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Structural, Dielectric and Impedance Characterization of $Pb(Ba_{1/3}Nb_{2/3})O_3$ *

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Abstract: Paper reports dielectric properties and complex impedance spectroscopic studies of lead based ferroelectric ceramic $Pb(Ba_{1/3}Nb_{2/3})O_3$. X-ray diffraction pattern has shown that the material is almost pure orthorhombic perovskite phase with lattice constants $a=3.6983A^0$ $b=16.2704A^0$, $c=12.7872A^0$. Grain size was found ≈1μm. The observed phase transition is almost diffuse type in character. Activation energy is found to 0.59 eV. Cole-Cole plot confirms the major contribution to the impedance coming from grains and grain boundary.

Keywords: Relaxor Materials, Diffuse Phase Transition, X-ray diffraction, Ferroelectrics.

1. Introduction

Lead based ferroelectric oxides with a general formula $Pb(B'_{1/3}B''_{1/3})O_3$ (where A = Mg, Zn, Ni etc.; B= Nb and Ta) have drawn attention because of their attractive relaxor characteristics or diffuse phase transition (DPT) useful for a wide range of industrial application such as electrical, optical, electromechanical device[1-4]. 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 these materials. Though several synthesis techniques have been tried to avoid the formation of undesirable pyrochlore phase[5-7], addition of small amount (5-10%) of PbO was found effective[8]. The role of excess amount of PbO in the formation of pure in $Pb(A^{2+}_{1/3}Nb_{2/3})O_3$ is still not clear. Mixed phase $Pb(Ba_{1/3}Nb_{2/3})O_3$

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(PBN) relaxor material was earlier prepared by our group[9]. In the present study we have tried to prepare phase pure perovskite $Pb(Ba_{1/3}Nb_{2/3})O_3$ and studied structural, microstructural and electrical behavior of the material by using impedance spectroscopy.

2. Experimental

The polycrystalline samples of $Pb(Ba_{1/3}Nb_{2/3})O_3$ were prepared by two steps solid state reaction route or columbite method. First, columbite structure was formed by pre-reacting Nb_2O_5 (99.9 % Loba Chemie Pvt. Ltd., India) with $BaCO_3$, $CaCO_3$ (99.9% pure, M/s B. D. H. Chemicals U. K) followed by calcination at 1100°C for 6 h. Calcined powder was then characterized by an X-ray diffraction technique (XRD) to ensure the formation of columbite structure. The precursor material was then reacted with PbO (99.5 % Loba Chemie Pvt. Ltd., India) at 1000 °C for 6 h to get the pyrochlore free desired compound.

3. Result and Discussion

3.1 Structural and Microstructural characterization

Observed peaks are indexed by least squares method using x-ray interpretation and analysis computer software POWDMULT. The lattice parameters were refined using the least-squares method so that $\Sigma\Delta d$ ($\Delta d = d_{obs} - d_{cal}$) is minimum.

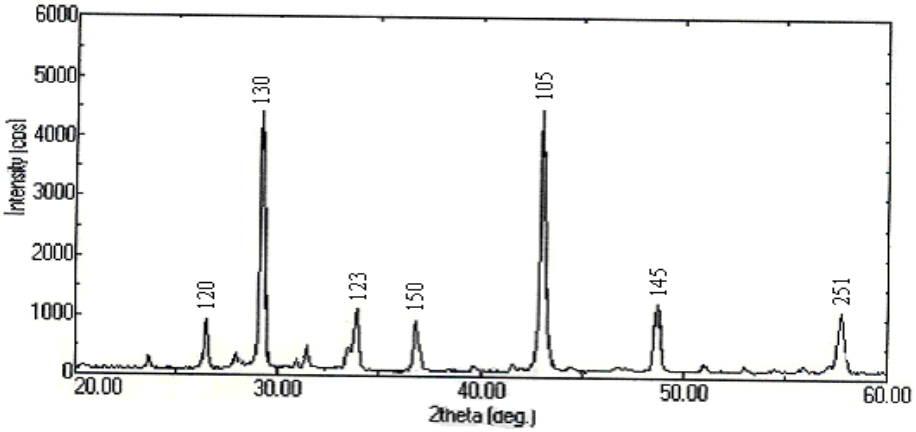

Figure-1: XRD profile of PBN at room temperature.

X-ray diffraction pattern shows (Fig 1) pure orthorhombic perovskite phase with lattice constants $a=3.6983A^0=16.2704A^0$, $c=12.7872A^0$.

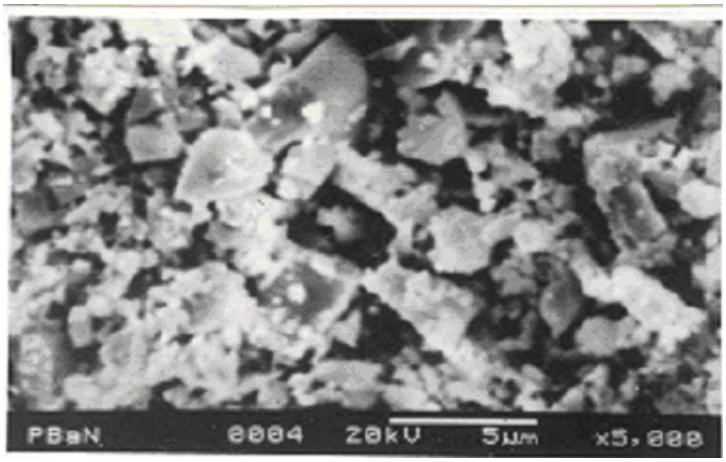

Figure-2: SEM micrograph of PBN.

The SEM micrograph of the compounds at room temperature (Fig.2) exhibits heterogeneous grain distribution with average grain size of 1 µm.

3.2 Dielectric Studies: Diffuse Phase Transition

The dielectric constant increase with increase in temperature and a peak evolves at 43^0C (ε_m = 2250) (Fig 3). The dielectric constant increases with rise in temperature up to its maximum value (ε_{max}) at the Curie temperature (Tc), and then decreases with further increase in temperature.

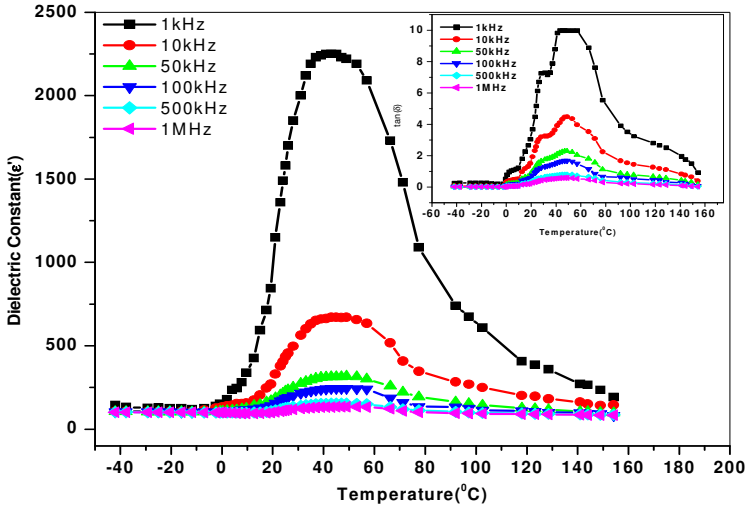

Figure 3: temperature dependence of dielectric constant for PBN;
Inset shows dielectric loss.

The value of □' decreases with rise in frequency, but the value of □' increases with increasing temperature. There is a step or gradual increase of

□' with increasing frequency. This is the typical characteristic of ferroelectric materials. At lower temperatures, the values do not attain saturation due to high frequency relaxation. Activation energy associated is 0.59 eV.

A modified Curie law is used to explain the dielectric behaviour of complex ferroelectrics with diffuse phase transition, which is described as follows[10]

$$1/\varepsilon - 1/\varepsilon_m = C(T-T_m)^{\gamma}$$

where γ and C are measured to be constants, the value of γ varies between 1 and 2 . When γ =1 the material are called normal ferroelectrics and when $1< \gamma <2$, they are called relaxor ferroelectrics, whereas γ =2 corresponds to a so-called 'complete' diffuse phase. Figure 4 shows the plot of log $(1/\varepsilon - 1/\varepsilon_m)$ as a function of log$(T-T_m)$ for the prepared sample at 1KHz. A linear relationship was obtained by linear fitting to the experimental data. The slope of curve was used to determine the values of γ. The value of γ estimated from the slope of the graphs for PBN is 1.98 indicating that material has almost complete diffuse phase transition characteristics.

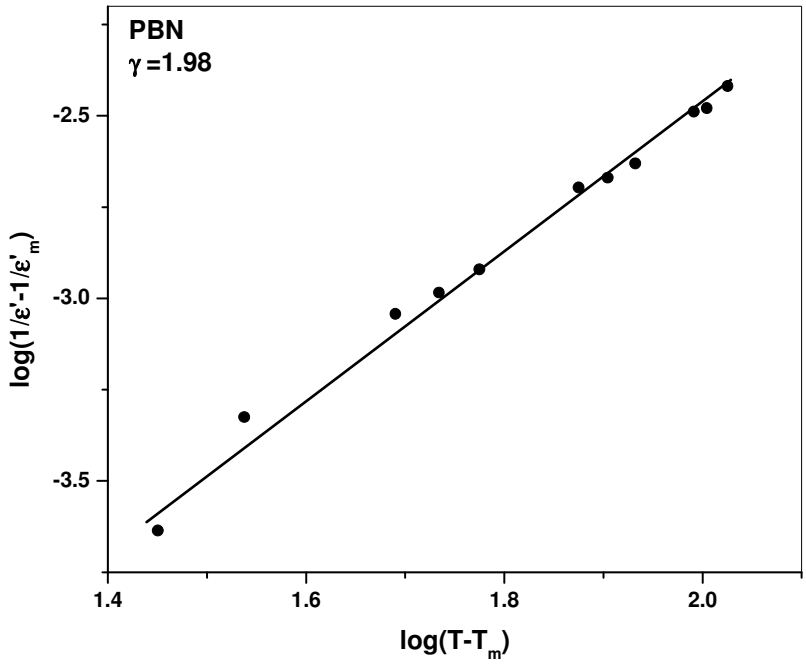

Figure- 4: log $(1/\varepsilon - 1/\varepsilon_m)$ as function of log$(T-T_m)$ for PBN at 1KHz

Frequency dependence of the real (Z') and imaginary (Z'') part of the electric impedance revealed that material has mainly grain (bulk) resistance contribution. Study of frequency dependence of impedance indicate that the relaxation mechanism of the material is almost temperature independent,

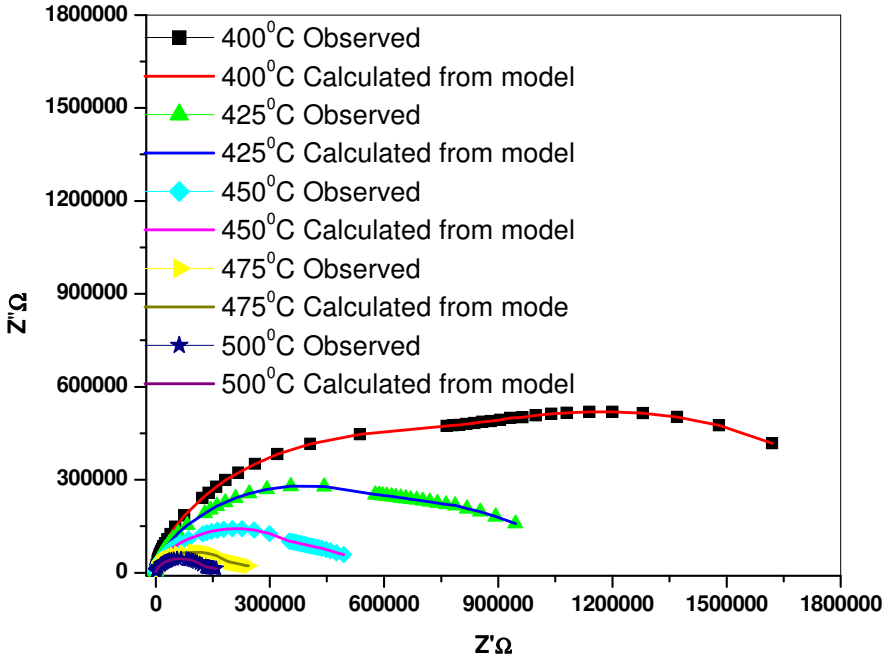

Figure-5: Explicit impedance plots between Z' and Z'' fitted with proposed model for PBN.

Explicit impedance plot (Fig 5) confirms that both grains and grain boundaries contribute to the impedance. Further, the arc crosses the Z' axis at lower values with increasing temperatures showing that the grain resistance decreases with temperature.

4. Conclusions

Structural and microstructural properties of the material have been evaluated by means of XRD and SEM analysis, respectively. X-ray diffraction pattern has shown that the material is almost pure orthorhombic perovskite phase with lattice constants $a=3.6983A^0$ $b=16.2704A^0$, $c=12.7872A^0$. Grain size was found ≈1μm. Temperature dependence of relative dielectric constant exhibits diffuse phase transition in the material. Activation energy calculated from Z' data is found to 0.59 eV. Nyquist plot confirms the major contribution to the impedance coming from grains and grain boundary. Study of frequency dependence of impedance indicates that

the relaxation mechanism of the material is almost temperature independent, and has bulk contribution only in a wide temperature range.

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