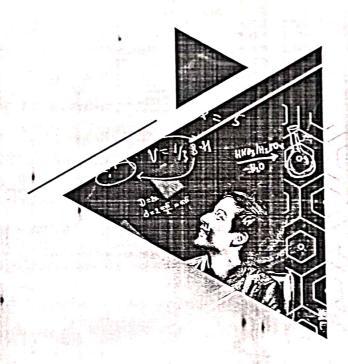
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Role of State and Market: In The Context of Indian Higher Education Sector

Edited By

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The Crystal Structure, Refinement and Dielectric Properties of Ba and Mn Substituted Bismuth Ferrite

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• Abstract. The effect of Ba and Mnsubstitution on the crystal structure and dielectric properties of BiFeO₃ has been studied using X-ray diffraction at room temperature, Rietveld refinement and dielectric properties measurements technique. Single phase Bi_{0.8}Ba_{0.2}Fe_{1.x}Mn_xO₃ (x=0.01, 0.05)multiferroics have been synthesized by two stage solid state reaction method. Rietveld refinement of both the samples revealed thatthe synthesized ceramics exhibit rhombohedral structure with space group R3c as of parent BiFeO₃. The dielectric response of both samples was analyzed in the frequency range 100 Hz-2 MHz at different temperatures revealing dispersion in dielectric constant (ε') and in dielectric loss (tanδ) at lower frequencies. Both ε' and tan δ increase with increase of Mn content.

INTRODUCTION

Now a day, there has been revival of interest in multiferroics materials in which magnetism and ferroelectricity exists in single phase. Such materials are relatively rare and interesting due to the physics behind them [1, 2]. Among all multiferroic materials, Bismuth Ferrite has gain so much attention as it is the only known material which has ferroelectric and antiferromagnetic orders (ferroelectric Curie temperature $T_C \sim 1100 K$ and high antiferromagnetic Neel temperature $T_N \sim 640 K$) well above room temperature. This behavior makes it suitable for various practical applications like sensors, actuators, memory devices etc.BiFeO₃ (BFO) has a rhombohedrally distorted perovskite structure with space group R3c in which polar cation (Bi³⁺) is present at A-site and magnetic cation (Fe³⁺) at B-site with G-type antiferromagnetic order [3-4]. Apart from the positives BFO has some problems as well which are (i) it has spiral spin structure which inhibits the macroscopic magnetization (ii) synthesis of single phase BFO (iii) high leakage current and low electrical resistivity [3-5]. Many solutions have been tried up and among them ionic substitution is found to be suitable to minimize these issues. So in this present work; substitution of diamagnetic divalent ion i.e., Ba is done at Bi site and transition metal ion i.e., Mn at Fe site is done and there structural and dielectric properties has been studied.

EXPERIMENTAL DETAILS

Conventional two stage solid state reaction method has been employed to synthesize the $Bi_{0.8}Ba_{0.2}Fe_{1-x}Mn_xO_3(x=0.01, 0.05)$. The appropriate materials Bi_2O_3 , $BaCO_3$, Fe_2O_3 , and Mn_2O_3 , ($\geq 99\%$ pure) reagents were taken in stoichiometric ratio, mixed properly and grounded in an agate mortar to obtain a homogenous mixture. These mixtures were calcined at 673 K for 4h at the rate of 5 K /minand grinding was again done for 1 hour to get

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more homogeneous mixture. Final sintering was carried out at 1123 K for 4 hours for and cooled at room temperature to obtain a single phase perovskite. Structural Characterization was done by X-ray diffraction at room temperature, XRD patterns were collected by using RigakuMiniflex-II diffractometer with CuK_n radiation ($\lambda = 1.54\text{Å}$) in the 20 range from 20° to 80° with the scanning rate of 2° min⁻¹ at room temperature. Rietveld Refinement of XRD data has been earried out using FullProf program. The impedance measurement was performed using an impedance/gain phase analyzer (Newton's 4th Ltd.). Dielectric data was recorded in the frequency range of 100 Hz to 1 MHz and temperature range 313 K to 623 K.

RESULT AND DISCUSSION

XRD pattern of polycrystalline Bi_{0.8}Ba_{0.2}Fe_{1.x}Mn_xO₃ (x=0.01, and 0.05 and henceforth designated as Mn 01 and Mn 05 respectively) multiferroics (Figure 1) exhibit single phase perovskite structure with traces of impurity phases (Bi₂Fe₄O₉, Bi₂₅FeO₃₉). Absence of any 'extra peak in both the sample indicates that no complete structural' transformation takes place.

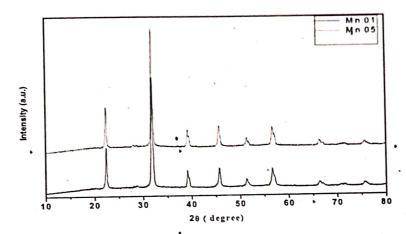
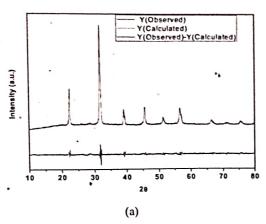


FIGURE 1.XRD patterns of $Bi_{0.8}Ba_{0.2}Fe_{1-x}Mn_xO_3$ (x = 0.01, and 0.05) multiferroic samples at room temperature.

In order to analyse the structural properties, the observed XRD patterns of both the samples have been refined using the Rietveld refinement method by FullProf program. Structure of Bi_{0.8}Ba_{0.2}FeO₃ has been ascribed to rhombohedral with space group R3c as reported earlier [4]. The ground state space group does not change with Mn substitution which is also reported by Yin et al [6]. Therefore Rietveld refinement of Mn01, Mn 05 samples was performed using same space group i.e. R3c and the structural model allow us to reproduce all the observed peaks. The observed, simulated and difference XRD pattern resulting from refinement are shown in Figure 2.



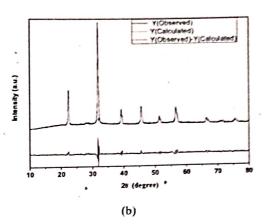


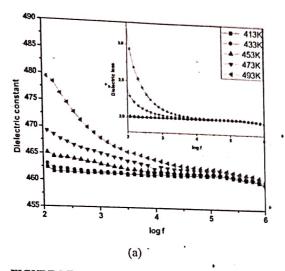
Figure 2.Observed, calculated and difference of Rietveld refined XRD patterns of $Bi_{0.8}Ba_{0.2}Fe_{1-x}Mn_xO_3$ (a) x = 0.01, (b) x = 0.05 samples.

The refined parameters are listed in table 1. With increase in the content of Mn, lattice parameters 'a', 'c' and volume decreased. But ionic radii of Mn³⁺ are same as that of Fe³⁺ i.e. 0.645 Å, which normally suggests that there should be no change in the lattice parameters with increase in the manganese content. But Fe and Mn are versatile species with multiple oxidation state, which points towards that Mn exists in Mn⁴⁺ state as also reported earlier [7].

TABLE 1. Refined structural parameters of $\mathrm{Bi}_{0.8}\mathrm{Ba}_{0.2}\mathrm{Fe}_{1-x}\mathrm{Mn}_x\mathrm{O}_3$ samples only.

		Mn=0.05
Concentration	Mn=0.01	Rhombhohedral
Crystal Structure Lattice paramters	Rhombhohedral a = 5.6359Å c = 13.6926Å V = 376.661Å ³	a=5.6314Å c=13.6905Å V=376.457Å ³
Atomic Positions	Bi/Ba(0, 0, 0.2361) Fe/Mn (0, 0, 0) O (0.8018, 0.6270, 0.423	Bi/Ba(0, 0, 0.2391) • Fe/Mn (0, 0, 0) O (0.7912, 0.6053, 0.4304)
R-factors	$R_p = 4.14$ $R_{wp} = 5.38$ $\gamma^2 = 3.49$	$R_p = 4.81$ $R_{wp} = 6.43$ $\chi^2 = 4.91$

Figure 3 represents the frequency dependence response of dielectric constant (ε') and dielectric loss (tan δ) for all the ceramics at different temperature. The dielectric constant for all the samples shows dispersion behaviour at low frequencies, and becomes constant at higher frequencies. Large values of ε' at low frequencies may be ascribed to the interfacial dislocations, oxygen vacancies, grain boundary effect etc., while as frequency is increased the charge carriers are not able to follow the applied external applied field and so there is a decrease in dielectric constant. This type of behaviour may be explained on the basis of Maxwell Wagner type interfacial polarization [8-9]. According to M-W model, the dielectric material is made up of well conducting layer of grains that are separated by grain boundaries which are highly resistive. At low frequency, grain boundaries have more impact than the grains and due to this charge accumulate near the boundary causes high dielectric constant. Howsoever at high frequency are grains comes into play which in turn reduced the probability of hoping conduction mechanism, results in the decrement in dielectric constant in that region and become constant at high frequency regime [10]. Similar behavior was observed in dielectric loss. At low frequency, grain boundary offered high resistance leads to large energy dissipation and high value of dielectric loss. On the contrary, at high frequency low resistance is offered by grains, causes small value of dielectric loss[8-10].



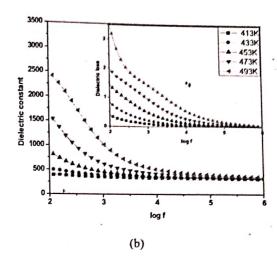


FIGURE 3.Frequency dependence of real part of dielectric constant (ϵ') and dielectric loss (tan δ) at inset of Bi_{0.8}Ba_{0.2}Fe₁- $_x$ Mn_xO₃ for (a) x = 0.01, (b) x = 0.05.

As the temperature increases, dielectric constant also increases due to the thermal conduction hopping mechanism. With increase in concentration of Mn dielectric constant increase appreciably which is the desirable result. Improvement in dielectric properties may be attributed to the suppression of oxygen vacancies created by the substitution of divalent ion (Ba²⁺) in place of volatile trivalent ion (Bi³⁺) by high valance of Mn ion to neutralise the charge [10, 11].

CONCLUSIONS

 $Bi_{0.8}Ba_{0.2}Fe_{1.x}Mn_xO_3(x=0.01, 0.05)$ multiferroics were synthesized by solid state reaction method. XRD pattern and Rietveld refinement shows that all the samples are phase pure and crystallized in rhombohedral structure with space group R3c. Dispersive behavior of dielectric constant (ϵ ') and dielectric loss ($\tan \delta$) is observed at low frequency. Improved dielectric properties are attributed to the suppression of oxygen vacancies by Mn ion.

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Structural, dielectric and magnetic properties of (Ho, Ti) modified BFO

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Structural, Dielectric and magnetic Properties of (Ho, Ti) Modified BFO

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Abstract. Bi_{0.80}HQ_{0.20}Fe_{0.80}Ti_{0.20}O₃multiferroicswas synthesized by method of mixed-oxide route. The XRD, dielectric properties and magnetic measurements of the compound were carried out. The X-ray structural analysis shows mixed phase. Rietveld refinement of the XRD patterns deduce that the found it fit by the mixed phase setting of rhombohedral R3c and triclinic P1 space group. The change in crystal structure is attributed to the distortion of FeO₆ octahedra due to replacing a part of B- site Fe ions by Ti ions. Magnetic evaluation were performed at room temperature up to an external magnetic field of ±6kOelt was observed that the Ti co-dopingshows a significant role for the improving multiferroics properties.

INTRODUCTION

The materials in which at least two of ferroelectric, ferromagnetic and ferro-elastic ordering exhibit in the same phasesimultaneously have been under concentrated study recently [1-2]. These materials have greatuse in the large magneto electric effect and have potential application which include information storage, spintronic devices, sensors etc. BiFeO₃ (BFO) belongs to this class [3] at room temperature. It is only single phase fascinating multiferroic material because of its high ferroelectric Ctrie temperature, ($T_c=1143 \cdot K$) and antiferromagnetic (AFM) Neel temperature ($T_N=643K$) [3-4]. The simultaneous doping of titanium and lanthanide can enhance together electrical and magnetic properties of BiFeO₃. Some other exciting results also have been reported in literature for BiFeO₃ when codoped with La and Ti;Dy and Ti[5].In this study, we have fabricated BiFeO₃ ceramics with codoping of Ho and Ti and found enhancement in electrical and magnetic properties.

Various attempts have been made by many researchers to enhance the multiferroicscharacteristics of BFO by co-doping at the sites A and B simultaneously. As Ho possesses high magnetic moment, so Bi has been substituted with it in the present work and therefore, co-doped BiFeO₃ceramic samples in which doping is done by Ho at A-site and Ti at B-site.

EXPERIMENTAL DETAILS

High quality oxide powders of Bi₂O₃, Ho₂O₃, Ti₂O₃ and Fe₂O₃ procured from Sigma Aldrich, their particular amount in stochiometric ratio was grounded thoroughly with the help of mortar and pestle for 2 hours and then calcinated for 3 hours at 400°C. The calcinated compound then grounded for 1 hour and sintered for 1 hour at 820°C in an alumina crucible. Structural analysis were performed using X-ray diffraction (XRD) using Rigaku-Miniflex II Desktop X-Ray diffractometer, scanning electron microscopy. The quality XRD pattern was further analyzed using a Rietveld refinement and Edper program in FullProf suite software. Micrographs evaluation were carried out using JEOL scanning electron microscope (SEM), respectively. Magnetization measurements were performed at room temperature using vibrating sample magnetometer (VSM) (model Lakeshore,7304).

Sample	Model	Cell (Å)	Atom	<u> </u>	v	Z	R-factor
Bi _{0.80} Ho _{0.20}	R3c (66.42%)	a= 5.5693 b= 5.5693 c=13.6702 V= 367.204(Å ³)	Bi/Ho Fe/Ti O	0.0000 0.0000 -0.1984	0.0000 0.0000 1.6068	0.02485 0.25115 0.7148	$R_p = 4.90$
Fe _{0.80} TiO _{.20} O ₃	P1 (33.58%)	a=4.3307 b=4.0994 c=3.8903 V=68.2819(Å3)	Bi/Ho Fe/Ti O1 O2	0.16159 0.63868 1.5028 2.8796	7.85772 8.46743 1.8327 0.7321	0.37914 0.91230 0.1741 -1.0982	$R_{wp} = 6.27$ $\chi^2 = 4.88$
			O3	-1.2690	1.1918	5.6569	

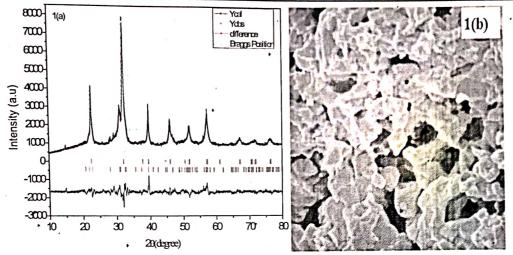


Fig 1.The Rietveld refined XRD patterns and 1(b) SEM micrographs ofBi_{0.80}Ho_{0.20}Fe_{0.80}TiO_{.20}O₃ ceramic.

Fig. 1 shows the Rietveld refined XRD spectrums of Bi_{0.80}Ho_{0.20}Fe_{0.80}Ti_{0.20}O₃ The Rietveld refinement of XRD pattern was best fitted by the mixed phase assumption including rhombohedral R3c (≈66.42%) and triclinic P1 (≈33.58%).

The parameters obtained from refinement are summarized in Table I.

Table 1. Rietveld refined structural parameters of Bi0.80Ho0.20Fe0.80Ti0.20O3 of XRD.

Fig. 1(b) explain scanning electron micrographs (SEM) of Bi_{0.80}Ho_{0.20}Fe_{0.80}Ti_{0.20}O₃. The micrographs represent the dense and uniform morphology of the sample. It signifies that Ti doping suppressesthe growth of grainsresulting in small grain sizes of highly doped sample reflects in the SEM micrographs. Another possible reason of decrease in grain sizes is the dissimilarity in the ionic radius of Bi³⁺ and Ti³⁺. Earlier studies suggested that the reduction in the grain size is ascribed to the suppression of oxygen vacancies with the Ti doping. Since the motion of oxygen vacancies during the sintering mechanismare responsible forgrowth of grains. Structural symmetry for (Ni, Co, Cd, Nd, Ho with Ti)-co-doped BFO is summerized in Table 2.

TABLE 2.Structural symmetry for (Ni,Co,Cd,Nd,Ho with Ti) co-doped BFO is summerized.

S. No.	Compounds Name	XRD Structure	Average Crystallite Size	Reference
1.	Bi(Ni _{1/4} Ti _{1/4} Fe _{1/2})O ₃	Orthorhombic Symmetry	28 nm	[2]
2.	Bi(Ni _{0.45} Ti _{0.45} Fe _{0.10})O ₃	Tetragonal Symmetry	30 nm	[4]
3.	Bi(Ni _{0.40} Ti _{0.40} Fe _{0.20})O ₃	Orthorhorhbic Symmetry	36 nm	[1]
• 4.	Bi(Co _{1/4} Ti _{1/4} Fe _{1/2})O ₃	Orthorhombic Symmetry	30 nm	[3]
5.	Bi _{0.90} Nd _{0.10} Fe _{0.93} Ti _{0.07} O ₃	Triclinic Symmetry		[5]
6.	Bi _{0.80} Ho _{0.20} Fe _{0.80} Ti _{0.20} O ₃	Triclinic+ Orthorhombic Symmetry	26 nm	Present work

MAGNETIC ANALYSIS

Prestine BFO exhibiting a spatially modulated spin configuration along with G-type antiferromagnetic ordering which does not permitthe resulting net magnetization [2]. On the basis of various reports it is concluded that Tico-doping at B-site of BFO is very effective in order to enhance the magnetic properties of BFO. Fig. 2 shows M-H hysteresis curves of the synthesised sample with a maximum field of ±10kOe at room *temperature. The magnetic parameters calculated from M-H loop and comparison with published report are listed in Table3

TABLE 3. Comparison between magnetic parameters for co-doping (Ti) BFO.

S. No.	Compounds Name		Magnetic Parameters		Reference	
			M ₅ (emu/g)	H _C (Oe)	Reference	
1.	Bi(Ni _{1/4} Ti _{1/4} Fe _{1/2})O ₃		0.131	298.98	[2]	
2.	Bi(Ni _{0.40} Ti _{0.40} Fe _{0.20})O ₃		0.363	389	[1]	
3.	Bi(Co _{1/4} Ti _{1/4} Fe _{1/2})O ₃	+	2.66	653.75	[3]	
4.	Bi _{0.80} Ho _{0.20} Fe _{0.80} Ti _{0.80} O ₃		0.144	67.77	Present work	

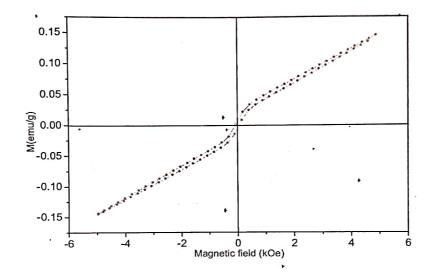


Fig 2 M-H hysteresis loop recorded at room temperature of $\mathrm{Bi}_{0.80}\mathrm{Ho}_{0.20}\mathrm{Fe}_{0.80}\mathrm{Ti}_{0.20}\mathrm{O}_3$

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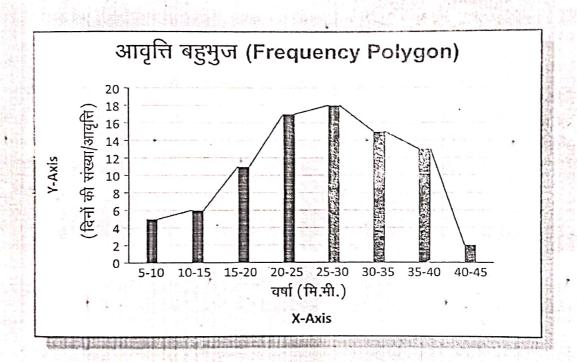
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Statistical Methods in Geography

DIFFERENTIAL EQUATION WITH NUMERICAL METHODS

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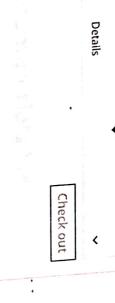
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Summary

Catalysis by functionalized nanomaterials is the contemporary discipline of of mankind. Nanocatalysts, being lying at the frontier of homogeneous and nanoscience which is expanding exceptionally to meet the upcoming global demands stability, enhanced activity, better selectivity, recoverability, reusability, and energy heterogeneous catalysts, offer multiple benefits of atom economy, remarkable efficiency, thereby allowing optimum feedstock utilization and minimal chemical waste. However, with time, it was diagnosed that some of these very active during catalysis, which was later resolved to a great extent by modifying their surface nanocatalysts suffer with the limitation of stability causing them to agglomerate composition via functionalization. The functionalization of these nanocatalysts with various biocompatible and active species serving as weak ligands not only enhances functionalization of nanomaterials also has considerable effect reflected in their their stability and selectivity but also facilitates their easy separation along with structure, morphology, optical, electrical, magnetic, and other properties owing to the preventing their undue coagulation during catalysis. Besides these, the novel theory of quantum effects, enabling a control of their catalytic activity.

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Carbon Nanotubes Loaded on Graphene Microfolds as Efficient Bifunctional Electrocatalysts for the Oxygen Reduction and Oxygen Evolution Reactions



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This is the first handbook that provides an integrated approach for functionalized nanomaterials (FNMs) based catalytic materials.

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Functionalized Nanomaterials for Catalytic Application: Trends and Developments

Meena Kumari^{1*}, Badri Parshad², Jaibir Singh Yadav³ and Suresh Kumar^{4†}

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Abstract

Catalysis by functionalized nanomaterials is the contemporary discipline of nanoscience which is expanding exceptionally to meet the upcoming global demands of mankind. Nanocatalysts, being lying at the frontier of homogeneous and heterogeneous catalysts, offer multiple benefits of atom economy, remarkable stability, enhanced activity, better selectivity, recoverability, reusability, and energy efficiency, thereby allowing optimum feedstock utilization and minimal chemical waste. However, with time, it was diagnosed that some of these very active nanocatalysts suffer with the limitation of stability causing them to agglomerate during catalysis, which was later resolved to a great extent by modifying their surface composition via functionalization. The functionalization of these nanocatalysts with various biocompatible and active species serving as weak ligands not only enhances their stability and selectivity but also facilitates their easy separation along with preventing their undue coagulation during catalysis. Besides these, the functionalization of nanomaterials also has considerable effect reflected in their structure, morphology, optical, electrical, magnetic, and other properties owing to the novel theory of quantum effects, enabling a control of their catalytic activity.

This Chapter will cover nanocatalysis, factors affecting catalytic performance, different functionalization strategies and application of these functionalized nanocatalysts in various fields.

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