Study of Pb($Zr_{0.65}Ti_{0.35}$)O$_3$(PZT(65/35) doping on structural, dielectric and conductivity properties of BaTiO$_3$(BT) ceramics

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ABSTRACT

$(1-x)$BaTiO$_3$–xPZT(65/35) ceramics were prepared by high temperature solid state reaction technique. Structural properties of the compounds were examined using an X-ray diffraction (XRD) technique to confirm the formation of phase at room temperature. Detailed studies of dielectric properties of $(1-x)$ BaTiO$_3$–xPZT(65/35) for all compositions were in temperature range 30- 200 ^{o}C reveal that the compound have transition temperature well above at the room temperature. While pure BaTiO$_3$ ceramics exhibited a sharp phase transformation expected for normal ferroelectrics, phase transformation behavior of the $(1-x)$ BaTiO$_3$–xPZT(65/35) solid solutions became more diffuse with increasing PZT(65/35) contents. The diffusivity of the dielectric peaks in the compound exhibited the values between 1 and 2 where the higher value indicates the greater disorder in the systems. This was primarily evidenced by an increased broadness in the dielectric peak, with a maximum peak width occurring at $x = 0.5$. The temperature dependence of ac conductivity indicated that the electrical conductivity decrease above T$_C$ on increasing the PZT(65/35) contents. This increase in the conductivity is attributed to the increase in polarizability of the materials around T$_c$, due to oxygen vacancies. Copyright © 2011 VBRI press.

Keywords: Perovskite; ferroelectrics; dielectric properties; SEM.

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Introduction

There has been considerable interest in the solid solutions of BT-PZT(65/35) with a perovskite ABO_3 type (A = mono or divalent, B = tri or hexavalent ion) structure due to its possible fore front application in the area of research as well as industrial application [1-6]. Among the many ferroelectric materials, barium titanate ($BaTiO_3$ or BT) has been one of the best known and widely used materials for electric ceramics due to its excellent dielectric, ferroelectric, and piezoelectric properties, in which cations and anions are displaced in opposite directions of the polar axis. This is the result of net dipole moment, which consequently depends on the extent of tetragonal distortion in the unit cell. Lead zirconate titanate (Pb (Zr_x, Ti_{1-x})O_3 are representative perovskite ferroelectric and piezoelectric prototypes because of their excellent electrical properties [7, 8]. However, the best dielectric and piezoelectric properties of PZT have been found near MPB [9]. Due to these technically sound properties of PZT, it has many potential applications in electronic devices, such as nonvolatile memories, infrared sensors, optical shutters, modulators etc. While, barium titanate is a normal ferroelectric with a high dielectric constant and a relatively low T_C (~120 ^{0}C), lead zirconate titanate has a higher T_C of 390 ^{0}C which allows PZT(65/35) based piezoelectric devices to be operated at relatively higher temperatures [10]. Although BT ceramic has better mechanical properties than PZT, the sintering temperature is also higher [7, 8]. Thus, mixing PZT(65/35) with BT is expected to decrease the sintering temperature of BT-based ceramics, a desirable move towards electrode of lower cost [11]. Moreover, since BT–PZT(65/35) is not a pure-lead system, it is easier to prepare single phase ceramics with lower amount of undesirable pyrochlore phases. It is expected that excellent properties can be obtained from ceramics in BT-PZT system. So far, there have been only a few studies on BT-PZT(65/35) system [12-13]. These studies have focused mainly on powder preparation and some electrical properties.

In the present study, we have synthesized barium titanate- lead zirconate titanate ((1-x) BT-xPZT(65/35) systems with various compositions using solid state reaction technique and studied the effect of PZT (65/35) doping on structural, dielectric and conductivity properties of the prepared system.

Experimental

The (1−x) $BaTiO_3$–xPZT compositions with $0.20 \leq x \leq 0.50$ were prepared by standard solid state reaction method. The starting raw materials were PbO, ZrO_2, TiO_2 and $BaCO_3$. For $BaTiO_3$ powder, $BaCO_3$ and TiO_2 were homogeneously mixed in agate mortar in acetone for 4 h. The mixture was dried and then claimed at 1050 ^{o}C for 2 h to form BT. A high temperature solid state reaction method was used to prepare polycrystalline PZT(65/35) using analytical grade oxides of PbO, ZrO_2 and TiO_2. The oxides were mixed thoroughly in stoichiometric ratios in acetone medium for 4 h. The mixture was calcined at 1050 ^{o}C for 4 h to form PZT(65/35). The prepared polycrystalline samples of BT and PZT(65/35) were carefully weighed in stoichiometric proportions and mixed thoroughly in agate mortar for 2 h.

The powder was calcined at 1050 ^{o}C for 2 h. This step is necessary to make sure that all composition reacts well with each other to form the desired phase. The calcined powder was then pressed into disks of thickness 1.2 mm and diameter 10 mm using polyvinyl alcohol as a binder. The final sintering of the pellets was done at 1100 ^{o}C for 2 h with heating rate of 5 ^{o}C/min. Preliminary Crystal structure and phase identification of sintered pellets was carried out by X-ray diffractometer (Bruker's D-8 Advance diffractometer) with Cu K_α radiation (1.54 Å) in a wide range of Bragg's angles 2θ ($20 \leq 2\theta \leq 60$) at the scanning rate of 1^0/min. The grain morphology and size were directly imaged using scanning electron microscopy (SEM). For dielectric measurements, silver paste was coated on the smooth flat surfaces of each pellet, which act as an electrode. The pellets were then fired at 200 ^{o}C for 30 min to remove moisture. Dielectric measurements were performed using LCR meter (Model 3532-50, HIOKI) in a temperature range 30 -200 ^{o}C and in a frequency range from 100 Hz to 1 MHz.

Results and discussion

Fig. 1 shows the XRD pattern of (1−x) BT–xPZT(65/35) ceramics. The diffraction pattern of composition x=0.20 match with diffraction pattern of $BaTiO_3$. With increasing PZT content, the diffraction peaks shifted towards lower angle and the diffraction peak around 2θ of 43–46° was found to split at composition x = 0.30 onwards as shown in **Fig. 1**. This observation suggests that 0.7BT–0.3PZT composition may lead to a diffuse morphotropic phase boundary (MPB) between the tetragonal and rhombohedral PZT phases. The XRD patterns with high degree of PZT(65/35) content ($x \leq 0.30$) showed the co-existence of both tetragonal and rhombohedral phases as clearly shown in **Fig. 1**.
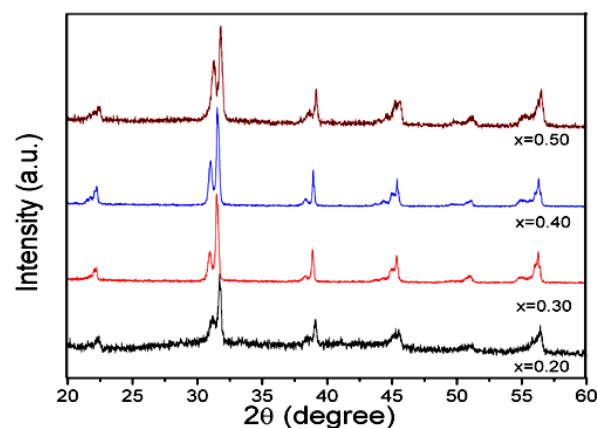

Fig. 1. X-ray diffraction pattern of (1−x) BT–x PZT(65/35) ceramics (x = 0.20, 0.30, 0.40, 0.50).

The crystallite size (D) of the samples was calculated from the broadening of few XRD peaks using Scherrer's formula equation, $D = K\lambda/\beta_{1/2}\cos\theta$

where K = 0.89, $\beta_{1/2}$ is full width at half maximum [14]. The value of crystallite size (D) of the BT-PZT(65/35) compounds under consideration was found in the range of

0.025 μm. We observed that the crystallite size first increased and then decreased on increasing the PZT (65/35) contents shown in **Table 1**.

Table 1. **Crystallite** size, Grain Size and activation energy for different compositions of (1−x) BT–x PZT(65/35) ceramics.

Sl. No.	Composition name	Grain size (μm)	Crystallite size (μm)	Activation energy (E_a T>T_c in eV)
1.	0.8BT-0.2PZT	2.36	0.02042	0.13
2.	0.7BT-0.3PZT	2.32	0.02918	0.18
3.	0.6BT-0.4PZT	2.29	0.02723	0.16
4.	0.5BT-0.5PZT	2.22	0.02242	0.25

The Scanning Electron Micrographs (SEM) of prepared samples of (1−x) BT–xPZT (65/35) ceramics are shown in **Fig. 2**. Well-developed and single shaped grain distribution is observed throughout the sample in all the compositions. The grain growth is homogeneous and grains are small, randomly oriented and densely distributed with significant porosity over the entire surface of ceramics. The average grain size was calculated using linear intercept method and found to be in the range of 2-2.36 μm. The grain size decreases with increasing PZT (65/35) composition as shown in **Table 1**.
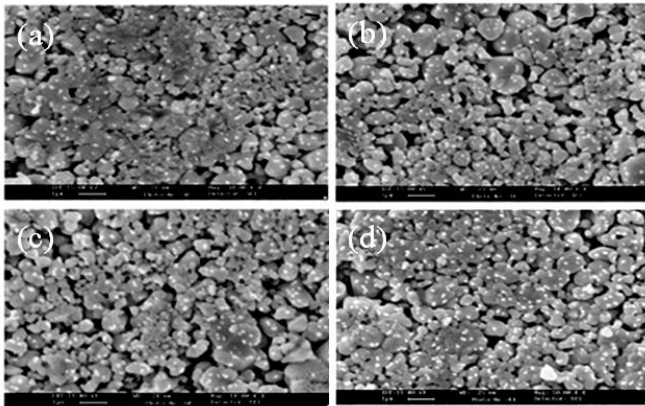

Fig. 2. SEM images of (1-x) BT- x PZT(65/35) ceramics (x=0.20, 0.30, 0.40, 0.50).

Fig. 3 shows variation of dielectric constant and dielectric loss tangent with frequency for (1-x) BT-xPZT(65/35) ceramics (x = 0.20, 0.30, 0.40, 0.50) in a wide frequency range (100 Hz to 1 MHz) at room temperature (35 °C). It is clear from the graph that all the (1-x) BT-xPZT(65/35) ceramics (x = 0.20, 0.30, 0.40, 0.50) show dispersion in dielectric constant and dielectric loss at low frequency. Both parameters (dielectric constant and dielectric loss tangent) initially showed a decreasing trend with increasing frequency, and then became constant up to 1 MHz. This behavior may be attributed to the dipole relaxation phenomenon. This phenomenon reflects about the delay time of the dipoles subjected to an electric field in the frequency response. This delay time is occurred due to the inability of dipoles (responsible for polarization) to follow the oscillations of the electric field at particular frequencies.
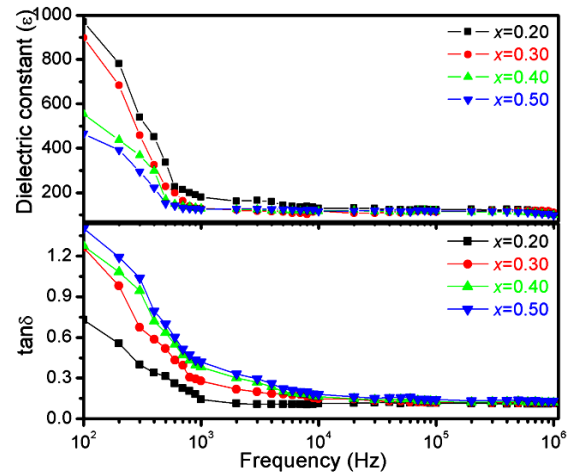

Fig. 3. Variation of Dielectric constant (ε) and Dielectric loss tangent (tanδ) with frequency at room temperature for (1-x) BT- x PZT(65/35) ceramics (x=0.20, 0.30, 0.40, 0.50).

Fig. 4 shows the temperature dependence of dielectric constant (ε) at three different frequencies ranging from 1 kHz to 100 kHz. It was found that dielectric constant of each sample decreases with increase of frequency which may be considered as normal behavior of the ferroelectric /dielectric materials [**15**]. The dielectric constant was almost constant upto 100 °C, then ε increases gradually attaining a maximum value $ε_{max}$ at Curie temperature and thereafter it decreases with the further increase in temperature. This dielectric anomaly indicates a phase transition from ferroelectric to paraelectric phase at that particular temperature (Curie temperature, T_c).
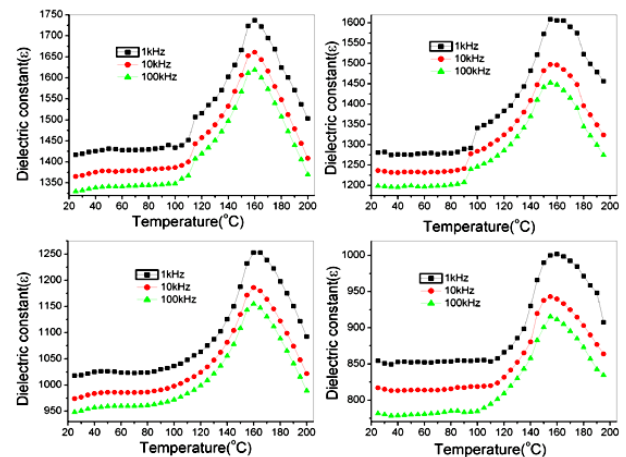

Fig. 4. Temperature dependence of dielectric constant of (1-x) BT- x PZT(65/35) ceramics (x = 0.20, 0.30, 0.40, 0.50).

The Curie temperature of BT is 130 °C. The Curie temperature shift towards higher temperatures (T_c~160 °C) with PZT(65/35) doping concentration x=0.20 and no shift was found in Curie temperature (T_c) with further increase in PZT(65/35) contents. From **(Fig. 4),** it is evident that the

value of ε decreases with increase of PZT content. The dielectric peaks broadened rather than a sharp peak (as in normal ferroelectrics) around T_c, which is one of the characteristic of disordered perovskite structure with diffuse phase transition. This broadening is believed to be due to the compositional fluctuation [16] or substitution disordering in the arrangement of cation in one or more crystallographic sites [17] in the structure leading to a microscopic heterogeneity in the composition and thus in a distribution of different local Curie points.

As described above, a combination of BT with PZT(65/35) introduces dielectric system; we look at these behaviors through Curie–Weiss law. For a normal ferroelectric such as BT and PZT, above the Curie temperature the dielectric constant follows the Curie–Weiss law:

$$\varepsilon = c/T - T_0 \qquad \ldots\ldots\ldots\ldots (1)$$

where c is the Curie constant and T_0 is the Curie–Weiss temperature [1]. For a ferroelectric with a diffuse phase transition (broad peak), the following equation:

$$1/\varepsilon = (T - T_m)^2 \qquad \ldots\ldots\ldots\ldots (2)$$

It has been shown to be valid over a wide temperature range instead of the normal Curie–Weiss law, Eq. 1 [18]. In Eq. 2, T_m is the temperature at which the dielectric constant is maximum. Further examination of the diffuseness in the studied materials was carried out by using the following expression [19, 20]:

$$(1/\varepsilon - 1/\varepsilon_{max}) \propto (T - T_C)^\gamma \qquad \ldots\ldots\ldots\ldots (3)$$

where ε_{max} is the maximum value of ε at T_c. The value of γ (diffusivity) was found to be between 1 and 2, which confirms the diffuse phase transition in the material. The diffusivity (γ) can be estimated from the slope of the dielectric data shown in **Fig. 5**, which should be linear. The values of γ are material constants depending on the composition and structure of materials.
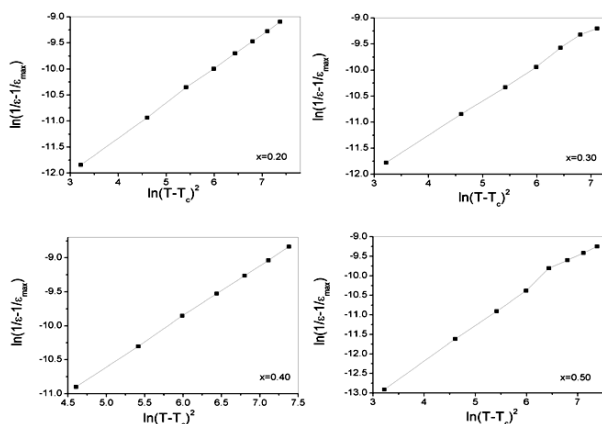

Fig. 6. Temperature dependence of conductivity of (1-*x*) BT- *x* PZT(65/35) ceramics (*x* = 0.20, 0.30, 0.40, 0.50) at 10 kHz.

where σ_0, E_a and K_B represent the pre-exponential factor, activation energy of the mobile charge carriers and

Boltzmann constant, respectively. It is observed that there is a increase in conductivity above T_C for all the doping compositions. This increase in the conductivity is attributed to the increase in polarizability of the materials around T_c. This is the typical behavior of the dc component of the conductivity [21]. The value of the activation energies of the (1-*x*) BT-*x* PZT(65/35) compounds is given in table 1, which shows that the activation energy depend on ionization level of oxygen vacancy [22, 23]. At low temperatures, the value of activation energy of the samples less than 1 eV refers to ferroelectric region which may be possibly caused due to presence of singly ionized oxygen vacancies in the conduction process.

Fig. 6 shows the plot of ac conductivity of (1-*x*) BT- *x* PZT(65/35) ceramics x=0.20, 0.30, 0.40, 0.50) against inverse of absolute temperature $10^3/T$ ^{0}K at 10 kHz. A nature of variation of curves over a wide temperature range supports the temperature dependence of transport properties of the materials obeying Arrhenius equation:

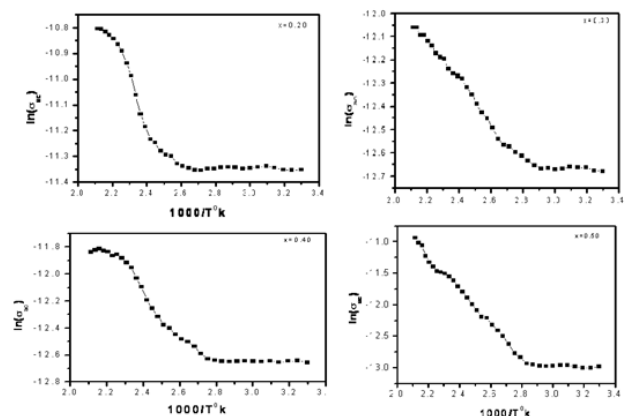$$\sigma_{ac} = \sigma_0 \exp\left(-\frac{E_a}{K_B T}\right)$$

Fig. 6. Temperature dependence of conductivity of (1-*x*) BT- *x* PZT(65/35) ceramics (*x* = 0.20, 0.30, 0.40, 0.50) at 10 kHz.

where σ_o, E_a and K_B represent the pre-exponential factor, activation energy of the mobile charge carriers and Boltzmann constant, respectively. It is observed that there is a increase in conductivity above T_C for all the doping compositions. This increase in the conductivity is attributed to the increase in polarizability of the materials around T_c. This is the typical behavior of the dc component of the conductivity [21]. The value of the activation energies of the (1-*x*) BT-*x* PZT(65/35) compounds is given in table 1, which shows that the activation energy depend on ionization level of oxygen vacancy [22, 23]. At low temperatures, the value of activation energy of the samples less than 1 eV refers to ferroelectric region which may be possibly caused due to presence of singly ionized oxygen vacancies in the conduction process.

Conclusion

In the present work, we have reported the BT-PZT(65/35) ceramics with composition *x* = 0.20, 0.30, 0.40, 0.50 prepared by mixed oxide method. X-ray diffraction studies confirmed tetragonal symmetry for *x* = 0.20 composition and tetragonal and rhombohedral symmetries for other

synthesized compositions. The grain size and crystallite first increased and after that decreased with increasing the PZT(65/35) doping. A study of dielectric constant suggests diffuse type of phase transition in the material. With PZT(65/35) doping, dielectric constant was found to decrease, whereas Curie temperature shifts towards higher temperatures ($T_c \sim 160\ ^oC$) for $x = 0.20$ composition and remained same for all the prepared compositions. The electrical conductivity increase above T_C for all the prepared compositions. This increase in the conductivity is attributed to the increase in polarizability of the materials around T_c. At low temperature, the value of activation energy of the samples less than 1 eV refers to ferroelectric region which may be possibly caused due to presence of singly ionized oxygen vacancies in the conduction process.

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