Structural and Physical Properties of Y-doped BiFeO$_3$ Material Prepared by Sol-gel Method

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Abstract: Y-doped BiFeO$_3$ materials were prepared by a sol–gel method. X-ray diffraction (XRD) measurement has been carried out to characterize crystal structure and to detect the impurities existing in these materials. The results showed that both lattice constants $a$ and $c$ of the unit cell of BiFeO$_3$ substance become smaller as the Y$^{3+}$ content is increased. The effect of introducing Y$^{3+}$ was to decrease the optical band gap for doped samples Bi$_{1-x}$Y$_x$FeO$_3$ ($x = 0.00$ + 0.20). Magnetic properties of Y-doped BiFeO$_3$ were investigated by vibrating sample magnetometer (VSM) measurements at room temperature, using maximum magnetic field of about 10 kOe. These materials exhibited a weak ferromagnetic behavior and magnetization of the sample was improved as presence of Y$^{3+}$ ions. When $x = 0.15$, 0.20, structural and magnetic properties change sharply. Y doping BiFeO$_3$ material modifies its physical properties.

1. Introduction

Ferroelectromagnetic materials, multiferroics, exhibit ferroelectric properties in combination with the ferromagnetic properties [1]. Additionally they exhibit the phenomenon called magnetoelectric coupling, magnetization induced by an electric field and electric polarization in a magnetic field. Recently, partial substitution of Bi$^{3+}$ ions by lanthanides has been shown to improve ferroelectric properties and magnetization [2–3]. Zhang et al. [4] and Das et al. [3] suggested that La$^{3+}$ substitution for Bi$^{3+}$ eliminates impurity phases and destroys the cycloidal spin structure resulting in uniform canted antiferromagnetic ordering. Zhang also reported that the structure changes from rhombohedral to orthorhombic at 30 mol% La. In the studies on dopant effects of Sm reported by Nalwa et al. [2] and Yuan [5] and those of Nd reported by Yuan et al. [6] in BiFeO$_3$, changes in the crystal structure of the materials were observed, which resulted in improving piezoelectric properties, long-range

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ferroelectric and canted antiferromagnetic orders. On the other hand, Uniyal and Yadav [7] claimed that 10 mol% Gd substituted for bismuth in the sample compound did not change the crystal structure but only reduced the volume fraction of impurity phases, while decreasing the Neel temperature \( T_N \) from 370 °C to 150 °C, and enhancing the magnetization to the extent of allowing the generation of the ferroelectric hysteresis loops [7]. The report of Hou Zhi – Ling et al. [8] shown that demonstrates the lattice contraction and magnetic properties improved due to 5 mol% Y substituted for bismuth. Our report shows effect of Y – doping on structure and physical properties of \( \text{Bi}_{1-x}\text{Y}_x\text{FeO}_3 \) materials. In this paper, we choose Y-content from \( x = 0.00 \) to \( x = 0.20 \) because of two reasons (i) with \( x \) small, the properties of Y doping have no significant changes; (ii) with \( x > 0.20 \), it may attribute to structural transition from rhombohedral (\( R_{3c} \)) to orthorhombic (\( P_{nma} \)) by Y substitution [9]

2. Experimental

Multiferroic \( \text{Bi}_{1-x}\text{Y}_x\text{FeO}_3 \) (\( x = 0.00 \pm 0.20 \)) powders have been synthesized by a sol – gel method. The chemicals used to create the samples are ferric nitrate \( \text{Fe(NO}_3\text{)}_3\cdot 9\text{H}_2\text{O} \), bismuth nitrate \( \text{Bi(NO}_3\text{)}_3\cdot 5\text{H}_2\text{O} \), yttrium nitrate \( \text{Y(NO}_3\text{)}_3\cdot 6\text{H}_2\text{O} \), citric acid and ethylene glycol. In the first step, these chemicals were mixed in correct weight contribution and an aqueous solution of citric acid was prepared in distilled water. Then ferric nitrate, bismuth nitrate and yttrium nitrate were added in turn with constant stirring at temperature 50 – 60 °C to avoid precipitation and obtain a homogeneous mixture. Now ethylene glycol was added into the solution with citric acid/ethylene glycol ratio of 70/30. After that water was evaporated at temperatures 100 °C to obtain colloidal gel bath. Finally, the gel was heated at temperatures of 700 °C for 6 hours to remove organics in the samples.

The samples were characterized by using different techniques. X-ray diffraction diagrams was used for phase identification and crystal structural analysis. The optical properties and electrical properties were determined by the absorption spectra. Vibrating sample magnetometer was used to measure the magnetic properties of the samples.

3. Results and discussion

Figure 1a shows the X-ray diffraction patterns of \( \text{Bi}_{1-x}\text{Y}_x\text{FeO}_3 \) samples (\( x = 0.05 \pm 0.20 \)). The XRD patterns are in excellent accordance with the powder data of JCPDS Card No. 71-2494 for \( \text{BiFeO}_3 \) crystals. Generally, for all samples, the second phase peaks attributed to Fe or Bi rich phases \( \text{Bi}_2\text{Fe}_4\text{O}_9 \) and \( \text{Bi}_{25}\text{FeO}_{40} \) (asterisk in Fig. 1a) were routinely observed as shown in previous results [10]. While Y substituted at the Bi site, the phase impurities can not be observed. However, with increasing Y content, another phase \( \text{Y}_3\text{FeO}_{12} \) appears in the \( x = 0.10, 0.15 \) and 0.20 powder samples [11]. For Y-doped \( \text{BiFeO}_3 \), all peaks are indexed according to the \( R_{3c} \) cell of \( \text{BiFeO}_3 \). The lattice parameters deduced for pure \( \text{BiFeO}_3 \) rhombohedral unit cell were found to have values \( a = 5.587 \text{ Å} \) and \( c = 13.872 \text{ Å} \). The results showed that both lattice constants \( a \) and \( c \) of the unit cell of \( \text{BiFeO}_3 \) substance become smaller as the \( \text{Y}^{3+} \) content is increased in the figure 1b. It is because the \( \text{Y}^{3+} \) ion radius (1.02
is smaller than that of Bi$^{3+}$ ion (1.17 Å) [12]. Crystallite size (d) was evaluated using the well-known Scherrer formula \(d = \frac{0.94\lambda}{\beta \cos \theta}\) [12, 13], where \(\beta\) is the full width at half-maximum of the chosen diffraction line (here we have chosen (012), (104), (110) and (024) intense peaks), \(\theta\) the Bragg diffraction angle and \(\lambda\) the wavelength of CuK\(\alpha\) radiation (1.5406 Å). The result is shown in figure 1b. The crystalline size is about 46 nm for pure sample and decreases as Y-doping is increased from \(x = 0.00\) to \(0.20\), which is attributed to the smaller ion radius of Y$^{3+}$ than that of Bi$^{3+}$ [8].

Figure 1. (a) XRD patterns of Bi$_{1-x}$Y$_{x}$FeO$_{3}$ powders; (b) a, c structure parameters depend on the Y content; and the insert shows average crystallite size depend on the Y content.

Figure 2 shows the Raman scattering spectroscopy of Bi$_{1-x}$Y$_{x}$FeO$_{3}$ samples (\(x = 0.00\) to \(0.20\)) measured at room temperature. The previous report has shown that the Raman active modes of the rhombohedral (R$_{3c}$) BiFeO$_{3}$ can be summarized using the following irreducible representation: \(\Gamma = 4A_{1} + 9E\) [12-14]. In present study we have observed 4A$_{1}$ modes (at wavenumbers of 170, 210, 464, and 549 cm$^{-1}$) and 6E modes (at wavenumbers of 134, 256, 281, 340, 368, and 517 cm$^{-1}$). The intensities of E modes are greater than that of A$_{1}$ modes in the present study. Since Raman scattering spectroscopy is sensitive to atomic displacements, the evolvement of Raman normal modes with increasing Y content can provide valuable information about ionic substitution and electric polarization. The stereochemical activity of the Bi electron pair plays major role in the change, both in Bi–O covalent bonds and characteristic modes observed at 170, 210, 256, 281, 340 and 368 cm$^{-1}$ for pure BiFeO$_{3}$. These modes are supposedly believed to be responsible for the ferroelectric nature of the bismuth ferrite samples [15-16]. With increasing in substitution ions, there is a change of Bi–O covalent bonds as a result of the decline in the stereochemical activity of the Bi lone electron pair and thus in long range ferroelectric order. If the mode frequency is governed by local factors, such as the force constant and ionic mass it will be proportional to \((k/M)^{1/2}\), where \(k\) is the force constant and \(M\) is the reduced mass [13]. Since ionic radius of Bi$^{3+}$ is similar to Y$^{3+}$, \(k\) is assumed to be independent of substitution ions. However, the shifting of Raman modes at higher frequencies, attrition of the prominent modes and the change in crystal structure is likely due to the A-site disorder created by Y substitution, having lower atomic weight 88.9 g as compared to Bi 209.0 g.
Figure 2. Raman scattering spectra of Bi$_{1-x}$Y$_x$FeO$_3$ materials (x = 0.00 – 0.20) at room temperature.

The UV–Vis absorption spectra of the Bi$_{1-x}$Y$_x$FeO$_3$ materials were showed in Fig. 3a. In the previous research, using chemical methods Zhike Liu et al. reported particle size of 150 ÷ 200 nm and the optical band gap ($E_g$) material of about 2.10 eV for BiFeO$_3$ [17]; approximate values of optical band gap were observed on BiFeO$_3$ thin films [18-19]; Theoretical calculations of Fan et al. showed BiFeO$_3$ material have the optical band gap to 2.5 eV [20]. By analyzing the absorption spectra (in Fig. 3a), we can obtain the values of optical band gap in the range of 2.01 ÷ 2.08 eV. In the guide to eyes, $E_g$ decreases with increasing the Y-doped content. The insert in Fig. 3b shows a plot of $(\alpha h \nu)$ as a function of photon energy. Analysis of the density of states indicated that the valence band was consisted with Fe-d and O-p states, and the conduction band was composed of Fe-d and Bi-p states [17]. Outside the absorption spectrum also shows the absorbance at 700 nm position receptors. This may be related to minor absorption happens when the electron is excited from $t_{2g}$ bands to $e_g$ bands [20].

Figure 3. (a) UV–Vis absorption spectra of the Bi$_{1-x}$Y$_x$FeO$_3$ (x = 0.00 – 0.20) materials; (b) the optical band gap of samples and insert shows a plot of $(\alpha h \nu)^2$ as a function of photon energy.
Figure 4. Room-temperature magnetization hysteresis loops of Bi$_{1-x}$Fe$_x$O$_3$ powders with $x = 0.00 \div 0.20$ for (b) – (f) and the insert saturation magnetization (Ms) and remnant magnetization (Mr) versus $x$ value (a).
The magnetization-magnetic field (M-H) curves of Bi$_{1-x}$Y$_x$FeO$_3$ powders measured with a maximum magnetic field of 10 kOe, as shown in Fig. 4. The partly enlarged curves are shown in the corresponding insert. In fact, BiFeO$_3$ is known to be antiferromagnetic having a G-type magnetic structure [21], but has a residual magnetic moment due to a canted spin structure (weak ferromagnetic) [22]. However, the Y-doped specimens exhibited a magnetic hysteresis loops, referring to a ferromagnetic behavior. As shown in Fig. 4, the curves are clearly not colinear. The saturation magnetization ($M_s$) are 0.052, 0.045, 0.106, 0.172 and 0.349 emu/g for samples $x = 0.00$, $0.05$, $0.10$, $0.15$ and $0.20$, respectively. The remnant magnetizations ($M_r$) are 0.010, 0.007, 0.011, 0.007 and 0.035 emu/g, respectively. The $M_s$ and $M_r$ values as the function of $x$ are plotted in the insert of Fig. 4a. A relevant research [23] reported that the Y-substitution could suppresses the spin cycloid of BiYFeO$_3$. Further analysis reveals that the $M_s$ and $M_r$ values of Bi$_{1-x}$Y$_x$FeO$_3$ with $x = 0.15$ and $0.20$ are significantly bigger than those of others, suggesting that with smaller value of $x = 0.10$. The Y-substitution can only suppress but can not destruct the spin cycloid, which is responsible for the limited and smooth increase of the $M_s$ and $M_r$ values. However, when $x \geq 0.10$, the Y substitution results spin cycloid, so that the latent magnetization locked the cycloid may be released, and a significant increasing of $M_s$ and $M_r$ value is observed. Another phase, such as Y$_3$Fe$_5$O$_{12}$ can also be found evidently, which may contribute to the increasing of magnetization value, it is consistent with predictions in reports of Feng et al. [11]. The reports of Hou Zhi-Ling et al. [8] had shown the Y ions, occupying the lattice sites, resulted in the changes of Fe-O-Fe bond angles which affected the super exchange Fe-O-Fe interactions. Although the Y-doping element does not contain 4f electrons, a small amount of doping can induce a strong magnetization [8]. In reports of Luo et al. [24] Bi$_{1.0-}$

$\times$Y$_x$FeO$_3$ ($0.00 < x < 0.30$) ceramics were synthesized by method, results showed that with $x < 0.20$ remnant magnetization and saturate magnetization have no significant changes. With increasing $x$ up to 0.30, a clear hysteresis loop can be observed, indicating the ferromagnetic properties. The saturate magnetization ($M_s = 0.31$ emu/g) of Bi$_{0.74}$Y$_{0.26}$FeO$_3$ increases significantly compared to those values of BiFeO$_3$ and has been attributed to structural transition from rhombohedral (R$_{3c}$) to orthorhombic (P$_{nma}$) [24]. The difference in our report, with increasing $x$ up 0.20 no structural transition, the saturate magnetization ($M_s = 0.349$ emu/g). This results are good for the application of Y-doped BiFeO$_3$ materials. For Y-substitution can improve the saturation magnetization so much should be discussed more and another effective analytical method should be introduced to assist.

4. Conclusion

We have successfully fabricated the Bi$_{1-x}$Y$_x$FeO$_3$ materials with different Y doping concentration in the range from $x = 0.00$ to 0.20 by sol-gel method. The presence of BiFeO$_3$ rhombohedral phase in all the samples was confirmed by XRD results. The values of unit cell parameters $a$ and $c$ were found to decrease with increase in Y-doping. Crystallite size, which was in agreement with the XRD results, decreases as Y-doing is increased. The optical band gap of Bi$_{1-x}$Y$_x$FeO$_3$ samples deduced from the UV–vis spectra decrease with increasing Y-content. Magnetic analysis reveals ferromagnetic nature of all samples at room temperature. The remanent magnetization and the
saturation magnetization increase with increasing Y-doping concentrations. It can be concluded that the sample with 20% Y-doping has enhanced multiferroic properties with larger magnetization.

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