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Neutron Diffraction Studies On Cobalt Substituted $BiFeO_3$

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Abstract. A dilute concentration of single phase Cobalt substituted Bismuth ferrite, $BiFe_{1-X}Co_XO_3$; (x=0, 0.02) is prepared by sol-gel auto combustion method. Room temperature neutron diffraction patterns show no change in the crystal and magnetic structure upon cobalt doping. The calculation of magnetic moments shows 3.848 μ_B for Fe^{3+} and 2.85 μ_B for Co^{3+}. The cobalt is found to be in intermediate spin state.

Keywords: Sol-gel method, LS-IS transition, Neutron Diffraction.
PACS: 75.10.Pq, 75.25.-j, 75.47.Lx, 75.10.Nr

INTRODUCTION

Since its discovery, $BiFeO_3$ (BFO) has been the only prototype among all the multiferroics, and it exhibits G-type antiferromagnetism (T_N = 643 K) superimposed with an incommensurate cycloidal spin arrangement of Fe^{3+} ions with a periodicity of 62 nm resulting in zero net magnetization[1,2]. A special interest of many researchers is for the improvement of the magnetic behavior via some suitable doping at Bi or Fe site[3,4] either by disrupting the cycloidal structure or by inducing lattice distortion. In addition, spin/ cluster glass behavior is observed via chemical substitution with some improved magnetization[5] in the sample. Recently, Xu et al observed a cluster glass behavior in $BiFe_{0.95}Co_{0.05}O_3$[6]. It is well known that Co^{3+} ion exhibits thermally stimulated spin state transitions from low spin (LS; T< 100K) to high spin (HS; T>500K) via an intermediate spin state (IS; 100K<T<500K)[7] which is attributed to the comparable energy of crystal field splitting (Δ_{CF}) of Co-d states and Hund's exchange energy (Δ_H)[8]. All these phenomena motivated us to study the magnetic behavior of Co substituted $BiFeO_3$.

EXPERIMENTAL DETAILS

$BiFe_{1-X}Co_XO_3$ (X=0, 0.02) samples were prepared by a sol-gel auto combustion method[9]. The single phase is confirmed by Reitveld refinement of X-ray diffraction (XRD) data. The structure of the parent as well as doped BFO is rhombohedral, R3c (No.161)[9]. The room temperature (RT) neutron diffraction (ND) measurements were performed at a wavelength of 1.48 Å on the focusing crystal based powder neutron diffractometer set up by the UGC-DAE CSR at Dhruva reactor.

RESULTS AND DISCUSSIONS

Magnetization studies of $BiFe_{1-x}Co_xO_3$; x=0, 0.01 and 0.02 show various magnetic states (superparamagnetic, antiferromagnetic and weakly ferromagnetic, respectively) along with an indication of magnetic field induced first order transition in the Arrot plot[9]. The above mentioned first order transitions strengthens on increasing Co content in the sample. Considering the various spin states exhibited by Co^{3+} as a function of temperature, a cycloidal spin model is proposed to explain these induced magnetic states and the above mentioned spin state transitions in Co doped $BiFeO_3$. In this model, it is considered that substitution of Co^{3+} ion at the Fe site leads to the creation of a weak link between two neighboring HS Fe^{3+} ions in the cycloid (see fig 1). This weak link is more pronounced when Co^{3+} goes to LS state on lowering the temperature. Hence because of these weak links, the long cycloidal structure virtually splits in various smaller segments, which upon application of magnetic field may re-orient accordingly. Though the present model successfully explains the observed magnetic phenomenon, a direct evidence of various spin states acquired by Co^{3+} on lowering the temperature is very much needed. Hence in order to confirm our

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proposition and strengthen the proposed model, ND measurements were carried out for X=0 and 0.02 samples.

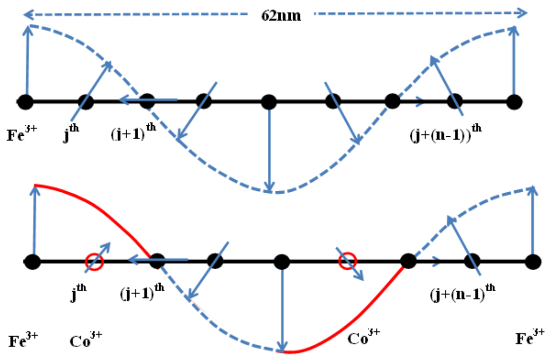

FIGURE 1. A schematic model showing the status of a cycloidal spin arrangement of $BiFe_{1-X}Co_XO_3$(X=0, 0.02). Here the Fe^{3+} and Co^{3+} are represented by solid black and hollow red spheres respectively. The arrow stands for the magnetic moments of iron (big) and cobalt (small). The solid portion of the curve represents the region of weak link formed by Co^{3+} in the cycloidal spin structure.

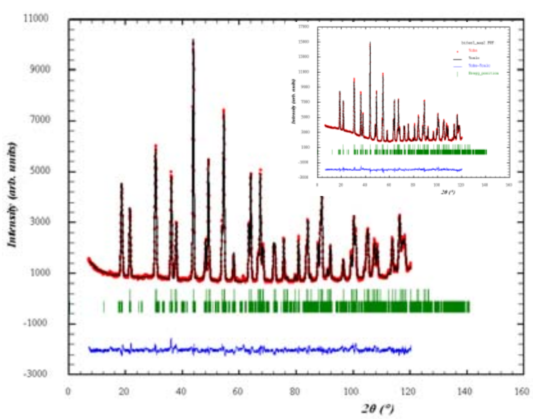

FIGURE 2. Reitveld refinement of the neutron diffraction pattern of $BiFe_{1-X}Co_XO_3$ (X=0 (inset), 0.02).

The ND data confirm the single phase of both parent and cobalt doped BFO. The magnetic structure at room temperature (RT) is solved by refining the ND data for both parent and doped sample. G-type antiferromagnetism with a long range cycloidal spin structure propagating along the [110] direction is confirmed for both the samples. Lattice parameters so obtained for x=0 are *a* = 5.58 Å and *c* = 13.87Å and no apparent change is observed due to cobalt doping. This is probably due to the similar ionic radius of Fe and Co. The magnetic refinement shows random substitution of Co at Fe sites. At x=0.02, nearly two Co^{3+} ions substitute the Fe^{3+} ions in one complete cycloid[9]. At RT, the Co^{3+} ions are supposed to be in IS state (S=1; $\mu = 2\sqrt{S(S+1)} = 2.828\ \mu_B$). The magnetic moment of Fe^{3+} in x=0 is found to be 3.848 μ_B and in x=0.02, it is found to be 3.828 μ_B. Since this value is the net effect due to both Fe^{3+} and Co^{3+}, the magnetic moment of Co^{3+} is obtained using the relation,

$$\mu_T = 0.98(\mu_{Fe(III)}) + 0.02(\mu_{Co(III)}) \qquad (1)$$

which is found to be 2.85 μ_B. This result is in agreement with one of our proposition that Co^{3+} is in IS state at RT. ND measurements are in progress to confirm the IS to LS transition of Co^{3+} at low temperature. A slight increase in the Fe-O and Bi-O bond lengths due to cobalt doping is also observed via refinement of neutron data as shown in Table 1.

Table1: Structural parameters obtained from ND

	$BiFeO_3$	$BiFe_{0.98}Co_{0.02}O_3$
Bi	0,0,0	0,0,0
Fe	0.2209	0.2211
O	0.446,0.0165, 0.9524	0.4471,0.0175, 0.9528
Bi-O	2.5313(6) Å	2.5335(9) Å
Fe-O	2.1109(12) Å	1.9496(9) Å
O-Fe-O	89.4357(9) deg	88.1023(6) deg

CONCLUSIONS

Single phase cobalt substituted Bismuth ferrite ($BiFe_{1-X}Co_XO_3$; x=0, 0.02) nanoparticles are prepared by the sol-gel method. The cycloidal spin structure along [110] propagating direction is found for x=0 sample, with IS spin state of Co^{3+} at room temperature. The calculation of magnetic moment for both the sample shows 3.848 μ_B for Fe^{3+} and 2.85 μ_B for Co^{3+}.

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