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Structural study of yttrium substituted BiFeO_3

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Abstract. Yttrium-substituted $\text{Bi}_{1-x}\text{Y}_x\text{FeO}_3$ ($x=0, 0.03, 0.07, 0.15, 0.2$ and 0.5) samples were prepared by solid state reaction technique. Morphological analysis was obtained by Scanning Electron Microscopy (SEM) technique indicating mainly granular behaviour. In addition, the substitution of yttrium promotes smaller particle size of BiFeO_3 . The obtained samples were also studied by X-ray diffraction (XRD). The crystal structure and the lattice parameters were confirmed by XRD. Rietveld refinement of experimental X-ray diffraction patterns showed that substituted BiFeO_3 compounds crystallize in a $R3c$ type structure and the lattice parameters decrease as Y concentration increases.

1. Introduction

BiFeO_3 (BFO) is a multiferroic material with special structural and magnetic properties (magnetoelectric coupling at room temperature) [1-2]. This perovskite has a rhombohedral $R3c$ crystallographic structure with larger Bi^{3+} ions occupying the cube-octahedral positions and the medium sized Fe^{3+} ions in octahedral coordination (see Figure 1). The lattice parameters are $a=5.57874\text{\AA}$ and $b=13.8688\text{\AA}$ [3].

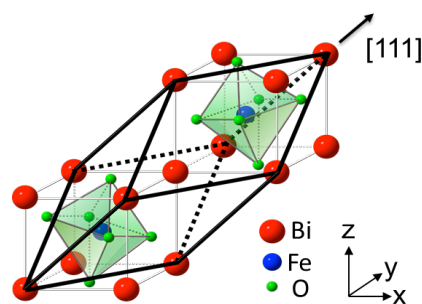


Figure 1. Crystal structure of BiFeO_3 .

BFO can be obtained by different methods of synthesis [4-6]. One of them is solid state reaction route, where the resulting final product (presence of impurities, changes in the structure) depends on the temperature conditions [6].

Rare-earth elements can be used to substitute Bi ions in the structure of BFO, which can affect the electrical, magnetic and specifically, structural properties [7-13] (by comparison, all the references here mentioned, used solid state route as synthesis method). Different Dy concentrations have been used to investigate the substitution of this element in BFO. Zhang et al. [7] synthesized $\text{Bi}_{1-x}\text{Dy}_x\text{FeO}_3$ ($x=0-0.3$).



They found that the presence of dysprosium prevents the appearance of impurities. The size of the grains are smaller as Dy concentration increases. These results are also obtained for other authors independent of the sintering conditions of solid state route [8-9]. The structural, optical, magnetic and dielectric properties of $\text{Bi}_{1-x}\text{Eu}_x\text{FeO}_3$ samples ($x=0, 0.03, 0.05, 0.07, 0.1, 0.12$ and 0.15) were investigated [10]. It was established that for $x>0.03$ impurities such as $\text{Bi}_2\text{Fe}_4\text{O}_9$ are eliminated. However, for $x>0.15$ distortion of the rhombohedral structure is evidenced. Small size and also better densification of the grains are obtained. Samples of BFO doped with yttrium were obtained for different few authors [11-13]. The investigations of these researchers show similar results as obtained for the others rare earth elements (presence of impurities, structure distortion and small grain size). But, low concentrations have been used (up to 0.2).

In the present work, $\text{Bi}_{1-x}\text{Y}_x\text{FeO}_3$ ($x=0, 0.03, 0.07, 0.15, 0.2$ and 0.5) ceramics were synthesized by the solid state route. The purpose is to make a rigorous analysis of the structural properties using a broad range of concentrations. The results are based on X-ray Diffraction (XRD) and Scanning Electron Microscopy (SEM).

2. Experimental

Samples of $\text{Bi}_{1-x}\text{Y}_x\text{FeO}_3$ ($x=0, 0.03, 0.07, 0.15, 0.2$, and 0.5) were prepared by using high purity Fe_2O_3 , Bi_2O_3 and Y_2O_3 powders in a conventional solid state reaction technique. The ground oxide mixtures were pressed into pellets. Then, the samples were presintered at 750°C for 6h in an alumina crucible. The resulting mixtures were ground, pressed and subjected to a second heat treatment at 750°C followed by quenching at room temperature (the temperature and time were kept constant for all x values). Phase analysis was done by X-ray diffraction. The XRD patterns were recorded using an X'Pert PRO PANalytical diffractometer with Co-K radiation ($\lambda=1.7902\text{\AA}$). GSAS software was used for Rietveld refinements. Morphological study of the samples was performed by Scanning Electron Microscopy (JEOL JSM 6490-LV).

3. Results and discussion

XRD patterns of the $\text{Bi}_{1-x}\text{Y}_x\text{FeO}_3$ samples are shown in Figure 2. It was found that the main phase in all the samples is rhombohedral structure BiFeO_3 . Few other peaks in the XRD patterns have been observed for secondary phases. For $x\leq 0.2$, traces of $\text{Bi}_2\text{Fe}_4\text{O}_9$ are found, which increase as Y concentration increases. For $x=0.2$, an Yttrium rich component starts to appear, becoming dominant for higher Y concentrations.

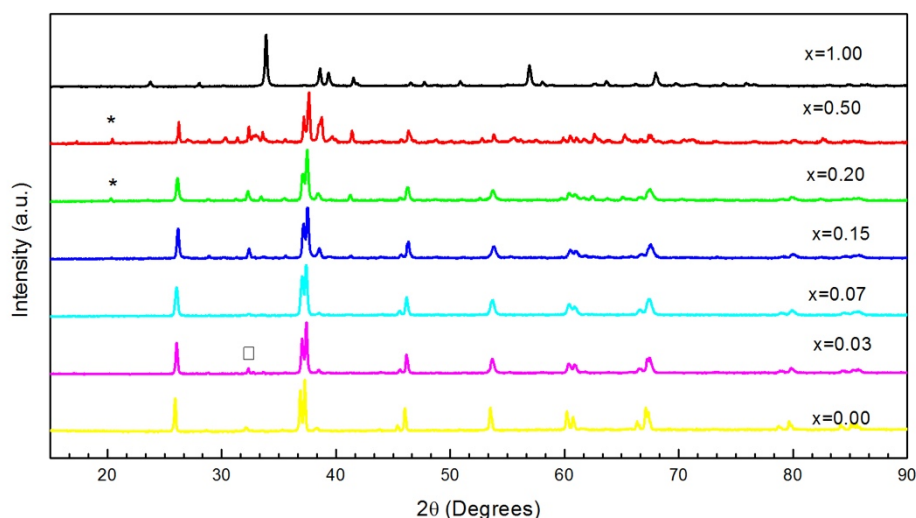


Figure 2. XRD patterns obtained for $\text{Bi}_{1-x}\text{Y}_x\text{FeO}_3$ compounds. The symbol (□) represents the $\text{Bi}_2\text{Fe}_4\text{O}_9$ phase and (*) $\text{Y}_3\text{Fe}_5\text{O}_{12}$.

The coexistence of orthorhombic phase of Pn21a/Pnma/Pbnm space group along with R3c space group is ruled out. The addition of some rare-earth elements in the BFO synthesis can cause a compositional phase transition from rhombohedral to other type of structure [10,14].

The lattice parameters for $\text{Bi}_{1-x}\text{Y}_x\text{FeO}_3$ samples were obtained from Rietveld analysis. They are summarized in Table 1. It shows that a and c values become smaller with increasing yttrium concentration. Similar values for $x = 0.15$ and 0.2 were obtained as those reported by Singh et al. [12] (independent of the sintering conditions during the synthesis in both investigations). This fact evidences that the substitution of Yttrium in the BFO structure is not affected for the synthesis procedure in solid state reaction method. The decrease in the lattice parameters values can be attributed to the substitution of Y^{3+} ($0.9\text{\AA}$) for Bi^{3+} ($1.03\text{\AA}$) in A-sites of BFO structure [12]. Other earth rare elements substituting Bi^{3+} ions can cause the same effect [7-10,14].

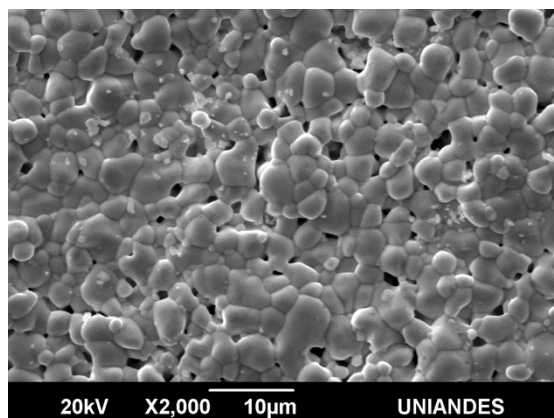
The average crystallite size of the samples was calculated using Scherrer's equation ($D = K\lambda/\beta_{1/2}\cos\theta_{\text{hkl}}$), where K (shapefactor) was set to 0.9; $\lambda = 1.7902\text{\AA}$, $\beta_{1/2}$ is the full width at half maxima (FWHM) and θ_{hkl} is the Bragg angle. These values are displayed in Table 1. The results show that the average crystallite size values decrease as Y substitution increases. The reduction in crystallite size creates high lattice strain [8].

Table 1. Comparison of lattice parameters a and c , the grain size (GS) obtained by SEM and crystallite size (D) by Scherrer's formula. All the values are for the phase BiFeO_3 .

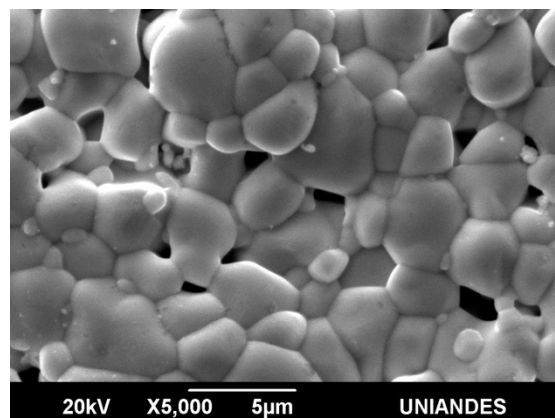
x	a ($\text{\AA}$)	c ($\text{\AA}$)	GS (μm)	D (nm)
0	5.5792	13.8723	6.42	95.9(5)
0.03	5.5757	13.8542	5.66	77.3(1)
0.07	5.5723	13.8471	5.10	56.4(9)
0.15	5.5713	13.8431	4.01	61.2(7)
0.20	5.5637	13.8325	----	52.0(6)
0.50	5.5576	13.8310	----	42.4(6)

SEM micrographs of some $\text{Bi}_{1-x}\text{Y}_x\text{FeO}_3$ samples are displayed in Figure 3. For $x=0-0.07$, the grains have a rounded shape and the average grain sizes decrease (GS, summarized in Table 1) with increasing Y doping level. The micrographs for $x=0.15-0.5$ show high interconnection between the grains, which makes difficult to calculate the average grain size. However, visual inspection evidences smaller size compared with lower yttrium concentrations. Doping can suppress oxygen vacancy concentration which lead to smaller grain sizes, which is common in the substitution of rare earth elements into BFO structure [7-13]. The difference between the values for crystallite and grain size can be explained for the formation of polycrystalline grains.

It can also be observed that there are secondary phases (which agrees with the XRD measurements) in a form of agglomerates.



(a)



(b)

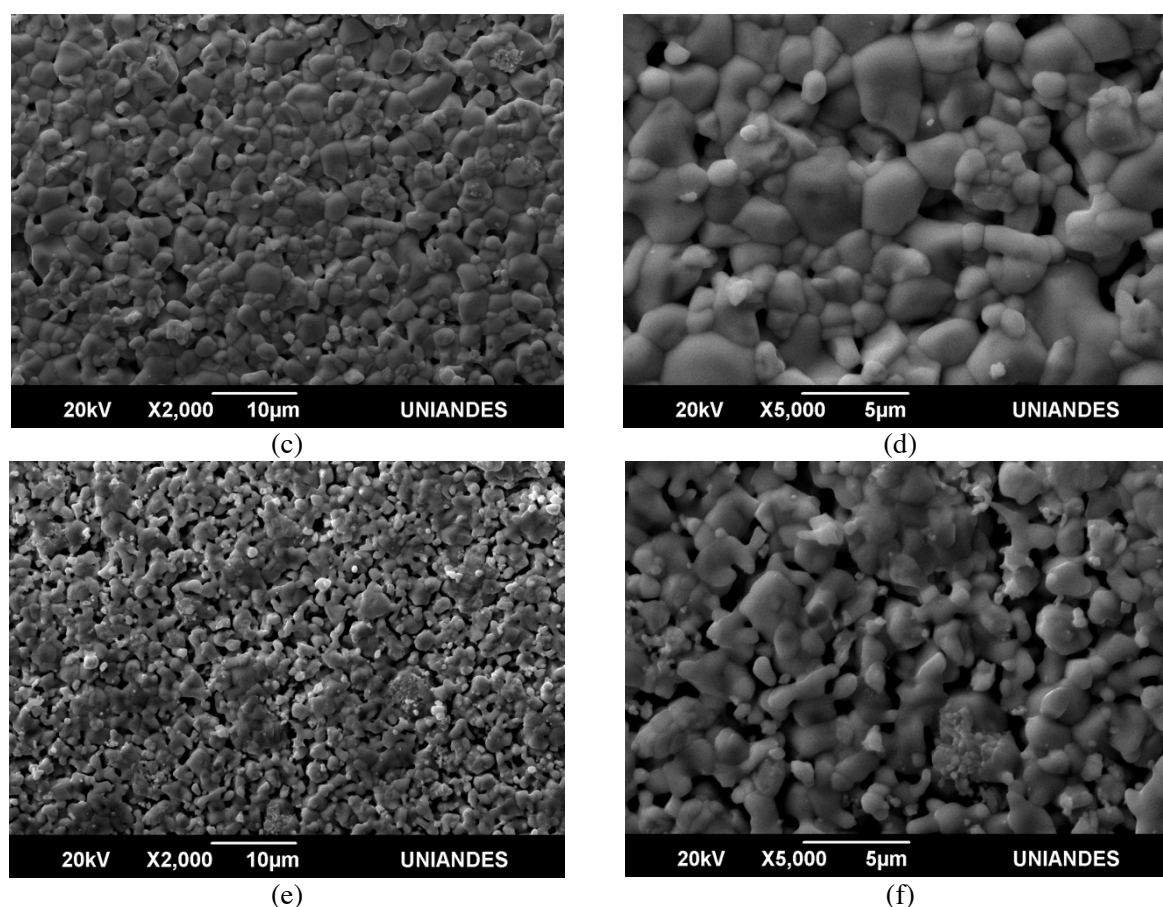


Figure 3. SEM micrographs of some $\text{Bi}_{1-x}\text{Y}_x\text{FeO}_3$ samples. (a) and (b) $x=0$, (c) and (d) $x=0.03$, (e) and (f) $x=0.2$.

4. Conclusions

Samples of BFO were prepared by conventional solid-state reaction technique. The results obtained from XRD are consistent with the changes in the structural properties by Y doping. SEM images indicates the reduction of the grain sizes of BFO by the replacement of Y in A-sites.

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