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Phase formation and dielectric phase transition in $Ba_{1-x}Ca_xTi_{0.6}Zr_{0.4}O_3$ solid solutions

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Abstract

Perovskite types $Ba_{1-x}Ca_xTi_{0.6}Zr_{0.4}O_3$ (with $x = 0.0$–0.5) ceramics have been prepared through solid state reaction route. The room temperature XRD study suggests the compositions with $x = 0.0$ and $x = 0.1$ have single phase cubic symmetry. With further increase in Ca content, solid solution breaks and an orthorhombic $CaTiO_3$ like phase is developed. The dielectric study on single phase compositions ($x = 0.0$ and 0.1) reveals that the materials are of relaxor type and undergo a diffuse type ferroelectric phase transition. In the Ca containing composition higher transition temperature is observed than the pure $BaTi_{0.6}Zr_{0.4}O_3$ materials. In the paraelectric region (above T_c) lower diffusivity is observed in the Ca containing composition. The strength of relaxation is calculated and found to be more in Ca containing material than that of pure $BaTi_{0.6}Zr_{0.4}O_3$ composition.

Keywords: D. Dielectrics

1. Introduction

Recently a new wave of interest has risen on relaxor ferroelectrics with complex perovskite structure due to its wide use in fabrication of multilayer ceramic capacitors, electrostrictive actuators, and electromechanical transducers. The ferroelectric-relaxor behavior, which is characterized by diffuse phase transition, has been studied extensively both theoretically as well as experimentally since a long time [1–9]. Various physical models have been proposed to explain the properties of relaxor behavior, e.g., microscopic composition fluctuation [2], order–disorder transition [3], microdomain and macrodomain switching [4], 'dipolar-glass' model [5], and quenched random field model [6]. Despite of continuous fundamental investigations on relaxor ferroelectrics in recent years, the nature of their extraordinary properties has not yet been understood completely, and they are still the subject of intensive research. It is accepted that the relaxor nature is related to the micropolar regions induced by B-site substitution, and the atomic radii and chemical valence differences of ions will often affect the relaxor effect. Most relaxor ferroelectrics belong to family of complex lead-based perovskite oxides, such as $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN), which is often considered as a model system. However, these compounds have the obvious disadvantages associated with the volatility and toxicity of PbO. Lead-free relaxor materials present great interest both for applications in field of environmental protection and for fundamental studies. Recently, relaxor behavior has been found in many lead-free materials, such as, $KNbO_3$–$BaTiO_3$ [7], $KNbO_3$–$BaTiO_3$–$CaTiO_3$ [9] and $BaTiO_3$–$BaZrO_3$–$BaLiF_3$ [10].

In $BaTiO_3$–$BaZrO_3$ system, it has been reported [11] that at ~15 atom% Zr substitution, the three transition temperatures of $BaTiO_3$, rhombohedra to orthorhombic, orthorhombic to tetragonal and tetragonal to cubic, merge near room temperature and the doped material exhibits enhanced dielectric constant. With further increase in Zr contents beyond 15 atom%, a diffuse dielectric anomaly in ceramic has been observed with the decrease in the

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transition temperature [12] and the material showed typical relaxor–like behavior in the range 25–42 atom % Zr substitution [13]. Unfortunately, these lead-free materials show their relaxor properties at relatively low temperature (<250 K). In the present study an attempt has been made to shift the T_C of $BaTi_{0.6}Zr_{0.4}O_3$ (BTZ) relaxor composition towards room temperature.

2. Experimental

The samples were prepared through solid state reaction route. The compositions with different values of x ($=0.0$, 0.1, 0.2, 0.4 and 0.5) in $Ba_{1-x}Ca_xTi_{0.6}Zr_{0.4}O_3$ were prepared from $BaCO_3$ (S.D. Fine Chem., Mumbai), $CaCO_3$ (S.D. Fine Chem., Mumbai), TiO_2 (E. Merck India Ltd.) and ZrO_2 (Loba Chem., Mumbai). All the chemicals were more than 99% pure. The raw powders were thoroughly mixed in agate mortar using IPA. The homogeneous mixtures were calcined successively at: 1300 °C for 4 h; 1350 °C for 4 h; and finally 1400 °C for 6 h with intermediate mixing and grinding. The synthesized powders were characterized with respect to phase identification and lattice parameter measurements, using Cu-K$_\alpha$ XRD (PW-1830, Philips, Netherlands). The structural refinements were carried out using Rietveld refinement program MAUD [14] and as reported elsewhere [15]. For electrical property measurement of the single phase compositions, the disks were pressed uniaxially at 200 MPa with 2 wt% PVA solution added as binder and that were sintered at 1400 °C for 6 h. The diameter and thickness of the sintered disks were measured and found to be 12 and 2 mm respectively. Disk densities were evaluated using Archimedes principle and found to be ~97% of their theoretical density. The average grain sizes were measured through optical microscope connected with a PC and found to be 22.7 and 5.8 μm for the composition with $x=0.0$ and $x=0.1$ respectively. Silver electrodes were printed on to opposite disk faces and were sintered at 700 °C for 15 min. Dielectric measurements were carried out over range 10 Hz to 5 MHz using HP-4192A LF impedance analyzer, connected with a PC. The temperature was controlled with a self-designed programmable oven. All the dielectric data were collected at an interval of 3 °C, while heating at a rate of 0.5 °C min^{-1}. The results were found to be reproducible.

3. Results and discussion

Fig. 1 shows the room temperature XRD pattern of the $Ba_{1-x}Ca_xTi_{0.6}Zr_{0.4}O_3$ samples with different Ca (x) concentrations. The compositions, $x=0.0$ and $x=0.1$, i.e., $Ba(Ti_{0.6}Zr_{0.4})O_3$ and $Ba_{0.9}Ca_{0.1}Ti_{0.6}Zr_{0.4}O_3$ were indexed in cubic symmetry with space group pm3 m. It can be noticed from the figure that peaks are shifting towards higher angle indicating decrease in lattice parameters in the single phase compositions. In the compositions with higher Ca content, these peaks were shifting towards lower angle and an orthorhombic $CaTiO_3$ (CT) like phase is observed along with tetragonal $Ba_{0.9}Ca_{0.2}Ti_{0.6}Zr_{0.4}O_3$ phases. Recently, Levin et al. [16] reported that solubility of CaO in $BaZrO_3$ increases from few percent at 1400 °C to about 30% at 1650 °C. But in the present study at 1400 °C/6 h the solubility of Ca, in Ba $(Ti_{0.6}Zr_{0.4})$ O_3 fails at around 20 atom%. The Zr^{4+} ion is chemically more stable than Ti^{4+} ion [17] may be the one cause for breaking of solid solution at the studied temperature. The detailed structural parameters and quantities of the phases present in the Ca-rich compositions were studied [15] using Rietveld refinement technique.

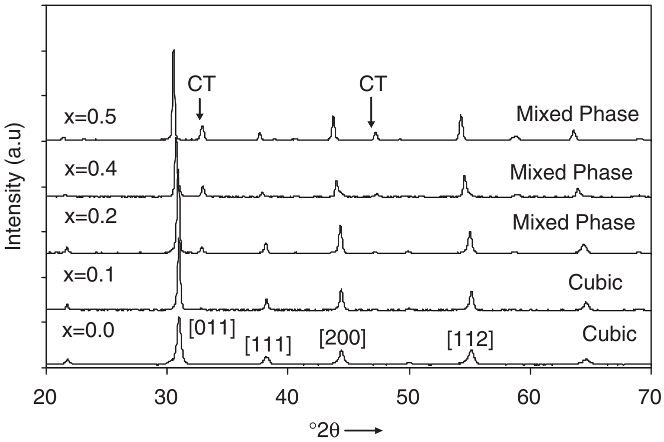

Fig. 1. XRD pattern of $(Ba_{1-x}Ca_x)$ $Ti_{0.6}Zr_{0.4}O_3$ ceramics with different Ca (x) contents.

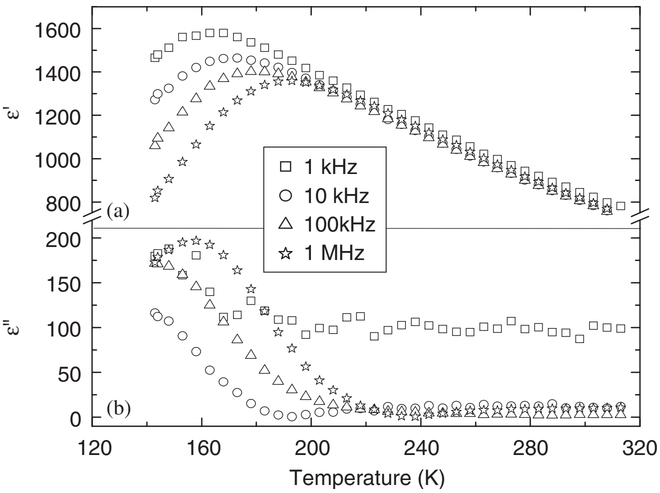

Fig. 2. Temperature dependency of permittivity of $BaTi_{0.6}Zr_{0.4}O_3$ at various frequencies: (a) real part; (b) imaginary part.

Figs. 2 and 3 show the temperature dependency of the permittivity and dielectric loss of bulk $BaTi_{0.6}Zr_{0.4}O_3$ and $Ba_{0.9}Ca_{0.1}Ti_{0.6}Zr_{0.4}O_3$ single phase compositions at different frequencies. The figures show, the value of ε′ increases gradually to a maximum value (ε_m) with increase in temperature up to the transition temperature and then decreases smoothly indicating a phase transition. The maximum of dielectric permittivity, ε_m and the corresponding

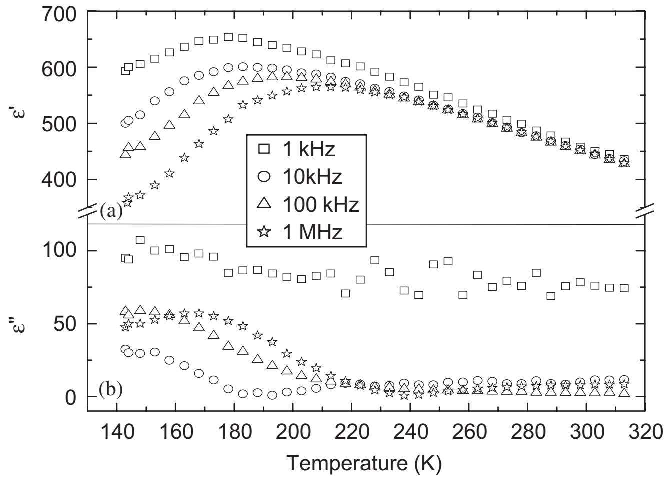

Fig. 3. Temperature dependency of permittivity of $Ba_{0.9}Ca_{0.1}Ti_{0.6}Zr_{0.4}O_3$ at various frequencies: (a) real part; (b) imaginary part.

temperature maximum T_m, depend upon the measurement frequency for all the compositions. The magnitude of dielectric constant decreases with increase in frequency and the maximum shifts to higher temperature. This indicates that the dielectric polarization is of relaxation type in nature such as dipolar glasses. In analogy with spin glasses, such a behavior of the dynamic susceptibility in disordered ferroelectric is supposed to be concerned with the existence of the broad spectrum of relaxation times. It is generally considered that the Debye model is based on the assumption of a single relaxation time. The model fails because of the existence of a distribution of relaxation times. Such a distribution of relaxation time implies that the local environment seen by individual dipoles differs from site to site. As shown in the figures, the dielectric loss values of the ferroelectric phase were reduced substantially in the paraelectric phase (above T_m). The observed lower temperature (below T_m) frequency dispersion may also have some contribution from the space charge effect. The high value of dielectric loss at 1 kHz is due to the presence of all types of polarizations including space charge effect. A gradual decrease of space charge is observed at higher frequency. An increase in the values of ε'' at lower temperature region may also be due to the presence of space charge polarization and those were reduced substantially at temperatures near paraelectric phase. The space charge effects are more prominent in the both low frequency and low temperature regions [18].

As a rule [11] this relaxation occurs in disorder ionic structures, particularly in solid solution. Within the curie range of temperature, dielectric permittivity achieves very high value and displays very large dispersion, which is reminiscent of that found for orientational glasses [19]. The two cations $Ti^{4+}$and Zr^{4+} in the B sites are all ferroelectrically active, so these cations are off-centered in the octahedral site and give rise to a local dipolar moment [20]. Qualitatively, the strongly broadened dielectric peak indicates that the phase transition is of a diffuse type near the transition temperature (T_m) which is caused by inhomogeneous distribution of the Zr ion on Ti site and mechanical stress in the grain [21]. It can be also noticed from the figures, that higher transition temperatures (T_ms) are observed in the Ca containing composition than the pure BTZ. When Ca is substituted in 12 coordination sites, it traps eight near neighbors Oxygen and four more distant ones. That modification assumes a possible displacement of Ca^{2+} out of the oxygen dodecahedron center to induce a dipolar moment whose occurrence may lead to increase in transition temperature. The diffuse nature of the transition in the case of ferroelectric ceramics is usually attributed to a distribution of grain sizes and/or to a gradient of quadraticity which leads to a distribution of transition temperature. This is more pronounced in samples containing both Ti and Zr may be due to the difference in ionic radius. Here additional spatial fluctuations in the mixture of Ti and Zr ions lead to the coexistence of regions of different Curie temperatures depending up on their concentration [22] in the solid solution. It is reported [23], as the grain size decreases, the maximum dielectric constant and transition temperature decreases. The effect of grain size originates from the higher surface tension in smaller grains [24], which acts in the same manner as hydrostatic pressure thus decreasing the Curie point [25]. In addition, the force experienced by the atoms and ions in the vicinity of, or far from, the surface of grain are not similar. These considerations suggest that a quadraticity gradient may exist between the surface and the bulk of grains [26]. For smaller grain sizes, however, the superficial layers of the grains represent a significant fraction and may dominate the structural and the dielectric measurement [22].

A diffuse phase transition is generally characterized by (a) broadening of dielectric constant versus temperature curve (b) a relatively large separation (in temperature) between the maximum of the real (dielectric constant) and imaginary (dielectric loss) part of the dielectric spectrum (c) a deviation from Curie–Weiss law in the vicinity of T_m; (d) frequency dispersion of both ε' and tan δ (dielectric loss) in transition region thereby implying a frequency dependency of T_m.

It is known that the dielectric permittivity of a normal ferroelectric above the Curie temperature follows the Curie–Weiss law described by

$$\varepsilon' = C/(T - T_0), (T > T_C),$$

where T_0 is the Curie–Weiss temperature and C is the Curie–Weiss constant. Fig. 4 shows the plot of inverse dielectric constant versus temperature at different frequencies of two different single phase compositions in the system $Ba_{1-x}Ca_xTi_{0.6}Zr_{0.4}O_3$; (a) $x = 0.0$, (b) $x = 0.1$. A clear deviation from Curie–Weiss law can be seen in all representative frequency. The parameters obtained at 1 kHz and 1 MHz are listed in Table 1. The parameter ΔT_m, which describes the degree of the deviation from the

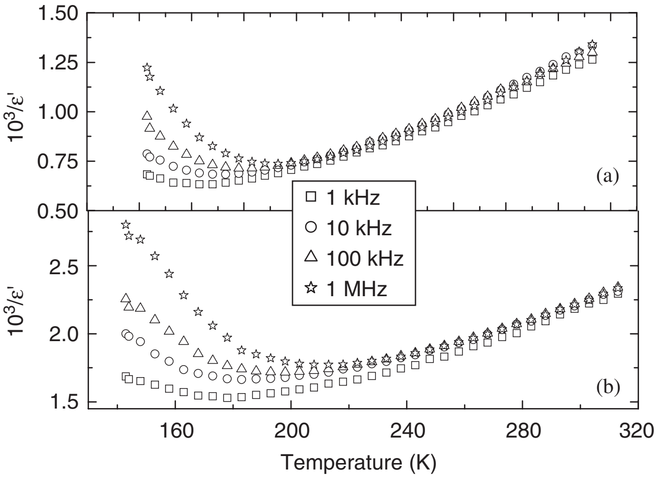

Fig. 4. Temperature dependency of $1/\varepsilon'$ for $Ba_{1-x}Ca_xTi_{0.6}Zr_{0.4}O_3$ at various frequencies: (a) $x = 0.0$ and (b) $x = 0.1$.

Table 1
Parameters obtained from temperature dependency dielectric study on the composition $Ba_{1-x}Ca_xTi_{0.6}Zr_{0.4}O_3$ at 1 kHz and 1 MHz

	$X = 0.0$		$X = 0.1$	
	1 kHz	1 MHz	1 kHz	1 MHz
T_m(K)	163.5	192.713	167.47	198.79
T_o(K)	189.41	211.60	186.6	214
$C(10^5$K)	1.67	1.665	1.45	1.42
ΔT_m	88.81	74.89	79.64	68.73
T_{cw}	251.3	267.6	247.11	267.52
ε_m	1598.7	1370.4	657.44	572.21

Curie–Weiss law, is defined as

$$\Delta T_m = T_{CW} - T_m.$$

where T_{cw} denotes the temperature from which the permittivity starts to deviate from the Curie–Weiss law and T_m represents the temperature of the dielectric maximum. The Curie temperature determined from the graph by extrapolation of the reciprocal of dielectric constant of the paraelectric region and the value obtained at 1 kHz and 1 MHz are given in Table 1.

A modified Curie–Weiss law has been proposed by many research groups to describe the diffuseness of a phase transition as

$$\frac{1}{\varepsilon'} - \frac{1}{\varepsilon_m} = (T - T_m)^\gamma / C',$$

Where γ and C' are assumed to be constant. The parameter γ gives information on the character of the phase transition; for $\gamma = 1$, a normal Curie–Weiss law is obtained, for $\gamma = 2$, it reduces to the quadratic dependency which describes a complete diffuse phase transition. The plot of log $(1/\varepsilon' - 1/\varepsilon_m)$ vs log $(T–T_m)$ at 100 kHz for two different compositions is shown in Fig. 5. Linear relationships are observed.

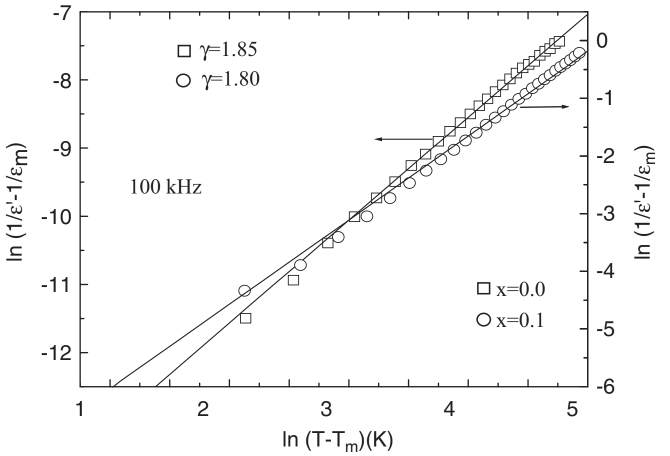

Fig. 5. Log $(1/\varepsilon' - 1/\varepsilon_m)$ vs log $(T–T_m)$ for $Ba_{1-x}Ca_xTi_{0.6}Zr_{0.4}O_3$ at 100 kHz.

The slopes of the fitting curve are used to determine the parameter γ value. The values of γ at 100 kHz are found to be 1.85 and 1.8 for $x = 0.0$ and $x = 0.1$ compositions, respectively, indicating transitions are of diffuse type. The values of the γ show that the materials are highly disordered. The decreased value of γ with Ca content indicates the decrease in diffusivity. The broadened dielectric maximum (in ε' vs temperature curve) and its deviation from Curie–Weiss law are the main characteristics of a diffuse phase transition of the material. The diffuse phase transition and deviation from Curie–Weiss type may be assumed due to disordering. The broadness in ε' vs temperature curve is one of the most important characteristics of the disordered perovskite structure with diffuse phase transition. The broadness or diffusiveness occurs mainly due to compositional fluctuation and structural disordering in the arrangement of cation in one or more crystallographic sites of the structure. This suggests a microscopic heterogeneity in the compound with different local Curie points. The nature of the variation of dielectric constant and non polar space group suggests that the material may have ferroelectric phase transition.

The plot of log (ν) vs $1/T_m$ is shown in Fig. 6 for two different compositions. The nonlinear nature indicates that the data cannot be fitted with a simple Debye equation. The Debye medium is a classic dielectric. Its dielectric constant is described by the Debye equation;

$$\varepsilon = \varepsilon_\infty + \Delta\varepsilon/(1 + \omega^2\tau^2),$$

where τ is the dielectric relaxation time of the dipole polarization, $\Delta\varepsilon$, the contribution of the dipole polarization to the static dielectric constant and ε_∞ is the high frequency dielectric constant, which remains nearly constant with the change of temperature.

In Debye medium, the dipoles (or molecules) are free to rotate and are thermally activated; the dipole moments of dipoles have the same value, and there is no interaction

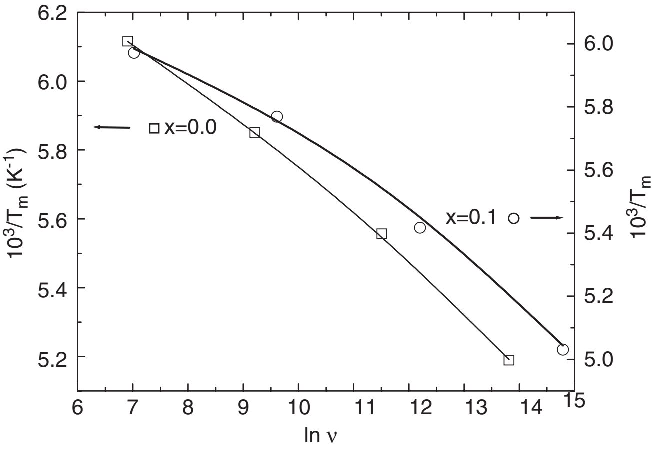

Fig. 6. $1/T_m$ as function of the measured frequency of $Ba_{1-x}Ca_xTi_{0.6}Zr_{0.4}O_3$. The symbols are the experimental data points and the line is corresponding fitting to the Vogel–Fulcher relationship.

between the dipoles. This means that the dipoles can be frozen only at temperature 0 K, and thus, τ is dependent on the temperature according to

$$\tau = \nu_0 \exp\left(T_0/T\right),$$

where ν_0 is the attempt frequency of the molecules (or the Debye frequency) and T_0 is the equivalent temperature of activation energy.

In any material system, it is impossible that all the dielectrics are free, so the dipoles in the Debye model are nonrealistic. The more realistic dipole is not free as in glass which is another classic dielectric. The dipoles in the glass do interact with their neighbors. The interaction makes the dipole freeze into a configuration devoid of long-range order at T_f. That is, the effect of T_f in glass is same as that of 0 K in Debye medium. Therefore, the relaxation time in a glass can be expressed by Vogel–Fulcher law [27,28].

In order to analyze the relaxation features, i.e., relation between ν and T_m of the ceramics, the experimental curves were fitted using the Vogel–Fulcher formula [27,28].

$$\nu = \nu_0 \exp\left[\frac{-E_a}{k_B(T_m - T_f)}\right],$$

Where ν_0 is the attempt frequency, E_a is the measure of average activation energy, and k_B is the Boltzman constant, and T_f is the freezing temperature. T_f is regarded as the temperature where the dynamic reorientation of the dipolar cluster polarization can no longer be thermally activated. The fitting curves are shown in Fig. 6. The fitting parameters for different compositions are; for $x = 0.0$, $E_a = 0.1020$ eV, $T_f = 106$ K, $\nu_0 = 8.5 \times 10^{11}$ Hz; for $x = 0.1$, $E_a = 0.0461$ eV, $T_f = 130$ K, and $\nu_0 = 2.51 \times 10^9$ Hz. The close agreement of the data with the V–F relationship suggests that the relaxor behaviors in the systems are analogous to that of a dipolar glass with polarization fluctuations above a static freezing temperature. The observed difference in average activation energy may be due to the large difference in grain size. The activation energy and pre-exponential factor are both consistent with thermally activated polarization fluctuations.

The empirical relaxation strength describing the frequency dispersion of T_m is defined as

$$\Delta T_{res} = T_{m(1\,MHz)} - T_{m(10\,kHz)},$$

where ΔT_{res} was derived from the dielectric measurement of the ceramics. The values of ΔT_{res} are found to be 20.14, and 25.44 for the compositions with $x = 0.0$ and $x = 0.1$, respectively. The relaxor behavior as observed in this ceramics can be induced by many reasons such as microscopic compositions fluctuation, the merging of micropolar regions in to macropolar regions, or a coupling of order parameter and local disorder mode through the local strain [28–30]. Vugmeister and Glinichuk reported that the randomly distributed electrical field of strain field in a mixed oxide system was the main reason leading to the relaxor behavior [31].

In the studied compositions of solid solutions $Ba_{1-x}Ca_xTi_{0.6}Zr_{0.4}O_3$, Ba and Ca ions occupy the A sites of the ABO_3 perovskite structure and Zr and Ti ions occupy the B site. As previously mentioned both Ti and Zr are ferroelectrically active and these cations are off-centered in the octahedral site, giving rise to a local dipolar moment [20]. In perovskite-type compounds, the relaxor behavior appears when at least two cations occupy the same crystallographic site A or B. The ionic radius of Zr^{4+} (0.98 Å) is larger than that of Ti^{4+} (0.72 Å). Therefore an inhomogeneous distribution results at the B site of the structure. A cationic disorder induced by B-site substitution is always regarded as the main derivation of relaxor behavior. However, according to our present results, it implies that the observed higher relaxation strength should attribute to a cationic disorder induced by both A-site and B-site substitutions. The different effects of A-site substitution on cation ordering and the stability of the polar region are considered to be based on the polarizability of cations and the tolerance factor of the perovskite structure. For perovskites with the general formula of ABO_3, the following equation can be used to calculate the tolerance factor (t) [20]:

$$t = \frac{(R_A + R_O)}{\sqrt{2}(R_B + R_O)},$$

where R_A is the radius of A, R_B is the radius of B, and R_O is the radius of O. As the t increases, the normal ferroelectric phase becomes stabilized. So Ba^{2+} cations can stabilize the normal ferroelectrics due to the larger ionic diameter and the higher polarizability. While Ca^{2+} cations in A sites behave as a typical destabilizer against normal ferroelectrics and induce paraelectric behavior due to smaller ionic diameter and lower polarization. In this case, more macrodomains (long-range ordered regions) in Ca substituted ceramics will breakup into micropolar regions than that in pure BTZ ceramics. Mechanical stress in the grain, is the cause of the relaxor behavior in the Ti and Zr mixed composition [28–30]. Stresses were introduced into the lattice during cooling after sintering process, which is due to the transition from a cubic to rhombohedral phase below the Curie temperature [32]. On the other hand, it is known that $BaZrO_3$ shows nonferroelectric (cubic paraelectric phase) behavior at all temperatures because, the Zr ion locates at the central equilibrium position of the $BaZrO_3$ lattice. In this case the macrodomain in $BaTiO_3$ could be divided into the microdomains which probably cause the relaxor behavior.

4. Conclusion

Perovskite type $Ba_{1-x}Ca_xTi_{0.6}Zr_{0.4}O_3$ (with $x = 0.0$, 0.1, 0.2, 0.4 and 0.5) ceramics have been prepared through solid state reaction route. The room temperature XRD study suggests that the compositions with $x = 0.0$ and 0.1 have single phase cubic symmetry with space group Pm3 m. With further increase in Ca content the solid solution breaks at the experimental temperature. An orthorhombic $CaTiO_3$ like phase is observed along with tetragonal $Ba_{0.8}Ca_{0.2}Ti_{0.6}Zr_{0.4}O_3$ phase. The dielectric study on single phase compositions reveals that the materials are of relaxor type and undergo a diffuse type ferroelectric phase transition. An improvement of transition temperature is observed in the Ca containing composition. Lower diffusivity and higher strength of relaxation is observed in the Ca containing compositions as compared to the pure $BaTi_{0.6}Zr_{0.4}O_3$ materials.

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