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Synthesis and dielectric properties of substituted barium titanate ceramics

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ABSTRACT

Barium titanate is one of the most studied ferroelectric materials which has been used in various forms, e.g. bulk, thin and thick films, powder, in a number of applications. In order to achieve a material with desired properties, it is modified with suitable substituents. Most common substituents have been strontium, calcium and zirconium. Here, we report studies on lead and zirconium substituted barium titanate. The material series with compositional formula $Ba_{0.80}Pb_{0.20}Ti_{1-x}Zr_xO_3$, with x varying from 0 to 0.1, was chosen for investigations. The material was synthesized by solid-state reaction method. Reacted powders compacted in the form of circular discs were sintered at 1300 °C. All the samples were subjected to X-ray diffraction (XRD) analysis and found to have single phase perovskite structure. Dielectric behavior was studied as a function of frequency and temperature. Curie temperature (T_c) was found to decrease with increasing x.

1. Introduction

Barium titanate (BT) has become one of the most important electroceramics since the discovery of its versatility in multilayer ceramic capacitors (MLCC), positive temperature coefficient of resistance (PTCR) thermistors, piezoelectric sensors, transducers, actuators and ferroelectric random access memories (FRAM) and electro-optic devices [1,2]. Its properties can be further improved by doping or by forming solid solutions with other systems or by controlling its microstructural characteristics by varying process parameters. The solid solution $BaTiO_3$–$BaZrO_3$ (BT–BZ) is also of great interest due to its different character of the dielectric response which can be tuned by composition. The dielectric data reported for $BaZr_xTi_{1-x}O_3$ ceramics suggest a normal ferroelectric behavior for $0 < x < 0.1$, a diffuse phase transition in the range $0.1 < x < 0.20$ and non-ferroelectric character for $x > 0.20$ [3,4]. On MgO doping, dielectric anomalies corresponding to lower phase transformations were broadened and depressed, while an anomaly for a cubic-tetragonal transformation remained and shifted to a lower temperature [5–7]. The influence of zirconium on the dielectric properties of barium titanate has been widely reported [8–10]. However, the influence of substitution of zirconium on the dielectric properties of $Ba_{0.80}Pb_{0.20}TiO_3$ is rarely found in literature. In the present work, we are reporting the results of a dielectric study of $Ba_{0.80}Pb_{0.20}Ti_{1-x}Zr_xO_3$ ceramics prepared by solid-state reaction route. Ferroelectric properties of these materials have already been published by us [11].

2. Experimental details

2.1. Sample preparation

$Ba_{0.80}Pb_{0.20}Ti_{1-x}Zr_xO_3$ (BPZT) ceramics were prepared by solid-state reaction technique using the following chemical reaction:

$$0.80(BaCO_3) + 0.20(PbO) + (1-x)TiO_2 + xZrO_2 \rightarrow Ba_{0.80}Pb_{0.20}Ti_{1-x}Zr_xO_3 + CO_2\uparrow \quad (1)$$

with x ranging from 0 to 0.10 in the steps of 0.02.

Proportionate amounts, as per above formula, of AR grade starting materials ($BaCO_3$, PbO, TiO_2 and ZrO_2) were weighed and wet-mixed by ball-milling for 16 h using zirconia balls as grinding media. Distilled water was used as wetting agent. The slurry was dried and calcined in alumina crucible at 900 °C for 4 h with heat-

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Table 1
Lattice constants (a & c), tetragonality (c/a), X-ray density (d_{xrd}), experimental density (d_{ex}), porosity and grain size of all the samples.

x	a (Å)	c (Å)	c/a	d_{xrd} (g/cc)	d_{ex} (g/cc)	Porosity (%)	Grain size (μm)
0	3.9760	4.0552	1.0199	6.76	6.33	6.4	17.7
0.02	3.9750	4.0542	1.0199	6.43	5.93	7.8	2.4
0.04	3.9755	4.0541	1.0198	6.45	5.87	9.0	3.1
0.06	3.9755	4.0382	1.0158	6.50	5.85	10.0	5.1
0.08	3.9861	4.0435	1.0144	6.48	5.81	10.3	7.3
0.10	4.0000	4.0542	1.0136	6.44	5.78	10.3	6.7

ing/cooling rates of 5 °C/min [12,13]. Calcined powders were ball milled again, dried and pressed using uniaxial press to form discs of diameter ~15 mm. Small amount of diluted PVA (3% solution in distilled water) was added as binder. The compacted discs were sintered at 1300 °C for 4 h with constant heating/cooling rates of 5 °C/min. To minimize lead loss, sintering was carried out in closed alumina crucibles in lead rich atmosphere. Density of the final sintered products was determined using the Archimedes principle [14].

2.2. Characterization

In order to evaluate the electrical properties, sintered samples were grounded to thickness ~0.8 mm and flat surfaces were polished. Silver electrodes were then fired on both sides of the samples at 400 °C for 30 min. The dielectric properties were measured at four discrete frequencies 100 Hz, 1 kHz, 10 kHz and 100 kHz using an Agilent 4263B LCR meter in the temperature range 25–250 °C with a heating rate of 1 °C/min using an automated system. XRD patterns were recorded for all the samples using Bruker, D-8 Advance X-ray diffractometer.

3. Results and discussion

3.1. Structural properties

XRD analysis shows all the samples to have pure perovskite phase with tetragonal structure. XRD patterns are shown in Fig. 1. From the observed d values, lattice parameters (a & c) were computed. Lattice constants (a & c), tetragonality (c/a), X-ray density (d_{xrd}) computed from lattice parameters, experimental density (d_{ex}) measured using Archimedes principle, porosity = $(d_{xrd}-d_{ex}) \times 100/d_{xrd}$ and grain size determined from SEM micrographs, reported recently by us for these materials [11], are given in Table 1. Tetragonality (c/a) was found to decrease with increasing x. Experimental density decreases with increasing substitutional parameter x and porosity was found to increase with increasing x. Grain size was found to decrease drastically for the first substituted sample (x = 0.02) and increases after that.

3.2. Dielectric properties

It was realized very early that substitution of Pb^{2+} for Ba^{2+} in $BaTiO_3$ raises the Curie point [15]. Complete solid solution occurs between the two end member compounds ($BaTiO_3$ and $PbTiO_3$) [16]. Although lead titanate has strong ferroelectric distortion and large polar moment [17], its high coercive field makes it difficult to accomplish enough poling. The substitution of Pb^{2+} for Ba^{2+} raises the Curie point monotonically towards that of $PbTiO_3$ (490 °C). It also lowers the orthorhombic-tetragonal and rhombohedral-orthorhombic transition temperatures [18]. Zr^{4+}, a well known substituent for Ti^{4+}, which causes depression of the Curie point and causes a rise in the orthorhombic-tetragonal transition temperature, so that the orthorhombic phase becomes stable at room temperature. This causes a rise in ferroelectric polarization at room temperature. The variation of the room temperature dielectric constant with composition (x) is shown in Fig. 2.

The dielectric properties were studied as a function of temperature at four different frequencies. Dielectric constant increases with increasing temperature and shows a peak, which is characteristic of ferroelectric materials. The variation is shown in Fig. 3. From the dielectric constant vs temperature plot transition temperature was determined. Transition temperature decreases with increasing zirconium contents. The Curie point, room temperature dielectric constant and maximum dielectric constant (at T_c) for the sample with composition $Ba_{0.80}Pb_{0.20}TiO_3$, measured at 10 kHz, are 217 °C, 265 and 3390, respectively. Variation of T_c with x is shown in Fig. 4.

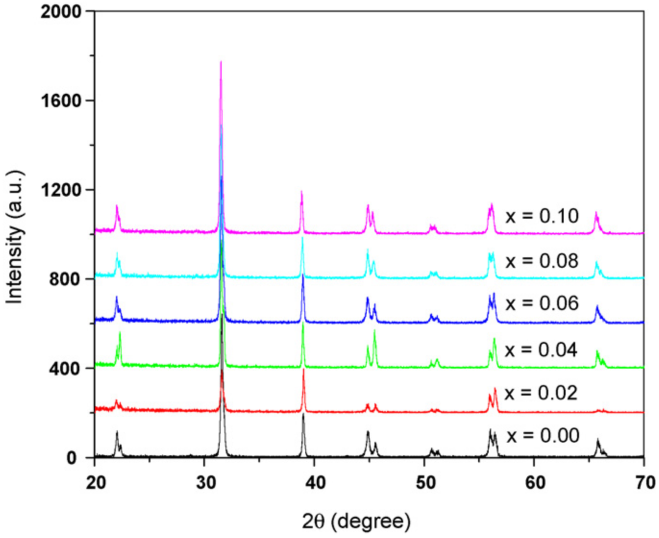

Fig. 1. XRD patterns for the samples with x = 0.00 to x = 0.10.

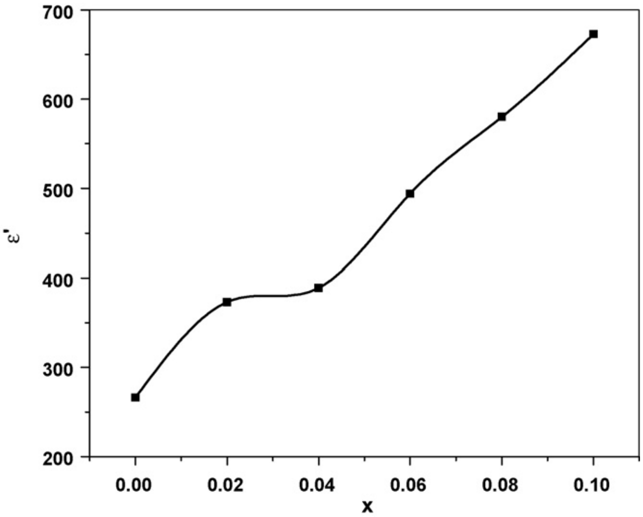

Fig. 2. Variation of dielectric constant (ε′) with zirconium content (x) at 10 kHz.

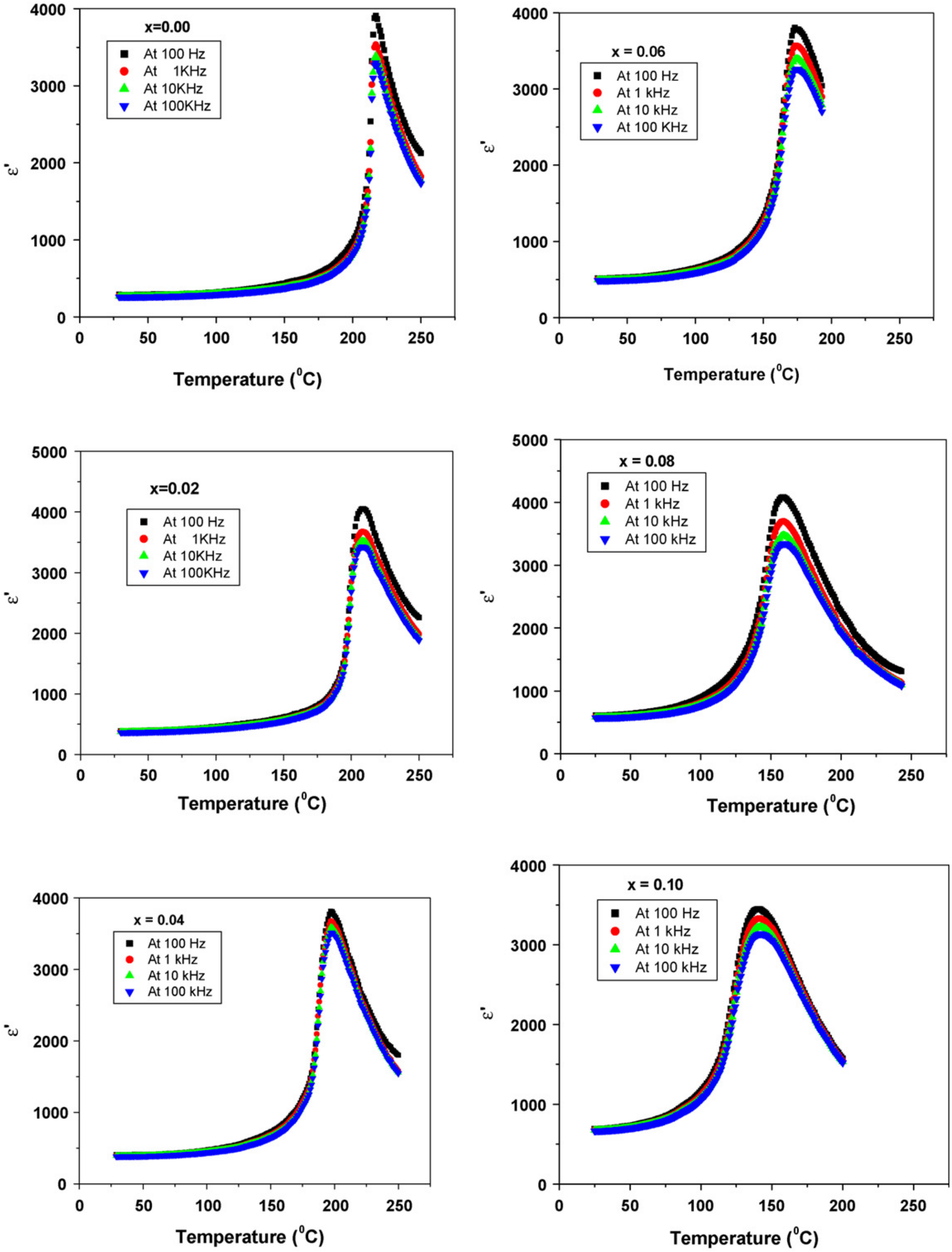

Fig. 3. Temperature dependence of dielectric constant (ε') at different frequencies.

Variation of dielectric constant with temperature, for the samples with different zirconium contents at a single frequency (10 kHz), is shown in Fig. 5.

From Fig. 3, it is clear that in general maximum value of dielectric constant decreases with increasing zirconium contents and the observed behavior may be attributed to decrease in tetragonality. However, the broadening of the peaks increases with increase in zirconium substitution, which is a characteristic of diffused phase transition. This may be due to disorder in the arrangement of various atoms, leading to a microscopic heterogeneity in the composition and thus a distribution of different local Curie points [19]. The structural disorder in the compounds arises due to the presence of a number of voids and impurities of different sizes.

Values of $\tan\delta$ at room temperature (RT) and T_c are given in Table 2. At RT, the value of $\tan\delta$ decreases with increasing x and it

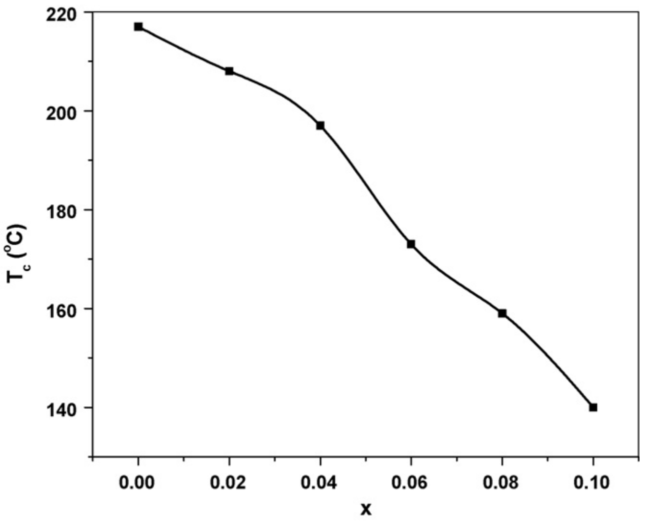

Fig. 4. Curie temperature (T_c) as a function of zirconium content (x).

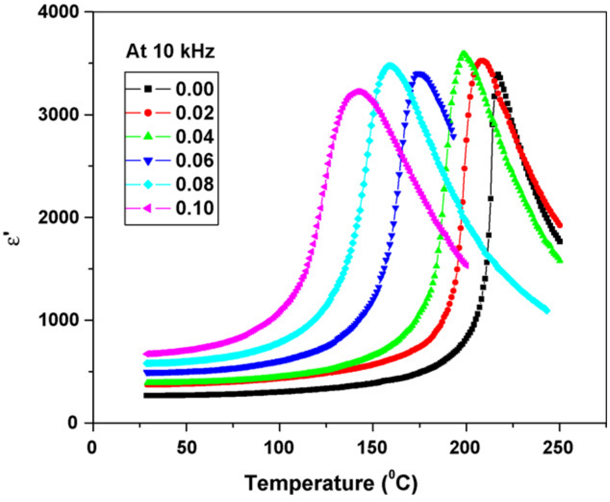

Fig. 5. Temperature dependence of dielectric constant (ε') for all values of x at 10 kHz.

is between 0.6% and 1.6% which is taken as a very good value for any application point of view.

The temperature dependence of dielectric loss for the samples with $x = 0.04$ and 0.10 at four different frequencies is shown in Fig. 6. The temperature dependence of dielectric loss for all the samples at 10 kHz is shown in Fig. 7.

Table 2
Variation of dielectric constant and tan δ measured at 10 kHz with different values of x.

x	T_c (°C)	ε (at RT)	tan δ (at RT)	ε (at T_c)	tan δ (at T_c)
0	217	265	0.016	3390	0.026
0.02	208	375	0.011	3525	0.026
0.04	197	390	0.011	3590	0.017
0.06	173	495	0.010	3390	0.033
0.08	159	580	0.009	3480	0.035
0.10	140	675	0.006	3220	0.021

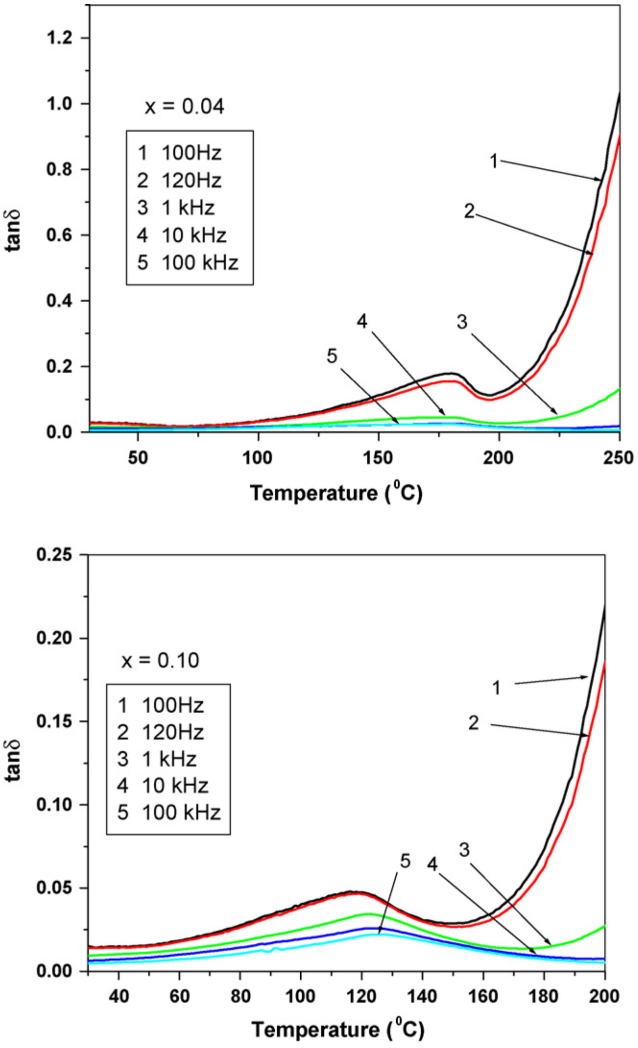

Fig. 6. Temperature dependence of dielectric loss (tan δ) for $x = 0.04$ and 0.10 at different frequencies.

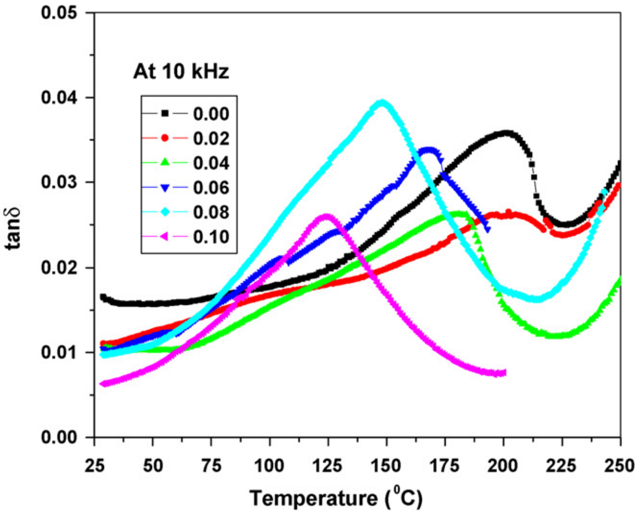

Fig. 7. Temperature dependence of dielectric loss (tan δ) for all samples at 10 kHz.

4. Conclusions

XRD analysis of all the sintered samples confirmed that all the samples are in pure perovskite phase with tetragonal structure. Room temperature dielectric constant increases with increase in zirconium content whereas the dielectric loss has values between 0.6% and 1.6%. The Curie temperature is found to be decreasing with increasing x, while the dielectric peaks widened with increase in x.

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