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Dielectric properties of $Pb(Mg_{1/4}Zn_{1/4}Nb_{1/2})O_{11/4}$

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Abstract. Polycrystalline samples of $Pb(Mg_{1/4}Zn_{1/4}Nb_{1/2})O_{11/4}$ have been synthesized by high temperature columbite precursor solid state reaction technique. Using X-ray diffraction (XRD) technique, compound formation in single phase cubic structure was observed and XRD analysis provided preliminary structural data. Detailed studies of dielectric properties of the compound reveal that this compound has high dielectric constant and diffuse phase transition in a wide range of temperatures around the Curie temperature. The charge deficiency of the compound presumably gets compensated in the high temperature columbite precursor process of sample preparation which is supported by single phasic form of the material.

Keywords. Relaxor ferroelectrics; X-ray diffraction analysis; diffuse phase transition.

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1. Introduction

Complex compound $Pb(Mg_{1/3}Nb_{2/3})O_3$, abbreviated as PMN, a member of cubic perovskite family of general formula ABO_3 (A = mono or divalent, B = trid, tetrad or pentavalent ions), has ferroelectric properties ($T_c = -8°C$), [1], with relaxor effect. Since the discovery of relaxor behaviour and diffuse phase transition in PMN, many compounds of the general formula $A^{2+}[(B_1)^{2+}_{1/3}(B_2)^{5+}_{2/3}]O^{2-}_3$ have been studied to know about phase transition mechanism in them. Though this relaxor effect was found in $Pb(Zn_{1/3}Nb_{2/3})O_3$(PZN) also, it was extremely difficult to synthesize single cubic perovskite phase of the compound. However, two-stage precursor method [2] was found useful for this purpose. It has been found that the relaxor properties of PMN and PZN are quite different, but both are useful for high dielectric capacitor and electrostrictive devices [3–8]. Though some work has already been reported on PZN, no work seems to have been done on more complex compounds of this family $Pb(Mg_{1/4}Zn_{1/4}Nb_{1/2})O_{11/4}$ (PMZN). In order to find out the existence of ferroelectrics, relaxor behaviour and basic crystal structural of the kind of PMZN, we have completed preliminary structural and detailed dielectric studies of a complex family with general formula $A^{2+}[(B^{I}_{1/4})^{2+}(B^{II})_{1/4}(B^{III})^{5+}_{1/2}]O^{2-}_{11/4}$; the present communication is a part of it.

2. Experimental

The polycrystalline samples of the PMZN of the type indicated above were prepared by double-stage high temperature solid-state reaction technique known as columbite precursor method from stoichiometric mixtures of PbO(99·9%), MgO(99·5%), ZnO(99·0%)

and Nb_2O_5(99·5%), all from Loba Chemicals. These oxides were thoroughly mixed in agate-mortar for three hours and then calcined at 1000°C in a 99% pure alumina crucible for about 6 h to get $MgZnNb_2O_7$. Requisite amounts of $MgZnNb_2O_5$ and PbO powders were again thoroughly mixed and calcined for 6 h at 1000°C to get homogeneous fine powders of the required PMZN. The pellet samples of diameter 1·15 cm and thickness 1–2 mm were compacted at room temperature from these powders at a pressure of $6{\cdot}5 \times 10^7 kg/m^2$ using a hydraulic press. Polyvinyl alcohol (PVA) was used as a binder to make pellets which has burnt out at 500°C during sintering process. The pellets were sintered in a platinum crucible at 1100°C for 4 h in $PbZrO_3$ atmosphere to compensate for PbO loss by evaporation. The quality and formation of perovskite compound was checked by X-ray diffraction technique.

The X-ray powder diffractogram (XRD) of the sample was taken using diffractometer (Rigaku-Miniflex, Japan) with CuK_α radiation ($\lambda = 1{\cdot}5418$ Å) in wide range of Bragg angles ($10° \leqslant 2\theta \leqslant 90°$), at scanning rate of 2°/min. The grain size, particle distribution and morphology of the compound were examined on pellet samples by a 'CAMSCAN' scanning electron microscope (SEM). The grain size and the degree of packing of the grains in the pellet govern the density of the pellet and hence ε, the dielectric constant and the loss (tan δ) of the ceramic.

For dielectric measurements, both the faces of the pellet samples were electroded with high purity and ultrafine silver particle paste. Measurements of dielectric constant (ε) and loss (tan δ) were carried out as a function of frequency (f) (400 Hz to 10 kHz), and temperature (− 150°C to + 200°C) using GR 1620 AP capacitance measuring assembly in small temperature interval.

3. Results and discussion

The cell parameters of PMZN type prepared was obtained by least-squares refinement method using a standard computer program from 10 indexed reflections widely spread in 2θ, of the powder diffraction profile.

The refined lattice constant was found to be 4·2240 Å which is close to the reported value of other members of this family [9]. The sharp single peaks (figure 1) and good agreement between observed and calculated d values suggest that while preparing the compound by high temperature double stage of columbite precursor technique, the pyrochlore phase formation has been bypassed [4].

The linear particle size P of the compound has been calculated from some strong X-ray reflections, using the following Scherrer's equation

$$P = \frac{0{\cdot}89}{\beta_{1/2}\cos\delta} \quad (\beta_{1/2} = \text{half width}).$$

The particle size was found to be approximately 200 Å.

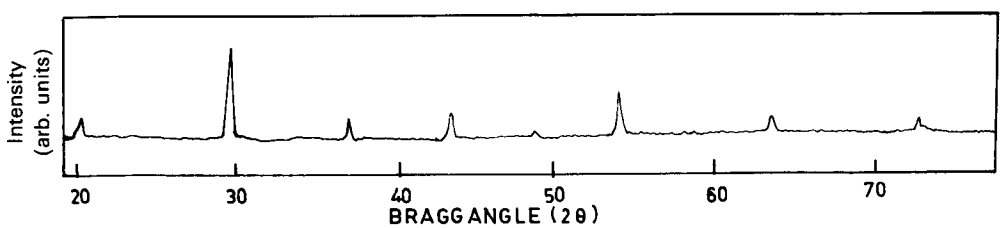

Figure 1. Room temperature X-ray diffractogram of $Pb(Mg_{1/4}Zn_{1/4}Nb_{1/2})O_{11/4}$.

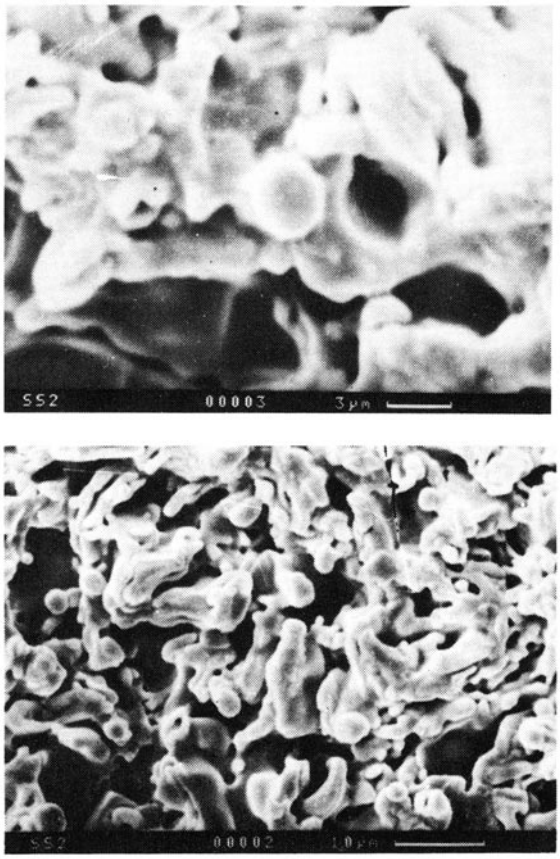

Figure 2. SEM (scanning electron micrographs) of $Pb(Mg_{1/4}Zn_{1/4}Nb_{1/2})O_{11/4}$ at (**a**) 3 μm, (**b**) 10 μm.

The SEM photographs (figure 2) shows that the particle distribution in the sample is homogeneous and uniform with average size of 2·5 μm. However, there are some pores/islands present in the pellets which suggest that the density of the compound is not very big which is consistent with the density determined by us separately ($\sim 90\%$ of the theoretical value).

Figure 3 shows the frequency dependence of dielectric constant and loss between 400 Hz to 10 kHz at room temperature. It has been observed that in this frequency region the compound shows normal dielectric behaviour. Below 400 Hz, it was not possible to balance the bridge of the ε and tan δ measuring assembly. Hence, the existence of a peak in tan δ vs frequency curve below 400 Hz cannot be ruled out.

Figures 4 and 5 show the variation of ε and tan δ of the material with temperature at two frequencies, $f = 1$ kHz and 10 kHz. In the dielectric response, ε reaches a higher peak value of 7200 at $f = 1$ kHz to T_c which is typical of a perovskite ferroelectric, but the (flat) dielectric maximum does not mark a phase change of the ferroelectric as the temperature of the maximum increases with frequency; this is in a manner typical of a relaxor dielectric. These relaxor show dispersion of maximum ε as a function of frequency in addition to a broad transition region. As the frequency increases from 1 kHz to 10 kHz, the value of ε_{max} decreases and T_c is shifted to higher

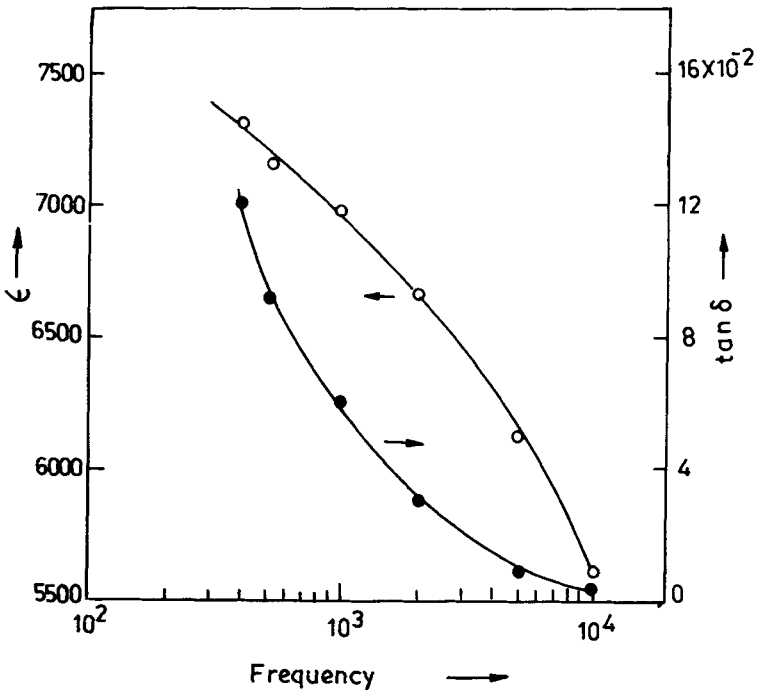

Figure 3. Variation of dielectric constant (ε) and loss (tan δ) of $Pb(Mg_{1/4}Zn_{1/4}Nb_{1/2})O_{11/4}$ at room temperature (20°C), with frequency (f).

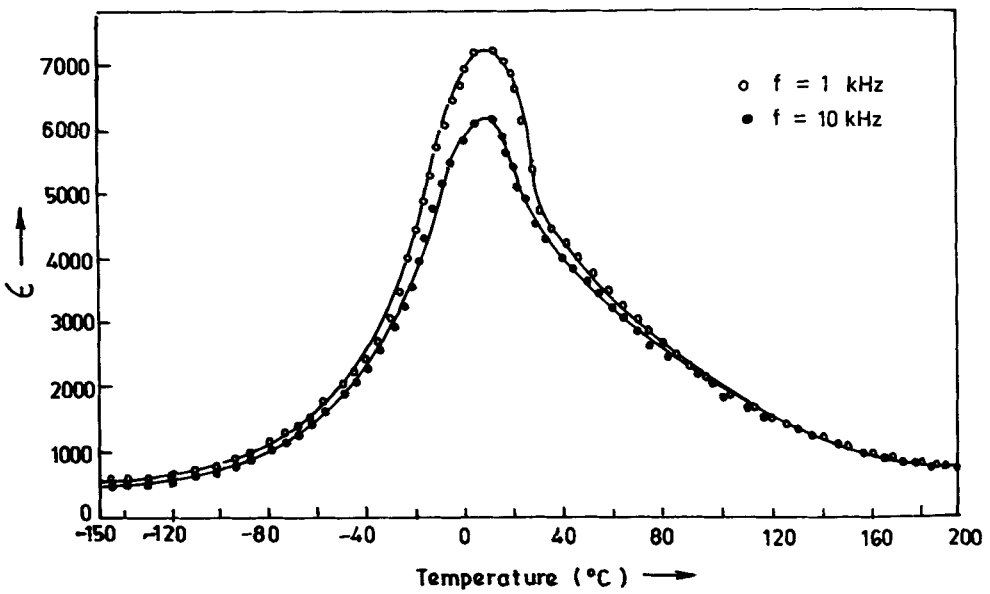

Figure 4. Temperature dependence of dielectric constant (ε) of $Pb(Mg_{1/4}Zn_{1/4}Nb_{1/2})O_{11/4}$ at $f = 1$ kHz and 10 kHz.

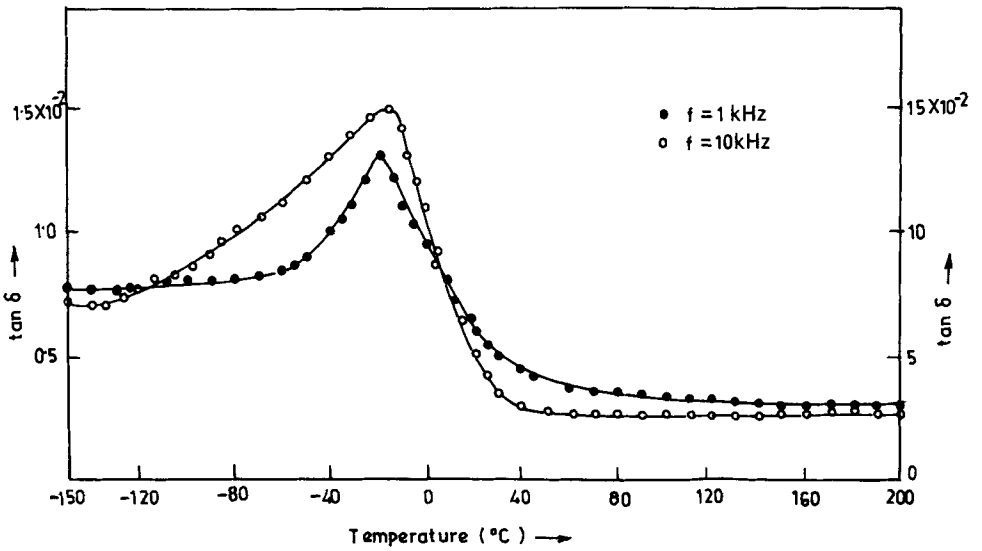

Figure 5. Temperature dependence of loss (tan δ) of $Pb(Mg_{1/4}Zn_{1/4}Nb_{1/2})O_{11/4}$ at $f = 1$ kHz and 10 kHz.

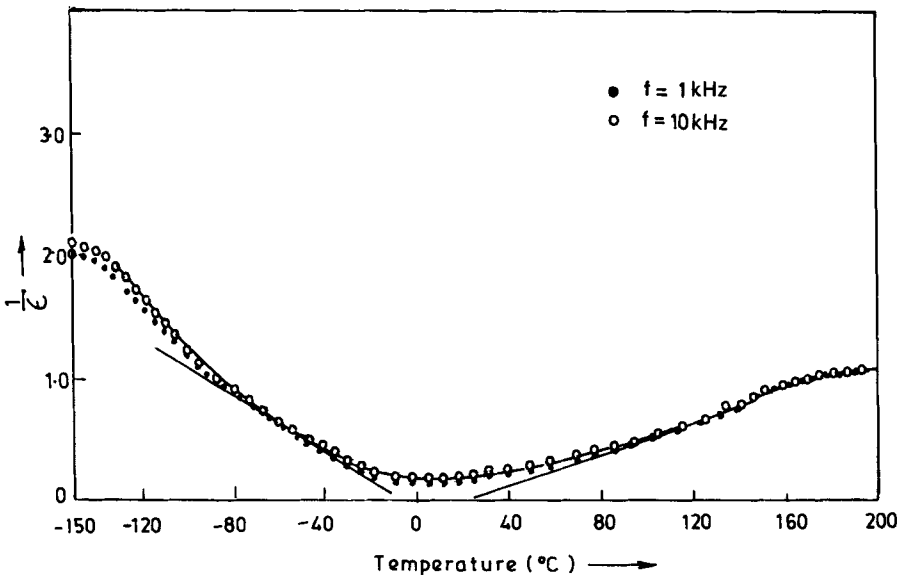

Figure 6. Temperature dependence of dielectric stiffness ($1/\varepsilon$) of $Pb(Mg_{1/4}Zn_{1/4}Nb_{1/2})O_{11/4}$ at $f = 1$ kHz and 10 kHz.

temperature side. The associated maxima in tan δ has also a typical behaviour of relaxor response. Because of the disordered distribution of the Mg^{2+}, Zn^{2+} and Nb^{5+} ions at identical B-lattice sites, the ferroelectric phase transition occurs gradually in PMZN, similar to the cases of other ferroelectrics of disordered perovskites [10]. Some temperature difference in peak dielectric constant (ε_{max}) and the dielectric loss is an automatic consequence of Kramer–Krönig relations [11] when there is a temperature dependent relaxation. Broadness in ε vs T curve is one of important characteristics of a ferroelectric with disordered perovskite structure. This is shown

in figure 6 for the material investigated. The dielectric stiffness ($1/\varepsilon$) vs temperature curve shows the temperature region of diffuse phase transition to be from $-40°C$ to 90°C, i.e. over a range of 130°C about the T_c, and the distinct deviation from the Curie–Weiss law in the temperature range of 25°C to 90°C. Following Yokomizo *et al* [12], the temperature range $-40°C$ to 90°C is the Curie range of the material.

The diffuseness of the compound has been examined by the following formula [8]:

$$\left(\frac{1}{\varepsilon}-\frac{1}{\varepsilon_{max}}\right)\propto(T-T_{max})^{\gamma}$$

or

$$\frac{1}{\varepsilon}+\frac{1}{\varepsilon_{max}}=C(T-T_{max})^{\gamma}$$

or

$$\log\left(\frac{1}{\varepsilon}-\frac{1}{\varepsilon_{max}}\right)=\log C+\gamma\log(T-T_{max}).$$

From figure 7 it has been shown that, the experimental results are in very good agreement for $\gamma = 1{\cdot}87$, which is an intermediate value between $\gamma = 1$ for a normal Curie–Weiss type dielectric and $\gamma = 2$ for a typical diffuse transition type [13] relaxor. Thus, the diffuse phase transition with relaxor effect and high dielectric constant in $Pb(Mg_{1/4}Zn_{1/4}Nb_{1/2})O_{11/4}$ has been observed.

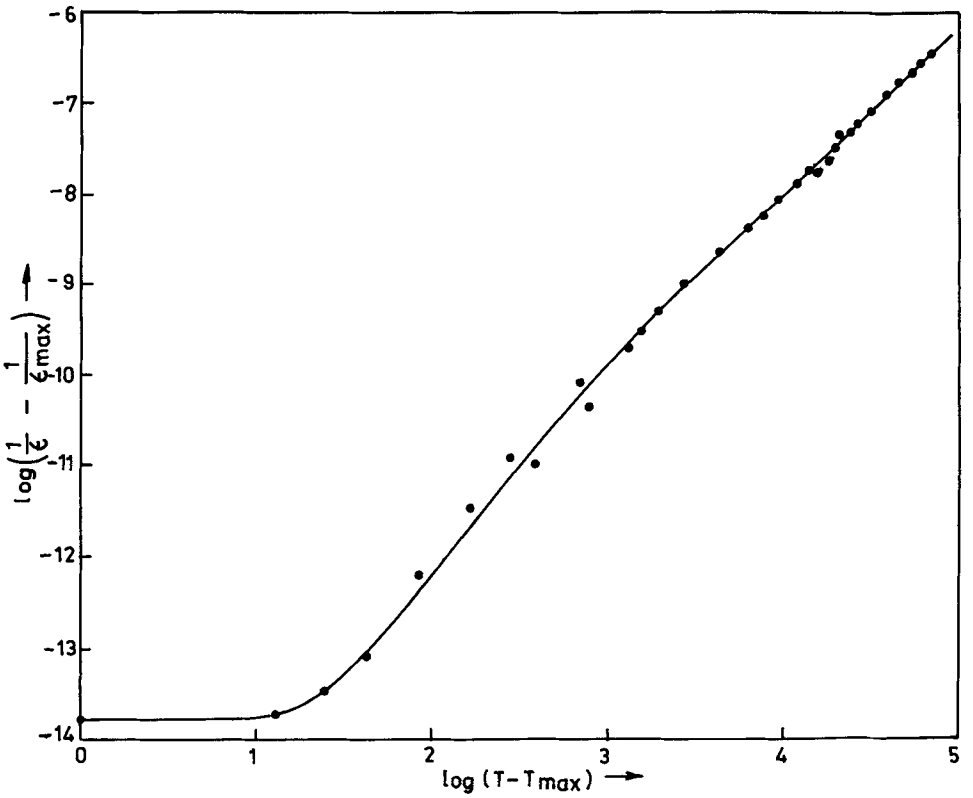

Figure 7. Variation of $\log[1/\varepsilon-(1/\varepsilon_{max})]$ with $\log(T-T_{max})$ for $Pb(Mg_{1/4}Zn_{1/4}Nb_{1/2})O_{11/4}$ at $f = 1$ kHz.

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