

# Dielectric behaviour of spray dried $\text{Pb}_{0.98}(\text{La}_{1-x/3}\text{Na}_x)_{0.02}(\text{Zr}_{0.53}\text{Ti}_{0.47})_{0.9950}\text{O}_3$ system

D. K. MAHATO, R. K. CHAUDHARY

Material Science Centre, National Institute of Technology, Jamshedpur 831 014, India

E-mail: drdevkumar@yahoo.com

S. C. SRIVASTAVA

National Metallurgical Laboratory, Jamshedpur 831 007, India

Sodium modified PLZT,  $\text{Pb}_{0.98}(\text{La}_{1-x/3}\text{Na}_x)_{0.02}(\text{Zr}_{0.53}\text{Ti}_{0.47})_{0.9950}\text{O}_3$  (PLNZT) with  $x = 0.0, 0.5, 1.0, 1.5, 2.0, 2.5$ , ceramics have been synthesized by spray drying technique. Rhombohedral phases of PLNZT ceramics were confirmed by XRD. Pellets prepared from the calcined powders were sintered at  $1100^\circ\text{C}$ . Micro-structural studies show the grains were spherical and homogeneous. Dielectric behaviour of these compounds has been studied as a function of temperature at 10 KHz frequency. Diffusivity of these compounds calculated from  $\varepsilon$ - $T$  plots were found to lie between 1 and 2, which suggests that the compounds have diffuse phase transition (DPT). The dielectric constant ( $\varepsilon$ ) as found to increase initially upto  $x = 1.5$  and then to decrease with increasing Na—concentrations. © 2005 Springer Science + Business Media, Inc.

## 1. Introduction

Recent investigations have shown that La modified PZT (PLZT) ceramic material that adopts tetragonal and/or rhombohedral phases has attracted considerable scientific interest as a source of unusually high dielectric constant material. PLZT ceramic have been extensively studied because of their excellent piezo and ferro-electric properties bearing significance to device applications such as MLCs, transducers, modulators, non-volatile memories etc., [1–3] and have been considered as a candidate of recent investigation [4–7]. PLZT generally has higher dielectric and piezoelectric properties than pure PZT because of their donor effect [3, 8, 9] i.e., divalent Pb ions are substituted by trivalent La-ones, creating A-Site vacancies in  $\text{ABO}_3$  structure [10]. It has been observed that PLZT has relaxation behaviour [11] and undergoes diffuse phase transition (DPT) [7–9, 12–14]. The relaxor-type perovskite are characterized by their high dielectric constant, excellent piezo-electric properties, diffuse phase transition and relatively low firing temperatures. Recently it was observed that dielectric and piezoelectric properties of PLZT relaxor materials are strongly influenced by the addition of other additives. It is, therefore, interesting to study the effect of Na-ions in La-site of PLZT with Zr/Ti = 53/47 ratio close to morphotropic phase boundary (MPB). In the present investigation we have extensively studied these properties of  $\text{Pb}_{0.98}(\text{La}_{1-x/3}\text{Na}_x)_{0.02}(\text{Zr}_{0.53}\text{Ti}_{0.47})_{0.9950}\text{O}_3$  ( $x = 0.0, 0.5, 1.0, 1.5, 2.0, 2.5$ ) (PLNZT) system synthesized using spray drying techniques.

Addition of  $\text{K}^+$  ions in PLZT has been reported to increase the dielectric constant ( $\varepsilon$ ) by about 5% [15] in samples having Zr/Ti = 65/35. Shanigrahi *et al.*, has re-

ported an increase of 20% in the value of dielectric constant for K-modified PLZT having Zr/Ti = 60/40 [5]—both samples prepared through sol-gel technique. In the present investigations addition of  $\text{Na}^+$  ions (1.5 at.%) in PLZT ceramics prepared through spray drying technique found to enhance the dielectric constant by 3.2% in samples having Zr/Ti = 53/47.  $\text{Na}^+$  ions added in concentrations higher than 1.5 at.% in PLZT has been observed to reduce the dielectric constant. This shows that addition of  $\text{Na}^+$  ions in PLZT only in small concentrations will increase the dielectric constant and such materials may be useful in devices where high dielectric constant is required. The materials being observed to be of diffuse transition type may help devices to have high dielectric constant over a considerable region of temperatures.

## 2. Experimental procedure

The  $\text{Pb}_{0.98}(\text{La}_{1-x/3}\text{Na}_x)_{0.02}(\text{Zr}_{0.53}\text{Ti}_{0.47})_{0.9950}\text{O}_3$  ceramic system with  $x = 0.0, 0.5, 1.0, 1.5, 2.0$  and  $2.5$  were prepared by spray drying technique using analytical grade of  $\text{Pb}(\text{NO}_3)_2$ ,  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ ,  $\text{TiCl}_4$ ,  $\text{NaNO}_3$  and  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  as starting materials in proper stoichiometry. Lead and Lanthanum nitrates were further purified by precipitating their aqueous solutions as hydroxides and then dissolving them in dil  $\text{HNO}_3$ . Chlorides of zirconium and titanium were converted separately into their nitrates by precipitating their aqueous solutions as hydroxides and redissolving the chloride free hydroxides in dil  $\text{HNO}_3$ .  $\text{NaNO}_3$  was however, used as such without further purification.

The composite nitrate solutions of the above composition were prepared by mixing the respective nitrate

TABLE I Some physical parameters of PLNZNZT ceramics

Physical parameters	X = 0.0	X = 0.5	X = 1.0	X = 1.5	X = 2.0	X = 2.5
Lattice parameter 'a' (Å)	4.0998	4.1113	4.1109	4.1209	4.1138	4.1117
Angle ' $\alpha$ '	89.962	89.963	89.979	89.998	89.982	89.983
Volume V (Å) <sup>3</sup>	68.91	69.49	69.38	69.98	69.59	69.51
$\epsilon_{\max}$	7450	7500	7598	7690	7300	7050
(tan $\delta$ ) <sub>max</sub>	0.046	0.042	0.037	0.034	0.048	0.052
T <sub>c</sub> (°C)	214	225	240	255	275	285
$\gamma$	1.5	1.60	1.75	1.63	1.44	1.38
$\delta_g$	64.6	70.3	68.3	81.9	77	66.4

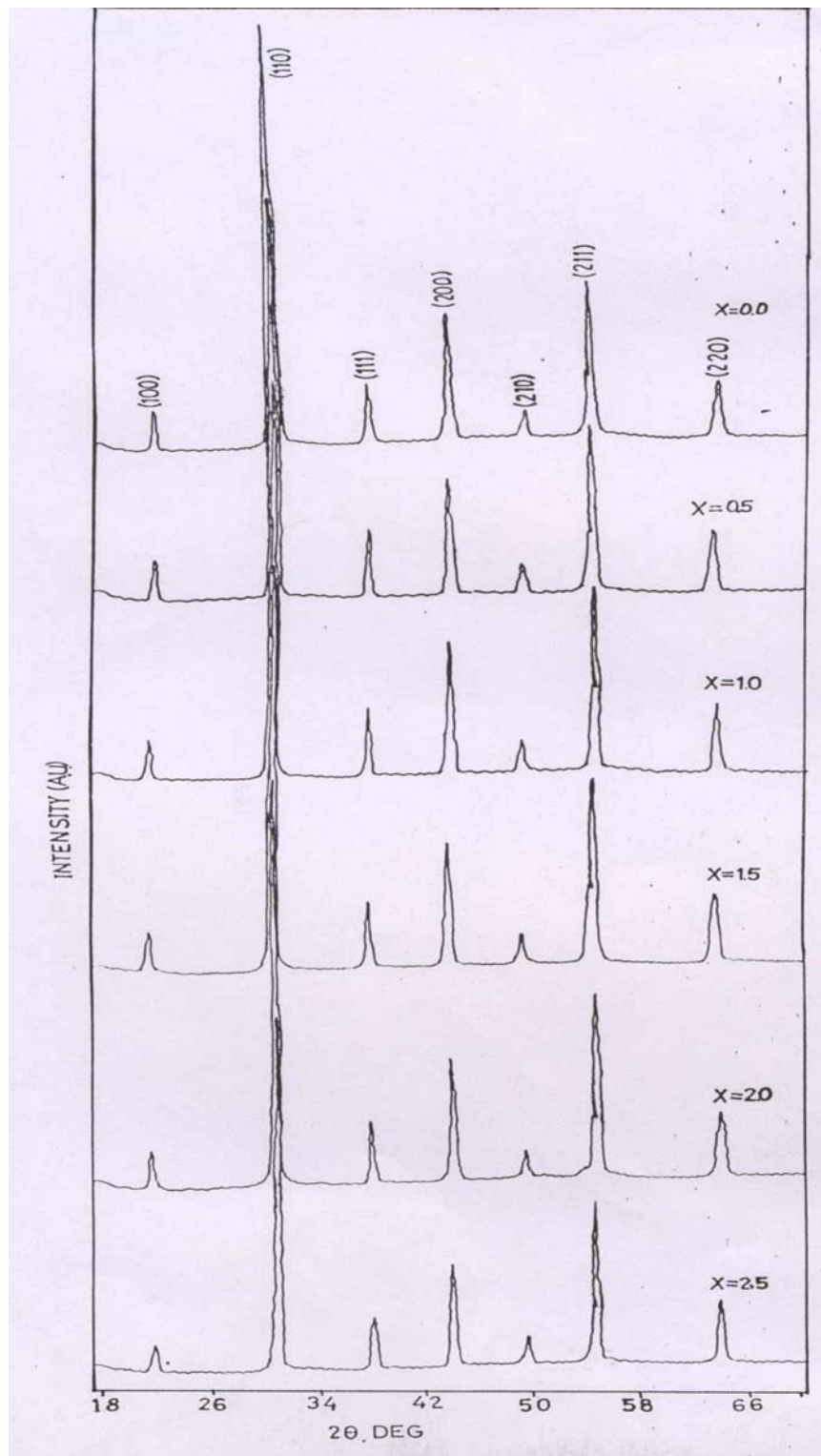


Figure 1 XRD patterns of PLZT (x = 0.0) and PLNZNZT.

solutions in right-proportions and converted into homogeneous powders by spray dryer. The spray-dried powders were transferred to platinum crucibles and calcined at 800°C for 6 h. The calcined powders were mixed with 1% solution of poly vinyl alcohol (PVA) as binder and cold pressed into pellets at a pressure of 150 MPa using a hydraulic press. The PVA binder was burnt out during sintering at 1100°C for 3 h. To prevent PbO loss of vaporisation during high temperature sintering, equilibrium PbO vapour pressure was established using PbZrO<sub>3</sub> powder. X-ray diffraction patterns of the resulting pellets were recorded using Cu K<sub>α</sub> radiation at room temperature with scanning rate 2°/min. Microstructure of the freshly polished surfaces of sintered pellets with a thin layer of graphite coating were observed using SEM (Jeol JSM-840 model of M/s. Jeol Ltd., Japan). Dielectric constant ( $\epsilon$ ) and tangent loss ( $\tan\delta$ ) of the high purity silver electroded samples were measured using a GR 1620 AP capacitance measuring assembly with a three terminal sam-

ple holder in a wide range of temperatures at 10 kHz frequency.

### 3. Results and discussion

All the XRD peaks of samples sintered at 1100°C were indexed using peaks interplanar spacing ( $d_{hkl}$ ) corresponding to  $2\theta$  values and intensity of each peak appearing in the diffraction patterns of each composition. On the basis of these values crystal phases of all compositions were found to be rhombohedral at room temperature using powder diffraction file [16]. It is found that the crystal structure is unaffected by substitutions of the Na<sup>+</sup> ions. However, small changes in lattice parameters and cell volume were observed (Table I) and negligible shifting of diffraction peaks towards higher angle with increasing  $x$ -value i.e., Na<sup>+</sup> concentration (Fig. 1) were observed.

The scanning electron micrographs of selected samples sintered at 1100°C are shown in Fig. 2. The grain

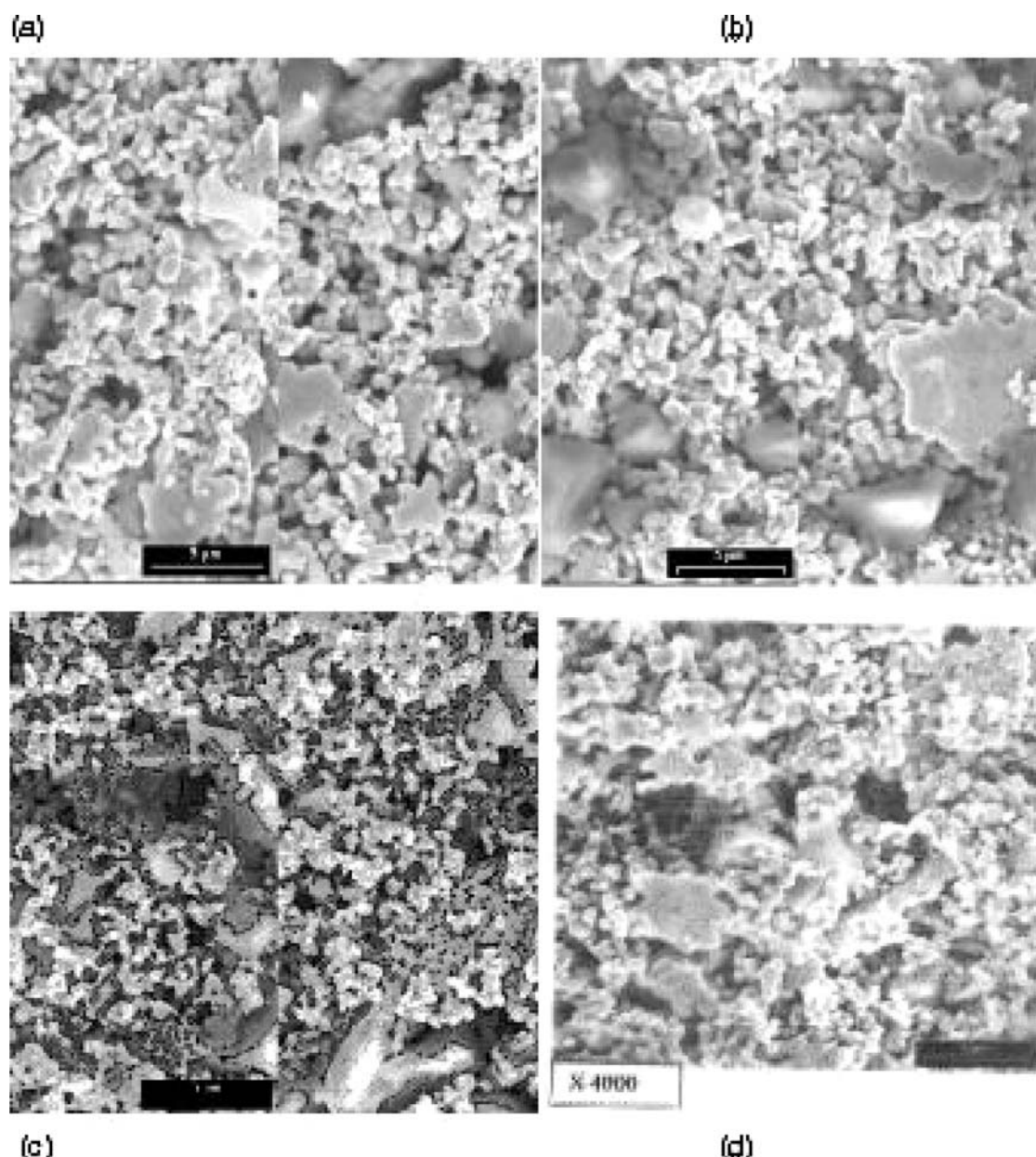


Figure 2 Scanning electron micrographs of PLZT and PLNZT sintered at 1100°C for (a)  $x = 0.0$ , (b)  $x = 0.5$ , (c)  $x = 1.5$  and (d)  $x = 2.5$ .

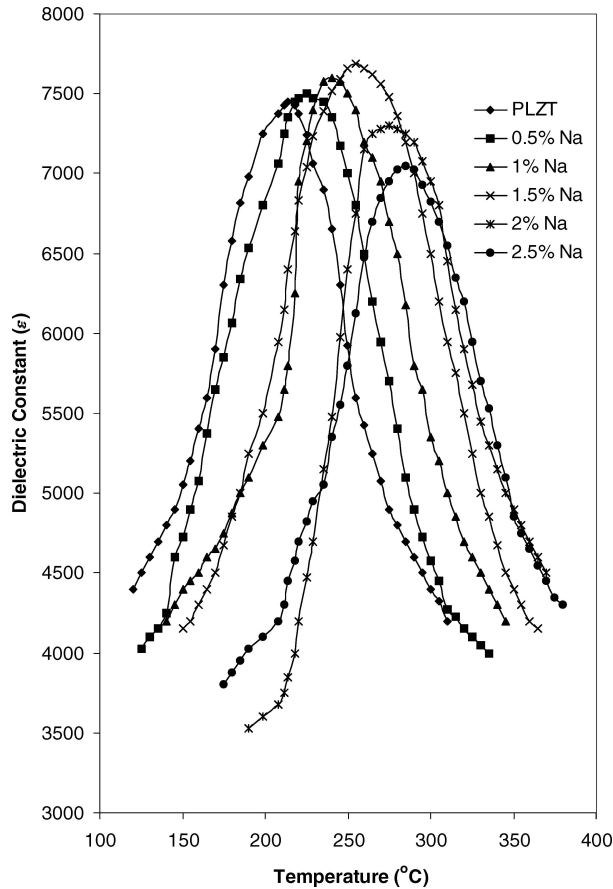


Figure 3 Variation of dielectric constant ( $\epsilon$ ) of PLZT and PLNzT as a function of temperature at 10 kHz.

size range of PLNzT for  $x = 0.0, 0.5, 1.5$  and  $2.5$  are  $0.85\text{--}2.47\ \mu\text{m}$ ,  $0.48\text{--}1.56\ \mu\text{m}$ ,  $0.54\text{--}1.47\ \mu\text{m}$  and  $0.82\text{--}1.73\ \mu\text{m}$  respectively. It is clear that (Fig. 2) the grain size range decreases with increase in  $x$ -value. The grains are nearly spherical and uniform with a grain size range of  $0.67\text{--}1.81\ \mu\text{m}$  on average.

Figs 3 and 4 show the variation of dielectric constant ( $\epsilon$ ) and tangent loss ( $\tan\delta$ ) of PLZT ( $x = 0$ ) and PLNzT as a function of temperature at 10 kHz respectively. It

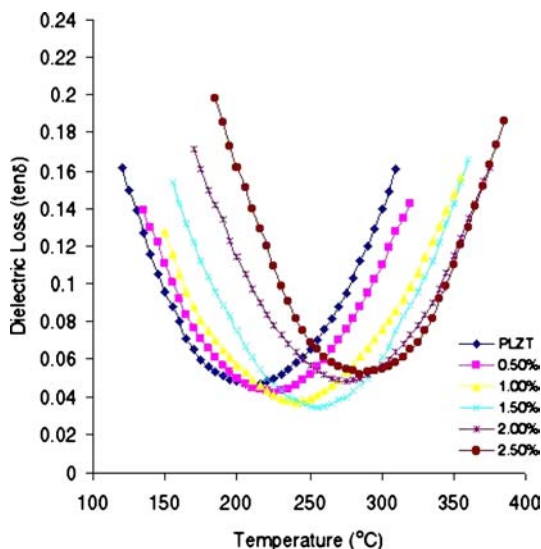


Figure 4 Variation of dielectric loss ( $\tan\delta$ ) of PLZT and PLNzT as a function of temperature at 10 kHz.

is observed that there is a sharp rise in dielectric constant ( $\epsilon$ ) to its maximum value ( $\epsilon_{\text{max}}$ ) with increase in temperature upto transition temperature ( $T_c$ ) and then starts decreasing with further increase in temperature for all compositions like normal ferro-electric (obeying Curie-Weiss Law), indicating ferro-electric phase transition in PLNzT. But, the dielectric peaks in the compounds have been found to be broadened, which indicates that these materials undergo ferro-electric phase transition of a diffuse type (characteristics of disordered perovskite) [15, 17]. This broadening of dielectric peak and variation of  $\epsilon_{\text{max}}$  are attributed to the variation of grain size and structural disorder [11] in the arrangement of the cations at the A-site and/or B-site of the crystal structure leading to microscopic heterogeneity in the composition and a distribution of local Curie points [5]. In addition, it is also observed that the transition temperature of the PLNzT ceramics increases with the increase in the value of  $x$ , whereas  $\epsilon_{\text{max}}$  increases initially upto  $x = 1.5$  and decreases with further increase in the value of  $x$  (Table I). A similar behaviour was observed by Rukmini *et al.*, in case of K-modified PLZT [15]. This can be attributed to the fact that the effect of  $\text{La}^{3+}$  doping increases the dielectric constant by creating A-site vacancies in PZT lattice thereby facilitating the motion of ferro-electric domains whereas  $\text{Na}^+$  doping creates hindrance to the motion of ferro-electric domains and hence the decrease in dielectric constant at room temperature [18]. With increase in temperature, lattice vibrations also increase

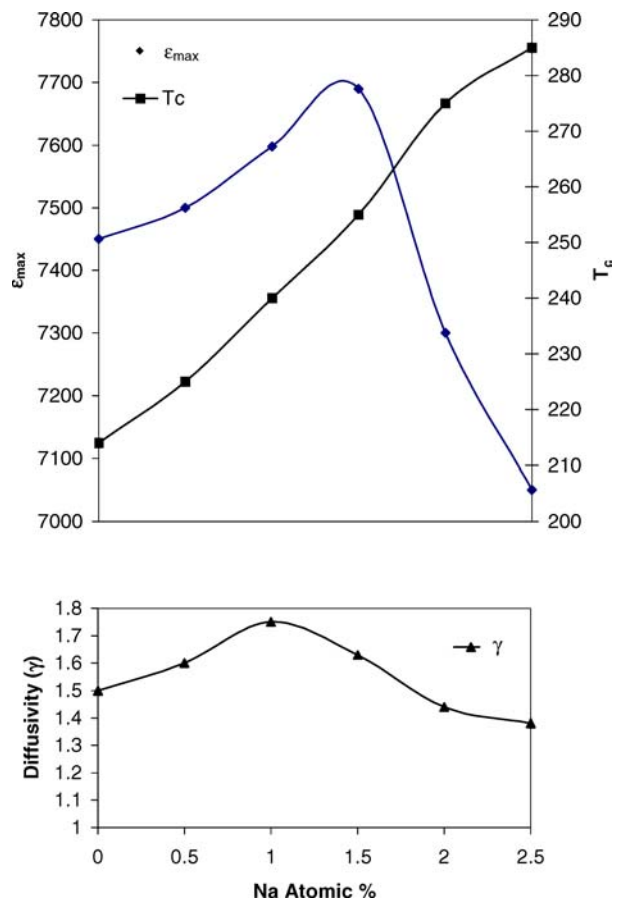


Figure 5 Variation of  $\epsilon_{\text{max}}$ ,  $T_c$  and  $\gamma$  of PLZT and PLNzT as a function of  $\text{Na}^+$  concentration.

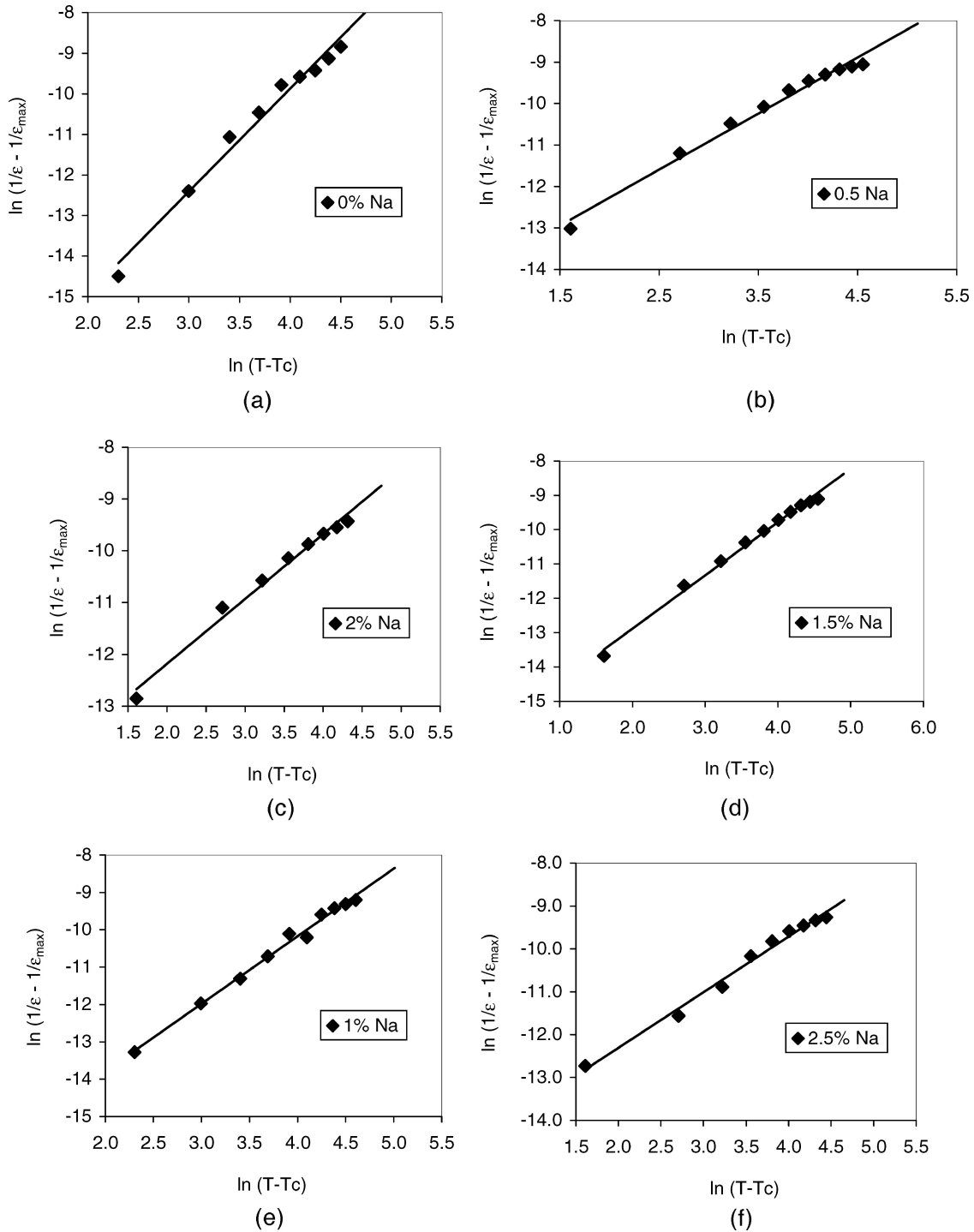


Figure 6 a-f: Plot of  $\ln(\frac{1}{\epsilon} - \frac{1}{\epsilon_{\max}})$  vs.  $\ln(T - T_c)$  for PLZT and PLNZT: (a)  $x = 0.0$ , (b)  $x = 0.5$ , (c)  $x = 1.0$ , (d)  $x = 1.5$ , (e)  $x = 2.0$ , and (f)  $x = 2.5$ .

and the interaction between the increase/decrease of vacancies created by  $\text{La}^{3+}/\text{Na}^+$  doping in PZT lattice may be responsible for the change in  $\epsilon_{\max}$  value and the corresponding  $T_c$  values. The  $\epsilon_{\max}$  values going to its maximum for 1.5 at.% at  $\text{Na}^+$  along with  $\text{La}^{3+}$  doping in PZT may be a result of the fact that predominance of vacancies (created by  $\text{La}^{3+}$ ) reduces beyond 1.5 at.%  $\text{Na}^+$  doping (i.e.,  $x = 1.5$ ). The change of ' $T_c$ ' and  $\epsilon_{\max}$  with  $\text{Na}^+$  concentration has been shown in Fig. 5. The tangent loss ( $\tan\delta$ ) of PLNZT has similar trend (Fig. 4). The  $(\tan\delta)_{\max}$ —values are given in Table I for all compositions.

The quantitative assessment of the degree of diffuseness of the broadened peak of the sample in the

paraelectric phase was evaluated from the expression  $(\frac{1}{\epsilon} - \frac{1}{\epsilon_{\max}})$  [19], where  $\epsilon$  is the dielectric constant at temperature  $T$ ,  $\epsilon_{\max}$  is the maximum value of  $\epsilon$  at  $T_c$  and  $\gamma$  is the measure of diffuseness. Plots of  $\ln(\frac{1}{\epsilon} - \frac{1}{\epsilon_{\max}})$  vs.  $\ln(T - T_c)$  for PLNZT as shown in Fig. 6a-f are almost linear. The values of ' $\gamma$ ' were calculated from slope of these st. lines and found to be between 1 (normal ferro-electrics) and 2 (disordered ferro-electrics), which confirms the diffuse phase transition in PLNZT material [4]. The variation of ' $\gamma$ ' with Na-concentration is shown in Fig. 5. Besides these, the Gaussian diffuseness ' $\delta g$ ' in PLNZT has been calculated using the relation  $\ln(\frac{\epsilon_{\max}}{\epsilon}) = \frac{(T - T_c)}{d\delta g^2}$ , [12] where over a limit  $1 \leq \frac{\epsilon_{\max}}{\epsilon} \leq 1.5$ . The variation of  $\frac{\epsilon_{\max}}{\epsilon}$  vs.  $(T - T_c)^2$  is plotted in

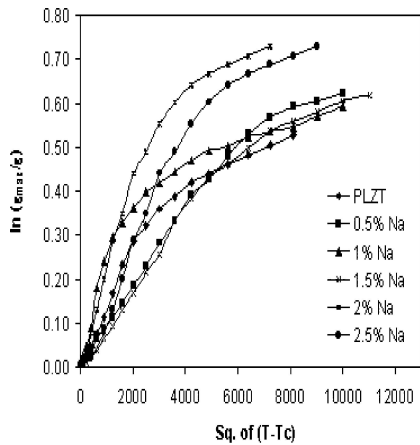


Figure 7 Variation of  $\ln(\epsilon_{\max}/\epsilon)$  vs.  $(T - T_c)^2$  of PLZT and PLNZT.

Fig. 7. Which shows clearly that the variation is non-linear.

#### 4. Conclusions

The spray dried PLNZT ceramics show good homogeneity and reactivity. The grains are nearly spherical and homogeneous. The grains size range decreases with increase in  $\text{Na}^+$  concentration. The dielectric constant is found to be high. The dielectric constant initially increases upto 1.5%  $\text{Na}^+$  and thereafter decreases with further increase in the  $\text{Na}^+$  concentration. The transition temperature is found to increase with the increase of  $\text{Na}^+$  concentration.

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