

Structural and electrical behaviour of $\text{Pb}(\text{Mn}_{1/4}\text{Cu}_{1/4}\text{Mo}_{1/2})\text{O}_3$ ceramics

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The polycrystalline samples of $\text{Pb}(\text{Mn}_{1/4}\text{Cu}_{1/4}\text{Mo}_{1/2})\text{O}_3$ were synthesized by a high-temperature solid-state reaction technique. A preliminary X-ray structural study of the compound at room temperature shows the formation of a single-phase compound with a non-centrosymmetric space group $\text{P}2_12_12_1$ of orthorhombic structure. Studies of dielectric constant (ϵ) and loss tangent ($\tan \delta$) both as a function of frequency (500 Hz-10 kHz) at room temperature and temperature (-100-250 °C) at 10 kHz suggest that the compound undergoes a phase transition at 57 °C. The activation energy (E_a) of the compound was calculated from the plot of dc conductivity versus inverse of absolute temperature. Variation of dc resistivity with electric field (8.55-85.47 kV/m) at room temperature and variation of dc resistivity (10^{12} - $10^6 \Omega\text{m}$) with temperature (100-300 °C) at a constant electric field of 85.47 kV/m showed the semiconductor characteristics of the material.

1 Introduction

Ferroelectric oxides synthesized by single crystal, thin film and ceramic routes are now widely used in computer memory and display devices, pyroelectric and gas sensors, electro-optical modulators, hydrophones, transducers and other electronic applications¹⁻⁸. Among all the ferroelectric oxides, some oxides with perovskite structure of a general formula ABO_3 (A = mono or divalent, B = tri-hexavalent ions) have extensively been studied in search of new compounds for the said devices following the conditions of charge neutrality and Goldschmidt tolerance factor⁹. For more than two decades lead-based complex perovskites (e.g., PbTiO_3 , $\text{Pb}(\text{ZrTi})\text{O}_3$ and $(\text{PbLa})(\text{ZrTiO}_3)$, etc.) have been playing a very important role in ferro-, piezo- and pyroelectric devices⁷. Extensive literature survey on Pb-based complex perovskite show that, except a few studies, not much work has been reported on complex PbWO_3 and PbMoO_3 because of their high electrical conductivity and dielectric loss at low frequencies and high temperatures. Recently a diffuse phase transition has been observed in many complex tungstate/molybdate ceramics modified with alkali and rare-earth ions¹⁰⁻¹¹. This attracted us to make other complex compounds modified with other isovalent ions such as $\text{Mn}^{2+}/\text{Mg}^{2+}$ and/or Cd^{2+} , Zn^{2+} , Ni^{2+} , Cu^{2+} , etc. at W- or Mo-sites. Therefore, the systematic studies of

phase transitions in $\text{Pb}(\text{Mn}_{1/4}\text{Cu}_{1/4}\text{Mo}_{1/2})\text{O}_3$ compounds have been carried out. Preliminary structural, detailed dielectric and resistive properties of $\text{Pb}(\text{Mn}_{1/4}\text{Cu}_{1/4}\text{Mo}_{1/2})\text{O}_3$ (hereafter PMCM) for a better understanding of its phase transition have been reported.

2 Experimental Details

Polycrystalline samples of PMCM were prepared by high-temperature solid-state reaction technique. Precursors used were PbO (99.9% M/s Aldrich Chemical Company, Inc., USA), MnCO_3 (AR Grade M/s Loba Chemie Industrial Co., India), CuO (99% M/s S.D. Fine Chemicals, India) and MoO_3 (99% M/s BDH, England). The desired stoichiometric mixtures of oxides and carbonates were thoroughly mixed in methanol in an agate mortar for 4h. The air-dried powder was then calcined at 860 °C for 12h. The mixing and calcination were repeated till the formation of the compound was formed. The fine calcined powder was cold-pressed into pellets at an isostatic pressure of $6 \times 10^7 \text{ N/m}^2$ using a hydraulic press and then sintered at 850 °C for 12h.

The quality and formation of the desired single-phase compound were checked by X-ray diffraction (XRD) technique. XRD patterns were recorded at room temperature using an X-ray powder diffractometer (Phillips PW 1710, Holland) using

CoK $_{\alpha 1}$ radiation. ($\lambda = 0.1789$ nm) for a wide range of Bragg angles ($20^\circ \leq 2\theta \leq 70^\circ$) with a scanning rate of 2° min^{-1} . A fine silver paste was applied on the flat surface of the sintered pellets. It was then dried at 150°C and cooled to room temperature before taking any electrical measurements to overcome the effect of moistures, if any. Measurements of dielectric constant (ϵ) and loss tangent ($\tan \delta$) were carried out with both as a function of frequency (500 Hz-10 kHz) at room temperature and temperature (-150 - 250°C) at 10 kHz using a 1620 capacitance measuring assembly with a laboratory made 3-terminal sample holder which compensates all sorts of stray capacitances. The dc electrical resistivity was measured both as a function of biasing electric field (8.55-85.47 kV/m) at room temperature and temperature (100 - 300°C) at a constant electric field of 85.47 kV/m with the help of a Keithley-617 programmable electrometer, laboratory made sample holder, chromel-alumel thermocouple and PID temperature controller (Indo therm 401D). The measurements of dc electrical resistivity as a function of temperature were taken in a cooling mode to get a reproducible data.

Table 1 — Comparison of some observed and calculated d -values (in $\text{\AA}$) of some reflections for PMCM compound at room temperature

h	k	l	d_{obs}	d_{cal}	I/I_0
0	1	2	4.9137	4.9319	20
2	2	0	3.5847	3.5853	24
2	2	1	3.4007	3.4161	81
1	1	3	3.3315	3.3234	22
1	3	0	3.2305	3.2344	100
3	1	1	3.0595	3.0600	56
2	2	2	3.0164	3.0235	50
0	3	2	2.9291	2.9204	36
2	1	3	2.8831	2.8828	32
1	0	4	2.7098	2.7085	32
1	1	4	2.6185	2.6187	28
0	4	0	2.5632	2.5626	18
2	4	0	2.2846	2.2822	19
4	0	3	2.0854	2.0850	20
0	5	1	2.0171	2.0169	25
3	4	2	1.9164	1.9130	23
4	4	0	1.7931	1.7927	17
3	4	3	1.7850	1.7881	18
2	5	3	1.6951	1.6933	15
0	5	4	1.6557	1.6568	16
6	1	0	1.6513	1.6506	22
3	4	4	1.6479	1.6484	22
4	4	3	1.6175	1.6174	31

3 Results and Discussion

The sharp and single peaks of the X-ray diffraction (XRD) patterns of calcined powder samples, which were different from those of the constituents, suggested the formation of single-phase compound. All the peaks in the XRD pattern were indexed and cell parameters were determined in various crystal systems with a standard computer program 'PowdMult' using observed d -values of strong, medium and low intensity reflections spread over wide 2θ range. Finally a particular unit cell in orthorhombic system was selected for which $\sum \Delta d = \sum (d_{\text{obs}} - d_{\text{cal}})$ was found to be minimum. Table 1 shows a good agreement between the observed and calculated d -values, which suggests the correctness of the selection of the crystal system and unit cell parameters. The lattice parameters of the unit cell were then refined by a least-squares method and found to be $a = 10.0348$ (42) $\text{\AA}$, $b = 10.2503$ (42) $\text{\AA}$ and $c = 11.2518$ (42) $\text{\AA}$. Even with limited number of reflections of XRD pattern, the space group of the material was found to be $P2_12_12_1$ suggesting the compound to be antiferroelectric. The double hysteresis loop of the sample has been observed. Attempts are being made again to modify the Sawyer-Tower circuit for this sample. Surface morphology of the sintered pellets was examined using a scanning electron microscope (CAMSCAN 180). The micrograph (Fig. 1) suggested that the



Fig. 1 — SEM micrograph of PMCM at 10 μm

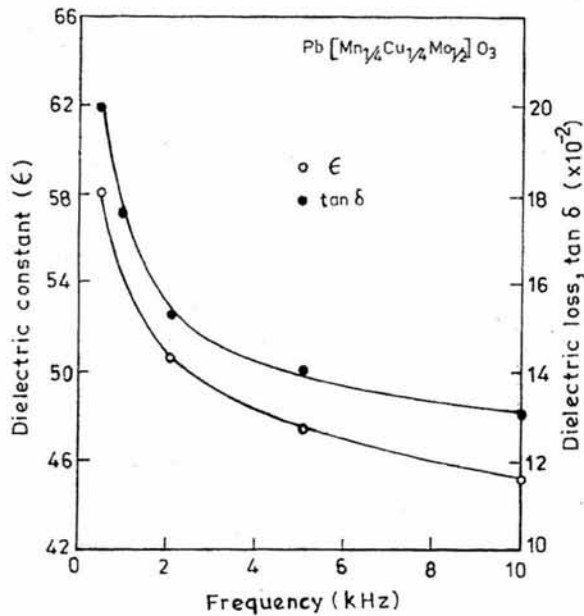


Fig. 2 — Variation of dielectric constant (ϵ) and loss ($\tan \delta$) of PMCM as a function of frequency at room temperature

sintered pellets were reasonably dense with a uniform grain distribution. There were however a few islands and holes present on the surface of the sintered pellets. The average grain size was found to be 2.3 μm . The average particle size was estimated

from some strong and medium intensity reflections of low 2θ range using Scherrer's equation¹²: $P_{hkl} = 0.89 \lambda / \beta_{1/2} \cos \theta_{hkl}$, where $\beta_{1/2}$ is the half-width and was found to be 150 Å. The smaller particle size is of great importance as it offers a higher rate of densification due to both an increase in driving forces for sintering and to the smaller distances of mass transport needed to fill the pores, thus permitting lowering of sintering temperature and the achievement of fine grain ceramics.

Fig. 2 shows the variation of ϵ and $\tan \delta$ of PMCM with frequency at room temperature. It has been found that both parameters decrease with increasing frequency, which is the normal behaviour of a dielectric.

Fig. 3 shows the variation of ϵ and $\tan \delta$ with temperature at a frequency of 10 kHz. Here, the dielectric constant increases gradually with an increase in temperature and has the maximum value at 57 °C and then decreases smoothly to 106 °C. Above 106 °C it increases with increase in temperature which may be caused by space charge polarization. Thus, a dielectric anomaly relating to ferroelectric-paraelectric phase transition was observed at 57 °C which may be considered as the transition temperature of PMCM. The loss tangent also varies in a similar way. The anomaly observed

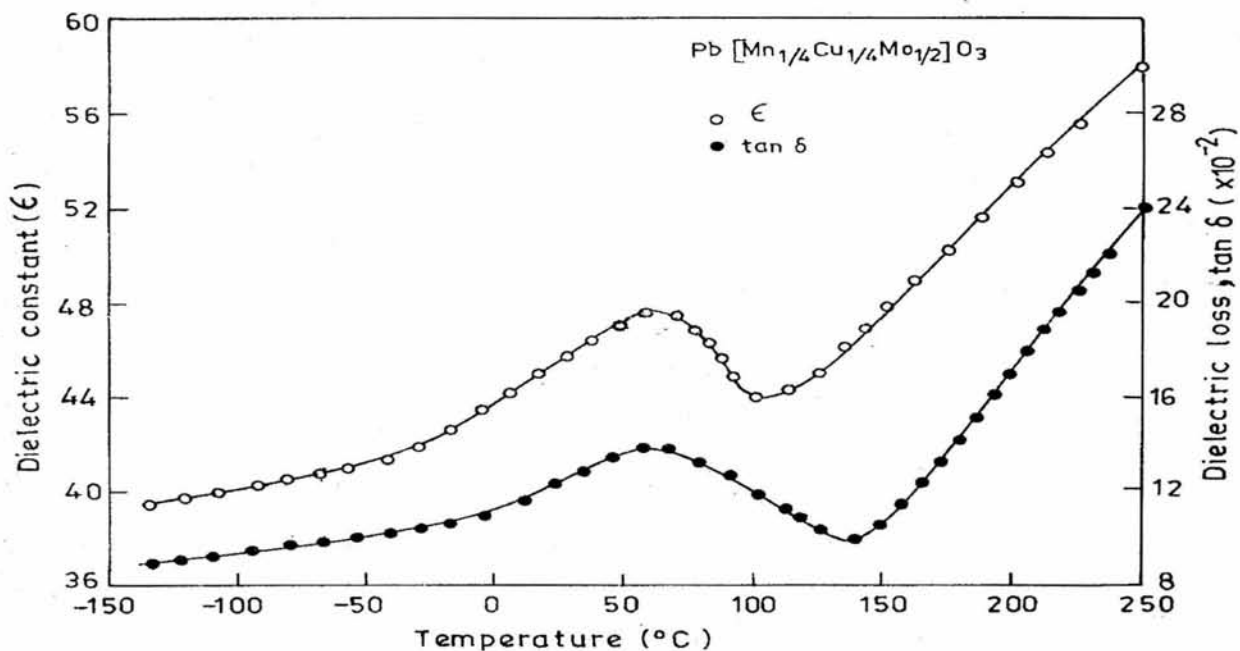


Fig. 3 — Variation of dielectric constant (ϵ) and loss ($\tan \delta$) of PMCM as a function of temperature at 10 kHz

in ϵ versus temperature and $\tan \delta$ versus temperature are presumably positioned around the phase transition. A small temperature difference between the peaks of dielectric constant and loss tangent is consequently an outcome of Kramers-Kronig relation accounting for the broadening of phase transition in the material¹⁴. Further, in the sublattice of ions, Mn^{2+} , Cu^{2+} and Mo^{6+} occupy octahedral positions. This suggests that in PMCM, the fluctuations in the statistical distribution of Mn^{2+} , Cu^{2+} and Mo^{6+} are too small to be conspicuous for providing a fairly broadened phase transition as found in its isomorphous compound PMCW¹³.

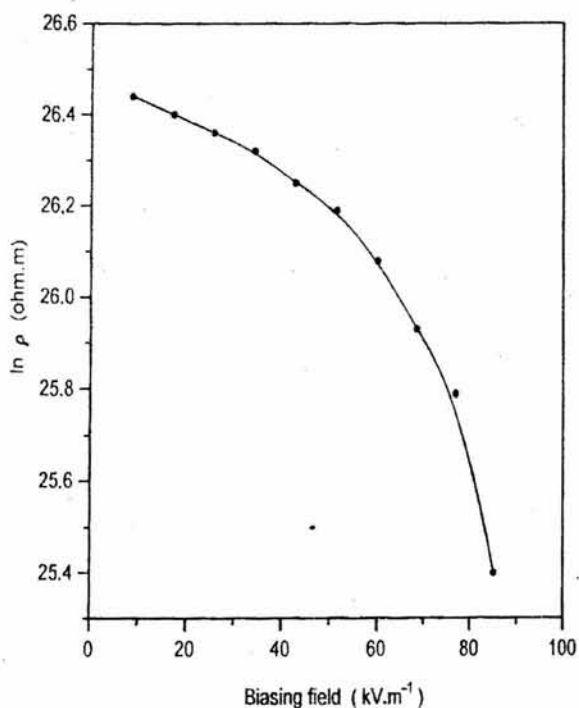


Fig. 4 — Variation of dc resistivity ($\ln \rho_{dc}$) of PMCM as a function of field at room temperature

Fig. 4 shows the variation of dc electrical resistivity with biasing field at room temperature. The resistivity decreases with the increase of bias field. It is observed that there is a very little variation with biasing field at room temperature. However at higher fields the decrease in resistivity is rather fast. This may be due to the following reasons: (a) ionization occurs in homogeneous dielectrics mainly through the mechanism of partial discharge of gases moistures from the pores or cracks present in the ceramics; the electric field results in the generation of local heat which in turn

results in the generation of thermal stresses and increase of local conduction; the stresses can generate more pores/cracks leading to further ionization up to a certain field, (b) electrons may be ejected from the electrodes material. These electrons are then accelerated through the sample and collide with ions or atoms in the solid knocking out other electrons and thus ionization takes place. So, resistivity comes down with increasing biasing field¹⁵.

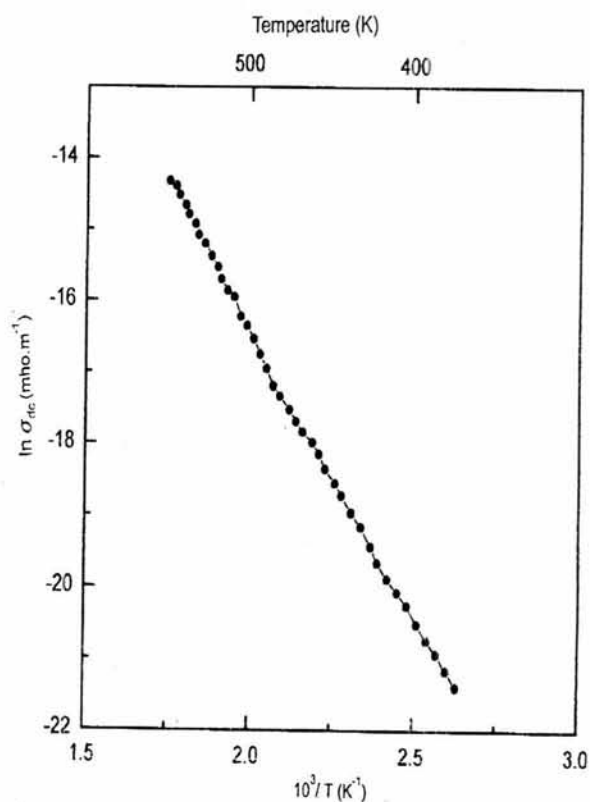


Fig. 5 — Variation of dc conductivity ($\ln \sigma_{dc}$) as a function of temperature at a constant electric field (85.47 kV/m)

Fig. 5 shows the variation of dc conductivity of PMCM with temperature at a constant biasing field of 85.47 kV/m. It is found that conductivity of the compound has a low value $\sim 10^{-12} (\Omega\text{m})^{-1}$ at room temperature which increases to a value of $\sim 10^{-6} (\Omega\text{m})^{-1}$ at 300 °C. Therefore the study of conductivity of the material was possible only at higher temperature (>150 °C) because of the difficulties in making measurements, when the materials become highly resistive at room temperature. The increase in conductivity at high temperature may, however, be possibly due to supply of more and more thermal energy to the

material as the temperature increases. This results in the creation of more and more free electrons that could be set free from the oxygen ions. When an electron is introduced in the sample it might be associated with cations and hence results in an unstable valence state. The activation energy (E_a) calculated from the slope of the $\ln \sigma_{dc}$ versus $10^3/T$ was found to be 0.71 eV in the higher temperature region. Similar behaviour in the nature of variation of dc conductivity with temperature was observed in our PMCW work¹³. In PMCW, the activation energy was found to be 0.85 eV. From such a low value of activation energy, it is again confirmed that oxygen may be the main carrier in the electrical conduction. Further, it may be recalled that though both the compounds PMCM and PMCW are chemically isomorphous but their dielectric behaviour is significantly different. The compound PMCM undergoes a normal phase transition at 57 °C while PMCW undergoes a diffuse phase transition at 190°C.

4 Conclusions

Finally, it is concluded that the compound PMCM has orthorhombic structure at room temperature and undergoes a weak dielectric anomaly at 57 °C. The nature of variation of ϵ with temperature and non-polar space group suggests that like PMCW, PMCM is also an anti-ferroelectric compound. However, conclusions to this may be drawn only by the detailed single crystal structural analysis and observations of double hysteresis loop on poled samples.

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