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+}(B_2)^{5+}]O_2^{2-} 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_{1/4})^{2+} (B_{11/4})^{-1/4}(B_{11/4})^{5+}]O_{11/4}^{2-}; 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 Nb₂O₅(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 MgZnNb₂O₇. Requisite amounts of MgZnNb₂O₅ 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 6.5 x 10⁷ kg/m² 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 PbZrO₃ 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 CuKα radiation (λ = 1.5418 Å) in wide range of Bragg angles (10° ≤ 2θ ≤ 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

\[ P = \frac{0.89}{\beta_{1/2}\cos \delta} \quad (\beta_{1/2} = \text{half width}). \]

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}.](image)