Role of pentagon spin frustration in magnetoelectric $Bi_2Fe_{4-x}Co_xO_9$ $(0 \leq x \leq 0.8)$

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Abstract: Geometrically frustrated systems have attracted considerable interest because the spin frustration leads to exceptionally rich physical properties ranging over spin-liquid, quantum phase transition, anomalous large thermoelectric response and magnetoelectric (ME) properties. Recently, the spin-driven ferroelectricity due to triangular spin frustration has been observed in various antiferromagnetic compounds $Ni_3V_2O_8$, hexagonal $RMnO_3$, $CuCrO_2$, and $AgCrO_2$. But the role of pentagon spin frustration on the spin driven ferroelectricity is poorly understood. $Bi_2Fe_4O_9$ belongs to rare class of compounds where ferroelectricity is being observed due to spin frustration in pentagon symmetry. But the microscopic picture of pentagon spin frustration is still under debate. Here, we report the preparation of magnetoelectric $Bi_2Fe_4O_9$ and Co doped $Bi_2Fe_4O_9$ by solid state route using bismuth oxide (Bi_2O_3), iron oxide (Fe_2O_3) and cobalt oxide (Co_3O_4). Our X-ray diffraction (XRD) results confirm that there is no change in crystal structure due to Co doping. Scanning Electron Microscopy image shows grain size increases due to doping which is in agreement with XRD analysis. From dielectric constant measurement we conclude that dielectric constant increases due to Co doping. UV-Visible plot shows due to Co doping band gap energy decreases.

❑ Introduction:

- Multiferroics possess two or more ordered states such as magnetism and ferroelectricity that coexist and are coupled to each other.
- Coupling between these order parameters is called the magneto-electric (ME) effect which allows control of magnetization by electric field and vice versa in the materials. This can be represented as :

$$\vec{P}_i = \alpha_{ij}H_j + \frac{\beta_{ijk}}{2}H_jH_k + \ldots$$
$$\mu_0\vec{M}_i = \alpha_{ij}E_j + \frac{\gamma_{ijk}}{2}E_jE_k + \ldots$$

Where $\vec{P_i}$ = ith component of electrictric polarization, $\vec{M_i}$ = ith component of magnetization, E_j, E_k = jth & kth component of electric field, H_j, H_k = jth & kth component of magnetic field and α, β are the linear and nonlinear magnetoelectric susceptibilities.

- $Bi_2Fe_4O_9$ belongs to rare class of compounds where due to unique kind of pentagon frustration of magnetic lattice of Fe atoms give rise to magnetoelectric coupling.

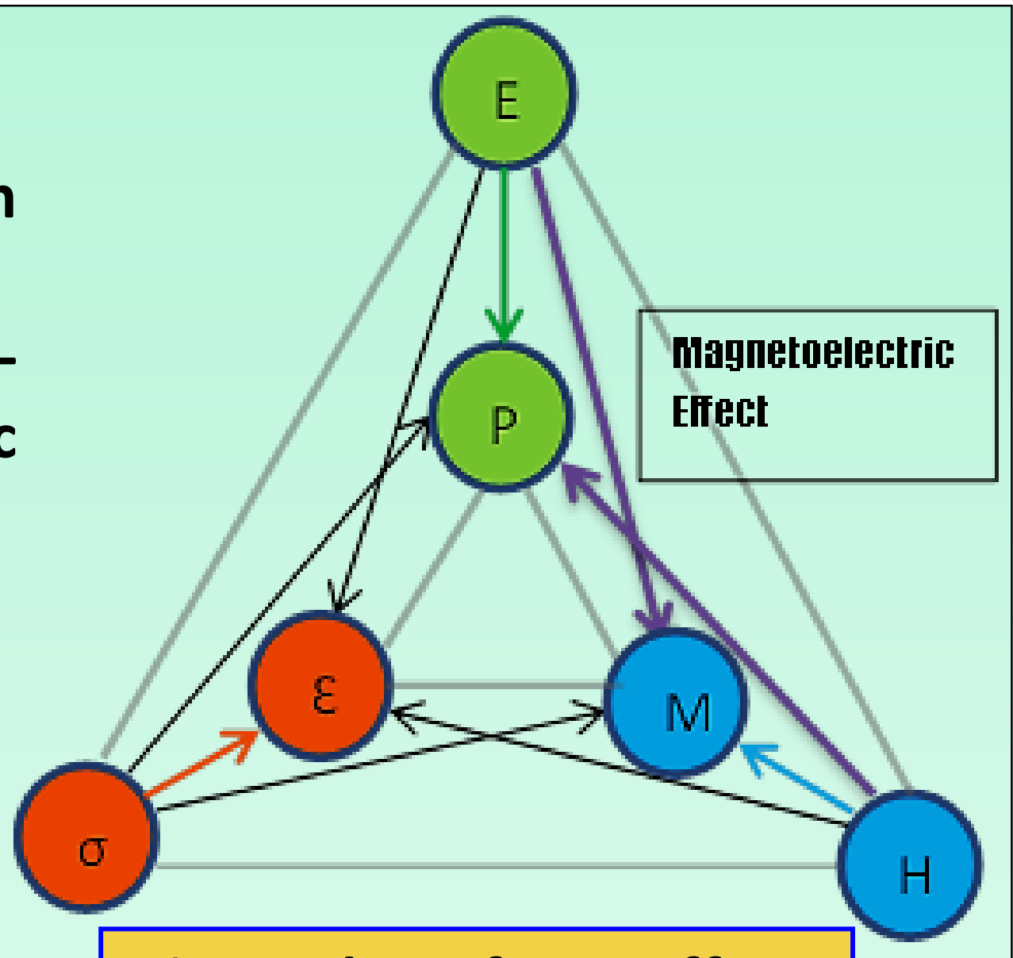


Fig 1: Idea of ME effect

❑ Crystal & Magnetic Structure Of $Bi_2Fe_4O_9$:

- ✓ $Bi_2Fe_4O_9$ crystallizes in orthorhombic structure with space group *'Pbam'.*
- ✓ The lattice constants of this structure are: a = 7.973Å, b = 8.441Å, c = 6.002Å.
- ✓ The antiferromagnetic transition of $Bi_2Fe_4O_9$ was reported to be ~260 K.
- ✓ In fig 3, there are four octahedral Fe ions on the sides of the cell (light green colour) and the remaining four tetrahedral Fe ions are in the interior (dark green colour).
- ✓ By the super-exchange route tetrahedral Fe spins interact anti-ferromagnetically among themselves and with the octahedral Fe spins while there is a ferromagnetic coupling within a pair of octahedral spins. This competing exchange interactions generate spin frustration.

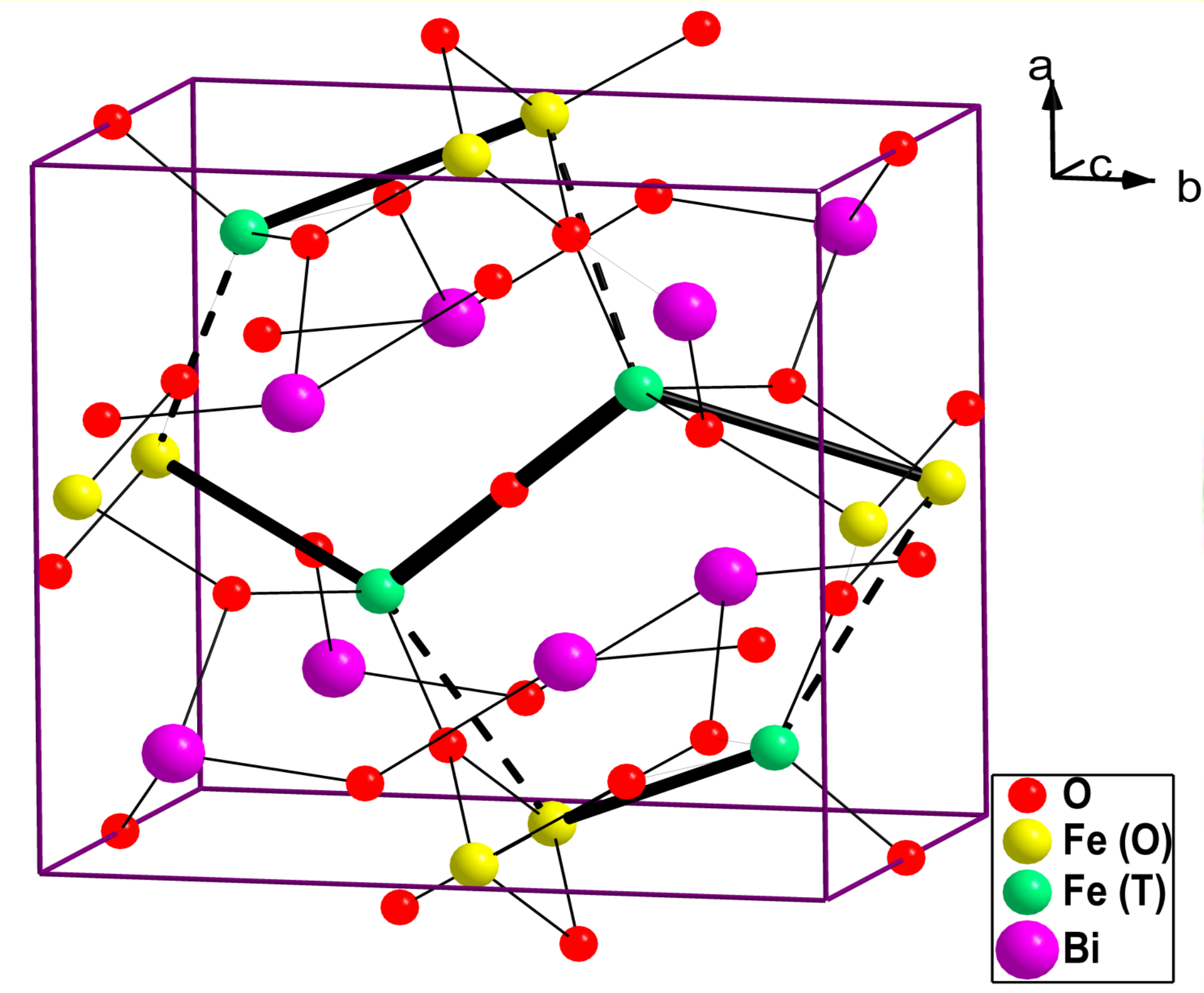


Fig 2: Unit cell of $Bi_2Fe_4O_9$ (Crystal structure)

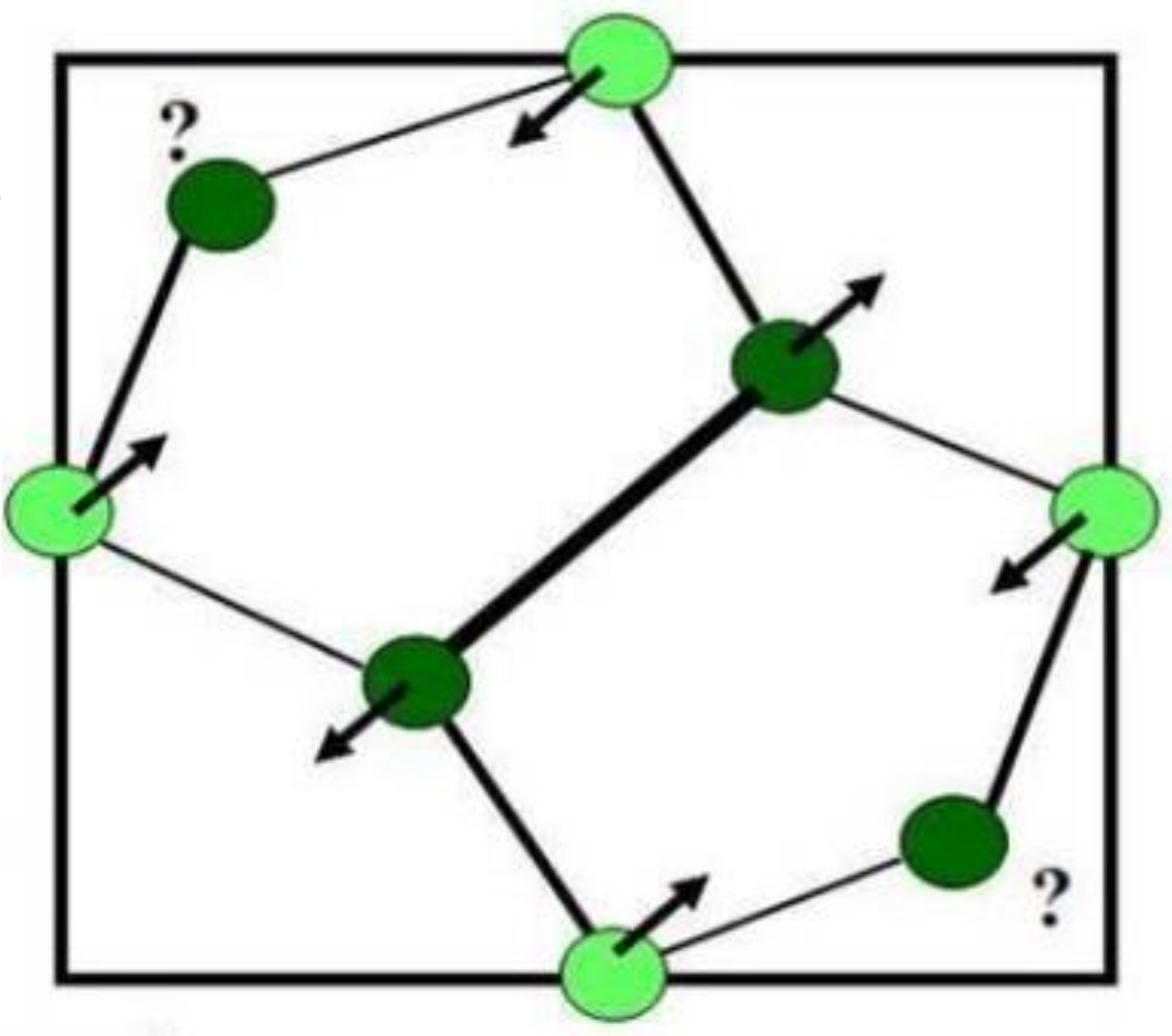
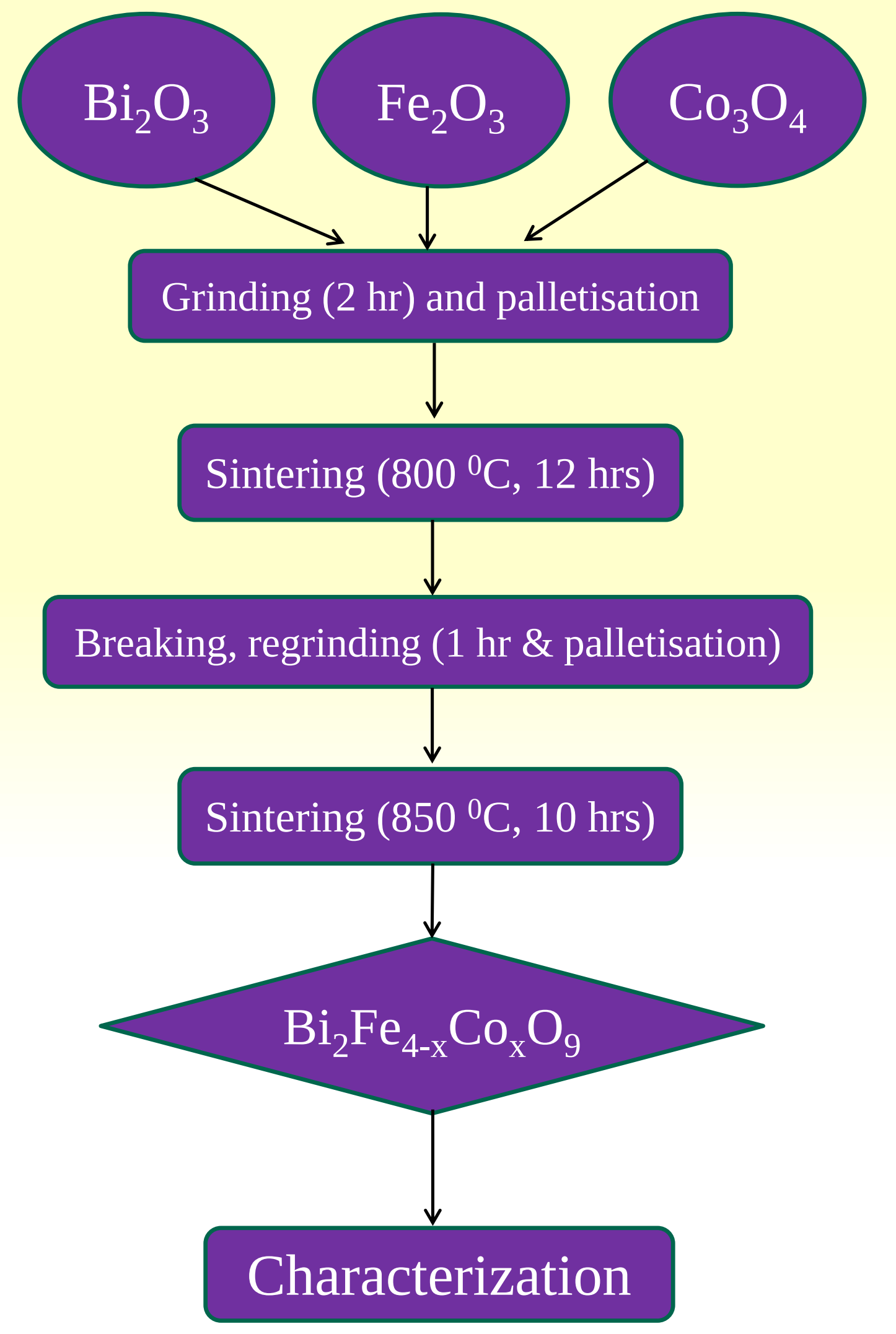


Fig 3: Spin frustration in $Bi_2Fe_4O_9$ (Magnetic structure)

❑ Sample Preparation:

Solid state route (Tubular Furnace)

$$Bi_2O_3 + 2(1\text{-}x)\,Fe_2O_3 + 4x/3\,Co_3O_4 \longrightarrow Bi_2Fe_{4-x}Co_xO_9 \quad (0 \leq x \leq 0.8)$$



Bi_2O_3 / Fe_2O_3 / Co_3O_4

Grinding (2 hr) and palletisation

Sintering (800 ⁰C, 12 hrs)

Breaking, regrinding (1 hr & palletisation)

Sintering (850 ⁰C, 10 hrs)

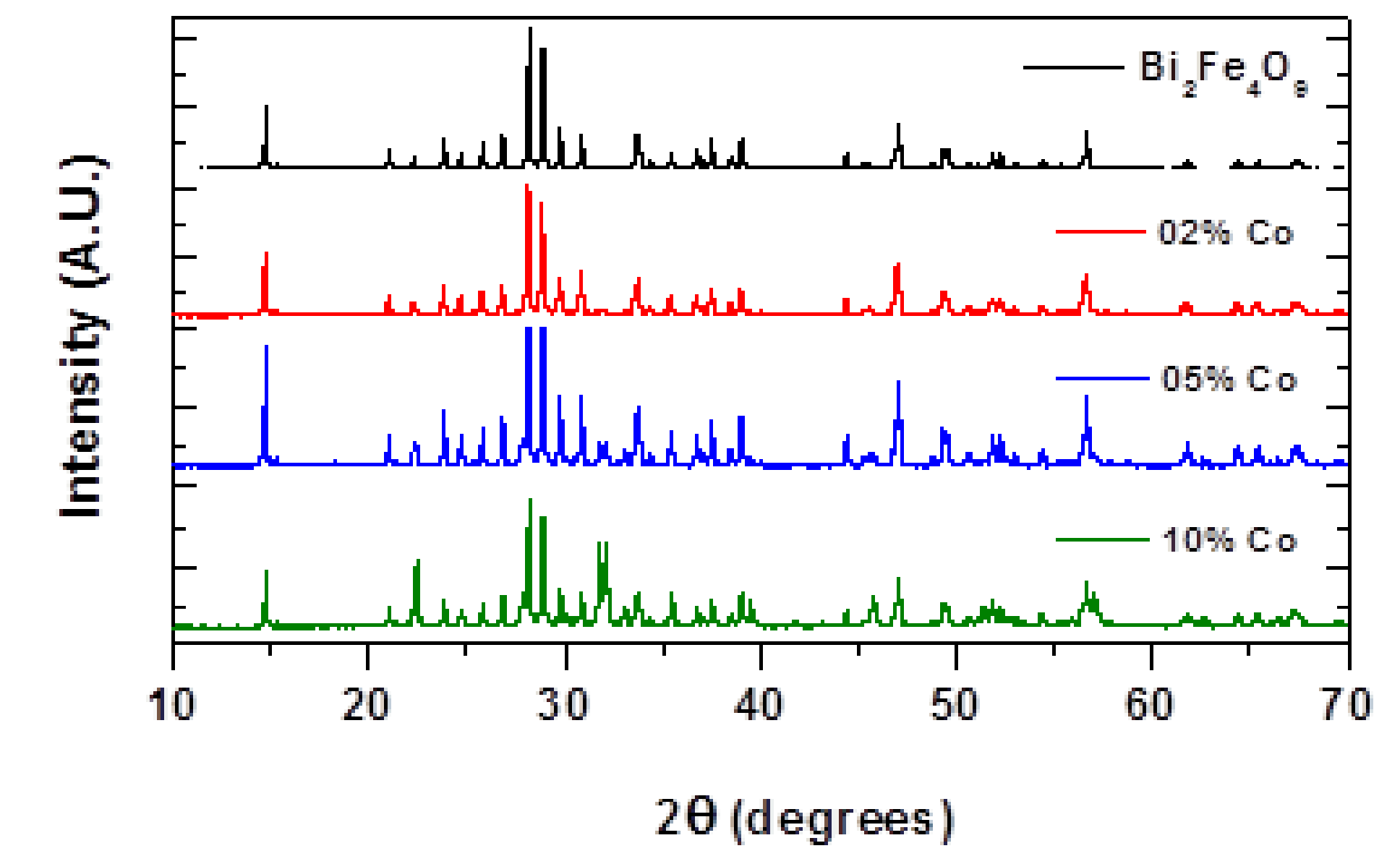
$Bi_2Fe_{4-x}Co_xO_9$

Characterization

❑ Characterisation:

- ○ The samples were characterized by X-ray diffraction (Rigaku- JAPAN).
- ○ The dielectric constant (ε) and tanδ were measured from room temp to high temperature (500⁰C) by varying frequencies using High precission impedance analyzer (6500B Wayne Kerr).
- ○ The FESEM and EDAX data were obtained using Nova Nano SEM/FEI.
- ○ Magnetization study was carried out at Dhruva reactor, BARC, Mumbai.
- ○ UV-visible spectroscopy was done using Perkin Elmer UV/VIS spectrometer (Lambda 35).
- ○ DSC & TG data were obtained using model NETZSCH, STA409C, Germany.

❑ X-Ray Diffraction Study:



Using Scherer formula crystallite size for $Bi_2Fe_4O_9$ and its various doping constituents (2% Co, 5% Co, 10% Co) are found to be 51.26 nm, 51.39nm, 51.51nm and 51.69nm respectively.

❑ Acknowledgement:

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❑ Results and Discussions:

X-ray diffraction:

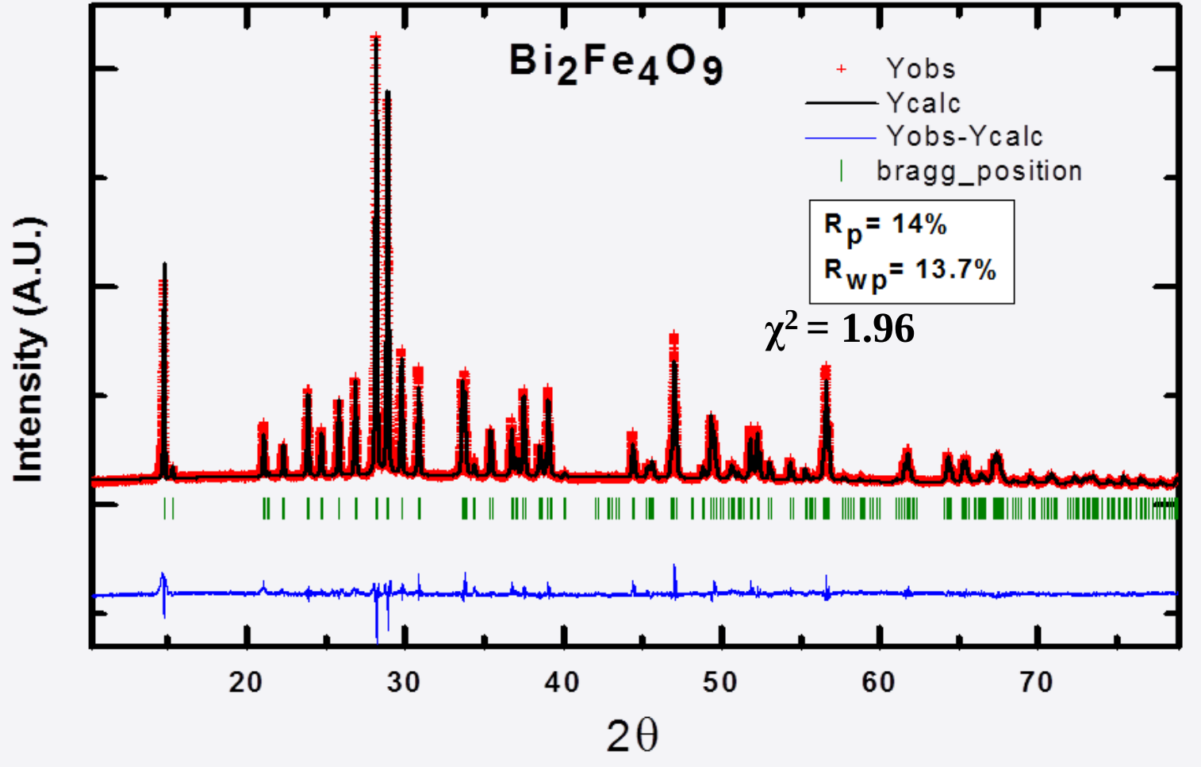


Fig 4: Reitveld refinement of $Bi_2Fe_4O_9$.

Field Emission Scanning Electron Microscopy:

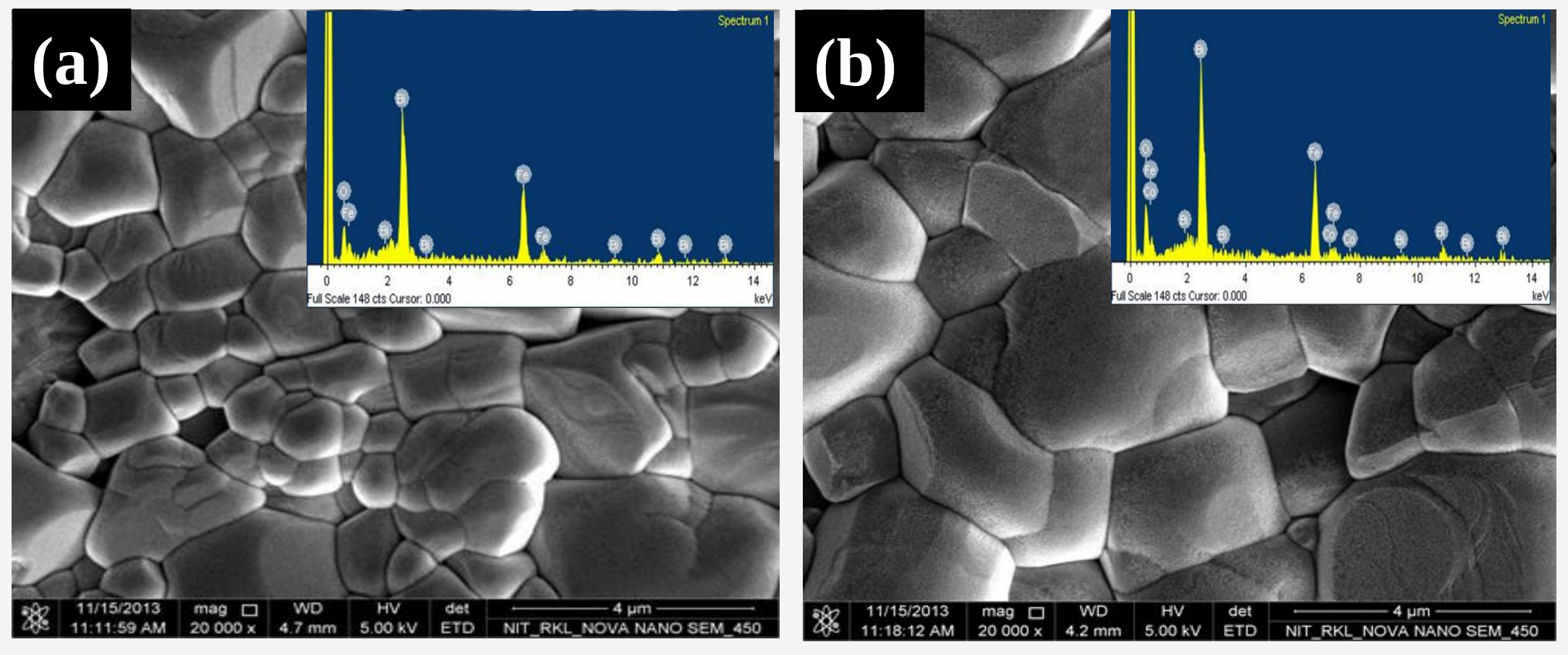


Fig 5: FESEM of (a) $Bi_2Fe_4O_9$ and (b) 5% Co doped $Bi_2Fe_4O_9$. Ionic radii of Fe^{3+}= 78.5pm and Co^{3+} = 75pm

Dielectric measurement:

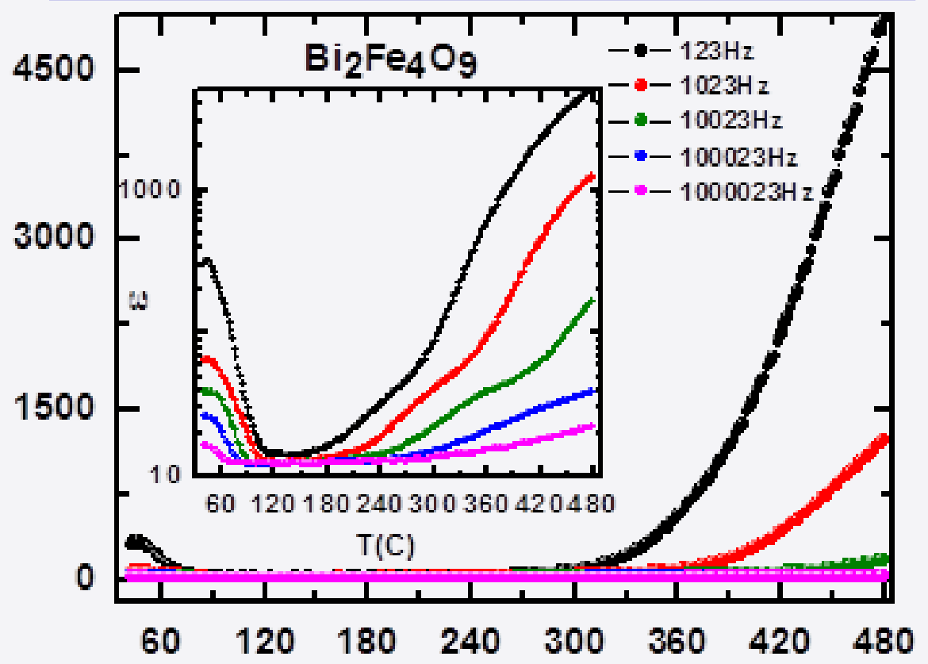


Fig 6(a)

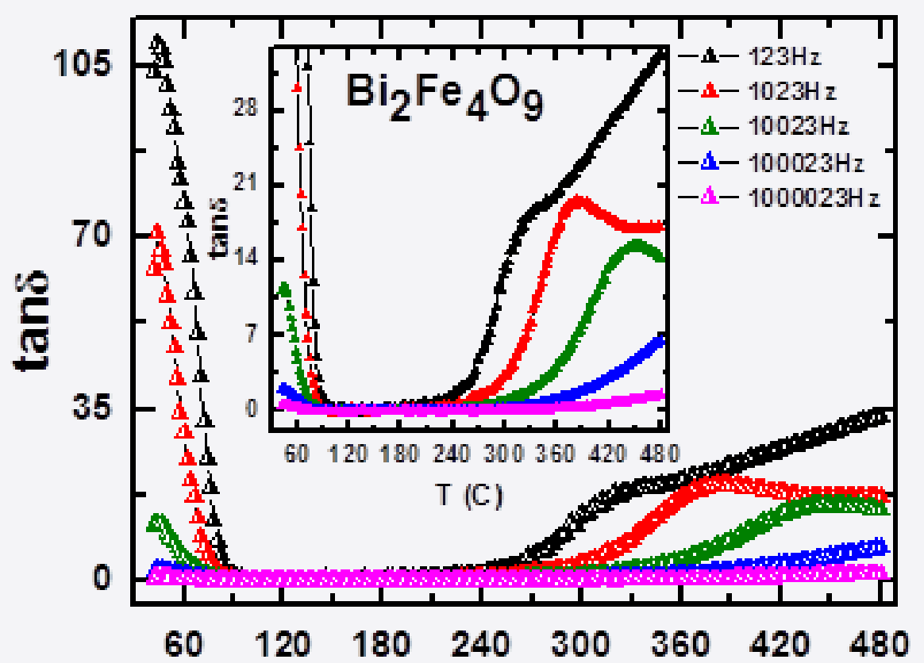


Fig 6(b)

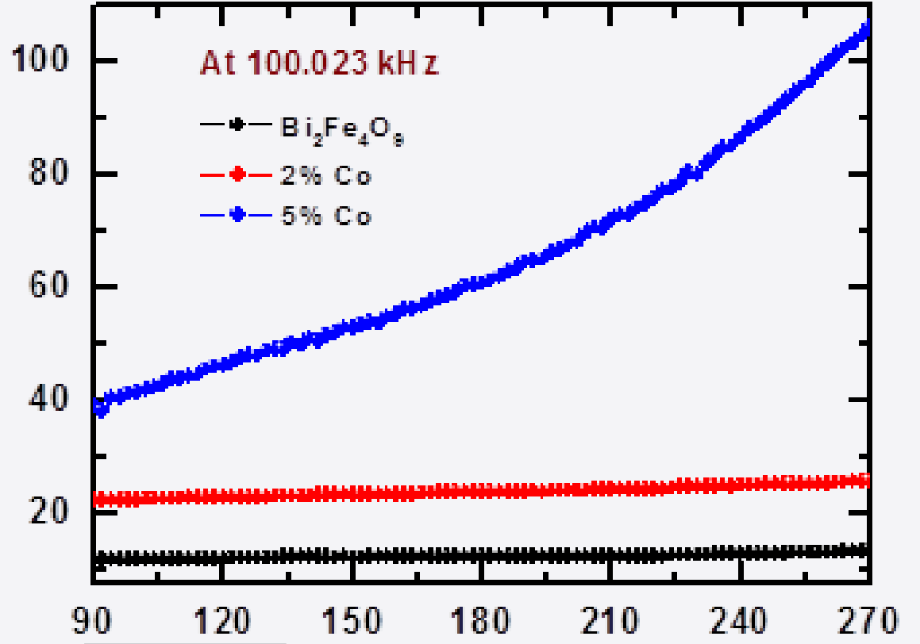


Fig 6(c)

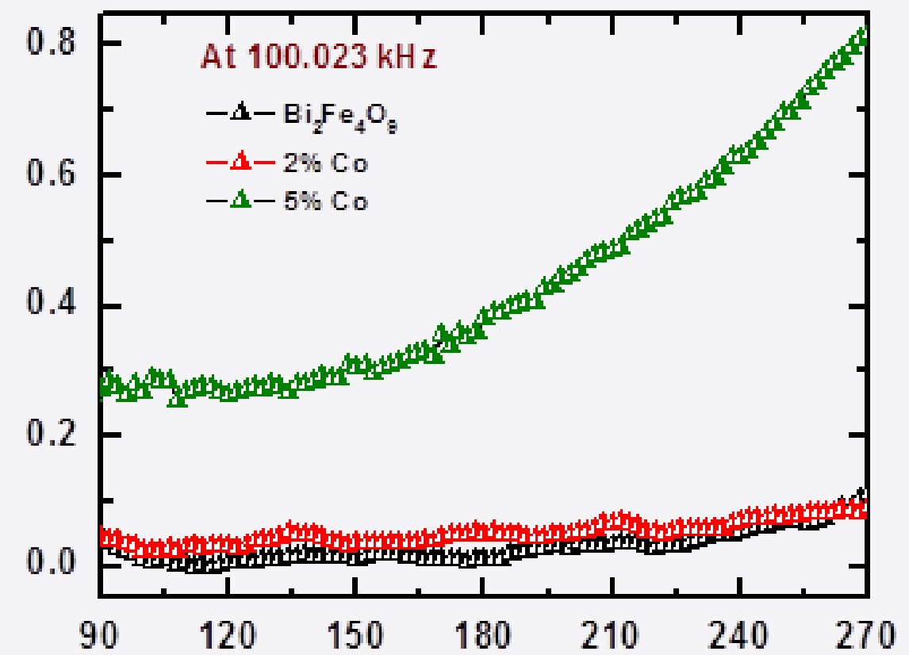


Fig 6(d)

Magnetization Study:

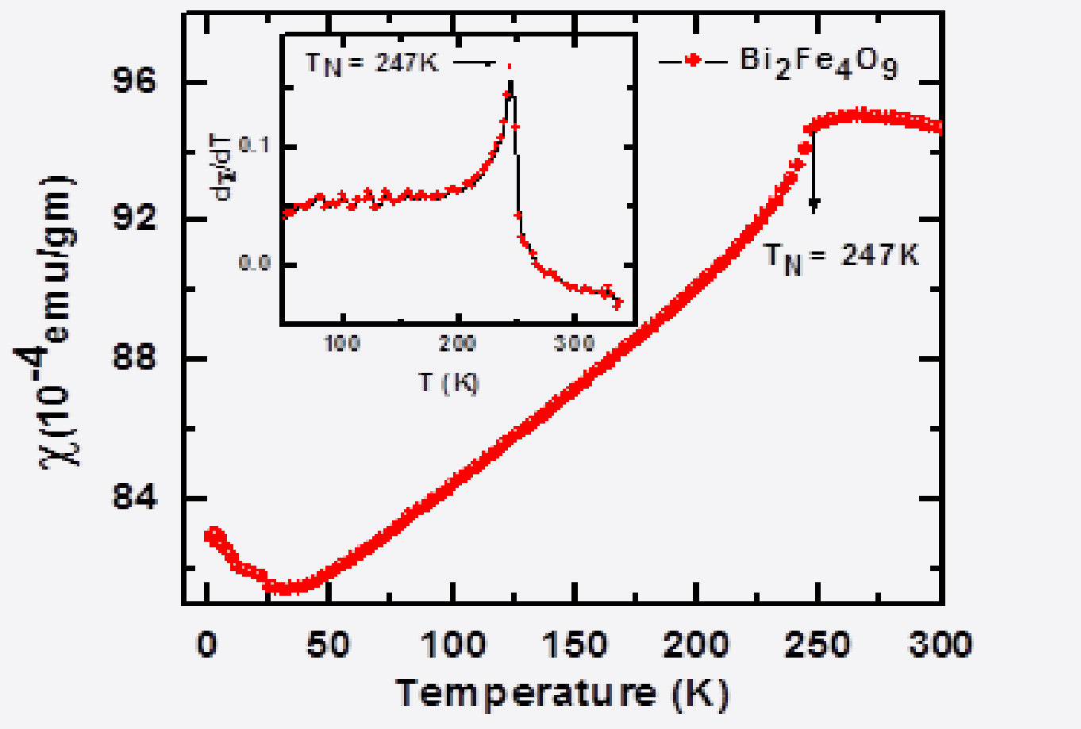


Fig 7: Temperature dependance of DC susceptibility of $Bi_2Fe_4O_9$. Inset shows the derivative of χ with respect to the temperature.

Fig 6(a) and 6(b) shows the variation of dielectric constant and tangent loss w.r.t temperature respectively for different frequencies of $Bi_2Fe_4O_9$.
Fig 6(c) shows at 1023Hz, dielectric constant(ϵ) increases due to Co doping. Fig 6(d) is also in agreement with fig 6(c).

UV Visible Spectroscopy:

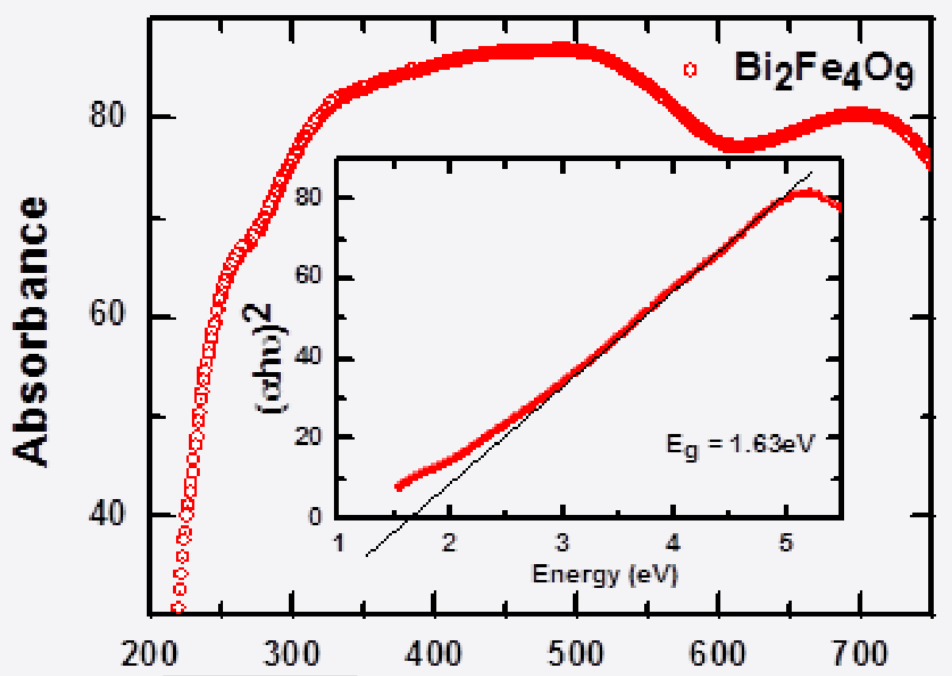


Fig 8(a)

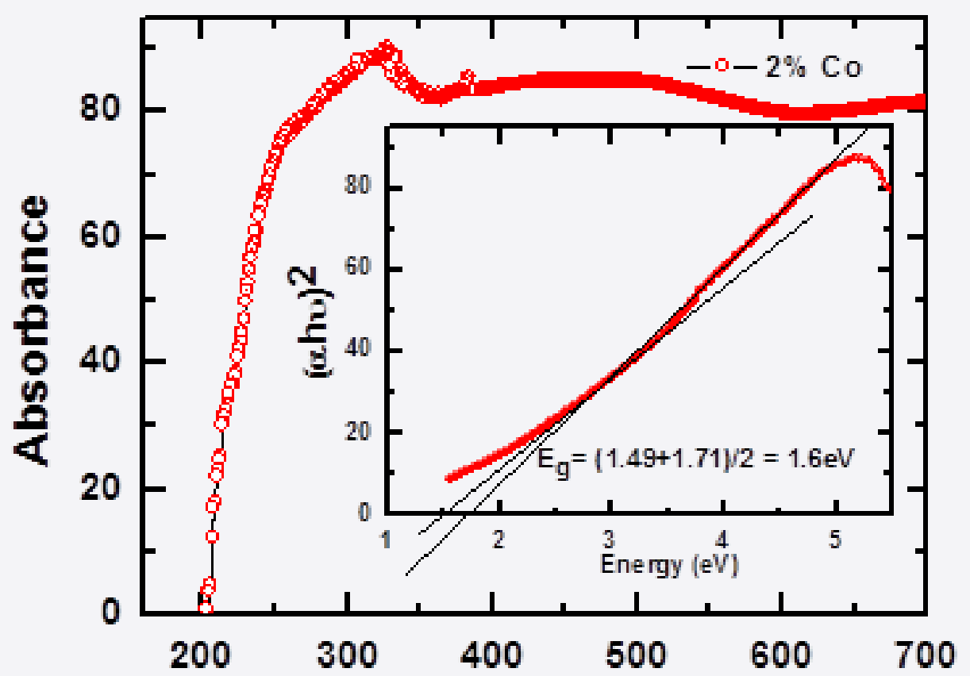


Fig 8(b)

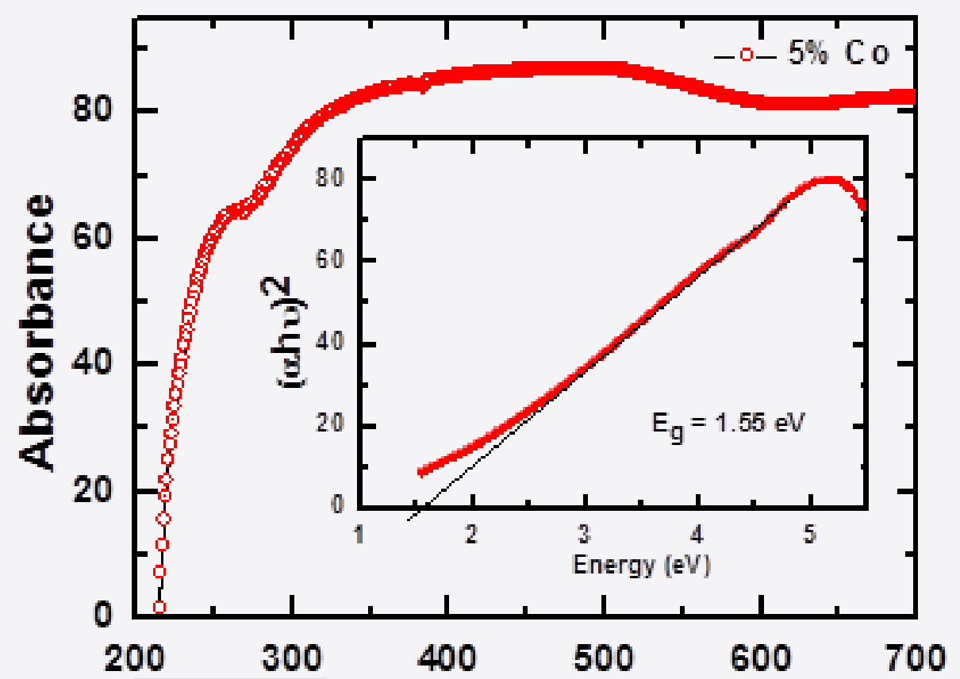


Fig 8(c)

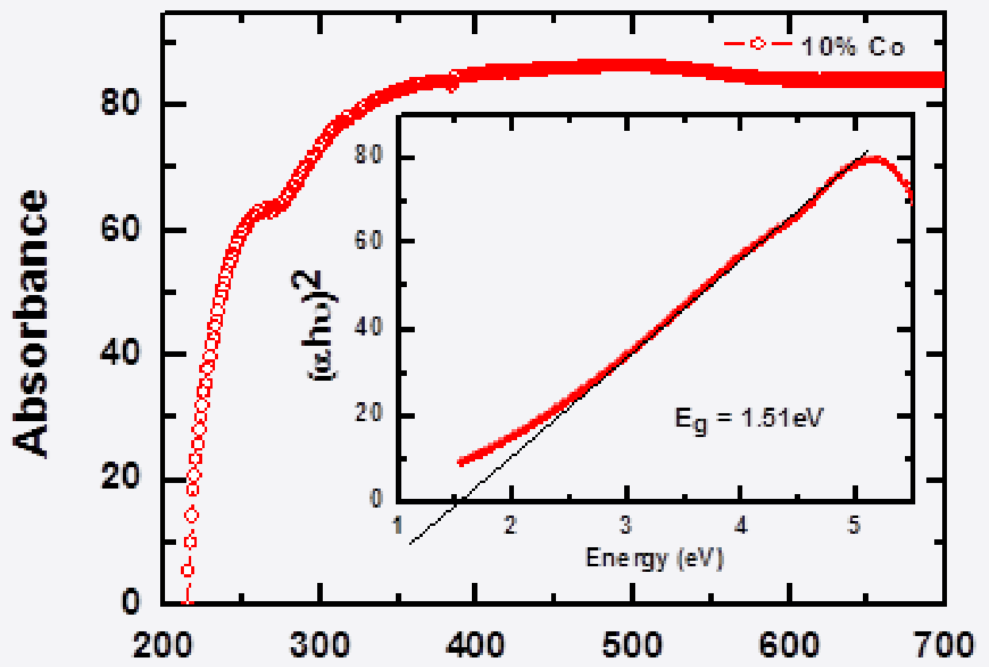
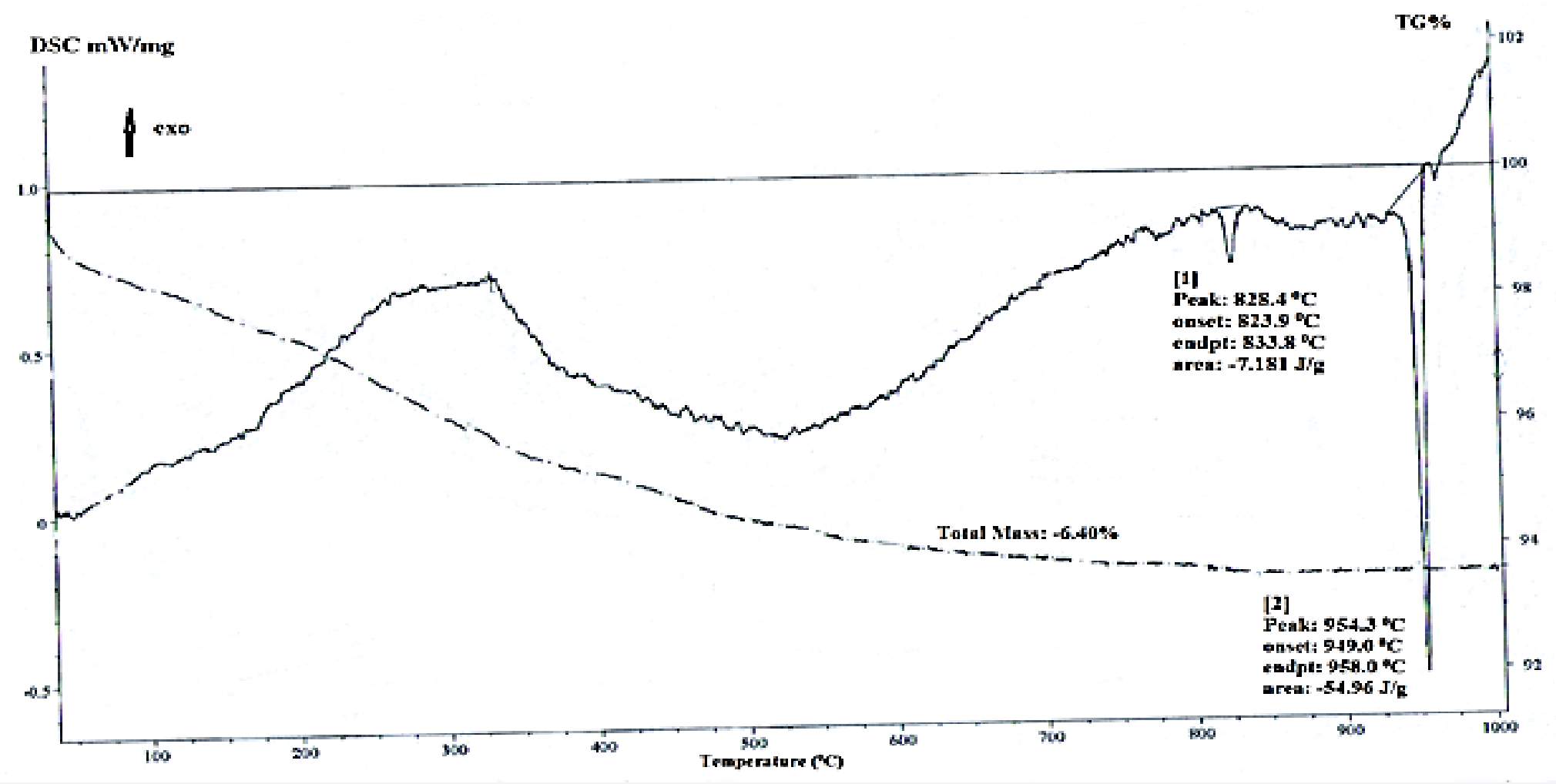


Fig 8(d)

Fig. 4(a-d)- Absorbance versus Wavelength graph of $Bi_2Fe_4O_9$ and different % of Co doped $Bi_2Fe_4O_9$. Inset shows Energy band gap of pure and different % of Co doped $Bi_2Fe_4O_9$.

DSC- TG Study:



❑ Conclusion:

- XRD analysis shows that there is no much significant change in crystal structure due to Co doping.
- FeSEM image shows grain size increases due to Co doping which is in agreement with XRD analysis. EDAX spectrum also confirmed showing $Bi_2Fe_{4-x}Co_xO_9$ $(0 \leq x \leq 0.4)$peaks corresponding to Bi, Fe and Co.
- From dielectric constant measurement we conclude that it shows substantial enhancement in dielectric constant due to Co doping.
- The magnetization versus temperature was measured using SQUID magnetometer in a constant magnetic field of 5000 Oe under Zero field cooled (ZFC) condition. The DC susceptibility shows a plateau below 280K followed by AFM transition at 247K (T_N).
- UV-Visible Spectroscopy plot shows that the band gap energy decreases duo to Co doping. The band gap energy E_g for $Bi_2Fe_4O_9$ was found to be 1.63 eV whereas for 2%, 5% and 10% Co doped $Bi_2Fe_4O_9$, band gap energy (Eg) calculated were 1.6 eV, 1.55eV and 1.51eV respectively.

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