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Manisha Rangi, Sujata Sanghi, Ashish Agarwal, Sandhaya Jangra, and Jogender Sangwan

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

Manisha Rangi[1,a)], Sujata Sanghi[2,b)], Ashish Agarwal[2,c)], and Sandhaya Jangra[2,d)], Jogender Sangwan[2,e)]

[1]*Department of Physics, Vaish College, Rohtak -124001, Haryana, India*
[2]*Department of Physics, Guru Jambheshwar University of Science and Technology, Hisar125001,Haryana,India*

[a)]Corresponding author: mrangi100@gmail.com
[b)]sutkash@yahoo.com
[c)]aagju@yahoo.com
[d)]sndh17@gmail.com
[e)]jogy.sangwan@gmail.com

Abstract. The effect of Ba and Mnsubstitution on the crystal structure and dielectric properties of $BiFeO_3$ has been studied using X-ray diffraction at room temperature, Rietveld refinement and dielectric properties measurements technique. Single phase $Bi_{0.8}Ba_{0.2}Fe_{1-x}Mn_xO_3$ (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 $BiFeO_3$.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 $T_C \sim 1100K$ and high antiferromagnetic Neel temperature $T_N \sim 640K$) well above room temperature. This behavior makes it suitable for various practical applications like sensors, actuators, memory devices etc.$BiFeO_3$ (BFO) has a rhombohedrally distorted perovskite structure with space group R3c in which polar cation (Bi^{3+}) is present at A-site and magnetic cation (Fe^{3+}) 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, (≥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 at673 K for 4h at the rate of 5 K /minand grinding was again done for 1hour 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_α radiation (λ = 1.54Å) in the 2θ range from 20° to 80° with the scanning rate of 2° min^{-1} at room temperature. Rietveld Refinement of XRD data has been carried 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 $Bi_{0.8}Ba_{0.2}Fe_{1-x}Mn_xO_3$ (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 ($Bi_2Fe_4O_9$, $Bi_{25}FeO_{39}$). Absence of any extra peak in both the sample indicates that no complete structural transformation takes place.

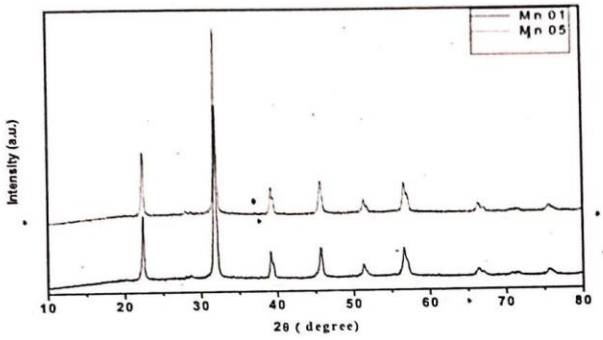

FIGURE 1.XRD patterns of $Bi_{0.8}Ba_{0.2}Fe_{1-x}Mn_xO_3$ (x = 0.01, and 0.05) multiferroic samples at room temperature.

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 $Bi_{0.8}Ba_{0.2}FeO_3$ 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.

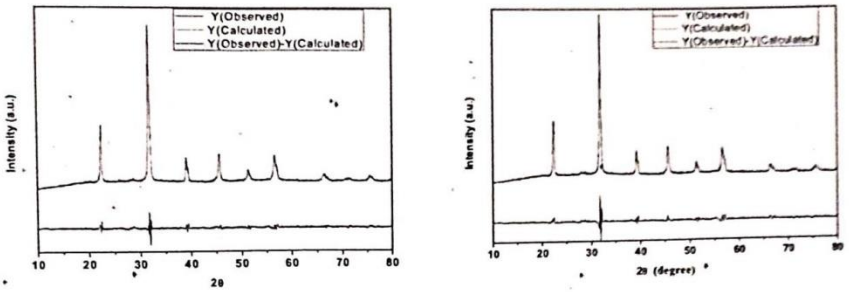

Figure 2. Observed, calculated and difference of Rietveld refined XRD patterns of $Bi_{0.8}Ba_{0.2}Fe_{1-x}Mn_xO_3$ (a) x = 0.01, (b) x = 0.05 samples.

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 Mn^{3+} are same as that of Fe^{3+} 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 Mn^{4+}state as also reported earlier [7].

TABLE 1. Refined structural parameters of $Bi_{0.8}Ba_{0.2}Fe_{1-x}Mn_xO_3$ samples only.

Concentration	Mn=0.01	Mn=0.05
Crystal Structure	Rhombhohedral	Rhombhohedral
Lattice paramters	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, 0.4288)	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 χ^2 = 3.49	R_p = 4.81 R_{wp} = 6.43 χ^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 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].

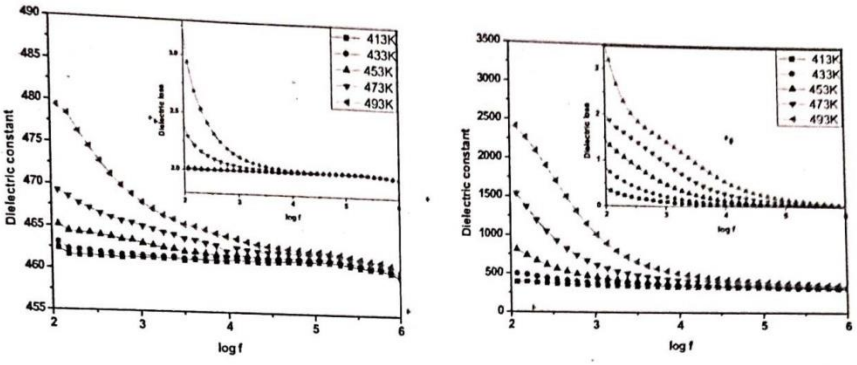

FIGURE 3. Frequency dependence of real part of dielectric constant (ε') and dielectric loss (tan δ) at inset of $Bi_{0.8}Ba_{0.2}Fe_{1-x}Mn_xO_3$ for (a) x = 0.01, (b) x = 0.05.

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 (Ba^{2+}) in place of volatile trivalent ion (Bi^{3+}) 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') anddielectric loss (tan δ) is observed at low frequency. Improved dielectric properties are attributed to the suppression of oxygen vacancies by Mn ion.

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