Dielectric behaviour of Pb-substituted BZT ceramics

PARVEEN KUMAR[1,4], **SANGEETA SINGH**[2], **J K JUNEJA**[3], **K K RAINA**[4] and
CHANDRA PRAKASH[5,*]

[1]Electroceramics Research Laboratory, [2]Department of Physics, G.V.M. Girls College, Sonepat 131 001, India
[3]Department of Physics, Hindu College, Sonepat 131 001, India
[4]School of Physics and Material Science, Thapar University, Patiala 147 004, India
[5]Directorate of ER&IPR, DRDO, DRDO Bhawan, New Delhi 110 105, India

Abstract. Material series with compositional formula $Ba_{1.0-x}Pb_xTi_{0.90}Zr_{0.10}O_3$ ($0 \le x \le 0.20$, in steps of 0.05) were prepared by conventional solid state method. All the samples were subjected to X-ray diffraction (XRD) studies and found to be single phase with perovskite structure. SEM measurements were done in order to collect micro-structural information. Different transition temperatures were found to depend on the Pb content. Tetragonality (c/a) and Curie temperature (T_c) increase with increase in lead content x. Dielectric properties were studied as a function of temperature and frequencies.

Keywords. BZT; dielectric properties; XRD; transition temperature; tetragonality.

1. Introduction

Among all the ferroelectric materials, barium titanate (BT) is the most studied material which has been used in various forms, e.g. bulk, thin and thick film and powder, in a number of applications. It has become one of the most important electroceramics in multilayer ceramic capacitors (MLCC), positive temperature coefficient of resistance (PCTR) thermistors (Haertling 1999; Uchino 2000; Mbenkum *et al* 2005). Barium strontium titanate (BST) is also widely used as dielectrics in capacitors because of its high dielectric constant due to which it has become a promising candidate for dynamic random access memory (DRAM) applications (Rhim *et al* 2000). Due to greater stability of Zr^{4+} ion as compared to Ti^{4+} ion, barium zirconium titanate (BZT) ceramics have low dielectric losses, and thus they can be used as potential candidates for capacitor applications. Furthermore, BZT-based ceramics show interesting dielectric behaviour with different Zr/Ti ratios. Because of its large ionic radii, substitution of Zr^{4+} for Ti^{4+} ion results in increasing the lattice cell volume by decreasing its tetragonality. This results in a decrease in the ferroelectric to paraelectric (tetragonal to cubic) phase transition temperature (T_c) and increase in other two ferroelectric to ferroelectric (rhombohedral to orthorhombic and orthorhombic to tetragonal) phase transition temperatures (T_{r-o} or T_{o-t}). Thus, dielectric peak width increases with increase in zirconium substitution because all the three phase transitions merge into each other. BZT

with 10 mol% Zr shows only one broad peak with decreased dielectric loss, and so the material can be used in a number of dielectric based applications. On further substitution of Zr^{4+}, ferroelectric to paraelectric phase transition changes to diffused phase transition (Kell and Hellicar 1956; Ravez and Simon 1997; Farhi *et al* 1999; Zhi *et al* 2002; Simon *et al* 2004; Dixit *et al* 2006). Pb^{2+} is a well-known substitution for Ba^{2+} ion which monotonically increases T_c towards Curie temperature of $PbTiO_3$ (490°C) while the other two transition temperatures shift towards lower temperature. Thus, substitution of Pb^{2+} results in decrease in room temperature dielectric constant and greater temperature stability in the dielectric behaviour (Perry *et al* 1967; Pilgrim *et al* 1990). This makes the Pb-substituted BZT (10/90) material suitable for more applications. Thus, in the present work, material series with compositional formula $Ba_{1-x}Pb_xTi_{0.90}Zr_{0.10}O_3$ ($0 \le x \le 0.20$ in steps of 0.05) were studied. Their structural and dielectric properties and their interrelationship were investigated and discussed here.

2. Experimental

Polycrystalline ceramic samples with compositions $Ba_{1.0-x}Pb_xTi_{0.90}Zr_{0.10}O_3$ with $0 \le x \le 0.20$ in the steps of 0.05 were prepared by conventional solid state reaction technique. The starting raw chemicals were AR-grade $BaCO_3$, PbO, TiO_2 and ZrO_2 powders. The weighed raw materials were mixed and grounded by wet ball milling for 16 h using high-density zirconia balls as milling media. The dried powder was calcined at 900°C for 4 h in alumina

*Author for correspondence (cprakash@hqr.drdo.in)

crucibles. The calcined powder was ball-milled again for 8 h and dried. A small amount of diluted binder was added to give mechanical strength for easy transportation from pressing to furnace for sintering. Circular pellets, uniaxially pressed at pressure of 10 ton, were placed on platinum sheet in a closed alumina crucible and sintered at 1300°C for 4 h at a heating rate of 5°C/min. Lead-rich environment was maintained to minimize lead escape during sintering. XRD patterns were recorded for all the samples using Bruker, D-8 Advance. SEM micrographs were also observed to collect structural information. Silver electrodes were deposited onto both main sides of the compacts to conduct dielectric measurements. The dielectric properties were measured over a frequency range of 20 Hz to 1 MHz using an Agilent 4284A LCR meter from 30°C to 200°C using an automated system.

3. Results and discussion

Figure 1 shows the XRD patterns for all the sintered samples. The presence of sharp single peaks of varying intensity in the XRD pattern indicates formation of single phase polycrystalline samples. All the peaks in the XRD pattern could be indexed and the lattice parameters were determined using interplanar spacing d. The samples with $x = 0$ and 0·05, were found to have rhombohedral and orthorhombic structure, respectively. Further increase in x caused the change of structure from orthorhombic to tetragonal. Existence of splitted peaks (200) and (002) in the XRD pattern of the sample with $x = 0·20$ clearly indicates that the sample has tetragonal structure. Tetragonality was found to increase with increase in x. Lattice parameters (a and c) and tetragonality as a function of x are shown in figure 2.
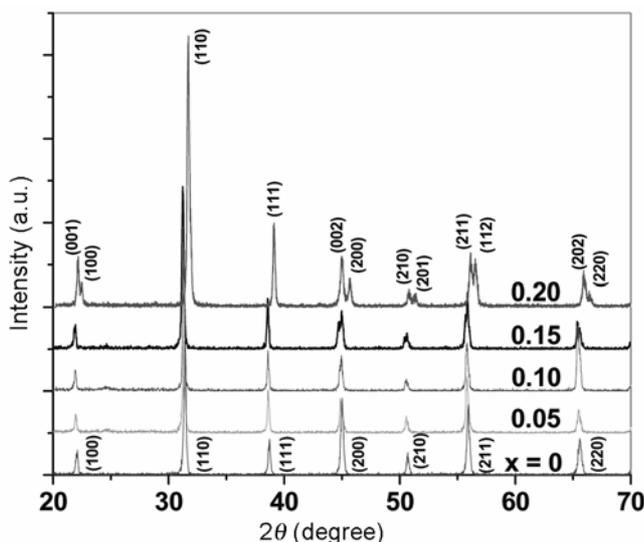
Figure 3 shows the SEM micrographs of fractured cross sections of sintered $Ba_{1·0-x}Pb_xTi_{0·90}Zr_{0·10}O_3$ ceramic samples for $x = 0$, 0·05 and 0·20. Comparatively large grains can be observed for $x = 0·20$. Variation of dielectric constant and $\tan \delta$ with frequency at 30°C is shown in figure 4.

Dielectric constant (ε) and loss tangent ($\tan \delta$) decrease with increase in frequency, which is a general behaviour of a ferroelectric. A higher value of the dielectric constant at low frequency is due to the presence of all types of polarizations (i.e. electronic, ionic, dipolar, interfacial, etc) in the material samples near room temperature. Since electronic polarization dominates over all other polarizations at higher frequencies, the value of dielectric constant decreases with increase in frequency (Thakur and Chandra Prakash 2003).

The dielectric properties were measured as a function of temperature up to well above the transition temperature, T_c, of the corresponding samples at four different frequencies. The dielectric constant increases with increasing temperature and shows a peak which is characteristic of ferroelectric materials. Variations of the dielectric constant with temperature for $x = 0·05$ are shown in figure 5. The dielectric constant does not show much dependence on frequency at temperature below T_c, but the effect of both frequency becomes pronounced as the temperature approaches T_c. The temperature dependence of the dielectric constant and $\tan \delta$ for all the samples measured at 100 kHz is shown in figure 6.

For ceramic sample with $x = 0·05$ another smaller dielectric peak was observed at temperature lower than T_c. This hump corresponds to orthogonal to tetragonal phase transition for the material. This may be attributed to the fact that substitution of Pb^{2+} for Ba^{2+} decreases ferroelectric to ferroelectric phase transitions (T_{r-o} or T_{o-t}) towards lower temperature. While material samples with $x > 0·05$, no such peak is there, which clearly indicates that
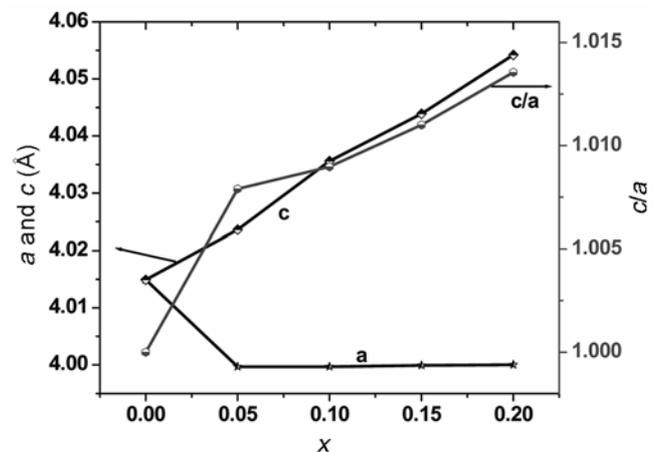

Figure 1. XRD patterns of sintered $Ba_{1·0-x}Pb_xTi_{0·90}Zr_{0·10}O_3$ ceramics.

Figure 2. Variation of lattice parameters (a & c) and tetragonality (c/a) as a function of x.
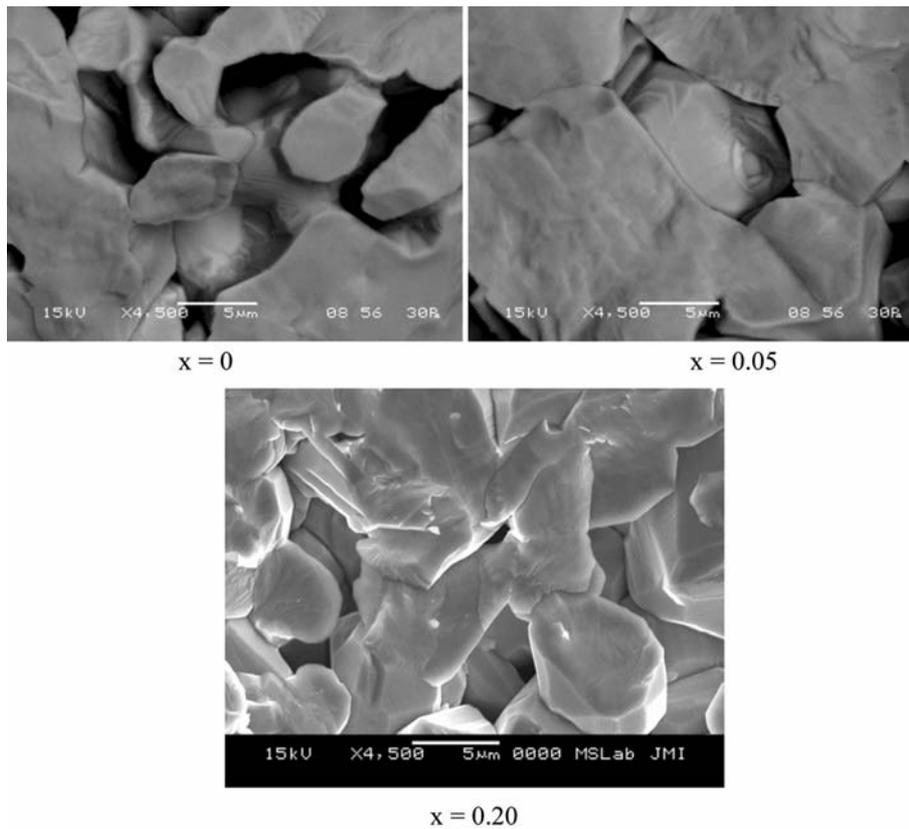
Figure 3. SEM micrographs of sintered $Ba_{1.0-x}Pb_xTi_{0.90}Zr_{0.10}O_3$ ceramics for $x = 0$, 0·05 and 0·20.
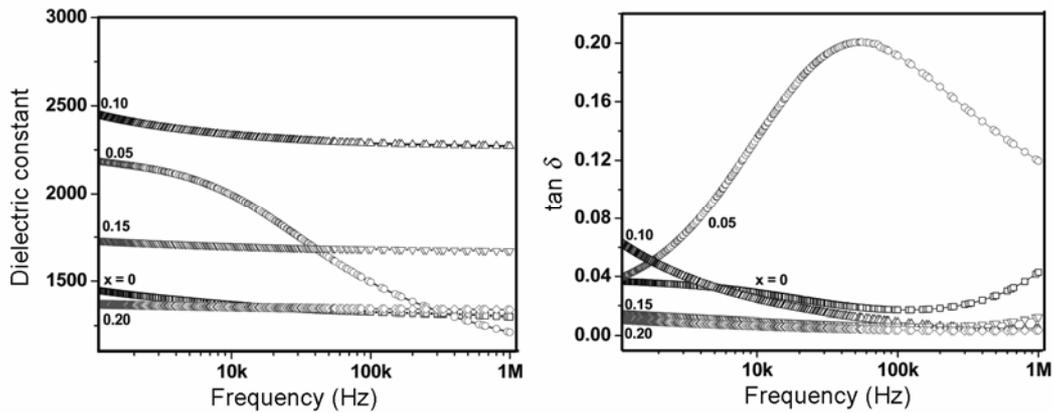

Figure 4. Variation of dielectric constant and tan δ as a function of frequency.

material phase is tetragonal at room temperature (Shirane and Suzuki 1951; Jaffe *et al* 1971; Kuang *et al* 2009). Increase in tan δ with temperature may be due to increase in conductivity with temperature (Kuharuangrong 2001). From the comparative plot of dielectric constant with temperature, it can be observed that T_c shifts towards higher temperature with increase in x, which is an expected result of Pb^{2+} substitution. Since sample with

$x = 0·05$ have larger grains, long-range ordered polarization may occur, which results in dielectric peak with greater height as compared to samples with other values of x. Large-sized grains can be achieved for other values of x by sintering the material samples at temperature higher than 1300°C (Hsu *et al* 2004). Since lead is volatile, this limits the sintering temperature. Greater stability of dielectric constant over a certain range of temperature can
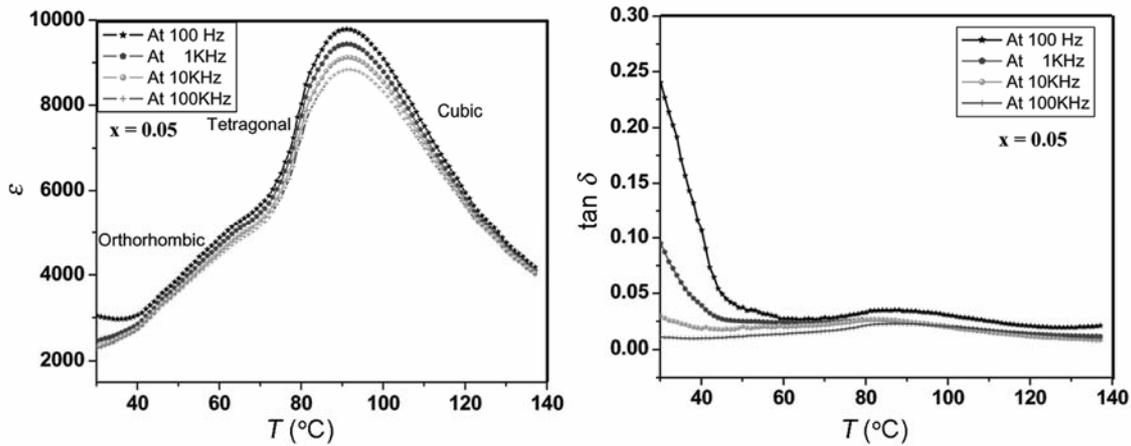
Figure 5. Variation of dielectric constant and tan δ of sintered $Ba_{1\cdot 0-x}Pb_xTi_{0\cdot 90}Zr_{0\cdot 10}O_3$ ceramics as a function of temperature for the sample with $x = 0.05$.
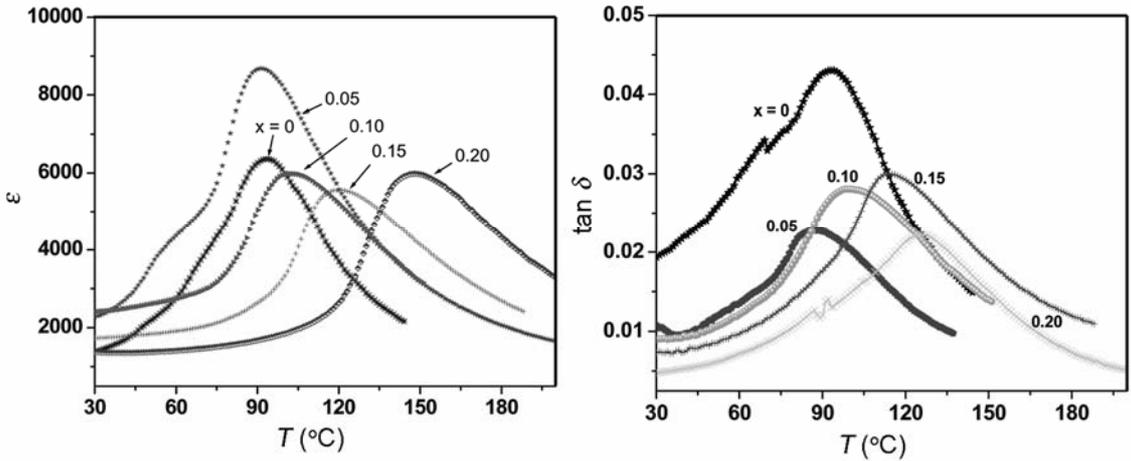

Figure 6. Variation of dielectric constant and tan δ with temperature for all x at 100 kHz.
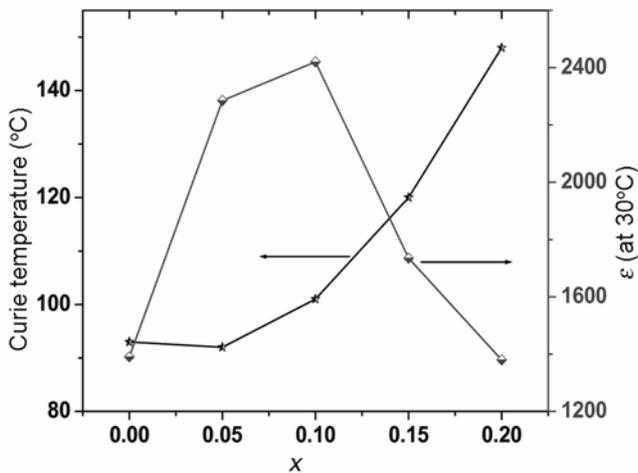

Figure 7. Room temperature dielectric constant and T_c of $Ba_{1\cdot 0-x}Pb_xTi_{0\cdot 90}Zr_{0\cdot 10}O_3$ ceramics samples.

also be observed for samples with higher values of x. This is also an expected result of Pb^{2+} substitution. Tangent loss found to decrease with increase in Pb^{2+} content.

Figure 7 shows the variation of room temperature (at 30°C) dielectric constant and T_c of the material samples as a function of x. T_c increases with increase in x, while room temperature dielectric constant increases up to $x = 0\cdot 10$ and then decreases for further values of x. We observed behaviour in room temperature dielectric constant up to $x = 0\cdot 10$ because of shifting of T_{r-o} and T_{o-t} towards lower temperature.

4. Conclusions

Material series with compositional formula $Ba_{1\cdot 0-x}$ $Pb_xTi_{0\cdot 90}Zr_{0\cdot 10}O_3$ ($0 \leq x \leq 0\cdot 20$) were prepared by conventional solid state route. XRD analysis confirmed single phase with perovskite structure. Dielectric properties and

different transition temperatures were found to depend on the Pb content. T_c increases with increase in Pb substitution. Room temperature dielectric constant first increases up to $x = 0 \cdot 10$ and then decreases for further values of x, while tan δ decreases with increase in the value of x.

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