 h in alcohol and calcined at 1050°C for 4 h. Then, 1 mol% CuO (purity $\geq 99.8\%$, Sinopharm Chemical Reagent Co. Ltd.)

powder was added into the synthesized BTSZ powder. The mixtures were ball-milled again for 12 h. The powder was dried and further pressed into pellet discs of 15 mm diameter and 1.0 mm thickness. Sintering was performed in the air under the condition of 1190°C, 2 h. For electrical evaluation, the sintered ceramics were coated with silver paint on the upper and bottom surfaces and fired at 575°C for 20 min. Poling was accomplished at 100°C in silicon oil under 3.0 kV/mm for 30 min. The d_{33} was measured with a Berlincourt-type d_{33} -meter (YE 2730, Wuxi). The k_p , k_t , k_{33} and Q_m were obtained from resonance-antiresonance frequencies, which were measured using an Agilent 4294 A precision impedance analyzer. Thermal aging stability was assessed in such a way that the experimental specimen was first raised to the designed testing temperature and maintained for 1 h. After being restored to room-temperature, the d_{33} value was measured again. For characterizations of microstructure and domain configuration, the poled specimens were polished and chemically etched in a dilute HCl-acid solution. Optical observation was performed under an Olympus BX51 polarizing microscope, and microscopic images were recorded by an Olympus DP70 digital camera. The polarization-electric field loops were measured using the Radiant Workstation (Germany).

3. Results and Discussion

Table 1 lists the mass density of various CuO-modified BTSZ ceramics as well as their dielectric and piezoelectric properties measured at room-temperature. It can be seen from Table 1 that all the CuO-modified BTSZ ceramics exhibit high density and good piezoelectric properties at room-temperature. With the decrease of Sn^{4+} concentration, the d_{33} values decrease slightly from 400 pC/N to 350 pC/N while the k_p , k_t and k_{33} do not change much. In particular, the CuO-modified BTSZ ceramic with $x = 0.01$ shows quite similar piezoelectric properties as CuO-modified $\text{Ba}(\text{Ti}_{0.96}\text{Sn}_{0.04})\text{O}_3$ ceramic, while the Curie temperature of CuO-modified $\text{Ba}(\text{Ti}_{0.96}\text{Sn}_{0.01}\text{Zr}_{0.03})\text{O}_3$ ceramic is much higher than that of CuO-modified $\text{Ba}(\text{Ti}_{0.96}\text{Sn}_{0.04})\text{O}_3$ ceramic. Figure 1 shows the temperature dependence of dielectric permittivity ϵ' for

Fig. 1. Temperature dependence of dielectric permittivity ϵ' for various CuO-modified BTSZ ceramics.

CuO-modified BTSZ ceramics. With the decrease of x , the Curie temperature T_C increases remarkably from 82.1°C to 97.9°C. The orthorhombic–tetragonal phase transition temperature (T_{O-T}) also shifts gradually from 35°C to about 45°C and the orthorhombic phase range is extended to high temperatures correspondingly.

The temperature dependences of k_p values for various CuO-modified BTSZ ceramics were presented in Fig. 2. It can be seen that in the commonly used temperature range, all the CuO-modified BTSZ ceramics show good temperature stabilities. Particularly, the CuO-modified $\text{Ba}(\text{Ti}_{0.96}\text{Sn}_{0.01}\text{Zr}_{0.03})\text{O}_3$ ceramic show nearly temperature-independent high k_p values in the temperature range from -1°C to 5°C . Moreover, in the temperature range between -50°C and 70°C , the k_p values are all larger than 40%. On the other hand, the k_p values are close to those of CuO-modified $\text{Ba}(\text{Ti}_{0.96}\text{Sn}_{0.04})\text{O}_3$ ceramics in the commonly-used temperature range and higher than those of other CuO-modified BTSZ ceramics.

Figure 3 shows the thermal aging behavior of various CuO-modified BTSZ ceramics in terms of d_{33} values. It can

Fig. 2. Temperature dependence of k_p value for various CuO-modified BTSZ ceramics.

Table 1. Room-temperature properties for various CuO-modified BTSZ ceramics.

	$x = 0.04$	$x = 0.03$	$x = 0.02$	$x = 0.01$
ρ (g/cm ³)	5.97	5.98	5.95	5.90
ϵ' at 1 kHz	3450	3300	2900	3100
$\tan \delta$ (%)	1.2	1.8	2	1.3
d_{33}	400	380	360	350
k_p	50.0	48.6	46.4	49.5
k_t	47.0	45.8	44.4	45.7
k_{33}	64.5	66.5	60.8	63.5
Q_m	391	221	248	310
T_c (°C)	82.1	87.6	91.5	97.9

Fig. 3. Thermal aging behavior of various CuO-modified BTSZ ceramics in terms of d_{33} value.

be seen that all these ceramics show excellent thermal aging stabilities. The d_{33} values of all these CuO-modified BTSZ ceramics kept almost unchanged until the thermal aging temperatures were nearly 5°C higher than their Curie temperatures. When the thermal aging temperatures were further raised, the d_{33} values decreased drastically to about zero. The CuO-modified $\text{Ba}(\text{Ti}_{0.96}\text{Sn}_{0.01}\text{Zr}_{0.03})\text{O}_3$ ceramic shows the best thermal aging stability and the d_{33} shows a temperature-independent value of 350 pC/N until the temperature of 100°C.

The optical images of various CuO-modified BTSZ ceramics are shown in Fig. 4. It can be seen that all these

CuO-modified BTSZ ceramics show dense microstructures consisting of small and uniformly distributed grains. The CuO-modified $\text{Ba}(\text{Ti}_{0.96}\text{Sn}_{0.01}\text{Zr}_{0.03})\text{O}_3$ ceramic has the smallest average grain size of 3.5 μm while the CuO-modified $\text{Ba}(\text{Ti}_{0.96}\text{Sn}_{0.02}\text{Zr}_{0.02})\text{O}_3$ ceramic shows the largest average grain size of 12.5 μm . The average grain sizes for CuO-modified $\text{Ba}(\text{Ti}_{0.96}\text{Sn}_{0.03}\text{Zr}_{0.01})\text{O}_3$ and $\text{Ba}(\text{Ti}_{0.96}\text{Sn}_{0.04})\text{O}_3$ ceramics are 8.8 μm and 9.5 μm , respectively. As to the domain structures, besides the 180°- and 90°-domains, 60°- and 120°-domains were also observed in these CuO-modified BTSZ ceramics. The average domain widths for these CuO-modified BTSZ ceramics do not vary much and are all around 380 nm.

In the following part, we will discuss the possible mechanism for the high piezoelectric properties and good temperature stabilities of CuO-modified BTSZ ceramics. In our previous studies, we have demonstrated that the piezoelectric properties of BaTiO_3 ceramics were much more stable in the orthorhombic phase than in the tetragonal phase.⁸ Partially substituting Ti^{4+} with Sn^{4+} or Zr^{4+} can shift the $T_{\text{O-T}}$ upward and extended the orthorhombic region. Compared with Sn^{4+} substitution, Zr^{4+} substitution is more effective in shifting the $T_{\text{O-T}}$ upward while keeping a higher Curie temperature. In Fig. 1, it can be seen that the CuO-modified $\text{Ba}(\text{Ti}_{0.96}\text{Sn}_{0.01}\text{Zr}_{0.03})\text{O}_3$ ceramic shows the highest $T_{\text{O-T}}$ and T_{C} . On the other hand, the room-temperature piezoelectric properties of CuO-modified BTSZ ceramics usually decrease with the increase of Zr content. This could be interpreted in the following two aspects. First, the remnant polarization of CuO-modified BTSZ ceramics will decrease

Fig. 4. The optical images of the domain structures for various CuO-modified BTSZ ceramics. (a) $x = 0.01$; (b) $x = 0.02$; (c) $x = 0.03$; (d) $x = 0.04$.

Fig. 5. Polarization versus electric field loop for various CuO-modified BTSZ ceramics.

with the increase of Zr content, as shown in Fig. 5. CuO-modified $\text{Ba}(\text{Ti}_{0.96}\text{Sn}_{0.04})\text{O}_3$ ceramic shows the largest remnant polarization of $11.4 \mu\text{C}/\text{cm}^2$ and CuO-modified $\text{Ba}(\text{Ti}_{0.96}\text{Sn}_{0.02}\text{Zr}_{0.02})\text{O}_3$ and $\text{Ba}(\text{Ti}_{0.96}\text{Sn}_{0.01}\text{Zr}_{0.03})\text{O}_3$ ceramics show the similar remnant polarization of $5.6 \mu\text{C}/\text{cm}^2$. The second aspect is that with the increase of Zr content, the $T_{\text{O-T}}$ at which the d_{33} of CuO-modified BTSZ ceramics reach the maximum values shifts upward. When measured at room-temperature, the d_{33} of CuO-modified BTSZ ceramics become further away from the peak with the increase of Zr content. Nevertheless, in this study, the piezoelectric properties of CuO-modified $\text{Ba}(\text{Ti}_{0.96}\text{Sn}_{0.01}\text{Zr}_{0.03})\text{O}_3$ ceramic are quite close to the CuO-modified $\text{Ba}(\text{Ti}_{0.96}\text{Sn}_{0.04})\text{O}_3$ ceramic. This can be explained by the piezoelectric grain-size effect of BaTiO_3 ceramics reported in our recent studies.¹¹ It has been found that the piezoelectric constant d_{33} of BaTiO_3 ceramics increase significantly at room-temperature with the reduction of the average grain size g . The CuO-modified $\text{Ba}(\text{Ti}_{0.96}\text{Sn}_{0.01}\text{Zr}_{0.03})\text{O}_3$ ceramic shows the smallest average grain size. Therefore, the domain walls of CuO-modified $\text{Ba}(\text{Ti}_{0.96}\text{Sn}_{0.01}\text{Zr}_{0.03})\text{O}_3$ ceramic has smaller areas and lighter inertia masses, thus can respond more actively to an external electrical signal.¹² The relatively low piezoelectric properties of CuO-modified $\text{Ba}(\text{Ti}_{0.96}\text{Sn}_{0.02}\text{Zr}_{0.02})\text{O}_3$ ceramic could be ascribed to the large average grain size.

The good thermal aging stabilities of CuO-modified BTSZ ceramics can be explained well by the aging effect based on the defect dipolar model. Cu^{2+} may partially replace Ti^{4+} in the sintering process and in order to maintain charge neutrality, an oxygen vacancy is formed around the Cu^{2+} in the oxygen octahedron. So in a unit lattice cell, there may be a defect dipole formed by Cu^{2+} and oxygen vacancy. The defect dipole can reorientate due to the mobility of the oxygen vacancy inside each oxygen octahedron.^{13,14} The reorientation of defect dipole is a hard diffusion process and may take several hours. Within a single domain, the defect dipoles tend to align parallel to the spontaneous polarization P_s after aging because the energy is lowest in that case.¹⁵ Therefore, when the as-prepared CuO-modified BTSZ

ceramics were poled, most of the spontaneous polarizations tend to align in the same direction. After aging for several hours, a large part of the defect dipoles will also align in the same direction and a large internal electric bias was formed. Therefore, the domain configurations of CuO-modified BTSZ ceramics are quite stable due to the aligned defect dipoles.^{16,17} Even when the aging temperatures were a little higher than their Curie temperatures, the CuO-modified BTSZ ceramics can still have high d_{33} when cooled to room-temperature. When the aging temperatures were further raised, the oxygen vacancy has enough energy to diffuse randomly and the domain configurations become unstable at higher temperature, thus the d_{33} decrease dramatically to zero.

4. Conclusion

In this study, Sn^{4+} and Zr^{4+} are co-doped in CuO-modified BaTiO_3 ceramics. Compared with the single-doped CuO-modified BaTiO_3 ceramics, the CuO-modified $\text{Ba}(\text{Ti}_{0.96}\text{Sn}_{0.01}\text{Zr}_{0.03})\text{O}_3$ ceramic exhibits both high piezoelectric properties and good temperature stabilities in the common usage temperature range. The high piezoelectric properties of CuO-modified $\text{Ba}(\text{Ti}_{0.96}\text{Sn}_{0.01}\text{Zr}_{0.03})\text{O}_3$ ceramic are ascribed to the small average grain size. On the other hand, the CuO-modified $\text{Ba}(\text{Ti}_{0.96}\text{Sn}_{0.01}\text{Zr}_{0.03})\text{O}_3$ ceramic shows a stable thermal aging behavior. This can be explained well with the defect dipolar model. Therefore, CuO-modified $\text{Ba}(\text{Ti}_{0.96}\text{Sn}_{0.01}\text{Zr}_{0.03})\text{O}_3$ ceramic could be considered as a promising low-cost lead-free piezoelectric material for practical applications.

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References

- ¹R. Bechmann, Elastic, piezoelectric, and dielectric constants of polarized barium titanate ceramics and some applications of the piezoelectric equations, *J. Acoust. Soc. Am.* **28**, 347 (1956).
- ²B. Jaffe, W. R. Cook and H. Jaffe, *Piezoelectric Ceramics* (Academic, London, 1971).
- ³H. Takahashi, Y. Numamoto, J. Tani, K. Matsuta, J. Qiu and S. Tsurekawa, Lead-free Barium Titanate ceramics with large piezoelectric constant fabricated by microwave sintering, *Jpn. J. Appl. Phys.* **45**, L30 (2006).
- ⁴T. Karaki, K. Yan, T. Miyamoto and M. Adachi, Lead-free piezoelectric ceramics with large dielectric and piezoelectric constants manufactured from BaTiO_3 nano-powder, *Jpn. J. Appl. Phys.* **46**, L97 (2007).
- ⁵S. Wada, K. Takeda, T. Muraishi, H. Kakemoto, T. Tsurumi and T. Kimura, Preparation of [110] grain oriented Barium Titanate

- ceramics by templated grain growth method and their piezoelectric properties, *Jpn. J. Appl. Phys.* **46**, 7039 (2007).
- ⁶H. Takahashi, Y. Numamoto, J. Tani and S. Tsurekawa, Considerations for BaTiO₃ ceramics with high piezoelectric properties fabricated by microwave sintering method, *Jpn. J. Appl. Phys.* **47**, 8468 (2008).
- ⁷S. F. Shao, J. L. Zhang, Z. Zhang, P. Zheng, M. L. Zhao, J. C. Li and C. L. Wang, High piezoelectric properties and domain configuration in BaTiO₃ ceramics obtained through the solid-state reaction route, *J. Phys. D: Appl. Phys.* **41**, 125408 (2008).
- ⁸P. Zheng, J. L. Zhang, S. F. Shao, Y. Q. Tan and C. L. Wang, Piezoelectric properties and stabilities of CuO-modified Ba(Ti,Zr)O₃ ceramics, *Appl. Phys. Lett.* **94**, 032902 (2009).
- ⁹J. L. Zhang, Z. Zhang, S. F. Shao, P. Zheng and C. L. Wang, High piezoelectric performance and relevant physical mechanism of CuO-modified Ba(Ti_{0.96}Sn_{0.04})O₃ ceramics, *J. Adv. Dielect.* **1**, 79 (2011).
- ¹⁰Z. Zhang, J. L. Zhang, S. F. Shao, P. Zheng and C. L. Wang, Influence of CuO additive on physical properties of BaTiO₃ ceramics, *Mater. Sci. Forum* **687**, 287 (2011).
- ¹¹P. Zheng, J. L. Zhang, Y. Q. Tan and C. L. Wang, Grain-size effects on dielectric and piezoelectric properties of poled BaTiO₃ ceramics, *Acta. Mater.* **60**, 5022 (2012).
- ¹²G. Arlt and N. A. Pertsev, Force constant and effective mass of 90° domain walls in ferroelectric ceramics, *J. Appl. Phys.* **70**, 2283 (1991).
- ¹³W. L. Warren, K. Vanheusden, D. Dimos, G. E. Pike and B. A. Tuttle, Oxygen vacancy motion in perovskite oxides, *J. Am. Ceram. Soc.* **79**, 536 (1996).
- ¹⁴C. Schaffrin, Oxygen diffusion in BaTiO₃ ceramic, *Phys. Stat. Sol. (a)* **35**, 79 (1976).
- ¹⁵G. H. Jonker, Nature of aging in ferroelectric ceramics, *J. Am. Ceram. Soc.* **55**, 57 (1972).
- ¹⁶U. Robels and G. Arlt, Domain wall clamping in ferroelectrics by orientation of defects, *J. Appl. Phys.* **73**, 3454 (1993).
- ¹⁷D. Z. Sun, X. B. Ren and K. Otsuka, Stabilization effect in ferroelectric materials during aging in ferroelectric state, *Appl. Phys. Lett.* **87**, 142903 (2005).