

Study of Structural and Dielectric Properties of PZT (La, Na) Ceramics

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Abstract

Polycrystalline samples of PLNZT with the composition of $\text{Pb}_{1-x}(\text{La}_{1-z}\text{Na}_z)_x(\text{Zr}_y\text{Ti}_{1-y})_{1-x/4}\text{O}_3$; (where $x=0.05$, $y=0.65$, $z=0.0, 0.1, 0.2, 0.3$) have been synthesized by solid state reaction method. Grain size and its distribution have been studied by SEM micrographs and the distribution is found uniform and the size is almost spherical. X-ray studies of the compounds suggest the formation of a doublet (split) phases in the material due to compositional fluctuations. Dielectric properties as a function of frequency (10 Hz to 10^6 Hz) and as a function of temperature (30°C to 300°C) at 100 Hz, 1 kHz, 10 kHz, and 100 kHz frequencies suggest that the compound has relaxor behavior and undergoes a diffuse type of phase transition.

Keywords: Ceramics, Ferroelectrics, Diffuse phase transition, PZT, hysteresis loop.

Introduction

The ferroelectric properties in BaTiO_3 [1] initiated the study of a large number of pure and complex oxides having perovskite structure of the type ABO_3 (A = mono- or di-valent; B= tri-, tetra- or penta-valent cations). The $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$ (PZT) perovskite ferroelectric ceramic has been used successfully as a basic material for transducers, sensors and actuators. Ferroelectric oxides are widely used in computer memory, display devices, electro optical modulators, and other electronic applications [2-9]. The electromechanical properties of PZT ceramics can be tailored by adding small quantities of mono, di, trivalent ions (e.g., lanthanum, neodymium, tantalum or niobium) at the Pb sites. Among various dopants at the A-site of the PZT unit cell,

La^{3+} is the most suitable for many piezoelectric, pyroelectric and other device [10-13]. The $[(\text{PbLa})(\text{Zr-Ti})\text{O}_3]$ (PLZT) ceramic with 10% La concentration, being in the near vicinity of Morphotropic phase boundary (MPB), has been reported to be a potential quadratic modulator material [14]. It is therefore of interest to explore the possibility of fine-tuning the characteristic of PLZT with the aid of an additional dopant (like Na, Bi, Li, K etc.) at the Pb-site. Most of the reported work has been done to study the effects of various dopants in varying concentrations (x) at the A and B sites of PZT and resulting applications. A large amount of work has been carried out on PLNZT with single doping, double doping and multi-doping [15] and show the effect of a doping technique on physical properties as well as on di-electrical properties.

The conventional (high-temperature solid state reaction) method [16] of preparing PLZT powders causes compositional fluctuations and chemical inhomogeneity, which impairs the electromechanical properties of the finished products. Here a study of structural and dielectric properties of $\text{Pb}_{1-x}(\text{La}_{1-z}\text{Na}_z)_x(\text{Zr}_y\text{Ti}_{1-y})_{1-x/4}$, where $x=0.05$, $y=0.65$, $z=0.0, 0.1, 0.2, 0.3$) prepared by solid state reaction method has been presented.

Experiment

Polycrystalline ceramic samples of composition of $\text{Pb}_{1-x}(\text{La}_{1-z}\text{Na}_z)_x(\text{Zr}_y\text{Ti}_{1-y})_{1-x/4}$, where $x=0.05$, $y=0.65$, $z=0.0, 0.1, 0.2, 0.3$ (hereafter PLNZT) were prepared from the raw materials: lead nitrate, zirconyl nitrate, tetraisopropyl titanate, lanthanum nitrate, and Sodium carbonate of AR grade ($> 98.5\%$) supplied by Merck. Firstly, PZT was prepared by dissolving $\text{Pb}(\text{NO}_3)_2$, $\text{Zr}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$, and $\text{C}_{12}\text{H}_{28}\text{O}_4\text{Ti}$ in the desired ratio in double-distilled water. Then, the compound was coprecipitated by adding NH_3 solution to the nitrate solution. The precipitate was vacuum filtered, dried at 150°C and then first calcined at 1000°C for 2 hrs and then 1100°C for 4 hrs followed by intermediate grinding.

$\text{La}(\text{NO}_3)_3$ and Na_2CO_3 were added in the required stoichiometry to this calcined compound and were wet milled in alcohol. The powder was cold pressed in the form of discs at a pressure of $5.8 \times 10^8 \text{ N-m}^{-2}$ using a uniaxial hydraulic press. The disc shaped samples of about 1-2 mm thick and 13mm diameter were obtained by using the hydraulic press. These pellets were then sintered at 1100°C for 2h. To prevent loss of PbO during high-temperature sintering, the pellets were placed along with PbZrO_3 powder sealed in alumina crucibles.

The formation and quality of the PLNZT compound in the sintered pellets were checked with XRD, using a PANalytical, X-ray diffractometer (X' Pert Pro MPD) and $\text{Cu K}\alpha$ ($\lambda=1.5418\text{\AA}$) radiation. The size, shape and distribution of the grains were determined from SEM micrographs taken by Zeiss, Scanning Electron Microscope (EVO).

Sintered disc samples were ground and lapped to make the surface flat, parallel and subsequently electroplated by applying silver paste on both flat faces. Measurement of the electrical properties like impedance (Z), dielectric constant (ϵ) and the dielectric loss ($\tan\delta$) were carried out on a LCR HiTESTER (Hioki 3532 – 50,

Japan) as a function of frequency from (10 Hz to 10^6 Hz) as well as a function of temperature (from room temperature to 300°C) at 100 Hz to 100 kHz. A three-terminal sample holder was used to compensate for the stray capacitance.

Results and Discussion

The XRD patterns of the sintered specimens are shown in figure (1). The pattern indicates that the diffraction lines are very sharp and in doublet (split) for composition (a) $z=0.0$ to (d) $z=0.3$. Na doped material has been studied for (a) $z=0.0$ to (d) $z=0.3$ (at intervals of 0.1) and found splitting in the XRD patterns with rhombohedral perovskite-type structure.

The splitting of their reflections in doublets and triplets takes place [17,18] in compositional fluctuations leading to the coexistence of tetragonal and rhombohedral phases. This is attributed to the greater homogeneity of the prepared powders, which restricts compositional fluctuations in the sintered ceramics. All the reflection peaks of the sample were indexed and their cell parameters **a** and **α** of **$\text{Pb}_{1-x}(\text{La}_{1-z}\text{Na}_z)_x(\text{Zr}_y\text{Ti}_{1-y})_{1-x/4}$** , where $x=0.05$, $y=0.65$, $z=0.0, 0.1, 0.2, 0.3$ are obtained (Table1) from the least-squares refinement method. These parameters are found to be consistent with other reported values [19,20]. The agreement of calculated and observed d values of all diffraction lines of different compositions suggests that there is no change in the basic crystal structure of PZT or PLZT by substitution of Na from $z=0.0$ to $z=0.3$ (at intervals of 0.1). The preliminary X-ray analysis indicates that the specimens were of **rhombohedral**

Table 1: Structural properties of Na-doped PLZT.

Composition	crystallite size	grain size	Lattice Constant α (Angle)
$x = 0.05, y=0.65$	(nm)	(nm)	(a)Å
$z=0.00$	19.36	470	4.1096 89.64
$z=0.01$	20.21	370	4.1054 89.62
$z=0.02$	21.43	350	4.1131 89.72
$z=0.03$	24.65	340	4.1181 89.79

structure. By increasing the concentration from $z=0.0$ to $z=0.3$, a small difference in the d -value(s) have been observed but keeping the final structure invariant however a systematic change in intensity of the few reflections have been observed. This change in intensity may be due to (i) variation of particle size and (ii) the presence of Na dopants in different x , y or z -values. The average linear particle size of all samples, calculated from Scherrer's equation (3.1) is given in Table1.

$$P=K\lambda / \beta_{1/2} \cos \theta \quad (K=0.89,) \quad \text{-----}(3.1)$$

Where $K=0.89$ and $\beta_{1/2}$ is FWHM. Crystallite size varies from 19.36 nm to 24.65 nm as shown in table (1). It may be noted that for the composition $z=0.0$ crystallite size is minimum i.e 19.36 nm and increases from $z=0.1$ to $z=0.3$ is almost linearly.

SEM micrographs of the sintered pellets are shown in figure (2). They show spherical grains for $\text{Pb}_{1-x}(\text{La}_{1-z}\text{Na}_z)_x(\text{Zr}_y\text{Ti}_{1-y})_{1-x/4}$, where $x=0.05$, $y=0.65$, $z=0.0, 0.1, 0.2, 0.3$. These grains are uniformly and homogeneously distributed, which suggests that sintered pellets were reasonably dense. It has been observed (Table 1) that average grain size decreased markedly by Na-doping in the PLZT ceramics.

The variation of impedance (Z), dielectric constant (ϵ) and the dielectric loss ($\tan\delta$) as a function of frequency at room temperature for PLNZT is shown in figure (3, 4 and 5).

Table 2 The variation of the electrical parameter at room temperature for 1 kHz frequency.

Composition	Impedance (Z)	Dielectric Constant (ϵ)	Dielectric Loss ($\tan\delta$)
$x=0.05, y=0.65$			
$z=0.0$	120	550	0.08
$z=0.1$	200	430	0.06
$z=0.2$	150	470	0.05
$z=0.3$	210	275	0.07

It is found (Figure 3) that the impedance at room temperature decreases with increase in frequency for all compositions and can be explained on the basis of the following equation (3.2).

$$Z = [R^2 + (2\pi f L \sim d/2\pi f \epsilon_0 A)^2]^{1/2} \quad \text{-----}(3.2)$$

The decrease in impedance ' Z ' with increase in frequency indicate the regular increase in ac conductivity. In figure (4) and figure (5) a regular decrease in the dielectric constant and in dielectric loss as the frequency increases is a normal behavior for any dielectric material. The dielectric dispersion was large at lower frequencies and is attributed to the space charge polarization. The loss tangent initially increases and then decreases with the increases in the frequency indicating the disappearance of the conducting boundary layers

The variation of the Impedance, Dielectric Constant and Dielectric Loss for 1 kHz frequency are compared in Table 2. It is clearly visible that the variation is non-linear for impedance, dielectric constant and dielectric loss.

The nature of the ferroelectric phase transition, is determined by the variation of ϵ and $\tan\delta$ of the samples with temperature. The variation of impedance, dielectric constant (ϵ) and dielectric loss ($\tan\delta$) at different frequencies with increment of temperature is shown in figure (6-8) for all four different compositions. The observed variation of impedance as temperature varies from 30°C to 280°C at different

frequency range (100 Hz to 100 kHz) is shown in figure (6). At 100 Hz and at low temperature impedance is quite high and starts to decrease as temperature increases. But at minimum temperature and 1 kHz frequency, impedance is quite low compare to other frequencies and further reduces as temperature increases. It is clearly visible in figure (6) for 10 kHz frequency, impedance increases very rapidly to the highest point at minimum temperature and then reduces as a function of temperature which was also observed at lower frequencies. The decreasing pattern of impedance with temperature is almost same for all frequencies. It is found that with increase in temperature the impedance of the sample decreases. This may be due to the increase in capacitance/dielectric constant of the sample which is also evident from equation (3.2). So, it can be concluded that whatever the frequency at high temperature (240⁰C to 280⁰C) AC conductivity increases.

The dielectric constant increases gradually with increase in temperature like a normal ferroelectrics. It is apparent from figure (7) that the variation of ϵ with temperature (30⁰C to 280⁰C) at different frequencies for all four compositions has a broadened peak rather than a sharp peak (as in normal ferroelectrics) around T_c (Curie temperature), which is one of the most important characteristics of a disordered perovskite structure with a diffuse phase transition (Figure 9 & 10). This broadening is believed to be due to the compositional fluctuations or substitutional disordering in the arrangement of cations in one or more crystallographic sites of the structure, which leads to the microscopic or nanoscopic heterogeneity in the compound, with different local Curie points [21,22].

The changes are ascribed to the lead vacancies and the resulting increase in domain wall mobility [23]. It is also clear that an increase in frequency causes a decrease in the maximum value of the dielectric constant, where as only a small shift in curie temperature could be observed as shown in figure 7(a) to 7(d). This dispersion of maximum dielectric permittivity and the shift in T_c confirm the relaxor behavior of PLZT ceramics [24-25]. Further examination of the diffuseness in the studied materials was carried out by using the following relation

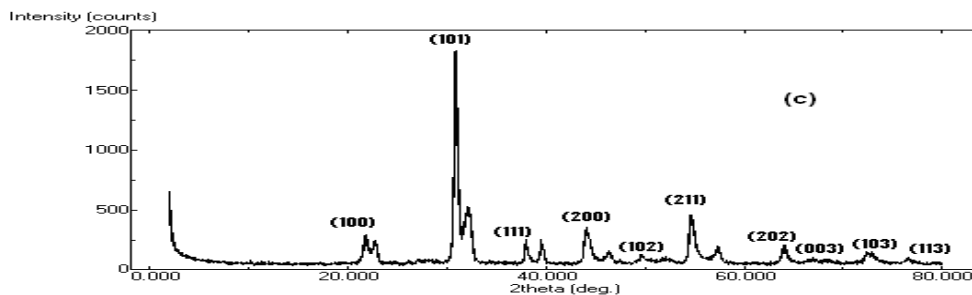
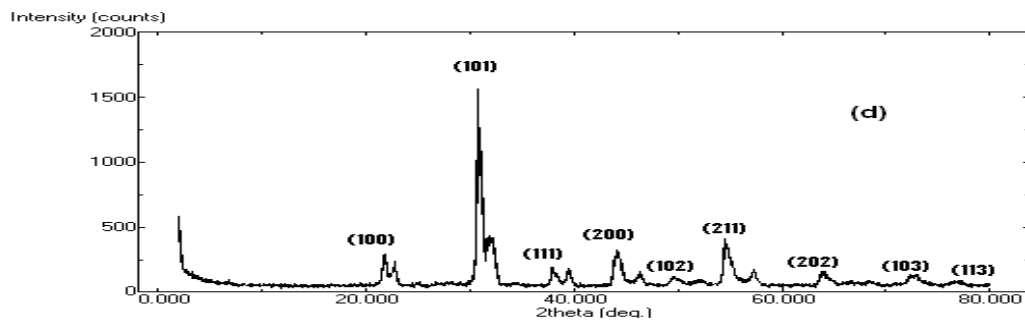
$$\left(\frac{1}{\epsilon} - \frac{1}{\epsilon_{\max}} \right) = (T - T_c)^\gamma \quad \text{----- (3.3)}$$

Where $\epsilon_{\max}$, is the maximum value of ϵ at T_c (figure 9 and table 3). The value of γ (diffusivity) given in table 3, was found to be between 1 and 2, which confirms the second-order diffuse phase transition in the material (Figure 11). we have noticed that the peak dielectric constant decreased with doping (Table 2 & 3), which implies that the substitution of (La, Na) ions at A-site reduces the dipole moment of the lattice and lowers the peak dielectric constant [26].

Table 3: Dielectrical properties of Na-doped PZT.

Composition	grain size	$\epsilon_{\max}$	T_c	γ	Diffused Temp.
$x=0.05, y=0.65$	(nm)	at 100 kHz	at 100 kHz	Range	
$z=0.0$	470	1280	255 ⁰ C	1.91	35 ⁰ C
$z=0.1$	370	1084	246 ⁰ C	1.45	54 ⁰ C
$z=0.2$	350	0858	244 ⁰ C	1.28	48 ⁰ C
$z=0.3$	340	0475	244 ⁰ C	1.16	50 ⁰ C

The $\tan\delta$ versus temperature curves for $\text{Pb}_{1-x}(\text{La}_{1-z}\text{Na}_z)_x(\text{Zr}_y\text{Ti}_{1-y})_{1-x/4}$, (where $x=0.05, y=0.65, z=0.0, 0.1, 0.2, 0.3$) shown in figure 8. It can be seen from the figure that the variation pattern of dielectric loss for 100 Hz to 100 KHz frequency is same for one doping of Na. For low frequency the loss is high while for high frequency the loss is minimum. But for different value of z , variation pattern of dielectric loss is different which is confirmed by figure 8. It might be possible due to the doping effect. However the dielectric loss is found to be very small but it is approx. same for all compositions. In general, the dielectric losses and dielectric constant follow the similar temperature behavior. In case of sharp ferroelectric-paraelectric phase transition both dielectric constant and dielectric losses peak at the same temperature and both follow the Curie-Weiss behaviour as expected from Kramer-KrÖnig relations [26].



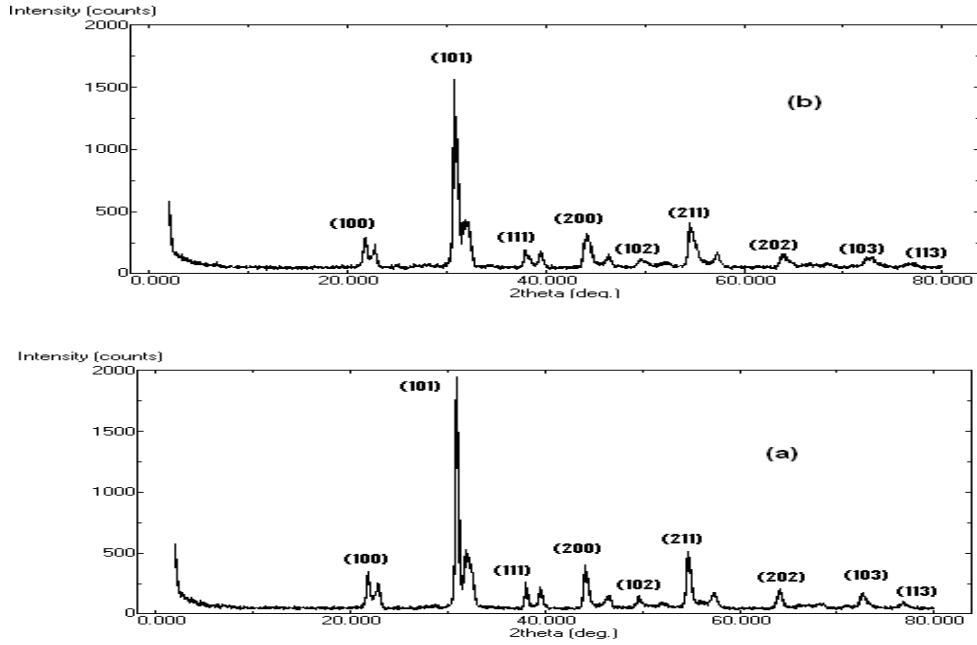


Figure 1: X-Ray Diffraction pattern of $\text{Pb}_{1-x}(\text{La}_{1-z}\text{Na}_z)_x(\text{Zr}_y\text{Ti}_{1-y})_{1-x/4}\text{O}_3$ sintered at 1100°C for 2 hrs. in which $x=0.05$, $y=0.65$ and (a) $z=0.0$, (b) $z=0.1$, (c) $z=0.2$ (d) $z=0.3$.

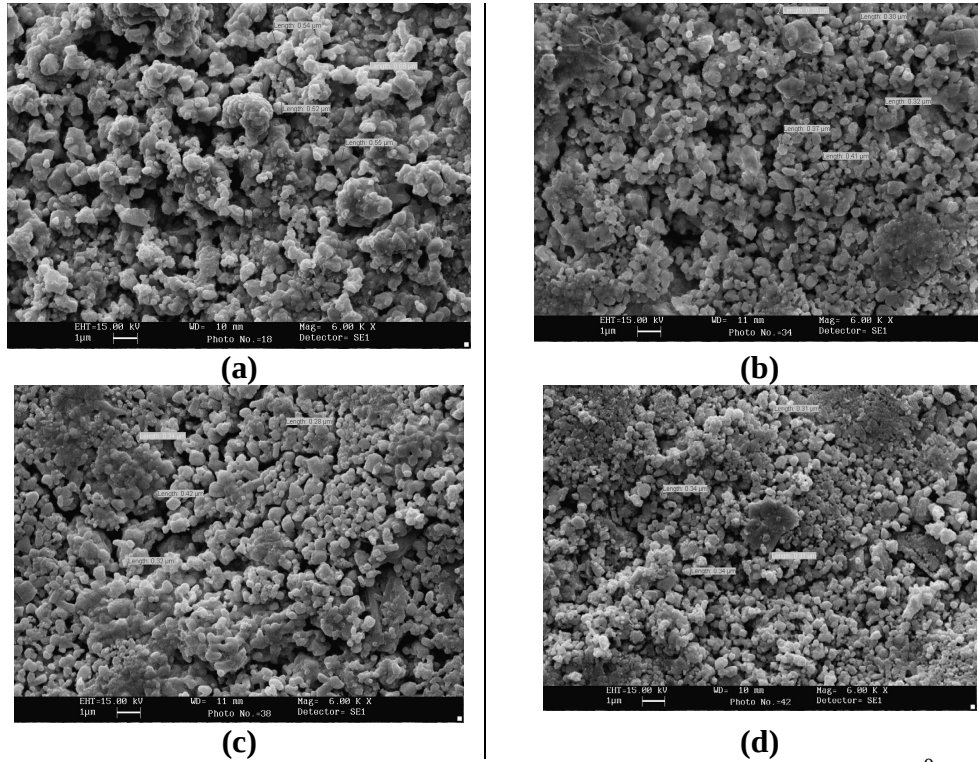


Figure 2: SEM of $\text{Pb}_{1-x}(\text{La}_{1-z}\text{Na}_z)_x(\text{Zr}_y\text{Ti}_{1-y})_{1-x/4}\text{O}_3$ sintered at 1100°C for 2 hrs. in which $x=0.05$, $y=0.65$ and (a) $z=0.0$, (b) $z=0.1$, (c) $z=0.2$ (d) $z=0.3$.

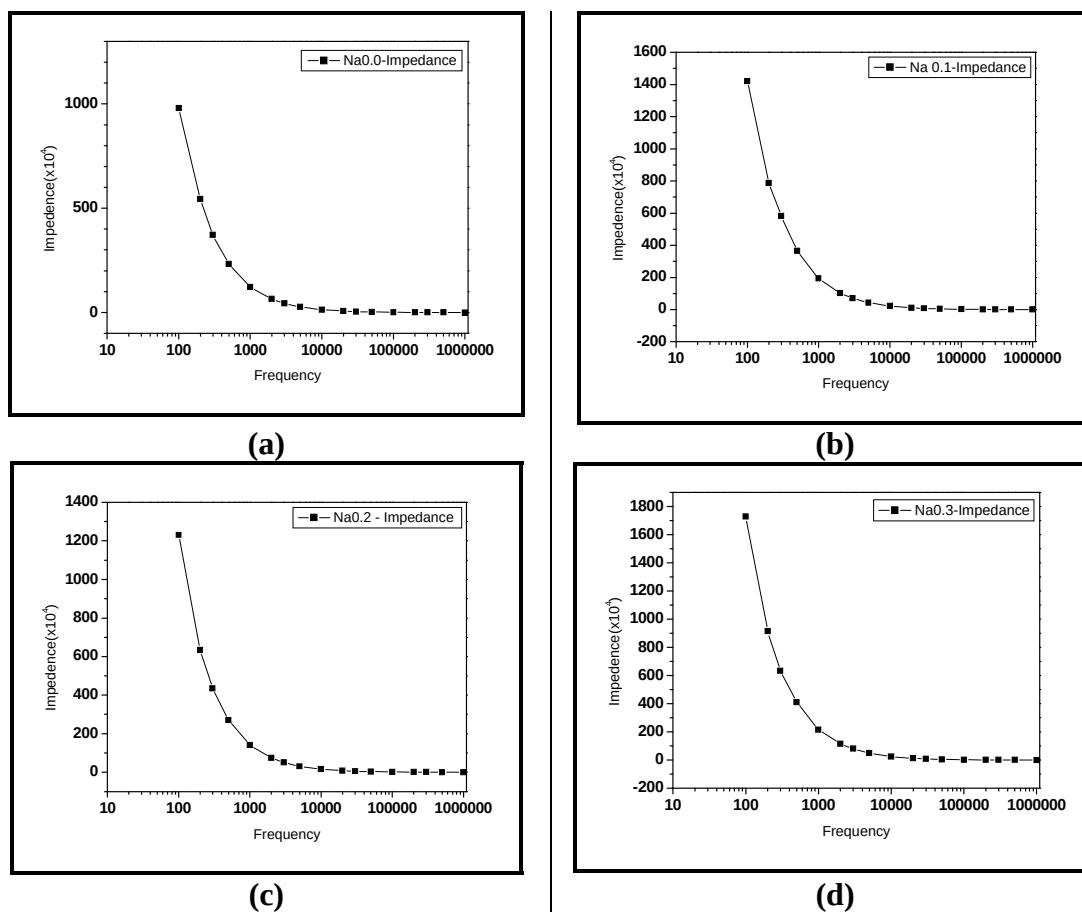
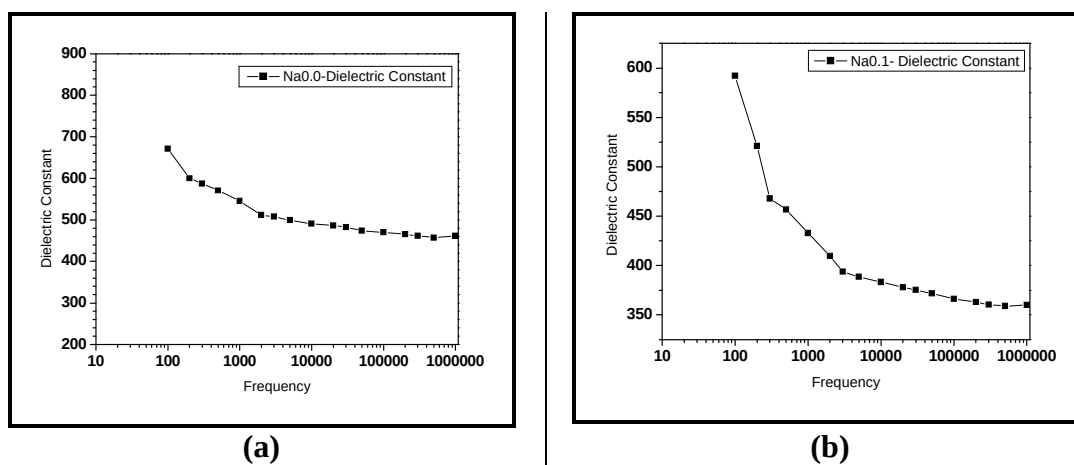


Figure 3 Variation of Impedance as a function of frequency at room temperature for $\text{Pb}_{1-x}(\text{La}_{1-z}\text{Na}_z)_x(\text{Zr}_y\text{Ti}_{1-y})_{1-x/4}\text{O}_3$ sintered at 1100°C for 2 hrs. in which $x=0.05$, $y=0.65$ and (a) $z=0.0$, (b) $z=0.1$, (c) $z=0.2$ (d) $z=0.3$.



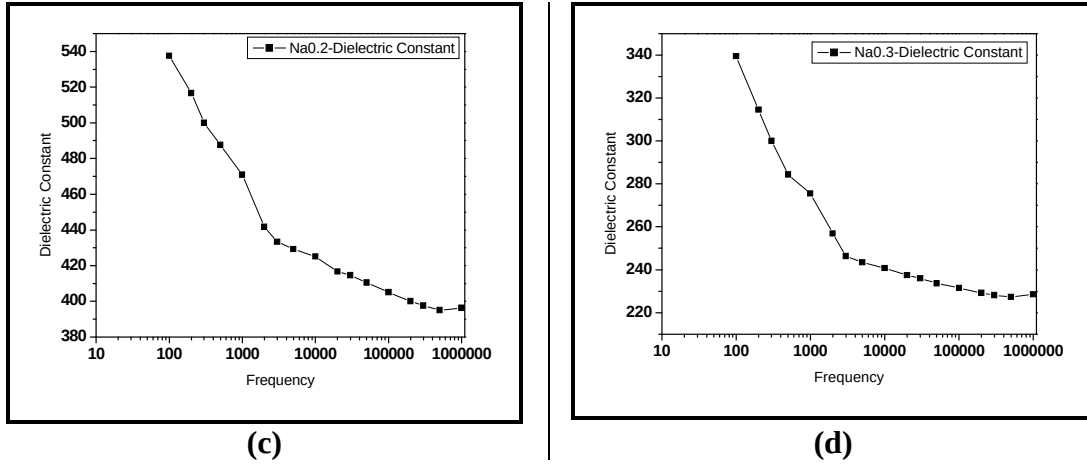


Figure 4: Variation of Dielectric Constant as a function of frequency at room temperature for $\text{Pb}_{1-x}(\text{La}_{1-z}\text{Na}_z)_x(\text{Zr}_y\text{Ti}_{1-y})_{1-x/4}\text{O}_3$ sintered at 1100°C for 2 hrs. in which $x=0.05$, $y=0.65$ and (a) $z=0.0$, (b) $z=0.1$, (c) $z=0.2$ (d) $z=0.3$.

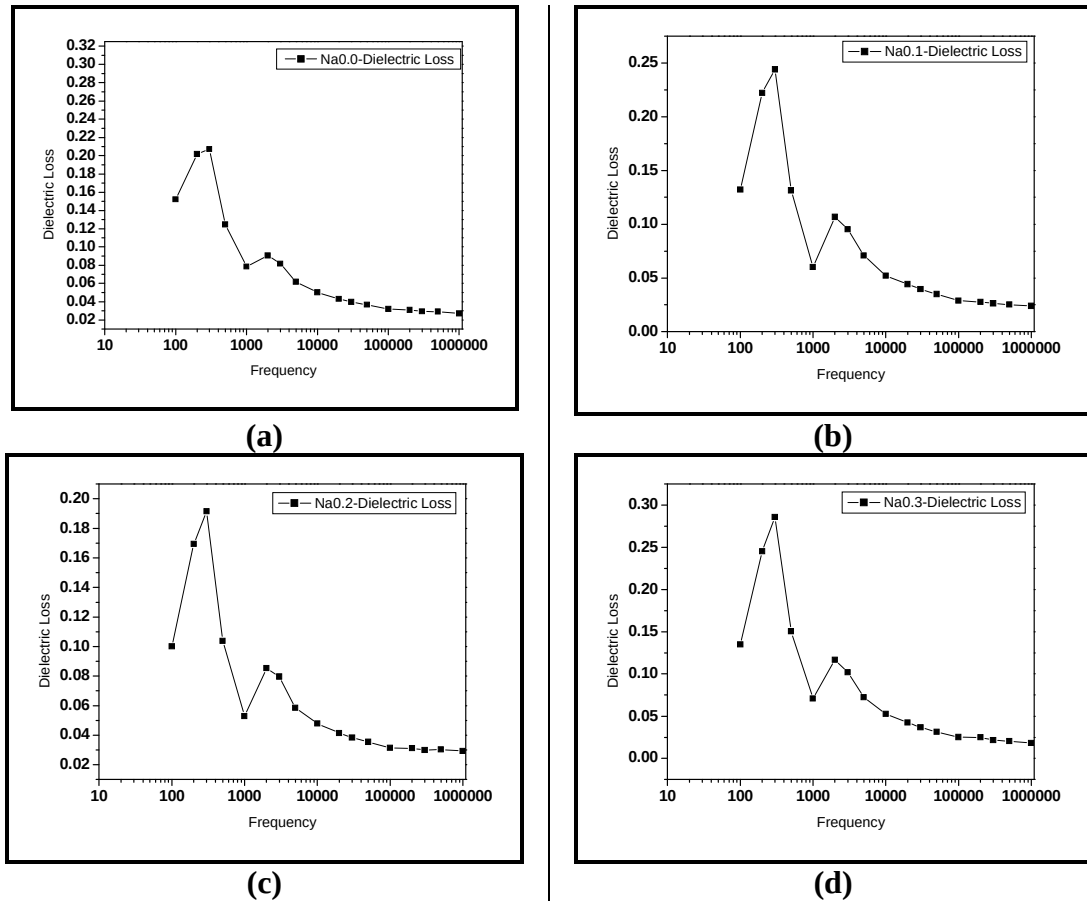
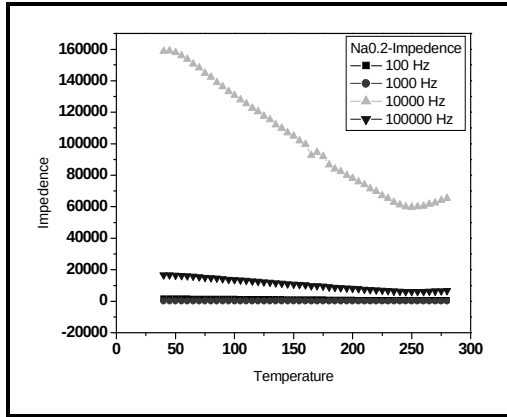
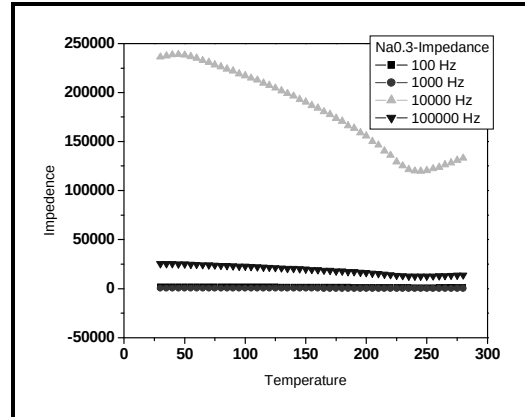


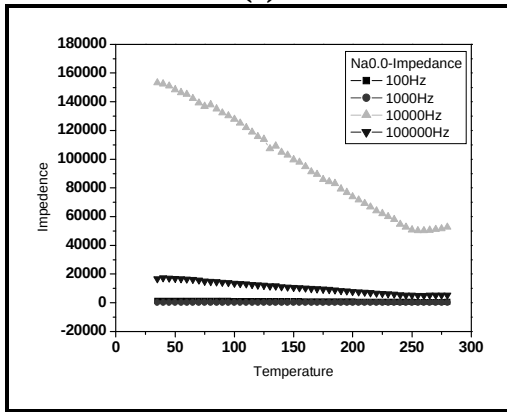
Figure 5 Variation of Dielectric Loss as a function of frequency at room temperature for $\text{Pb}_{1-x}(\text{La}_{1-z}\text{Na}_z)_x(\text{Zr}_y\text{Ti}_{1-y})_{1-x/4}\text{O}_3$ sintered at 1100°C for 2 hrs. in which $x=0.05$, $y=0.65$ and (a) $z=0.0$, (b) $z=0.1$, (c) $z=0.2$ (d) $z=0.3$



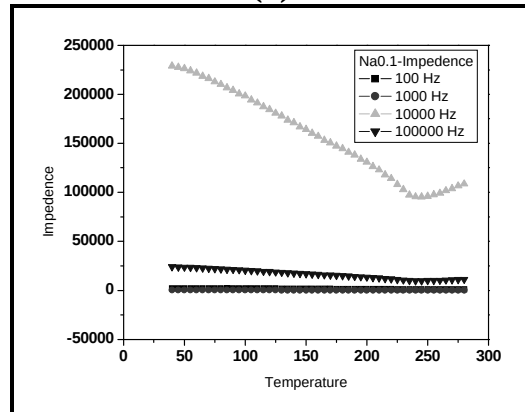
(c)



(d)

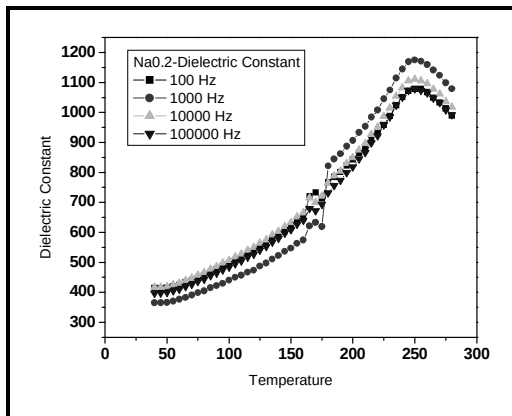


(a)

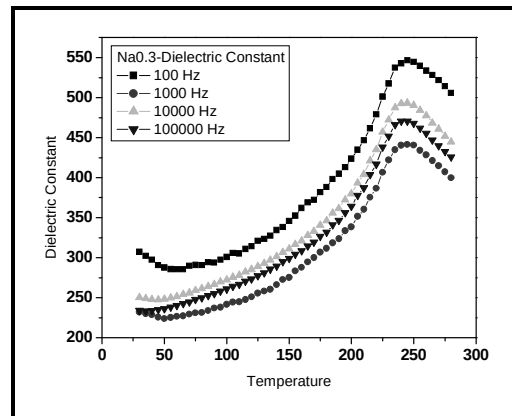


(b)

Figure 6 Impedance of $\text{Pb}_{1-x}(\text{La}_{1-z}\text{Na}_z)_x(\text{Zr}_y\text{Ti}_{1-y})_{1-x/4}\text{O}_3$ as a function of temperature at different frequency sintered at 1100°C for 2 hrs. in which $x=0.05$, $y=0.65$ and (a) $z=0.0$, (b) $z=0.1$, (c) $z=0.2$ (d) $z=0.3$



(c)



(d)

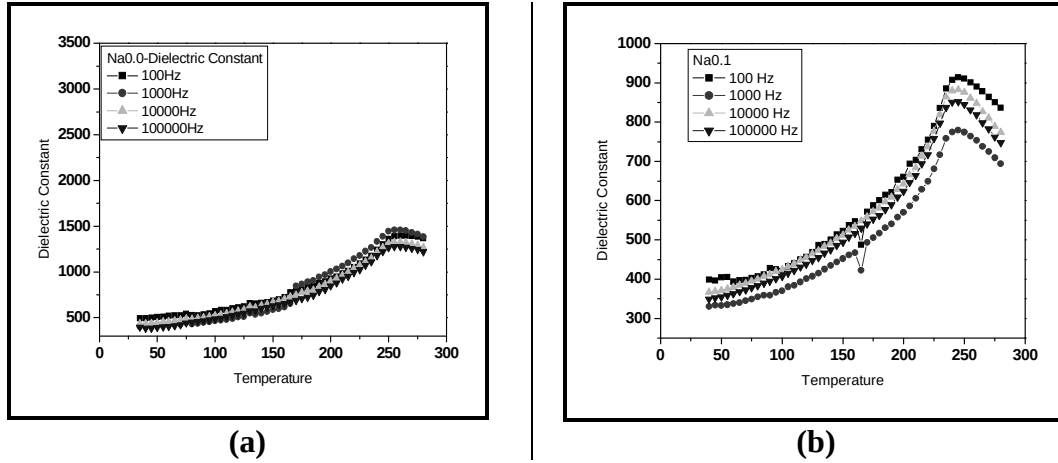


Figure 7: Dielectric Constant for $\text{Pb}_{1-x}(\text{La}_{1-z}\text{Na}_z)_x(\text{Zr}_y\text{Ti}_{1-y})_{1-x/4}\text{O}_3$ as a function of temperature at different frequency sintered at 1100°C for 2 hrs. in which $x=0.05$, $y=0.65$ and (a) $z=0.0$, (b) $z=0.1$, (c) $z=0.2$ (d) $z=0.3$.

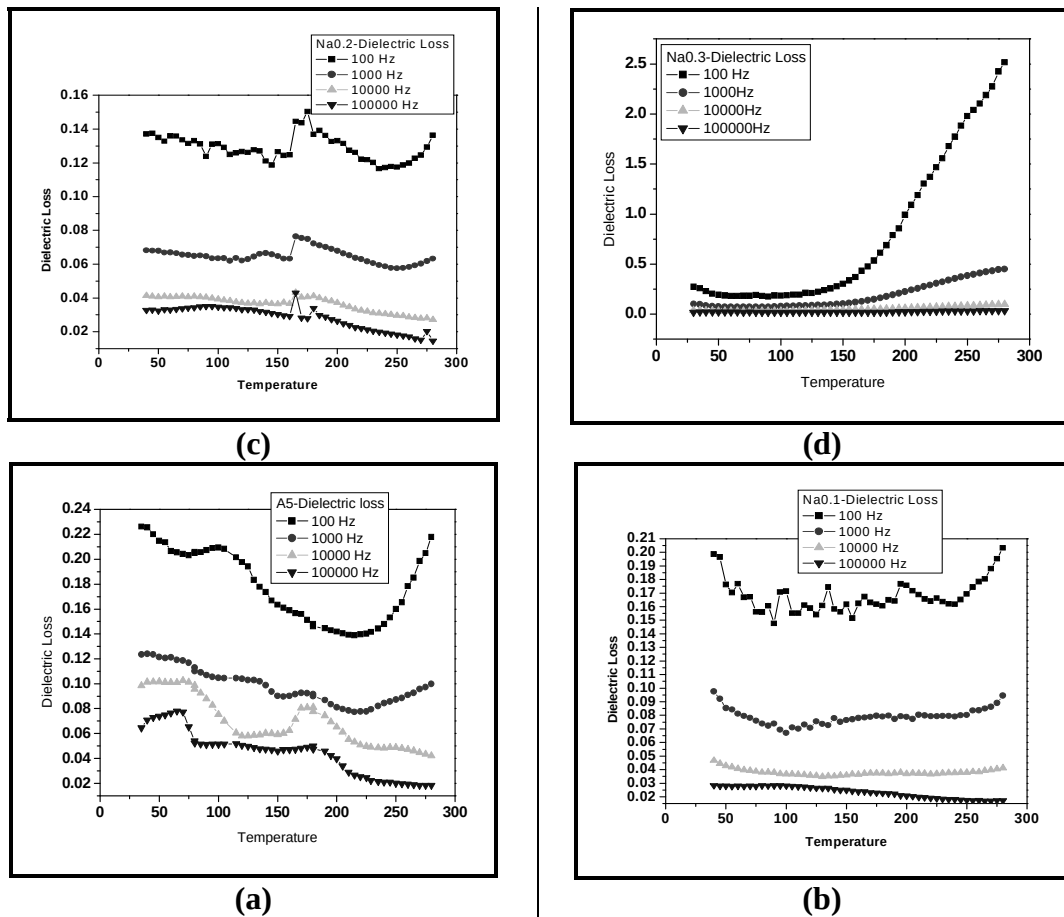


Figure 8 Dielectric Loss for $\text{Pb}_{1-x}(\text{La}_{1-z}\text{Na}_z)_x(\text{Zr}_y\text{Ti}_{1-y})_{1-x/4}\text{O}_3$ as a function of temperature at different frequency sintered at 1100°C for 2 hrs. in which $x=0.05$, $y=0.65$ and (a) $z=0.0$, (b) $z=0.1$, (c) $z=0.2$ (d) $z=0.3$

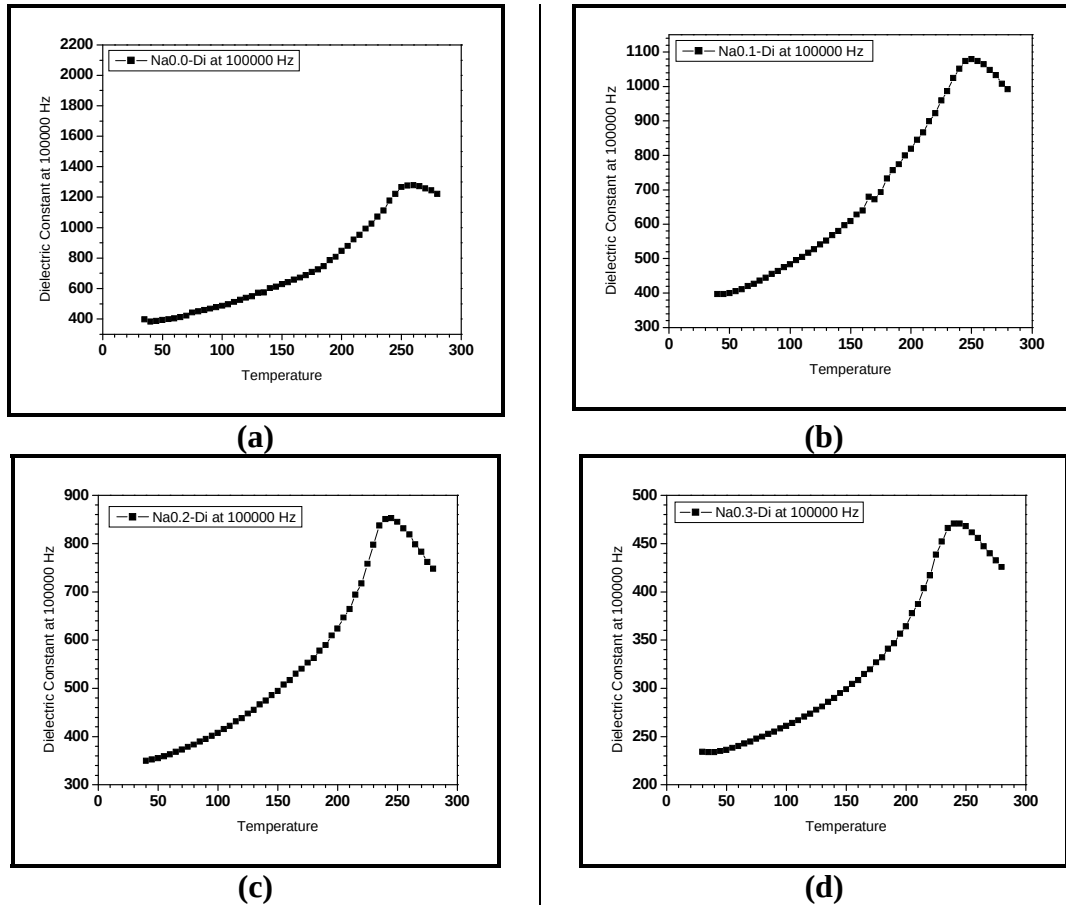
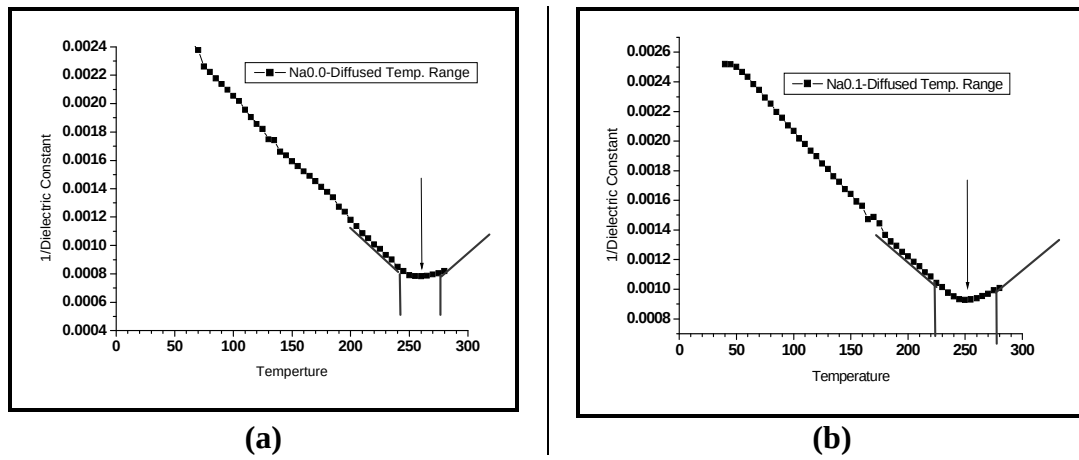


Figure 9 Max dielectric constant and curie temp. point for $\text{Pb}_{1-x}(\text{La}_{1-z}\text{Na}_z)_x(\text{Zr}_y\text{Ti}_{1-y})_{1-x/4}\text{O}_3$ as a function of temperature at 100 kHz frequency sintered at 1100°C for 2 hrs. in which $x=0.05$, $y=0.65$ and (a) $z=0.0$, (b) $z=0.1$, (c) $z=0.2$ (d) $z=0.3$



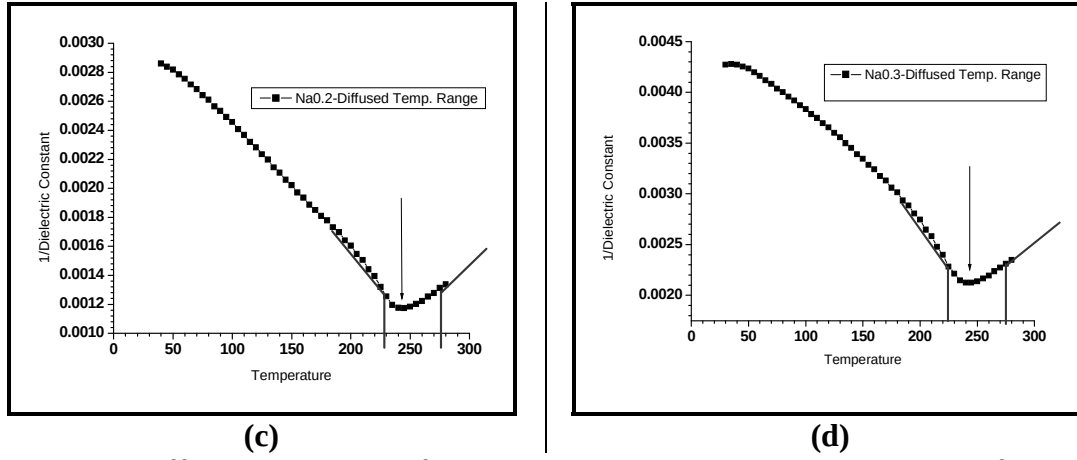


Figure 10 Diffused temp. range for $\text{Pb}_{1-x}(\text{La}_{1-z}\text{Na}_z)_x(\text{Zr}_y\text{Ti}_{1-y})_{1-x/4}\text{O}_3$ as a function of temperature at 100 KHz frequency sintered at 1100°C for 2 hrs. in which $x=0.05$, $y=0.65$ and (a) $z=0.0$, (b) $z=0.1$, (c) $z=0.2$ (d) $z=0.3$

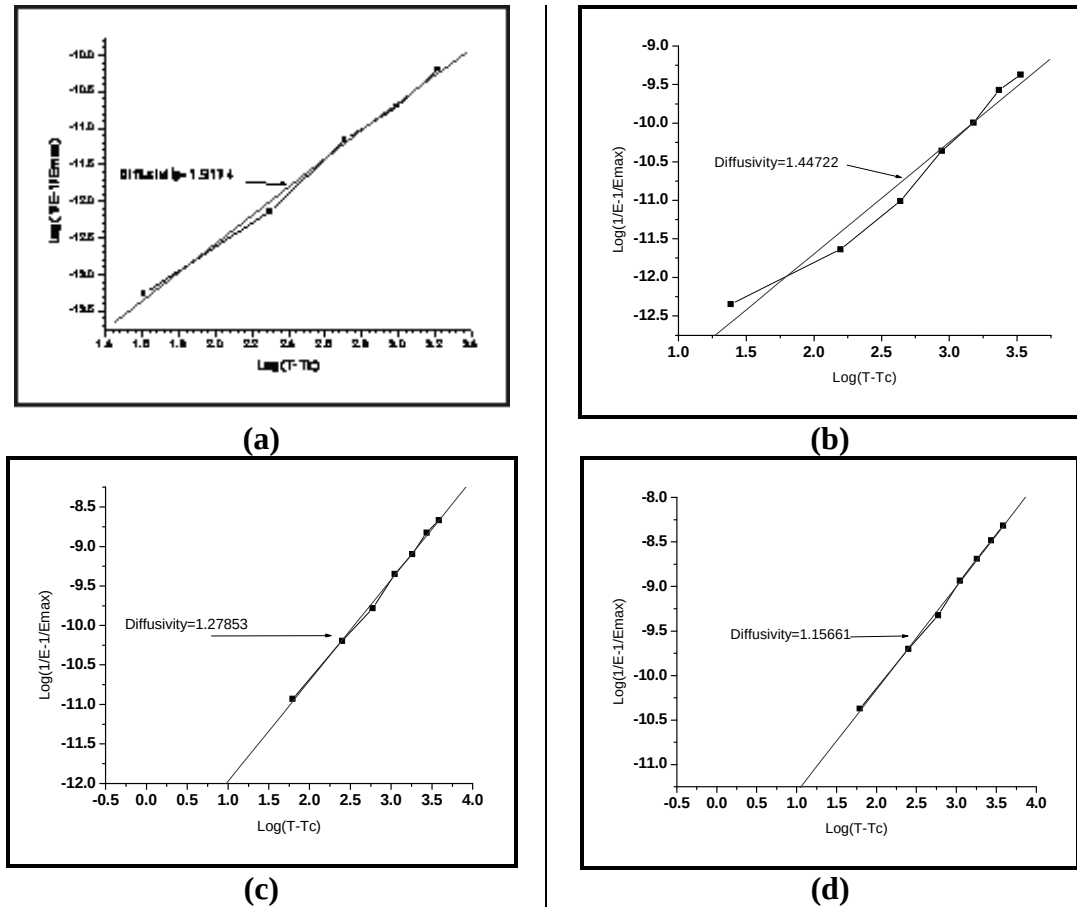


Figure 11 Diffusivity for $\text{Pb}_{1-x}(\text{La}_{1-z}\text{Na}_z)_x(\text{Zr}_y\text{Ti}_{1-y})_{1-x/4}\text{O}_3$ as a function of temperature at 100 kHz frequency sintered at 1100°C for 2 hrs. in which $x=0.05$, $y=0.65$ and (a) $z=0.0$, (b) $z=0.1$, (c) $z=0.2$ (d) $z=0.3$

Conclusions

The effect of Na doping on the structural and dielectric properties of chemically prepared PZT system has been reported. X-ray diffraction studies confirm the formation of pure phase and homogeneous ceramics, having a rhombohedral symmetry due to the presense of doublet peaks in these compounds. Scanning electron micrographs show a uniform grain distribution and the grain size and shapes were changed upon Na addition. Increase in Na content causes a decrease in average grain size of the material. Dielectric measurement demonstrate a decrease in the dielectric constant and variation in dielectric loss with increasing Na doping. The prepared ceramics have very low dielectric loss, high dielectric constant and high transition temperature which may be useful for device applications.

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