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The effect of La doping on the electrostriction and electric hysteresis of $0.85Pb(Zn_{1/3}Nb_{2/3})O_3$–$0.10BaTiO_3$–$0.05PbTiO_3$ ceramics

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Abstract

Lanthanum-doped $0.85Pb(Zn_{1/3}Nb_{2/3})O_3$–$0.10BaTiO_3$–$0.05PbTiO_3$ ternary system ceramics were synthesized by the columbite method. The effect of lanthanum doping on dielectric, electrostrictive properties and electric hysteresis of the specimens was investigated. With the increase in lanthanum content, the content of perovskite phase and dielectric constant decreased, but the thermostablity of the dielectric properties improved. When lanthanum content increased, electrostriction and electrostrictive coefficients decreased. The electric hysteresis of La-doped speciments also decreased, i.e. the remanent polarization and coercive fields decreased. © 2000 Published by Elsevier Science Ltd. and Techna S.r.l. All rights reserved.

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1. Introduction

Relaxor ferroelectrics based on $Pb(Zn_{1/3}Nb_{2/3})O_3$ (abbreviated as PZN) exhibit excellent physical properties such as high dielectric constant, large electrostriction and little hysteresis. They have received special attention as electrostrictive materials applied for actuators, micro-positioner and optical devices [1]. As pure PZN is very difficult to synthesize, various methods have been carried out to stabilize its perovskite phase, but the results are not ideal [2]. Later it was found that with some amounts of $BaTiO_3$ (abbreviated as BT) and/or $PbTiO_3$ (abbreviated as PT) added to pure PZN, a 100% perovskite structured PZN–BT–PT solution ceramics were easy to obtain [3–5]. Still there is a barrier, i.e. their bad thermostability, affecting the applications of PZN–BT–PT ceramics. As a result, several approaches had been proposed to increase their thermostability [6,7].

Lanthanum doping in PMN-based ceramics [8–10] had been studied extensively and it was proved that lanthanum doping increased their thermostability. But the properties of lanthanum doped PZN-based ceramics were seldom reported; in particular, the effect of lanthanum doping on electrostriction and electric hysteresis has never been investigated until now. The purpose of this study is to investigate the effects of different contents of lanthanum on the electrostriction and electric hysteresis of PZN–BT–PT solution ceramics.

2. Experimental procedure

The specimens studied in this investigation were fabricated according to formula $0.85Pb(Zn_{1/3}Nb_{2/3})_3$–$0.10BaTiO_3$–$0.05PbTiO_3 + x$ mol%La (abbreviated as x/85/10/5 hereafter), where x was 0, 0.01, 0.02, 0.05, 0.10 respectively. The specimens were prepared by columbite precursor method [11] and the purity of all starting raw powders were 99%. The columbite precursor ($ZnNb_2O_6$) was first prepared by mixing predetermined amounts of ZnO and Nb_2O_6 and ball-milled for 12 h in polyethylene jars, then the slurry was dried and calcined for 4 h at 1000°C to form $ZnNb_2O_6$. The columbite precursor was then mixed and ball-milled with pre-determined amounts of PbO,TiO_2,$BaCO_3$ and La_2O_3 powders and calcined at 880°C for 4 h. The calcined powders were ground, ball-milled again and pressed into disks using PVA as a binder and a uniaxial hydrostatic pressure of 150 MPa. After burning off PVA, the pellets were sintered in a sealed aluminate

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crucible at a soaking temperature of 1100°C for 1 h. In order to compensate for PbO loss from the pellets, a PbO-rich atmosphere was maintained by placing an equi-molar mixture of PbO and ZrO_2 inside the covered aluminate crucible.

The relative amounts of pyrochlore and perovskite phases were determined using XRD patterns of powder samples by measuring the major X-ray peak intensities for perovskite and pyrochlore phases, i.e. (110) and (222), respectively. The percentage of perovskite phase was calculated by the following equation:

$$\text{Content of perovskite phase (\%)} = I_{\text{perov}(110)} / \left(I_{perov(110)} + I_{pyro(220)} \right)$$

where I_{perov} and I_{pyro} stand for the intensities of the major peaks (110) and (220) for perovskite and pyrochlore phases, respectively.

The dielectric response was measured at the frequency of 1 kHz using an automatic LCR meter (WK4225) at a temperature range from −70 to 120°C. Electrostriction was measured with a standard strain gauge method and polarization–electric hysteresis loops (P–E loop) were observed with a standard Tower-Sawyer circuit.

3. Results and discussion

3.1. Phases analysis and dielectric properties

The specimens contained 0, 1, 2, 5 and 10% mol La^{3+} were numbered 1#, 2#, 3#, 4# and 5#, respectively. According to XRD patterns, their perovskite and pyrochlore phases contents and other physical parameters were shown in Table 1.

As listed in Table 1, with increasing lanthanum content, the amounts of perovskite phase of the specimens decreased gradually, which is similar to the case of lanthanum doping in PMN-based ceramics. It was explained that the charge imbalance due to lanthanum doping was compensated for by the adjustment of the B-site cation concentrations [9]. Ti^{4+} and Nb^{5+} ions have approximately the same ionic radii, i.e. 0.68 and 0.70 a.u., respectively; we believe that charge imbalance was compensated for by the removal of Nb^{5+} ions and the entering of an equivalent number of Ti^{4+} onto their positions [9]. The experiment proved that La substitution resulted in Nb-rich and Ti-rich regions. The Nb-rich regions became pyrochlore phases and Ti-rich regions became perovskite phase. We could satisfactorily conclude that the more lanthanum content there was, the more pyrochlore and the less perovskite phase resulted.

As shown in Table 1, the perovskite phase lattice shrank gradually with increasing lanthanum content. Obviously the radius of La^{3+} ion is smaller than that of Pb^{2+} ion. When La^{3+} ions entered into the perovskite structure, the lattice parameter was certain to decrease.

The relative dielectric constant (at 1 k Hz) vs temperature curves of lanthanum doped PZN–BT–PT specimens are shown in Fig. 1. As the content of lanthanum ions increased, both the relative dielectric constant and Curie temperature decreased significantly. In addition to this, the thermostablity of dielectric properties improved.

There are several reasons for the decrease of the relative dielectric constant in lanthanum doped PZN-based ceramics. First, and most importantly, the pyrochlore phase content increased with the increment of lanthanum content. It is known that the pyrochlore phase is detrimental to dielectric property [2,12]. Second, lanthanum doping made the Nb^{5+} ions content decrease and Ti^{4+} ions content increase in the perovskite phase, i.e. the number of NbO_6 octahedrons decreased and the number of TiO_6 octahedrons increased [9]. The space charge of polarization caused by NbO_6 octahedrons was less than that by TiO_6 octahedrons, which also decreased the dielectric constant. Third, as shown in Table 1, the lattice constant of the perovskite phase decreased by lanthanum doping, which made the movable space of B-sites ions become smaller and affect dielectric properties. Lastly, lanthanum doping may have resulted in some lead vacancies which had a strong effect on dielectric properties [13–16].

Table 1
Some physical parameters of the La-doped specimens

	Specimen number				
	1#	2#	3#	4#	5#
Composition (xLa/PZN/BT/PT)	0/85/10/5	1/85/10/5	2/85/10/5	5/85/10/5	10/85/10/15
Content of pyrochlore phase (%)	–	1.2	3.8	6.1	11.7
Content of perovskite phase (%)	100	98.8	96.2	93.9	88.3
Lattice constant (10^{-9} m)	4.051	4.049	4.041	4.034	4.032
Curie temperature (°C)	80	60	35	−5	−50
Peak dielectric constant (at 1 kHz)	6598	5916	3943	3402	1388
Density (g/cm^3)	8.1784	8.1148	8.0321	7.9594	7.8967

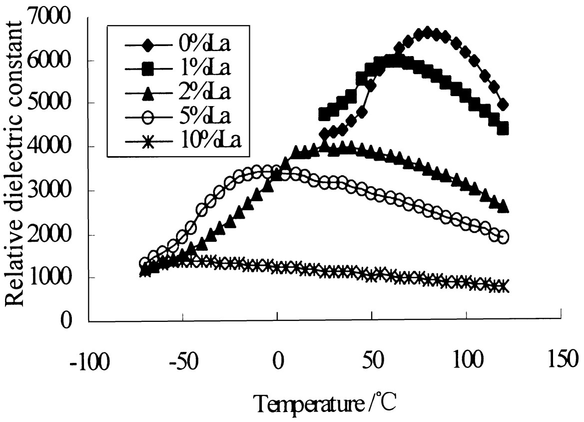

Fig. 1. The curves of temperature vs relative dielectric constant of the La-doped specimens.

3.2. Electrostrictive properties

The transverse and longitudinal electrostriction of the specimens measured at 30°C are given in Table 2. The curves of longitudinal electrostriction vs electric field of specimens 1#, 2# and 4# at 30°C were shown in Fig. 2. From Table 2 and Fig. 2, we can see that with the increasing of lanthanum content, both the transverse and longitudinal electrostriction decreased, while the transverse and longitudinal electrostrictive coefficients also decreased.

The decrease of electrostriction with lanthanum doping may have resulted from the following reasons: Firstly, the decrease of dielectric properties caused electrostriction to decrease. Secondly, lanthanum doping made spontaneous polarization decrease [9]. Since spontaneous polarization is related closely with electrostriction, lanthanum doping made electrostriction decrease. Thirdly, pyrochlore phases by lanthanum doping was responsible for the reduction of electrostriction. Pyrochlore phase caused perovskite phase to be isolated from each other and to be formed into very small islands which are readily re-oriented by electric fields and which readily release strains, so that electrostriction decreased with the existence of pyrochlore phase.

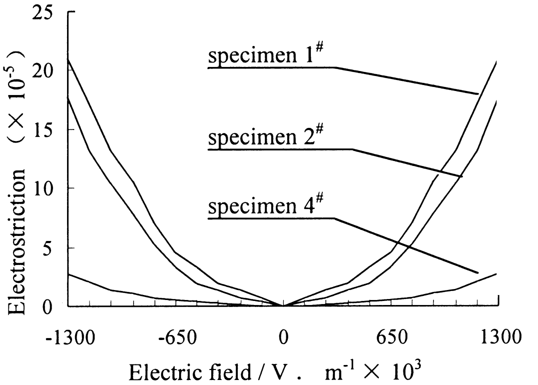

Fig. 2. The plot of longitudinal electrostriction vs electric field of specimens 1# , 2# and 4#.

3.3. Electrical hysteresis

The electric hysteresis parameters of the specimens 1#, 2# , 4# and 5# at 0, 40 and 60°C were listed in Table 3. At the same temperatures, with the increase of lanthanum content, remanent polarization and coercive field decreased. We believe that the decrease of hysteresis resulted from the following reasons: First, pyrochlore phase was responsible for this decrease of hysteresis, which has been discussed in Section 3.2. Because of the existence of the pyrochlore phase, the perovskite phase broke into very small domains which were readily re-oriented by the electric field. Second, when the content of La^{3+} ions increased, the Curie temperature of the specimens moved to a lower temperature range. Different specimens hold different Curie temperatures, so the same temperature was within different phase-transformation-temperature-ranges for different specimens; for example, 40°C was at the mixture of ferroelectric and paraelectric phases for specimen 2#, while 40°C was at paraelectric phase for specimen 5#. And third, lead vacancy was also a reason that made hysteresis decrease.

In summary, the remanent polarization and coercive field decreased gradually when temperature and/or lanthanum content increased, which was consistent with published literature.

Table 2
The effect of content of lanthanum on electrostriction and electrostrictive coefficients of the specimens

	Specimen number				
	1#	2#	3#	4#	5#
Composition (xLa/PZN/BT/PT)	0/85/10/5	1/85/10/5	2/85/10/5	5/85/10/5	10/85/10/5
Transverse electrostriction (1.3 kV/mm, 30°C)	-1.6×10^{-4}	-8.0×10^{-5}	-7.0×10^{-5}	-0.4×10^{-5}	–
Transverse electrostrictive coefficient Q_{12} (m^4/C^2)	-6.475×10^{-2}	-2.594×10^{-2}	-2.224×10^{-2}	-2.07×10^{-2}	–
Longitudinal electrostriction (1.3 kv/mm, 30°C)	2.1×10^{-4}	1.7×10^{-4}	1.5×10^{-4}	2.8×10^{-5}	–
Longitudinal electrostriction coefficients Q_{11} (m^4/C^2)	8.634×10^{-2}	5.242×10^{-2}	5.012×10^{-2}	2.086×10^{-2}	–

Table 3
The parameters of electric hysteresis of La-doped specimens

	Coercive field (kV/cm)			Remanent polarization (C/m^2)			Spontaneous polarization (C/m^2)
Specimen number	60°C	40°C	0°C	60°C	40°C	0°C	40°C
1#	1.11	1.41	2.50	0.042	0.060	0.091	0.27
2#	0.83	1.22	2.02	0.025	0.035	0.069	0.22
4#	0.30	0.50	1.03	0.015	0.020	0.041	0.10
5#	0.05	0.07	0.15	0.007	0.008	0.013	0.03

4. Conclusions

The dielectric, electrostrictive properties and polarization-electric field hysteresis of lanthanum doped PZN-based ceramics were investigated. With the increase of lanthanum content, dielectric constant and the amount of perovskite phase decreased, the lattice constant shrank from 4.051 to 4.032 pm, but their thermostability improved. When the content of lanthanum changed from 0 to 0.05 mol, at the condition of 1.3×10^6 V/m and 30°C, the longitudinal electrostriction decreased from 2.1×10^{-4} to 2.8×10^{-5}, the longitudinal electrostritive coefficient from 8.634×10^{-2} to 2.086×10^{-2} m^4/C^2, while the transverse electrostriction decreased from -1.6×10^{-4} to -0.4×10^{-5}, the transverse electrostritive coefficient from -6.475×10^{-2} to -2.07×10^{-2} m^4/C^2. With the increment of lanthanum content and/or measuring temperatures, the remanent polarization and coercive field decreased gradually.

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