

Production and structural and magnetic characterization of a $\text{Bi}_{1-x}\text{Y}_x\text{FeO}_3$ ($x = 0, 0.25$ and 0.30) system

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Abstract. The production and the structural and magnetic characterization of the $\text{Bi}_{1-x}\text{Y}_x\text{FeO}_3$ ($x = 0, 0.25$ and 0.3) system is reported in this work. The system was produced through the solid-state reaction technique. The morphological characterization obtained by scanning electron microscopy technique evidences the granular behavior. The structural properties were studied by means of X-ray diffraction technique. Magnetization measurements in function of temperature of the $\text{Bi}_{1-x}\text{Y}_x\text{FeO}_3$ ($x = 0, 0.25$ and 0.3) system were performed with the magnetometer VSM by means of the Zero Field Cooled–Field Cooled method. The results obtained from all the techniques evidence the effect of yttrium on the physical properties of BiFeO_3 .

1. Introduction

Multiferroic materials exhibit simultaneous ferromagnetic, ferroelectric and/or ferroelastic ordering [1]. Bismuth ferrite (BiFeO_3) is one of such materials with antiferromagnetic behavior ($T_N = 643$ K) and a ferroelectric ordering ($T_C = 1103$ K), with both properties coexisting at room temperature [2-3]. This compound has ABO_3 Perovskite structure belonging to the $R3c$ space group in which A represents the larger Bi^{3+} ions occupying the cube-octahedral positions and B represents the medium sized Fe^{3+} ions in octahedral coordination [4]. In BiFeO_3 , the Fe magnetic moments are coupled ferromagnetically within the pseudocubic (111) planes and antiferromagnetically between the near planes; this is called the G-type antiferromagnetic order. Additionally, this compound exhibits a spatial spin-modulated structure (SSMS). The destruction of this SSMS must lead to ferromagnetism and a magnetoelectric effect [2, 5]. In spite of this complex magnetic behavior, this compound has a great potential for information storage, sensors, and electric field controlled devices. It has been shown that by substitution of elements at the A-site (Bi) or B-site (Fe), the SSMS can be suppressed and, therefore, enhancement of the magnetic properties is evidenced [6-15]. Rare-earth elements (La, Nd, Eu, Dy, Gd, Ho, Y, etc.) can be substituted at the A-site and, thus, improve ferroelectric and magnetic properties [7, 8, 12-15]. Guo *et al.* [15] reported that Gd doped BiFeO_3 nanoparticles synthesized via sol-gel method increase remnant magnetization with the increase of the Gd substitution. However, the photocatalytic activity was found to decrease as Gd concentration increases. James *et al.* [14] obtained bismuth iron based pigments $\text{Bi}_{1-x}\text{M}_x\text{FeO}_3$ ($\text{M} = \text{Y, La}$; $x = 0, 0.05, 0.1, 0.15, 0.2$) by conventional solid state route. X-ray diffraction (XRD) results indicated that a pure phase was formed up to 10 mol% yttrium; for higher concentrations impurity phases are detected. Doping of lanthanum did not strongly



affect the lattice parameters due to the similar ionic radii of La^{3+} and Bi^{3+} . In addition, smaller particles were obtained with the substitution of these elements. Magnetic properties of BiFeO_3 with substitution of yttrium (10 mol%) were studied by Rao *et al.* [12]. The compounds were obtained via solid-state method. It was suggested that the remnant magnetization was enhanced with the substitution of Y in the A-site due to the suppression of the spin-modulated structure.

Given that the substitution of rare earths is a way of influencing the physical properties of multiferroic BFO, it is relevant to expand research on doping with yttrium concentrations above 10 mol% and establish the effects of this element. In this work, $\text{Bi}_{1-x}\text{Y}_x\text{FeO}_3$ ($x = 0, 0.25$ and 0.3) ceramics were synthesized by the solid-state route. The results are based on XRD, scanning electron microscopy (SEM) and magnetization studies on the phase formation using two different concentrations of yttrium.

2. Experimental

Bismuth ferrite samples were prepared by means of the conventional solid-state reaction technique, starting from high purity Fe_2O_3 , Bi_2O_3 , and Y_2O_3 powders. The ground powders were pre-calcined at 700°C for 2 h in an alumina crucible. The calcined material was ground thoroughly and further calcined at 750°C for 2 h (the synthesis temperature and time were kept constant for all doping levels) followed by cooling in air by taking the sample out of the furnace. The crystal structure was studied by XRD experiments, with a nickel-filtered Cu-K radiation ($\lambda = 1.5406 \text{ \AA}$) of an X'Pert PRO PANalytical diffractometer. Morphological studies of the samples were performed via SEM experiments. For the SEM analysis, the cleaned and dried samples were measured in a JEOL JSM 6490-LV machine. The magnetization hysteresis (M-H) loop, zero field cooling (ZFC), and field cooling (FC) studies of the BiFeO_3 system were carried out by using vibrating sample magnetometers (VSM). Magnetization measurements were performed at several magnetic fields (field range of $-3 \text{ T} - 3 \text{ T}$) and magnetic hysteresis measurements were done at different temperatures, including room temperature (temperature range of $50 - 300 \text{ K}$).

3. Results and discussion

The XRD patterns of the $\text{Bi}_{1-x}\text{Y}_x\text{FeO}_3$ ($x = 0, 0.25$ and 0.3) samples are shown in Figure 1. It was found that all compounds crystallize in rhombohedral structure with the $R3c$ group, indicating the lack of orthorhombic phases with the yttrium substitution [12]. Besides the main phase BFO, few other peaks in the XRD diffractograms have been observed for secondary phases, for example, that in $32-35^\circ$ of 2θ . Through the literature review and by means of a Rietveld analysis (performed by GSAS code), the extra peaks observed are $\text{Bi}_2\text{Fe}_4\text{O}_9$.

Changes in the split peaks (012) and (110), typical for BiFeO_3 , with Y doping suggest the existence of structural effects. The lattice parameters for a $\text{Bi}_{1-x}\text{Y}_x\text{FeO}_3$ system obtained from Rietveld analysis are summarized in Table 1. For the BiFeO_3 phase the lattice parameter a is smaller and the lattice parameter c is bigger compared to that reported by other authors [18].

It is important to notice that the results obtained in the present work contradict those obtained in reference [16], which concludes that for higher concentrations of yttrium 10 mol% other Y-phases are formed. In contrast, the content of the impurity $\text{Bi}_2\text{Fe}_4\text{O}_9$ increases as the yttrium concentration increases. In addition, the mechanisms of BFO formation during synthesis process in the presence of yttrium are still unclear.

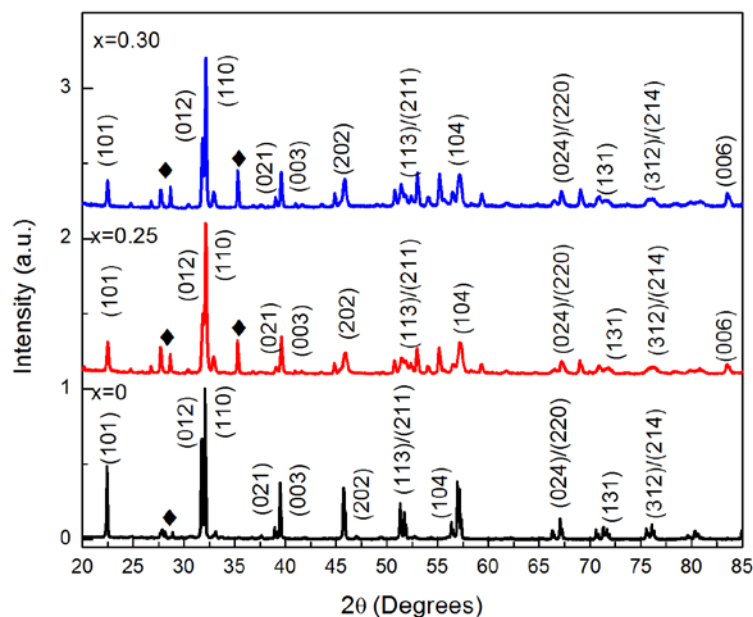


Figure 1. XRD patterns obtained for $\text{Bi}_{1-x}\text{Y}_x\text{FeO}_3$ compounds. The symbol (♦) represents the $\text{Bi}_2\text{Fe}_4\text{O}_9$ phase

The SEM micrographs of the $\text{Bi}_{1-x}\text{Y}_x\text{FeO}_3$ samples are displayed in Figure 2. For $x = 0$, the grains have a rounded shape and their grain size distribution is estimated to be from 0.5 to about 1 μm (counting around 100 particles). A secondary phase can also be observed (which agrees with the XRD measurements) in a form of agglomerates bigger than 1 μm . With $x = 0.25$, the rounded shape of the grains has already changed exhibiting a high interconnection of the grains. Such an effect is even stronger with $x = 0.30$, where bigger agglomerations are observed.

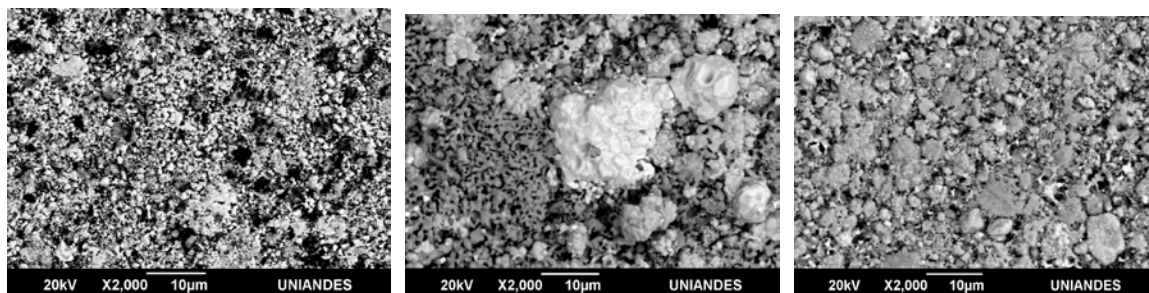


Figure 2. SEM micrographs of the $\text{Bi}_{1-x}\text{Y}_x\text{FeO}_3$ samples. From left to right, $x = 0, 0.25$, and 0.35

Magnetization hysteresis (M-H) loops taken at room temperature and 50 K are observed in Figure 3. As shown, the conventional loop for BFO at room temperature is very thin, but non-zero remnant magnetization. The values of M_s and M_r are similar for samples reported by Maurya *et al.* [19] synthesized through the same method for the BiFeO_3 sample. On the other hand, the samples with the presence of yttrium exhibit higher values for remnant magnetization and lower coercive field, inferring that the substitution of Y in the A-site influences the magnetic properties of BFO systems. The ionic radius of Y^{3+} is smaller compared to that of Bi^{3+} , therefore, doping with this rare earth element affects the bonds between Bi-O and Fe-O. The magnetic behavior of the samples at 50 K (Figure 3 left) is similar to that at 300 K (Figure 3 right) except for saturation magnetization values, which are higher in the first case (Table 1).

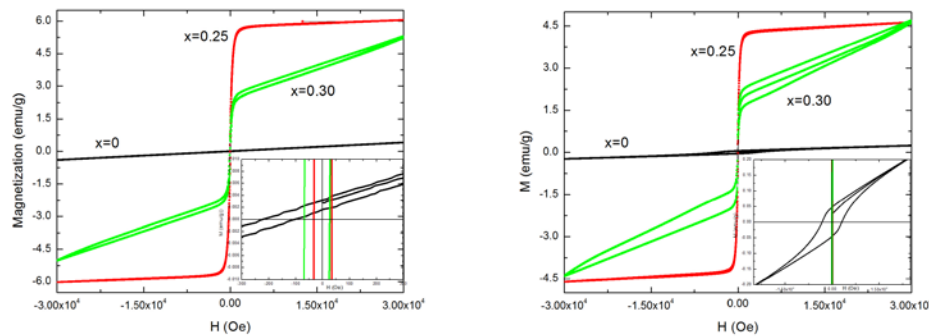


Figure 3. Magnetization hysteresis loops at 50 K (left) and 300 K (right) of $\text{Bi}_{1-x}\text{Y}_x\text{FeO}_3$ samples. Black, red, and green lines correspond to $x = 0, 0.25$, and 0.30 , respectively

Table 1. a , c lattice parameters and magnetic values obtained for the $\text{Bi}_{1-x}\text{Y}_x\text{FeO}_3$ system

x	$T = 300 \text{ K}$					$T = 50 \text{ K}$		
	a (Å)	c (Å)	H_c (Oe)	M_r (Emu/g)	M_s (Emu/g)	H_c (Oe)	M_r (Emu/g)	M_s (Emu/g)
0.00	5.059	13.968	3120	0.05	0.17	212	0.003	-----
0.25	6.519	15.721	11	0.51	6.00	35	0.600	4.60
0.30	6.519	15.722	52	0.90	2.42	54	0.800	2.69

In order to analyze the magnetic ordering in the samples, the temperature dependence of ZFC and FC magnetization curves is presented in Figure 4. The most interesting phenomena are observed in the sample with zero concentration (Figure 4 left). Firstly, the FC and ZFC cycles do not coincide, which implies possible spin glass-like ordering [16]. In addition, comparing these cycles to those obtained by other authors, some differences exist [16-18]. It is possible to notice an anomalous dependence on magnetization temperature, such as a decrease in magnetization that starts at 150 K (which is different from previously reported results), besides being accompanied by a significant difference at about 230 K (this kind of phenomenon was published in ref [18] but it was not explained). One of the reasons for such an anomalous magnetization may be the oxygen vacancy concentration and the existence of Fe^{2+} ions [17], another possible explanation could be the contribution of the impurity phases. In these experiments, it is also noted that the substitution of yttrium affects the magnetic response of BFO as observed in Figure 4 right.

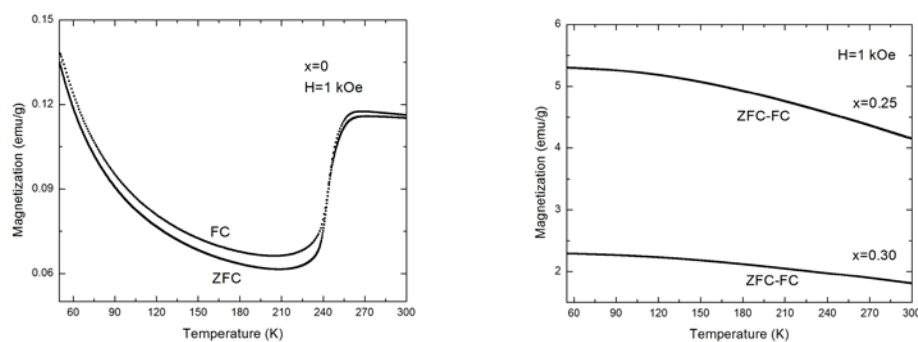


Figure 4. M vs T curves for the samples with zero (left) and with $x = 0.25$ and 0.30 (right)

4. Conclusions

Bismuth ferrite samples were prepared by conventional solid-state reaction technique. The magnetic responses obtained are typical of ferromagnetic behaviour in a BFO system, affected by the percentage increase of yttrium. The results obtained from XRD and SEM techniques are consistent with changes in the structural properties by Y doping.

5. References

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