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# Dielectric and piezoelectric properties and PTC behavior of $Ba_{0.9}Ca_{0.1}Ti_{0.9}Zr_{0.1}O_3-x$La ceramics prepared by hydrothermal method

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ABSTRACT

Lead-free $Ba_{0.9}Ca_{0.1}Ti_{0.9}Zr_{0.1}O_3$–$x$La ($x$=0.000, 0.005, 0.010, 0.015, and 0.020) ceramics have been prepared by hydrothermal method and were assisted by fast microwave sintering, and the effects of La-doping on the electrical properties of $Ba_{0.9}Ca_{0.1}Ti_{0.9}Zr_{0.1}O_3$ were studied. The single orthorhombic phase was observed in the composition of $x \leq 0.10$ and the coexistence of orthorhombic and tetragonal phase were detected at $x$=0.015 and 0.020. The substitution of small amount of $La^{3+}$ resulted in an decreasing of dielectric constant and dielectric loss, and they both possessed a minimum value at $x$=0.010. With the addition of $x \geq 0.015$, the $Ba_{0.9}Ca_{0.1}Ti_{0.9}Zr_{0.1}O_3$–$x$La ceramics became semi-conductors and the PTC behavior was observed. The piezoelectric constant ($d_{33}$) measured at 50 °C of the ceramics were increased after the partial substitution of $La^{3+}$ because of the enhancement of coexistence of orthorhombic and tetragonal phases. The $T_C$ was decreased with increasing $La^{3+}$, and the ferroelectric and piezoelectric properties cannot be detected at samples with $x$=0.02.



## 1. Introduction

For a half century, Pb-based piezoelectric ceramics, such as lead zirconium titanate [$PbTiO_3$–$PbZrO_3$ (PZT)], have dominated the field of piezoelectric ceramics worldwide. However, because lead oxides are highly toxic, the use of the lead based ceramics has caused serious environmental problems. Therefore, it is necessary to develop lead-free piezoelectric ceramics. In 2009, BZT-BCT ferroelectric system with a super high $d_{33}$ was designed, and since then, BCTZ system materials have attracted considerable attention and been considered as one of the promising candidates for lead-free piezoelectric ceramics. Some high valence metal ions such as $La^{3+}$ and $Nb^{5+}$ have been frequently used to substitute in the piezoelectrics for increasing the $d_{33}$ and decreasing the dielectric loss [1–3]. However, there is little work on $La^{3+}$ doping for BCTZ ceramics and the BCTZ ceramics were mainly prepared by conventional solid-state method. In present work, the $Ba_{0.9}Ca_{0.1}Ti_{0.9}Zr_{0.1}O_3$–$x$La ceramics were prepared by hydrothermal method and the effects of La-doping on the electrical properties of the ceramics were studied.

## 2. Experimental

$Ba_{0.9}Ca_{0.1}Ti_{0.9}Zr_{0.1}O_3$–$x$La ceramics with different $x$ values were prepared by hydrothermal method and the $BaCl_2 \cdot 2H_2O$ (SCRC), $CaCl_2$, $TiCl_4$, $ZrOCl_2 \cdot 8H_2O$ and $La(NO_3)_3$ were used as raw materials. $BaCl_2 \cdot 2H_2O$, $CaCl_2$ $ZrOCl_2 \cdot 8H_2O$ and $La(NO_3)_3$ were first dissolved in distilled water respectively and then were mixed. The $TiCl_4$ was added into the mixtures dropwise to obtain the precursors. Finally the NaOH was added to regulate the pH > 14. The three precursors were put into the heating-autoclave, followed by distilled water until the total volume reached to ~80% of the autoclave. The hydrothermal reactions were carried out at 180 °C for 10 h and finally the three powders were mixed before dried. After that, the powders were pressed into pellets of 12 mm diameter and the pellets were sintered at 1280 °C for 10 min under microwaves. Phase structure was examined using an X-ray diffraction (D/max 2200pc, Rigaku, Tokyo, Japan) with CuKα radiation. Dielectric and ferroelectric measurements were measured by Agilent 4980A impedance analyzer and a ferroelectric analyzer (Premier II, Radiant, USA). The ceramics were poled under a DC field of 4.5 kV/mm in silicon oil bath for 10 min at different temperatures and the $d_{33}$ of the poled ceramics was measured using a quasi-static meter $d_{33}$ meter (ZJ-4AN, China).

## 3. Results and discussion

The XRD patterns of the $Ba_{0.9}Ca_{0.1}Ti_{0.9}Zr_{0.1}O_3$–$x$La ceramics are shown in Fig. 1. All the ceramics have a pure perovskite structure and no second phases were detected, suggesting that $La^{3+}$ were incorporated into the BCTZ lattices to form a solid solution. The BCZT ceramics for $x \leq 0.10$ possess single orthorhombic structure

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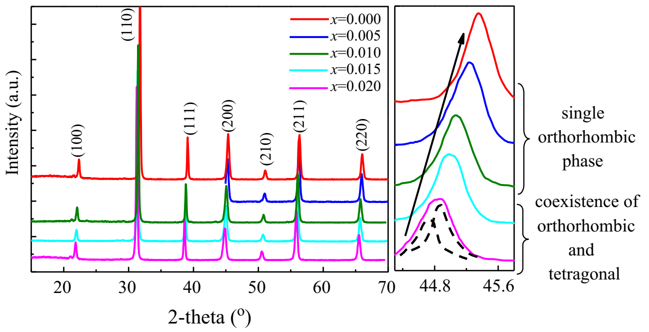


**Fig. 1.** X-ray patterns of the $Ba_{0.9}Ca_{0.1}Ti_{0.9}Zr_{0.1}O_3$–$x$La ceramics with different $x$ values.

and the coexistence of orthorhombic and tetragonal phase were detected with $x \geq 0.015$, which can be characterized by the broadening of (200)/(002) peak, seen from the smaller range of 44.3–45.8°. It is also noticed that the (200)/(002) peak shifts towards lower degree of $2\theta$ with increasing $La^{3+}$ content for the increasing lattice parameter $d$ [4,5].

Fig. 2 shows the temperature dependence of dielectric constant and dielectric loss at 1–1000 kHz and the temperature dependence of resistivity for the BCTZ–$x$La ceramics with different $x$ values. The samples for $0.005 \leq x \leq 0.020$ display two obvious polymorphic phase transitions corresponding to the orthorhombic to tetragonal ($T_{O-T}$) and tetragonal to cubic phase ($T_m$) while the sample with $x=0.000$ only shows $T_m$. The $T_m$ transition peak shifts towards lower temperature slightly with increasing $La^{3+}$ addition,

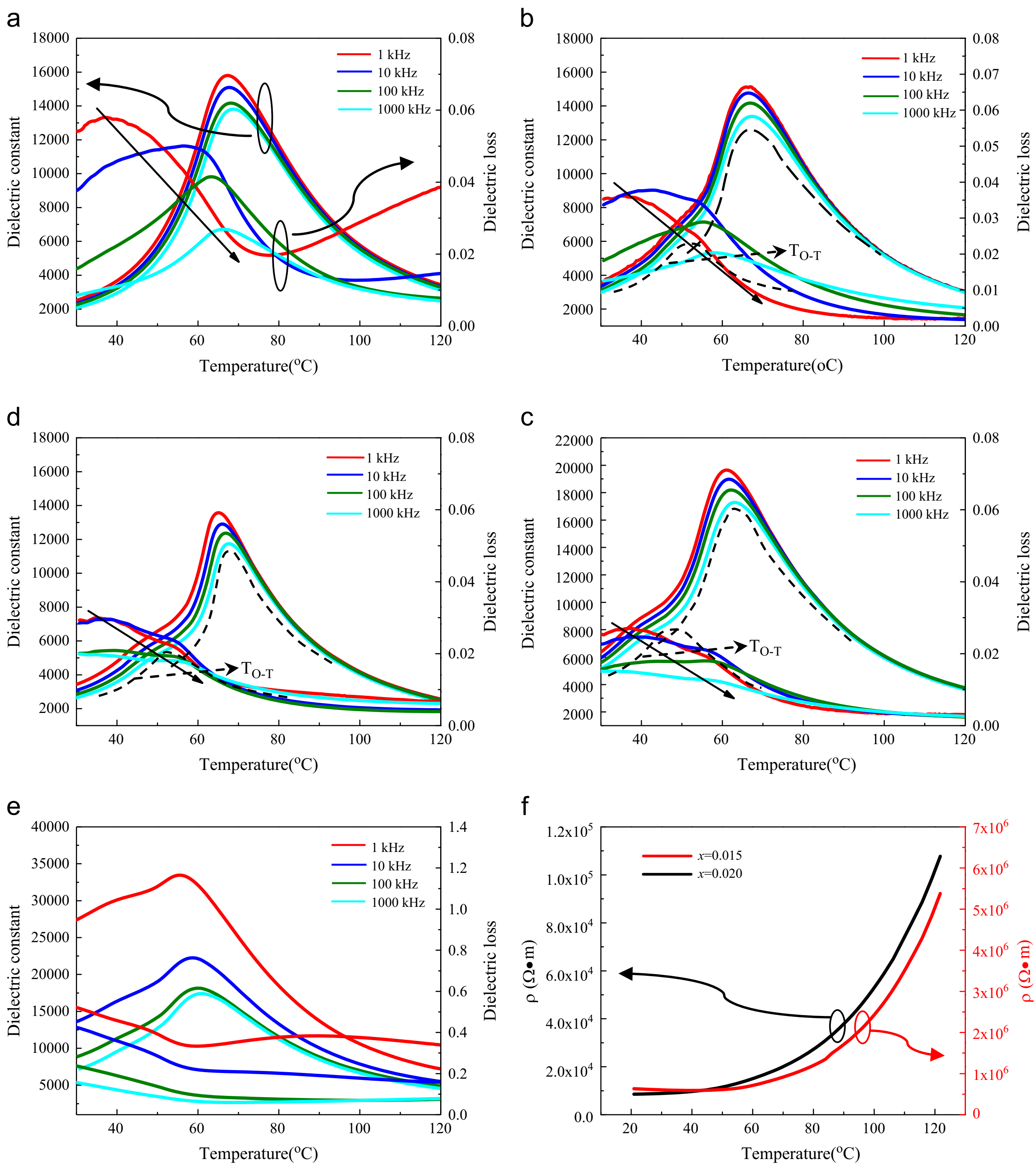


**Fig. 2.** Temperature dependence of dielectric constant and dielectric loss and the temperature dependence of resistivity for the $Ba_{0.9}Ca_{0.1}Ti_{0.9}Zr_{0.1}O_3$–$x$La ceramics with different $x$ values: (a) $x=0.000$; (b) $x=0.005$; (c) $x=0.010$; (d) $x=0.015$; (e) $x=0.020$; and (f) $\rho$–$T$ curves of samples with $x=0.015$ and 0.020.

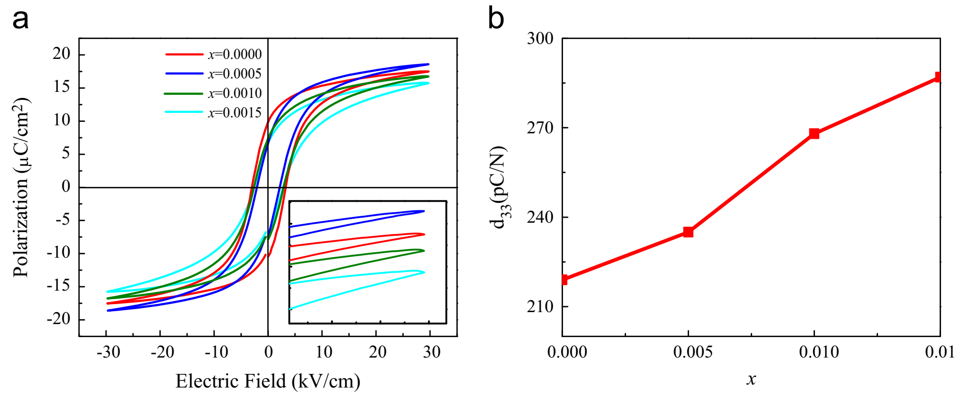


**Fig. 3.** The $P$–$E$ loops and the variations of the $d_{33}$ with $x$ for the $Ba_{0.9}Ca_{0.1}Ti_{0.9}Zr_{0.1}O_3$–$x$La ceramics with different $x$ values. (a) $P$–$E$ loops and (b) $d_{33}$–$x$ curves.

and the permittivity decreases with $x=0.000$–$0.010$ then increases with further addition. For samples with $x=0.015$ and 0.020, the permittivity is relatively higher and the temperature dependence of resistivity of these two samples are shown in Fig. 2(f), indicating that these ceramics can be used as semi-conductor materials and show a PTC behavior. It is also noticed in Fig. 2(e) that the permittivity of $Ba_{0.9}Ca_{0.1}Ti_{0.9}Zr_{0.1}O_3$–0.020La is nearly reach up to 35,000 below 60 °C, which can be used as giant dielectric constant materials in certain temperature range [6,7].

These phenomenons can be probably explained as followings: the substitution of of $La^{3+}$ can both increases the permittivity of $T_{O-T}$ peak and decreases the temperatures of phase transitions. The radius of $La^{3+}$ (0.10132 nm) is very close to those of $Ba^{2+}$ (0.161 nm) and $Ca^{2+}$ (0.134 nm) of the BCTZ ceramics. Therefore, according to the principles of crystal chemistry, $La^{3+}$ most likely occupy the A site firstly. With increasing $x$, more $Ba^{2+}/Ca^{2+}$ were substituted by $La^{3+}$, remaining one $e^-$ in the lattice for one substitution. When $x$ was increased to 0.020, the amount of $e^-$ obtained a threshold for semiconducting, exhibiting electronic relaxation polarization in the $Ba_{0.9}Ca_{0.1}Ti_{0.9}Zr_{0.1}O_3$–0.020La ceramic. Compared with other fast polarizations, the electronic relaxation polarization can not keep pace up with the electrical field with higher frequency ($f \geq 10$ kHz), only making contribution in increasing the permittivity significantly at $f=1$ kHz. Thus, $Ba_{0.9}Ca_{0.1}Ti_{0.9}Zr_{0.1}O_3$–0.020La ceramic shows such giant permittivity at 1 kHz. It also can be observed that the degree of frequency dispersion increases with increasing $La^{3+}$ addition which is due to the grain size [8].

At higher $x$, the defect chemical reaction of $La^{3+}$ substitution for A-site ions is represented as

$$La^{3+} \xRightarrow{Ba^{2+}} La_{Ba}^{\cdot} + e$$

$$La^{3+} \xRightarrow{Ca^{2+}} La_{Ca}^{\cdot} + e$$

The new emerged $e$ is served as carriers in ceramics and thus the samples with higher $La^{3+}$ content show a positive temperature coefficient behavior and can be used as PTC semi-conductors. The dielectric loss decreases with increasing $La^{3+}$ content, showing a minimum value at $x=0.015$. And then increases sharply at $x=0.020$ for slow polarizations such as electronic relaxation polarization always lead to high dielectric loss [9–11].

The $P$–$E$ loops and the variations of the $d_{33}$ with $x$ for the BCTZ–$x$La ceramics are shown in Fig. 3. Samples with $0.000 \leq x \leq 0.015$ show standard hysteresis loops and the ferroelectric properties can not be detected in $Ba_{0.9}Ca_{0.1}Ti_{0.9}Zr_{0.1}O_3$–0.020La ceramic. That is because the $x=0.020$ sample is no longer dielectrics but semi-conductors for its relative low resistivity, which is easily to be broken down under a high voltage. The value of $E_c$ of BCZT ceramics was maximum at $x=0.000$ and then decreased with increasing $La^{3+}$ content. The $P_s$ exhibits a maximum at $x=0.005$ and then decreases with further addition of $La^{3+}$. The piezoelectric constants ($d_{33}$) measured at 50 °C of samples at $0.000 \leq x \leq 0.015$ are shown in Fig. 3(b). The $d_{33}$ increases with increasing $La^{3+}$ content and the piezoelectric properties can not be detected in sample at $x=0.020$. That is due to the enhancement of coexistence of orthorhombic and tetragonal phases at 50 °C of $Ba_{0.9}Ca_{0.1}Ti_{0.9}Zr_{0.1}O_3$–$x$La ceramics [1,3,8].

## 4. Conclusions

Lead-free $Ba_{0.9}Ca_{0.1}Ti_{0.9}Zr_{0.1}O_3$–$x$La ceramics have been prepared by hydrothermal method and the effects of $La^{3+}$ on the electrical properties of these ceramics were studied. With $La^{3+}$ addition, the $T_{O-T}$ emerged and the permittivity and $T_C$ both decreased with increasing $La^{3+}$ content for samples at $0.000 \leq x \leq 0.015$. $La^{3+}$ was firstly substituted into A-site with smaller amount and entered oxygen octahedron with further addition, which leads to a PTC behavior. $Ba_{0.9}Ca_{0.1}Ti_{0.9}Zr_{0.1}O_3$–0.015La ceramic is a promising dielectric and ferroelectric materials for its high dielectric constant, low dielectric loss and standard $P$–$E$ loop. For $Ba_{0.9}Ca_{0.1}Ti_{0.9}Zr_{0.1}O_3$–0.020La ceramic, it can be used as semi-conductor and giant permittivity materials at 0.1 kHz below 60 °C.

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