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Presence of dielectric anomaly and spontaneous magnetization in $Pb(Mn_{1/2}Nb_{1/2})O_3$

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Abstract

Polycrystalline lead manganese niobate [$Pb(Mn_{1/2}Nb_{1/2})O_3$] has been prepared by a solid-state reaction technique. A preliminary structural analysis indicates a tetragonal crystal structure. A broad dielectric anomaly at 520 K is observed in the permittivity versus temperature pattern. Differential thermal analysis (DTA) shows a change in slope near the temperature corresponding to the dielectric anomaly. The ac conductivity obeys the Arrhenius law over a wide range of temperatures with a peak at 520 K. A peak in the magnetization (M) versus temperature (T) curve is observed at 16 K with a bifurcation between ZFC and FC curves below this temperature. Although the sample is found to be in a paramagnetic state at room temperature, considerable hysteresis is found in the M–H curve at 2 K. Moreover, Arrott's plot at 2 K has given a clear indication of the presence of spontaneous magnetization in the system.

1. Introduction

Ferroelectric materials with perovskite structure have been found to have applications in a multitude of devices like high permittivity ceramic capacitors, piezoelectric transducers, memory devices etc [1, 2]. Among all the perovskites studied so far, the lead-based complex perovskites of the general formula $Pb(B'_xB''_{1-x})O_3$ are fascinating materials because of their high dielectric constant, frequency dispersive behavior and diffuse phase transition. Their properties vary from relaxor to normal ferroelectric, depending upon the degree of disorder at the B-site sublattice [3–7]. When both d^0 ion (ferroelectric active) and the partially filled d orbital ion (magnetically active) are accommodated at the B site of these complex lead-based perovskites of the general formula $Pb(B^{+3}_{1/2}B^{+5}_{1/2})O_3$, they give multiferroic properties (simultaneous occurrence of magnetic and ferroelectric order in the same phase) [8–13]. This idea was first conceived by Russian scientists in the 1950s leading to the synthesis of many multiferroic materials like $Pb(Fe_{1/2}Nb_{1/2})O_3$, $Pb(Fe_{1/2}Ta_{1/2})O_3$, $Pb(Mn_{1/2}Nb_{1/2})O_3$, etc [11, 14–17]. However, in this group of multiferroic materials $Pb(Mn_{1/2}Nb_{1/2})O_3$ has not been studied extensively. Though an attempt was made to prepare the material by Smolenskii *et al* [17] in 1959 and subsequently by Filipev *et al* [18] in 1963, the single-phase material could not be achieved. Then Drobyshev *et al* [19] investigated the magnetic characteristics of single-crystal $Pb(Mn_{1/2}Nb_{1/2})O_3$ and found a transition to the antiferromagnetic state at 11 K. Though they mentioned about a ferroelectric transition at 293 K, no study of dielectric properties was done in support of this transition temperature. Also during this period Astrov *et al* [20] had reported that the two ferroelectric substances $Pb(Fe_{1/2}Nb_{1/2})O_3$ and $Pb(Mn_{1/2}Nb_{1/2})O_3$ possessed a spontaneous magnetic moment, which was of magnetoelectric origin in nature. Later Brunskill *et al* [21] reported a pseudo-cubic structure of the single crystal of this material. But a detailed study of dielectric, electrical and magnetic properties of this material is lacking. As in recent years a renewed and intense research in multiferroics has taken place, a detailed analysis of a new or less studied material in this field will add more impetus to progress in this direction. Therefore, in this paper we report detailed dielectric, electrical and magnetic properties of $Pb(Mn_{1/2}Nb_{1/2})O_3$.

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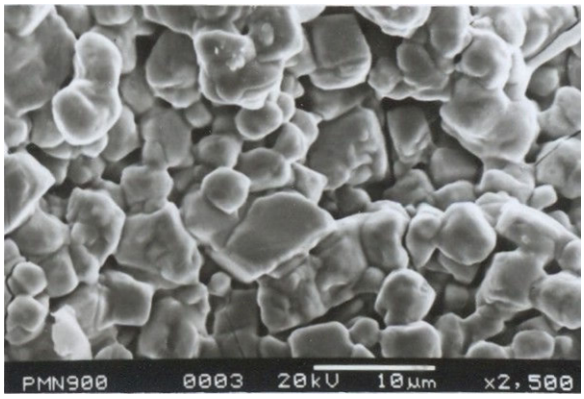

Figure 1. The SEM micrograph of the sintered pellet of $Pb(Mn_{1/2}Nb_{1/2})O_3$.

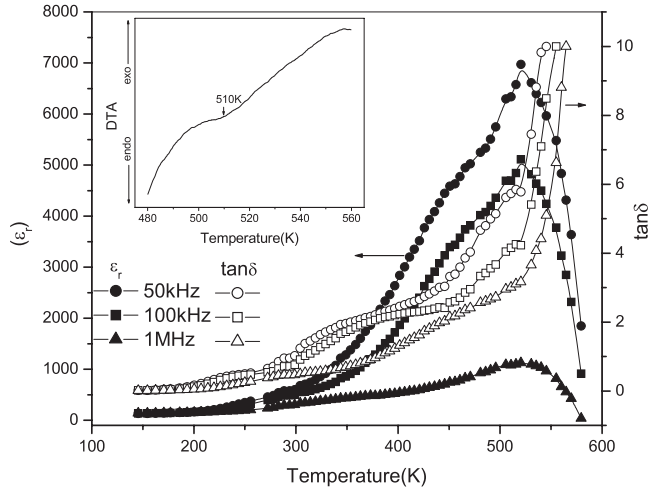

Figure 2. Variation of dielectric permittivity and loss tangent with temperature at different frequencies. The DTA curve of the sample is shown in the inset.

2. Experimental details

The polycrystalline samples of $Pb(Mn_{1/2}Nb_{1/2})O_3$ were prepared by a solid-state reaction method using high purity starting materials, PbO, Mn_2O_3 and Nb_2O_5. The physical mixture of the above chemicals in required stoichiometry with 3% excess PbO (to compensate for lead loss) were calcined at an optimized temperature/time (1123 K for 6 h) in a platinum crucible and in air atmosphere. Differential thermal analysis (DTA) was recorded for the powder samples of $Pb(Mn_{1/2}Nb_{1/2})O_3$ using a Pyris Diamond TG/DTA STA unit at a scan rate of 10 °C min^{-1} in a platinum crucible. The calcined powder was cold pressed into small cylindrical pellets which were subsequently sintered at 1173 K for 6 h in air atmosphere. The SEM micrographs at different magnifications were taken using the scanning electron microscope JEOL JSM-5800. Electrical measurements were done on a cell, Ag | pellet |Ag in the frequency range 100 Hz–1 MHz using a Hioki LCR Hi Tester (Model: 3532) and for a temperature range of 145–579 K. The magnetic measurements were carried out in a 14 T PPMS-VSM of Quantum Design for a temperature range from 2–300 K.

3. Results and discussion

The preliminary structural analysis of the polycrystalline $Pb(Mn_{1/2}Nb_{1/2})O_3$ ceramic sample suggests tetragonal structure of the compound at room temperature with lattice parameters, $a = 4.0027(28)$ Å, $c = 4.0090(28)$ Å (the number in parentheses is the estimated S.D.), with $c/a = 1.0016$. The low tetragonality (∼1) and absence of peak splitting (not shown here) suggest the centro-symmetric pseudo-cubic structure of the material. The SEM micrograph of the sintered pellet of the sample is shown in figure 1. The micrograph reveals microstructure comprising grains of varying sizes with clearly defined boundaries and uniform distribution of grains.

The variations of relative permittivity (ε_r) and loss tangent ($\tan\delta$) with temperature at different frequencies are shown in figure 2. At each frequency ε_r increases very slowly up to 315 K, beyond which it increases rapidly till it attains a broad maximum at 520 K and then its value decreases continuously. A small kink is also observed in the $\tan\delta$ pattern at 520 K. Strong frequency dispersion in both permittivity and loss pattern above 315 K is also evident from this figure. No dielectric anomaly at 293 K showing any transition is observed here, contrary to the previous report [19]. The low frequency dispersion at elevated temperature in both permittivity and loss pattern indicates the presence of appreciable dc conductivity in the system [22]. This was a hindrance for poling the material to get any hysteresis loop. To get more insight into the reason behind the observed dielectric anomaly, we have carried out thermal analysis (DTA) of this sample. The DTA curve is shown in the inset of figure 2. Though we do not get a clear endothermic peak (anomaly) in support of the phase transition temperature, certainly a change in slope is observed at 510 K, which is close to the temperature of the dielectric anomaly. The above anomalies are not sufficient to draw any conclusions about the occurrence of a ferroelectric phase transition in the material. However, these anomalies may be attributed to non-ferroelectric phase transitions arising from defect contributions as explained by Scott in the case of $KMnF_3$ [23]. The variation of ac conductivity (σ_{ac}) with the inverse of absolute temperature ($1000/T$) at different frequencies is shown in figure 3. It is evident from the figure that there is a peak at 520 K below which the graph appears to be linear for the most part. The linear variation may be approximated to be governed by the relation: $\sigma_{ac} = \sigma_0 e^{-Ea/kT}$, where Ea is the activation energy and k is Boltzmann's constant. The activation energy evaluated using this relation works out to be 0.21 eV. Probably due to the coexistence of a small amount of different oxidation states of Mn along with Mn^{3+}, there might be few oxygen vacancies created in the crystal lattice. Considering the low value of activation energy, only a single ionized oxygen vacancy may be involved in the conductivity process along with some polaronic contribution [24–26]. Also the lattice strains associated with order–disorder changes may induce the conduction by small polarons where the carrier transport is by hopping charge. The anomaly observed in ac conductivity

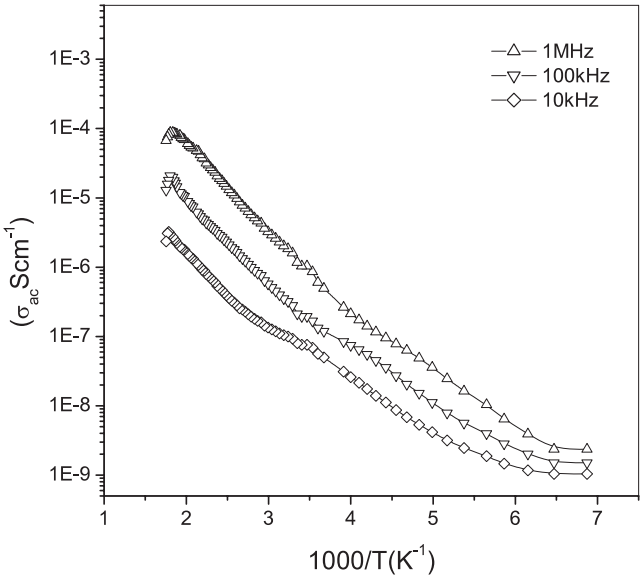

Figure 3. Variation of ac conductivity σ_{ac} with inverse of absolute temperature at different frequencies.

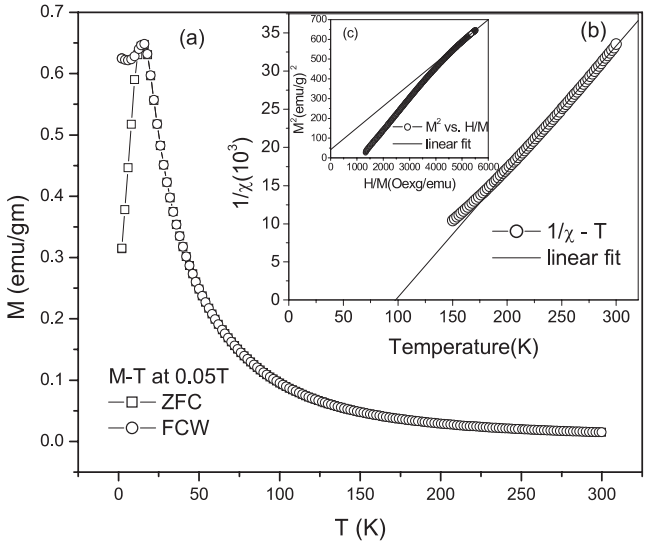

Figure 4. (a) Variation of magnetization (M) with temperature (T) in ZFC and FC mode at 0.05 T. $1/\chi$ versus temperature graph in the range of 150–300 K is shown in the inset (b) and Arrott's plot is also shown in the inset (c).

near the transition temperature is a typical behavior of many ferroelectric materials [27].

Figure 4(a) shows the variation of magnetization (M) with temperature (T) for the $Pb(Mn_{1/2}Nb_{1/2})O_3$ sample in both zero-field-cooled (ZFC) and field-cooled (FC) mode in 0.05 T magnetic field. Both ZFC and FC magnetization show a sharp rise below 100 K and a peak around 16 K. Below this peak the ZFC and FC magnetization bifurcate. Figure 5 shows the M–H curves for 300 and 2 K. Above 215 K, the sample appears to be in the paramagnetic state, which is evident from the Curie–Weiss plot (figure 4(b)) and also the linear M–H at 300 K (upper inset of figure 5). However, the sharp increase in M may be attributed to ferrimagnetic interactions which is clear from a large +ve intercept of $1/\chi$ on the temperature axis in the Curie–Weiss plot [28]. The nonlinearity in M–H with finite hysteresis at 2 K is the manifestation of this ferrimagnetic interaction in the system. To confirm the presence of spontaneous magnetization, Arrott's plot (M^2 versus H/M) is carried out from the M–H data at 2 K (figure 4(c)). The positive intercept on the M^2 axis in Arrott's plot indicates a spontaneous magnetization in the sample [29–31]. Super-exchange resulting from Mn–O–Mn interactions might give rise to the magnetic ordering at low temperature. The peak in the M–T graph around 16 K and a bifurcation between the ZFC and FC magnetization indicate a canted state at low temperature [32].

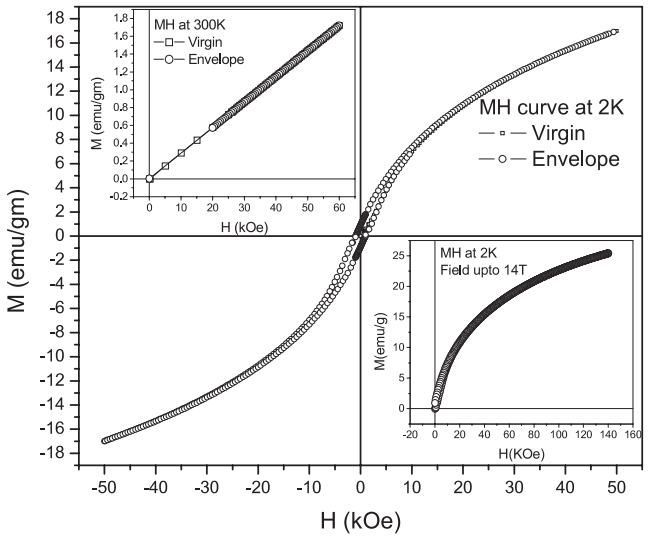

Figure 5. M–H curve for the sample at 2 K. M–H curve at 2 K with applied field 14 T (inset) and M–H curve at room temperature (inset).

4. Conclusion

The polycrystalline $Pb(Mn_{1/2}Nb_{1/2})O_3$, prepared by a solid-state reaction technique, was formed in a single phase with tetragonal/pseudo-cubic unit cell structure. It is a lossy material with high dielectric permittivity and showing strong frequency dispersion. The temperature-dependent permittivity pattern shows a broad peak at 520 K. This peak/anomaly may be related to non-ferroelectric phase transition, and due to defects. The material shows high conductivity with low activation energy. The magnetization versus temperature graph shows a peak at 16 K. Though at room temperature the material shows paramagnetic behavior, evidence of spontaneous magnetization is found in the system.

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