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Piezoelectric properties of Ca-modified $Pb_{0.6}Bi_{0.4}(Ti_{0.75}Zn_{0.15}Fe_{0.10})O_3$ ceramics

Fei-fei An [a], Fei Cao [b], Jian Yu [a,*]

[a] Functional Materials Research Laboratory, Tongji University, Shanghai 200092, China
[b] Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, China

Abstract

Perovskite-structured $Pb_{0.6}Bi_{0.4}(Ti_{0.75}Zn_{0.15}Fe_{0.1})O_3$ ceramics was reported with high Curie temperature T_C of 705 °C and tetragonality of $c/a = 1.10$, promising for high temperature applications with large piezoelectric anisotropy. In this paper, it was experimentally demonstrated to ease poling processing and enhance piezoelectricity through substituting lead with calcium of $Pb_{0.6-x}Ca_xBi_{0.4}(Ti_{0.75}Zn_{0.15}Fe_{0.1})O_3$. For the $x = 0.18$ sample, electromechanical coupling factor ratio of $k_t/k_p \rightarrow \infty$, dielectric constant of 380, piezoelectric coefficient d_{33} of 80 pC/N, mechanical quality factor Q_m of 50 and Curie point T_C of 237 °C were obtained, which exhibits better piezoelectric performance than the $(Pb_{0.76}Ca_{0.24})(Ti_{0.96}(Co_{0.5}W_{0.5})_{0.04})O_3$. The enhanced piezoelectric response was analyzed with relation to the reduction of tetragonality and Curie temperature.

Keywords: A. Powders: solid state reaction; B. X-ray methods; C. Piezoelectric properties; D. Perovskites

1. Introduction

Lead titanate ($PbTiO_3$) has both high Curie temperature of $T_C = 490$ °C and large electromechanical and piezoelectric anisotropy, which is promising for high temperature transducer, high frequency ultrasonic imaging devices and underwater hydrophones. Owing to sintering difficulties, the practically applied $PbTiO_3$ ceramics are usually modified with Ca and/or Sm to obtain strong mechanical ceramic patches and improve piezoelectric performances. This anisotropy effect has been shown to result from the statistical orientation of the crystallites in the ceramics and the material properties due to this orientation [1–3]. In contrast to most of $PbTiO_3$-based solid solutions with decreasing tetragonality and Curie temperature, Chen et al. found experimentally that modifying $PbTiO_3$ with 30 mol% $Bi(Zn_{1/2}Ti_{1/2})O_3$ and 10 mol% $BiFeO_3$ to form ternary solid solution exhibits a near-zero thermal expansion coefficient and the Curie temperature upward about 700 °C, substantial for high thermal stability while extending transducer application temperature [4]. Recently, the authors obtained robust insulating $Pb_{0.6}Bi_{0.4}(Ti_{0.75}Zn_{0.15}Fe_{0.1})O_3$ ceramic patches with dielectric constant of $\varepsilon_r = 204$, dielectric loss of $\tan \delta = 1.7\%$, piezoelectric constant of $d_{33} = 2.0$ pC/N, tetragonality of $c/a = 1.100$ and $T_C = 705$ °C for the 1.0 mol% Nb + 0.5 mol% Mg co-doped samples [5,6]. It was noted that such small d_{33} may be attributed to ceramic poling difficulty of overcoming large strain energy due to a large c/a ratio. In this paper, pure and 1 mol% Nb + 0.5 mol% Mg co-doped Ca-modified $Pb_{0.6}Bi_{0.4}(Ti_{0.75}Zn_{0.15}Fe_{0.1})O_3$ ceramics (termed as PCBTZF-0 and PCBTZF-Nb(1.0)/Mg(0.5), respectively) were prepared with the conventional electroceramic processing, and their structure, dielectric, piezoelectric, electromechanical and ferroelectric properties were investigated related to calcium concentration. Piezoelectricity was observed to be enhanced remarkably by the Ca-modification and analyzed.

2. Experimental procedures

The PCBTZF-0 and PCBTZF-Nb(1.0)/Mg(0.5) ceramic patches were prepared using solid state reaction method with PbO, $CaCO_3$, Bi_2O_3, TiO_2, ZnO, Fe_2O_3, Nb_2O_5 and MgO as starting raw materials. Stoichiometric mixtures of the raw powders were calcined at 800 °C for 5 h. The 10 mm and 13 mm green disks were pressed uniaxially under 250 MPa, and then sintered at temperature between 1000 °C and 1050 °C for

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* Corresponding author. Tel.: +86 21 65980544; fax: +86 21 65985179.
E-mail address: jyu@tongji.edu.cn (J. Yu).

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various soaking time. The details of processing were described in our previous reports [5,6]. For piezoelectric and temperature-dependent dielectric characterizations, the ceramic pellets were polished, coated with different silver paste and fired at 600 °C or 800 °C for 10 min, respectively. Their crystallographic phase and microstructure was analyzed using an X-ray diffraction (XRD) and scanning electron microscopy (SEM), respectively. The temperature-dependent dielectric properties were investigated with Agilent precision LCR meter. The polarization-electric field hysteresis loops were measured with Radiant ferroelectric materials analyzer. The ceramic poling was carried out at 160 °C under DC electric field of 6.0–8.0 kV/mm. The piezoelectric constant d_{33} was measured using a quasi-static piezoelectric d_{33} meter and electromechanical coupling factor with Agilent precision impedance analyzer.

3. Results and discussion

For the PCBTZF-0 and PCBTZF-Nb(1.0)/Mg(0.5) ceramic disks with x between 0.05 and 0.20 sintered at temperatures between 1000 and 1050 °C, XRD measurements showed that all of them were well crystallized in the tetragonal structure [5,6]. For an illustration, Fig. 1 presents XRD patterns of the PCBTZF-Nb(1.0)/Mg(0.5) ceramic pellets with various calcium concentration. It was seen from Fig. 1 that the (0 0 2) peak shifts downward but the (2 0 0) upward, that is to say the tetragonality of c/a ratio decreasing, with increasing calcium concentration. c/a was calculated as 1.095 for $x = 0.05$, 1.085 for 0.10, 1.059 for 0.15, and 1.030 for 0.20 from the (0 0 2)/(2 0 0) diffraction peaks. Judging from the shrinkage rate and measured density, the ceramic disks obtained here were well densified with relative density above 94% [6]. For instance, Fig. 2 shows the SEM pictures of the microstructure of fracture surface for the $x = 0.10$ and 0.15 pure ceramic disks sintered at 1020 °C, of which the spherical morphology and average grain size about 1 μm were observed.

The piezoelectric constant d_{33}, dielectric constant ε_r and dielectric loss tan δ at 1 kHz were measured at room temperature, among which d_{33} and ε_r presented in Fig. 3 for the PCBTZF-0 and PCBTZF-Nb(1.0)/Mg(0.5) ceramic disks sintered at 1020 °C and summarized in Table 1. From Fig. 3 and Table 1, it was observed that the dielectric constant increase monotonically with x increasing but the piezoelectric constant exhibits a high response around $x = 0.18$ in our experiments. The co-doping with Nb and Mg enhances the piezoelectric constant and dielectric constant but decrease the dielectric loss. The impedance magnitudes for both radial and thickness modes were measured and illustrated in Fig. 4 for the $x = 0.10$, 0.125,

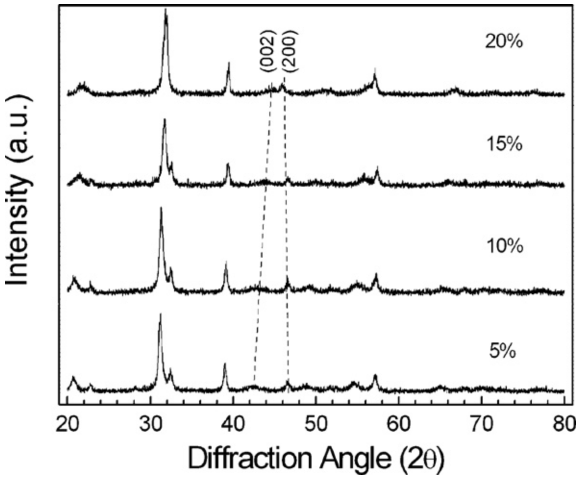

Fig. 1. XRD patterns of the PCBTZF-Nb(1.0)/Mg(0.5) ceramic pellets with various x sintered at 1020 °C for 1 h. The dashed lines only for viewing shift of the (0 0 2) and (2 0 0) peaks.

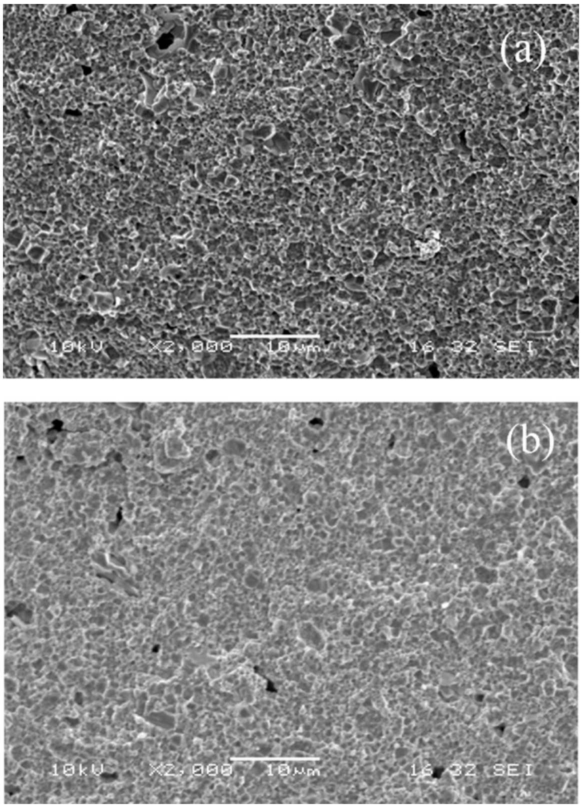

Fig. 2. SEM microstructure pictures of the fracture surface of the PCBTZF-0 (a) $x = 0.10$ and (b) $x = 0.15$ samples sintered at 1020 °C.

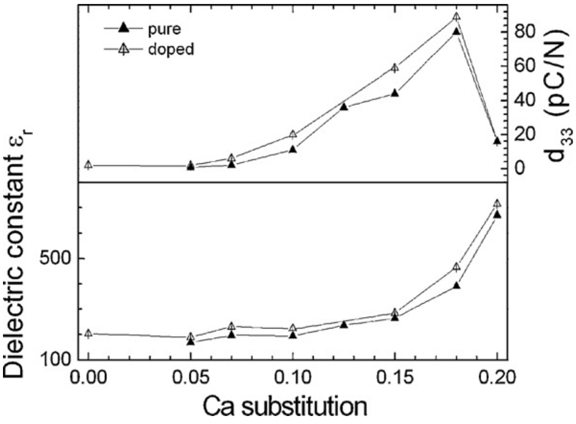

Fig. 3. piezoelectric constant d_{33} and dielectric constant ε_r as a function of calcium concentration obtained at room temperature for the PCBTZF-0 and PCBTZF-Nb(1.0)/Mg(0.5) samples sintered at 1020 °C. The segments are only for view.

Table 1
Dielectric constant and dielectric loss, piezoelectric constant, electromechanical coupling factor and Curie temperature measured for the PCBTZF-0 samples sintered at 1020 °C for 1 h. The values in the brackets for the corresponded sample co-doped with 1 mol% Nb and 0.5 mol% Mg.

x	ε_r	tan δ (%)	d_{33} (pC/N)	k_t	T_C (°C)
0.05	169 (190)	1.9	0.6 (1.8)		644 (635)
0.10	195 (224)	2.3	11 (20)	0.15	465 (439)
0.125	230	2.6	36	0.27	407
0.15	265 (284)	2.7	44 (58)	0.31	296 (278)
0.18	380 (466)	2.8	80 (89)	0.38	237
0.20	670	4.4	16		192

and 0.15 samples. It was seen clearly that the radial modes were negligible and the thickness modes only exist, implying large electromechanical anisotropy with $\zeta = k_t/k_p \rightarrow \infty$. The electromechanical coupling factor k_t was calculated as 0.15, 0.27, 0.31 and 0.38, respectively, for the $x = 0.10$, 0.125, 0.15 and 0.18 sample. It is of interest to note that the obtained piezoelectric properties of PCBTZF-0 ($x = 0.18$) ceramics are better than those of $(Pb_{0.76}Ca_{0.24})(Ti_{0.96}(Co_{0.5}W_{0.5})_{0.04})O_3$ ceramics with $\zeta \rightarrow \infty$, $\varepsilon = 250$, $d_{33} = 70$ pC/N, $T_C = 240$ °C [2].

To understand the piezoelectric and dielectric behavior with respect to calcium substitution, measurements of ferroelectric hysteresis loop and temperature-dependent dielectric constants were further performed for the samples sintered at 1020 °C. Fig. 5 presents polarization–electric field hysteresis loops measured at room temperature for the pure and doped $Pb_{0.6-x}Ca_xBi_{0.4}(Ti_{0.75}Zn_{0.15}Fe_{0.1})O_3$ pellets with various x. It was seen from Fig. 5 that both the pure and co-doped samples are strong insulating to sustain electric field higher than 7 kV/mm and that the remanent polarization at zero field obtained from the P–E loop increases with x increasing for both kinds of samples. Compared with the doped $Pb_{0.6}Bi_{0.4}(Ti_{0.75}Zn_{0.15}Fe_{0.1})O_3$ of remanent polarization less than 0.25 μC/cm^2 [5,6], the Ca substitution of Pb makes the polarization switching easier. In particular, a typical ferroelectric polarization-electric field hysteresis loop was observed with remanent polarization $P_r = 3.31$ μC/cm^2 and coercive field $E_c = 33.0$ kV/cm for the $x = 0.20$ pure sample, the Nb/Mg co-doping increases $P_r = 6.18$ μC/cm^2 but reduces $E_c = 26.2$ kV/cm.

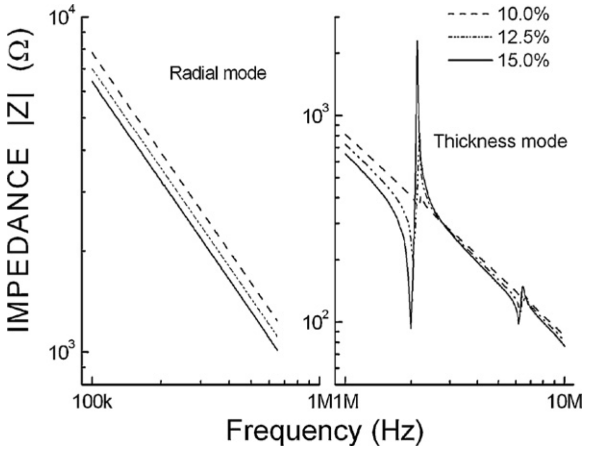

Fig. 4. Impedance magnitudes measured at room temperature for the PCBTZF-0 ($x = 0.10$, 0.125, and 0.15) ceramic disks sintered at 1020 °C with the diameter/thickness ratio of 12.

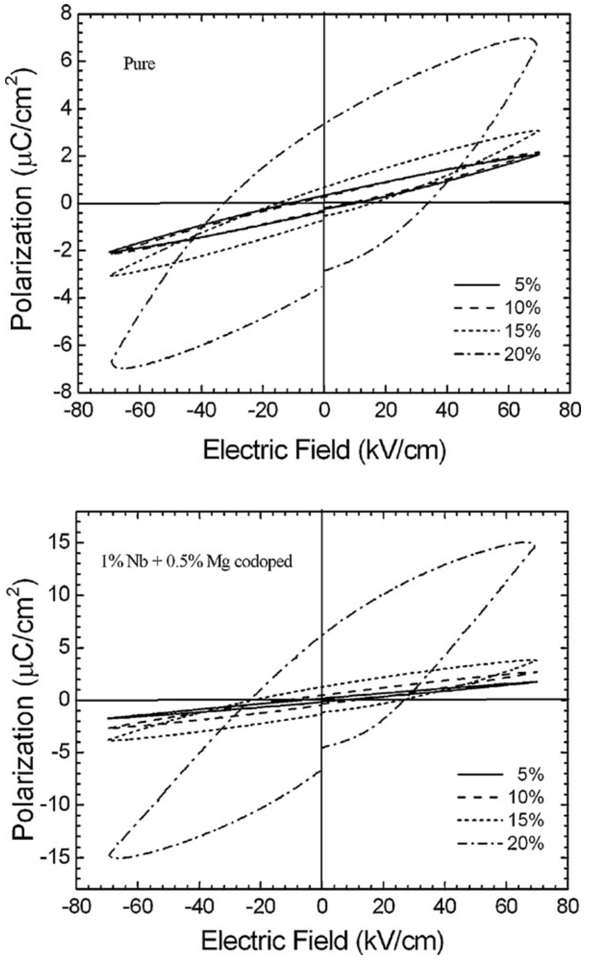

Fig. 5. Polarization–electric field hysteresis loops measured at room temperature for the PCBTZF-0 and PCBTZF-Nb(1.0)/Mg(0.5) ceramic pellets sintered at 1020 °C.

From the temperature-dependent measurements of dielectric constant, the ferroelectric–paraelectric phase transition Curie temperature was determined as the dielectric peak position and summarized in Table 1. The phase transition Curie temperature was observed decrease monotonically with x increasing upward 0.20. Similar to the cases of $PbTiO_3$, $PbTiO_3$–$BiFeO_3$ and $PbTiO_3$–$Bi(Zn_{1/2}Ti_{1/2})O_3$ [7,8], the reduction of Curie temperature correlates closely with the decrease of tetragonality in the $Pb_{0.6-x}Ca_xBi_{0.4}(Ti_{0.75}Zn_{0.15}Fe_{0.1})O_3$. Compared with the Nb/Mg co-doped $Pb_{0.6}Bi_{0.4}(Ti_{0.75}Zn_{0.15}Fe_{0.1})O_3$ ceramic with $T_C = 705$ °C and $c/a = 1.100$ [6], the Ca substitution of Pb reduces the Curie temperature and tetragonality, which can be well understood by the reduction of covalent bond character at the A-site by substituting Pb with Ca [9,10]. So far, it can be concluded that the reduction of tetragonality and Curie temperature ease the polarization re-orientation and 90° domain rotations during poling processing [2,3]. Moreover, in contrast to monotonic trend of tetragonality, Curie temperature and dielectric constant with respect to Ca concentration, the anomalous decrease of d_{33} for the $x = 0.20$ samples may come from the thermal-depoling effect during cooling after removing poling electric field, due to the used poling temperature of 160 °C being close to the phase transition temperature. When the poling was performed at temperature of 120 °C, d_{33} was obtained as 35 pC/N. On the other hand, for a PCBTZF-Nb(1.0)/Mg(0.5) ($x = 0.15$) sample with $d_{33} = 53$ pC/N, the remaining piezoelectric constant of 47 pC/N but very small 2.0 pC/N and 1.7 pC/N were observed after heat treatment at 200, 250 and 350 °C for 24 h, respectively.

4. Summary

Pure and Nb/Mg co-doped $Pb_{0.6-x}Ca_xBi_{0.4}(Ti_{0.75}Zn_{0.15}Zn_{0.15}Fe_{0.1})O_3$ perovskite-structured ceramics were prepared with the conventional electroceramic processing and their piezoelectric properties were investigated experimentally. It was demonstrated that the calcium substitution of lead eases the ceramic poling and enhances the piezoelectric properties of $Pb_{0.6}Bi_{0.4}(Ti_{0.75}Zn_{0.15}Fe_{0.1})O_3$ ceramics, with a maximum of piezoelectric response around $x = 0.18$ for the pure and Nb/Mg co-doped samples. The enhanced piezoelectric performance observed here was experimentally analyzed with relation to the reduction of tetragonality and Curie temperature.

Acknowledgements

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