

## **Physical Sciences**

# **Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub> as a potential candidate for multiple state memory and magnetic field sensor application**

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**Keywords:** Magneoelectric coupling, magnetic field sensors, magnetization, dielectric constant

### **Abstract**

Phase pure polycrystalline Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub> is prepared using the conventional solid state reaction route. X-ray diffraction (XRD) reveals Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub> to possess an orthorhombic crystal structure with space group '*Pbam*'. Optical characterization confirms Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub> to be a direct band gap material with E<sub>g</sub> ~ 1.5 eV. Magnetization measurement shows compound to be antiferromagnetic (AFM) with AFM transition temperature ~150 K. The dielectric response of the compound was recorded in the temperature range 10-300 K with the probing frequency from 500 Hz-5 MHz. Here, we report remarkable magnetic field tunable dielectric properties of polycrystalline Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub> near its AFM transition temperature. Thus, Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub> can be further stimulated for various other magnetic field sensors, multiple state memory and other ferroelectric applications.

# $\text{Bi}_2\text{Fe}_4\text{O}_9$ as a potential candidate for multiple state memory and magnetic field sensor application

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# Abstract

Phase pure polycrystalline  $\text{Bi}_2\text{Fe}_4\text{O}_9$  is prepared using the conventional solid state reaction route. X-ray diffraction (XRD) reveals  $\text{Bi}_2\text{Fe}_4\text{O}_9$  to possess an orthorhombic crystal structure with space group 'Pbam'. Optical characterization confirms  $\text{Bi}_2\text{Fe}_4\text{O}_9$  to be a direct band gap material with  $E_g \sim 1.5$  eV. Magnetization measurement shows compound to be antiferromagnetic (AFM) with AFM transition temperature  $\sim 150$  K. The dielectric response of the compound was recorded in the temperature range 10-300 K with the probing frequency from 500 Hz-5 MHz. Here, we report remarkable magnetic field tunable dielectric properties of polycrystalline  $\text{Bi}_2\text{Fe}_4\text{O}_9$  near its AFM transition temperature. Thus,  $\text{Bi}_2\text{Fe}_4\text{O}_9$  can be further stimulated for various other magnetic field sensors, multiple state memory and other ferroelectric applications.



# Plan of talk

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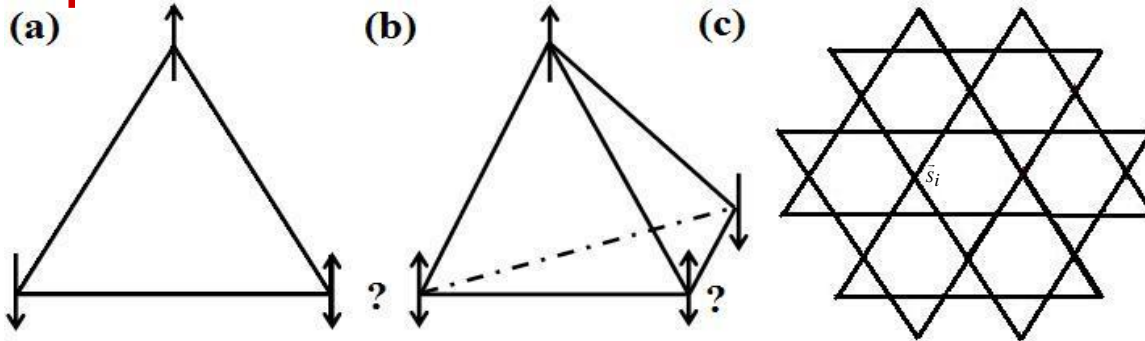
- Introduction
- Motivation
- Experimental techniques used
- Results and discussion
- Conclusion

# Introduction

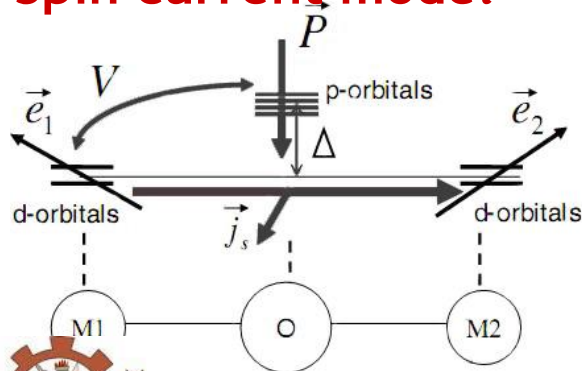
## Multiferroics

➤ Multiferroics are rare materials that exhibit two or more switchable states such as polarization, magnetization, or strain and possibly exhibiting coupling among them. *Spaldin, Science 309, 391 (2005)*

## Spin frustration

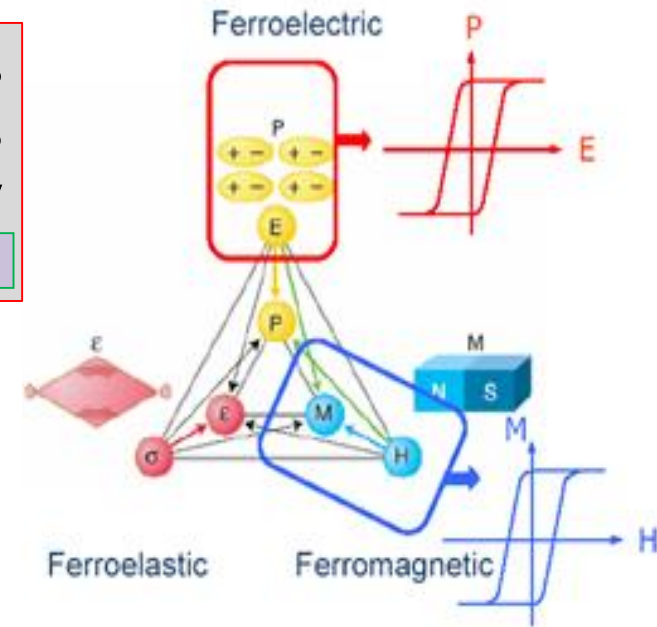


## Spin current model



$$\vec{P} = A e_{ij} \times (\vec{S}_i \times \vec{S}_j)$$

$\vec{S}_i, \vec{S}_j$ : magnetic moments  
 $\vec{e}_{ij}$ : unit vector connecting site  $i, j$   
 $\vec{P}$ : polarization  
 $\vec{J}_s$ : spin current



# Examples of Multiferroics

- The most promising multiferroic materials are the Perovskites having structure like  $ABO_3$ . d-shell electrons plays the important role. e.g.  $SrTiO_3$ ,  $BaTiO_3$ ,  $PbVO_3$  etc.
- Bi and Pb Perovskites : lone pair plays the role.  
e.g.  $BiMnO_3$ ,  $BiFeO_3$
- Hexagonal magnanites: Same formula as perovskite has .  
But different crystal and electronic structure e.g.  $YMnO_3$ .
- Ferroelectricity due to magnetic ordering e.g.  $Ni_3V_2O_8$ .
- Recently discovered  $RMn_2O_5$  and  $CdCr_2S_4$



# Applications of Multiferroics

## ✓ Magnetic field Sensors

[Appl. Phys. Lett. **88**, 62510 (2006), Nat. Mater. 7, 94 (2009)]

## ✓ Data storage, and recording

[J. Appl. Phys. **103**, 07F506 (2008), J. Appl. Phys **102**, 44504 (2007)]

## ✓ Quantum electromagnet [Science **312**, 1481(2006)]

## ✓ Solar cells [Science 324, 64 (2009), Appl. Phys. Lett. 95, 62909 (2009)]

## ✓ Microelectronics

[J. Phys.: Condens. Mater 17, L39 (2005)]

## ✓ Transducers

## ✓ Detectors (SONAR) :

## ✓ Filter probes and filters

## ✓ Spintronics applications



# Scarcity of multiferroics: why?

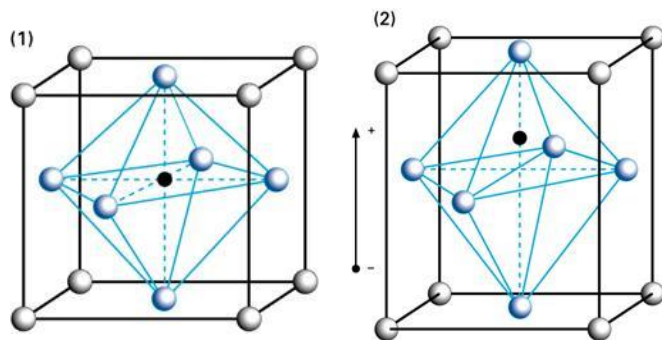
There are some limiting factors that prevent a material to be simultaneously ferromagnetic and ferroelectric :---

- ✓ **Symmetry:** There are 122 no. of Shubnikov point groups. Among these 31 are allowed for electric polarization **P**, and 31 are allowed for magnetic polarization **M** & 13 point groups are common to both.
- ✓ **Electric property:** Ferroelectric materials must be an insulator and Ferromagnets are often metal. So it is difficult to exist both these ferroic properties in a same material.
- ✓ **d<sup>0</sup>-ness:** Ferroelectric material have d<sup>0</sup> configuration but ferromagnetism needs partially d-filled orbital. Again contradiction.
- ✓ **Size of the cations:**
- ✓ **Magnetism versus d-orbital Occupancy:** The existence of d-electrons on the B-site cations reduces the tendency of perovskite oxides to display the ferroelectricity.

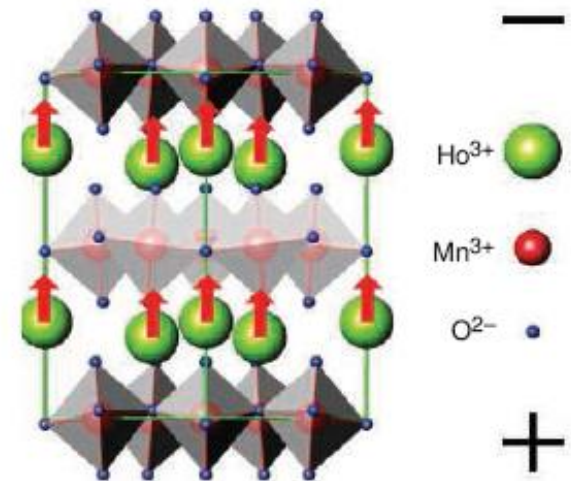




✓ **Structural distortion:** Ferroelectric materials must undergo a phase transition that does not have a center of symmetry (achieved in perovskite ferroelectrics). For a cation with certain d-orbital occupancy, the tendency to undergo a J-T distortion is strong and likely to be dominant structural effect. This subterfuges the non-centro symmetric structure.



**Perovskite Structure**  
( A: Grey, B: Black, O: Blue )



Multiferroic HoMnO<sub>3</sub>

Science 309, 391 (2005)

*Two Phase composite multiferroics e.g.  $PbZr_{1-x}Ti_xO_3$  and  $Tb_{1-x}Dy_xFe_2$  have been successfully tried out. YMnO<sub>3</sub> is a better candidate because it contains heavy and easily oxidized elements and it is free from elements such as Pb and Bi*

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# Motivation

- Is it possible to observe multiferroic property in a spin frustrated material very near to room temperature?
- What is the microscopic origin of the coupling between electric and magnetic order in frustrated magnetic system?
- Are the bulk properties giving some kind of indication for the application of  $\text{Bi}_2\text{Fe}_4\text{O}_9$ ?
- How doping will affect the ME coupling in pentagon spin frustrated  $\text{Bi}_2\text{Fe}_4\text{O}_9$ ?



# Experimental techniques used

## Sample preparation

- Solid state reaction
- Sol gel

## Crystal and magnetic structure

- X-ray diffraction
- Neutron diffraction

## Surface morphology and compositional study

- Scanning electron microscopy
- Energy dispersive spectroscopy

## Optical characterization

- UV-Visible spectroscopy
- Raman spectroscopy

## Magnetic characterization

- SQUID

## Magnetoelectric coupling study

- Magneto-dielectric study

## Thermodynamic measurement

- PPMS

## Ferroelectric characterization

- PE measurement
- CV measurement



# Crystal structure

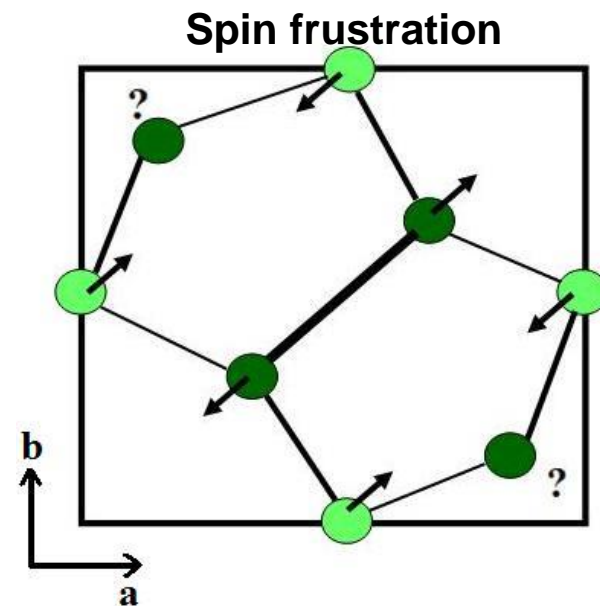
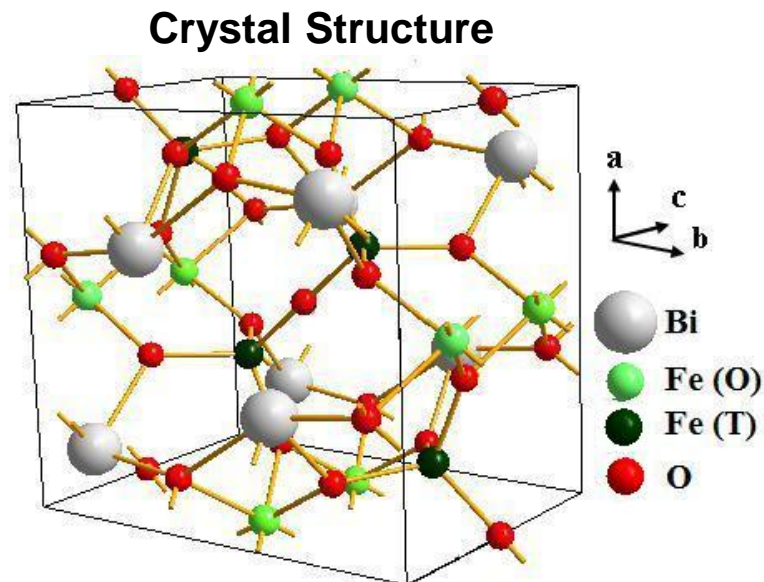
- Orthorhombic structure
- Space group  $Pbam$
- Two formula units per unit cell
- $T_N = (265 \pm 3)$  K
- Magnetic moment =  $4.95 \mu_B$ , compared with the value of  $5 \mu_B$  for the  $Fe^{3+}$  free ion.
- There are four octahedral Fe ions on the sides of the cell and the remaining four tetrahedral Fe ions are in the interior.

## Sample preparation

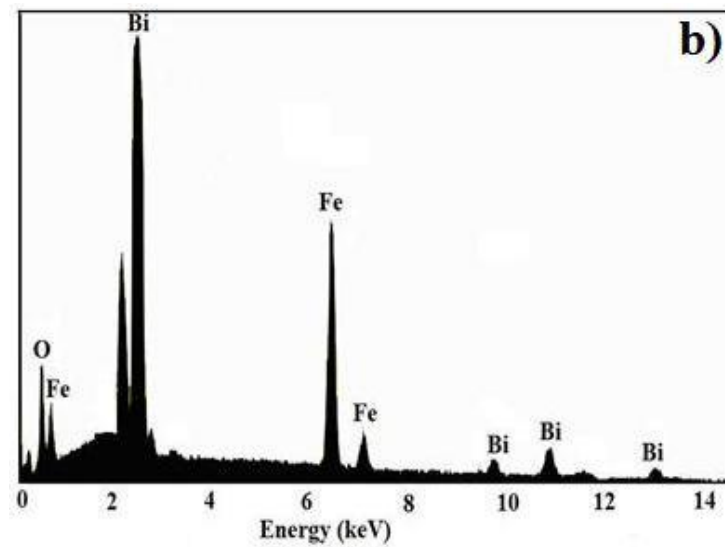
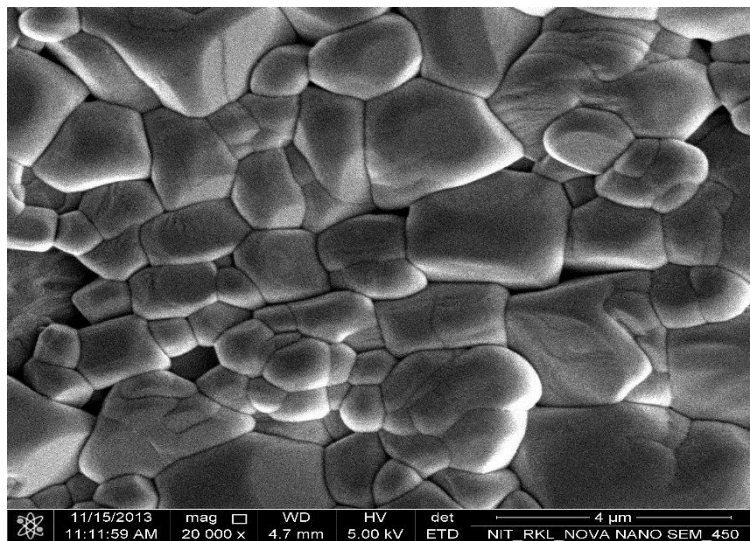
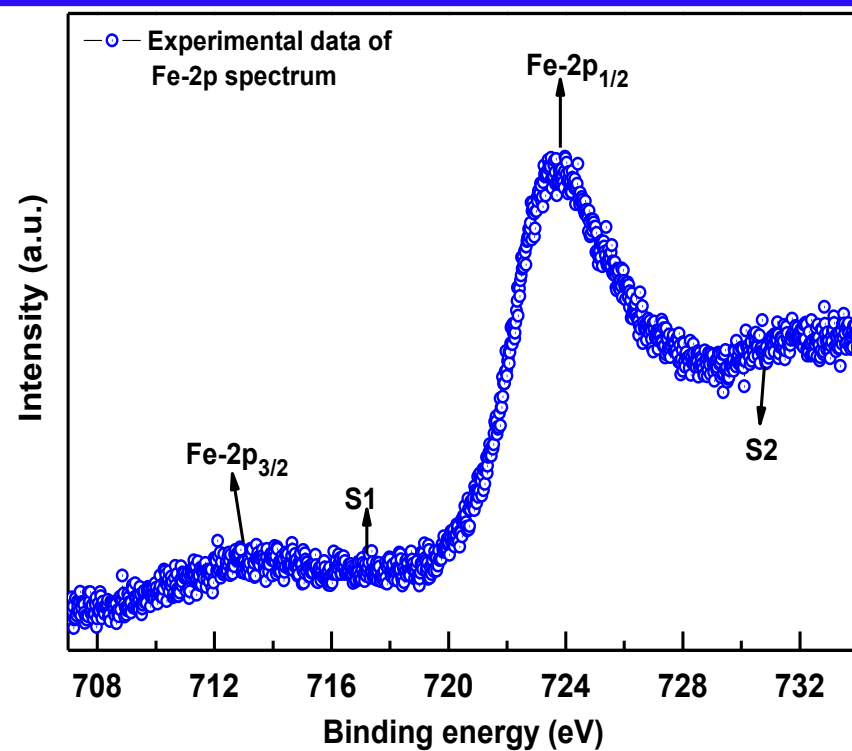
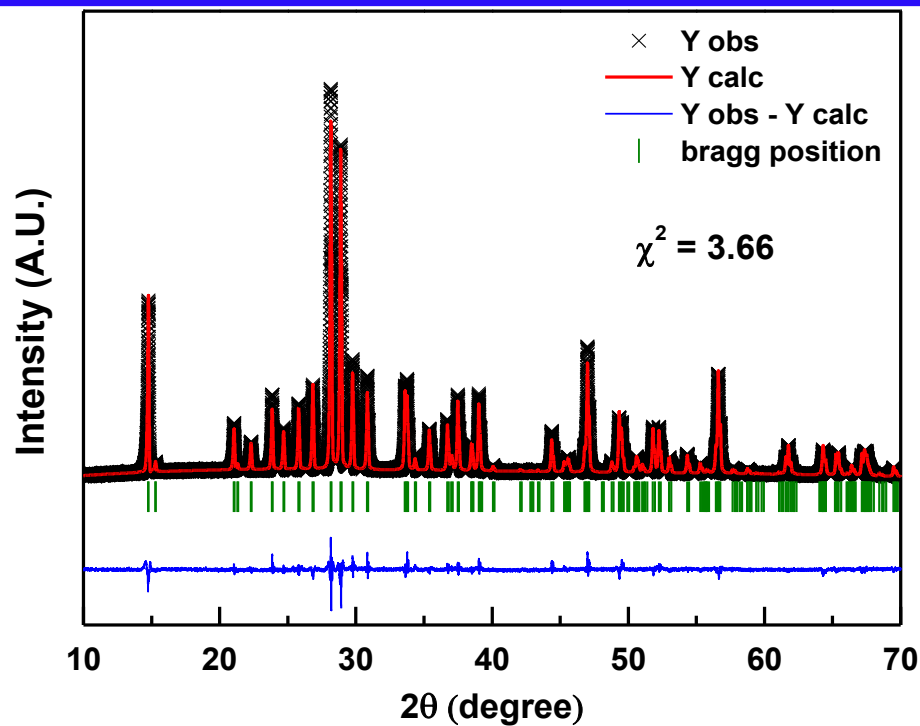
○ Polycrystalline samples of  $Bi_2Fe_4O_9$  were prepared by conventional solid state reaction process at  $850^\circ C$  at ambient pressure for 12 hours.



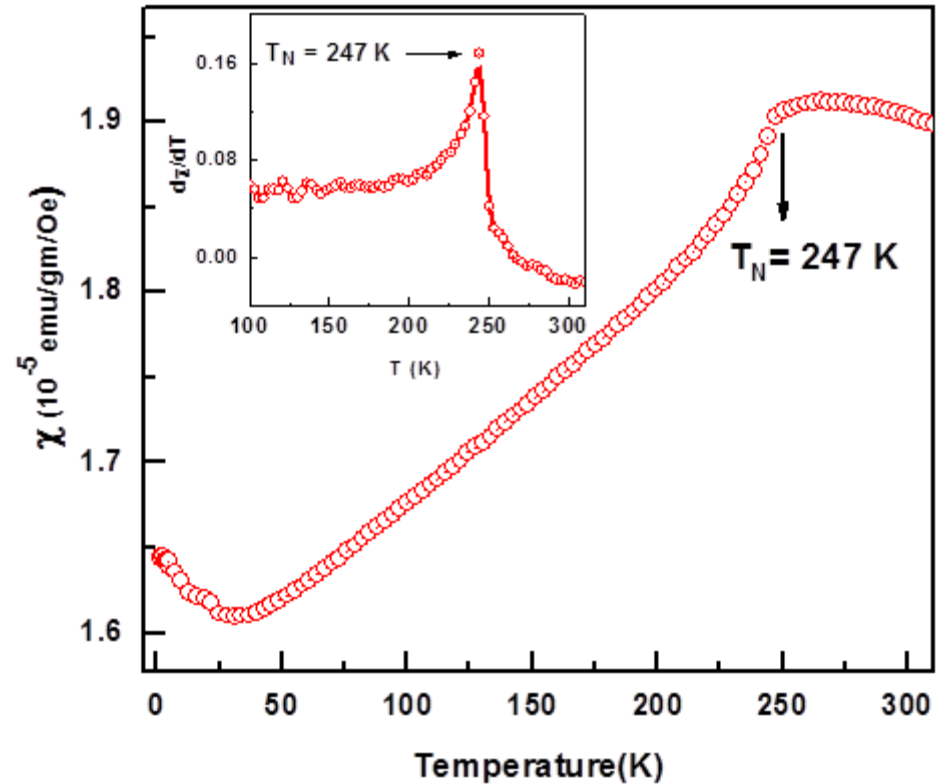
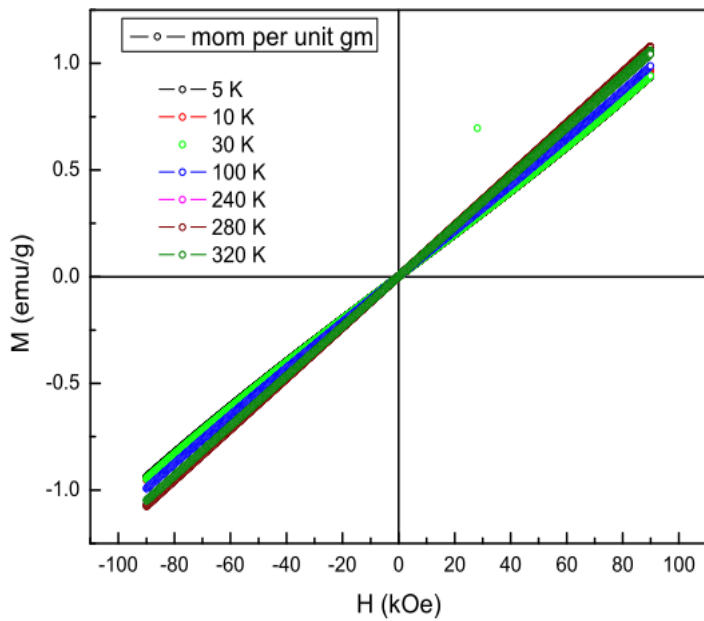
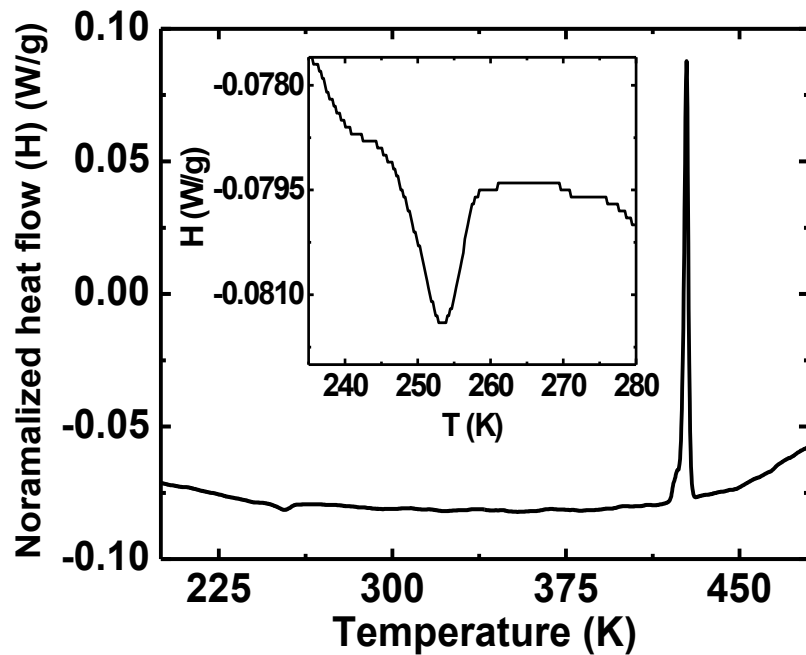
○ To ensure the stoichiometry, homogeneity and density of the pellets, the grinding and sintering process was repeated thrice.



# XRD, FESEM, EDS and XPS Data



# DSC, and SQUID Data

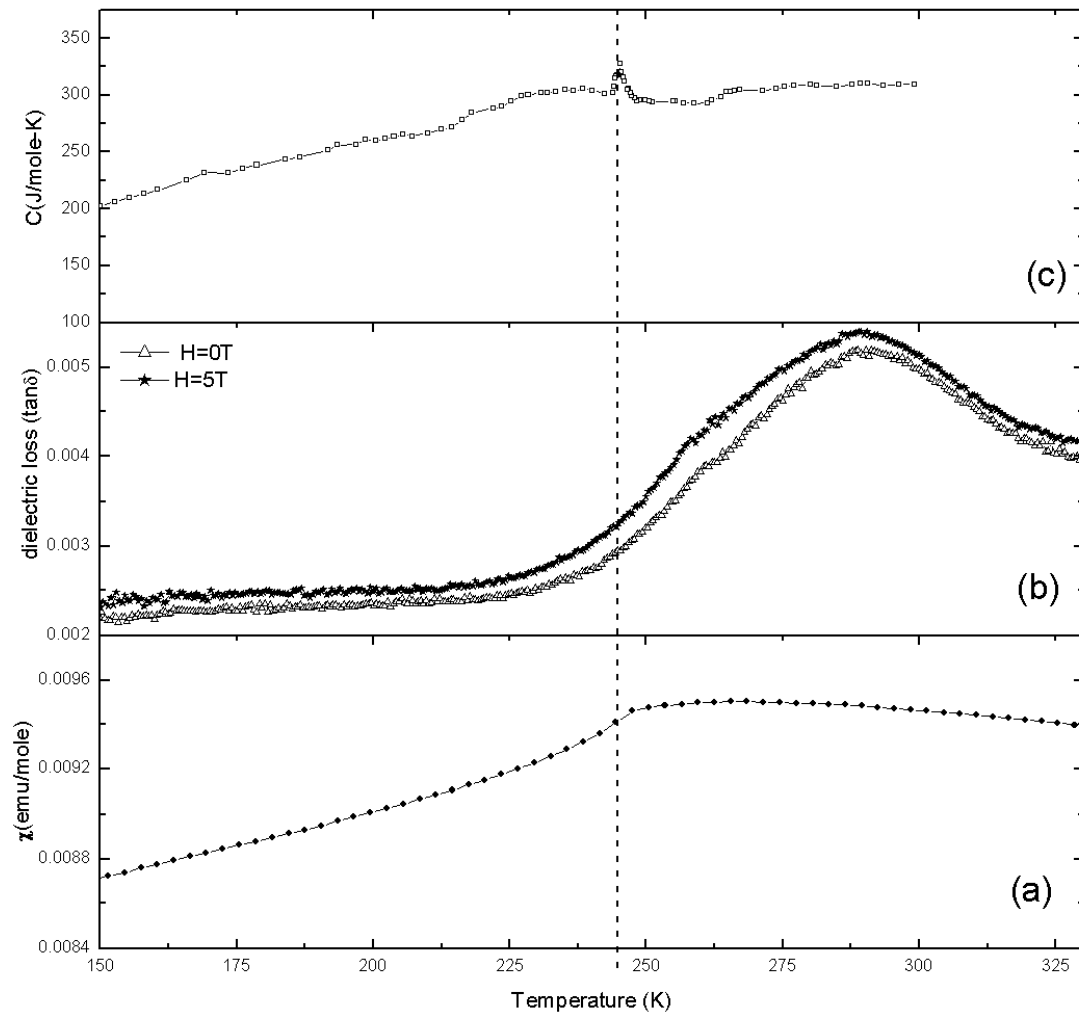
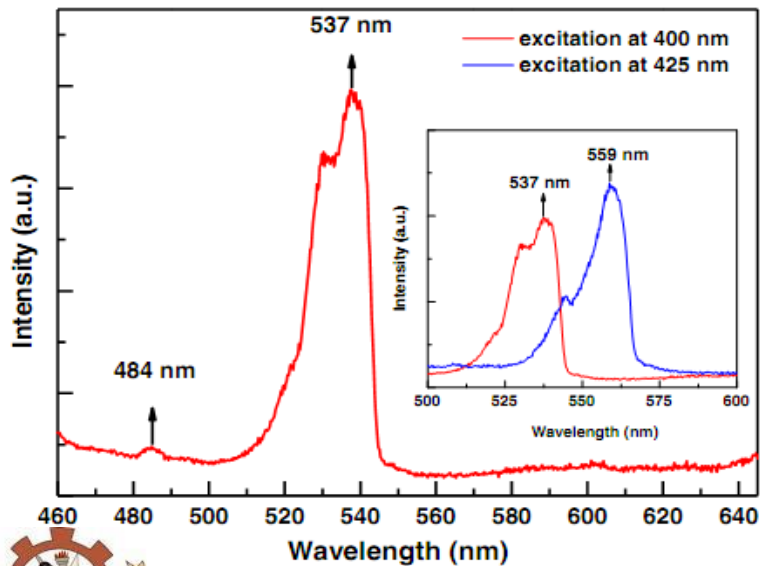
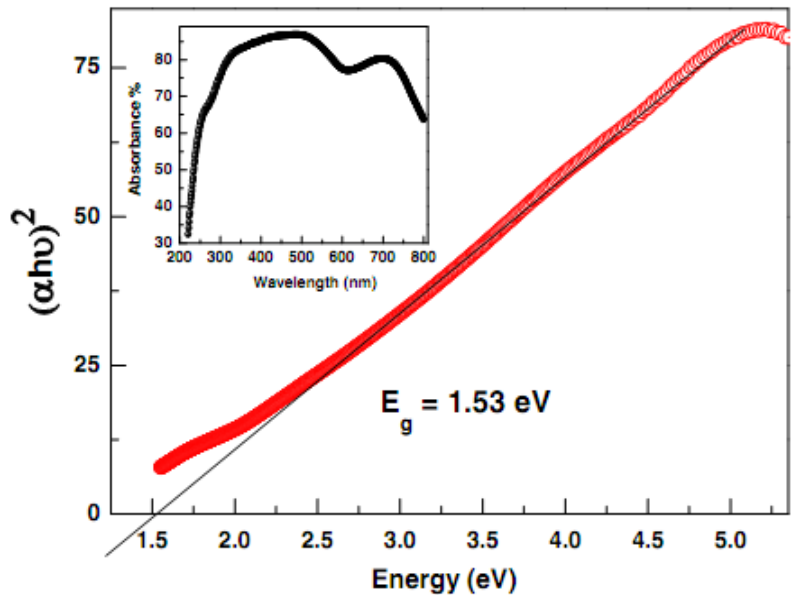


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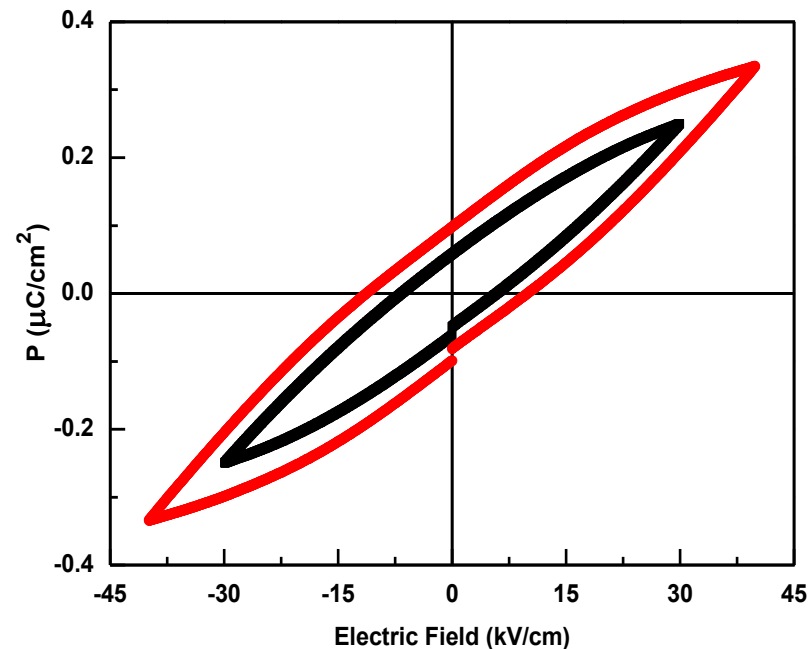
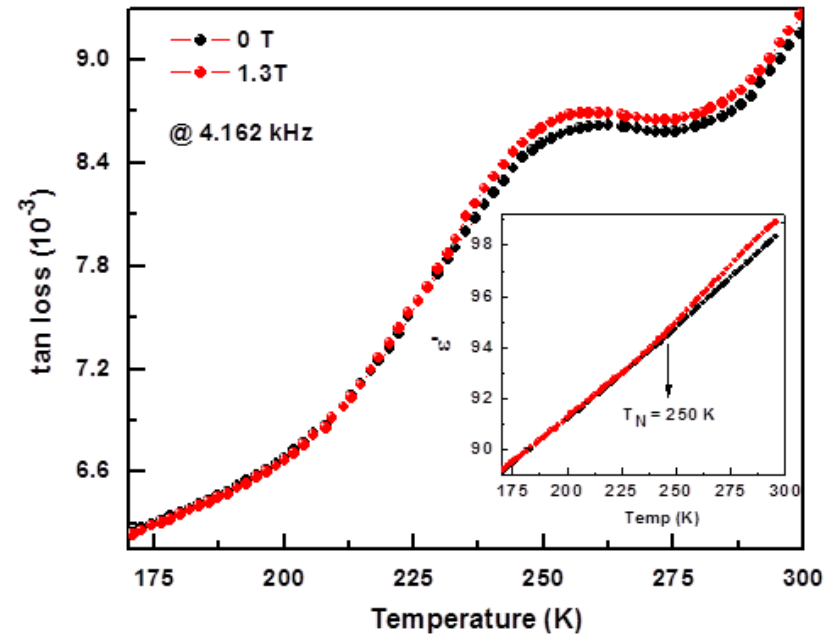
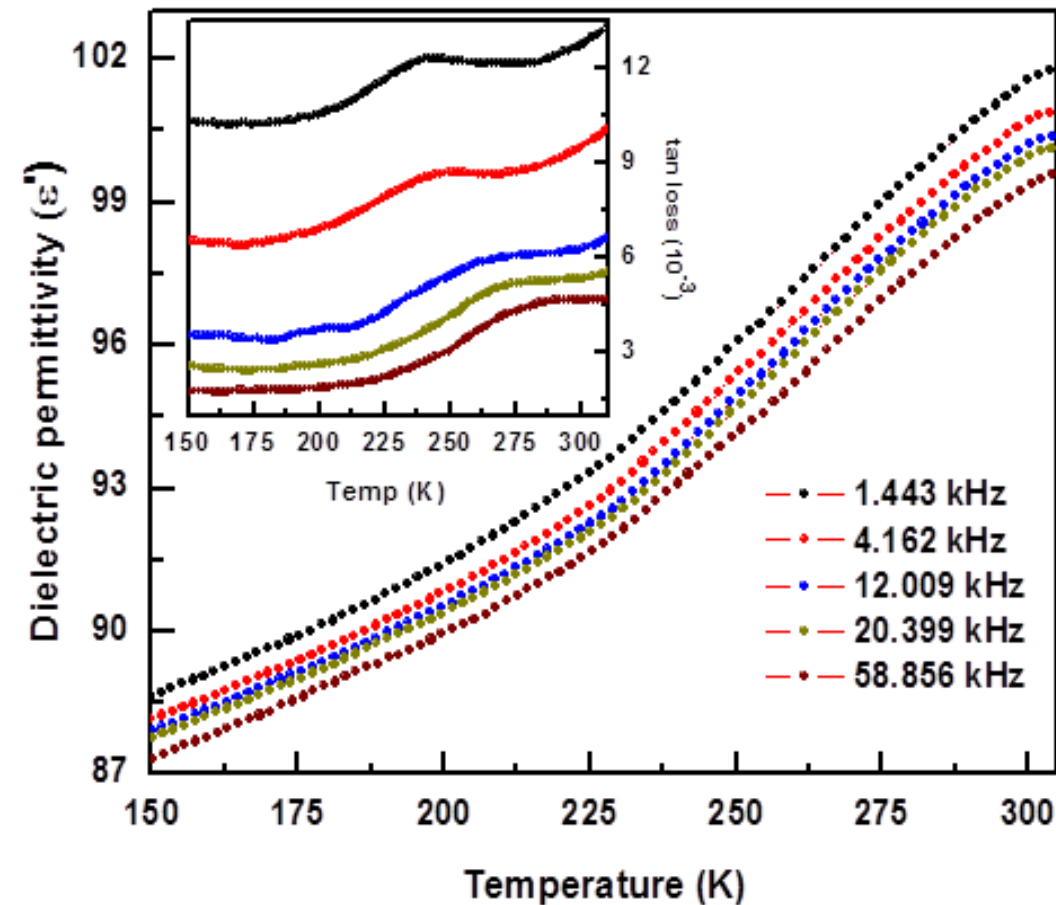




# UV-visible spectroscopy and Heat capacity Data

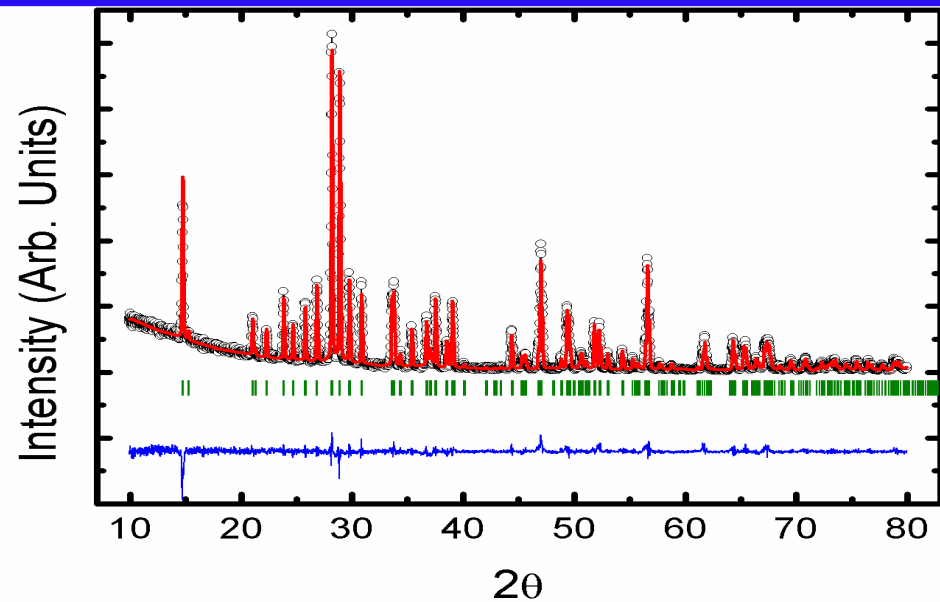


# Dielectric, ME coupling, PE measurement

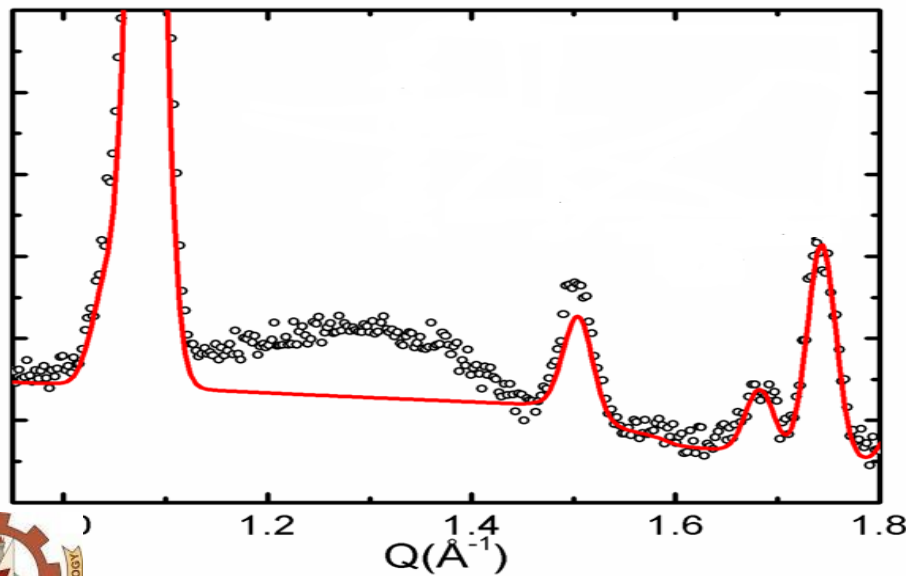
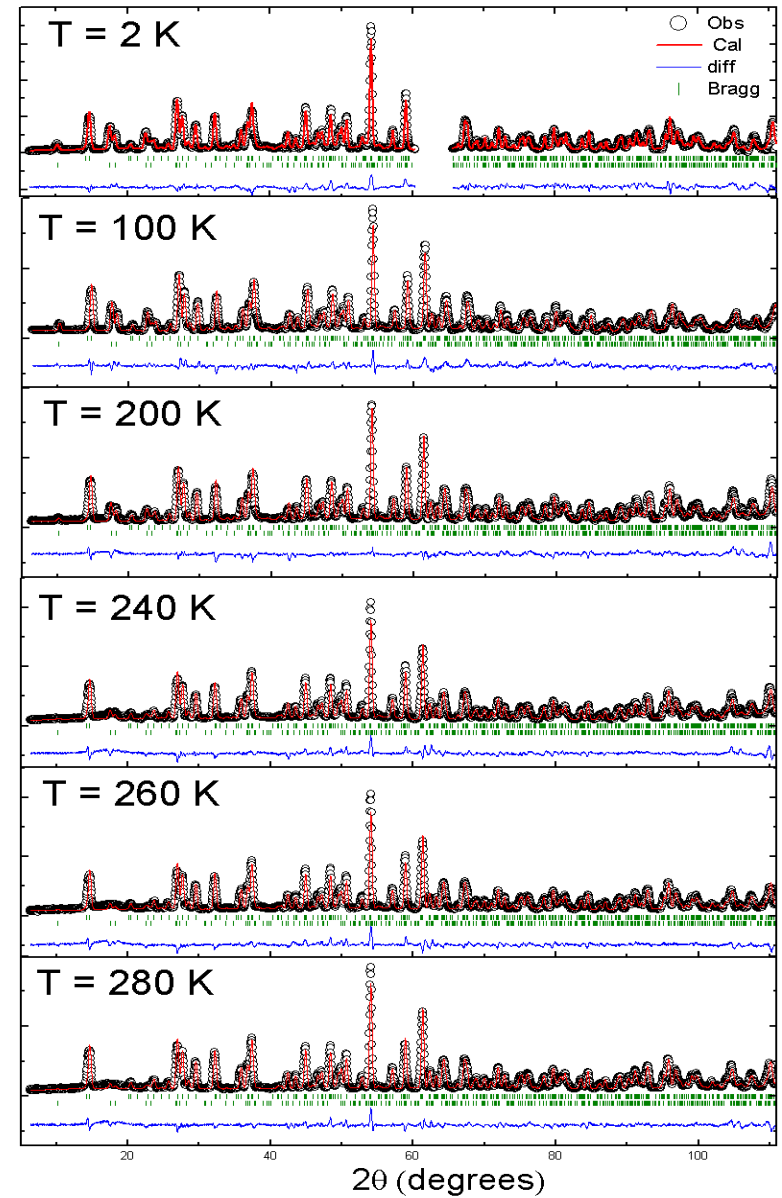




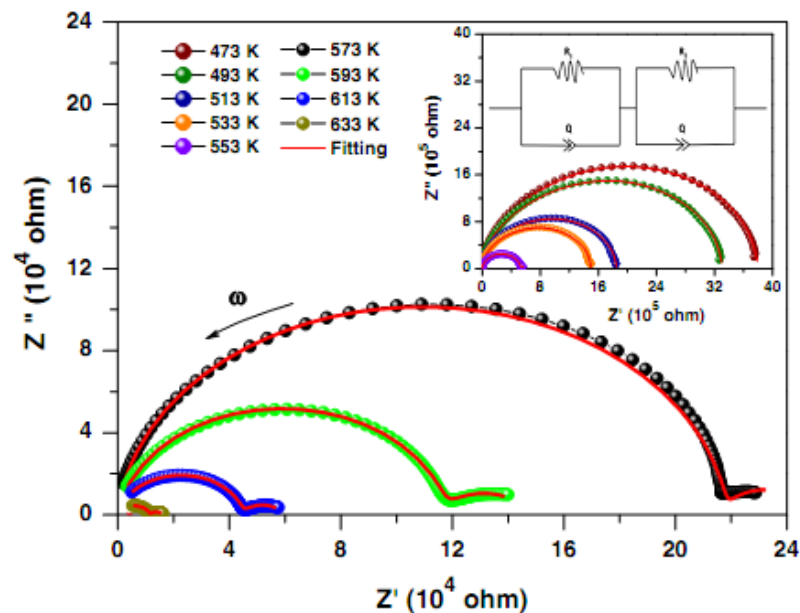
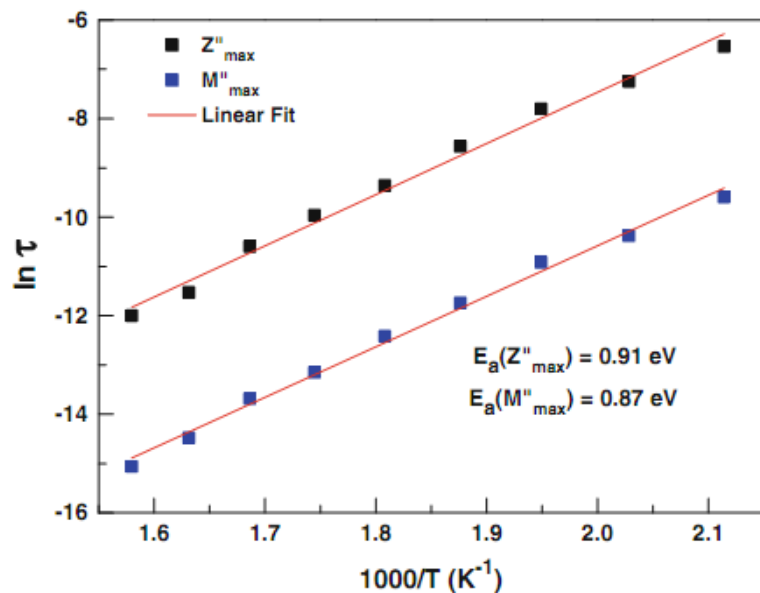
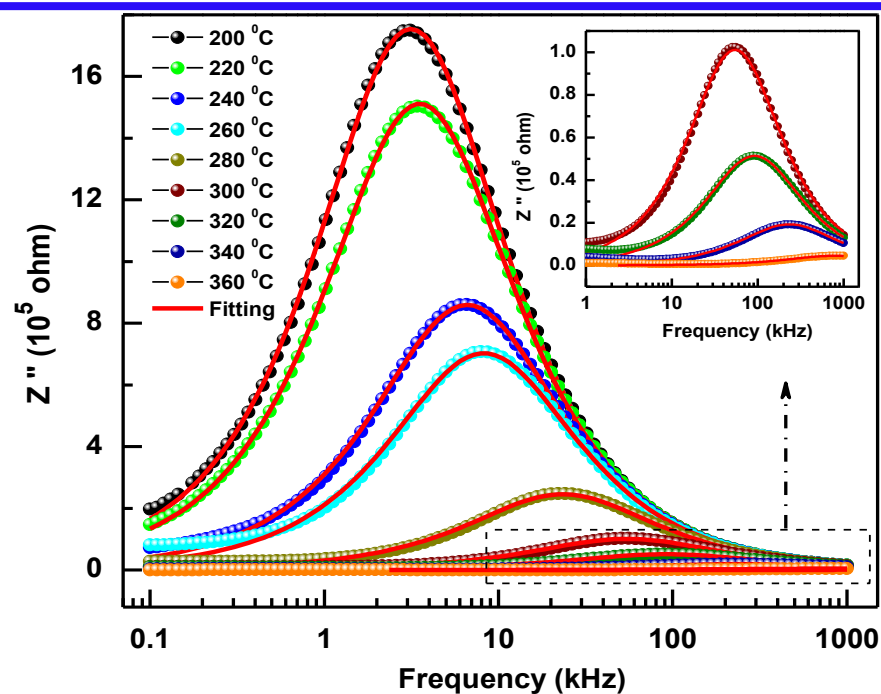
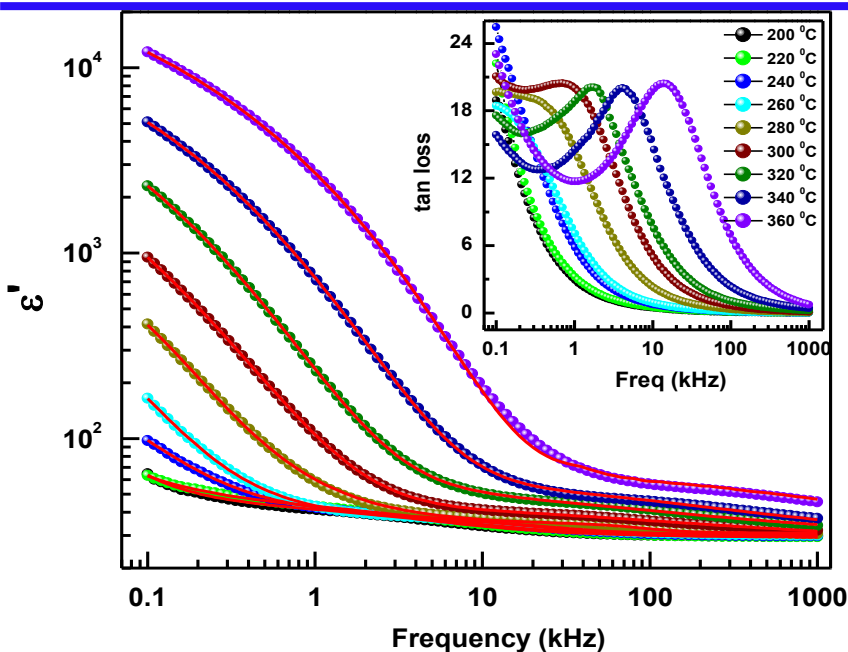
# Neutron diffraction results



Intensity (Arb. Units)



# High temperature dielectric and conduction mechanism



# Conclusion

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- ❖  $\text{Bi}_2\text{Fe}_4\text{O}_9$  shows novel magnetoelectric property very near to room temperature.
- ❖ BFO has a great potential to be used as a magnetic field sensor as its ME coupling at room temperature is  $\sim 8\%$  for 1.4 T magnetic field.
- ❖ Its semiconducting properties enables us to use this material for solar cell application.
- ❖ BFO can also be used as multiple state memory application.

## References

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# Acknowledgement

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THANK U FOR YOUR KIND  
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