

Structural, Optical and Dielectric Property of Co Doped $\text{Bi}_2\text{Fe}_4\text{O}_9$

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Abstract. Multiferroic $\text{Bi}_2\text{Fe}_4\text{O}_9$ and Co doped $\text{Bi}_2\text{Fe}_4\text{O}_9$ are prepared by solid state route reaction method using bismuth oxide (Bi_2O_3), iron oxide (Fe_2O_3) and cobalt oxide (Co_3O_4). Their structural optical and dielectric properties are studied and compared. X-ray diffraction (XRD) results confirm that there is no change in crystal structure due to Co doping. 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 increases.

Keywords: Multiferroics, Spin frustration, UV-visible spectroscopy.

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INTRODUCTION

Compounds which exhibit both an ordered magnetic phase and a ferroelectric phase are termed as magnetic ferroelectrics or multiferroics [1]. The most promising candidates for such controllable multiferroic have been found among the materials with inherent geometric magnetic frustration. Frustration usually arises due to specific lattice structure when all pairs of magnetic interactions are not simultaneously satisfied. The recent discovery of giant magnetoelectric coupling effect in some frustrated manganites as TbMnO_3 and TbMn_2O_5 has further enhanced the interest in other spin frustrated systems [2, 3]. $\text{Bi}_2\text{Fe}_4\text{O}_9$ belongs to rare class of compounds where due to unique pentagon frustration of magnetic lattice gives rise to magnetoelectric coupling [4, 5].

$\text{Bi}_2\text{Fe}_4\text{O}_9$ crystallizes in orthorhombic structure with space group $Pbam$ [4, 5]. The lattice constants of this structure are $a=8.06\text{\AA}$, $b=8.56\text{\AA}$, $c=6.01\text{\AA}$. The antiferromagnetic transition of $\text{Bi}_2\text{Fe}_4\text{O}_9$ was reported to be $\sim 260\text{ K}$. The iron ions in the $\text{Bi}_2\text{Fe}_4\text{O}_9$ lattice are evenly distributed between the tetrahedral and octahedral positions with each octahedral magnetic Fe^{3+} is surrounded by six O^{2-} forming FeO_6 unit, while tetrahedral magnetic Fe^{3+} are surrounded by four O^{2-} forming FeO_4 unit. On the other hand, nonmagnetic Bi^{3+} is surrounded by eight O^{2-} with mutually orthogonal shorter BiO_3 and longer BiO_5 units. The tetrahedral Fe^{3+} interact with each other and with the octahedral Fe^{3+} spins antiferromagnetically, whereas

the octahedral Fe^{3+} mutually interact ferromagnetically [3]. Because of these competing exchange interactions, the magnetic configuration is frustrated and the moments are canted. In the present contribution we have explored the effect of Co doping in $\text{Bi}_2\text{Fe}_4\text{O}_9$ on its structural, dielectric and optical properties at room temperature.

EXPERIMENTAL TECHNIQUES

Polycrystalline $\text{Bi}_2\text{Fe}_4\text{O}_9$ and $\text{Bi}_2\text{Fe}_{3.5}\text{Co}_{0.5}\text{O}_9$ samples were synthesized from high purity Bi_2O_3 , Fe_2O_3 and Co_3O_4 by solid state reaction route. The powders were ground under acetone, pressed into pellets and heated at $850\text{ }^\circ\text{C}$ for 12 hours. Then the samples were characterized by X-ray diffraction. The dielectric constant (ϵ) were measured at room temperature at various frequencies using impedance analyzer N4L-PSM1735. UV-visible spectroscopy was done using Perkin Elmer UV/VIS spectrometer (Lambda 35).

RESULTS AND DISCUSSION

The X-ray diffraction data of polycrystalline samples of $\text{Bi}_2\text{Fe}_4\text{O}_9$ and 10% $\text{Bi}_2\text{Fe}_4\text{O}_9$ are shown in Figure 1. We confirm the correct orthorhombic structure (SG $Pbam$) without any impurity phases. The lattice parameters for $\text{Bi}_2\text{Fe}_4\text{O}_9$ and $\text{Bi}_2\text{Fe}_{3.5}\text{Co}_{0.5}\text{O}_9$ are calculated to be $a=8.10\text{ \AA}$, $b=8.63\text{ \AA}$, $c=6.09\text{ \AA}$ and $a=8.16\text{ \AA}$, $b=8.66\text{ \AA}$, $c=6.22\text{ \AA}$ respectively. Thus due

to 10% co doping c-axes get elongated by ~3% without changing its crystal structure.

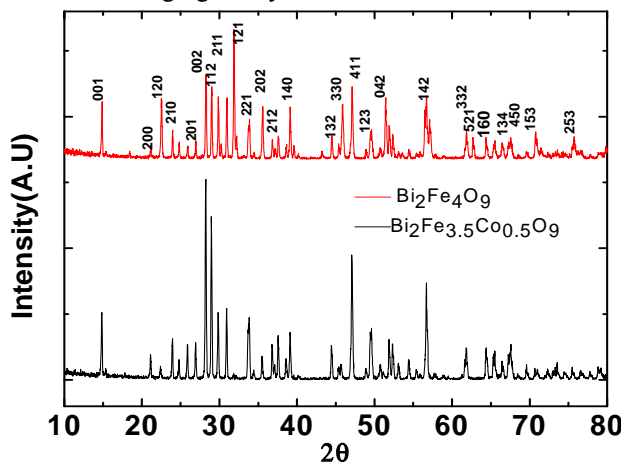


FIGURE 1. XRD pattern of bulk sample of both $\text{Bi}_2\text{Fe}_4\text{O}_9$ and $\text{Bi}_2\text{Fe}_{3.5}\text{Co}_{0.5}\text{O}_9$.

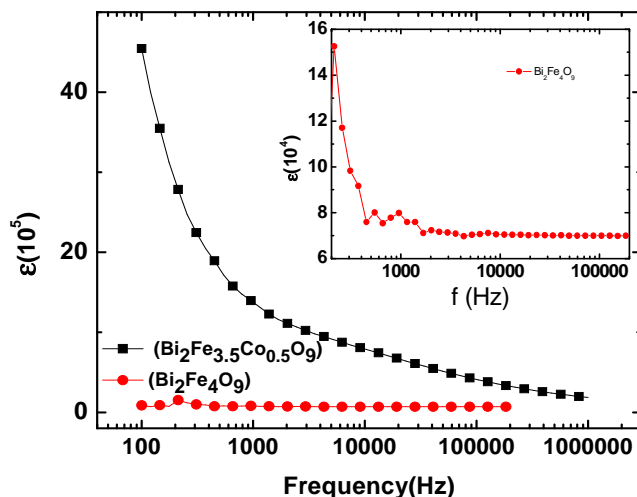


FIGURE 2. Variation of dielectric constant (ϵ) as a function of frequency for both $\text{Bi}_2\text{Fe}_4\text{O}_9$ and $\text{Bi}_2\text{Fe}_{3.5}\text{Co}_{0.5}\text{O}_9$. Inset shows the ϵ versus frequency for $\text{Bi}_2\text{Fe}_4\text{O}_9$.

Shown in Fig 2 is the frequency dependence of dielectric constant (ϵ) with $\text{Bi}_2\text{Fe}_4\text{O}_9$ and $\text{Bi}_2\text{Fe}_{3.5}\text{Co}_{0.5}\text{O}_9$ pallets in the cell at room temperature. A rapid rise in capacitance (dielectric constant $\epsilon = C / C_0$, with $C_0 = \epsilon_0 A / d$, A and d being the circular area and thickness of the pallet) is observed at the lower frequencies. Clearly, 10% Co doping in $\text{Bi}_2\text{Fe}_4\text{O}_9$ increases ϵ by ~200% at 100 Hz and ~20% at 100 kHz.

Optical transmission spectrum of $\text{Bi}_2\text{Fe}_4\text{O}_9$ and $\text{Bi}_2\text{Fe}_{3.5}\text{Co}_{0.5}\text{O}_9$ was measured in the wavelength range of 200 - 1100 nm. The absorption coefficient (α) was calculated from transmittance measurement using the relation $\alpha = -\log(T/100)$ and wavelength was converted

into energy using relation $E = hv = \frac{1240}{\lambda(\text{nm})} \text{eV}$. The plot of

α^2 versus band gap energy is shown in fig 3. In order to determine the nature of band gap (direct or indirect) associated with the absorption bands, optical absorption coefficient data near these points were fitted to relation $\alpha = C(h\nu - E_g)^t$, where $t=1/2$ and $t=2$ correspond to direct and indirect band gap respectively. In the linear region, fitting was done to both the exponents corresponding to $t = 1/2$ and $t = 2$. For $\text{Bi}_2\text{Fe}_4\text{O}_9$, the χ^2 values of the fitting were found to be 1.5×10^{-4} and 1.0×10^{-3} corresponding to $t=1/2$ and $t=2$ respectively. By comparing χ^2 values, we conclude that $\text{Bi}_2\text{Fe}_4\text{O}_9$ is a direct band gap material. The band gap energy of $\text{Bi}_2\text{Fe}_4\text{O}_9$ and $\text{Bi}_2\text{Fe}_{3.5}\text{Co}_{0.5}\text{O}_9$ were calculated to be of about 4.6 eV and 4.8 eV respectively.

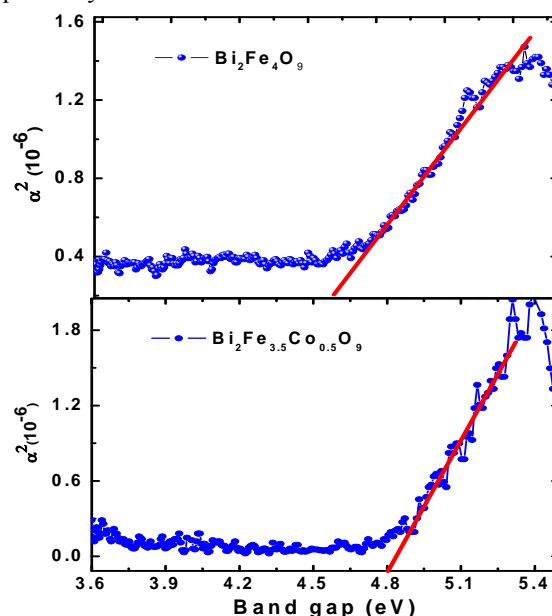


FIGURE 3. Absorption spectra of Co doped $\text{Bi}_2\text{Fe}_4\text{O}_9$.

CONCLUSION

XRD analysis shows that due to 10% Co doping there is no change in crystal structure that remains the same as pure compound. Dielectric measurement shows substantial enhancement in dielectric constant due to Co doping. UV-visible spectroscopy measurement confirms the enhanced band gap.

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