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Short communication

Influence of calcium substitution on structural and electrical properties of substituted barium titanate

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Abstract

$Ba_{0.80-x}Ca_xPb_{0.20}Ti_{0.90}Zr_{0.10}O_3$ ceramics ($x = 0$, 0.10 and 0.20) were synthesized by solid state reaction. Samples microstructure and dielectric, ferroelectric and piezoelectric properties were studied. Dielectric constant (ε), coercive field (E_c), remanent polarization (P_r) and ratio of remanent to spontaneous polarization (P_r/P_s) were studied at different temperatures. Sample with $x = 0.10$ was found to have maximum and comparatively more stable P_r/P_s ratio over a wide temperature range. Dielectric loss was found to improve with increase in x whereas piezoelectric charge coefficient d_{33} was found to decrease with increase in x.

Keywords: Ferroelectrics; XRD; BZT; Dielectric loss; Piezoelectric; Microstructure

1. Introduction

$BaTi_{1-x}Zr_xO_3$ (BZT) ferroelectric ceramics with low dielectric loss have been chosen as an alternative to $BaTiO_3$ in the fabrication of ceramic capacitors because Zr^{4+} is chemically more stable than Ti^{4+} [1–3]. The nature of ferroelectric phase transition at the transition temperature of BZT is known to change with Zr content. For $x > 0.08$, $BaTi_{1-x}Zr_xO_3$ ceramics show a broad dielectric constant vs temperature curve near the transition temperature [4–8]. It is reported that Pb substituted BZT ceramics exhibit improvements in tangent loss, dielectric constant and ferroelectric properties [9,10]. It is also reported that calcium substituted BZT ceramics exhibit a broad dielectric constant vs temperature curve near T_c with high value of dielectric constant [11]. Thus for the present study, calcium modified BPZT ceramics $Ba_{0.80-x}Ca_xPb_{0.20}Ti_{0.90}Zr_{0.10}O_3$ (for $x = 0$, 0.10 and 0.20) were synthesized by solid state reaction. Structural, dielectric and ferroelectric properties and their inter relationship were studied.

2. Experimental

$BaCO_3$, PbO, TiO_2, ZrO_2 and $CaCO_3$ were used as starting raw materials which were weighed according to stoichiometric ratio, mixed and subjected to wet ball milling for 16 h using distilled water as wetting agent. After drying, the powder was calcined at 900 °C for 4 h in alumina crucibles then ball milled again for 8 h and dried. Small amount of PVA diluted solution was added and then the powder was uniaxially pressed in to circular discs and sintered at 1300 °C for 4 h with a heating rate of 5 °C/min. X-ray diffraction (XRD) patterns were recorded (Bruker, D-8 Advance model). The dielectric properties were measured at frequencies from 100 Hz to 100 kHz (Agilent 4284A LCR meter) in the temperature range 25–250 °C. P.E. hysteresis loops were recorded at different temperatures. Piezoelectric charge coefficient d_{33} was measured (Piezometer system of Concord Electroceramics Ind., India).

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3. Results and discussion

3.1. Structural properties

XRD (Fig. 1) show the samples to be single phase with perovskite tetragonal structure. Shifting of peaks towards higher angles with the amount of Ca substitution indicates the smaller Ca^{2+} (1.48 Å) ions to replace the larger Ba^{2+} (1.75 Å) ions [12] with consequent reduction of the lattice parameter as x increases (Table 1).

3.2. Dielectric properties

Dielectric peaks observed in the ε–T graphs (Fig. 2) show typical ferroelectric behavior in all samples. From these peaks, the ferroelectric to paraelectric phase transition temperature (T_{max}) can be determined (Table 1). The value of ε decreases with the increase in frequency (100 Hz to 100 kHz) because of reduced contribution from space charge, ionic and orientational

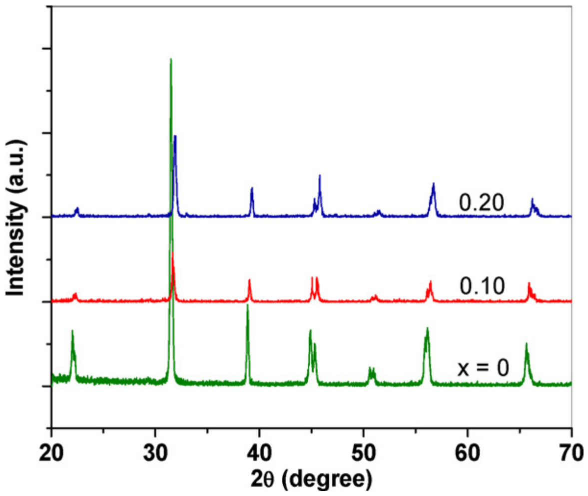

Fig. 1. XRD patterns of $Ba_{0.80-x}Ca_xPb_{0.20}Ti_{0.90}Zr_{0.10}O_3$ ceramics.

Table 1
Lattice parameters (a, c), relative density and dielectric properties (at 100 kHz).

x	c (Å)	a (Å)	Relative density (%)	T_{max} (°C)	ε_{RT}	tan δ_{RT}	ε_{max}	tan $\delta_{T_{max}}$
0	4.0542	4.0000	89.75	148	1375	0.04	5985	0.025
0.10	4.0206	3.9838	86.65	142	970	0.002	7930	0.010
0.20	4.0004	3.9607	85.83	142	950	0.012	4970	0.009

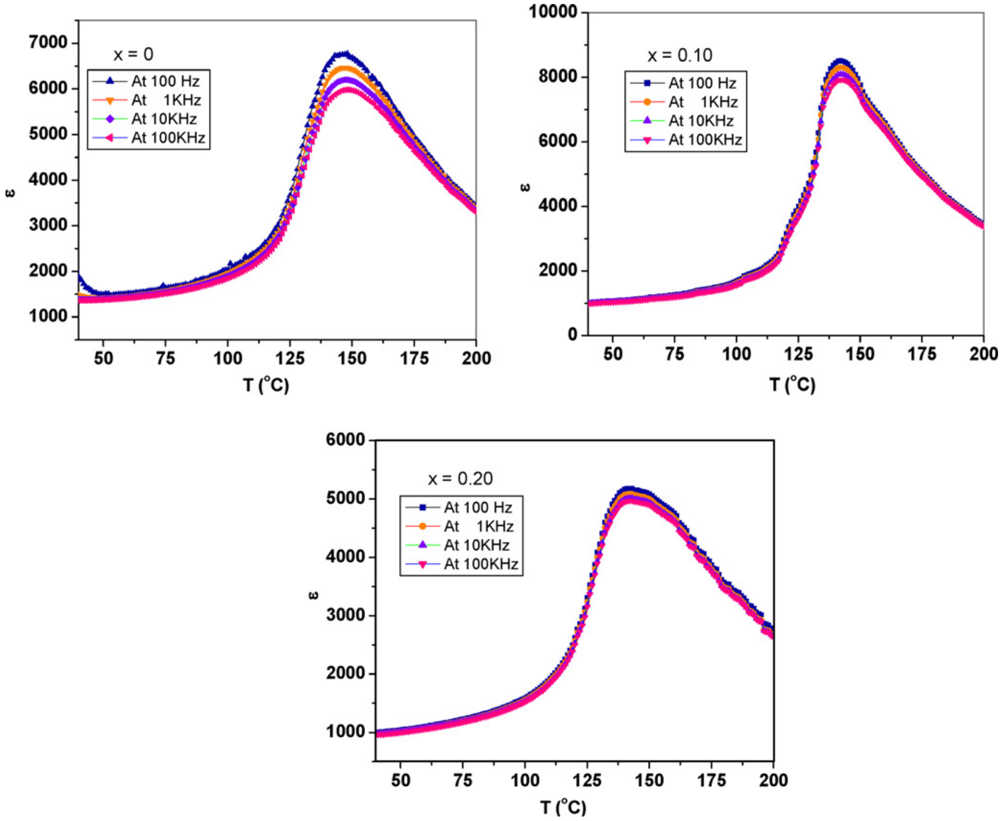

Fig. 2. ε–T curves for all x.

polarizations at higher frequencies. ε_{max} has maximum value for $x = 0.10$ (Table 1) whereas for $x = 0.20$ the dielectric peak broadens, as expected. However this broadening may be due to micro compositional fluctuations resulting in different local transition temperatures which also results in decrease in dielectric maxima [13,14].

ε_{RT} decreases as x increases from 0 to 0.20, which may be attributed to substitution of Ca to strongly lower the tetragonal–orthogonal transition temperature. This is of great practical value in improving the temperature stability of dielectric properties for many engineering applications. A marked improvement in tan δ can also be achieved by Ca substitution. Sample with $x = 0.10$ has a value of tan δ_{RT} (0.2%) which is rarely reported in literature. This again indicates prepared materials to be potential candidates for dielectric applications like capacitors.

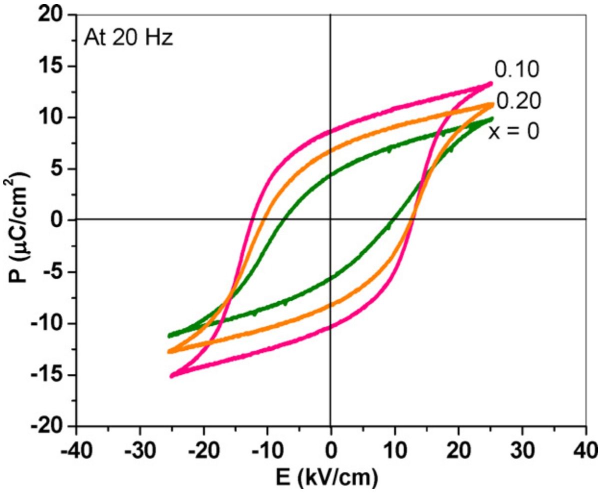

Fig. 3. P–E hysteresis loops at 30 °C.

3.3. Ferroelectric properties

P–E hysteresis loops recorded at 30 °C are shown in Fig. 3. P_r/P_s (squareness of P–E loop) improves by calcium substitution. This improvement in P_r/P_s ratio indicates that the material may be suitable for memory devices. It can be observed that sample with $x = 0.10$ has maximum value of E_c, P_r and P_r/P_s ratio (Table 2).

P–E loops were also recorded at different temperatures. The loops get shrink as temperature approaches the transition temperatures, T_{max} (Fig. 4). Sample with $x = 0.10$ shows a high P_r, reduced E_c with fast switching at 120 °C.

Variation of E_c, P_r, P_{max} and P_r/P_s ratio with temperature for all values of x is shown in Fig. 5. E_c decreases with temperature increase whereas an increase in P_r is observed for a certain range of temperature and it then decreases at higher temperature. Decrease in E_c shows that the material softens on heating. Increase in P_r is mainly due to increase in internal energy caused by thermal excitation resulting in greater dipole alignment. Existence of polarization beyond T_{max} may be due to induced polarization. Sample with $x = 0.10$, P_r/P_s ratio was found to be stable over a certain range of temperature and decreases as temperature approaches T_{max}.

3.4. Piezoelectric properties

k_p and k_t were determined by impedance spectroscopy (resonance–antiresonance method). Piezoelectric charge coefficient d_{33} and k_p decrease as x increases (Table 2). Although ceramic sample with $x = 0.10$ shows decreased dielectric constant at room temperature, k_p and d_{33} remain reasonably high. Such compositions may be possible candidates for use for ultrasonics and for underwater sound application.

Table 2
Coercive field (E_c), remanent polarization (P_r), P_r/P_s, d_{33}, k_p and k_t measured at 30 °C.

x	E (kV/cm)	P_r (μC/cm^2)	P_r/P_s	d_{33} (pC/N)	k_p (%)	k_t (%)
0	8.88	4.7	0.46	107	14.7	12.64
0.10	12.59	9.5	0.66	88	10.2	15.49
0.20	11.59	7.5	0.62	72	8.03	13.83

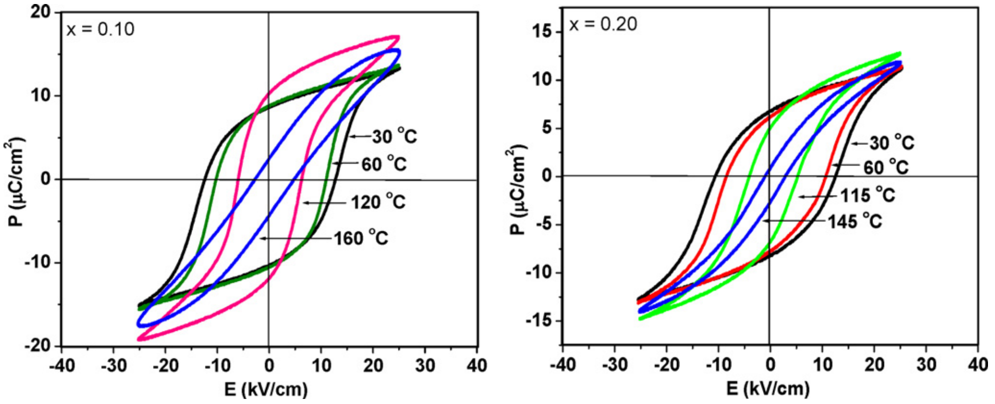

Fig. 4. P–E hysteresis loops at different temperatures for the samples with $x = 0.10$ and 0.20.

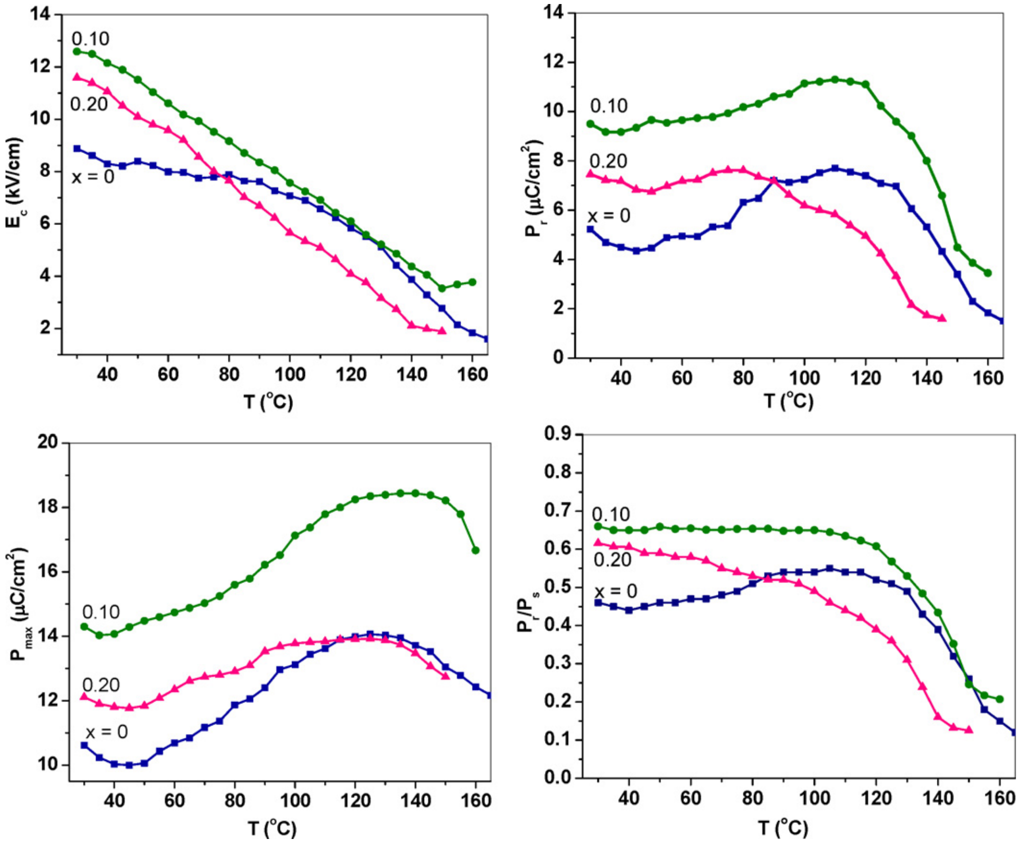

Fig. 5. Variation of E_c, P_r, P_{max} and P_r/P_s with temperature.

4. Conclusions

$Ba_{0.80-x}Ca_xPb_{0.20}Ti_{0.90}Zr_{0.10}O_3$ materials were synthesized by the conventional solid state reaction method. All the samples show tetragonal structure, the lattice constant decreasing with the increase of calcium content. Dielectric constant and tangent loss improved with calcium substitution. The sample with $x = 0.10$ showed the best ferroelectric properties at room temperature as well as at higher temperatures.

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