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## Relaxor Behaviour in $\text{Pb}(\text{Fe}_{0.5}\text{Nb}_{0.5})\text{O}_3$

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**Abstract** —The relaxor, ferroelectric lead iron niobate,  $\text{Pb}(\text{Fe}_{0.5}\text{Nb}_{0.5})\text{O}_3$  (PFN) is synthesized by Coulombite precursor method. Scanning electron micrograph taken at room temperature shows the compactness of the sample. The average grain size is found to be  $\sim 2 \mu\text{m}$ . The field dependence of dielectric response is measured in a frequency range, 0.1 kHz–1 MHz and in a temperature range from 27 °C to 200 °C. The temperature dependence of permittivity ( $\epsilon'$ ) shows broad maxima at various frequencies. The frequency dependence of the permittivity maximum temperature ( $T_m$ ) has been modeled using Vogel-Fulcher relation. Cole-Cole plot confirms the polydispersive nature of the relaxation time. It is proposed that the deviation from Debye behaviour is a result of the development of correlations between polar moments leading to the onset of non-ergodicity near freezing. The results also show that at  $T > T_m$ ,  $(1/\epsilon' - 1/\epsilon'_m)$  is proportional to the exponent  $\gamma$  and is found to be 1.844 at both 253 and 304 kHz.

Keywords : *Relaxor, Dielectric response, permittivity, Curie-Weiss law, Vogel-Fulcher relation.*

### INTRODUCTION

Perovskite based relaxor ferroelectric materials have generated considerable interest due to rich diversity of their physical properties and possible applications in various technologies like memory storage devices, micro-electro-mechanical system, multilayer ceramic capacitors and recently, in the area of opto-electronic devices [1-4]. It occupies a particular place among the complex oxides  $\text{A}(\text{B}'_m\text{B}''_{1-m})\text{O}_3$  with promising dielectric properties. In contrast to normal ferroelectrics, they are known to exhibit strong frequency dispersion of the dielectric constant in the temperature region of the diffuse permittivity maximum ( $T_m$ ) with no structural phase transition across  $T_m$ . The observed broadening in  $\epsilon'$ -T has generally been attributed to the presence of nano-

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regions resulting from local composition variation over length of 10-100 nm. Different nano-regions in a microscopic sample transforms at different temperatures giving rise to a range of transformation temperatures. In compositionally homogenous systems, quenched random disorder breaks the long-range polar order at unit cell level, leading to broad  $\epsilon'$ -T response [5]. Such materials exhibit slow enough relaxation dynamics and hence been termed as ferroelectric relaxor [6-7]. Burns and Decol [8] have proved the existence of polar-regions in relaxors at temperatures higher than  $T_m$ . Broadly, the relaxors are classified in two families: 1:2 family such as  $\text{Pb}(\text{Mg}_{0.33}\text{Nb}_{0.66})\text{O}_3$ , lead magnesium niobate (PMN) and 1:1 family such as  $\text{Ba}(\text{Fe}_{0.5}\text{Nb}_{0.5})\text{O}_3$ , barium iron niobate (BFN) [3].

In this paper we report the results of our studies on the relaxor behaviour of lead iron niobate  $\text{Pb}(\text{Fe}_{0.5}\text{Nb}_{0.5})\text{O}_3$  (PFN) that belongs to 1 : 1 family. An analysis of real and imaginary parts of the dielectric permittivity with frequency has been performed. The relaxor behaviour of PFN is obtained by monitoring the variation of its dielectric permittivity with temperature in the frequency range 0.1 kHz–1 MHz and in the temperature range from 27 °C to 200 °C. The micro structural study of the sample has been carried out by scanning electron micrograph (SEM).

## EXPERIMENTAL

**Materials :** The polycrystalline sample of PFN was synthesized by Coulombite precursor method using high purity oxides,  $\text{Fe}_2\text{O}_3$  (99.99% pure, Alfa acsar),  $\text{Nb}_2\text{O}_5$  (99.9% pure, Loba chemie) and  $\text{PbO}$  (~ 99% pure, Loba chemie) taken in stoichiometric ratio. First, the finely mixed powder of  $\text{Fe}_2\text{O}_3$  and  $\text{Nb}_2\text{O}_5$  is calcined at 1200 °C in an alumina crucible for 8 h. The calcined powder was then grinded and mixed by mortar and pestle with  $\text{PbO}$  for 6 h. At this stage of mixing 4-weight percentage of extra  $\text{PbO}$  is taken to compensate for the lead loss that might occur during calcination and sintering. Mixing had been done in acetone medium. The finely mixed powder was calcined at 1000 °C. The calcined powder was regrinded and used to make pellets of diameter 10 mm and thickness 1.6 mm of PFN using poly vinyl alcohol (PVA) as the binder. The pellets were sintered at 1050 °C for 4 h and then brought to room temperature gradually. First we brought from 1050 °C to 700 °C in 2 h then from 700 °C to 500 °C in 1 h and finally from 500 °C to room temperature in the next 1 h. The X-Ray diffraction of the sample shows rhombohedral phase, which resembles with the earlier results [11-12], and hence not presented here. Scanning electron micrograph of the sample was taken at room temperature. The sintered pellet is polished and silver electroded and connected to a LCR meter (Hioki, Japan) for dielectric measurement. The frequency dependence of dielectric constant and loss tangent were obtained using the LCR meter in the frequency range from 0.1 kHz – 1 MHz and in the temperature range from 27 °C to 200 °C.

All the dielectric data were recorded while heating the sample at a rate of  $0.5\text{ }^\circ\text{C min}^{-1}$ . The temperature was controlled by a programmable oven.

## RESULTS AND DISCUSSION

Fig. 1 shows the scanning electron micrograph (SEM) of PFN. The average grain size is found to be  $\sim 2\text{ }\mu\text{m}$ , which is uniformly distributed with some small pores/islands present on the surface of the pellets. The SEM micrograph predicts the proper compactness of the pellets. Fig. 2 shows the frequency dependence of real ( $\epsilon'$ ) and imaginary ( $\epsilon''$ ) parts of dielectric constant for PFN at various temperatures. It is seen that the values of  $\epsilon'$  and  $\epsilon''$  decrease with increasing frequency at any temperature. The temperature dependence of  $\epsilon'$  of PFN at various frequencies is shown in Fig. 3. There is a broad peak around  $112\text{ }^\circ\text{C}$  in the  $\epsilon'$ -T curve. With increasing frequency the permittivity maximum temperature  $T_m$  increases, while the magnitude of the peak value (the value of  $\epsilon'$  at  $T_m$ ) decreases. There is a strong dielectric dispersion in the frequency region around and below  $T_m$  in the  $\epsilon'$ -T curve. Diffuse maximum of  $\epsilon'$  is the characteristic of the relaxor ferroelectrics [9-10]. The above described

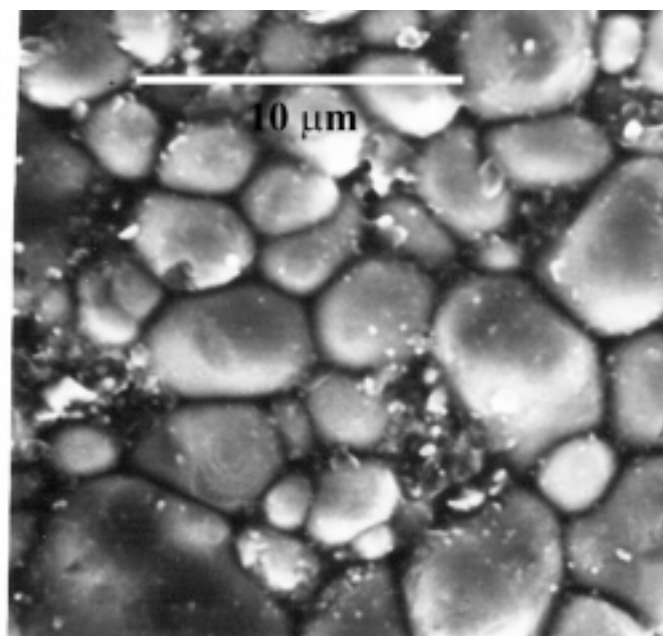


Fig. 1. Scanning electron micrograph of PFN.

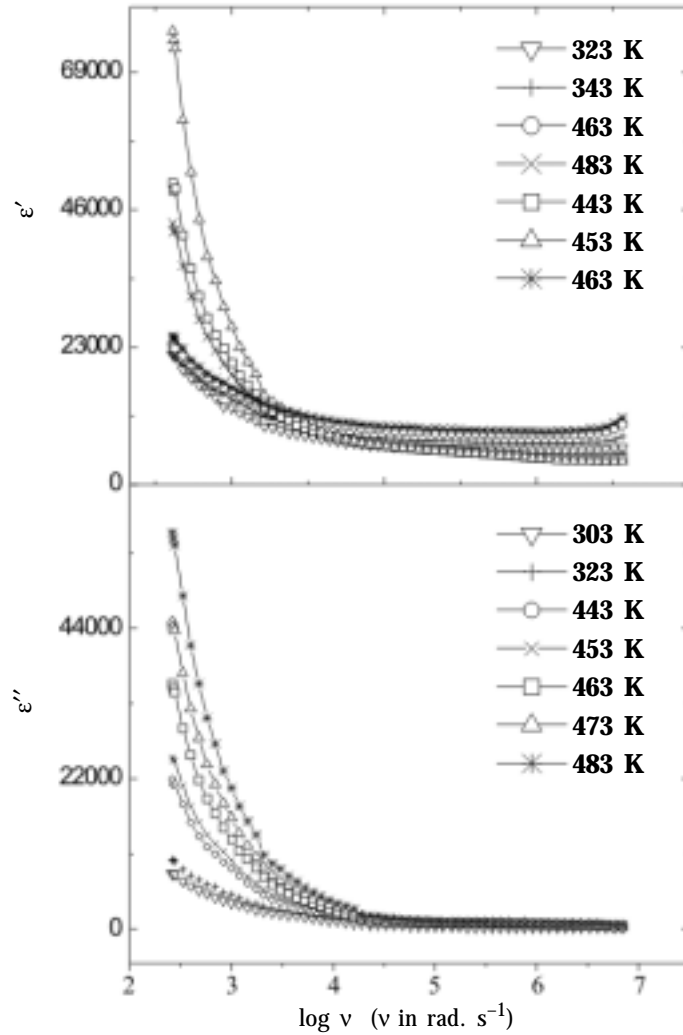


Fig. 2. Frequency dependence of  $\epsilon'$  and  $\epsilon''$  of PFN at various temperatures.

features in the  $\epsilon'$ - $T$  curve is very much similar to the observations by Cross, Yokosuka and many others [10-12] for various lead based ferroelectric relaxor materials.

It is well known that dielectric permittivity of normal ferroelectric above Curie temperature follows the Curie-Weiss law represented by the equation,

$$1/\epsilon' = (T-T_c)/C, (T > T_c) \quad (1)$$

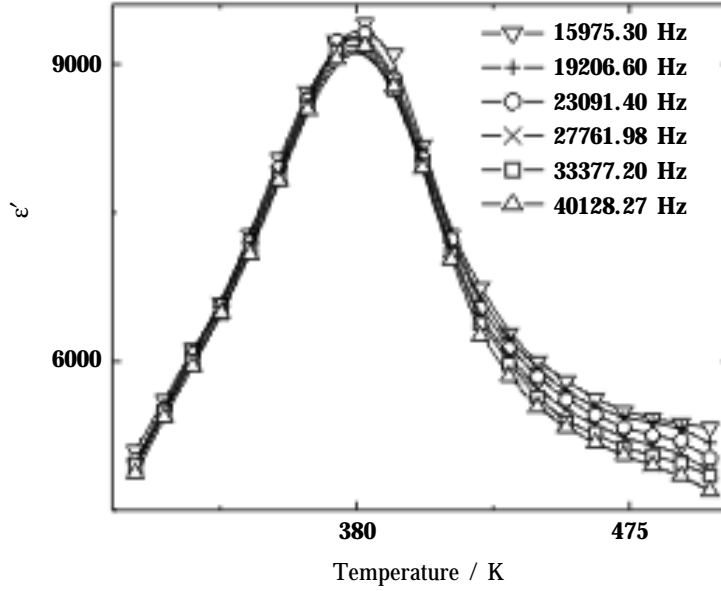


Fig. 3. Temperature variation of dielectric constant of PFN at various frequencies.

where  $T_c$  is the Curie temperature and  $C$  is the Curie-Weiss constant. Fig. 4 shows the inverse of  $\epsilon'$  as a function of temperature at 253 kHz and 304 kHz and the fitting of the experimental data to Curie-Weiss law. A deviation from Curie-Weiss law starting at  $T_{\text{dev}}$  can be seen clearly. The parameter  $\Delta T_m$ , which is often used to show the degree of deviation from the Curie-Weiss law, is defined as

$$\Delta T_m = T_{\text{dev}} - T_m \quad (2)$$

The  $T_{\text{dev}}$  as determined from the Curie-Weiss fit is found to be  $\sim 410$  K and hence  $\Delta T_m$  is found to be 25 K at 304 kHz. For such behaviour, a modified Curie-Weiss law has been proposed by Uchino and Nomura [12-13] to describe the diffuseness of the  $\epsilon'$  at and around  $T_m$ . It is given as

$$(1/\epsilon' - 1/\epsilon'_m) = (T - T_m)^\gamma / C_1 \quad (3)$$

where  $\epsilon'$  is the dielectric constant at temperature  $T$ .  $\gamma$  and  $C_1$  are modified constants. The values of  $\gamma$  lie in between 1 and 2 in the equation (3) of the Curie-Weiss law,  $\gamma = 1$  is the case for normal ferroelectric and quadratic dependence is valid for an ideal ferroelectric relaxor. In Fig. 5 the plot of  $\log(1/\epsilon' - 1/\epsilon'_m)$  as a function of  $\log(T - T_m)$  is shown with fitting to equation (3). The exponent  $\gamma$ , determining the degree of diffuseness, is obtained from the slope of  $(1/\epsilon' - 1/\epsilon'_m)$  vs.  $\log(T - T_m)$  plot

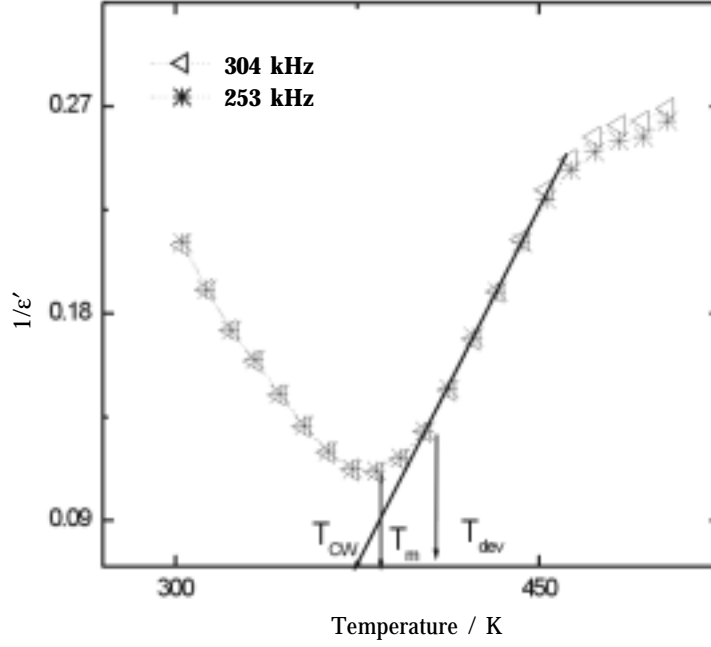


Fig. 4. The inverse dielectric constant ( $1/\epsilon'$ ) as a function of temperature at 253 kHz and 304 kHz for PFN. The symbol represents experimental data points and the solid line shows fitting to the Curie-Weiss law.

and is found to be 1.844 both at 253 and 304 kHz.

Yet another parameter, which is used to characterize the degree of relaxation behaviour in the frequency range of 0.1 kHz to 100 kHz, is described as

$$\Delta T_{\text{relax}} = T_m(0.1 \text{ kHz}) - T_m(100 \text{ kHz}) \quad (4)$$

The above characterization is done on the basis of Curie-Weiss law and the values of empirical parameters like  $\Delta T_m$ ,  $\gamma$  and  $\Delta T_{\text{relax}}$  ( $= 4\text{K}$ ) suggest that the permittivity of PFN follows Curie-Weiss law only at temperatures much higher than  $T_m$ .

The frequency dependence of  $T_m$  is shown in Fig.6. This frequency dependence of  $T_m$  can be modeled using the Vogel (1921) and Fulcher (1925) relation [14-15] given by

$$v = v_0 \exp \left[ -\frac{E_a}{k_B(T_m - T_f)} \right] \quad (5)$$

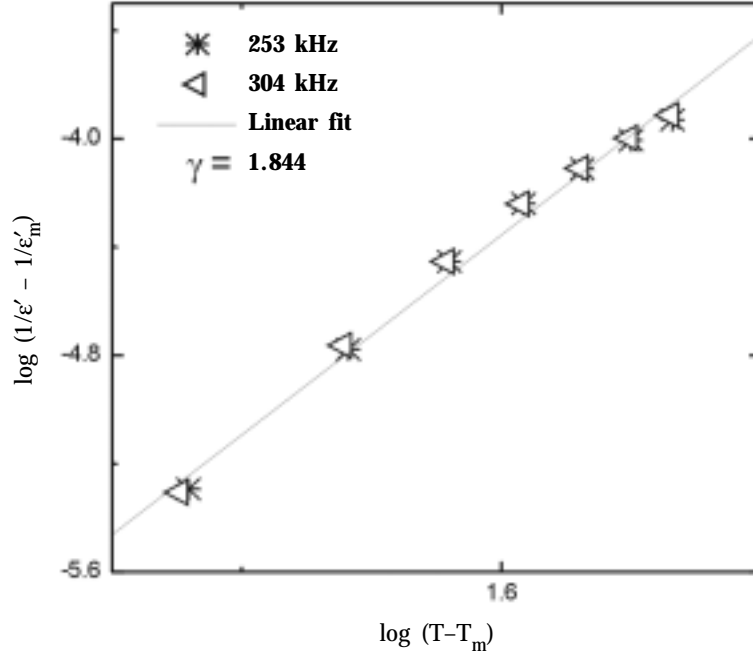


Fig. 5.  $\log (1/\epsilon' - 1/\epsilon'_m)$  vs.  $\log (T - T_m)$  plot for PFN at 253 kHz and 304 kHz, the symbols represent experimental data points and the solid line shows a linear fit to the data points.

where  $\nu$  is the frequency for a particular value of  $T_m$ ,  $k_B$  is Boltzmann's constant,  $\nu_0$  is the pre-exponential factor,  $E_a$  is the activation energy and  $T_f$  is the freezing temperature.  $T_f$  is regarded as the temperature where the dynamic reorientation of dipolar cluster polarization can no longer be thermally activated. The solid line in Fig.6 is the curve fitted to the data using equation (5). The values derived from the curve gave an activation energy of 0.756 eV, a pre-exponential factor of  $2.2 \times 10^{12}$  Hz and a static freezing temperature of 280 K. This value of  $T_f$  is very reasonable, as it is below the temperature where the maximum occurs. The close agreement of the data with the Vogel-Fulcher relationship suggests that the relaxor behaviour in the PFN is analogous to that of dipolar glass with polarization fluctuations above a static freezing temperature. The activation energy and pre-exponential factor are both consistent with thermally activated polarization fluctuations.

In Fig.7, we have plotted  $\epsilon''$  against  $\epsilon'$  usually known as Cole-Cole plot at temperatures 483 K and 503 K. For polydisperse relaxation, which is expected in PFN, the plots are close to circular arcs with end points on the axis of real and the centre below this axis. The complex dielectric constant in such situations is known

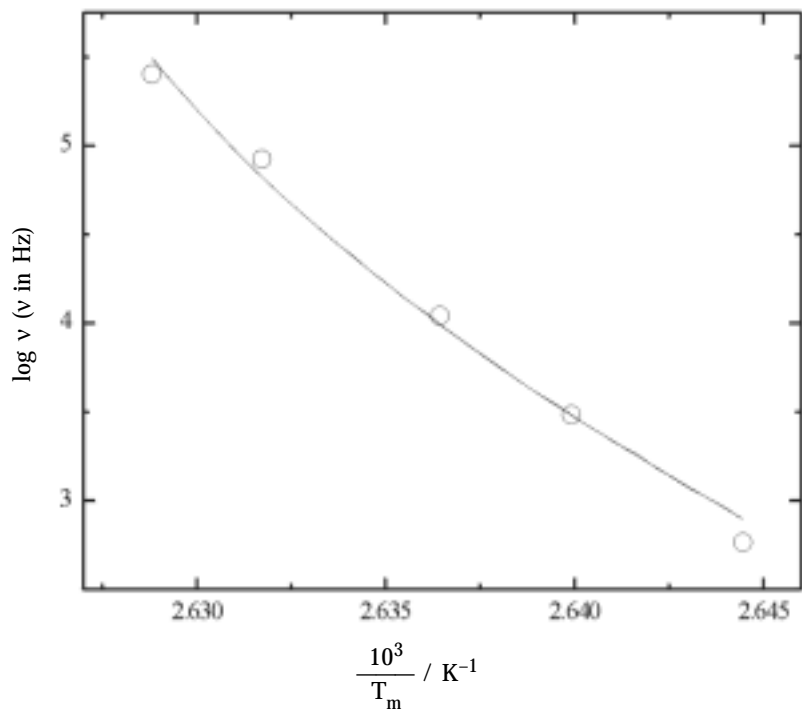


Fig. 6. Frequency dependence of  $T_m$  for PFN. The symbols indicate experimental data points and the solid line is the fit to Vogel-Fulcher relationship.

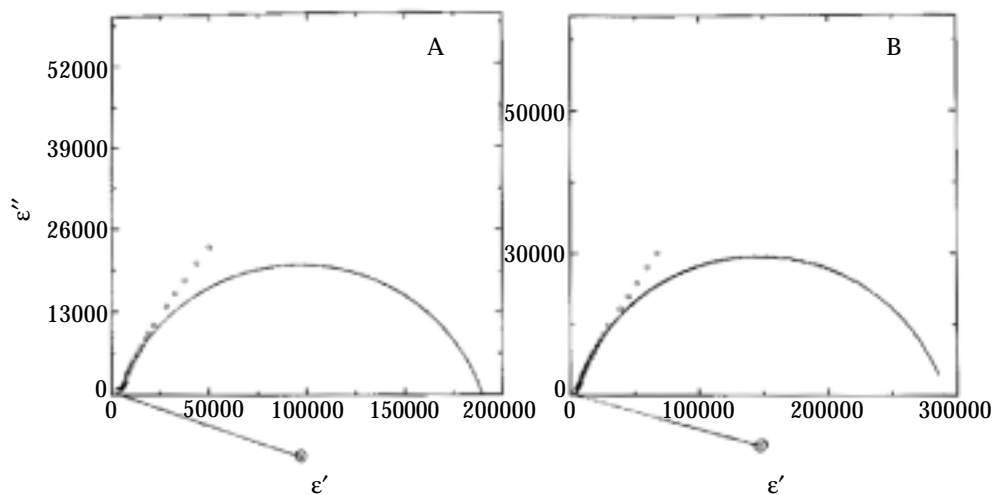


Fig. 7. Complex Argand plane plot between  $\epsilon''$  and  $\epsilon'$  at 483 K (A) and 503 K (B) for PFN.



to be described by the empirical relation

$$\varepsilon^* = \varepsilon' - i\varepsilon'' = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + (i\omega\tau)^{1-\alpha}} \quad (6)$$

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  $\omega = 2\pi\nu$ . The parameter  $\alpha$  can be determined from the location of the centre of the Cole-Cole circles, of which only an arc lies above the  $\varepsilon'$ -axis [16]. It is evident from the plots that the relaxation process differs from monodispersive 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 the origin of the  $\varepsilon''$ -axis [17-19], shows a very small increase in the interval [0.189, 0.133] with the decrease of temperature from 503 K to 483 K, implying a slight increase in the distribution of the relaxation time with decreasing temperature below  $T_m$ . All these analyses suggest that PFN is a relaxor ferroelectric.

## CONCLUSION

The relaxor behaviour of lead iron niobate,  $\text{Pb}(\text{Fe}_{0.5}\text{Nb}_{0.5})\text{O}_3$  (PFN), synthesized by Coulombite precursor method, is analysed with impedance spectroscopy in the temperature range from 27 °C to 200 °C and frequency range 0.1 kHz – 1 MHz. An analysis of real and imaginary parts of dielectric permittivity is performed. Cole-Cole plot shows that the relaxation in the sample is of polydispersive type. Diffuse maxima and frequency dispersion are observed in the permittivity-temperature plots. The results show that at  $T > T_m$ ,  $(1/\varepsilon' - 1/\varepsilon'_m)$  is proportional to exponent  $\gamma$  and is found to be 1.844 at both 253 and 304 kHz. The frequency dependence of temperature of the permittivity maximum ( $T_m$ ) has been modeled using Vogel-Fulcher relation. The scanning electron micrograph of the sample shows its proper compactness. The average grain size is found to be  $\sim 2 \mu\text{m}$ .

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