Crystal structure and magnetic properties variation at phase boundaries in Nd and La co-doped BiFeO$_3$

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Abstract: Nd and La co-doped $Bi_{0.8}Nd_{0.10}La_{0.10}FeO_3$ multiferroics have been synthesizedvia solid state reaction method. The XRD patterns recorded at room temperature indicate slights variations in crystal structure with composition. The refinement of the XRD patterns (shown in Fig.1reasoned mixed crystal structure formulation exhibiting rhombohedral R3c and orthorhombic Pbam phases in the prepared samples.The cause behind such transition may be attributed to the mismatch of the ionic radii among Bi^{3+} (1.03Å), Nd^{3+} (0.983Å) and La^{3+} (1.032Å) producing inhomogeneous lattice strains, which indeed transforms the crystal structure. The M – H loops obtained by VSM shows in Fig.2.

The presence of antiferroic orthorhombic Pbam phase in the prepared samples suggests the reorientation of magnetic dipoles and thus driving the structure towards weak ferromagnetic state.[1] Again rise of magnetisation proportionate with this orthorhombic Pbam phase confirms the modification in the spiral modulation.Moreover on comparing, the doping ofLa is found stabilise the orthorhombic symmetry and enhanced magnetisation as compared to Nd.

Introduction:

Multiferroic materials exhibiting more than one ferroic properties amongst ferroelectricity, ferromagnetism and ferroelasticity has become the worthy class for research and advanced device applications. Amongst the same, BiFeO3 Bismuth ferrite multiferroics has been in the advent area of research and implication prospective, as it exhibit magnetoelectric coupling through record high transitions temperature ranges with ferroelectric Curie temperature at 1103K and antiferromagnetic Neel temperature at 643K. The other multiferroics, reported till now, shows multiferroism either below room temperature or in short ranges of temperature. BiFeO3 crystallizes in distorted rhombohedral structure with R 3 c space group, which is in the form of a G-type canted antiferroic order associated with spatially modulated spiral spin (SMSS) structure. The wavelength associated with in the spiral structure is of the order of 62 nm, as result the macro magnetisation effect is seriously affected and the linear magnetic effects are hindered. Secondly, the volatile nature of Bi leads to give birth to secondary phases like Bi2Fe4O9, Bi29FeO39 and Bi36Fe24O57 in the process of synthesis. These phases cause serious current leakage problems and derive the compound away from the ferroelectric concept of BiFeO3.

Experimental Details

High quality Bi2O3, Nd2O3, BaCO3 and Fe2O3 reagents from Sigma Aldrich were taken in stochiometric amounts and ground well in agate mortar with pestle for 4 hours. Then calcination of the prepared mixture was done at 400˚C for 5hours in air starting from room temperature and taken out after natural cooling. Then the calcined powders were again ground for 2 hour in agate mortar. The sintering was performed at 800˚C for 2 hour in air starting from room temperature and the samples were taken out after natural cooling. The X-ray diffraction of the prepared samples was carried out by Rigaku Miniflex-II table top X-Ray diffractometer. The scan range and scan rate for collecting the XRD patterns were selected 10˚ - 80˚ and 2˚ per minute respectively. The refinement of the XRD patterns was performed through Rietveld method by FullProf suite. Magnetic properties were evaluated using vibrating sample magnetometer which was carried out at room temperature with a maximum applied field of 15 kOe.

Results and Discussion

Fig.1. Shows the XRD patterns of $Bi_{0.8}Nd_{0.10}La_{0.10}FeO3$ sample collected at room temperature. The XRD pattern shows changes in the peak shape in the vicinity of 32° of 2θ, indicating transitions in the crystal structure. The refinement of the XRD patterns confirms the transition in phase and deduces the occurrence of mixed phases in all the samples. The structure of whole series is found to comprise rhombohedral R3c and triclinic P1 phases but with interesting phases fraction evolution via the variation of co-dopant's concentration.
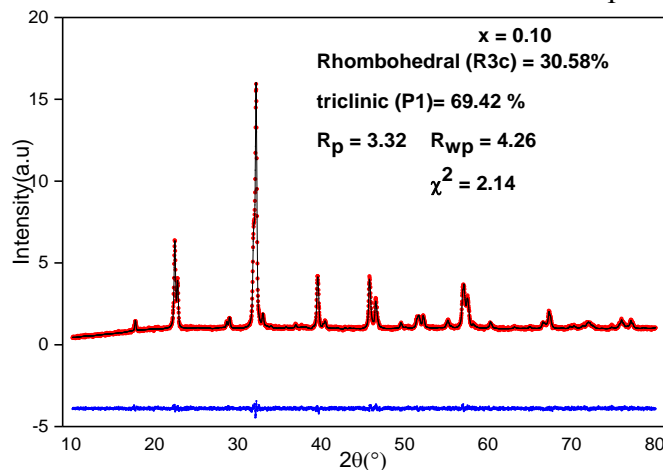

Fig.1 Refined XRD patterns of $Bi_{0.8}Nd_{0.10}La_{0.10}FeO3$ multiferroics.

TABLE 1. Crystal structure parameters obtained by Rietveld analysis of XRD patterns o.Bi0.8Nd0.10La0.10FeO3

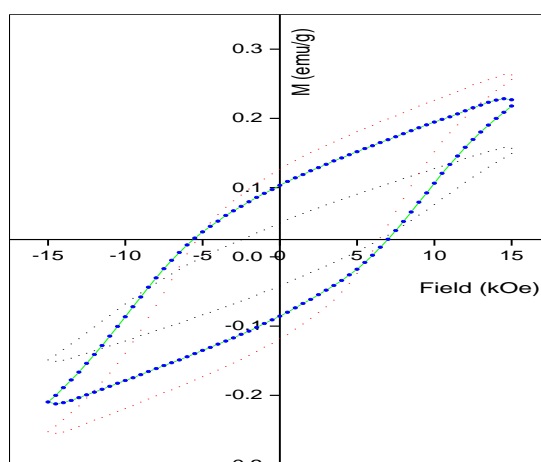| Sample Name	Space group	a (Å)	b (Å)	c(Å)	volume per unit cell (Å3)	χ^2
$Bi_{0.8}Nd_{0.10}La_{0.10}FeO_3$	R3c(≈30.58 %) +	5.5656	5.5656	13.8187	368.301	2..14
	P1(≈69.42 %)	4.3036	4.1022	3.8847	67.746	

Fig.2 M – H loops of $Bi_{0.8}Nd_{0.10}La_{0.10}FeO3$ multiferroics

The M – H loops obtained through VSM are shown in figure 2. The pristine BiFeO3 lacks in magnetisation via the presence of spin cycloid which renders the spins to be canted anti-ferro magnetically.

Conclusions

Two stage solid-state reaction method has been used to synthesised the Nd and La co-doped Bi0.8Nd0.10La0.10FeO3 multiferroics and their structural, magnetic properties have been reported. XRD analysis and Rietveld refinement show that sample have a mixed phase with combination of Rhombohedral (R3c) and triclinic (P1) symmetries. Highest value of magnetization is observed.

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