Magnetodielectric response of coexisting phases in half doped manganites

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Abstract

The magnetic field dependence of dielectric permittivity and resistivity have been measured simultaneously in two separate half doped managnites $Pr_{0.75}Na_{0.25}MnO_3$ and $Pr_{0.5}Ca_{0.5}Mn_{0.975}Al_{0.025}O_3$. A gigantic change in dielectric permittivity was detected near the percolation threshold. The hysteresis in dielectric permittivity as well as in resistivity supports the first order nature of the insulator-metal transition while the tunability is due to the coexisting of phases across the transition. A highly resistivity correlated dielectric behaviour has been observed throughout the insulator to metal transition evidencing the dielectric catastrophe phenomenon. The field dependent dielectric data are analyzed in the framework of Maxwell-Garnett theory in association with Mott-Hubbard model.

Keywords: Manganite, Multiferroics

I.INTRODUCTION

Half doped perovskite manganites of general formula $R_{0.5}A_{0.5}MnO_3$ have shown many interesting properties in the last decade, which includes the well known colossal magnteoresistnace (CMR)[1-3], orbital/charge ordering[3], phase separation[1] etc. The CMR effect, which correspond to the observation of drastic nonlinear responses to external stimulations, can be understood as a result of the intense competition between the ferromagnetic(FM)-metallic phase and antiferromagnetic (AFM) charge-ordered (CO) insulating phases[1-3] of contrasting order. The two phases in the materials are associated with a first order phase transition, in which one is growing at the expense of the other over a range of magnetic field and temperature[1-3]. In general, the magnetization and resistivity measurement are carried out with varying T, H etc to establish various intriguing phenomena associated with the systems. The increase in magnetization is due to part transformation from AFM to FM phase, while a large change in resistivity is achieved through the opening of percolating conducting path with the increasing of FM phase fraction. However, the dielectric property of such phase coexisting systems, especially in presence of high magnetic field, is rarely studied. A few investigations has been carried out recently in half doped manganites, which includes magnetically induced ferroeletricity and magnetoeletric coupling in $La_{0.5}Ca_{0.5}MnO_3$ by Giovannetti etal[4], multiferroic nature of half doped manganites[5] by Serrao etal, ordering of polarons at low temperature in $Pr_{0.5}Ca_{0.5}MnO_3$ by Levstik etal[6], glassiness in charge dynamics in a non-stoichiometric compound of $Pr_{0.5}Ca_{0.5}MnO_3$ by Karmakar etal[7] etc. All the systems are having AFM ground state and the dielectric permittivity has been studied as a function of temperature, frequency and in few cases, with small magnetic field which are further ascribed as magneto electric multiferroics. In a magnetoelectric, magnetic order is coupled to polarization and thus to the dielectric permittivity(ε) as well. Measuring ε(T) and looking for deviations around the magnetic transition can therefore be used to detect a multiferroic state. Since magnetic field effects magnetic ordering, the field also indirectly alters the dielectric permittivity of such systems and a large value of such parameter with field is a matter of concern for application purposes. Furthermore, near the percolation threshold, dielectric permittivity of the materials increases throughout IM transition if the transition is approached from the insulating side[8]. This phenomenon was called "dielectric catastrophe" by Mott[8] and was quite rarely evidenced in bulks[9,10] and thin films[11,12].

In this work, a detailed investigation of the dielectric properties of coexisting phases is carried out on two separate half doped manganites $Pr_{0.75}Na_{0.25}MnO_3$ (PNMO) and $Pr_{0.5}Ca_{0.5}Mn_{0.975}Al_{0.025}O_3$ (PCMAO), but having similar ground state(FM-M) properties[14,15]. Additionally, a distinctive evidence for dielectric catastrophe is also presented. These are excellent materials for this study as they reveal a first order Antiferromagnetic-Insulating (AFI) to Ferromagnetic-Metallic (FMM) or vice versa transition induced by magnetic field [13-15], while the I-M transition is percolative. At low temperature, the zero field cooled state of both the sample is AF-I which is rather an outcome of arrested kinetics of first order phase transformation whereas in field, they exhibits a tunable coexistence of phases of contrasting order[14,15].

II.EXPERIMENTAL

In this study we have used two single phase polycrystalline samples. The PNMO sample used in this study has been prepared by wet chemical route known as ’pyrophoric method’. Aqueous solution of the high purity Pr_6O_{11}, Na_2CO_3 and Manganese acetate were mixed together and then triethanolamine (TEA) is added (1:1:2 ratio) to make a viscous solution. The complex solution is heated at 120 ^{o}C with constant stirring to dehydrate and decompose, leaving behind organic based, black fluffy precursor powder. This powder was subsequently calcined and sintered at 700 ^{o}C and 1000 ^{o}C respectively for 3hr in air. The phase compositions were determined by an X-ray diffractometer (18 kW Rigaku Rotaflex RTC 300

RC) with Cu Kα radiation. The PCMAO sample is the same batch of the sample as used in[16,17]. The ε vs H for two samples were measured using an Impedance Analyzer (HP4192A) and a self design dielectric insert coupled to the PPMS Quantum design Cryostat(M/s. Quantum Design, USA). To test the optimal performance of the experimental set-up, a commercial KDP single crystal sample was measured and values similar to those reported in the literature was obtained. For in-field measurements of the resistivity, a standard four-probe technique is used with a commercial cryostat (Oxford Instruments Inc., UK) while the DC-magnetization were carried out using 14T PPMS-VSM.

III.RESULTS AND DISCUSSIONS

For the basic characterization of the samples, the zero field, ε(T) and resistivity(T) of the samples was measured and shown in Fig.1. A broad peak in dielectric permittivity and step in resistivity at ~ 220K (Fig.1a) depicts the CO transition of PNMO[13,14,18] and highly insulating below ~ 40K. In the low-T regime (below ~ 50K) where ε becomes frequency and T independent. The intrinsic static dielectric constant ($\varepsilon_0 = \varepsilon(T\rightarrow 0)$) can be determined directly from the data. The sharp increase of ε(ω), the onset of frequency dispersion with increasing temperature and differing in the temperatures of the maxima in tan δ (denoted T_{max}) and inflections in ε(T) rules out an intrinsic dipole response (i.e absence of any permanent dipole moment in the system), for which these features occur at the same temperature[7,19]. Furthermore, the peak corresponding to CO transition shifted with frequency (Fig.1b) which is a characteristic of relaxor ferroelectrics.

The magnetic field dependent of the above said properties in these systems has been measured at low-T. Fig.2 shows the ε and ρ vs H of PNMO sample at various representative T but below CO transition, after cooling the sample in zero field to the respective T. The ε vs H can be expressed as magnetodieletric coefficient($\Delta\varepsilon/\varepsilon(0) = [\varepsilon(H)-\varepsilon(0)] / \varepsilon(0)$). With field, the sample undergoes I to M even though the transition H is different for different T. The H dramatically increases the ε through IM transition and decreases it for MI. For instance, at 10 K, ε rises from 71 up to approx. 3200 at 7T for PNMO. A gigantic change in ε is observed in this state while ρ behaves in opposite way. This is an evidence for dielectric catastrophe phenomenon naturally taking place at the IM transition. Recently, a qualitatively similar phenomenon also has been seen in other manganites[20]. However, at other T one can see a distinguishable hysteresis signifies the FOPT in dielectric order parameter. Similar response also has been seen in PCMAO sample (not shown for conciseness).

The large value of ε in several manganites has been described by considering various models. For instance, a colossal dielectric response in $Pr_{0.6}Ca_{0.4}MnO_3$ arises from the Schottky barriers at electrical contacts[21] while similar response in La-Pr-Ca-Mn-O stems from the phase competition[22]. The effect of electrical contacts in the present work not affect so much as it's a direct contact method of measuring ε. In several phase competing systems, mostly effective media approximation is used to describe such dielectric response with respect to the controlling variables.

Quite similar albeit much smaller ρ correlated dielectric behaviour was observed in $Nd_{0.5}Sr_{0.5}MnO_3$ using magneto-optical studies[23]and discussed in terms of effective media approximation (EMA)[24]. The authors suggested that the rise in capacitance (C) can be explained as a result of increasing effective surface areas (A) of metallic clusters and decreasing the distances (d) between them (since $C = \varepsilon_0\varepsilon_r A/d$). The EMA is valid when fluctuations in the local microscopic values of dielectric permittivity are small, which can't be applied in present case as ρ of two phases differs by a huge factor ($\sim 10^6$). Furthermore, the contrasting behaviour between ρ and ε allows us to apply some different approach to describe such drastic effect in phase separated system. One such approach is the generalized Maxwell-

Garnet theory (MGT)[25] to describe such correlated but contrasting behaviour in a mixture for macroscopic analysis where the grain shape is assumed to be spherical.

When magnetic field is applied, the ferromagnetic conductive phases start to appear in antiferromagnetic matrix in the samples. The expression for effective dielectric permittivity $\varepsilon_{\mathrm{eff}}$ can thus given by[24,25];

$$\varepsilon_{eff} = \varepsilon_i + 3f\varepsilon_i \frac{\varepsilon_m - \varepsilon_i}{\varepsilon_m + 2\varepsilon_i - f(\varepsilon_m - \varepsilon_i)} \tag{1}$$

by taking the depolarization factor as 1/3 for spherical grains[28](assume both have similar grain shape). ε_i is the dielectric permittivity of the AFI phase, ε_m dielectric permittivity of the FMM phase, f is the volume fraction of the FM phase, which can be determined from the magnetization loop. Once the magnetic field is continuously increasing, f rises and finally reaches 100%. At a certain point it is no longer valid to consider a model in which FMM phase are surrounded by an AFI matrix. In fact it is rather opposite (in Fig.3c). As a consequence when the system approaches to the metal rich limit it is obvious that ε_i and ε_m should be interchanged. The higher the difference of ε between I and M phases, the larger change in ε_{eff} is expected. The subsequent field cycling at low temperature keeps the sample in a metallic state, where the sample is having a high effective dielectric permittivity. Such a high value indicates that, the capacitance and hence ε may not be associated with the area(A) and thickness(d) of the capacitor structure (as in Refs. 23 and 24), but more with the geometrical factors defined by the relative I and M phases of the system. This can also be explained in the following way; the ε is related to the electric susceptance (χ=P/E) in an isotropic material. If a conductor is having "bound" electrons in that they cannot leave the entire material, but are free to polarize across the entire length of a conductor. By applying external E, the entire conductor will polarize, such that the P causes the E inside the conductor to be zero (electrostatic equilibrium). However, in a normal dielectric, the bound electrons cannot move as far as in a conductor, they have a much smaller polarization. The definition of a dipole moment is charge times the separation distance. In a conductor/metal, the induced dipoles have distances of the magnitude of the size of the macroscopic object, which is much larger than the dipole distances of a dielectric. Hence, the polarization vectors or susceptance is therefore near infinite, and so is the relative permittivity.

Qualitative analysis of eq^n (1) indeed predicts increasing of ε_{eff} as a function of f in a phase separated samples. However, quantitative results differs with the expt. data, strongly suggests that additional mechanisms are involved as well. For instance, taking $\varepsilon_i = 163$, $\varepsilon_m = 3320$, $f = 0.37$ the resulting dielectric permittivity of PNMO at 2T(80K) (filled square in Fig.3a) will be 372, while experiment gives around 1800. Similarly in PCMAO, by taking $\varepsilon_i = 80$, $\varepsilon_m = 3960$, $f = 0.27$ the resulting dielectric permittivity at 4T(40K) (filled square in Fig.3b) will be 164, while experiment gives around 1915. Here note that, all these values specified here are derived from ε vs. H and M vs H graphs in Fig.3a and 3b. The ferromagnetic fraction f is calculated by considering the method used by Hardy *et al*[26]. It has also to be mentioned that, small modification of the M phase under applied H was recently suggested to contribute to the ε, in which the polaron activation energy (derived from the dielectric measurements) is suppressed by field[27]. Although MGT predicts additional contribution to the ε_{eff} as a volume of two fractions changes, it still cannot explain a huge value of ε of the M phase in both compounds. Therefore, microscopic contribution to the ε_{eff} has to be also taken into account. Among various proposed mechanisms of the MI transitions, the role of electron-electron interactions (Hubbard Ref. 30) in the formation of insulating (or conducting) phases has received a great deal of attention[28,29,30]. In case of our compounds also, similar mechanism leads to the screening of Coulomb interaction under H at IM transition and can be considered as so called Mott-Hubbard insulators. Also, anomalies related to ε (T) was previously observed in a nearly half doped compound[31], where it was considered as a Mott insulator close to an edge between a localized-delocalized state[31] to describe such anomalies. In the present case, the extra microscopic contribution to the electric susceptibility vis-a-vis dielectric constant can be explained by considering Mott-Hubbard mechanism[32]. Where at high Coulomb repulsion energy (insulator state), e_g electrons are localized close to Mn^{3+} ions (i.e., hopping is minimized) and formation of randomly oriented dipoles can occur of the average size *l*. Implies the huge increase of ε can be due to increase of the size of inequivalent Mn dipoles or from offcentering[33].

IV.CONCLUSIONS

In summary, an extensive dielectric properties study has been carried out in $Pr_{0.75}Na_{0.25}MnO_3$ and $Pr_{0.5}Ca_{0.5}Mn_{0.975}Al_{0.025}O_3$. The dielectric behaviour is highly correlated but in contrast in behaviour to their resistivity. The variation of dielectric permittivity with field is intrinsically associated with the coexisting phases of contrasting order. A several order increase of dielectric permittivity was found in both samples which is a benchmark in the applications of such material in current scenario. The same effect is expected to be seen in the system at IM transition induced by pressure, light and X-ray.

REFERENCES

[1] E. Dagotto, Nanoscale phaseseparation and colossal magnetoresistance (Springer-Verlag, Berlin, 2003) and references therein.

[2] Y Tokura, Rep. Prog Phys. **69**, 797 (2006).

[3] C. N. R. Rao and B. Raveau, *Colossal Magnetoresistance, Charge ordering and Related properties of Manganese Oxides* (World Scientific, Singapore, 1998).

[4] G. Giovannetti, S. Kumar, J. van den Brink and S. Picozzi, Phys. Rev. Lett **103**, 037601 (2009)

[5] C. Serrao, A. Sundaresan and C. N. R. Rao, J. Phys.: Condens. Matter, **19**, 496217 (2007).

[6] A. Levistik, C. Filipic, V. Bobnar, S. Drnovsek, J. Holc, Z. Trontelj and Z. Jaglicic, Solid State Communications, **150**, 1249 (2010).

[7] A. Karmakar, S. majumdar, S. Banerjee and S. Giri, Euro. Phys. Lett. **92**, 57009 (2010)

[8] N. F. Mott, Metal-Insulator Transition (Taylor & Francis, London, 1974).

[9] A. Pimenov, S. Tachos, T. Rudolf, A. Loidl, D. Schrupp, M. Sing, R. Claessen and V. A. M. Brabers, Phys. Rev. B **72**, 035131 (2005);

[10] T. G. Castner, Phil, Mag. B **42**, 873 (1980).

[11] J. J. Tu, C.C. Homes and M. Strongin, Phys. Rev. Lett. **90**, 017402 (2003).

[12] H. S. Choi, J. S. Ahn, J.H. Jung, T. W. Noh and D. H. Kim, Phys. Rev. B **54**, 4621 (1996).

[13] T. Tang, C. Tien, R.S. Huang, B.Y. Hou Solid State Communications **146**, 133 (2008).

[14] S. Dash, A. Banerjee and P. Chaddah, Private communication.

[15] A. Banerjee, K. Mukherjee, Kranti kumar and P. Chaddah, Phys. Rev. B **74**, 224445 (2006).

[16] S. Nair and A. Banerjee, J. Phys.: Condens. Matter **16**, 8335 (2004).

[17] S. Nair and A. Banerjee, Phys. Rev. Lett. **93**, 117204 (2004).

[18] T. Satoh, Y. Kikuchi, K. Miyano, E. Pollert, J. Hejtmaneak and Z. Jirak, Phys. Rev. B **65**, 125103 (2002)

[19] R. K. Grubbs, E. L. Venturini, P. G. Clem, J. J. Richardson, B. A. Tuttle, and G. A. Samara, Phys. Rev. B **72**, 104111 (2005).

[20] B. Kundys, N. Bellido, C. Martin and Ch. Simon, Eur. Phys. J. B **52**, 199 (2006)

[21] N. Biskup, A. de Andres, J. L. Martinez and C. Perca, Phys. Rev. B **72**, 024115 (2005).

[22] R. P. Rairigh, G. S. Bhalla, S. Tongay, T. Dhakal, A. Biswas and A. F. Hebard, Nat. Phys. **31**, 551 (2007).

[23] J. H. Jung, H. J. Lee, T.W. Noh, E. J. Choi, Y. Moritomo, Y. J. Wang and X. Wei, Phys. Rev. B **62**, 481 (2000).

[24] T. W. Noh, Y. Song, S. I. Lee, J.R. Gaines, H.D. Park and E.R. Kreidler, Phys. Rev. B **33**, 3793 (1986).

[25] R. W. Cohen, G.D. Cody, M. D. Coutts and B. Abeles, Phys. Rev. B **8**, 3689 (1973); L. D. Landau, E. M. Lifshitz and L. P. Pitaevskii, Electrodynamics of Continuous Media, 2nd Edition, Pergamonpress, 1960. pp. 42-44.

[26] V. Hardy, A. Wahl, C. Martin, and Ch. Simon Phys. Rev. B, **63**, 224403(2001)

[27] R. S. Freitas, J. F. Mitchell, and P. Schiffer, Phys. Rev. B **72**, 144429 (2005)

[28] X. Y. Zhang, M. J. Rozenberg, G. Kotliar, Phys. Rev. Lett. **70**, 1666 (1993).

[29] B. Valenzuela, S. Fratini and D. Baeriswyl, Phys. Rev. B **68**, 045112 (2003).

[30] J. Hubbard, Proc. R. Soc. London A **281**, 401 (1964).

[31] M. S. Andu jar, S. Y. Vilar, S. C. Garcia and M. A. S. Rodriguez, J. Solid State Chem. **181**, 1354 (2008)

[32] C. Aebischer, D. Baeriswyl and R. M. Noack, Phys. Rev. Lett. **86**, 468 (2001).

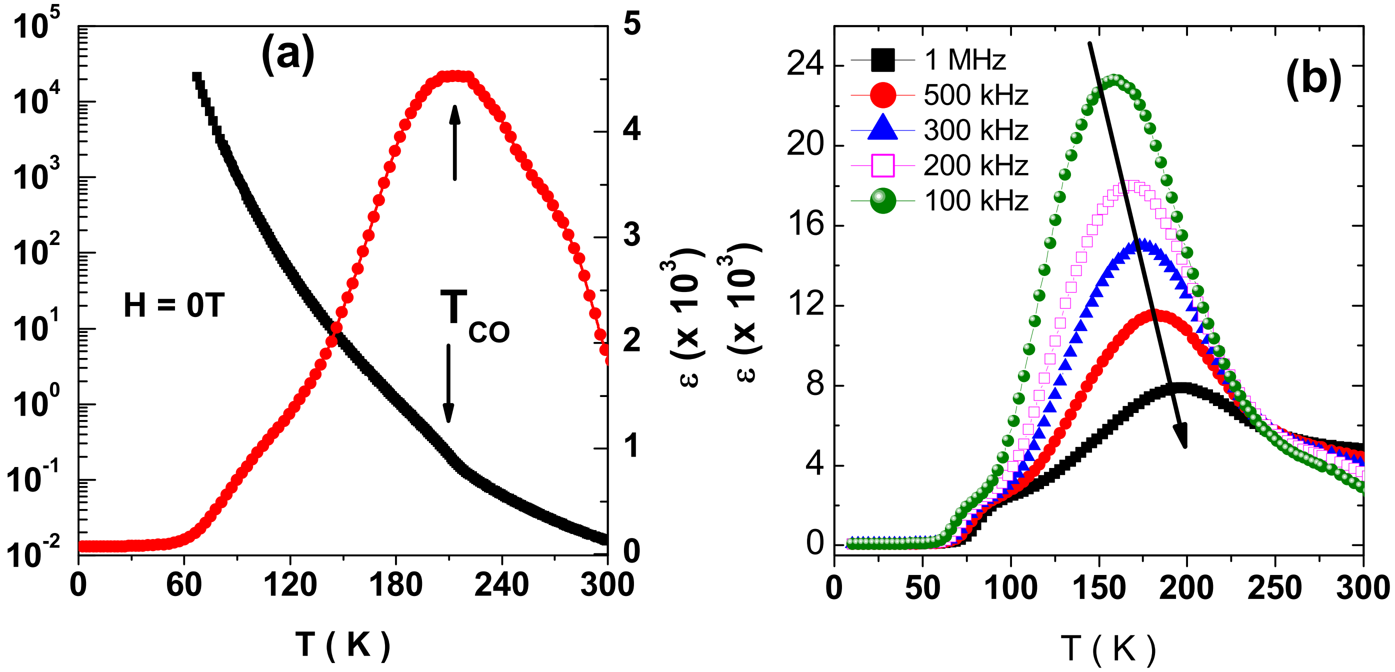
[33] V. Efremov, J. Van den Brink, D. I. Khomskii, Nature Materials **3**, 853 (2004).

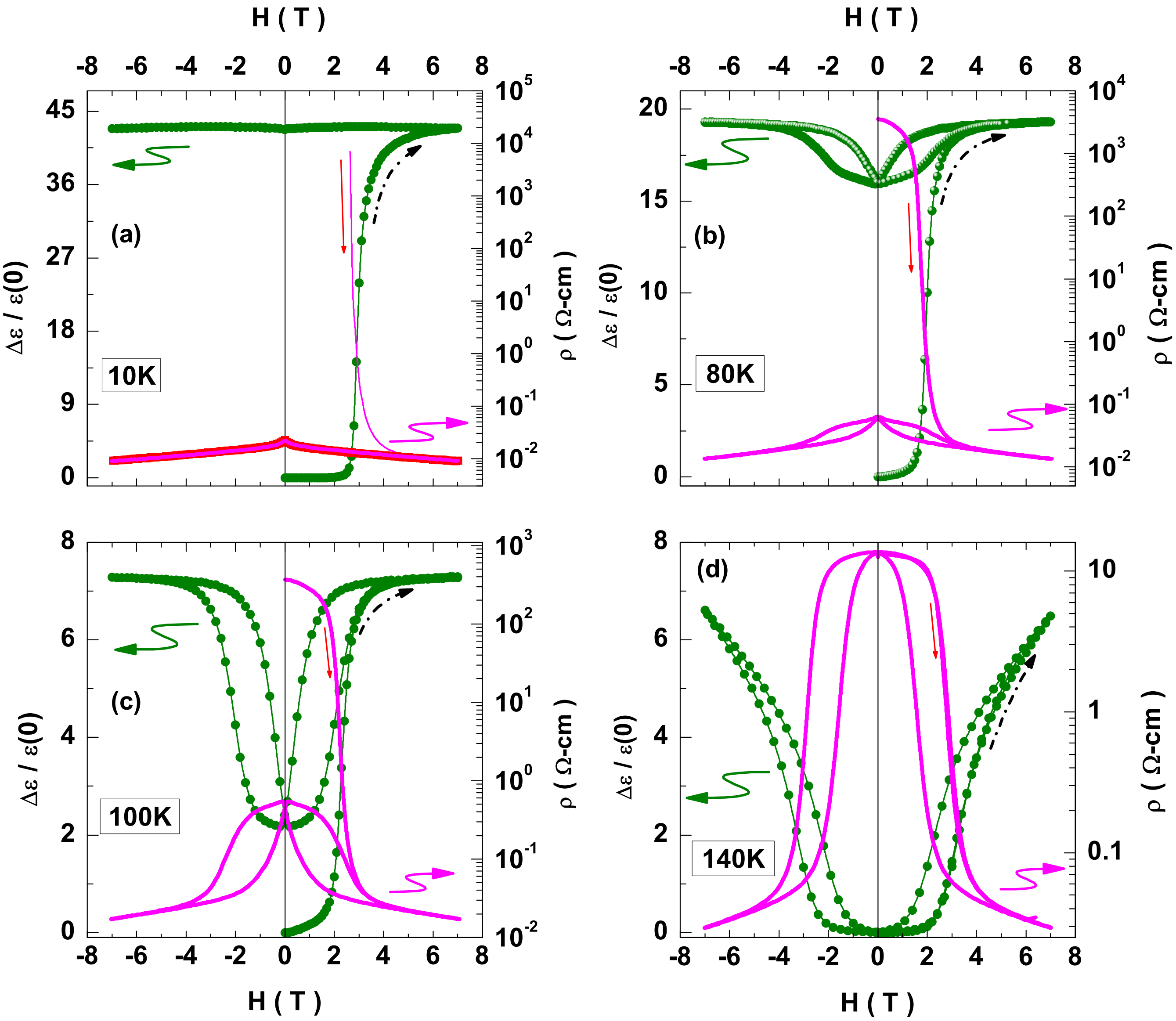
FIGURE CAPTIONS

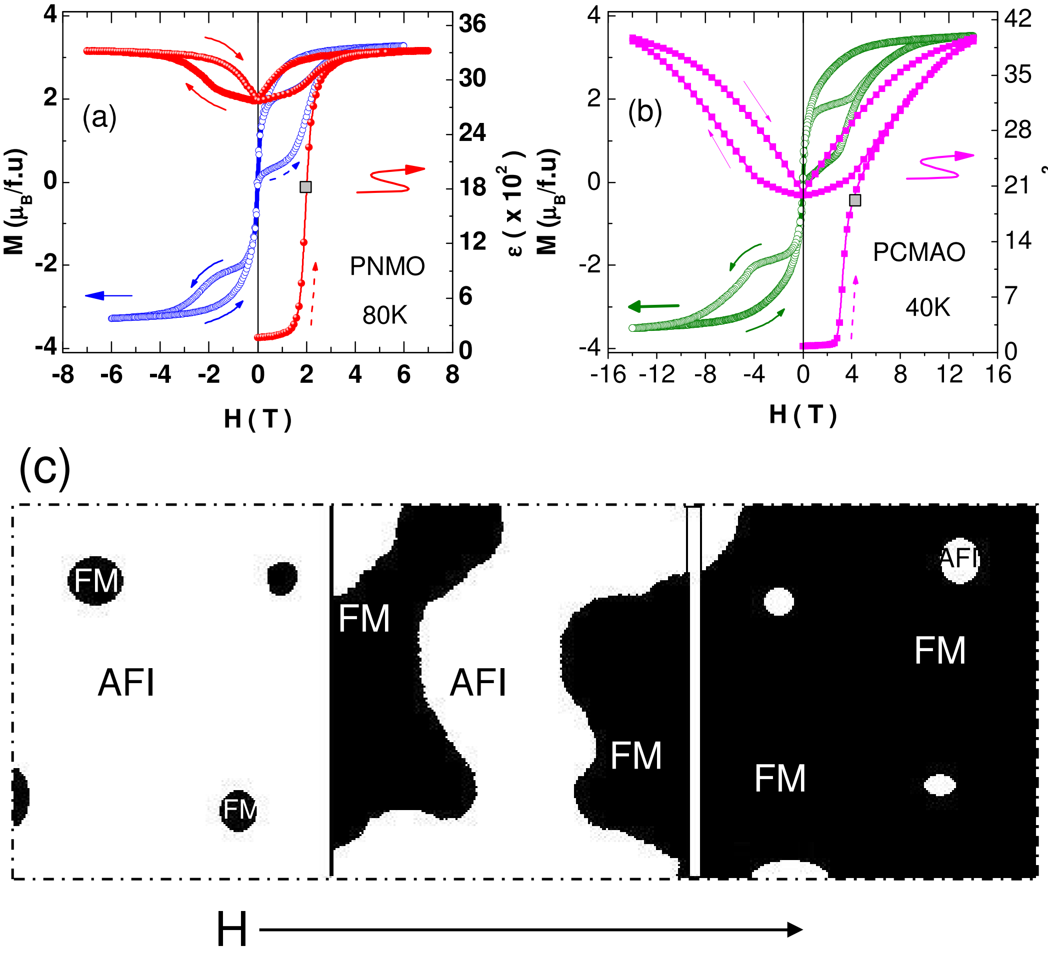
Fig.1 (a) Temperature dependent dielectric permittivity and resistivity for $Pr_{0.75}Na_{0.25}MnO_3$. (b) Frequency dependent dielectric permittivity.

Fig.2. Magnetodieletric and resistivity isotherms of $Pr_{0.75}Na_{0.25}MnO_3$ taken at 10K, 80K, 100K and 140K.

Fig.3. (a) and (b) show the effect of H on ε and M of the two samples. (c) Shows a schematic representation of evolution of the FM volume in an AFM matrix with respect to magnetic field. With increasing field, the nucleation of the FMM phase starts and finally reaches fully FMM (classical spin aligned value 3.5 μ_B/f.u.) at the higher field.


(a)
H = 0T
T_CO
ρ (Ω-cm)
10^5
10^4
10^3
10^2
10^1
10^0
10^-1
10^-2
ε (x 10^3)
5
4
3
2
1
0
0
60
120
180
240
300
T (K)
(b)
1 MHz
500 kHz
300 kHz
200 kHz
100 kHz
ε (x 10^3)
24
20
16
12
8
4
0
0
50
100
150
200
250
300
T (K)


H (T)
-8 -6 -4 -2 0 2 4 6 8
Δε / ε(0)
ρ (Ω-cm)
(a)
10K
45 36 27 18 9 0
10^5 10^4 10^3 10^2 10^1 10^0 10^{-1} 10^{-2}
(b)
80K
20 15 10 5 0
10^4 10^3 10^2 10^1 10^0 10^{-1} 10^{-2}
(c)
100K
8 6 4 2 0
10^3 10^2 10^1 10^0 10^{-1} 10^{-2}
(d)
140K
8 6 4 2 0
10 1 0.1


(a)
PNMO
80K
M (μ_B/f.u)
ε (x 10^2)
H (T)
4
2
0
-2
-4
36
30
24
18
12
6
0
-8
-6
-4
-2
0
2
4
6
8
(b)
PCMAO
40K
M (μ_B/f.u)
ε (x 10^2)
H (T)
4
2
0
-2
-4
42
35
28
21
14
7
0
-16
-12
-8
-4
0
4
8
12
16
(c)
FM
AFI
FM
FM
AFI
FM
FM
AFI
FM
FM
H