Structural and Dielectric Properties of Yttrium Doped Multiferroic Bismuth Ferrite (Bi$_{1-x}$Y$_x$FeO$_3$, x = 0, 0.18) Synthesized by Sol-Gel Method

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Abstract

Pure and Y-doped BiFeO$_3$ have been synthesized by sol–gel method. the gel have been heated at 150°C for 3 h, the low-temperature heating treatment was given to obtain uniform, homogenous, and smaller size. The crystal BiFeO$_3$ have been found after dried and grounded followed by calcination at 750°C for 4 h. The X-ray diffraction (XRD) patterns of pure and Y-doped BiFeO$_3$ are indexed and well matched with rhombohedral structure (R3c) and have been found secondary impurities such as Bi$_2$Fe$_4$O$_9$ (mullite) and Bi$_{25}$Fe$_2$O$_{39}$ (sillenite) were detected in pure and Bi$_{1-x}$Y$_x$FeO$_3$ (x=0, 0.18). The pattern of (104) and (110) peaks in Y-doped BiFeO$_3$ around $2\theta = 32°$ indicates reduction of the rhombohedral phase and increase that of the orthorhombic phase (Pbnm). Morphology of pure and Y-doped BiFeO$_3$ with FE-SEM the result doping Yttrium can be reduce particle size between 200 – 400 nm. The LCR study, the impedance (real and imaginer) BiFeO$_3$ and Y doped decreasing at low frequency (40 – 2 kHz) but after frequency 2 kHz is constant value. The impedance (imajiner) of pure is smaller of Yttrium doped BiFeO$_3$. The dielectric constant pure and Ydoped BiFeO$_3$ have been constan after frequency 2 kHz and decreasing at low frequency (40 – 2 kHz). The conductancy pure BiFeO$_3$ is smaller of Y doped BiFeO$_3$ at 42 Hz – 5 MHz and after frequency 2 kHz conductancy of Y doped increases significant.

Keywords : sol-gel, rhombohedral, orthorhombic, particle size, resistivity, conductancy, dielectric constant

1. Introduction

Multiferroics, having the coexistence of magnetic and ferroelectric orders, have attracted the attention of many researchers due to its potential applications for magneto-electric devices.[1] Among various types of multiferroic materials, perovskite-type BiFeO$_3$ (BFO) is the only room temperature multiferroic till today having the ferroelectric T$_C$ = 1043 K and T$_N$ = 647 K. However, the narrow synthesis area of single-phase BFO would result in the formation of secondary phases such as Bi$_2$Fe$_4$O$_9$ and Bi$_{25}$FeO$_{40}$ along with BFO. However, BiFeO$_3$ materials usually present a high electrical conductivity that hinders its practical applications. This high leakage current is mainly attributed to the presence of secondary phases, namely the Bi-rich sillenite type Bi$_{25}$FeO$_{39}$ phase and the Fe-rich mullite type Bi$_2$Fe$_4$O$_9$ phase, and to defects in the crystal structure, such as oxygen vacancies originated by the reduction of Fe^{3+} to Fe^{2+}.[2,3] The presence of these undesired phases is commonly attributed to a very narrow range of stabilization of the BiFeO$_3$ phase and to the presence of impurities at trace leveis that promote the stabilization of secondary phases,[4] These phases are often difficult to detect by X-ray diffraction because the Bi$_{25}$FeO$_{39}$ sillenite phase is not always well

crystallized and, also, because its high proportion of heavy Bi^{3+} ions (which, with 80 electrons, scatters X-rays much more efficiently than the much lighter Fe^{2+} and O^{2-}, with 24 and 10 electrons respectively) disguises the signal of the iron-rich $Bi_2Fe_4O_9$ phase.[4] Forthis reason, a rigorous microstructural characterization is always essential in order to detect traces of secondary phases.

In addition, leakage current and low magnetization in BFO limits its usage in multifunctional devices. The multiferroic properties of BFO are very sensitive to its intrinsic defects, such as vacancies. Highly dense materials without impurities are essential to avoid the leakage current and to exhibit good ferroelectric properties. The densification of these materials very much relies on synthesis route and sintering temperature. Many studies have focused on the synthesis of single phase BFO using different techniques.

The $BiFeO_3$ ceramics with *R3c* phase can be made prepared using *sol-gel* technique (SG) shows better reactivity than solid state reaction and fully densified samples can be obtained at a relatively lower temperature (750°C). The sol gel procedure involves molecular level mixing and results in the homogeneous material,[5]. The Sol gel technique also has an advantages over SS like low cost, generates less carbon residue and easy to prepare. Hence sol-gel has been considered as an alternative method for the preparation of BFO.

Many attempts are being done in order to obtain puré $BiFeO_3$ using methods such as chemical synthesis as such co-precipitation,[6], sol-gel[7], hydrothermal or solvothermal synthesis[8,9], mechanical activated synthesis[11], micro-wave assisted synthesis[12,13]. However, up to date, the obtaining of bismuth ferrite as a pure single phase product still represents a major challenge.

In the last few years many researches have tried to stabilize theBiFeO3 phase by partial substitution of A or B-site in the perovskite structure [10-15].

2. Experimental Procedure

Pure and Y-doped $BiFeO_3$ have been synthesized by sol–gel method. To prepare the YBFO using sol-gel method; the precursors, high purity (99.9 %) $Bi(NO_3)_3 \cdot 5H_2O$, $Y(NO_3)_3 \cdot 6H_2O$ and $Fe(NO_3)_3 \cdot 9H_2O$ of Sigma- Aldrich make were used. The analytical grade $Bi(NO_3)_2.5H_2O$, $Fe(NO_3)_3.9H_2O$, and $Y(NO_3)_3 \cdot 6H_2O$ in appropriate amounts, have been used to prepare the precursors in a stoichiometric molar ratio were dissolved in 1:5 HNO_3 to form an aqueous solution.

Citric acid $C_7H_8O_7$ was then added in appropriate proportion and stirred for 4 h at RT. Then, the mixture was heated at 250ºC on a hot plate with stirring, which leads to the evolution of gases. Furthermore, the gel have been heated at 150°C for 3 h heating rate 10°C, the brownish colour residue obtained finally, was heated at 600 ºC for 1 h to form the desired compound. These powders are made into pellets and sintered for densification at 750 ºC for 4 h.

3. Characterizations and measurements

Room temperature X-ray diffractogram was recorded on these ceramics using Phillips X-ray diffractometer with Cu Kα wavelength (1.5418 Å). The samples were characterized for its microstructure using Field Emission Scanning Electron Microscopy (FE-SEM) FEI INSPECT F50 and dielectric properties measurements were carried out using Agilent E4980A LCR meter at room temperature (RT).

4. Result and Discussion

4.1. *Structural analysis of Y doped BiFeO₃*

The calsined of $BiFeO_3$ on 600°C, 650°C, 700°C, and 750°C at 4 h and the crystal structure studies of $Bi_{1-x}Y_xFeO_3$ (x = 0.00, 0.18) have been carried out using X-ray diffractometer by Phillips with Cu-Kα (λ=1.54060 Å). The cylindrical pellets having dimensions 12 mm diameter and 2 mm thickness were prepared by hydraulic press with pressure of 10 ton/cm². The sintering of the pellets was carried out at 750°C for 4 h by heating at the rate of 40°C/min to remove any volatile impurities/organic materials (binder) from the pellets.
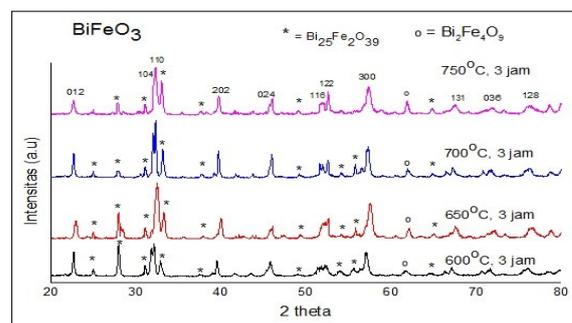

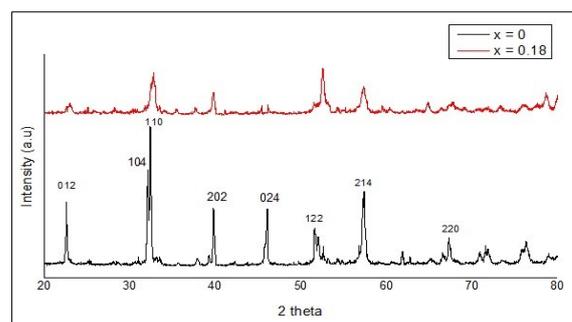Fig 1. The X-ray diffraction pattern of $BiFeO_3$ with calsined 600°C, 650°C, 700°C, and 750°C

Fig 2. The X ray diffraction pattern of pure and $Bi_{1-x}Y_xFeO_3$ (x = 0, 0.18)

Fig.1 shows the X-ray diffraction (XRD) patterns of $BiFeO_3$ with calsined on 600°C, 650°C, 700°C, and 750°C at 4 h. Single phase $BiFeO_3$ were given calsined early on 600°C and have been found secondary phase is $Bi_2Fe_4O_9$ (mullite) and $Bi_{25}Fe_2O_{39}$ (sillenite) as impurities. The phase is $Bi_2Fe_4O_9$ (mullite) and $Bi_{25}Fe_2O_{39}$ (sillenite) reduced with increaes calsined

The X ray diffraction pattern of pure and Y-doped $BiFeO_3$ are indexed and well matched with rhombohedral structure (R3c) and have been found secondary impurities such as $Bi_2Fe_4O_9$ (mullite) and $Bi_{25}Fe_2O_{39}$ (sillenite) were detected in pure and $Bi_{1-x}Y_xFeO_3$ (x=0, 0.18). However, XRD patterns of $Bi_{1-x}Y_xFeO_3$ (x = 0, 0.18) clearly reveal some other peaks indicated by ''*'' and "o" (Fig.2) have been observed and are attributed to secondary impurities phases. This indicates that $BiFeO_3$ doped with Yttrium remains pure with 'x' up to 0.18, indicating good the incorporation and dispersivity of ion Y^{3+} ions into $BiFeO_3$ crystal structure; further increase in Y content (x = 0.18) lead to formation of secondary phase impurities. This establishes that solution limitation for Y doped $BiFeO_3$ is around 18%. Therefore, the present study was carried out for $Bi_{1-x}Y_xFeO_3$ (x=0, 0.18).
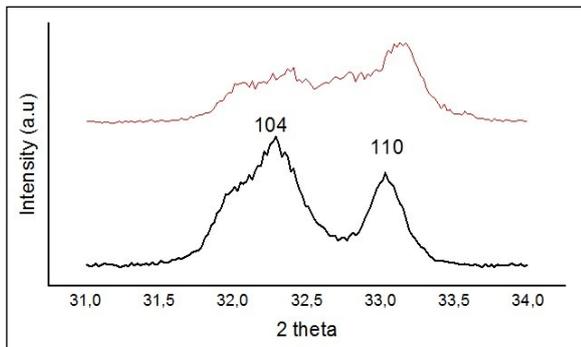

Fig 4. Magnified XRD pattern of indicated transformation rhombohedral to orthorombic for pure and $Bi_{0.82}Y_{0.18}FeO_3$

The XRD patterns (Fig.3) of clearly indicating the structural transformation because of increase in Y content in host $BiFeO_3$. Complete structural transformation from rhombohedral to orthorhombic takes place (Fig.4) as we increases Ydoping concentration from 0 to 18% in the host $BiFeO_3$. It is clear that the decrease in the splitting of (104) and (110) peaks in $Bi_{0.88}Y_{0.18}FeO_3$ around 2θ = 32° indicates reduction of the rhombohedral phase and increase that of the orthorhombic phase (Pbnm). Similar phenomenon of phase transformation with addition of rare earth metal in $BiFeO_3$ host material had been observed by the other groups[16].

The result rietveld refinement have been found crystal structure of $Bi_{1-x}Y_xFeO_3$ (x = 0, 0.18) is rhombohedral R3c to exist pure and 18% Y doped $BiFeO_3$ as show at Table 1. The refinement crystal

structure orthorombic Pbnm of 18% Y doped $BifeO_3$ is not report analysis.

Table 1. Structural parameters of $BiFeO_3$ and $Bi_{0.82}Y_{0.18}FeO_3$

Paramaters/ Compounds	$BiFeO_3$	$Bi_{0.82}Y_{0.18}FeO_3$
Crystal system	Rhombohedral	Rhombohedral
Space group	R3c	R3c
$a = b$ (Å)	5.579808	5.573200
c(Å)	13.866997	13.869400
Cell volume (Å^3)	373.8976	373.8732

4.2. Morphology study of Y doped $BiFeO_3$

In order to find the grain size distribution in Y doped BFO, the morphology of YBFO has been studied using FE-SEM. As shown in the Fig. 5, morphological characteristic on these smples exhibited that the sol-gel synthesis resulted in doping 18% Y in $BiFeO_3$, the grain shape continues to be rectangular but their average size reducing to 200 – 400 nm. However, addition of 18% Y in $BiFeO_3$ results in aggregated clusters with non-uniform morphology. Further, changing Y concentration to 18%, there results grains having still smaller size 100 – 400 nm. It is clear that the grain growth found to be suppressed with increase in Y content and helps in densification.
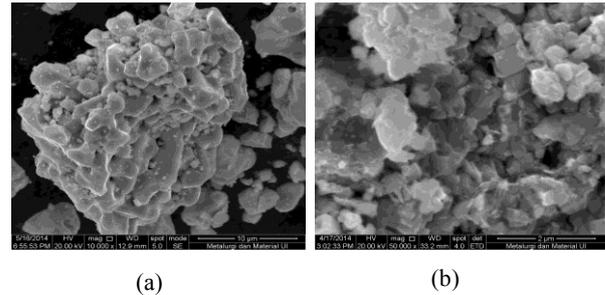

(a)   (b)

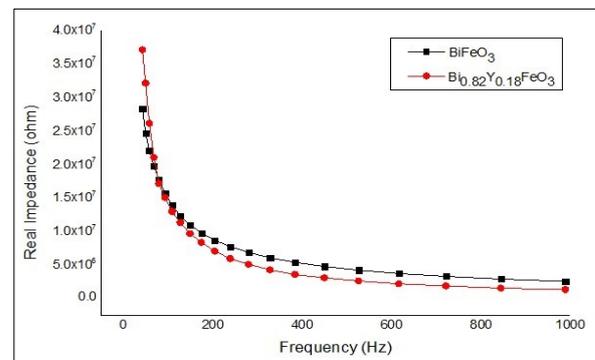Fig 5. The morphology of $BiFeO_3$ (a) pure
(b) $Bi_{0.82}Y_{0.12}FeO_3$

Fig 6. The real Impedance, Z(re) as function frequency of $BiFeO_3$ and Y doped $BiFeO_3$

4.3. Dielectric properties of Y doped $BiFeO_3$

The variation of resistivity (real and imaginer) of these samples as a function frequency in the range 40 Hz – 8

kHz is shown in Fig. 6 and 7 with the LCR analysis. With decreasing frequency the resistivity (real and imaginer) decreases at low frequency (40 Hz – 2 kHz). After frequency at 2 kHz show constant resistivity (real and imaginer) for pure and Y doped $BiFeO_3$. Fig.6. The real impedance of $BiFeO_3$ pure is smaller of Y doped $BiFeO_3$ and so the dielectric properties $BiFeO_3$ pure is bigger of Y doped $BiFeO_3$. Can be summary is Yttrium is magnetic properties and so that Yttrium can decreasing dielectric properties of $BiFeO_3$.
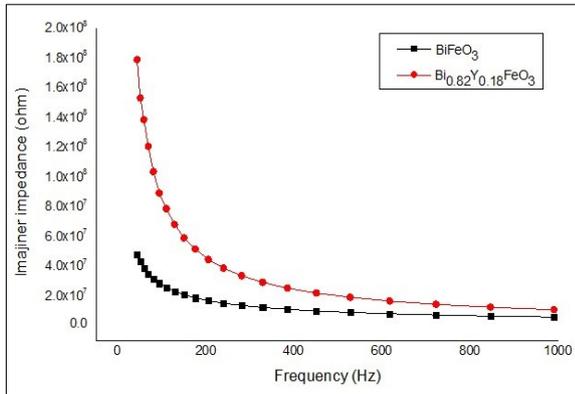

Fig 7. The imaginer impedance (Z_{im}) as frequency function of $BiFeO_3$ and Y doped $BiFeO_3$

Fig.7. The variation of imaginer resistivity of these samples as frequency function in the range 40 Hz – 8 kHz show is vice versa of real resistivity. The real resistivity measured form impendancy (Z) sample by the relation given in Equation :

$$Z = Z\,cos\theta + i\,Z\,sin\theta \qquad (1)$$

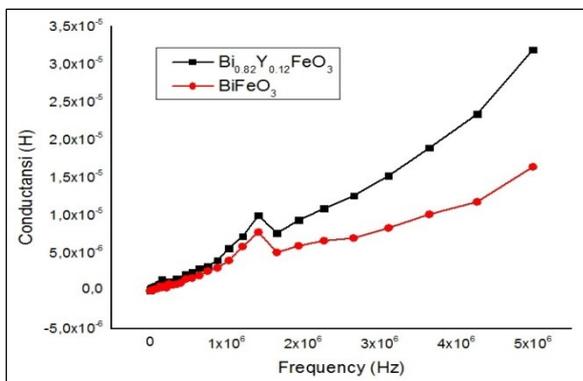where $Z\,cos\theta$ = R(re) and $Z\,sin\theta$ = R(im)

Fig 8. The conductancy as frequency function of $BiFeO_3$ and Y doped $BiFeO_3$

Fig.8.The variation of conductancy of these samples as a frequency function in the range 40 Hz – 5 MHz is showing conductancy $BiFeO_3$ is smaller of Y doped $BiFeO_3$ because dielectric properties Y doped $BiFeO_3$ is bigger and Yttrium is magnetic properties. After frequency at 2 kHz (high frequency region)

shown with increases frequency the conductancy increasing significant and difference conductancy of $BiFeO_3$ and Y doped $BiFeO_3$ are bigger. All the problem are conductancy value effected by frequency.

The variation of dielectric constant (K) of these samples as frequency function in the range 40Hz - 8 kHz prepared by *sol-gel* route is shown in Fig. 9. The LCR observed, the dielectric constant $BiFeO_3$ pure is bigger of Y doped $BiFeO_3$ and so that dielectric properties of Y doped $BiFeO_3$ is smaller.
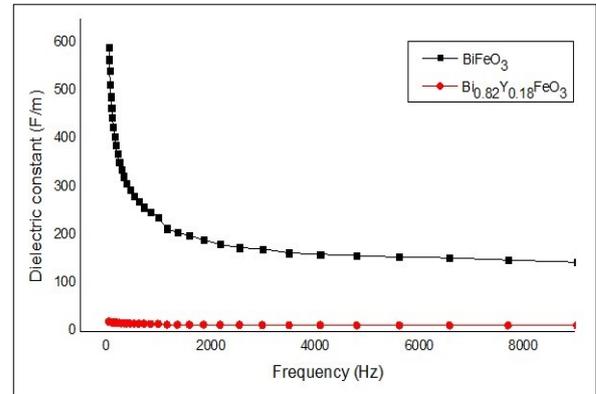

Fig 9. The dielectric constant as function frequency of $BiFeO_3$ and Y doped $BiFeO_3$

The dielectric constant can be ascribed by realtion given in Equation :

$$C = \varepsilon\,\frac{A}{d} \qquad (2)$$

where C is capacitancy of sample, ε is permitivity of sample, A is surface area of sample, and d is thickness of sample. Determine of Dielectric constant with equation :

$$K = \frac{\varepsilon}{\varepsilon_0} \qquad (3)$$

where K is dielectric constant and ε_0 is permittivity at vacum.

It is clearly observed that all the *sol-gel* prepared samples have a very high value of dielectric constant in low frequency region in comparison with the previous reports in other RE doped $BiFeO_3$[17,18]. The space charge polarization in these samples may result into such high value of dielectric constant at low frequencies.

5. Conclusions

The crystal structure of Yttrium doped $BiFeO_3$ have indicated change rhombohedral to orthorhombic system and the Yttrium doped to affect particle size decrease. The dielectric properties decreased with Yttrium doped $BiFeO_3$. Needed, the following research modified the other Yttrium doped $BiFeO_3$ and treatment particle size on pure and Yttrium doped $BiFeO_3$ and so that to have been particle size is smaller because to affect dielectric properties.

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