Structural and dielectric behaviour of barium substituted lead zinc niobate ceramics at low temperature

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The polycrystalline samples of \((\text{Pb}_{1-x}\text{Ba}_x)(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3\) (PBZN) ceramics have been synthesized by the columbite precursor method. X-ray diffraction analysis of PBZN synthesized for \(x = 0.15, 0.25, 0.35\) and 0.50 shows a cubic perovskite phase at room temperature. The changes in the structures are observed with increasing Ba contents in PBZN. The dielectric dispersion of the solid solutions has been studied as a function of temperature in the frequency range 100 Hz-1MHz. The temperature variation of the real components \((\varepsilon')\) at different frequencies of the dielectric permittivity shows a broad maximum. The diffuse peaks in \(\varepsilon'\) versus \(T\) confirm the relaxor behaviour of PBZN. The changes in the relaxor properties of the compounds are found to be compositional dependent. The frequency dependence of \(T_m\) in these compounds with barium substitution is modeled using Vogel-Fulcher relation.

Keywords: Relaxor ferroelectric, Barium substituted lead zinc niobate, Vogel-Fulcher

1 Introduction

Ferroelectric relaxor was first discovered by Smolenskii and Isuopov\textsuperscript{1} in \(\text{Ba(Ti}_{1-x}\text{Sn}_{x})\text{O}_3\) solid solution. It is characterized by a broad maximum in temperature dependence of permittivity and a strong relaxation dispersion of permittivity near the temperature of maximum permittivity\textsuperscript{2,3}. Besides these, relaxor ferroelectrics have other special characteristics distinguishing them from normal ferroelectrics, such as existence of spontaneous polarization above the temperature of dielectric maximum around which a phase change takes place in normal ferroelectrics. Relaxor ferroelectrics (RFE) with perovskite (ABO\textsubscript{3}) structure are of great interest because of their outstanding potential applications. An important potential application of these materials is in multilayer ceramic capacitors, where their very high permittivites and broad Curie temperature ranges can be exploited. Relaxor behaviour is closely related to the 1:1 ordered region dispersing in the disordered matrix, as found by transmission electron diffraction\textsuperscript{4,5}. Two important families of relaxor ferroelectrics are \(A^{2+}(B^{2+}_{1/3}B^{5+}_{1/3})\text{O}_3\) and \(A^{2+}(B^{2+}_{2/3}B^{5+}_{2/3})\text{O}_3\), in which ordered regions are consistent and inconsistent with the chemical stoichiometries, respectively. Since the ordered region of \(A^{2+}(B^{2+}_{2/3}B^{5+}_{2/3})\text{O}_3\), is inconsistent with the 1:2 stoichiometry, this family has more complicated properties.

It is well known that that perovskite phase of PZN cannot be stabilized in polycrystalline form even using the two-step columbite precursor method\textsuperscript{6}. The difficulty arises from the fact that PZN is thermodynamically unstable over a wide range of temperature in the range 600-1400°C, rapidly yielding pyrochlore phase and other phases and PbO as decomposition products ruling out the possibility of synthesizing dense polycrystalline form. This is mainly because the pyrochlore phase is thermodynamically more stable. Accordingly, pure perovskite PZN and PZN-PT ceramics cannot be synthesized by conventional mixed oxide process, but only under high pressure at elevated temperature\textsuperscript{7,8} (25 kbar, 800°-1000°C). To attain a stable perovskite phase in polycrystalline form under normal conditions, solid solutions being formed by substitution either at A-site\textsuperscript{9,12} by Ba or B-site\textsuperscript{13} by Ti\textsuperscript{4+}, Ta\textsuperscript{5+} have been reported. Barium zinc niobate\textsuperscript{14}, Ba(Zn\textsubscript{1/3}Nb\textsubscript{2/3})\text{O}_3 (BZN) and other structurally related Ba-based mixed B-site cation perovskites, Ba(B\textsubscript{1/3}B\textsuperscript{5+}_{2/3})\text{O}_3 are linear dielectrics. The crystal
structure is perovskite, analogous to PZN. This family of material is reported to undergo an ordered-disorder phase transformation\(^ {15,16}\). However, unlike PZN, the Ba-based mixed B-site cation materials can achieve complete long-range order upon annealing. The ordered structure has a triple unit cell, in distinction to the doubled unit cell of short-range-ordered PZN. The dielectric response of Ba-based mixed B-site cation perovskites is known to be dependent on the degree of long-range chemical ordering. The magnitudes of both the dielectric constant (\(\varepsilon^\prime\)) and dissipation factor (\(\tan\delta\)) have been reported to decrease with increasing order\(^ {14}\). The ordered materials are characterized by a frequency- and temperature-independent dielectric response in the frequency range below \(10^{10}\) with a loss factor less than \(10^{-4}\). As a consequence, ordered \(\text{Ba}(\text{Zn}_{\frac{1}{3}}\text{B}_{\frac{2}{3}})\text{O}_3\) materials have been investigated for potential applications in microwave dielectric resonators. Complete solid solutions between short-range-ordered PZN and long-range-ordered BZN \([(\text{Pb}_{1-x}\text{Ba}_{x})(\text{Zn}_{\frac{1}{3}}\text{Nb}_{\frac{2}{3}})\text{O}_3]\), (PBZN) can be formed, as the structures of these materials are isomorphic.

In the present work, the transition from relaxor to polar dielectric behaviour has been investigated, by systematically varying the composition for \(x\) values between 0 and 1. The manner in which the dielectric properties are influenced by \(\text{Ba}^{2+}\) substitution, provides insight into the changes in the dynamical behaviour of Polar Regions in these materials, which is useful for understanding the relaxor behaviour of these materials. A generalized Curie Weiss law is used to fit the real part of permittivity above \(T_m\) to compare the variation in relaxor for different compositions. Frequency dependence of \(T_m\) is analyzed using the Vogel-Fulcher (V-F) relation to understand the relaxation phenomena in the materials.

2 Experimental Details

Two PBZN compounds \((\text{Pb}_{1-x}\text{Ba}_x)(\text{Zn}_{\frac{1}{3}}\text{Nb}_{\frac{2}{3}})\text{O}_3\), with \(x=0.15, 0.25, 0.35\) and 0.50 were synthesized by the columbite precursor method in three stages to minimize the secondary phase formation. High purity of raw materials \(\text{PbO}, \text{BaCO}_3, \text{ZnO}\) and \(\text{Nb}_2\text{O}_5\) was used for the preparation. The columbite precursor \((\text{ZnNb}_5\text{O}_{14})\) was first prepared by mixing predetermined amounts of \(\text{ZnO}\) and \(\text{Nb}_2\text{O}_5\) (1:1 molar ratio). It was wet milled in acetone for a day and calcined at 1150°C for 3 h. In the second stage, \(\text{ZnNb}_5\text{O}_{14}\) and \(\text{BaCO}_3\) were mixed in stoichiometric ratio and calcined at 1200°C for 3 h for formation of BZN. In the third stage, \(\text{PbO}\) and BZN were mixed in stoichiometric ratio and calcined at 850°C for 2 h and brought to room temperature under controlled cooling. The pellets of the calcined materials were sintered at 1100°C for 1 h. At each stage of calcinations and final stage sintering, the phases were confirmed with XRD taken at room temperature. Each sintered disc of the prepared ceramic at room temperature was polished on different grades of emery paper to obtain parallel flat surfaces. Silver paste was used on both sides of the disc for electrical contacts. The temperature and frequency dependence of the electrical property was studied by impedance spectroscopy using an LCR meter in our laboratory, in the frequency range 50 Hz-1 MHz and in a temperature range from 133 K to room temperature. The temperature was controlled by a programmable controller. All the data were collected while heating at a rate of 0.5°C min\(^{-1}\).

3 Results and Discussion

XRD profiles at room temperature of developed structures in the system \((\text{Pb}_{1-x}\text{Ba}_x)(\text{Zn}_{\frac{1}{3}}\text{Nb}_{\frac{2}{3}})\text{O}_3\), at \(x=0.15, 0.25, 0.35\) and 0.50 are shown in Fig. 1 at room temperature. At \(x=0.15\) \([(\text{Pb}_{0.85}\text{Ba}_{0.15})(\text{Zn}_{\frac{1}{3}}\text{Nb}_{\frac{2}{3}})\text{O}_3\) stoichiometry], there is mixed phase of perovskite and cubic pyrochlore \((\text{Pb}_3\text{Nb}_5\text{O}_{15})\). The sintered pellets at \(x=0.25, 0.35\) and 0.50 show cubic perovskite phase. It is observed that there is more of the perovskite phase at the expense of the pyrochlore phase, as the substituent amount of barium is increased further.

Figures 2 and 3 show the real part \((\varepsilon^\prime)\) and imaginary part \((\varepsilon^\prime\prime)\) of dielectric permittivity of two compositions PBZN15 \((x=0.15)\) and PBZN25 \((x=0.25)\) as a function of temperature at various frequencies. The peak in the dielectric constant \(\varepsilon^\prime\) is shifted towards higher temperatures as the measuring frequency is increased, and a strong dispersion of \(\varepsilon^\prime\)
exists in the low temperature region [Figs 2(a) and 3(a)]. The peak value (ε′_{max}) of ε′ decreases with the increase of frequency. These indicate that the relaxor nature is retained in PBZN15 and PBZN25. It is observed that addition of Ba decreases not only the maximum permittivity but also shifts the T_m to lower temperature. The variations in T_m at different frequencies are presented in Table 1 for x=0.15 and 0.25.

Figures 2(b) and 3(b) show the temperature dependence of ε″ at various frequencies for PBZN15 and PBZN25, respectively. It is seen that the peak value (ε″_{max}) of ε″ increases with the increase in frequency which is typical characteristic of relaxor ferroelectric materials. The above described features of (ε′−T) and (ε″−T) variation shown in Figs 2 and 3 are very much similar to the observation by Smolensky et al. for various lead based materials.

Table 1 — Characteristic parameters determined and calculated from ε′(T) measurements

<table>
<thead>
<tr>
<th>Composition</th>
<th>Frequency</th>
<th>T_m (K)</th>
<th>θ (K)</th>
<th>T_B (K)</th>
<th>ΔT_m</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBZN15</td>
<td>9.19 KHz</td>
<td>238</td>
<td>252</td>
<td>294</td>
<td>56</td>
</tr>
<tr>
<td>PBZN25</td>
<td>11.05 kHz</td>
<td>223</td>
<td>218</td>
<td>257</td>
<td>34</td>
</tr>
</tbody>
</table>

Figure 4 shows the frequency dependence of ε″ at two temperatures for PBZN15 and PBZN25. It seems clear that the width of the loss peaks in Fig. 4(a & b) cannot be accounted for in terms of a monodispersive relaxation process and points towards the possibility of a distribution of relaxation times.

One of the most convenient ways for checking the polydispersive nature of dielectric relaxation is through complex Argand plane plots of ε″ against ε′, usually called Cole plots. For a pure monodispersive Debye process, one expects semicircular plots with
center located on the $\varepsilon'$-axis whereas, for polydispersive relaxation, these Argand plane plots are close to circulars arcs with end-points on the axis of real and the centre below this axis. The complex dielectric constant in such situations is known to be described by the empirical relation:

$$\varepsilon^* = \varepsilon' - i\varepsilon'' = \varepsilon_\infty + \frac{(\varepsilon_s - \varepsilon_\infty)}{1 + (\omega\tau)^{1-\alpha}} \quad \cdots (1)$$

where $\varepsilon_s$ and $\varepsilon_\infty$ are the low- and high-frequency values of $\varepsilon'$, $\alpha$ is a measure of the distribution of relaxation times, $\tau = \omega^{-1}$ and $\omega = 2\pi v$. The parameter $\alpha$ can be determined from the location of the center of the Cole-Cole circles of which only an arc lies above the $\varepsilon'$-axis. Figure 5(a and b) depicts two representative plots for $T = 186$ K and $148$ K for the PBZN15 and PBZN25. It is apparent from these plots that the relaxation process differs from the mono dispersive Debye process (for which $\alpha = 0$). The parameter $\alpha$ as determined from the angle subtended by the radius of the circle with the $\varepsilon'$-axis passing through origin of $\varepsilon''$-axis, shows a very small increase in the interval [0.578 and 0.66] with the decrease in the temperature from 186 to 148 K, implying a slight increase in the distribution of relaxation time with decreasing temperature below $T_m$.

The Cole-Cole plot confirms the polydispersive nature of the dielectric relaxation time of PBZN15 and PBZN25. However, the small variation in $\alpha$ with decreasing temperature is not convincing enough, keeping in mind the uncertainties in fitting the circle, which was done through visual fit to observed points. We can look at the distribution of relaxation times from yet another angle to compare the results with the dielectric behaviour of Debye relaxation system with

![Figure 4](image1.png)

**Fig. 4** — Frequency dependence of $\varepsilon''$ at two temperature for(a) PBZN15 and (b) PBZN 25. A comparison of the measured imaginary part of the dielectric permittivity of PBZN15 and PBZN25 with that calculated using Eq. (5) for the two different temperatures is shown, where open and solid circles and stars symbol represent the experimental and calculated points, respectively.

![Figure 5](image2.png)

**Fig. 5** — Cole-Cole plots at temperature of 186 K and 148 K for (a) PBZN15 and (b) PBZN25.
a broad relaxation spectrum \( g(\tau, T) \). If \( g(\tau, T) \) is the temperature-dependent distribution function for relaxation times, the complex dielectric constant can be expressed as:

\[
\varepsilon^*(T) = \varepsilon_0 \int_0^\infty \frac{d(\ln \tau)}{1 - j\omega \tau} g(\tau, T) \quad \text{(2)}
\]

which yields the real and imaginary part of dielectric constant.

\[
\varepsilon'(\omega, T) = \varepsilon_0 \int_0^\infty \frac{d(\ln \tau)}{1 + (\omega \tau)^2} g(\tau, T) \quad \text{(3a)}
\]

\[
\varepsilon''(\omega, T) = \int_0^\infty \frac{d(\omega \tau)}{(1 + (\omega \tau)^2)} g(\tau, T) \quad \text{(3b)}
\]

as shown by Courten for a broad relaxation distribution function \( g(\tau, T) \). \( \varepsilon''(\omega, T) \) can be approximated as:

\[
\varepsilon''(\omega, T) \approx \frac{\pi}{2} \varepsilon(0, T) g\left(\frac{1}{\omega}, T\right) \quad \text{(4)}
\]

Thus, the spectrum of dielectric loss gives direct information about \( g(1/\omega, T) \). In the limit of \( \tau_{\text{min}} \leq 1/\omega \leq \tau_{\text{max}} \), one can also obtain an important simple relation between real and imaginary parts of the dielectric permittivity.

\[
\varepsilon''(\omega, T) \approx \frac{\pi}{2} \frac{\partial \varepsilon(\omega, T)}{\partial (\ln \omega)} \quad \text{(5)}
\]

We have used our experimental data to verify the validity of the assumptions made to obtain Eq. (5). The results obtained are shown in Fig. 4(a & b) for PBZN15 and PBZN25. A good agreement between the directly measured value of \( \varepsilon'' \) and those calculated from the dispersion of \( \varepsilon' \) using Eq. (5) suggests that the spectrum \( g(1/\omega, T) \) is broad at low temperature as well as at high temperature.

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

\[
\left(\frac{1}{\varepsilon'}\right) = \frac{(T - \theta)}{C} \quad (T > \theta) \quad \text{(6)}
\]

(where \( \theta \) is the Curie-Weiss temperature and \( C \) is the Curie-Weiss constant). It is observed in the paraelectric phase only at temperatures much higher than \( T_m \) i.e. above Burns temperature, \( T_B \). Figure 6(a & b) show the inverse of \( \varepsilon' \) as a function of temperature at 9.19 kHz and 11.05 kHz for the PBZN15 and PBZN25 sample, respectively and it is a fit to the experimental data by Curie-Wiess law. A deviation from Curie-Wiess law starting at \( T_B \) can be clearly seen. The parameter \( \Delta T_m \), which is often used to show the degree of deviation from the Curie-Wiess law, is defined as:

\[
\Delta T_m = T_B - T_m \quad \text{(7)}
\]

The \( T_B \) as determined from the Curie-Wiess law fit and other characteristic parameters calculated are presented in Table 1. It is observed that the generalized empirical relation in Eq. (6) is obeyed in the paraelectric phase only at temperature much higher than \( T_m \) i.e. above Burns temperature, \( T_B \). In the temperature range between \( T_m \) and \( T_B \), the temperature
dependence of permittivity is known to deviate from the typical Curie-Weiss behaviour and obeys the empirical expression by a modified Curie-Weiss relationship \( \gamma \) to describe the diffuseness of the phase transition as follow:

\[
\left( \frac{1}{\varepsilon} - \frac{1}{\varepsilon_{\text{max}}} \right) = \frac{(T-T_{\text{\text{max}}})^\gamma}{C_1}
\]  

... (8)

where \( \gamma = 1 \) and \( C_1 \) are modified constants with \( 1 \leq \gamma \leq 2 \). The parameter gives the information on the character of the phase transition. Its limiting values are \( \gamma = 1 \) and \( \gamma = 2 \) in the expression given in Eq. (8) of the Curie-Weiss law, \( \gamma = 1 \) is for the case of a normal ferroelectric and the quadratic dependence is valid for an ideal ferroelectric relaxor, respectively. Thus, the value of \( \gamma \) can also characterize the relaxor behaviour. The plot of \( \log \{ (1/\varepsilon'(T)-1/\varepsilon_{\text{max}}') \} \) versus \( \log (T-T_{\text{\text{max}}}) \) is shown in Fig. 7 by fitting with Eq. (8). The exponent \( \gamma \), determining the degree of the diffuseness of the phase transition, is obtained from the slope of \( \log \{ (1/\varepsilon'(T)-1/\varepsilon_{\text{max}}') \} \) versus \( \log (T-T_{\text{\text{max}}}) \) plot. We obtain the value of the parameter \( \gamma = 1.672 \) and 1.62 at 1 kHz for PBZN15 \((x=0.15)\) and PBZN25 \((x=0.25)\), respectively. A clear linearity of this relation was observed for both the investigated samples from which \( \gamma \) is calculated. The value of \( \gamma \) deviates from 2 with the increase in Ba which indicates that there is decrease in relaxor nature within the solid solution where the relaxor nature is retained. However, Eq. (8) cannot explain the end product of the series of \((\text{Pb}_{1-x}\text{Ba}_x)(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3\) since the end product\(^{[14]}\) \( \text{BZN} \) neither show any phase transition nor exhibit any temperature and frequency dependent dielectric properties. Yet another parameter, which is used to characterize the degree of relaxation behaviour in the frequency range 100 Hz - 919.28 kHz, is described\(^{[24]}\) as follows:

\[
\Delta T_{\text{relax}} = T\varepsilon'_m(919.28 \text{kHz}) - T\varepsilon'_m(100 \text{Hz})
\]  

... (9)

The value of \( \Delta T_{\text{relax}} \) was determined to be 34.85 and 29.20 K for the sample PBZN15 and PBZN25, respectively. The above characteristic done on the basis of Curie-Weiss law and the value of empirical parameters like \( \Delta T_{\text{\text{\text{m}}}} \), \( \gamma \), and \( \Delta T_{\text{relax}} \) suggest that the permittivity of \((\text{Pb}_{1-x}\text{Ba}_x)(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3\) ceramics follow the Curie-Weiss law only at temperatures much higher than \( T_m \). Thus, large deviation from the Curie-Weiss behaviour, large relaxation temperature

\[ T_{\text{relax}}, \text{ and } \gamma \text{ suggests that } (\text{Pb}_{1-x}\text{Ba}_x)(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3 \text{ is RFE.} \]

It is well known that in the RFE, the frequency dependence of temperature \( T_m \) cannot be described by Arrhenius law, which is expected in the Debye relaxation process. This is due to the fact that the relaxation spectrum is broader. Therefore, the observed frequency dependence of \( T_m \) is usually empirically evaluated by the implementation of the Vogel (V) –Fulcher (F) relationship, adopted from the theory on magnetic relaxation in glass systems. A spin glass state is, generally, viewed as a system of interacting superparamagnetic clusters and not a system of clusters with independent localized behaviour. The universal characteristics of a spin glass, and in general, any glass behaviour, is the existence of a static freezing temperature. In structural glasses, the freezing temperature commonly known as the glass transition temperature, is determined by the
onset of measurable visco-elastic behaviour on observable time scales. In spin glasses, a static freezing temperature can be determined from the frequency dependence of the permittivity, which approaches a constant value at lower frequencies. The freezing of the magnetic moment in spin glasses is believed to arise due to competing interactions, both ferromagnetic and antiferromagnetic, between neighbouring clusters preventing the establishment of conventional long-range ordering. Instead, these systems become frustrated by establishing only local ordering, ferromagnetic or antiferromagnetic, between clusters. A dipolar glass is believed to exist due to competition between ferroelectric and antiferroelectric. All the glassy systems possess two important key elements: firstly, randomness due an underlying disordered usually with clustering, and secondly, frustration leading to freezing.

The frequency dependence of $T_m$ can be modeled using the Vogel and Fulcher relationship attributed to V-F is known to be described by the empirical relation:

$$\omega = \omega_0 \exp \left[ \frac{-E_a}{k(T_m - T_f)} \right]$$

where $E_a$ is the activation energy, $T_f$ the freezing temperature, $E_a$ the activation energy, $\omega_0$ the Debye frequency or pre-exponential factor, and $T_m$ is the temperature of the permittivity maximum. In dipolar glass system, $T_f$ is regarded as the temperature where the dynamic reorientation of dipolar cluster polarization can no longer be thermally activated. The solid line in Fig. 8 is the curve fitted to the data using Eq. (10). The value derived from the curve gave an activation energy of 0.086 eV and 0.078 eV, a pre-exponential factor of $1.5 \times 10^{11}$ and $1.8 \times 10^{12}$ and a static freezing temperature of 174 K and 170 K for the PBZN15 and PBZN25, respectively. This value of $T_f$ is very reasonable, as it is below the temperature where the maximum occurs at 250 K and 235 K for the PBZN15 and PBZN25, respectively. The close agreement of the data with V-F relationship, suggests that the relaxor behaviour in the present PBZN15 and PBZN25 system is analogous to a spin glass with polarization fluctuations above a static freezing temperature. The V-F relation may also be interpreted as normal Debye relaxation with temperature dependent activation energy. The activation energy increases as the temperature decreases becoming undefined as the freezing temperature is approached. In RFE, the $E_a$ represents the activation energy for polarization fluctuations of an isolated cluster with temperature dependence from the development of short-range order between neighbouring clusters with $kT_f$ being a measure of the interaction energy. It is certainly possible that the ferroelectric clusters interact via dipole-induced dipole exchanges. The possibility also exists that the clusters could interact elastically through local rhombohedral distortions, implying that clusters may freeze into an oriental glassy state and are superelastic above the freezing temperature.

It is known that the origin of the polar nano-regions in lead containing RFE of the perovskite structure (ABO$_3$) is caused by chemical disorder of A- and B-sites and dynamical disorder of A-site caused by the anharmonic motion of Pb atom. Dynamics of
polar nanoclusters, which appear below $T_B$ is considered to be responsible for the relaxor behaviour. The dispersion (frequency dependence) of the dielectric response may be attributed to the relaxation of individual NbO$_6$ octahedral out of the network of ferroelectrically-coupled NbO$_6$ octahedral. Thomas et al.$^{30}$ proposed a theoretical framework in that indirect coupling of ferroelectrically active NbO$_6$ octahedra through Pb is important to observe the relaxor behaviour. According to this model, the evolution of micro Polar Regions is retained showing weak relaxor behaviour. From the detailed analysis using the theoretical model and from the experimental observation of fall of $\varepsilon'_m$, $\varepsilon''_m$ and $T_m$, they inferred that the substitution of barium ion prevents coupling of neighbouring NbO$_6$ octahedra to the ferroelectric network. There is a progressive breakdown of relatively large Pb rich regions into smaller regions, which is evident from decrease of $T_m$ with increase in Ba content. Increase of Ba for Pb disrupts the coupling and leads to decrease in volume of micro polar regions. As a general rule, an addition of a non-ferroelectric component is known to cause smearing and shifting of the phase transition towards lower temperatures and promote an appearance of relaxor behaviour. Comparing with pure PZN, addition of $x=0.15$ and 0.25 of Ba shifts the dielectric permittivity maximum by almost from 250 to 235 K.

4 Conclusions

RFE (Pb$_{1-x}$Ba$_x$)(Zn$_{1/3}$Nb$_{2/3}$)$_3$O$_9$ ceramics is synthesized by columbite process. The X-ray diffraction patterns of the samples at room temperature show the dominant perovskite phase with cubic pyrochlore phase. The maximum temperature of dielectric decreases with the increasing barium concentration. The barium substitution at A-sites of Pb(Zn$_{1/3}$Nb$_{2/3}$)$_3$O$_9$ (PZN) shifts the transition temperature towards lower temperature. Detailed analysis using dielectric spectroscopy (DES) shows that there is evidence for Vogel-Fulcher-type relaxational freezing below $T_m$. Therefore, the dielectric relaxation in PBZN is found analogous to the magnetic relaxation in spin-glass system with polarization fluctuations above a static freezing temperature.

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