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

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Abstract

Phase pure polycrystalline Bi$_2$Fe$_4$O$_9$ is prepared using the conventional solid state reaction route. X-ray diffraction (XRD) reveals Bi$_2$Fe$_4$O$_9$ to possess an orthorhombic crystal structure with space group ‘Pbam’. Optical characterization confirms Bi$_2$Fe$_4$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 Bi$_2$Fe$_4$O$_9$ near its AFM transition temperature. Thus, Bi$_2$Fe$_4$O$_9$ can be further stimulated for various other magnetic field sensors, multiple state memory and other ferroelectric applications.
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Plan of talk

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

\[ P = A e_{ij} \times (S_i \times S_j) \]

- \( S_i, S_j \): magnetic moments
- \( e_{ij} \): unit vector connecting site I, j
- \( P \): polarization
- \( J_s \): spin current

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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$_3$V$_2$O$_8$.

Recently discovered RMn$_2$O$_5$ and CdCr$_2$S$_4$
Applications of Multiferroics

✓ Magnetic field Sensors

✓ Data storage, and recording

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

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

✓ Microelectronics

✓ Transducers

✓ Detectors (SONAR) :

✓ Filter probes and filters

✓ Spintronics applications
## Scarcity of Multiferroics: Why?

There are some limiting factors that prevent a material from being 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.

- **$d^0$-ness**: Ferroelectric material have $d^0$ 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.

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✓ **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.

Two Phase composite multiferroics e.g. $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ and $\text{Tb}_{1-x}\text{Dy}_x\text{Fe}_2$ have been successfully tried out. $\text{YMnO}_3$ 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 Bi$_2$Fe$_4$O$_9$?

• How doping will affect the ME coupling in pentagon spin frustrated Bi$_2$Fe$_4$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

Magneto-electric coupling study
- Magneto-dielectric study

Thermodynamic measurement
- PPMS

Ferroelectric characterization
- PE measurement
- CV measurement

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Crystal structure

- Orthorhombic structure
- Space group \( \text{Pbam} \)
- 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 \( \text{Fe}^{3+} \) 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 \( \text{Bi}_2\text{Fe}_4\text{O}_9 \) were prepared by conventional solid state reaction process at 850 °C at ambient pressure for 12 hours.
- \( \text{Bi}_2\text{O}_3 + 2\text{Fe}_2\text{O}_3 \rightarrow \text{Bi}_2\text{Fe}_4\text{O}_9 \)
- To ensure the stoichiometry, homogeneity and density of the pallets, the grinding and sintering process was repeated thrice.


http://www.natureasia.com/asia-materials/highlight.php?id=244
XRD, FESEM, EDS and XPS Data

\[ \chi^2 = 3.66 \]

![Intensity vs. 2θ (degree)]

![Intensity vs. Binding energy (eV)]

Experimental data of Fe-2p spectrum

Fe-2p\(^{3/2}\)

Fe-2p\(^{1/2}\)

S1

S2
Normalized heat flow (H) (W/g)

Temperature (K)

DSC, and SQUID Data

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UV-visible spectroscopy and Heat capacity Data

- Energy (eV)
  - $E_g = 1.53$ eV

- Absorbance (%)
  - Wavelength (nm)

- Intensity (a.u.)
  - Wavelength (nm)
  - $484$ nm
  - $537$ nm
  - $559$ nm

- Heat capacity (CJ/mole·K)
  - Temperature (K)
  - $H=0T$
  - $H=5T$

- Dielectric loss (tanδ)
  - Frequency (Hz)

Graphs showing spectral data and thermodynamic properties.
Dielectric, ME coupling, PE measurement

![Graphs showing dielectric permittivity and tan loss vs temperature for different frequencies and magnetic fields.]

- Electric Field (kV/cm)

![Graphs showing polarization vs electric field at 4.182 kHz.

- Temperature (K)

- P (µC/cm²)

- Electric Field (kV/cm)
Neutron diffraction results

Intensity (Arb. Units)

2θ

Intensity (Arb. Units)

Q(Å⁻¹)

T = 2 K

T = 100 K

T = 200 K

T = 240 K

T = 260 K

T = 280 K

2θ (degrees)
High temperature dielectric and conduction mechanism

Conclusion

- Bi$_2$Fe$_4$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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