Dielectric Characterization of Pb(Ni$_{1/3}$Nb$_{2/3}$)O$_3$ Multiferroic Material

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ABSTRACT Pb(Ni$_{1/3}$Nb$_{2/3}$)O$_3$ (PNN) prepared by two stage solid state route method and structurally characterized using XRD. The final phase XRD data shows that material was stabilized in mixed phase. Dielectric constant is order of lower magnitude may be due to another phase appeared in final phase of PNN. The calculated perovskite phase percentage is 72% in final phase. Temperature dependence dielectric data shows shifting of peak towards higher temperature with increase in frequency which is key point to be a relaxor. Dielectric dispersion follows Jonscher's power law.

1.1 INTRODUCTION

A ferroic material is basically a material which exhibits either ferroelectric or ferromagnetic or ferroelastic ordering, a feature typically demonstrated by the presence of a well defined hysteresis loop when the material is switched electrically, magnetically or mechanically. Hence, the term multiferroic would mean a material exhibiting two or more of the above ordering mechanisms. The multiferroic materials are either rare earth manganites or ferrites or transition metal perovskite oxides.

Currently there is enormous interest in multiferroic materials, especially the magneto-electrics, because of their potential applications in advanced sensor and actuator technology [1]. Pb(Ni$_{1/3}$Nb$_{2/3}$)O$_3$ (PNN) is a multiferroic showing a relaxor ferroelectric [2] and an anti-ferromagnetic transition at very low temperatures (~5K) [3].

Pb(Ni$_{1/3}$Nb$_{2/3}$)O$_3$ or PNN is one of the first known relaxor ferroelectrics reported by Smolenskii and Agranovskaya [2]. PNN have drawn attention because of their attractive relaxor behavior and/ or diffuse phase transition due to applications in electrical, optical, electromechanical devices [4-7]. Most common problem in the synthesis of lead-based single-phase ceramics is their strong inclination to form detrimental secondary pyrochlore phase/phases. The presences of the secondary phases reduce the dielectric, electrostrictive and other properties of the materials [8, 9]. Though various attempts have been made to solve this problem using different synthesis routes, columbite synthesis method [10] has been very effective to increase the % of perovskite phase to the highest possible level (i.e., to obtain single phase material). In this method, divalent (A^{2+}) oxides/carbonates and Nb$_2$O$_5$ are taken as precursors to obtain A^{2+}Nb$_2$O$_6$ type phase, that in sequence react with a stoichiometric amount of PbO to obtain Pb(A$^{2+}_{1/3}$Nb$_{2/3}$)O$_3$ (A=divalent cations) powders with dominant perovskite phase. To obtain pure perovskite phase in Pb(A$^{2+}_{1/3}$Nb$_{2/3}$)O$_3$, some important steps have been followed. PbO volatilization or deficiency is a main source of pyrochlore

phase in Pb(A$^{2+}_{1/3}$Nb$_{2/3}$)O$_3$ ceramics[1]. Though several synthesis techniques have been tried to avoid the formation of undesirable pyrochlore phase [11-13], addition of small amount (5-10%) of PbO (compensate PbO volatilization) was found effective [14-16]. The role of excess amount of PbO in the formation of pure in Pb(A$^{2+}_{1/3}$Nb$_{2/3}$)O$_3$ is however, still not clear. Only indirect effects of PbO excess has been reported on the dielectrics and micro-structural properties in PMN bulk ceramics [13-15]. Earlier, Pb(Ba$_{1/3}$Nb$_{2/3}$)O$_3$ (PBN) ceramic is prepared by Pastor et al [17]; it is not stabilized in pure perovskite phase.

PNN single-crystals showed typical relaxor ferroelectric behavior with a room temperature dielectric constant of ~ 2500 (measured at 1 kHz) that increased to ~ 4000 at the transition temperature (-120 °C). Further, the characterization of mixed phase materials without any excess of A/ B site oxides are not reported to the best of our knowledge. This is important, as the relaxor behavior in mixed phase may be useful in characterizing new materials that forms mixed phase. In this paper, we report the preparation, structural and electrical characterization of this well-established relaxor prepared without excess of PbO.

1.2 Experimental

Materials were prepared by two steps solid state reaction route. Pre-reacting Nb$_2$O$_5$ (99.5 % Loba Chemie Pvt. Ltd., India) with NiO (99.5 % Merk) to form precurser. The calcination was performed in an alumina crucible at 1200° C for 6 h. These materials are then reacted with PbO in a crucible at 1000° C. The fine and homogeneous powder of the material was pressed into cylindrical pellets of 10 mm diameter and 1-2 mm thickness under an uniaxial pressure of 100 MPa using a hydraulic press. Polyvinyl alcohol (PVA) was used as a binder to reduce the brittleness of the pellets. The pallets were fired first at 500° C to remove the binder and then sample Pb(Ni$_{1/3}$Nb$_{2/3}$)O$_3$ sintered at 1100° C for 6hours. Material was electrically characterized using dielectric and impedance measurements. The final phase material is also structurally analyzed using X ray diffraction

technique. The dielectric capacitance and dielectric loss data were measured as a function of temperature from room temperature up to 325° C using HIOKI 3532 LCR Hi TESTER.

1.3 Results and discussion
Room temperature XRD pattern of calcined powder of $Pb(Ni_{1/3}Nb_{2/3})O_3$ (PNN) is shown in figure 1.
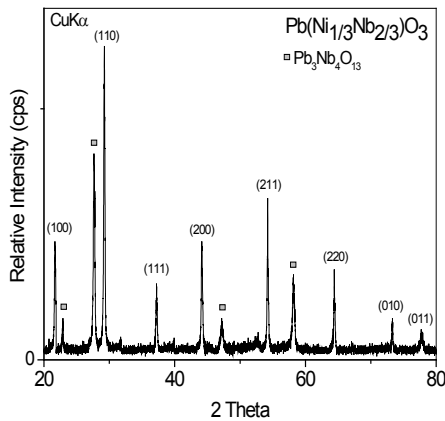

Figure: 1 XRD pattern of PNN electroceramic at room temperature.

Observed peaks are indexed by least square method using x-ray interpretation and analysis computer software POWD-MULT [18]. The best agreement between the observed and calculated interplanar spacing suggests that the prepared materials (PNN) stabilized in orthorhombic perovskite single phase. The lattice parameters were refined using the least-squares method so that Δd ($\Delta d = d_{obs}-d_{cal}$) is minimum. The lattice constants obtained for PNN are a=4.0849(3) (A°), b=7.2439(4) (A°) c=10.1318(9) (A°). The observed pyrochlore phase in prepared materials is mainly due to $Pb_3Nb_4O_{13}$.

Das *et.al* reported that the % of perovskite phase depends upon the nature of the pyrochlore phase. The relative amount of perovskite phase could also be determined using the method [19]. The percentage of perovskite is where I_{pero} and I_{pyro} are the integrated band intensities of perovskite (110) and pyrochlore (222) XRD peaks, respectively. Accordingly, the calculated perovskite phase percentage is 72% in final phase. The cubic pyrochlore gets stabilized along with the perovskite phase. Our basic aim has been to understand the nature of materials prepared using two step solid state route without any excess of oxides. Further, the sintering optimization was not made. It is important as the effect of various control parameters used to obtain the phase pure materials vary from one report to other.

The measured temperature dependence of both the dielectric constant Figs 2 and dielectric absorption (tan d) is shown in inset of Figs 2. These figures show the effect of frequencies on both T_m' (temperature where broad dielectric maxima occurs) and T_m'' (temperature where dielectric loss peak occurs) observed in relaxors. However, the value of dielectric constant is order of magnitude lower than that is reported for pure phase material. Dielectric properties are depressed by inclusion of pyrochlore phase in PNN. The characterization of dielectric behavior is very important

not only to the theory of the polarization mechanism but also to the applications. From application point of view, knowledge of the temperature and the frequency dependence of dielectric constant along with the frequency dependence of T_m are very important. The dielectric characterization of relaxors has mainly focused on its temperature dependence above Tm that is used for characterizing the degree of dielectric relaxation [20].
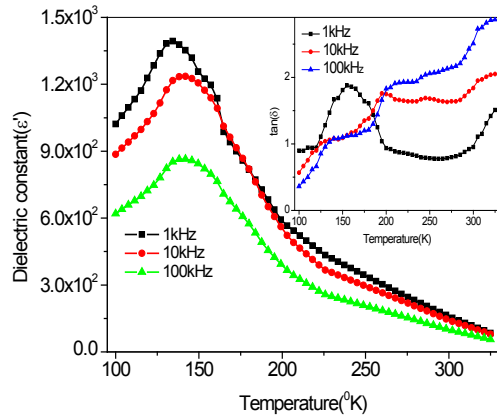

Figure: 2. Dielectric constant as function of temperature at different frequencies for PNN. Inset shows temperature dielectric loss at same frequencies.

Very few studies are performed below T_m.
However, there are contradictory reports regarding the temperature dependence of dielectric constant at high temperature above T_m. Therefore, the relation between temperature and dielectric constant still remains to be understood properly. The dielectric data calculated from figure 2 is given in table 1. It is clear from the data, dielectric peak shift towards higher temperature with increase in frequency which is key point to be a relaxor. Hence, PNN shows relaxor behaviour in elevated temperature.

Table: 1. Dielectric data calculated from temperature dependence dielectric constant plot.

Sample name	Frequency	T_m'	ε'
PNN	1KHz	134.3(K)	1397.6
	10KHz	140(K)	1240.4
	100KHz	144(K)	867.9

The frequency dependence of real (ε') and imaginary (ε'') part of dielectric constant in the 100-300°C temperature range on a log-log scale is shown in figures 3 and 4 respectively. Both ε' and ε'' show dispersions at higher frequencies and almost saturated at lower frequencies. The dispersions increase with increase in temperature. This is attributed to space charge accumulation effect. Such dispersions in both components of complex dielectric constant are observed commonly in ferroelectrics with appreciable ionic conductivity and are referred to as low frequency dielectric dispersion (LEDD) [21, 22]. The complex dielectric constant as a function of the frequency ω in accordance with the Jonscher's power law [23] is

$$\varepsilon^* = \varepsilon'-\varepsilon'' = \varepsilon_\infty + \sigma/\varepsilon_0\omega + (a(T)/\varepsilon_0)(i\omega^{n(T)-1})$$
(1)

where ε_∞ is the high frequency value of the dielectric constant, $n(T)$ is the temperature dependent exponent and $a(T)$ determines the strength of the polarizability arising from the universal mechanism in question. The real and imaginary parts of the complex dielectric constant are given as

$$\varepsilon' = \varepsilon_\infty + \ \sin(n(T)\tfrac{\pi}{2})\big(a(T)/\varepsilon_0 \big)(i\omega^{n(T)-1}) \qquad\text{--------(2)}$$

$$\varepsilon'' = \ \sigma/\varepsilon_0\omega + \cos(n(T)\frac{\pi}{2})\big(a(T)/\varepsilon_0 \big)(i\omega^{n(T)-1}) \qquad\text{------(3)}$$

Where the first term in equation (2) determines the lattice response and the second term corresponds to charge career contribution to the dielectric response. Similarly, in equation (3) the first term reflects the DC conduction contribution and the second term represents the charge career contribution to dielectric loss.
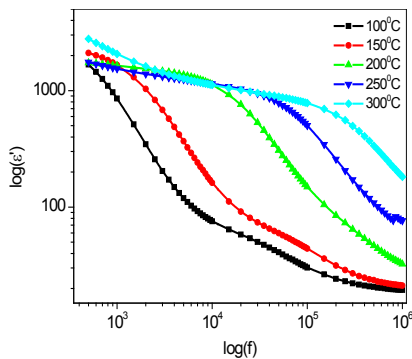

Figure: 3. Frequency dependence real part of dielectric constant on log-log scale.

At low frequencies, the contribution due to charge career term $(\sin(n(T)\tfrac{\pi}{2})\big(a(T)/\varepsilon_0 \big)(i\omega^{n(T)-1}))$ dominates and lattice response part ε_∞ can be neglected. Therefore, equation (2) for constant n yields a straight line with slope $(n-1)$. At higher frequencies, the charge careers fail to respond to the applied external field and the dielectric constant is mainly due to lattice contribution. This may account for the observed frequency dependence of dielectric constant; a linear decrease with frequency in low frequency region and frequency dependent plateau region at high frequencies. With increasing temperature, the range of frequencies in which charge career contribution dominates increase showing that charges have sufficient high energy to overcome the barrier and get released. The interaction between the charge careers contributing in the polarization process is characterized by $n(T)$; at low temperatures, n is almost 1, showing Debye type relaxation.
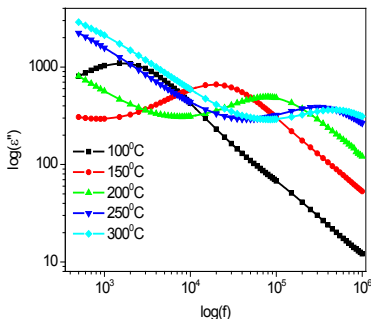

Figure: 4. Frequency dependence imaginary part of dielectric constant on log-log scale.

The behaviour of ε'' could be explained by Eq.(3). Frequency dispersion of ε'' gives two slopes, -1 in the low frequency region and $(n-1)$ in the high frequency region Fig 4. With increasing temperature, the frequency range with slope -1(DC conduction) increases and at higher temperatures dc conduction dominates the charge career conduction.

1.3Conclusion

Well known a multiferroic $Pb(Ni_{1/3}Nb_{2/3})O_3$ (PNN) is successfully prepared by two state solid state reaction method. The final phase stabilized in orthorhombic perovskite structure with small amount of pyrochlore phase. The lattice parameters were obtained a=4.0849(3) (A°), b=7.2439(4) (A°) c=10.1318(9) (A°). The calculated perovskite phase percentage is 72% in final phase. Temperature dependence dielectric data shows shifting of peak towards higher temperature with increase in frequency which is key point to be a relaxor. Dielectric dispersion follows Jonscher's power law.

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