Structural properties of bismuth ferrite synthesized by sol-gel method with variation of calcination temperature

M N Abdillah and D Triyono*

1Department of Physics, Faculty of Mathematics and Natural Sciences, Universitas Indonesia, Depok 16424, Indonesia

*Corresponding author: djoko.triyono@sci.ui.ac.id

Abstract. The effect of calcination temperature (500°, 600° and 700°C) on structural properties of BiFeO₃ synthesized by sol-gel method was studied. The structure of BiFeO₃ sample was investigated by using X-ray diffraction (XRD), Raman scattering spectroscopy, Fourier Transform Infrared spectroscopy (FTIR), and supported by UV-Visible spectrophotometry (UV-Vis) analysis. The XRD analysis revealed the stability of single-phase hexagonal crystal structure with R3c space group in calcination condition of 700°C. The Raman spectroscopy observed the presence of Fe—O stretching which is also confirmed by FTIR analysis. UV-Vis measurement described the slightly increasing of gap energy as calcination temperature increase.

1. Introduction
Multiferroics is one of the important functional material behavior in application as sensor design, actuators, and spintronic devices [1]. Perovskite BiFeO₃ is the one of multiferroics materials due to the ferromagnetic and ferroelectric coupling. BiFeO₃ has high transition temperature (Curie temperature 1100 K and Neel temperature 650 K) [2-3]. The pure perovskite BiFeO₃ has strong visible absorption and optical band gap of 2.27 eV [4].

Several research have been reported for synthesis method of BiFeO₃ caused the change in the structural and optical properties [4-5]. Jose Luis Ortiz-Quinonez et al [4] reported that BiFeO₃, synthesizing by using Glycine and Tartaric Acid as Ligands affected in the crystallite size (23 and 26 nm, respectively) and direct band gap (2.27 and 2.66 eV). Pavana et al [5], reported that BiFeO₃, synthesizing by low-temperature citrate sol-gel process, caused the increasing crystallite size with rise of heating temperature.

As an alternative to the previously reported methods, in this work BiFeO₃ was synthesized by sol gel method for obtaining single phase BiFeO₃ by varying the calcination temperature. The effect of calcination temperature on the structural properties of BiFeO₃ were investigated.

2. Experimental details
BiFeO₃ sample was prepared by sol-gel method with Bi(NO₃)₃·9H₂O, Fe(NO₃)₃·5H₂O, aquades, and citric acid as precursor. All precursors were mixed, stirred, and heated at 80° C using magnetic stirrer.
until the gel-phase was obtained. The gel was dried until the brown powder was formed. Then the powder was calcined with the variation temperature condition of 500°C, 600°C, and 700°C. The XRD patterns of BiFeO$_3$ samples were recorded by using X-ray Diffraction (XRD) type X’Pert PRO PANalytical with source radiation Cu Kα ($\lambda$=1.5405 Å). Raman scattering spectra were recorded in the range of 70 – 2000 cm$^{-1}$. FTIR analyze were recorded using PerkinElmer type Spectrum Two in the range 70 – 4000 cm$^{-1}$ and show the molecular and metal-oxide bonds from BiFeO$_3$ samples. Additionally, the optical band gap were determined using UV-VIS (Agilent Cary 100/300).

3. Results and discussion

3.1 X-ray diffraction analysis

Figure 1 presents the XRD pattern of calcined BiFeO$_3$. All the reflection peaks is agreement with the Hexagonal R3c space group. Bi$_2$Fe$_4$O$_9$ as the impurity phase is observed for 500 and 600°C (as shown in Figure 1), and disappeared for 700°C calcination condition. Similar condition has been reported by Luis Ortiz-Quinonez et al [4] for the appearance of Bi$_2$Fe$_4$O$_9$ during the synthesis process.

![Figure 1. The XRD patterns of BiFeO$_3$ with variation of calcination temperature ((A) 500°C, (B) 600°C and (C) 700°C).](image)

Tolerance factor (t) used to describe the stability of crystal structure. The tolerance factor are calculated using formula [6]:

$$t = \frac{(A-X)}{\sqrt{(B-X)}}$$

where ($A-X$) is the average of the measured bond length between A cation and the surrounding 12 anions and ($B-X$) is the average bond length between B cation and the surrounding 6 anions. Table 1 tabulates the structural parameters and calculated tolerance factor of BiFeO$_3$ samples. The tolerance factor, t-value >1 indicating the stability of hexagonal structure of BiFeO$_3$ samples [6]. The crystallite size is determined by Scherrer equation and found in the range of 39.2 – 97.0 nm. Table 1 show increasing crystal size as calcination temperature increase. Increasing crystal size at higher calcination temperature may due to more energy is given to the atoms to diffuse and reside at the suitable site in
the grains with less surface energy and crystal lattice will become larger [7]. Lattice parameter ‘a’ and ‘c’ are increase as calcination temperature increase as shown in Table 1. Lattice parameter increase might be attributed to the presence of point defects, oxygen vacancies or dislocation defects [7].

Table 1. The structural parameters and calculated tolerance factor of BiFeO$_3$ ((A) 500°C, (B) 600°C and (C) 700°C)

| Parameter                  | BiFeO$_3$          |
|----------------------------|--------------------|
|                            | A                 | B                 | C                 |
| Crystallography parameters |                    |                   |                   |
| Phase (Space Group)        | Hexagonal (R3c)    | Hexagonal (R3c)   | Hexagonal (R3c)   |
| a (Å)                      | 5.579             | 5.580             | 5.581             |
| b (Å)                      | 5.579             | 5.580             | 5.581             |
| c (Å)                      | 13.87             | 13.87             | 13.88             |
| Volume (Å$^3$)             | 373.86            | 374.08            | 374.14            |
| Crystallite size (Å)       | 392.99            | 741.76            | 970.07            |
| Density g/cm$^3$           | 8.34              | 8.33              | 8.33              |
| Wyckoff Factor             |                   |                   |                   |
| Bi                         | 6a                | 6a                | 6a                |
| Fe                         | 6a                | 6a                | 6a                |
| O                          | 18b               | 18b               | 18b               |
| Geometrical parameters     |                   |                   |                   |
| Bond length (Å)            |                    |                   |                   |
| Bi-O1                      | 2.288             | 2.287             | 2.23              |
| Bi-O2                      | 3.422             | 3.424             | 3.424             |
| Fe-O1                      | 1.97              | 1.973             | 1.956             |
| Fe-O2                      | 3.305             | 2.08              | 2.08              |
| Bond angle (°)             |                    |                   |                   |
| Bi-O-Bi                    | 90.91             | 90.89             | 90.79             |
| Fe-O-Fe                    | 156.15            | 156.07            | 155.55            |
| Tolerance factor <t>       | 1.76              | 1.99              | 1.99              |

3.2 Raman scattering analysis
Figure 2. The Raman spectra of BiFeO$_3$ ((A) 500°C, (B) 600°C and (C) 700°C). The dash line describes the fitting result by Lorentzian standard profile.

Figure 2 shows the Raman scattering spectra of BiFeO$_3$ compounds. According to previous report, R3c structure has 13 Raman active mode: 4A$_1$ + 9E at Raman finger print area (0-600 cm$^{-1}$) [8-9]. Yuan et al [10] reported 10 Raman modes for BiFeO$_3$ consist of three A$_1$ modes (152.6, 177.5 and 224.2 cm$^{-1}$) and six E modes (270, 298.8, 354.9, 473.3, 554.3 and 618.3 cm$^{-1}$). R. Palai et al [9] reported Raman spectra for BiFeO$_3$: A$_1$ modes at 74.2, 168, 212 and 350.4 cm$^{-1}$ and E modes at 79.6, 145, 175.9, 224.2, 277.7, 295.2, 371.5, 473 and 553 cm$^{-1}$. Polomska et al [11], reported that Raman spectra appear at ~610 cm$^{-1}$ for oxygen stretching vibrations, ~410 cm$^{-1}$ related to oxygen bending vibration, modes between 200 and 300 cm$^{-1}$ are oxygen tilt and bending vibration and the modes for Bi-vibration appear below 200 cm$^{-1}$.

The some specific of Raman phonon modes shown in figure 2 are tabulated in Table 2. The 13 phonon modes due to 4A$_1$ + 9E symmetries are observed for sample C (calcined at 700°C). They are assigned to A$_1$ modes (99.79, 166.42, 214.68 and 335.57 cm$^{-1}$) and the remaining peaks are assigned to E modes (119.47, 145.08, 179.71, 287.48, 370.89, 436.35, 474.9, 559.81 and 649.81 cm$^{-1}$). Bi-O bond are associated with the A$_1$ modes and E modes are related to Bi atoms [ ]. Raman modes for sample A and B (500 and 600°C) are observed less than sample C (as can be seen in Table 2) and similar with the previously reported [8-9]. The difference in Raman mode number might due to calcination temperature effect which affect the structural parameter from the sample [13].

| Table 2. Raman shift (cm$^{-1}$) and mode assignment of BiFeO$_3$ Samples |
|---|---|---|---|---|
|   | A    |   | B    |   | C    |   |
| Frequency (cm$^{-1}$) | Mode | Frequency (cm$^{-1}$) | Mode | Frequency (cm$^{-1}$) | Mode |
| 127.54 | A$_1$ | 143.07 | E | 99.79 | A$_1$ |
| 222.8  | A$_1$ | 176.73 | E | 119.47 | E |
| 267.71 | A$_1$ | 222.66 | A$_1$ | 145.08 | E |
| 476.23 | E | 267.23 | A$_1$ | 166.42 | A$_1$ |
| 956.26 | MPP | 474.42 | E | 179.47 | E |
| 1256.04 | MPP | 529.22 | A$_1$ | 214.68 | A$_1$ |
|        |     | 548.13 | E | 287.48 | E |
|        |     | 592.54 | E | 335.57 | A$_1$ |
|        |     | 616.31 | E | 370.89 | E |
|        |     | 1257.85 | MPP | 436.35 | E |
|        |     |        |     | 474.92 | E |
3.3 FTIR analysis

Figure 3 shows the Fourier transform infrared spectra (FT-IR) of BiFeO$_3$ samples. The FT-IR spectra show some peaks that consistent with the previous reports for BiFeO$_3$ [14-16]. The numerous absorption peaks are visible as seen in Table 3. The existence of absorption band around 526 – 533 cm$^{-1}$ ($\nu_1$) are characteristics of the Fe–O stretching vibration of octahedral FeO$_6$ groups indicating the formation of BiFeO$_3$ phase [14-15]. Another Fe–O peak are observed around 809-848 cm$^{-1}$ ($\nu_2$) suggesting the highly crystalline BiFeO$_3$ phase formation [15-16].

The presence of NO$_3^-$ stretching vibrations observed at 1384, 1371 and 1367 cm$^{-1}$ for BiFeO$_3$ samples. The NO$_3^-$ ions are distributed uniformly at gel matrix which limiting formation of nitrate crystallites. Accordingly, the diffraction peaks corresponding to nitrates are not observed in XRD (figure 1) [15]. Moreover, observed absorption band (sample A and B) around 1741 and 1216 cm$^{-1}$ can be assigned to C=O and C–O stretching vibrations, respectively [17]. The C=O and C–O stretching band are not observed after calcination at 700°C indicating the organics molecules has decomposed in this calcination condition.

![Figure 3. The FTIR patterns of BiFeO$_3$ ((A) 500°C, (B) 600°C and (C) 700°C). The dash line presents the vibration of symmetry bonding in lattice.](image)

| Calcination condition | $\nu_1$ | $\nu_2$ | $\nu_3$ | $\nu_4$ | $\nu_5$ |
|-----------------------|--------|--------|--------|--------|--------|
| A                     | 533    | 809    | 1216   | 1367   | 1743   |
| B                     | 526    | 810    | 1218   | 1371   | 1741   |
| C                     | 532    | 848    | -      | 1384   | -      |

Table 3. FT-IR band assignment of some specific absorption modes for BiFeO$_3$ ((A) 500°C, (B) 600°C and (C) 700°C)
3. UV-Vis analysis

![Graph of UV-Vis analysis](image1)

![Graph of UV-Vis analysis](image2)

**Figure 4.** (a) UV-vis absorption (b) diffuse reflectance spectra of BiFeO$_3$ (A) 500°C, (B) 600°C and (C) 700°C

Optical absorbance performance are one important properties of semiconductors materials to determine the band gap from materials. In order to estimate the optical band gap of BiFeO$_3$, UV-Vis spectroscopy has been done in the UV-Vis-NIR range. The strong UV absorption of BiFeO$_3$ samples is due to the electronic transition from the valence band to the conduction band [18]. As shown in figure 4(a) the BiFeO$_3$ samples can absorb considerable amount of visible light, indicating the potential of BiFeO$_3$ sample as photocatalytic material. Optical absorption edge (Figure 4) indicates slight shift to higher wavelength with increasing calcination temperature. The shift in absorbance spectrum edge might be due to the change of particle size [19].

Figure 4(b) shows the diffuse reflectance of BiFeO$_3$ samples. The Kubelka Munk function used to calculate the absorption coefficient based on the diffuse reflectance data which defined as [20]:

$$F(R) = \frac{\alpha}{s} = \frac{(1 - R)^2}{2R}$$

where $F(R)$ is Kubelka-Munk function, $\alpha$ is absorption coefficient, $s$ is the scattering coefficient, and $R$ is the diffused reflectance. From this, the energy dependence of the UV-Vis-NIR range was further described.
Figure 5 shows the plot of \((F(R)E)^2\) vs. \(h\nu\). The extrapolation of linear parts of the curves toward absorption equal to zero gives \(E_g\) for direct transition. The optical band gaps (\(E_g\)) are found in the range of 1.98 – 2.06 eV. This results are consistent with the reported direct energy gap value from previous work for BiFeO\(_3\) [19]. The gap energy increase with the rise of calcination temperature suggesting the decreasing of conduction response in materials.

Calcination effect on BiFeO\(_3\) can be explained according to the experiment result. Structure analysis show crystal structure (hexagonal) and crystal symmetry (R3c space group) for all sample. Change in Raman mode due to structural parameter as shown in Table 1 and Table 2. Bond length from sample decrease as calcination temperature increase. The shift in Raman mode with increasing calcination temperature indicating a change in FeO\(_6\) vibration octahedral due to the difference in Fe/Bi-O bond length. The existence of FeO\(_6\) vibration also confirmed by FTIR analysis. UV-Vis analyses confirm gap energy increase as calcination temperature increase caused by stronger atomic bonding as bond length decrease. Bond length decreasing cause charge carrier movement become harder, so the energy that needed to move to other sites (gap energy) increase.

4. Conclusion
The single phase BiFeO\(_3\) have been successfully synthesized using sol-gel method and obtained in calcination condition at 700°C. The vibrational analysis confirmed the presence of metal-oxide stretching and bending vibration suggesting the formation of oxide perovskite compounds. The optical band gap energy increases with increasing of calcination temperature.

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