

# **Tunable competition and possible coexistence of magneto-electric phases in a charge ordered manganite**

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The magnetoelectric (ME) effect, i.e., cross control of magnetization (electric polarization) by an external electric (magnetic) field, may introduce a new design principle for novel spin devices. However, it has been a long-standing challenge to enhance the magnetoelectric effect. There are two known magnetoelectric effects: a conventional linear magnetoelectric effect in a centrosymmetry-broken magnet and a recently explored nonlinear magnetoelectric effect associated with a magnetic phase transition. To enhance the ME signal, effective control of a phase competition has recently been revealed as a promising approach. Here, we report the magnetic field control of the distinct ME phases in a charge ordered magnet  $\text{Pr}_{0.75}\text{Na}_{0.25}\text{MnO}_3$ , in which an antiferromagnetic (AFM) phase is competing with a ferromagnetic (FM) phase. Charge ordered magnetic compounds are a far more promising class of materials with potentially large magnetoelectric coupling. The material is prepared by wet chemical route at low sintering time and temperature in order to maintain the Na stoichiometry. The phase purity and structure is well studied through different techniques. The temperature evolution of resistivity and dielectric shows anomaly at charge ordering (CO) transition. With rise in temperature raises the dielectric parameter upto CO and then decreases. The rise in this region is probably due to the formation of polar regions. However, at different frequency, the slope change in dielectric permittivity and peak in loss tangent are uncorrelated signifies this system to be a relaxor. The magnetic field dependent dielectric behavior is highly correlated but in contrast to their resistivity. Surprisingly, the dielectric parameter follows the magnetic signal. The variation of dielectric permittivity with field is intrinsically associated with the coexisting phases of contrasting order. However, the ground state of this system is proved to be ferromagnetic. Using suitably experimental protocol the magnetic phases as well as electronic phases can

be tuned effectively at low magnetic field vis-à-vis to enhance the ME signal. Moreover, the FM in the proximity of AFM phase enhance the functionality of this materials with a several order in the ME parameter. The apparent change in ME signal in accordance with macroscopic phase competition are modelled through Maxwell's dynamical theory. We envisage that this short of studies will renders valuable information for other materials which shows similar behavior.

***Keywords: Magnetolectric, manganite, competing phase, functional, spin device***

[1] DAGOTTO, E., 2003. Nanoscale Phase Separation and Colossal Magnetoresistance (Springer-Verlag, Berlin, 2003), and references therein.

[2] DASH, S., BANERJEE, A., & CHADDAH, P., 2013. Magnetodielectric response of coexisting phases in half doped manganites. *JAP*, 113, 17D912.

[3] SATOH, T., KIKUCHI, Y., MIYANO, K., & JIRÁK, Z., 2002, Irreversible photoinduced insulator-metal transition in the Na-doped manganite  $\text{Pr}_{0.75}\text{Na}_{0.25}\text{MnO}_3$ , *Phys. Rev. B* 65, 125103

[4] LANDAU, L. D., 1960. *Electrodynamics of Continuous Media*, 2nd ed. (Pergamon Press, 1960), pp. 42–44.

[5] COHEN, R. W., CODY, G. D. COUTTS, M. D. & ABELES, B. 1973, Optical Properties of Granular Silver and Gold Films, *Phys. Rev. B* 8, 3689-3701

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# Outline

- a] Magneto-electric Multiferroics
- b] Half doped Manganite
- c] Instrumentation
- d] Results
- e] Discussions with Theoretical Modelling
- f] Conclusions
- g] Future Aspects



# Magneto-electric Multiferroics

## Multiferroics:

*"Crystals can be defined as multiferroic when two or more of the primary ferroic properties [...] are united in the same phase."*

Primary ferroic  $\leftrightarrow$  formation of **switchable** domains:

Excludes anti-ferroic forms of ordering

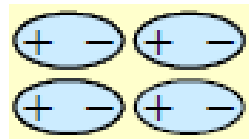
### Ferromagnetism

Spontaneous magnetization



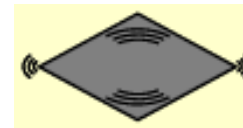
### Ferroelectricity

Spontaneous polarization



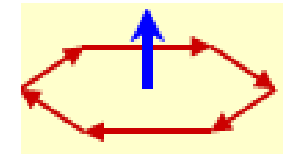
### Ferroelasticity

Spontaneous strain



### Ferrotoroidicity

Spontaneous magnetic vortex

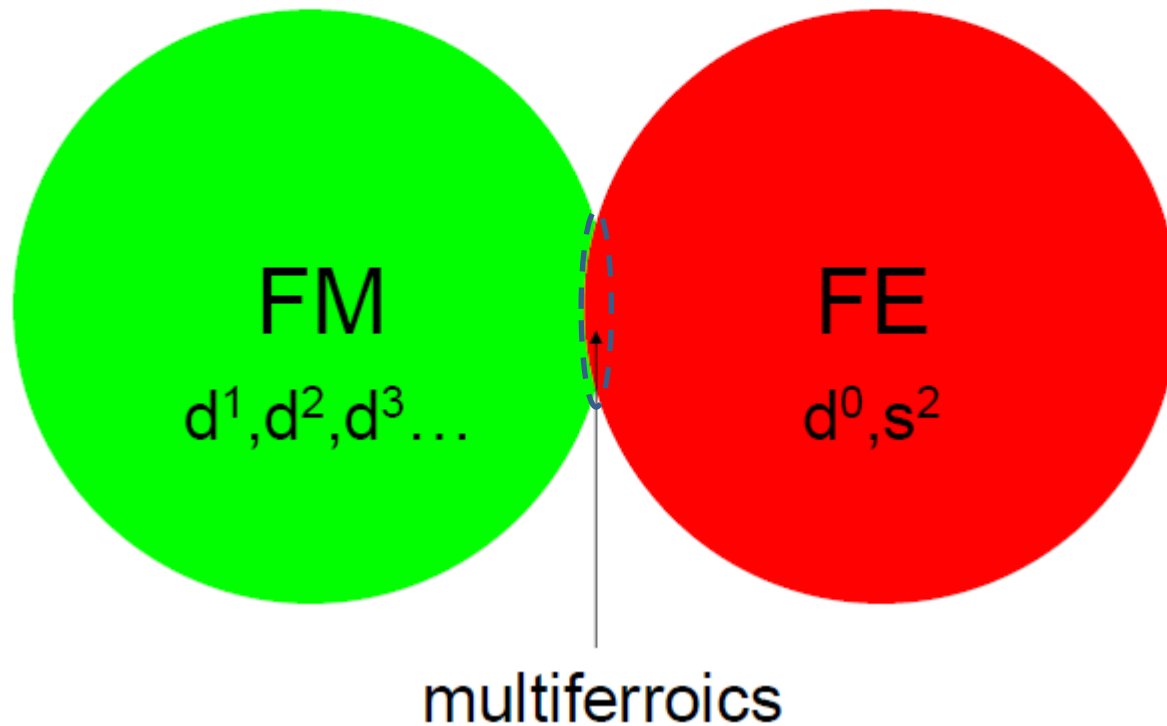


## Extension to anti-ferroic forms of ordering:

Compounds consisting of multiferroic sublattices (one or more of) whose primary ferroic properties cancel in the macroscopic crystal

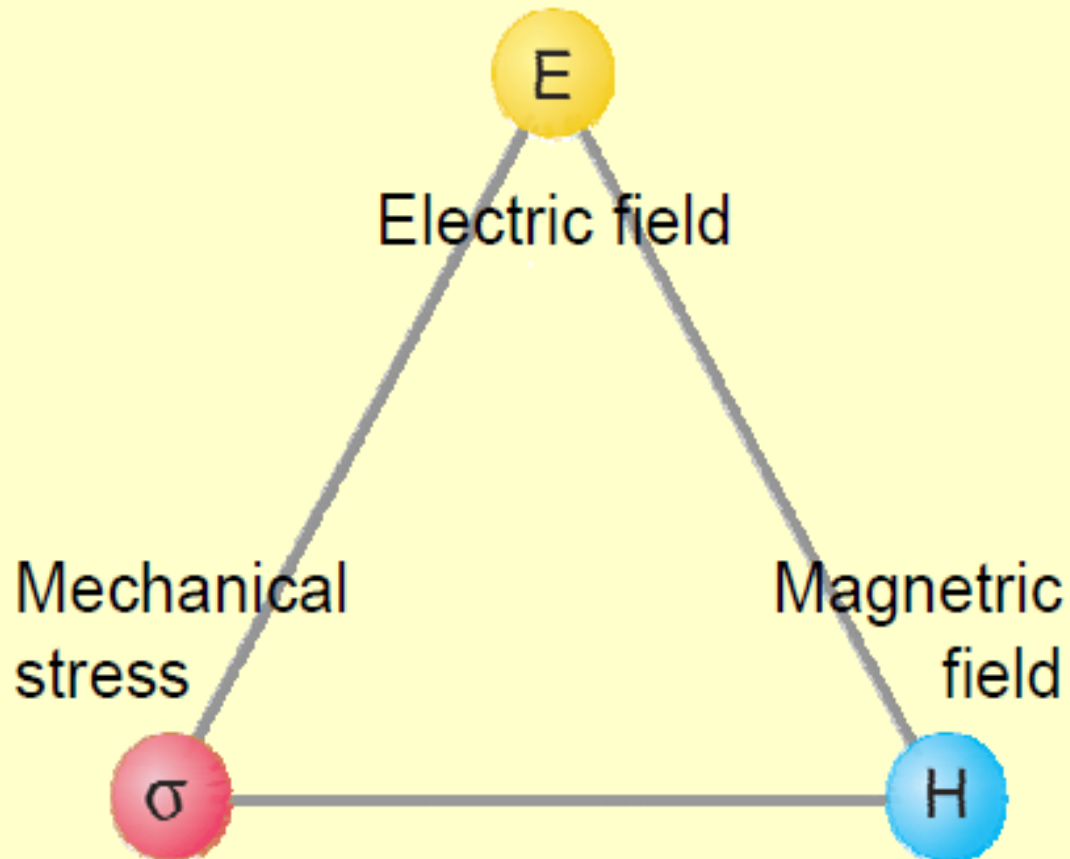
# Magneto-electric Multiferroics

No chemistry between  
magnetism and ferroelectricity

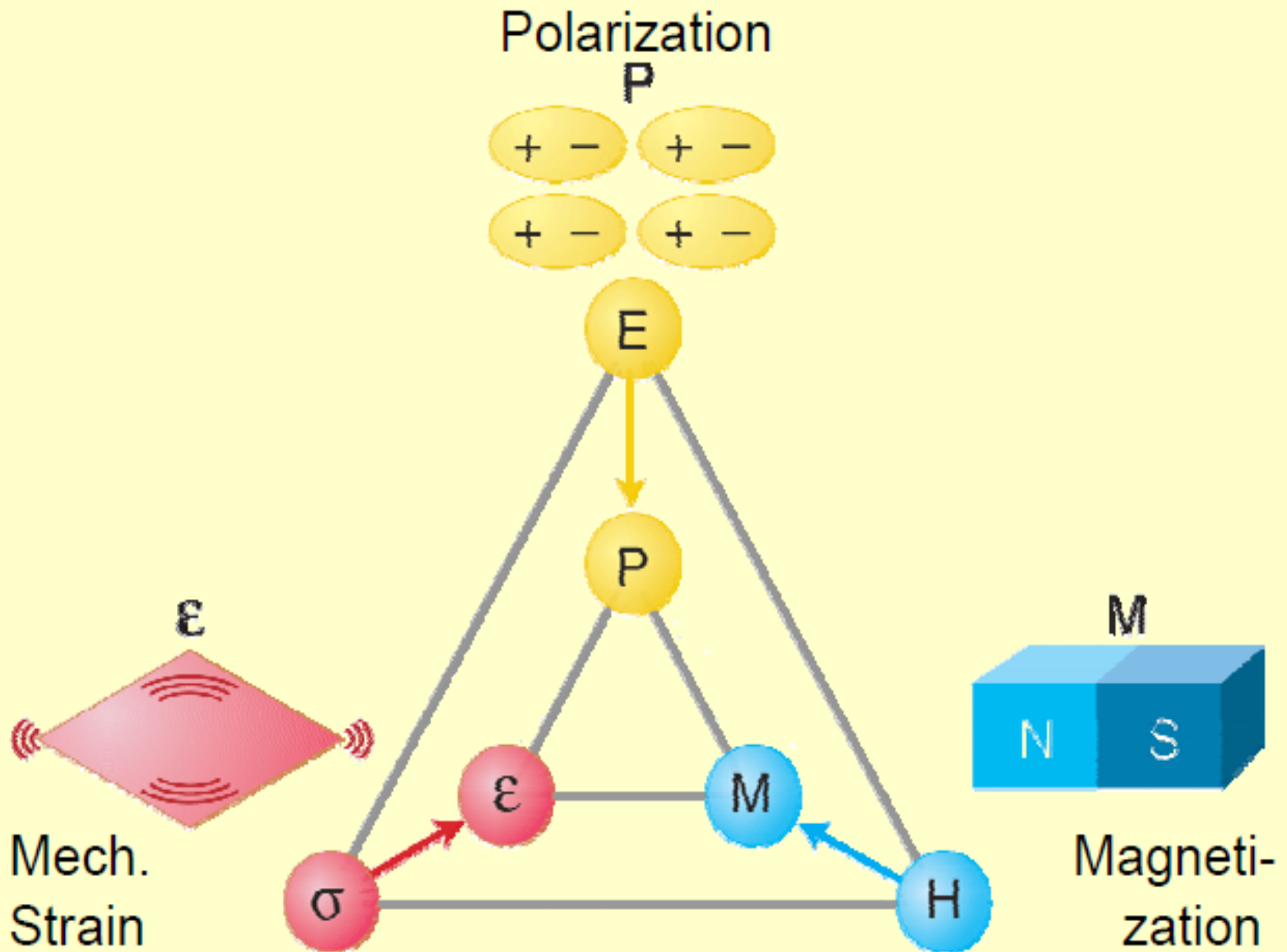


# Magneto-electric Multiferroics

## Idea of Magneto-electric effect



# Magneto-electric Multiferroics







# Magneto-electric Multiferroics

## Quantification

Free energy of magnetoelectric materials with “mixed terms” in E and H:

$$F(E_i, H_j) = -\alpha_{ij} E_i H_j - \frac{1}{2} \beta_{ijk} E_i H_j H_k - \frac{1}{2} \gamma_{ijk} E_i E_j H_k$$

**Magnetization:  $M(E) = -dF/dH$**

**Electric polarization:  $P(H) = -dF/dE$**

⊗ Requires breaking of time reversal and space-inversion symmetries

- ⊗ Linear magnetoelectric effect:  $P_i = \alpha_{ij} H_j$ ;  $M_j = \alpha_{ij} E_j$
- ⊗ Higher order terms for  $\beta \neq 0$ ,  $\gamma \neq 0$



**Not all magnetoelectric are multiferroics !**

**e.g:  $\text{Cr}_2\text{O}_3$  is a magnetoelectric antiferromagnet without electric ordering**



**Not all multiferroics are magnetoelectric !**

**e.g: Hexagonal  $\text{YMnO}_3$  is a ferroelectric antiferromagnet in which the magnetoelectric effect is forbidden by symmetry**



**All ferroelectric and ferromagnets can be magnetoelectrics**

**e.g:  $\text{Ni}_3\text{B}_7\text{O}_{13}$ !**

# Magneto-electric Multiferroics

## Limitations of the magnetoelectric effect:

Cannot be larger than the geometric mean of electric and magnetic permeability

$$\alpha_{ij}^2 < \chi_{ii}^e \chi_{jj}^m$$

### The magnetoelectric effect is small!

- Maximum value in  $\text{Cr}_2\text{O}_3$ :  $4.13 \text{ pT/Vm}^{-1}$   
(corresponding to reversal of one in a million spins at  $10^6 \text{ V/cm}$ )
- Record value found in  $\text{TbPO}_4$  :  $36.7 \text{ pT/Vm}^{-1}$

### Other problem:

- Limited choice of compounds
  - No general theoretical concept
- Decline of research activities after 1973



# Magneto-electric Multiferroics

## Single phase multiferroics: Overview

- **Perovskite type:**

$ABO_3$ ,  $A_2B'B''O_6$  (e. g.,  $BiFeO_3$ ,  $TbMnO_3$ )

- **Hexagonal structure:**

$RMnO_3$  with  $R = Sc, Y, Ho-Lu$

- **Boracites:**

$M_3B_7O_{13}X$  with  $M = Cr, Mn, Fe \dots$ ;  $X = Cl, Br, I$

- **Orthorhombic  $BaMF_4$  compounds**

$M = Mg, Mn, Fe, Co, Ni, Zn$

and further ones (about 100)

- **Non-multiferroic magnetoelectrics:**

$GdFeO_3$ ,  $LuFe_2O_4$

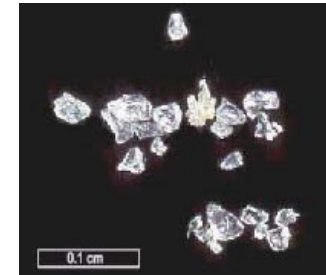
Multiferroics “unusual”  
because they circumvent the  
 $d^0 / d^n$  problem [1]

Most are **anti-ferroic** in one of  
the orders (magnetic / electric)  
→ small magnitude of  $M$  or  $P$

Very rare: **RT multiferroics**  
( $BiFeO_3$ : ferroelectric + antif.mag)

## Three natural crystal

Congolite  
 $Fe_3B_7O_{13}Cl$



Hubnerite  
 $MnWO_4$



Chambersite  
 $Mn_3B_7O_{13}Cl$

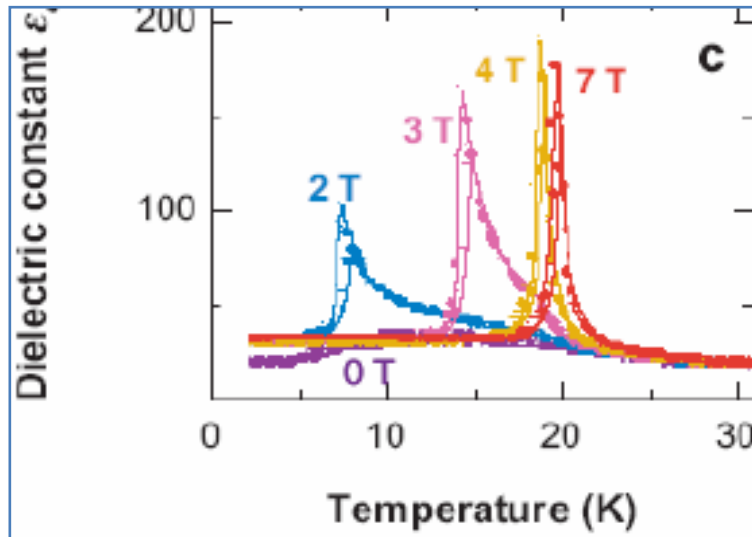


[1] C. Ederer and N. A. Spaldin, *Curr. Opin. Sol. Stat. Mat. Sci.* 9, 128 (05)

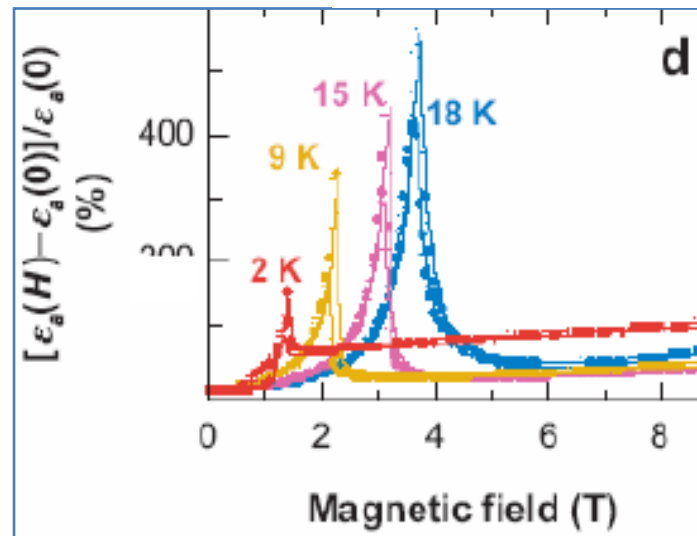
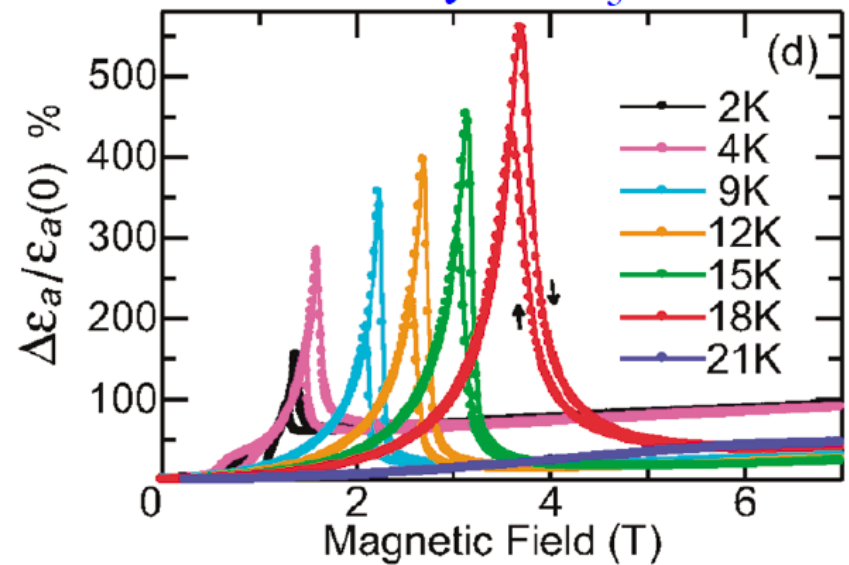


# Magneto-electric Multiferoics

Magnetic control of dielectric properties



Giant magnetocapacitance effect in DyMnO<sub>3</sub>

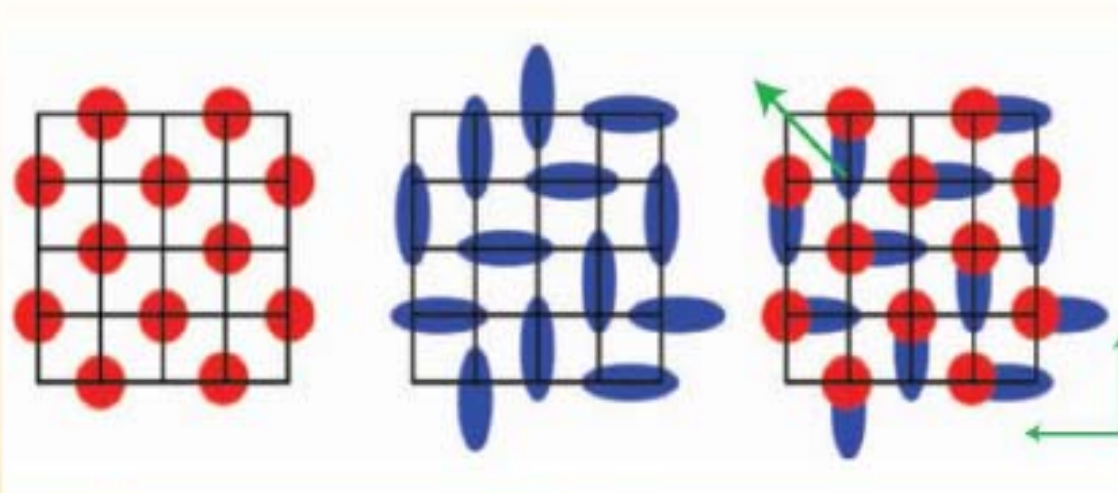


# Magneto-electric Multiferroics

## Charge-ordered compounds

Transition metal oxides (e. g.  $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ ):

$e_g$  electrons order in insulating phases



a) "site-centered"

b) "bond-centered"

c) intermediate

(a)  $\text{Mn}^{4+}$  order or  
(b) electron hole  
at the O ?

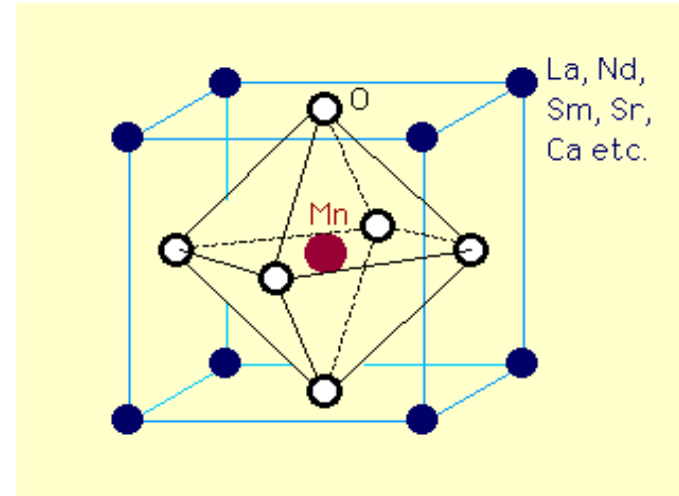
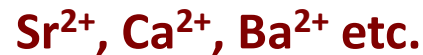
$\Omega$  Intermediate  
case (c) with  
broken space  
inversion  
symmetry



# Half doped Manganite



**R** is the rare earth element and **A** is alkali/alkaline earth element.



Perovskite structure

⇒ Hole doping : where %  $Mn^{4+} = x$        $x = 0.5$  (half doped)

Threshold for  $Mn^{4+}$  : Ferromagnetism > (6-8) %  $Mn^{4+}$

Metallicity > (12-16) %  $Mn^{4+}$

➤ Presence of  $Mn^{4+}$  gives rise to ferromagnetism, Metal insulator transitions, Colossal Magneto-resistance (CMR) , Charge Ordering (CO), Electronic Phase Separation (EPS) etc.

# Half doped Manganite

## Charge Ordering (CO)

- $\text{Mn}^{3+}$  &  $\text{Mn}^{4+}$  ions order into different planes.
- Electron localisation.
- The kinetic energy of the charge carriers loose out to the coulomb energy
- Resistivity shows a sharp increase at the charge ordering temperature
- Can be melted by large magnetic field, electric field pressure etc.

## Phase separation/phase coexistence

- Usually, simultaneous coexistence of FM metallic and AF insulating regions.
- origin in the unusual proximity of free energy of these very distinct FM and AF states.
- give rise to different interesting physics: unusual step in MH isotherms at low-T, CMR etc.





# Half doped Manganite

## Colossal magneto-resistance (CMR)

Magneto-resistance (MR) is the relative change in the electrical resistivity of a material produced on the application of magnetic field.

$$\text{MR} = (\Delta\rho/\rho(0)) = [\rho(H) - \rho(0)]/\rho(0)$$

$\rho(H)$  and  $\rho(0)$  are the resistivity in presence and absence of H.

### CMR can be classified into two types:

**CMR1** → Magnetic-field-induced transition from charge-ordered AF insulating state to a FM metallic state. This transition is of 1<sup>st</sup> order in nature and CMR is achieved through opening of percolative conducting path with the increase of coexisting FM-M phase fraction.

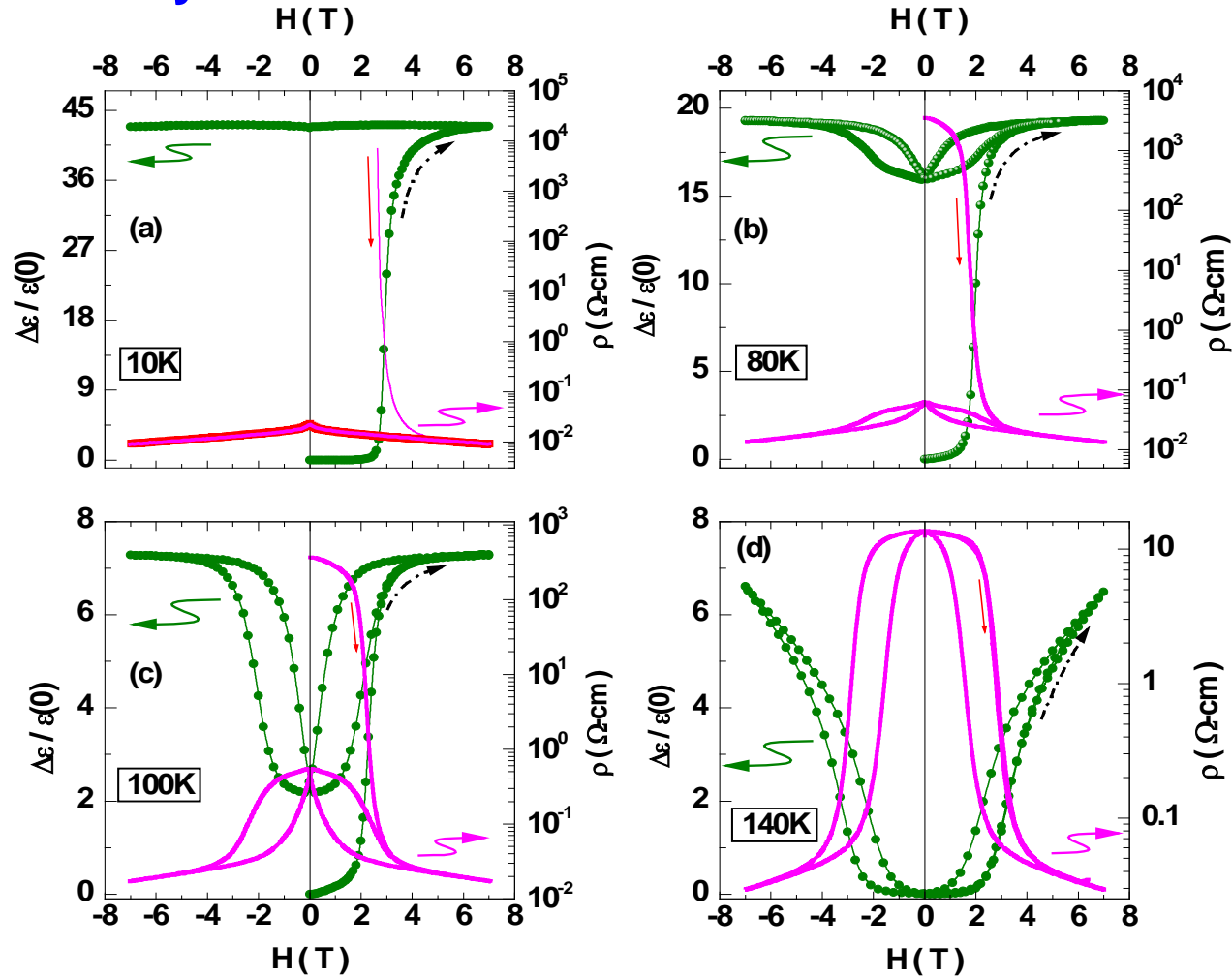
**CMR2** → Due to suppression of spin fluctuation by an applied magnetic field around  $T_C$  which favors Double Exchange mechanism.



## Magnetodielectricity:

## Simultaneous measurement

PNMO



## Resistivity correlated dielectric behaviour



# Conclusions

- **An extensive dielectric properties study has been carried out in  $\text{Pr}_{0.75}\text{Na}_{0.25}\text{MnO}_3$**
- The dielectric behavior is highly correlated but in contrast resistivity
- The variation of  $\epsilon$  with H is intrinsically associated with the coexisting phases and several order increase of  $\epsilon$  is an evidence for dielectric catastrophe at IM transition
- **In both materials, due to the application of H, the microscopic metallic phases gets created by overcoming the coulomb repulsion energy, which then additionally contribute to the magneto-dielectric effect through MGT theory.**
- Macroscopic MGT and extended Mott-Hubbard theory jointly are proposed to describe the experimental results



# Future Aspects

**i] The dielectric catastrophe effect is expected to be seen in the system at IMT induced by pressure, light and X-rays. Check?**

**ii] In light of unique resistivity correlated behaviour of dielectric permittivity near IM transition, it may be interesting to see how much dielectric properties of other manganites are correlated with the colossal magnetoresistance effects in these materials. Try....**

**The quest for compounds uniting strong ferroelectricity and strong ferromagnetism at 300 K is still far from being solved!**



# Thank You!

