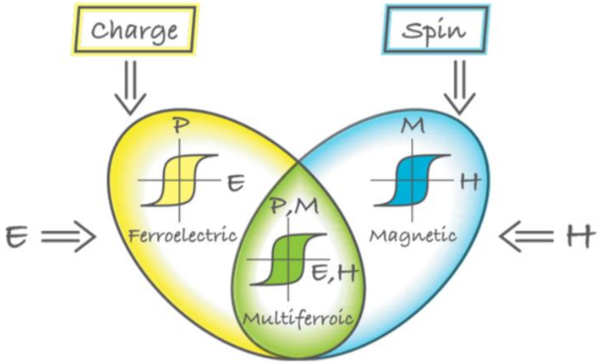
Role of Antisite Disorder in $MnSb_2Se_4$: *Multiferroicity* vs. *Spin-glass*

R Kumar and A. Sundaresan

School of Advanced Materials and Chemistry & Physics of Materials Unit, JNCASR, Bangalore

Multiferroicity

Materials that exhibit more than one primary ferroic properties, are called multiferroics.
In our case, magnetic and electric properties are coupled to each other.

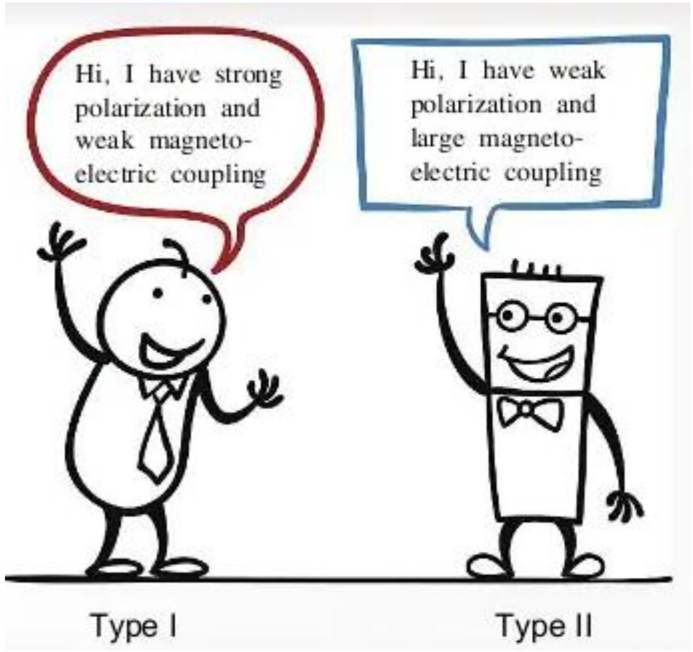


Type I

- Ferroelectricity and magnetism have different origin.
- **Origin of ferroelectricity:**
  - ⁎ Lone-pair effect,
  - ⁎ Geometrical frustration
  - ⁎ Charge ordering

Type II

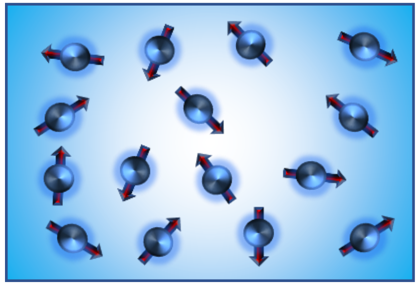
- Ferroelectricity originates from magnetism.
- **Mechanism of ferroelectricity:**
  - ⁎ Exchange striction
  - ⁎ Inverse DM interaction
  - ⁎ Spin dependent *p-d* hybridization.



$BiFeO_3$ $TbMnO_3$

Spin-glass

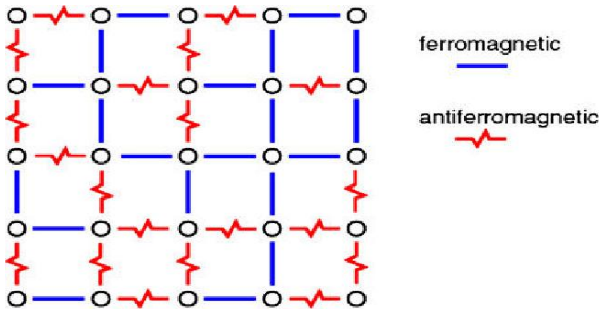
Spin-glass can be defined as a state having a large number of degenerate ground states which has spins frozen in random directions below a critical temperature.



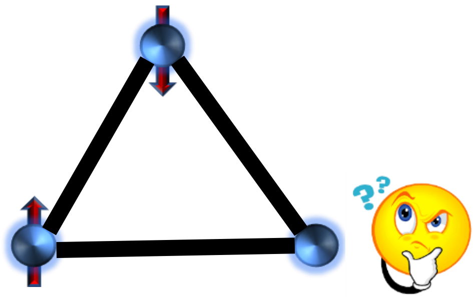
Ingredients of Spin-glass

1. Disorder

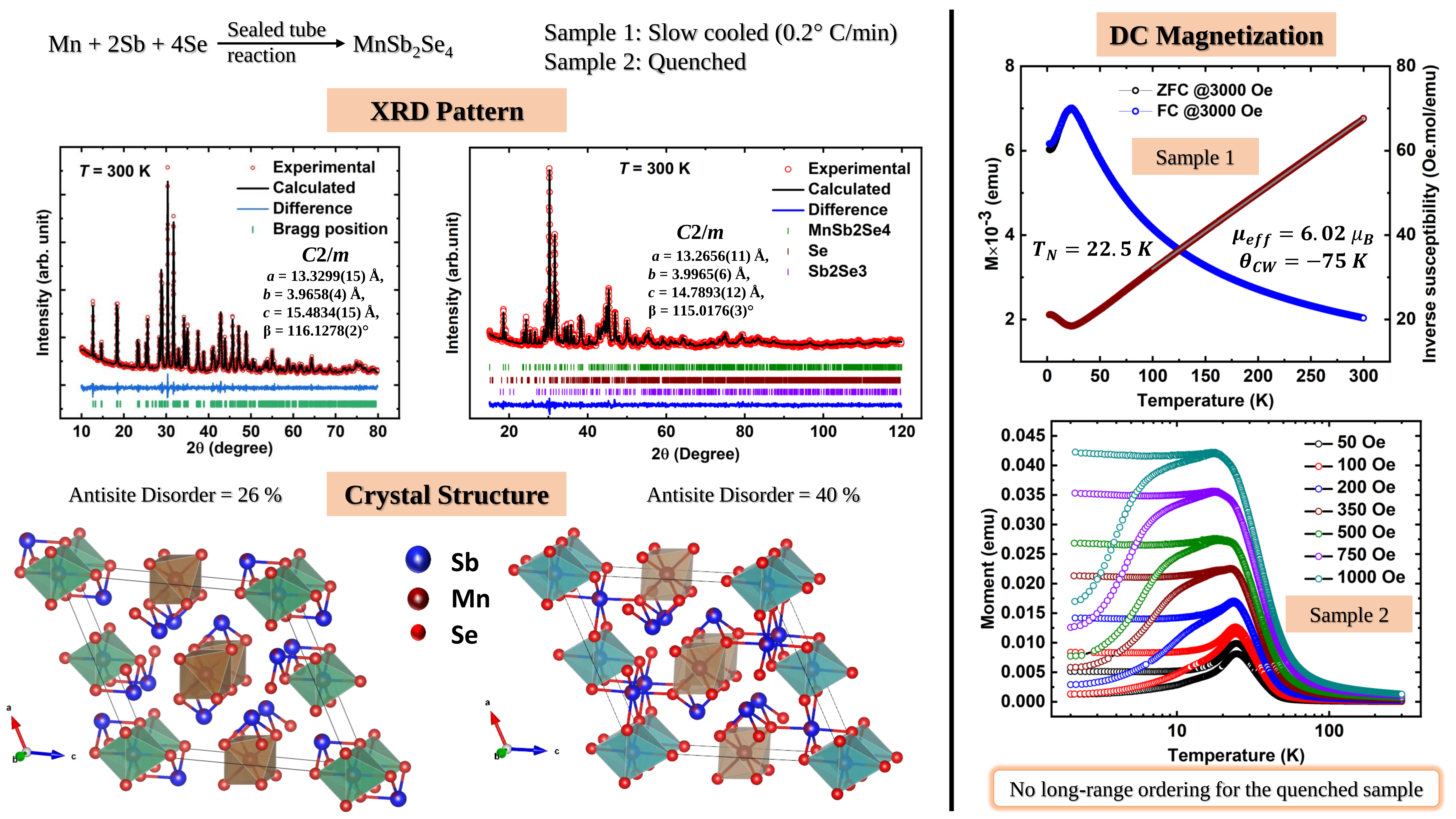
Can be due to site randomness or bond randomness. E.g.: $Cu_{1-x}Mn_x$, $Fe_{1-x}Mn_xO_3$



2. Frustration

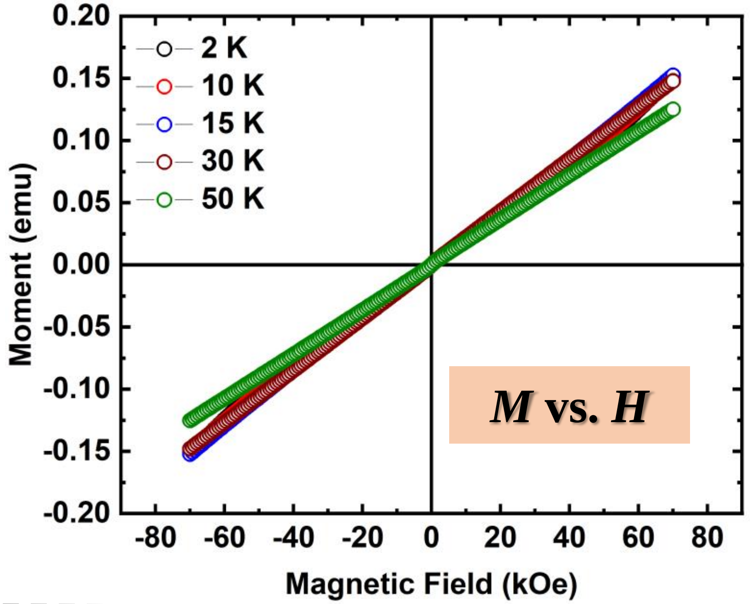


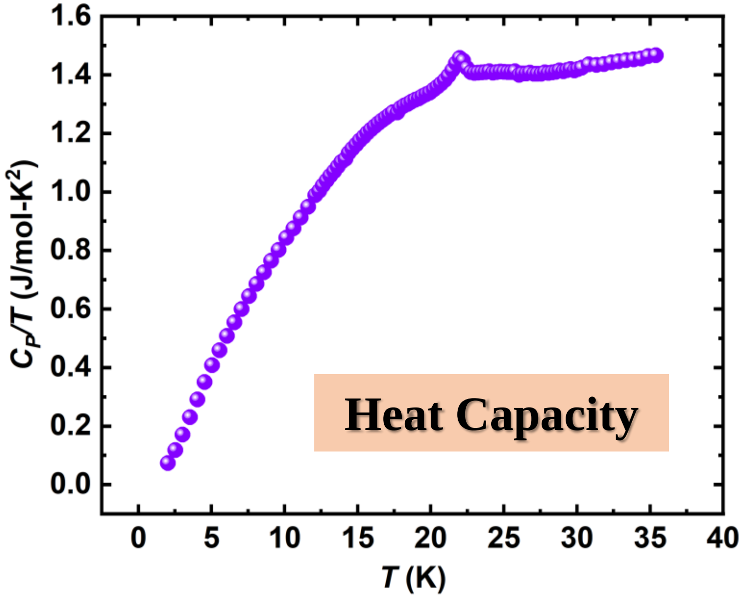
Lattice geometry inhibits ordered configurations.
Simplest example: Triangular lattice with antiferromagnetic ordering. E.g.: $Li_2Mn_3O_7$

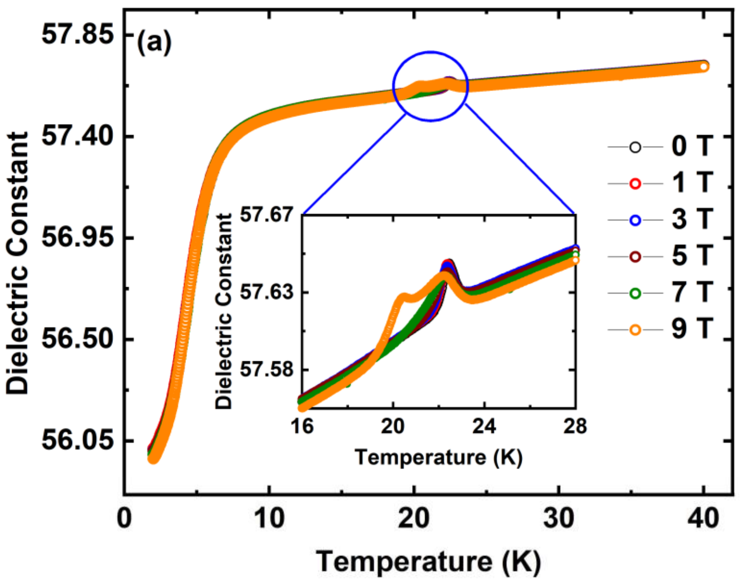


Mn + 2Sb + 4Se
Sealed tube reaction
MnSb2Se4
Sample 1: Slow cooled (0.2° C/min)
Sample 2: Quenched
XRD Pattern
T = 300 K
Experimental
Calculated
Difference
Bragg position
C2/m
a = 13.3299(15) Å,
b = 3.9658(4) Å,
c = 15.4834(15) Å,
β = 116.1278(2)°
Intensity (arb. unit)
2θ (degree)
T = 300 K
Experimental
Calculated
Difference
MnSb2Se4
Se
Sb2Se3
C2/m
a = 13.2656(11) Å,
b = 3.9965(6) Å,
c = 14.7893(12) Å,
β = 115.0176(3)°
Intensity (arb.unit)
2θ (Degree)
Antisite Disorder = 26 %
Crystal Structure
Antisite Disorder = 40 %
Sb
Mn
Se
DC Magnetization
ZFC @3000 Oe
FC @3000 Oe
Sample 1
T_N = 22.5 K
μ_eff = 6.02 μ_B
θ_CW = −75 K
M×10^-3 (emu)
Inverse susceptibility (Oe.mol/emu)
Temperature (K)
50 Oe
100 Oe
200 Oe
350 Oe
500 Oe
750 Oe
1000 Oe
Sample 2
Moment (emu)
Temperature (K)
No long-range ordering for the quenched sample

Magnetic and Dielectric Properties of Sample 1

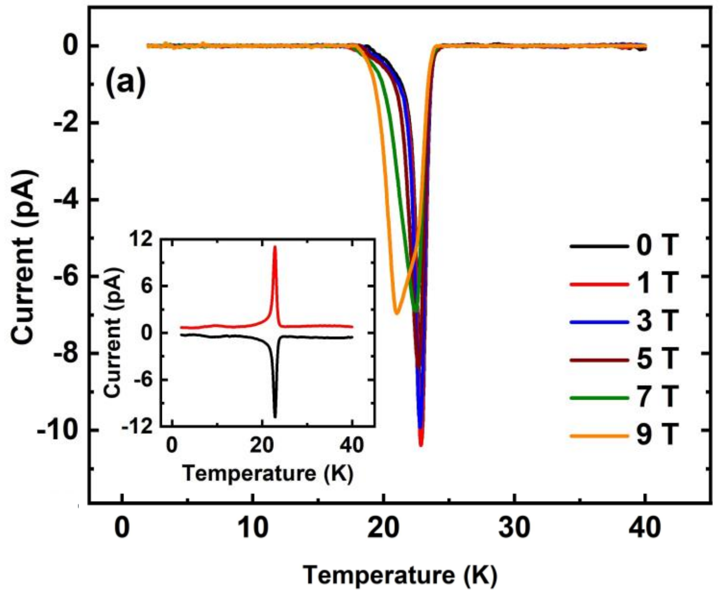




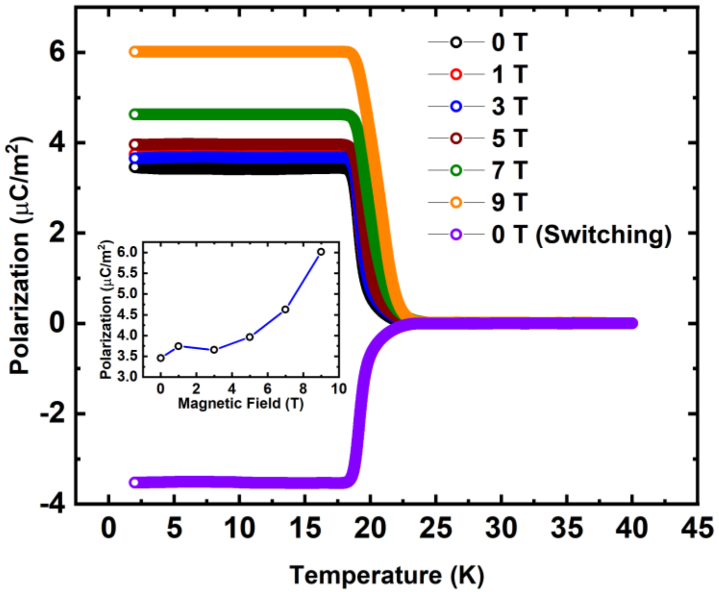


Dielectric Measurements

Pyroelectric Measurement

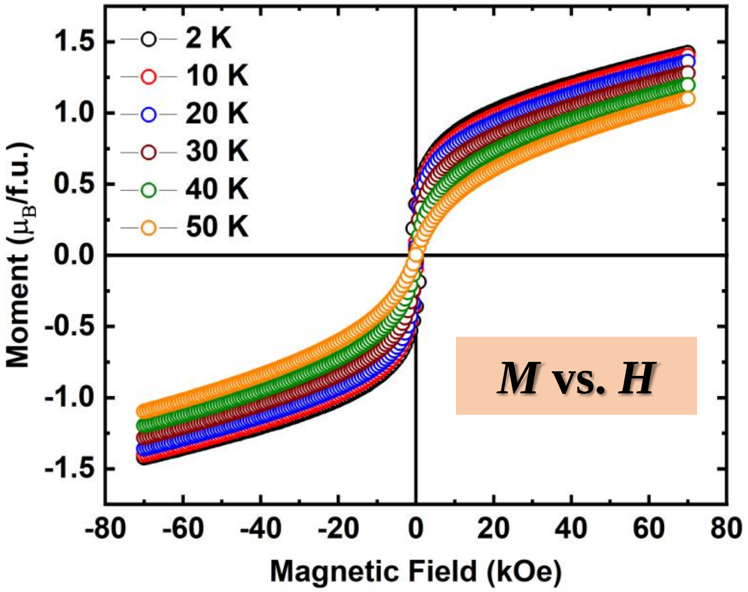


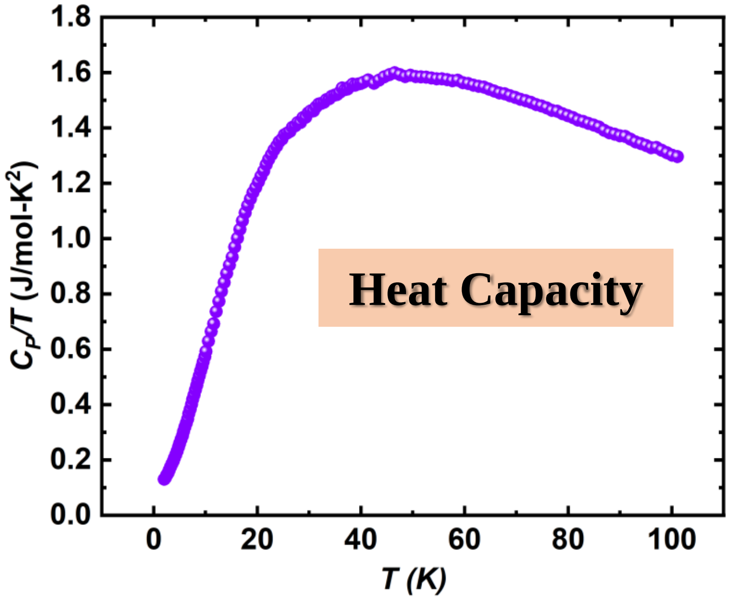
Polarization

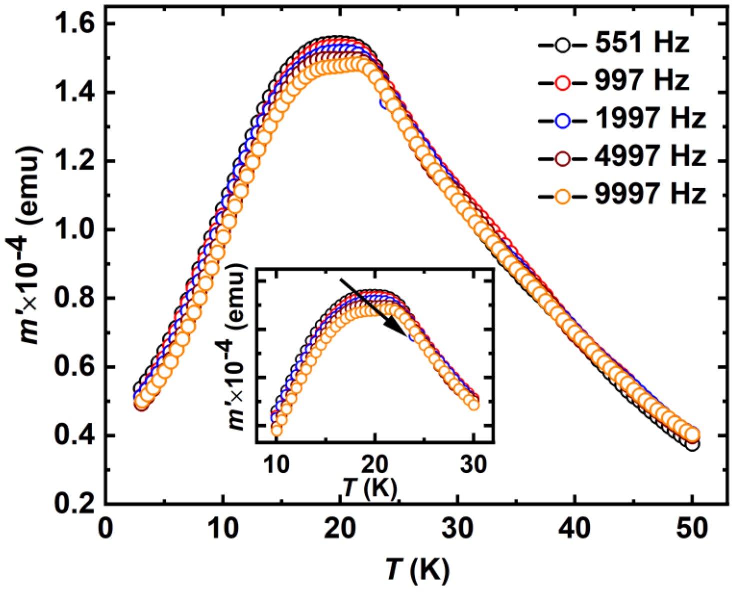


- Sample 1 shows AFM ordering below 22.5 K.
- Dielectric measurements also show anomaly at the magnetic transition temperature.
- Pyroelectric measurements confirm the ferroelectric nature of the dielectric anomaly.

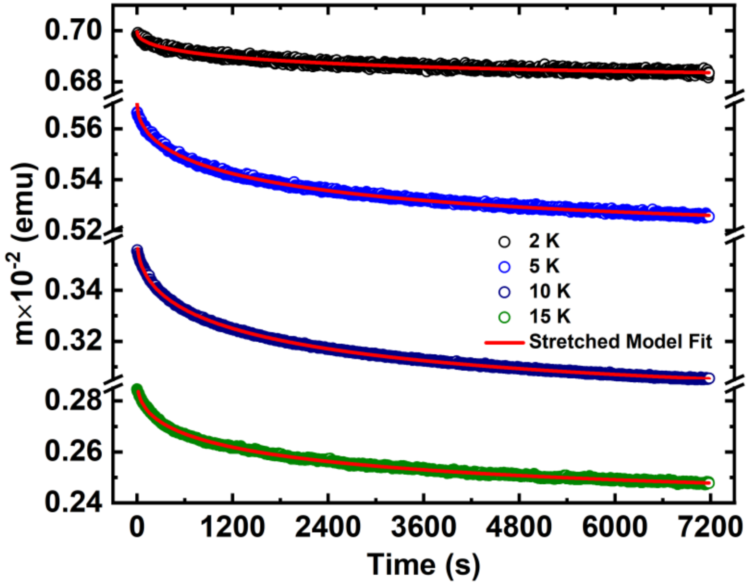
Magnetic Properties of Sample 2



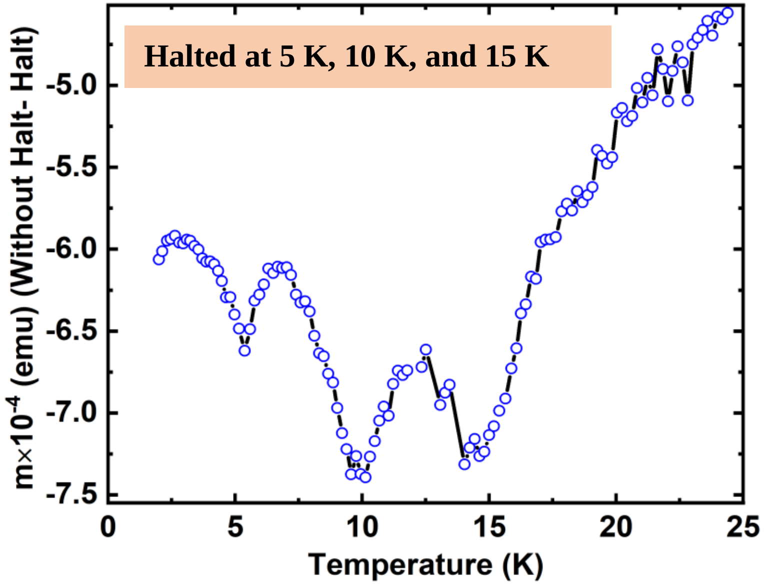




Relaxation Measurement



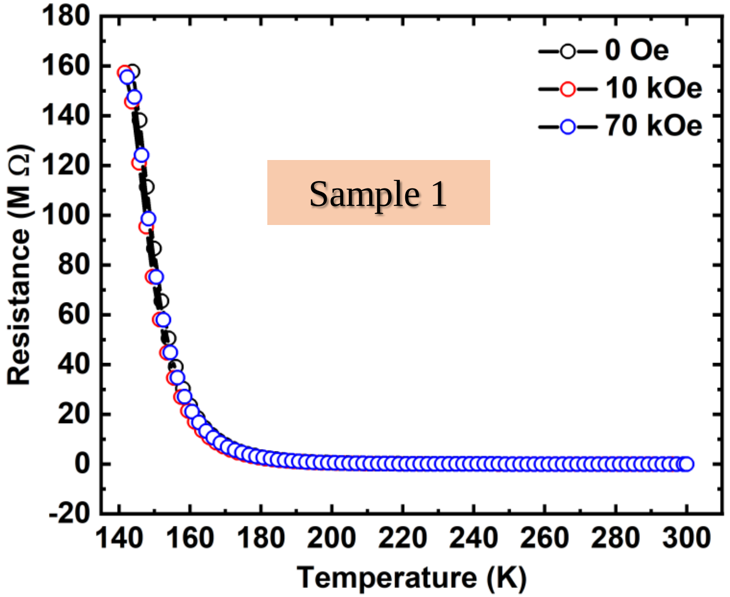
Magnetic Memory

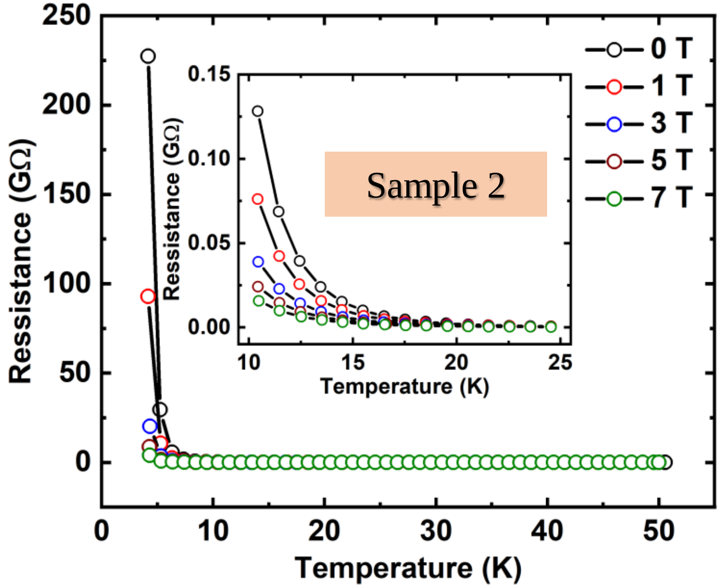


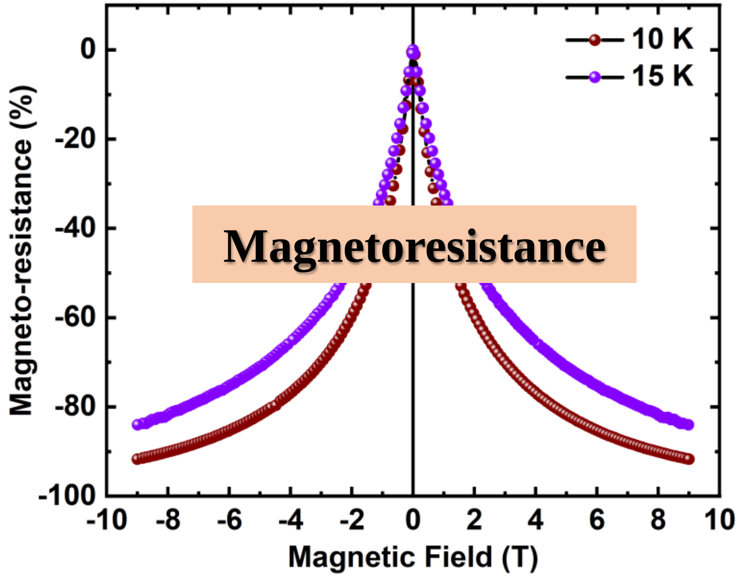
AC Susceptibility

- Sample 2 did not show any magnetic ordering.
- AC susceptibility shows shifting of peak position towards high temperature.
- Presence of magnetic relaxation and magnetic memory effect confirm the glassy state.

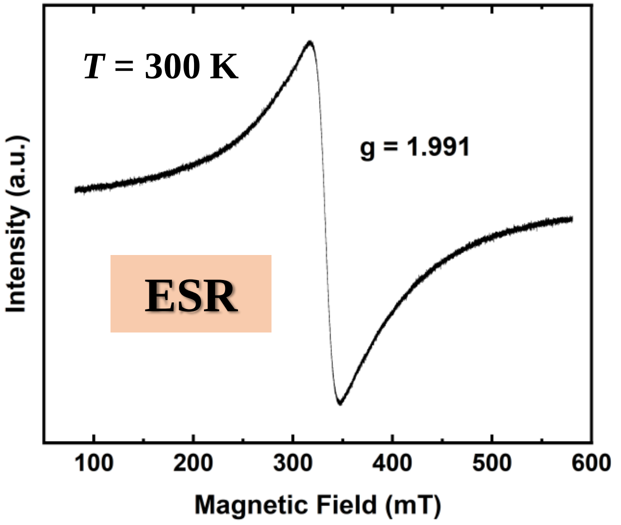
Comparison of Resistive Properties







A New Compound Having Negative Colossal Magnetoresistance!



- ❖ Resistivity data show gradual change from insulator to semiconductor to metallic state within a narrow temperature range.
- ❖ Increase in antisite disorder resulted into magnetic glassy state.
- ❖ With increase in magnetic field, spin-disorder decreased and hence resulted into lower resistivity. (Mechanism?)
- ❖ Absence of mixed valency, rules out the double exchange mechanism.
- ❖ Increase in magnetic field resulted in increased volume of ferromagnetic domains which reduced the electron scattering.

Conclusion

- Antisite-disorder plays an decisive role in determining magnetic ground state.
- Presence of ferroelectricity in sample 1 has magnetic origin as paramagnetic phase is centrosymmetric.
- Glassy behaviour of sample 2 is due to site randomness of the magnetic ion.
- A new non-manganite compound with negative colossal magnetoresistance.
- Origin of colossal magnetoresistance is not double exchange mechanism.

Acknowledgement

- Prof. A. Sundaresan, for his guidance and constant support.
- Prof. C. N. R. Rao, for his encouragement.
- Labmates, for making healthy environment in the lab.
- JNCASR, for all the experimental facilities.

Thank You