



STRUCTURAL AND MAGNETIC PROPERTIES OF PURE AND B-SITE SUBSTITUTED BISMUTH FERRITE.

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Abstract:

Multiferroic BiFeO_3 and $\text{BiFe}_{1-x}(\text{Co,Ni})_x\text{O}_3$ materials were synthesized by auto-combustion method using urea as a fuel. The crystal structure study was carried out using X-ray diffraction (XRD). All synthesized samples crystallized in a rhombohedrally distorted BiFeO_3 structure. With the increase in Ni doping concentration there is an increase in lattice parameters of the unit cell. However, the lattice parameters for Co doped samples are smaller than those for BiFeO_3 , which is due to the smaller ion diameter of Co^{3+} than that of Fe^{3+} . Room temperature magnetic study showed that in pure BiFeO_3 , the magnetization varies nearly linearly with the applied magnetic field confirming that sample is antiferromagnetic having a G-type magnetic structure. Compared with BiFeO_3 , the magnetic properties of doped samples were significantly enhanced.

Keywords: Multiferroics, magnetoelectric, auto-combustion, and BiFeO_3

Introduction :

Multifunctional materials that combine a spontaneous magnetization with a ferroelectric polarization are of tremendous fundamental and practical interest^[1-4]. Multiferroics are a class of materials with coupled electric, magnetic, and structural order parameters that yield simultaneous effects of ferroelectricity, ferromagnetism, and ferroelasticity in the same material^[5]. Magnetoelectric multiferroics are the focus of much experimental and theoretical research^[6-10] due to the potential to greatly impact the field of spin-based electronics (spintronics) including new forms of magnetic storage, logic, and memory^[11,12]. An ideal multiferroic would be a ferroelectric ferromagnet that exhibits coupling between these order parameters at room temperature. There has been growing recent interest in the magnetic, ferroelectric, and piezoelectric properties of bismuth based perovskite-structure oxides^[13-21]. In such



materials, the formally Bi^{3+} ion occupies the perovskite A site, and its stereochemically active $6s^2$ lone pair induces a symmetry-lowering structural distortion that can lead to ferroelectricity^[22]. The B-site substitutions are made by replacing the Fe^{3+} ions by other transition metal ions. Since the conduction band of BiFeO_3 is related to the d orbital state of the Fe^{3+} ion, B-site substitutions can have a strong influence on physical properties by changing the electronic structure near the Fermi level. In this work we analyze the magnetic properties of Bi-based multiferroics in order to understand the chemical and structural factors which affect the magnetic ordering.

BiFeO_3 is one such multifunctional material, which is ferroelectric ($T_c \sim 830^\circ\text{C}$) and the magnetic ordering is essentially G-type antiferromagnetic ($T_N \sim 370^\circ\text{C}$) with cycloidal spin magnetic ordering^[23]. The necessary condition to manifest multiferroic properties in BiFeO_3 is the suppression of spin cycloid, which is reported to be possible with application of high magnetic/electric fields, epitaxial strains, and chemical substitutions^[24]. However, BiFeO_3 usually exhibits a relatively high leakage current that is detrimental to ferroelectric performance and often makes BiFeO_3 practically unusable^[25,26]. It is also difficult to derive weak ferromagnetism in pure BiFeO_3 ^[27] whose space-modulated spin structure may lead to a cancellation of the possible nonzero remnant magnetization permitted by the canted G-type antiferromagnetic order^[28,29]. However to enhance the magnetic and ferroelectric properties of BiFeO_3 , chemical modification have been attempted with varying degrees of success^[30-32].

Inducing the lattice distortion is one way to enhance the magnetic properties of BiFeO_3 by enhancing the canting of the antiferromagnetic arranged neighboring spins. Ion substitution is an efficient way to induce the lattice distortion to improve the magnetic properties. Fe-site ion substitution with magnetic ions is also very attracting, and enhanced ferromagnetism was reported^[33]. In this paper, we present the structural and enhanced magnetic properties of BiFeO_3 by Co and Ni substitution.



Experimental :

The BiFeO_3 , $\text{BiCo}_x\text{Fe}_{1-x}\text{O}_3$ ($x=0.5, 0.8$) and $\text{BiNi}_x\text{Fe}_{1-x}\text{O}_3$ ($x=0.5, 0.8$) ceramics were prepared by auto-combustion synthesis. The chemicals $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (99.9% Merck), $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (99.9% Merck), $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (99.9% Merck), $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and Urea (Merck) used were analytical reagent grade and used without further purification. Stoichiometric amount of metal nitrate (oxidizer) and fuel when ignited undergo self-propagating, gas-producing combustion reaction to yield voluminous metal oxide in less than 5 min. The as-synthesized powders were crushed and grinded in an agate mortar^[34]. The oxidizer/fuel ratio was figured on the basis of oxidizing valencies of the metal nitrates and reducing valency of the fuel.

The synthesized powders were characterized by using various techniques. X-ray diffraction data was collected using a XPERT-PRO diffractometer with Cu $\text{K}\alpha$ radiation ($\lambda = 0.154056 \text{ nm}$) at step of 0.02 in the range $2\theta = 20^\circ$ to 80° . The magnetic properties were measured by a vibrating sample magnetometer (Lakeshore VSM 7410) at room temperature.

RESULTS AND DISCUSSION :

Structural Analysis

Room temperature powder x-ray diffraction pattern of pure BiFeO_3 and $\text{BiNi}_x\text{Fe}_{1-x}\text{O}_3$ ($x=0.5, 0.8$) is presented in Figure[1-3] . All the peaks could be indexed in the rhombohedral distorted perovskite structure with space group- $R3c$. The planes (hkl) in the XRD pattern for BiFeO_3 were matched by comparing them with the data of JCPD card of 86-1518. Using 2θ values from XRD plot and hkl values from the standard JCPD card the lattice parameters were found. The lattice parameters of pure BiFeO_3 are relatively close to the reported literature and the same are calculated to be $a=b=5.5730 \text{ \AA}$ and $c=13.862 \text{ \AA}$. The doped samples also exhibited similar rhombohedral perovskite structure.

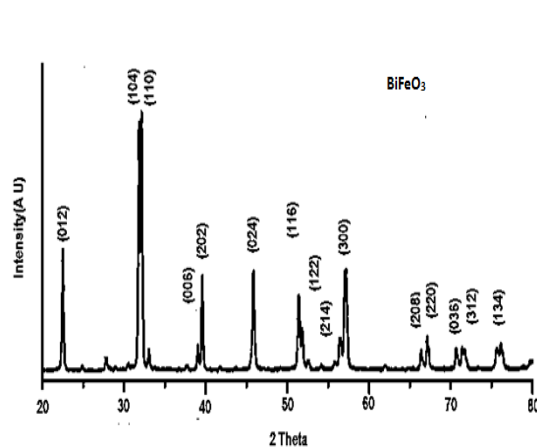


Fig [1]

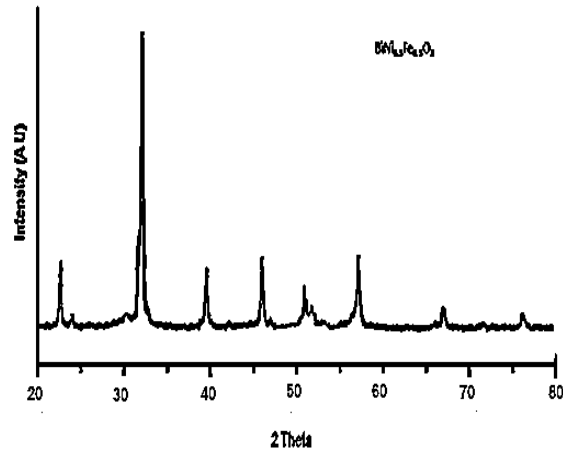


Fig [2]

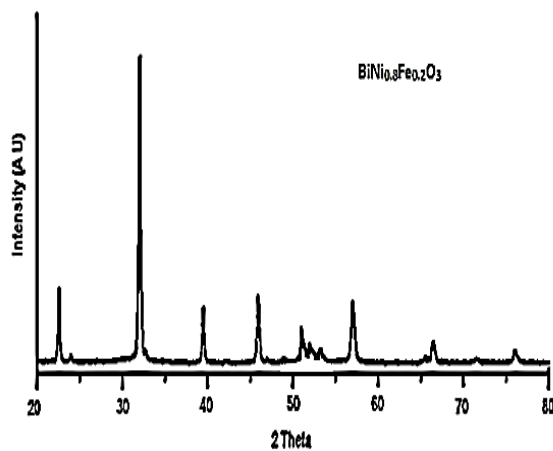


Fig [3]

The lattice parameters for 0.5 Ni doped BiFeO_3 are $a=b=5.5874 \text{ \AA}$ and $c = 13.879 \text{ \AA}$, whereas for 0.8, the values are $a = b = 5.5976 \text{ \AA}$ and $c = 13.89 \text{ \AA}$. It can be seen clearly that with the increase in Ni doping concentration there is an increase in both, a and c parameters of the unit cell. This is as expected, since the ionic radius of Ni^{2+} is slightly larger than that of Fe^{3+} . However, the lattice constant for Co doped samples are found to be smaller than those for BiFeO_3 , which is due to the smaller ion diameter of Co^{3+} than that of Fe^{3+} . Hence, small structure contraction can be expected, giving rise to a slight canting of the rhombohedral unit cell^[35]. Since there is a change in both, a and c parameters, the ratio c/a remains more or less unaffected, which is important for maintaining the ferroelectric properties in doped BiFeO_3 samples.



Magnetic properties :

The room temperature magnetic hysteresis loops are shown in figures[4]. In pure BiFeO_3 , the magnetization varies nearly linearly with the applied magnetic field confirming that sample is antiferromagnetic having a G-type magnetic structure [36] and having a residual magnetic moment due to canted spin structure (weak ferromagnetic). The magnetic parameters for $x=0.5$ Ni doped sample are $M_s=0.278$ emu/g and $M_r = 3.560$ emu/g while saturation magnetization $M_s = 0.687$ emu/g and remanant magnetization $M_r = 1.1235$ emu/g, i.e. for $x=0.8$ Ni doped sample are much larger than those of BiFeO_3 prepared under similar conditions $M_s = 0.004$ emu/g, $M_r = 0.942$ emu/g respectively.

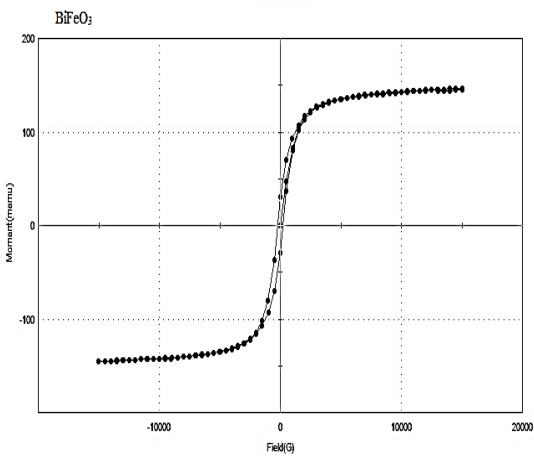


Fig [4]

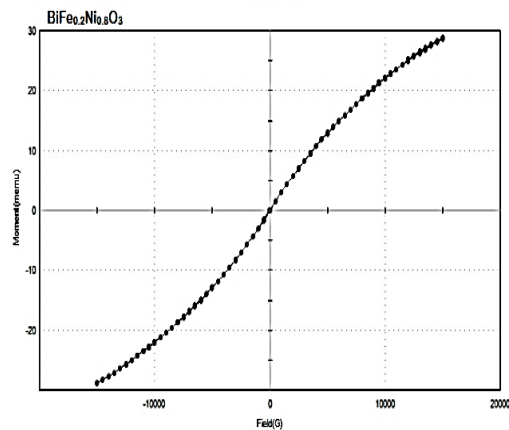


Fig [5]

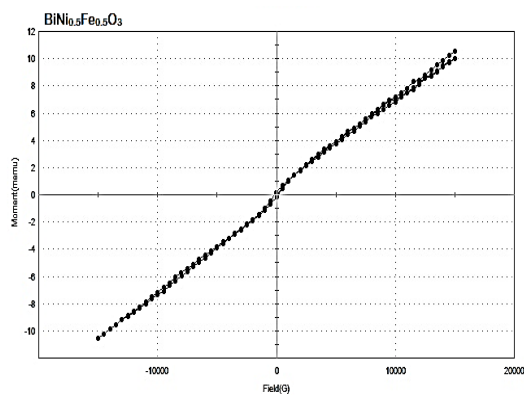


Fig [6]



An enhanced moment was observed for the higher Co-doped samples as well. The enhancement of the magnetic parameters might be related to the increased magnetoelectric coupling inside Co-doped BiFeO₃.

Conclusion:

BiFeO₃ and BiFe_{1-x}(Co,Ni)_xO₃ materials were synthesized by auto-combustion method. Co substitution at Fe site causes a structural distortion due to decrease in lattice parameter where as an increase in lattice parameter is observed for Ni substitution. Pure BiFeO₃ exhibits antiferromagnetic behavior at room temperature. The Co, Ni substitution has strengthened the magnetic properties of the bismuthferrite system. The spin structure in the magnetic ion substitution at Fe sites in BiFeO₃ needs further study to clearly understand the enhanced magnetic properties, and the room temperature multiferroic materials with enhanced properties might be realized.

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