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Absence of ferroelectric polarization in layered and rock-salt ordered $NaLnMnWO_6$ (Ln = La, Nd, Tb) perovskites

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The ordered perovskites, $NaLnMnWO_6$ (Ln = La, Nd, Tb) are reported to exhibit simultaneous ordering of A-site cations (Na and Ln) in layered arrangement and B-site cations (Mn and W) in rock salt structure. They have been shown to crystallize in a mononclinic structure with the polar space group $P2_1$. Based on density functional calculations and group theoretical analysis, it has recently been proposed that $NaLaMnWO_6$ should be ferroelectric with relatively a larlge polarization (16 $\mu C/cm^2$). Contrary to this prediction, our electrical measurements such as, conventional P-E loop, Positive-Up and Negative-Down (PUND), piezoelectric response and Second Harmonic Generation (SHG) reveal the absence of ferroelectric polarization on $NaLnMnWO_6$ (Ln = La, Nd, Tb). A dielectric anomaly is observed just below room temperature (~270 K) for all the three compounds, which is related to change in conductivity as revealed by temperature dependent ac and dc resistivity. A pyrocurrent peak is also observed at the same temperature. However, its origin cannot be attributed to a ferroelectric transition.

Introduction

Simple perovskite oxides (ABO_3) are one of most curious and useful family of materials where both A and B cations of different valence and size can be tuned and thus providing a large number of diverse and fascinating properties such as ferroelectricity[1], ferromagnetism, piezoelectricity[2], superconductivity[3], colossal magnetoresistance[4], ionic conductivity[5] etc. Recently, several perovskite oxides such as $BiFeO_3$ and $RMnO_3$ (R = Tb, Dy) are found to exhibit magnetoelectric multiferroic properties.[6-9] In the former, the Bi^{3+} ion with lone pair electrons provides ferroelectric polarization and Fe^{3+} ions with unpaired electron provide magnetism. In the later, a cycloidal ordering of Mn^{3+} spins breaks the inversion symmetry and renders the material ferroelectric.[7] Apart from different mechanisms which provide multiferroic properties, these materials are important from the view point of potential applications in multistate computer memory devices and spintronics.[10-12]

Recently, a family of ordered perovskites having the formula, $AA'BB'O_6$ has drawn much attention because of unusual ordering of cations at both A and B site of the perovskite structure.[13,14] For example, in $NaLnMnWO_6$ (Ln = La, Nd and Tb), Na and Ln ions order at the A-site in a layered form and Mn and W ions order at the B-site in a rock salt manner.[15] Such double ordering in the stoichiometric compound is unusual[16] and is known commonly in oxygen or cation deficient compounds.[17,18] It has been suggested that the layered ordering in the present compounds gives bond instability which could be compensated by the presence of highly charged d^0 cation on one of the B-site.[14,15] In addition to this rare cation ordering, these compounds were expected to show multiferroic properties because they crystallize in polar space group $P2_1$ according to the X-ray and neutron diffraction analysis[19,20] and Mn^{2+} ions impart magnetism. In fact, these compounds show antiferromagnetic ordering of Mn-moments at low temperatures (T_N ranging from 10 to 15 K) through the Mn-O-W-O-Mn superexchange interaction.

While the common octahedral tilting in distorted perovskites results in non-polar phases, the presence of layered cation ordering in $NaLaMnWO_6$, makes these rigid units as a building block of polar structure.[21] It has been suggested that the polar nature is induced through a trilinear coupling between the two unstable tilting modes. Based on density functional theory calculations and group theoretical analysis, it has been shown that the ferroelectric polarization would be as large as 16$\mu C/cm^2$ for $NaLaMnWO_6$.[21]

In this study, we made an attempt to determine the ferroelectric polarization experimentally in $NaLnMnWO_6$ with Ln = La, Nd and Tb. Using conventional P-E loop measurements, we found that none of these compounds showed a ferroelectric loop. For further confirmation, we have employed a well-established P-E loop measurement technique, called PUND (Positive-Up and

Negative-Down).[22] This method could overcome the experimental difficulty present in the conventional P-E method due to defects, porosity or high leakage current.[23,24] We have also studied piezoelectricity, SHG[25], dielectric permittivity, dc and ac conductivity and pyroelectric current measurements for all the three synthesized compounds. We have found very similar results for all the three compounds.

Experiments

Polycrystalline samples of $NaLnMnWO_6$ (Ln =La, Nd and Tb) were synthesized by the conventional solid state route. Rare earth oxides were preheated at 900 ^{O}C for 10 hours. $MnWO_4$ was first prepared by heating appropriate amount of Mn_2O_3 and WO_3 in air at 1200 ^{O}C for 40 hours. Rare earth oxides (La_2O_3, Nd_2O_3 and Tb_4O_7), $MnWO_4$ and Na_2CO_3 were mixed stoichiometrically in an agate mortar pestle. An excess of 5wt% of Na_2CO_3 was taken to compensate the loss of sodium. The mixture was first heated at 850 ^{O}C in air, and then it was ground again, and finally sintered at 1000 ^{O}C in a forming gas (5% H_2 and 95% Ar).

Powder X-ray Diffraction data were collected by Bruker D8 Advance –X-ray diffractometer and analyzed by Rietveld method using Full-prof Professional suite. Magnetization measurements were carried out on a Quantum Design SQUID VSM magnetometer and data were collected from 2 to 300 K with the increment of 3 K/min. Electrodes were made by gold sputtering and silver paints to measure the electrical properties. P-E loop, PUND, piezoelectricity measurements were performed using Radiant technology Precision Work station. Dielectric properties were measured in Agilent E4294A impedance analyzer. Pyroelectric current was recorded in a Keithley electrometer (model 6517A) in the temperature range 10 K to 370 K. SHG measurements were done at room temperature in DCR-11 equipped with Laser of 1064 nm wavelength.[25]

Results and discussion

Results of Rietveld refinement on the room temperature powder X-ray diffraction data of $NaLnMnWO_6$ are shown in Fig. 1 (a, b and c) for Ln = La, Nd and Tb respectively. The refinements made with the $P2_1$ space group gave a better fitting with less χ^2 value compared to $P2_1/m$. This is in good agreement with the reported X-ray diffraction analysis.[15] No trace of impurity was observed for $NaNdMnWO_6$ and $NaLaMnWO_6$ whereas a little amount of Tb_4O_7 was present as a secondary phase in $NaTbMnWO_6$ as indicated by an asterisk.

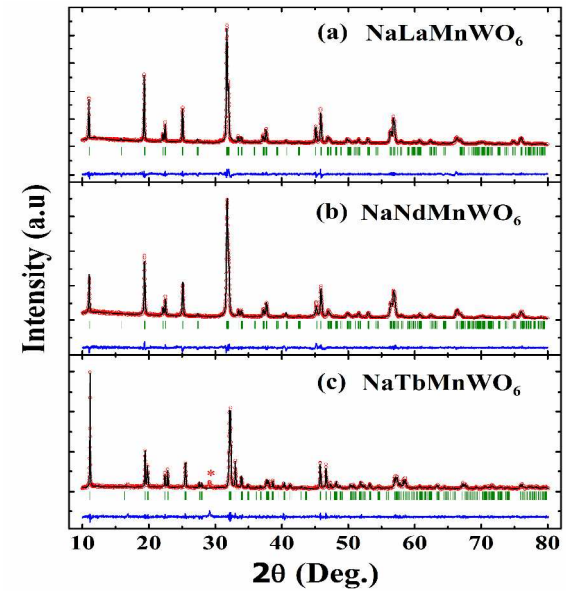

Fig. 1 Rietveld refinements on room temperature powder X-ray data of $NaLnMnWO_6$ (Ln =La, Nd and Tb). Red circles, black lines, blue lines below, green vertical lines are representing observed, calculated, difference intensity and Bragg's positions, respectively. Asterisk in fig **1(c)** shows impurity peak.

The values of lattice parameters and other structural parameters are consistent with those reported earlier.[15] Magnetization measurements confirm the magnetic ordering of Mn-ions at low temperatures (10 – 15 K) as shown in Fig. 2 (a, b and c) for $NaLnMnWO_6$ where Ln = La, Nd and Tb.

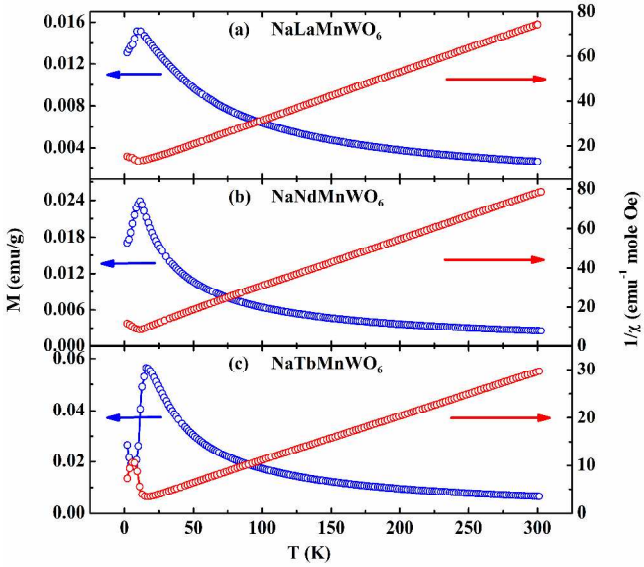

Fig. 2 Magnetization *vs.* temperature (blue circle left axis) and $1/\chi_m$ *vs.* temperature plot (red circle right axis) of $NaLnMnWO_6$ (Ln = La, Nd and Tb).

The Curie constant and the Weiss constant obtained from the Curie-Wiess fitting of the paramagnetic moment data between 150 K to 300 K, (Fig. 2), are consistent with the earlier reported values.[15]

Results of P versus E measurements carried out on $NaNdMnWO_6$ using a single wave (top panel) and PUND method (bottom panel) at several temperatures (15, 77, 150, 240, 250, 260, 270, 280 and 300 K) with voltage pulse of frequency of 1000 Hz and 10 Hz are shown in Fig. 3(a) and 3(b), respectively.

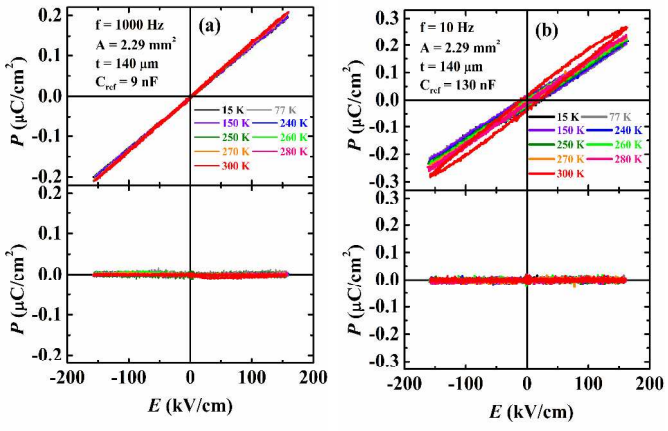

Fig. 3 P-E loop (upper panel), and PUND result (lower panel) of $NaNdMnWO_6$ measured with a voltage pulse frequency **(a)** 1000 Hz, **(b)** 10Hz. Different colors show the curve obtained at different temperature.

It can be seen that the single wave method gives either lossy or linear loop, which indicates a leaky material where other source of polarization such as capacitive and resistive dominates. With the conventional P-E method, it would be difficult to separate out intrinsic ferroelectric polarization from other sources. To determine the intrinsic ferroelectric polarization, if any, we performed the PUND measurements, which allow subtraction of extrinsic contribution arising from leakage[22,23] and the results are shown at the bottom panels of Fig. 3(a) and 3(b). It is obvious from these figures that there is no ferroelectric polarization in $NaNdMnWO_6$. Similar results were also found for the other two materials.

PUND results of $NaNdMnWO_6$ have been further analyzed from time dependent behavior of current (I).[26] In Fig. 4(a) and 4(b), upper most panels show the first negative applied electric field pulse with time. Lower panels show the response of current to the first negative pulse (black curve) and second negative pulse (red curve) with time at various temperatures at (a) 1000 and (b) 10 Hz.

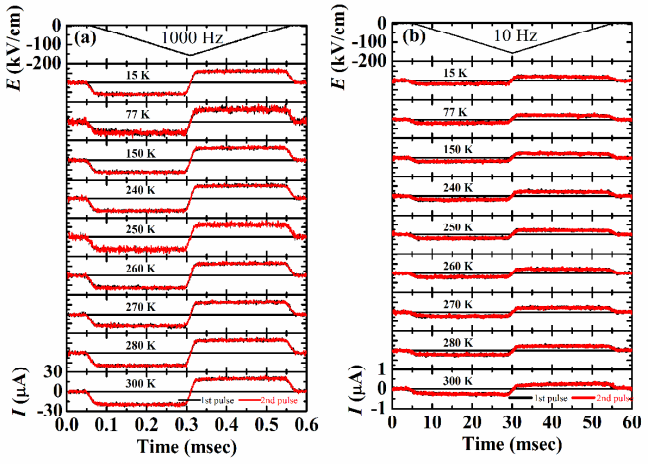

Fig. 4 Time-dependent current curves for $NaNdMnWO_6$. Upper most panels represents the 1st and 2nd electric field pulse for PUND measurement at **(a)** 1000 Hz, **(b)** 10 Hz. Lower panels represent the corresponding current responses at various temperatures. Black curves show the response of 1st voltage pulse and red curves show the response of 2nd voltage pulse.

For a ferroelectric material, we should observe a peak in the current curve in response to the first negative pulse which should be absent in the second negative pulse[27]. In the present data, we do not see any peak-like feature in both the first and second negative pulse. We have obtained similar results for positive-up pulse except the polarity and those results are not shown here for brevity. These results further confirm the absence of ferroelectricity.

As these materials are expected to show ferroelectricity from the symmetry aspects, we have carefully performed two more symmetry related experiments on $NaLnMnWO_6$ (Ln =La, Nd and Tb). Piezoelectric measurements measured at room temperature did not show any stress-strain loop.[25] SHG measurements[25,29] carried out at room temperature also showed nearly zero signals compared to KDP and urea. On the other hand, the SHG measurement on isostructural compounds $NaNdFeWO_6$ and $NaLaFeWO_6$ has been reported to show a positive SHG signal.[28] However, it is important to note that these materials also do not exhibit ferroelecticity which is in agreement with our results. The absence of ferroelectricity in these materials is in contrast to that expected based on neutron/X-ray diffraction studies and density functional theory calculations[21]. These contradicting results pose a question whether the actual crystal symmetry is polar ($P2_1$) or non-polar ($P2_1/m$ or tetragonal). The suggestion of the polar space group ($P2_1$) is obtained from the analysis of Rietveld refinement on x-ray and neutron diffraction data on polycrystalline sample and bond valence optimization using SPuDs program assuming a random distribution of the A site cation, suggesting a stable octahedral tilting ($a^-a^-c^+$) system.[19] $P2_1$ space group is expected for $a^-a^-c^+$ tilting along with both the cation ordering.[14] The present experimental results suggest that we may need to look for other tilt system with a non-polar symmetry. In addition, synchrotron x-ray and neutron diffraction data from a single crystal and/or an analysis of electron microscopy study could help the actual structure determination. In fact, transmission electron microscopy studies on related compounds have shown that the structure is not simple but incommensurately modulated.[15]

Dielectric permittivity and loss data of $NaLnMnWO_6$ (Ln = La, Nd and Tb) measured at various frequencies are shown in Fig. 5 (a, b and c) and 5 (d, e and f), respectively.

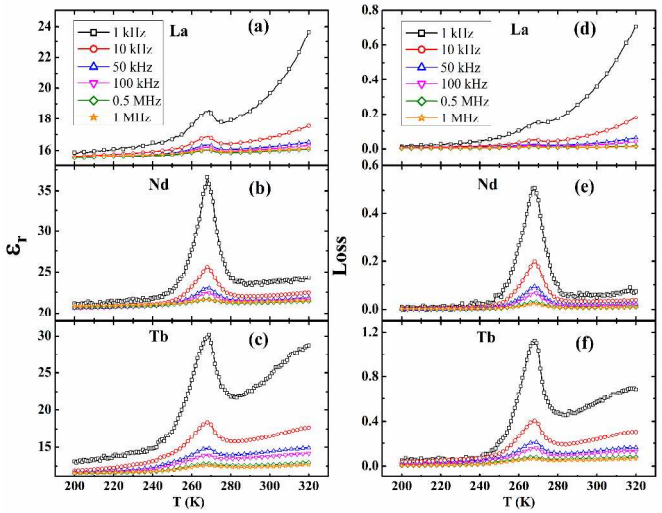

Fig 5. Variation of dielectric constant (a, b and c) and Loss (d, e and f) with temperature at various frequencies.

The value of dielectric constant is low and is almost independent of frequency and temperature up to 250 K. Intriguingly, it shows a peak at ~ 270 K with a dispersion in frequency. Correspondingly, the loss data also exhibit peaks

and similar frequency dispersion at the same temperature. Since the dielectric anomaly occurs around 270 K, one could argue that this anomaly may be related to possible frost on the sample or between the wires. As we do not see such an anomaly in other samples we suggest that this anomaly is intrinsic to the samples investigated here. At the same time, the dielectric anomaly cannot be attributed to ferroelectricity as we have not observed ferroelectric polarization over a wide range of temperatures above and below including the temperature at which the dielectric anomaly occurs. The lower value of dielectric constant and impedance spectroscopic analysis with Z' *vs.* Z" plot indicated that the space charge contributions from electrode material and grain boundaries are not significant. The dielectric anomaly temperature does not vary with frequency irrespective of the electrode materials (silver or gold) used, which indicates that the dielectric anomaly is not associated with any relaxation mechanism.

In order to understand the origin of the dielectric anomaly, temperature dependence of resistivity was measured using two-probe method by applying dc voltage. The resistivity value at room temperature is about 2 GΩ-cm for all the samples. The resistivity data for $NaNdMnWO_6$ as shown in the Fig. 6, shows a step like change and a broad peak with a thermal hysteresis near the temperature where the dielectric anomaly is seen.

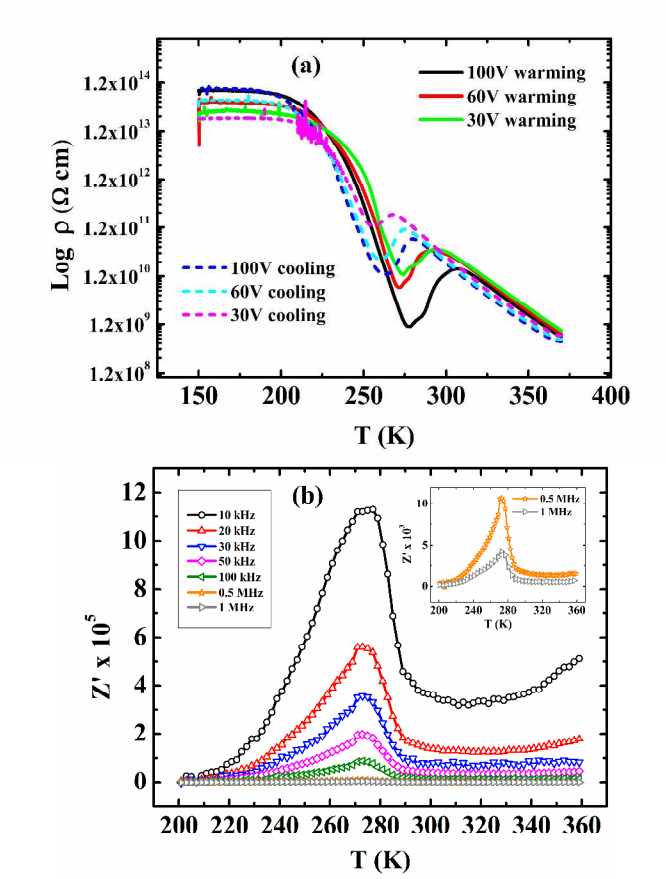

Fig. 6(a) Temperature variation of dc resistivity of $NaNdMnWO_6$. Continuous curves and dotted curves show the date measured while warming and cooling. **(b)** ac resistivity *vs.* temperature plot of $NaNdMnWO_6$ at various frequencies.

The dc conductivity data of all the samples are shown in the Fig. 7.

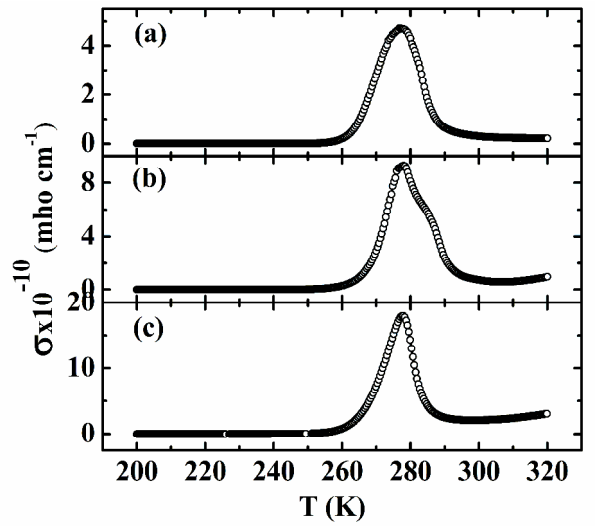

Fig. 7 DC conductivity *vs.* Temperature data while warming at 2 K/min.

It should be mentioned here that the dc conductivity does not necessarily always leads to the change in dielectric constant, but ac conductivity is related to dielectric constant through Kramers-Kornig relation.[30] To further confirm the resistive origin of the dielectric anomaly, we performed ac resistivity *vs.* temperature measurement in $NaNdMnWO_6$ and the result is shown in Fig. 6b. We see a broad anomaly in the vicinity of the dielectric anomaly temperature. Therefore, we suggest that the dielectric anomaly is due to change in conductivity which may arise from hopping of locally generated charge carrier[30,31] because of some local structural distortion and therefore the dielectric anomaly is not related to ferroelectricity. We believe that this mechanism is applicable to the other two samples as well.

We have also measured pyroelectric current as a function of temperature while warming at 4 K/min after an electric field poling across the dielectric anomaly temperature as shown in Fig. 8.

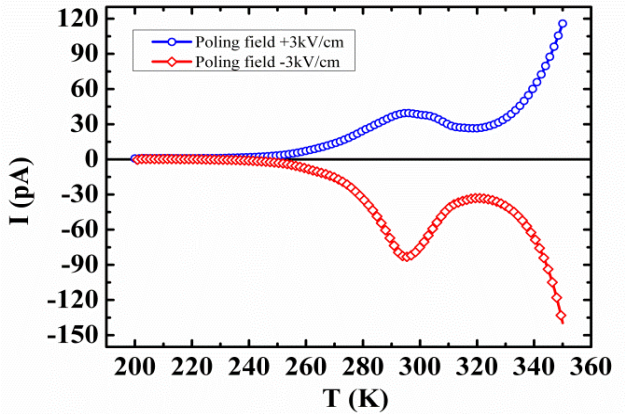

Fig. 8 Pyroelectric current data of $NaNdMnWO_6$ for positive and negative poling field.

Surprisingly, a pyroelectric current peak is seen in the vicinity of dielectric anomaly. Further, unlike the ferroelectric materials, the pyroelectric current peaks for positive and negative poling fields are highly asymmetric as depicted in Fig.8. The peak is also observed in the leakage current

measurement even after many heating and cooling cycles. It should be noted that this kind of leakage current peaks are generally not observed at the ferroelectric transition. Similar behavior is observed for the other two samples as well. The origin of such pyroelectric peaks is also related to the anomalous behavior of the resistivity and does not represent ferroelectric polarization. Our results further demonstrate that the presence of a pyroelectric current peak does not necessarily indicate ferroelectric polarization.[32]

Conclusions

Based on conventional P-E loop, PUND, Piezoelectric and SHG measurements we conclude that the $NaLnMnWO_6$ (Ln = La, Nd and Tb) materials are not ferroelectric and may not possess a non-centrosymmetric structure as well. Therefore, a further structural investigation on single crystal of this cation ordered materials is required. A substantial dielectric anomaly is found just below the room temperature for all the materials. It is suggested that the conductivity change at that temperature is responsible for such dielectric anomaly. These materials represent another clear case where the observed pyroelectric current peak does not represent ferroelectricity, cautioning the researcher that the observation of pyroelectric current peak is not always the indication of ferroelectricity.

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Notes

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