Studies of structural and electrical behaviour of Pb(Mg$_{1/4}$Zn$_{1/4}$Mo$_{1/2}$)O$_3$ ceramics

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Polycrystalline samples of Pb(Mg$_{1/4}$Zn$_{1/4}$Mo$_{1/2}$)O$_3$ (PMZM) have been prepared by a solid-state reaction technique. Preliminary X-ray studies show the formation of the single-phase PMZM compound with orthorhombic structure. SEM study shows the uniform distribution of spherical grains in the samples. Detailed studies of dielectric constant (ε) and loss tangent (tan δ) are carried out as a function of temperature (-150-250°C) at 10 kHz and also as a function of frequency (1-10 kHz). Observations of a strong dielectric anomaly as a ferroelectric phase transition at 30°C are supported by the polarization study. Variation of dc resistivity of the material with temperature shows semiconducting behaviour, usually called NTC (negative temperature coefficient) resistor.

Introduction

With the growing interest and suitability of ferroelectrics for device applications, a large number of ferroelectric ceramics have been developed in a wide variety and range of compositions and stable structures. Oxide ferroelectrics synthesized by single crystal, thin film and ceramics routes are now widely used for computer memory and display devices, electro-optical modulators, pyroelectric and gas sensors, transducers, hydrophones and other electronic applications. From an extensive literature survey, it has been found that a wide variety of perovskite ferroelectrics having a general formula ABO$_3$ (A = mono, divalent, B = tri-hexavalent ions) can be made by making suitable substitutions at A and/or B sites obeying the following conditions:

\[
\begin{align*}
(i) & \sum_{i=1}^{k} X_{A_i} n_{A_i} + \sum_{i=1}^{l} X_{B_i} n_{B_i} = 6 \\
(ii) & \frac{\overline{r}_A + r_0}{\sqrt{2(\overline{r}_A + r_0)}}
\end{align*}
\]

where \(t\) is the tolerance vector, \(\overline{r}_A\) and \(r_0\) are the average radii of the ions at A and B sites respectively and \(r_0 = 1.32\ \text{Å}\) (Goldschmidt ionic radius of O$^\text{2-}$). Using this formula, tolerance factor of a large number of simple and mixed perovskite ferroelectrics have been calculated. It has been found that for ideal or simple perovskite, \(t = 1\) but for other complex perovskite, it varies between 0.80 \(\leq t \leq 1.20\). Large deviations in tolerance factor indicate the large distortions of perovskite from its ideal value (i.e., \(t = 1\)).

Fig. 1 – SEM photograph of PMZM at 10 μm
The calculated value of \( r \) for lead based perovskite \( \text{Pb(Mg}_{0.5}\text{Zn}_{0.5}\text{Mo}_{0.5})\text{O}_3 \) is 0.84 (i.e. PMZM has distorted perovskite). Detailed literature survey reveals that not much work has been reported on modified lead tungstate and lead molybdate. As some members of this family show very interesting ferroelectric properties, we have carried out systematic studies of \( \text{Pb(Mg}_{0.5}\text{Zn}_{0.5}\text{Mo}_{0.5})\text{O}_3 \) ceramics. In this paper we report the preliminary structural and detailed dielectric, polarisation reversal and resistive properties of the compound.

2 Experimental Details

The polycrystalline sample of PMZM was prepared by a standard solid-state reaction technique with high-purity constituent oxides and carbonate: \( \text{PbO}(99.99\text{\%}, \text{M/s Aldrich Chemical, USA}), \text{MgCO}_3 \) (99.9\%, M/s s.d. Fine Chemical, India), \( \text{ZnO} \) (99\%, M/s Loba Chemie Co., India), \( \text{MoO}_3 \) (AR grade, John Baker Inc., Colorado, USA) in the desired stoichiometry. These oxides and carbonate were thoroughly mixed in an agate mortar for 4 hr in a wet medium (methanol) and calcined at 750°C for 12 hr. The process of grinding and calcination were repeated and finally the PMZM powder was calcined at 840°C for 18 hr in an air atmosphere. The fine powder of PMZM was cold pressed into small discs (pellets) under a uniaxial pressure of \( 6 \times 10^7 \text{ N/m}^2 \). Polyvinyl alcohol (PVA) was used as a binder. The pellets were then sintered at 850°C for 12 hr in a high-purity alumina crucible. PVA binder was burnt out during sintering of the pellets.

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The formation of single-phase PMZM compound was checked by an X-ray diffraction (XRD) technique with a powder diffractometer (Phillips PW 1710, Holland). For preliminary structural analysis of PMZM, the XRD data was collected with diffractometer on calcined as well as pellet sample using CuK\(_a\) radiation (\( \lambda = 1.5418\text{\AA} \)) in a wide range of Bragg angles (20° ≤ 2θ ≤ 70°) with a scanning rate of 2° min\(^{-1}\) at room temperature. High-purity silver paste was then painted on flat polished surfaces of the sintered pellets to act as an electrode. It was then dried at 150°C and cooled down to room
Fig. 3 - Variation of dielectric constant (\(\varepsilon\)) and dielectric loss (tan \(\delta\)) of PMZM as a function of temperature at 10 kHz.

Temperature before taking electrical measurements to avoid the effect of moisture, if any.

The dielectric constant (\(\varepsilon\)) and loss tangent of PMZM were measured both as a function of frequency (1 to 10 kHz) and temperature (-120 to 300°C) using a GR 1620 AP capacitance measuring assembly with a chromel-alumel thermocouple and a laboratory made 3-terminal sample holder. Measurement of polarization was carried out using a

Fig. 4 - Variation of spontaneous polarization \((P_s)\) and coercive field \((E_c)\) of PMZM as a function of temperature at 50 Hz.
modified Sawyer-Tower circuit with a dual trace oscilloscope at an a.c. field of 8.4 kV/cm and a frequency of 50 Hz.

![Graph of dielectric constant vs. biasing field](image)

Fig. 5 – Variation of dc resistivity of PMZM as a function of biasing field at room temperature

The dc electrical resistivity \( \rho_d \) was measured as a function of biasing electric field (4.4-6.7 kV/m) at room temperature and as a function of temperature (100-300°C) at a constant electric field 6.7 kV/m. This measurement was carried out with the help of a Keithley-617 programmable electrometer.

3 Results and Discussion

The room temperature XRD peaks of PMZM were found to be sharp and single indicating good homogeneity and formation of single-phase compound. All the reflection peaks were indexed and lattice parameters of PMZM were determined in various crystal systems using a computer program package (PowdMulti). Finally, a unit cell was selected for which a good agreement between observed and calculated interplanar spacing \( d \) \( (d_{\text{obs}} \) and \( d_{\text{cal}}) \) of all reflection lines was found in orthorhombic system. (Table 1). The least-squares refined lattice parameters of PMZM are \( a = 10.76579(32) \) Å, \( b = 12.1682 \) (32) Å and \( c = 16.9121(32) \) Å. It was not possible to determine the space group of the compound with a limited number of powder diffraction data. The linear particle size \( (P_{\text{th}}) \) of the sample was calculated from strong and medium intensity reflection peaks using Scherrer’s equation

\[ P_{\text{th}} = \frac{0.89\lambda}{\beta_{1/2}} \cos\theta_{1/2}, \]

where \( \beta_{1/2} \) = half peak width. The average particle size was found to be about 170 Å. SEM photographs (Fig. 1) of the sintered pellet suggested that spherical grains were uniformly distributed throughout the sintered surface with an average size of 200 Å.

![Graph of dc resistivity vs. temperature](image)

Fig. 6 – Variation of dc resistivity of PMZM as a function of temperature at a constant electric field (6.7 kV/m)

Fig. 2 shows the decrease of dielectric constant \( (\varepsilon) \) and loss tangent \( (\tan \delta) \) with increasing frequency which is a normal characteristic of a dielectric/ferroelectric. This type of variation suggests the presence of different types of polarizations (i.e. electronic, atomic, orientational, space charge, etc.) at low frequencies. However, unlike in many linear and/or nonlinear dielectrics at low frequencies, loss tangent becomes very high and hence it became very difficult to perform experiment by above instrument. The temperature variation of \( \varepsilon \) and \( \tan \delta \) at 10 kHz is shown in Fig. 3. The values of \( \varepsilon \) were found to be almost independent of temperature in the range -120 to -30°C. It increases slowly up to 10°C and then very sharply to its maximum value at 30°C. Above 30°C it decreases very fast. A strong dielectric anomaly was, therefore, found at 30°C, which may be considered as transition temperature of PMZM. The loss tangent also varies in a similar fashion. The observation of sharp transition and peak of \( \varepsilon \) and \( \tan \delta \) exactly at the same temperature suggests that
both follow Curie-Weiss law, as expected from the Kramer-Kroning relations$^4$.

Fig. 4 shows the variation of spontaneous polarization and coercive field as a function of temperature. As the ceramics have lower density than those of its single crystal counterpart, a higher electric field was required to get saturation polarization. Unfortunately at higher field, the ceramic sample breaks into several pieces. So we have optimized a field (8.4 kV/cm) to get the hysteresis loop. The spontaneous polarization decreases with increasing temperature until it becomes zero or very small. In ceramic samples, it has been found that a very small amount of spontaneous polarization remains above $T_c$ (determined from dielectric studies). This can be explained by the nature of domains present in the ceramics. The ceramic sample has a large number of domains having different directions of polarization instead of a single polarizing axis as in the single crystal. Due to the application of an external ac field, the dipoles in every domain experience a force to oscillate about their mean rest position with the frequency of the applied a.c. field. Due to thermal energy they may be agitated and regain their randomness. But some of the domains still have a definite value of dipole moment, which results in a small value of spontaneous polarization above $T_c$ (Ref. 20).

At room temperature the variation of dc resistivity ($\rho_d$) as a function of biasing field is shown in Fig. 5. It has been observed that the resistivity of PMZM decreases with increasing biasing electric field. The $\rho_d$ first decreases some what rapidly but above 5.35 kV/m the decrease in $\rho_d$ with respect to increase in field is rather small. With direct applied voltage, the diffusion of mobile impurity ions builds up a much larger charge at the surface until the reverse field so developed from the surface charge eventually arrests the current$^4$. As such with increase in dc field, the surface charge build up by the mobile ions is expected to increase, which explains the nature of $\rho_d$ versus biasing field curve in Fig. 5. The variation of dc resistivity with temperature at a constant electric field (6.7 kV/m) is shown in Fig. 6. It is found that resistivity of the sample at room temperature is $\sim 10^3 \Omega \cdot m$ which decreases rapidly to $10^2 \Omega \cdot m$ at 300°C. This can be attributed as follows: with the addition of thermal energy, electrons could be set free from oxygen ions. When an electron is introduced in the sample it might be associated with cations, which results in an unstable valence state$^4$.

4 Conclusions

It is now concluded that polycrystalline sample of PMZM has an orthorhombic structure and it undergoes phase transition at 30°C. It behaves as NTC thermistors and can be effectively used for sensor applications, if the accuracy and stability of sensor devices is adequately maintained$^4$.

References

4. Thomas A L, Ferroelectrics, 3 (1972) 231.