Structural, dielectric and transport properties of $Pb(Mn_{0.5}W_{0.5})O_3$

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Abstract. **Polycrystalline $Pb(Mn_{0.5}W_{0.5})O_3$, a ferroelectric oxide having perovskite structure, was prepared by high temperature solid state reaction technique. Preliminary X-ray diffraction analysis confirms single phase formation with the lattice parameters $a = 7.2501$ Å, $b = 8.1276$ Å and $c = 12.0232$ Å. Room temperature dielectric constant (e') and loss tangent (tan d) were scanned with respect to frequency in the range 100 Hz–1 MHz. Detailed study of dielectric constant and electrical conductivity reveals a phase change around 400 K, which is quite different from those in the other materials of the same type. Further, the seebeck coefficient (a) is temperature independent. The conduction is interpreted as due to small polaron hopping.**

Keywords. **Perovskite structure; X-ray diffraction; dielectric constant; phase transition; small polaron hopping.**

1. Introduction

There has been considerable interest in the ferroelectric ceramics due to their possible applications in transducers and in the piezoelectric, pyroelectric, electro-optic, acousto-optic and memory devices (Chowdhury and Roy 1993; Bera and Chowdhury 1995; Orlando *et al* 1998; Yamashita *et al* 1998). For the last few decades extensive research work has been devoted to oxide materials of perovskite type structure of general formula, ABO_3 (A = monovalent or divalent ion and B = tri, tetra, penta or hexa valent ion). Perusal of literature shows that few perovskite compounds exhibit simultaneous electric and magnetic ordering. In order to satisfy the necessary condition for the existence of magnetic and electric ordering simultaneously, ferroelectrically active as well as magnetic ions need to be introduced into the octahedral position. Therefore, in the present case, Mn^{+2} and W^{+6} ions were introduced in B site while Pb^{+2} ion in A site. It has been found that some Pb based pure or mixed oxides, such as $Pb(Fe, W)O_3$ (Ye and Schmid 1994), $Pb(Co, W)O_3$, $Pb(Fe, Nb)O_3$ and $Pb(Mg, W)O_3$, have very interesting properties which are useful in devices. In order to find the existence and mechanism of phase transition in mixed lead based ferroelectric materials we have carried out systematic and extensive study of their structural, electrical and thermal properties (Mathe *et al* 2001; Patankar *et al* 2001a). In this paper we report structural, electrical and dielectric properties of $Pb(Mn_{0.5}W_{0.5})O_3$ compound, abbreviated as PMW.

2. Experimental

Polycrystalline $Pb(Mn_{0.5}W_{0.5})O_3$ was prepared by high temperature solid state reaction technique using oxides and carbonates viz. PbO, $MnCO_3$ and WO_3. These oxide powders were taken in appropriate molar proportion and thoroughly mixed in agate mortar for couple of hours to get homogeneous mixture. The mixture was presintered at 800°C for 12 h followed by grinding. The fine homogenous powder of PMW was shaped to make pellets of 10 mm diameter and 3.13 mm thickness under a pressure of 5 tons. Saturated solution of polyvinyl alcohol (PVA) (MW = 124000) was used as a binder for pellets. These pellets were finally sintered at 1050°C for 24 h in air. X-ray diffraction pattern of final product was obtained using CuK_a ($I = 1.5453$ Å) radiation from X-ray powder diffractometer (model PW 3710). The pellets were polished with fine emery paper to make the surfaces flat, smooth and parallel for electrical measurements. The flat surfaces of the pellets were silver painted. The dielectric measurements were made using HP 4284A LCR bridge. These measurements were made as a function of frequency in the range 100 Hz–1 MHz at room temperature and as a function of temperature in the range 300–500 K at certain fixed frequency (1 kHz). The resistance as a function of temperature was measured at 1 kHz and 10 kHz using HP 4284A meter in the range 300–500 K. For thermoelectric power measurement a temperature difference of 25 K was maintained across the pellet with the help of a mini furnace fitted to the sample holder assembly. The temperature difference across the pellet was measured with the help of chromel–alumel differential thermocouple. The d.c. resistivity was measured

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as a function of temperature in the range 300–500 K by two-probe method. The pellet was sandwiched in the sample holder tightly. A constant low voltage was applied across the sample and current through the sample was measured. The whole assembly was kept in a regulated furnace (± 5°C), whose temperature was measured with the help of a chromel–alumel thermocouple.

3. Results and discussion

Figure 1 shows the X-ray diffraction pattern of PMW. The appearances of sharp diffraction peaks confirm the formation of single-phase compound. All the peaks were indexed from their observed *d* values. The structure was found to be orthorhombic with lattice parameters $a = 7.2501$ Å, $b = 8.1276$ Å and $c = 12.0232$ Å. These values are consistent with those for the other tungsten–lead oxide materials (Bera and Chowdhury 1995).

Figure 2 shows the variation of dielectric constant (*e′*) and tangent loss (tan *d*) as a function of frequency at room temperature. It shows that *e′* and tan *d* decrease rapidly at low frequencies and remain nearly constant after about 10 kHz. This is the general behaviour of the ceramics (Patankar *et al* 2001b,c).

Figure 3 shows the variation of *e′* and tan *d* with temperature at 1 kHz frequency. The dielectric constant initially increases with temperature, reaches a peak value

at around 400 K, and then exhibits a slightly upward trend. The peak in the dielectric constant around 400 K corresponds to T_c of PMW. Tan *d* on the other hand, shoots at about this temperature indicating phase transition.

The seebeck coefficient (*a*) was found to be temperature independent (figure 4). The seebeck coefficient measurement shows that the majority charge carriers are electrons. Non-dependence of seebeck coefficient on temperature is a result of small polaron hopping. In the hopping model the number of charge carriers are fixed. Hopping model considers that conductivity is due to the change in the mobility of carriers with temperature (Viswanathan and Murthy 1990).

The variation of log *s* vs $1/T$ for d.c. conductivity (*s*$_{d.c.}$) and for conductivity at 1 kHz and 10 kHz is as shown in figure 5. These plots show change in slope around 400 K, which corresponds to curie temperature. Similar behaviour is observed for other doped ABO_3 perovskites (Zha *et al* 2001). It is seen from figure 5 that the a.c. and d.c. conductivities follow the same trend of temperature variation but at room temperature as frequency changes from $f = 0$ (d.c.) to $f = 1$ kHz and $f = 10$ kHz, the conductivity increases. The reason for this increase should be searched in the frequency dependence of small polaron hopping conduction. It should be recalled that the conduction at lower temperature is due to impurities and defects while at higher temperature it is intrinsic
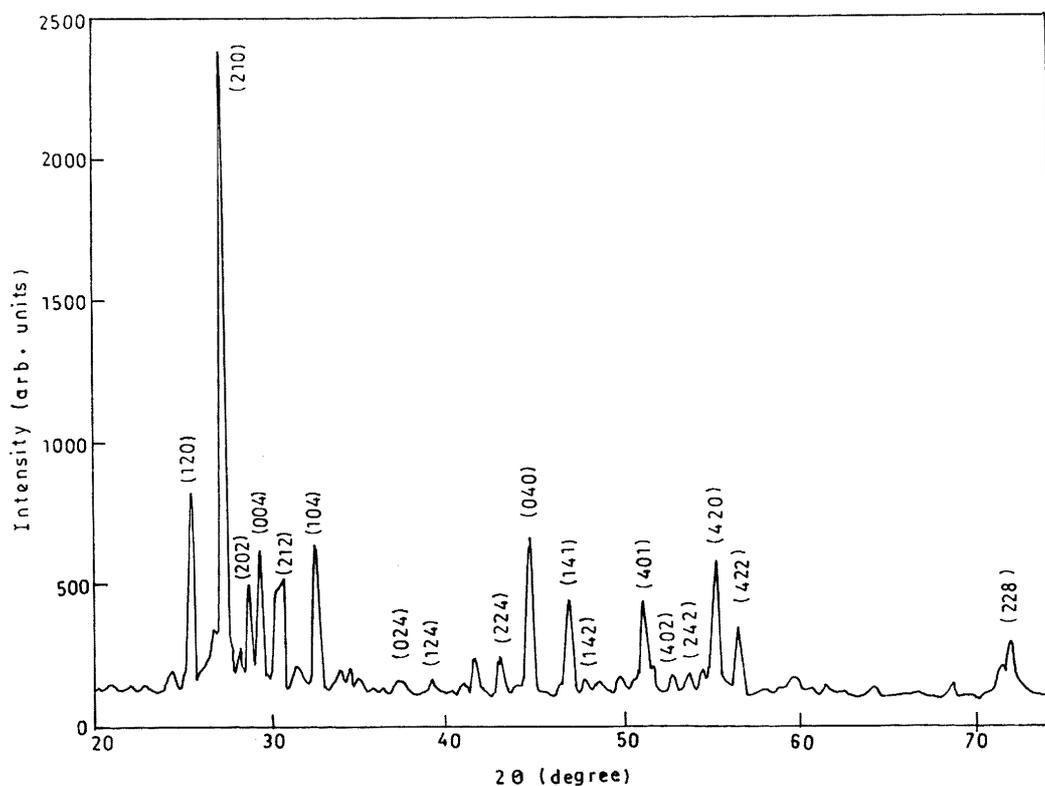

Figure 1. XRD pattern.

property of the material. The activation energies above 400 K are higher than those below this temperature as can be judged from the slopes of the curves. This is in agreement with the general behaviour of ferroelectrics (Gurerich 1969).

For ionic and low energy band solids the conduction is better explained in terms of small polaron (Apple 1968). The excess electrons in a narrow conduction band (or excess holes in a narrow valence band) due to their inter-action with lattice ions distort the surrounding in such a way that potential well thereby generated is deep enough to introduce localization leading to the formation of pola-ron. Polarons are divided into two categories: (i) large polarons and (ii) small polarons. If the conduction is due to large polarons it can be explained on the basis of band mechanism at all temperatures. Small polaron formation takes place in those materials whose conduction band belong to incomplete 'd' or 'f' orbital. In present case Mn^{+2} and W^{+6} have incomplete 'd' orbitals which are responsible for the formation of small polarons. Also that, for conduction due to large polarons the slopes of thermo-

electric power (α) vs $1/T$ and log s vs $1/T$ curves are identical. This is not the case with the curves of PMW. Therefore, the possibility of conduction due to large polarons is ruled out. The conduction mechanism due to small polaron at high temperature is of hopping type and is frequency independent but at low temperatures s depends upon frequency according to the expression (Alder and Feinleib 1970; Sirdeshmukh *et al* 1998)
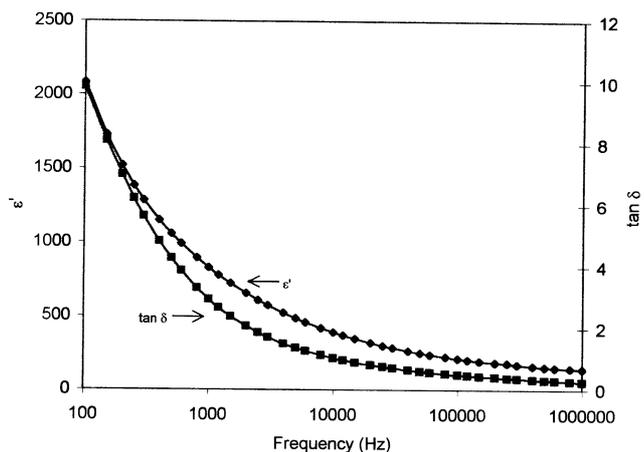

Figure 4. Temperature variation of seebeck coefficient.

Figure 2. Variation of dielectric constant (ε') and loss tangent (tan δ) with frequency at room temperature.
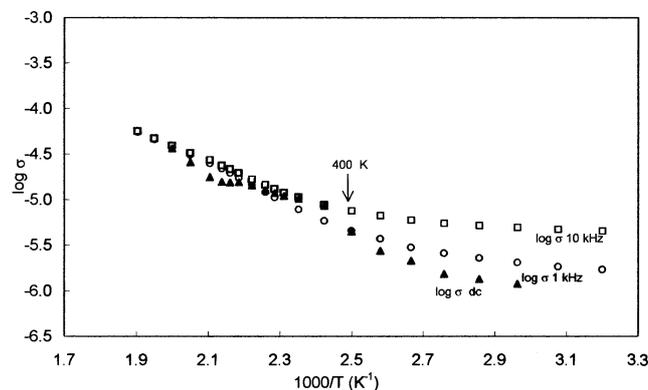
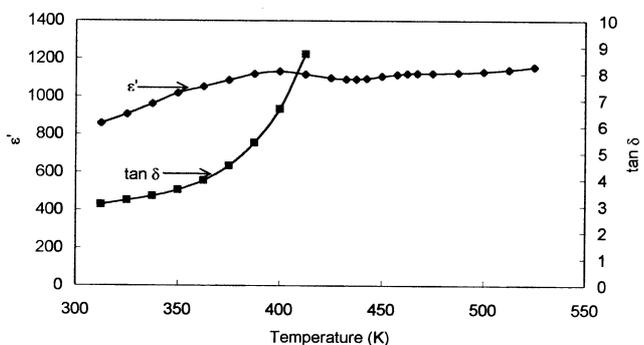**Figure 5.** Variation of log s (a.c. and d.c.) with temperature ($1/T$).

Figure 3. Variation of dielectric constant (ε') and loss tangent (tan δ) with temperature at 1 kHz.
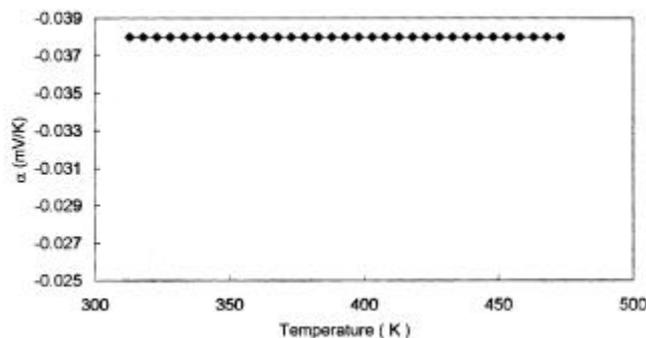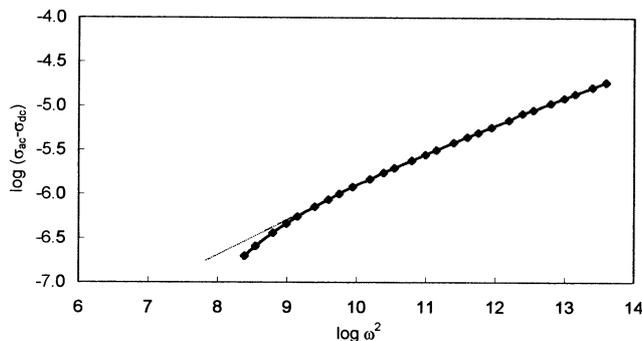

Figure 6. Plot of log($s_{a.c.} - s_{d.c.}$) vs log w^2.

$$(\boldsymbol{s}_{\mathrm{a.c.}} - \boldsymbol{s}_{\mathrm{d.c.}}) = \boldsymbol{w}^2\boldsymbol{t}/(1 + \boldsymbol{w}^2\boldsymbol{t}^2). \qquad (1)$$

From this relation one thing is clear that hopping conduction of small polarons is completely unobservable in d.c. measurements. It is possible to observe the hopping of small polarons bound to impurity sites as an additional contribution to a.c. conductivity. To get the idea of conduction mechanism we measured $\boldsymbol{s}$ as a function of frequency in the range 100 Hz to 1 MHz at room temperature. The result is shown in figure 6. Since conductivity increases with frequency one can expect hopping conduction of small polarons. In such a case $\boldsymbol{s}_{\mathrm{a.c.}}$ follows the relation (1). Since $\boldsymbol{t}$ is small ($\approx 10^{-10}$ sec), at frequencies $\boldsymbol{w} < 10^9$ Hz, $\boldsymbol{w}^2\boldsymbol{t}^2 \ll 1$ and hence it can be neglected from the denominator of (1). Thus in such a case a plot of $\log(\boldsymbol{s}_{\mathrm{a.c.}} - \boldsymbol{s}_{\mathrm{d.c.}})$ vs $\log \boldsymbol{w}^2$ should be a straight line, which is indeed the case in figure 6. Similar results have been observed by Lal and Dar (1976). A small deviation in the lower values may be due to the fact that at lower frequencies the dipoles have sufficient time to follow the frequency of applied field which is not the case at higher frequencies.

4. Conclusions

The $Pb(Mn_{0.5}W_{0.5})O_3$ compound has orthorhombic crystal structure at room temperature. It exhibits normal ferroelectric phase transition. The charge carriers are of n type and their concentration is temperature independent. The conduction is due to small polaron hopping. At low temperature this conduction is frequency dependent.

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