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Ferroelectric relaxor behaviour in Pb(Fe$_{0.5}$Ta$_{0.5}$)O$_3$

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Abstract : The relaxor ferroelectric lead iron tantalate, Pb(Fe$_{0.5}$Ta$_{0.5}$)O$_3$ (PFT) is synthesized by Coulombite precursor method. The X-ray diffraction pattern of the sample at room temperature shows a cubic phase. The field dependence of dielectric response is measured in a frequency range 0.1 kHz – 1 MHz and in a temperature range from 173–373 K. The temperature dependence of permittivity (ε') shows broad maxima at various frequencies. The frequency dependence of the permittivity maximum temperature (T_m) has been modelled using Vogel-Fulcher relation.

Keywords : Ceramics, dielectric constant, Curie temperature, relaxor.

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1. Introduction

Perovskite based relaxor ferroelectric materials have generated considerable interest due to rich diversity of their physical properties (one of these is high dielectric constant, ε') and possible applications in various technologies like memory storage devices, micro-electro-mechanical system, multilayer ceramic capacitors and opto-electronic devices [1–4]. In these materials, the cluster states have been shown to be long lived at temperature significantly below that of the average transformation temperature (T_m), as indicated by the dielectric response characteristic. Viehland *et al* [5(a)-(b)] have shown that this long-lived polar cluster state is characterized by glasslike behaviour in the macroscopic response characteristic and hence Vogel-Fulcher relation can be used.

In comparison with normal ferroelectrics, relaxors are known to exhibit strong frequency dispersion of the dielectric constant in the temperature range of the diffuse permittivity maximum (T_m) and no structural phase transition across T_m. The observed broadening in $\varepsilon'-T$ has generally been attributed to the presence of nano-regions

resulting from local composition variation over a length of 100–1000 Å. Different nano-regions in a microscopic sample transforms at different temperatures giving rise to a range of transformation temperature. In compositionally homogenous systems, quenched random disorder breaks the long-range polar order at unit cell level, leading to broad $\varepsilon'-T$ response [6]. Such materials exhibit slow enough relaxation dynamics and hence been termed as ferroelectric relaxor [7,8]. Burns and Decol [9] have proved the existence of polar-regions in relaxor at higher temperatures than T_m.

Broadly, the relaxors are classified in two families : 1 : 2 family such as lead magnesium niobate, $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) and 1 : 1 family such as barium iron niobate, $Ba(Fe_{1/2}Nb_{1/2})O_3$ (BFN) [3]. In this paper, we have studied lead iron tantalate, $Pb(Fe_{0.5}Ta_{0.5})O_3$ (hereafter PFT), a member of complex perovskite family having relaxor behaviour. The relaxor behaviour of PFT 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 173–373 K.

2. Experimental

The polycrystalline sample of PFT has been synthesized by Coulombite precursor method using Fe_2O_3 (~99.99% pure), Ta_2O_5 (~99.99% pure) and PbO (~99% pure) taken in stoichiometric ratio. First, the finely mixed powder of Fe_2O_3 and Ta_2O_5 is calcined at 1200°C in an alumina crucible for 7 h. The calcined powder is then grinded and mixed with PbO for 10 h. At this stage of mixing, 4-weight % extra of PbO is taken for compensating the lead loss during calcinations and sintering. Mixing has been done in acetone medium. The finely mixed powder is calcined at 1000°C. The calcined powder of PFT is regrinded and palletized into a disc of diameter 9.49 mm and thickness 1.16 mm using polyvinyl alcohol as binder. Finally, the disc is sintered at 1050°C for 4 h and cooled down to room temperature by adjusting the cooling rate. The colour of the sample is found to be blackish gray.

The X-ray diffraction pattern (XRD) of the sample is taken at room temperature using a Rigaku Miniflex-II X-ray powder diffractometer. For the dielectric characterization, the sintered disc is polished. Gold electrodes are evaporated on to both sides of the disc and the disc is connected to a LCR meter. The frequency dependence of dielectric permittivity and loss tangent of the sample is measured in the frequency range 0.1 kHz – 1 MHz and in the temperature range from 173–373 K. The temperature is controlled with a programmable oven. All the dielectric data are collected while heating at a rate of 0.5°C min^{-1}.

3. Results and discussion

Figure 1 shows the XRD of the sample taken at room temperature. All the reflection peaks of the X-ray profile are indexed and lattice parameters are determined using a least square method with the help of a standard program (POWDMULT). Good
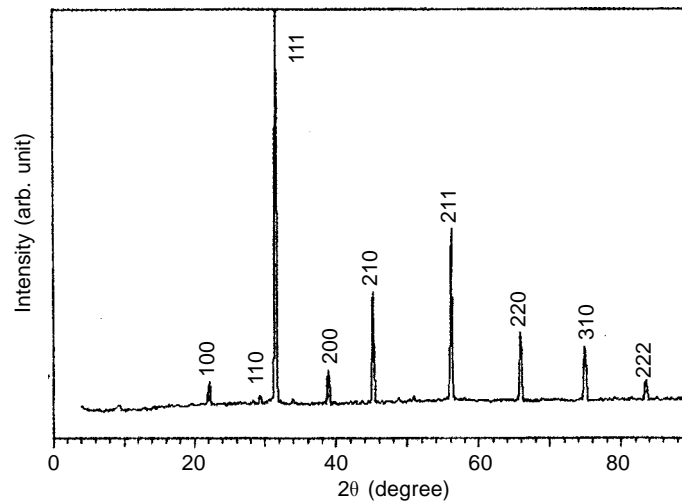
Figure 1. X-Ray diffraction pattern of PFT.

agreement between the observed and calculated inter-planer spacing (*d*-values) suggests that the sample has cubic structure at room temperature with $\alpha = 89.976°$ ($\alpha = b = c = 4.0772$ Å). It confirms that the sample has single phase.

The temperature dependence of ε' of PFT at various frequencies is shown in Figure 2. There are broad peaks around 263 K in the $\varepsilon'-T$ curve. With increasing frequency the permittivity maximum temperature T_m increases, while the magnitude of the peak value ε_m (the value of ε' at T_m) decreases. Diffuse maximum of ε' is the characteristic of relaxor ferroelectric [10,11]. This feature in the $\varepsilon'-T$ curve is very much similar to the observations by Cross, Yokosuka and many other researchers [11–13] for various lead based relaxors.
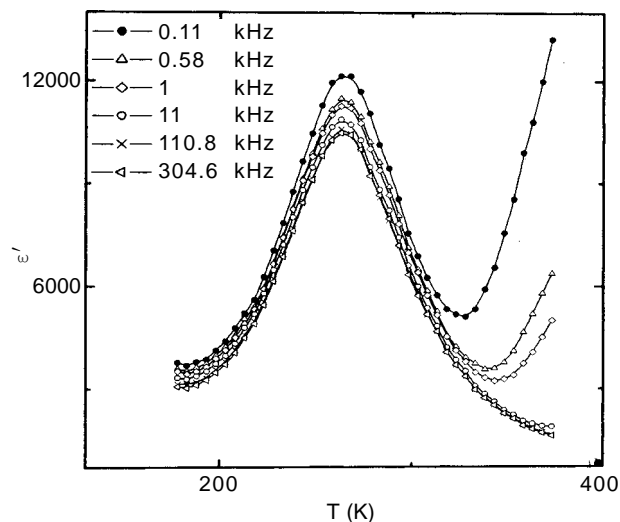

Figure 2. Temperature variation of dielectric constant of PFT at varous frequencies.

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

$$\frac{1}{\varepsilon'} = \frac{T - T_C}{C} \quad (T > T_c) \tag{1}$$

where T_c is the Curie temperature and C is the Curie-Weiss constant. Figure 3 shows the inverse of ε' as a function of temperature at 253.19 kHz and its fit to the experimental data by Curie-Weiss law. A deviation from Curie-Weiss law starting at
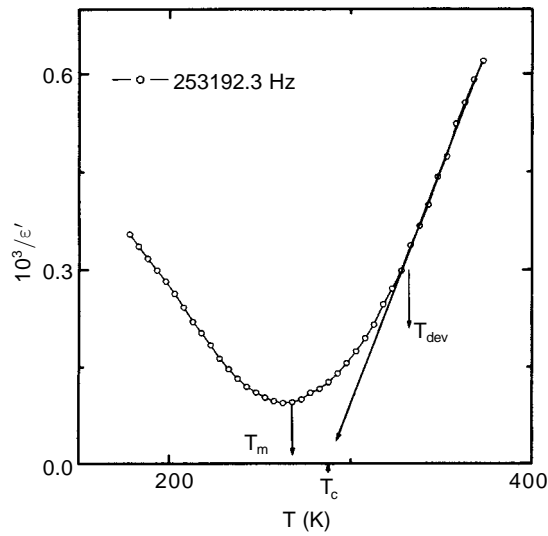
Figure 3. The inverse dielectric constant ($1/\varepsilon'$) as a function of temperature at 253.19 kHz for PFT. The symbol represents experimental data points and the solid line shows fitting of the modified Curie-Weiss law.

T_{dev} can be seen clearly. The parameter ΔT_m, which is often used to show the degree of deviation from the Curie-Weiss law, is defined as

$$\Delta T_m = T_{\mathrm{dev}} - T_m . \tag{2}$$

The T_{dev} as determined from the Curie-Weiss fit is found to be 330 K, and hence ΔT_m is found to be 73 K at 253.19 kHz. For such behaviour, a modified Curie-Weiss law has been proposed by Uchino and Nomura [13] to describe the diffuseness of the ε' at and around T_m, given as

$$\frac{1}{\varepsilon'} - \frac{1}{\varepsilon'_m} = \frac{(T - T_m)^{\gamma}}{C_1} \tag{3}$$

where ε' is the dielectric constant at temperature T. γ and C_1 are modified constant. The values of γ lie in between 1 and 2 in the expression (3). $\gamma = 1$ is the case for normal ferroelectric and quadratic dependence is valid for an ideal ferroelectric relaxor.

The plot of logarithmic frequency dependence of T_m for PFT is shown in Figure 4. The nonlinear nature indicates that the data cannot be fitted with a simple Debye
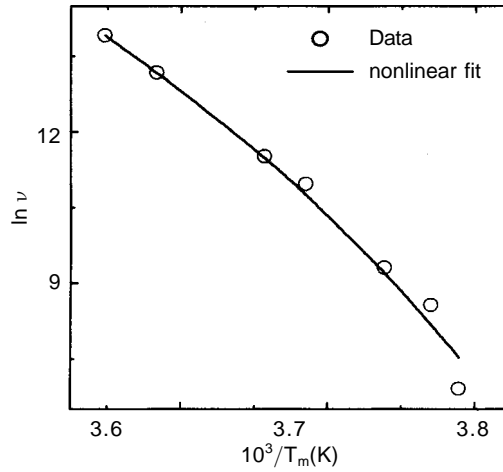
Figure 4. The frequency dependence of T_m for PFT. The symbols indicate experimental data points and the solid line is a fit to the Vogel-Fulcher relationship.

equation. The Debye medium is a classic dielectric. In Debye medium, the dipoles (or molecules) are free to rotate and are thermally activated. In any material system, it is impossible that all the dipoles 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 neighbours. The interaction makes the dipole to freeze into a configuration devoid of long range order at temperature 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 [14].

In order to analyze the relaxation features, *i.e.*, relation between frequency (ν) and T_m of PFT, the experimental curve is fitted using the Vogel-Fulcher formula [14],

$$\nu = \nu_0 \exp\left[-\frac{E_a}{k_B(T_m - T_f)}\right] \tag{4}$$

where ν_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 Figure 4 is the curve fitted to the data using expression (4). The values derived from the curve give an activation energy of 0.075 eV, a pre-exponential factor of 2.3 × 10^{12} Hz and a static freezing temperature of 254 K.

This value of T_f is very reasonable, as it is below the temperature T_m. The close agreement of the data with the Vogel-Fulcher relationship suggests that the relaxor behaviour in the PFT is analogous to that of dipolar glass with polarization fluctuations above a static freezing temperature. All these analyses suggest that PFT is a relaxor ferroelectric.

4. Conclusion

The relaxor behaviour of lead iron tantalate, $Pb(Fe_{0.5}Ta_{0.5})O_3$ (PFT), synthesized by Coulombite precursor method, is analysed with impedance spectroscopy in the temperature range from 173–373 K and frequency range 0.1 kHz – 1 MHz. The X-ray diffraction pattern of the sample at room temperature shows a cubic phase. An analysis of dielectric constant with frequency is performed at various temperatures. Diffuse maximum and frequency dispersion are observed in the dielectric constant (ε') *vs*. temperature plots. The frequency dependence of temperature of the permittivity maximum (T_m) has been modelled using Vogel-Fulcher relation.

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