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Structural and magnetic analysis of the $\text{Bi}_{x-1}\text{Sm}_x\text{FeO}_3$ ($x=0.04$ and 0.07) system

J D Suárez Londoño¹, S Segura Peña^{1,2}, E H Sáchica^{1,2}, A F Cruz Pacheco², A Sarmiento Santos² and C A Parra Vargas²

¹ Universidad Santo Tomas, Tunja, Colombia

² Universidad Pedagógica y Tecnológica de Colombia, Tunja, Colombia

E-mail: sully.segura01@usantoto.edu.co

Abstract. This work reports on the synthesis and characterization of the $\text{Bi}_{x-1}\text{Sm}_x\text{FeO}_3$ ($x=0.04$ and 0.07) systems, produced by the solid-state reaction method. The samples obtained were characterized by X-Ray Diffraction (XRD), Rietveld refinement and magnetization measurements as a function of the magnetic field applied and temperature. The structural characterization was performed by Rietveld refinement and allowed the identification of a perovskite type structure on all the materials with rhombohedral crystalline system and $R3c$ space group. The characterization by Scanning Electron Microscope (SEM) allowed to determine that the sintered solids present a homogenous microstructure. The magnetization curves as a function of magnetic field applied at 50 and 300K and as a function of the temperature at 5000Oe of the sintered solids exhibited a ferromagnetic behavior, with a rise of the permanent magnetization (M_r), the coercive field (H_c) and the magnetic susceptibility when the samarium concentration rose up. The structural and magnetic characteristics that are generated in the obtained solids make these materials of great interest as multiferroic components.

1. Introduction

Electronic devices play an important role in people's daily life. This is why there is a high demand for the evolution of these systems, producing everyday smaller, more efficient and affordable devices. However, the advance of this field is threatened by an invisible wall that limits the miniaturization of components for these elements.

During the last years, there has been a notable increase in the interest for components based on bismuth ferrite BiFeO_3 [1], several studies have been done in the area of multiferroics based on their potential applications in multiple state memory elements, sensors and spintronic devices. The advantages of BiFeO_3 over other materials are high ferroelectric transition temperature (Curie Temperature) which is around $T_C=1083\text{K}$ and its high antiferromagnetic temperature (Neel temperature) which is around $T_N=643\text{K}$, which places it really above its RT where it possesses a space group $R3c$, making it viable for practical applications [2].

This material is interesting not just for their multiferroic properties, there is not lead in their structure and therefore is a candidate to replace the traditional PZT in free lead ceramics. The BiFeO_3 has three big problems when it is obtained, as it is not pure due to the secondary phases presented, such as: $\text{Bi}_2\text{Fe}_4\text{O}_9$, $\text{Bi}_{25}\text{Fe}_{40}\text{O}_{40}$ and $\text{Bi}_{36}\text{Fe}_{24}\text{O}_{57}$, because of metastable state of BFO, phases that depend of the synthesis technique used, the other problem found is a decrease of the density at the moment of



obtaining pastilles [3–5], and last, the big leakage current and the difficulties to achieve the net magnetization since the magnetic order of these materials is the antiferromagnetic type [6], thus limiting the applications of this material in various devices. However, in order to improve the magnetic properties, various studies suggest the application of a big magnetic field or the ionic doping of rare earths, occupying the place of the Bi compound, favoring the magnetism and the stability of distorted structures ferroelectrically [6]. Others studies show an improvement in the introduction of lanthanides such as La^{3+} , Nd^{3+} , Sm^{3+} , Eu^{3+} , Gd^{3+} , etc. Currently, a lot of studies with respect to the magnetic properties BiFeO_3 doping with Sm over 10% of the doping concentration have been reported. But, there is a lot of work to be done below this level [7–10]. The present research is based on the synthesis and characterization of a ceramic oxide, perovskite type, based on the $\text{Bi}_{1-x}\text{Sm}_x\text{FeO}_3$ system with a level of Samarium cation ($x=0.04$ and 0.07).

2. Experimental

The Spuds software is used to predict the tolerance factor of formation from structures of $\text{Bi}_{0.9}\text{Sm}_{0.1}\text{FeO}_3$ system with $R3c$ space group as the most viable. For the synthesis of $\text{Bi}_{0.9}\text{Sm}_{0.1}\text{FeO}_3$ system, solid state method (RES) was used, starting with Bi_2O_3 (99,999%), Sm_2O_3 (99,9%) and Fe_2O_3 (99,995%) oxides, mixing and macerating them in a mortar of agate for 4 hours until the oxides get completely homogenized. The samples are compressed at 4MPa and calcined at 973K for 24 hours. The sintering process is performed at 1103K for 36 hours.

The crystallographic structure was determined with XRD using a X'Pert PRO PANalytical diffractometer with Cu-K radiation ($\lambda=1.540598\text{\AA}$). The Rietveld refinement analysis was carried out using PCW and GSAS software. The images of SEM were obtained in a microscope JEOL JSM 6490-LV brand. Finally, the M-H and M-T curves were made in a Versalab magnetometer with magnetic fields between -3T and 3T and temperatures between 50-320K.

3. Results and discussions

The Figure 1 shows the Rietveld refinement for $\text{Bi}_{0.96}\text{Sm}_{0.04}\text{FeO}_3$, it has not manifested secondary phases. The Rietveld refinement analysis for $\text{Bi}_{0.93}\text{Sm}_{0.07}\text{FeO}_3$ system, (Figure 2), show secondary phases of $\text{Bi}_2\text{Fe}_4\text{O}_9$, which are traces of around 4% and a principal phase of $\text{Bi}_{0.93}\text{Sm}_{0.07}\text{FeO}_3$ with 96%.

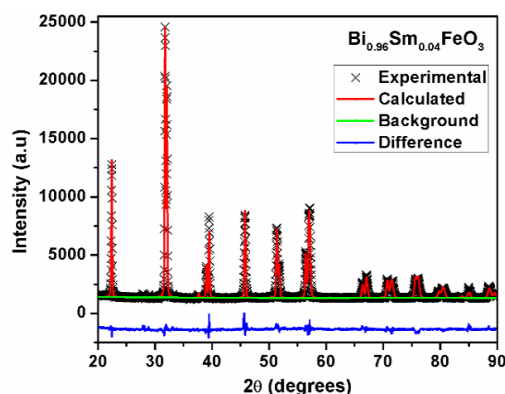


Figure 1. Rietveld refinement for $\text{Bi}_{0.93}\text{Sm}_{0.07}\text{FeO}_3$.

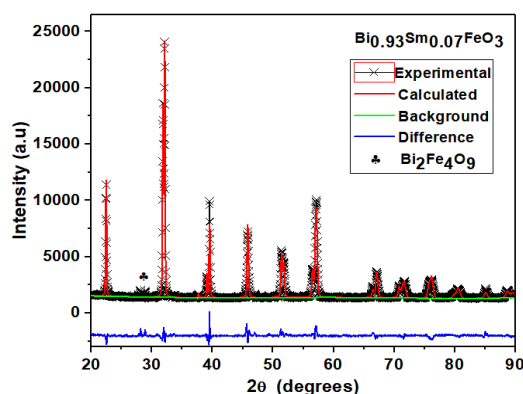


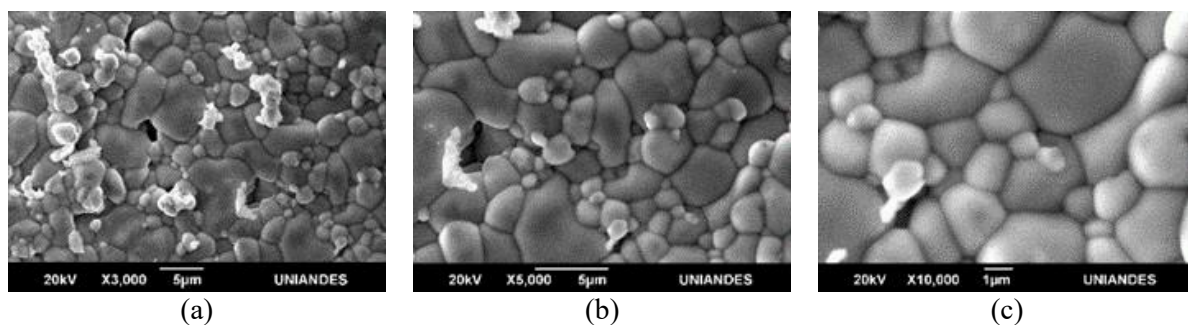
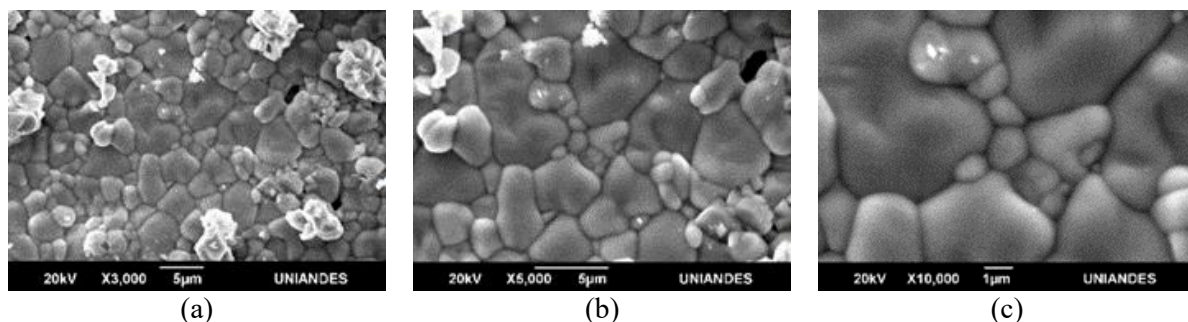
Figure 2. Rietveld refinement for $\text{Bi}_{0.96}\text{Sm}_{0.04}\text{FeO}_3$.

In Table 1, are shown the lattice parameters and atomic positions obtained by Rietveld refinement, with symmetry of space group $R3c$ or rhomboidally. The a , b and c values become higher with an increasing samarium concentration. The statistical parameters of the refinements were: For $\text{Bi}_{0.96}\text{Sm}_{0.04}\text{FeO}_3$ system $\chi^2=4.941$ and $R(F^2)=0.0742$, and for $\text{Bi}_{0.93}\text{Sm}_{0.07}\text{FeO}_3$ system $\chi^2=5.124$ and $R(F^2)=0.0565$.

Table 1. Structural parameters for $\text{Bi}_{1-x}\text{Sm}_x\text{FeO}_3$ ($x=0.04$ and 0.07) obtained with Rietveld refinement.

Lattice parameters				Bi _{0.96} Sm _{0.04} FeO ₃		Bi _{0.93} Sm _{0.07} FeO ₃		
a (Å)				5.5805		5.5819		
b (Å)				5.5805		5.5819		
c (Å)				13.8550		13.8440		
Atomic positions								
Atoms	x	y	z	OCC	x	y	z	OCC
Bi	0.0000	0.0000	0.7767	0.9333	0.0000	0.0000	0.7756	0.8688
Sm	0.0000	0.0000	0.2281	0.0519	0.0000	0.0000	0.7575	0.0119
Fe	0.0000	0.0000	0.9993	1.0132	0.0000	0.0000	0.9969	0.9828
O	0.8976	0.6534	0.4965	1.0045	0.8918	0.6596	0.4941	1.1345

Figure 3 (a), (b) and (c) shows the SEM micrographs for the $\text{Bi}_{0.96}\text{Sm}_{0.04}\text{FeO}_3$ system with a magnification degree of X3000, X5000 and X10000 respectively, and Figure 4(a), (b) and (c) shows the $\text{Bi}_{0.93}\text{Sm}_{0.07}\text{FeO}_3$ system with a magnification degree of X3000, X5000 and X10000 respectively.

**Figure 3.** SEM micrographs of the $\text{Bi}_{0.96}\text{Sm}_{0.04}\text{FeO}_3$ system at different magnifications, (c) X3000, (b) X5000 and (c) X10000.**Figure 4.** SEM micrographs of the $\text{Bi}_{0.93}\text{Sm}_{0.07}\text{FeO}_3$ system at different magnifications, (a) X3000, (b) X5000 and (c) X10000.

Both present grains with rounded shape and high interconnection between the grains and low porosity, in other words, a big homogeneity. Moreover, $x=0.04$ and $x=0.07$ have grain sizes around $5\mu\text{m}$, but only $x=0.04$ has a samarium grain size less than it. A visual inspection reveals the presence of a single second phase for $x=0.07$ like the XRD measurements. For more concentrations of samarium the grains are a little larger. On other hand, the $x=0.04$ micrographs do not have high concentrations of samarium grains.

Both magnetization hysteresis (M-H) loops for $\text{Bi}_{1-x}\text{Sm}_x\text{FeO}_3$ Perovskite systems ($x=0.04$ and 0.07) taken at room temperature and 50K, show a very thin hysteretic feature but non-zero remnant

magnetization as shown in Figures 5 and 6. The systems with the samarium samples exhibit higher values of remnant magnetization and low coercive field, so, it is possible to infer that the substitution of samarium in the A-site influences the magnetic properties of BFO system.

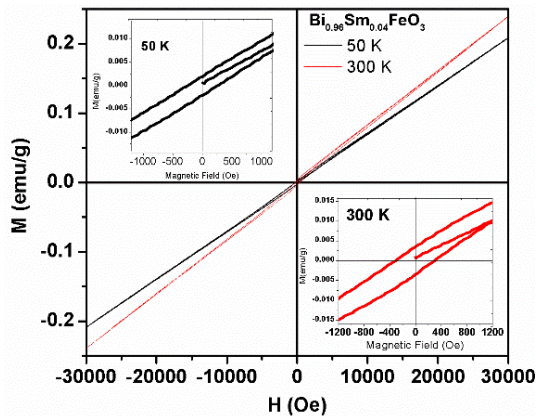


Figure 5. M-H curves hysteretic feature of $\text{Bi}_{0.96}\text{Sm}_{0.04}\text{FeO}_3$ system at 50K (red line) and 300 K (black line).

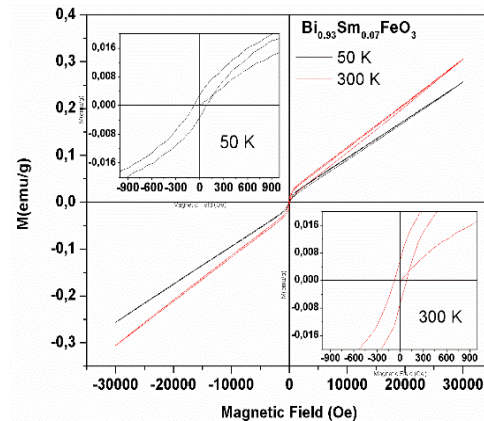


Figure 6. M-H curves hysteretic feature of $\text{Bi}_{0.93}\text{Sm}_{0.07}\text{FeO}_3$ perovskite at 50K (red line) and 300 K (black line).

As it can be seen in Table 2, the remnant magnetic fields are higher respect to the Sm concentration, but the coercive field decreases with that concentration. The ionic radius of Sm^{+3} is lower compared with the one for Bi^{3+} . Doping with this rare earth element affects the links between Bi-O and Fe-O, according with the reports by Gómez and collaborators [11].

Table 2. Magnetic values obtained for the $\text{Bi}_{x-1}\text{Sm}_x\text{FeO}_3$.

X	T=50K		T=300K	
	H_C (Oe)	M_r (emu/g)	H_C (Oe)	M_r (emu/g)
0.04	262	0.001919	296	0.0035
0.07	79	0.003015	80	0.0059

Figure 7 and 8 show the graphics of magnetization as a function of the temperature for the sample 0.04 and 0.07 respectively, with a constant field of 5000Oe. If we compare both samples it can be observed that the sample 0.04 is ferromagnetic, but the sample 0.07 shows a weak ferromagnetic state that transforms into anti-ferromagnetic at 130K; this behavior has been reported for Zatsiupa A. A. *et.al.* [12].

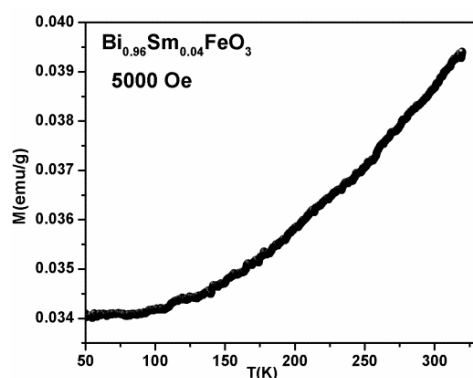


Figure 7. ZFC curves for $\text{Bi}_{0.96}\text{Sm}_{0.04}\text{FeO}_3$ samples at 5000Oe.

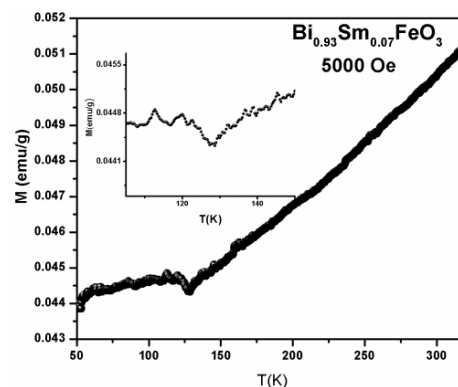


Figure 8. ZFC curves for $\text{Bi}_{0.93}\text{Sm}_{0.07}\text{FeO}_3$ samples at 5000Oe.

4. Conclusions

The crystallographic structure was obtained for both samples 0.04 and 0.07. The 0.04 one presented a single crystalline phase, while the second one presented a 96% pure phase and 4% Bi₂Fe₄O₉. At the same time was observed that the behaviour of the grain is the same for the produced samples. The magnetic answer corresponds to the typical behaviour of the BiFeO₃ materials. It was found that the remnant magnetic field increases with depending on the Sm concentration, but the coercive field decreases with the Sm concentration.

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