Crystal structure and phase transformation of BiFeO$_3$ multiferroics on the temperature variation

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Abstract. In this study, multiferroic of BiFeO$_3$ was successfully synthesized using solid state methods. The materials was calcined by variation temperature at 800, 840, 860, and 880ºC for 4 hours in air atmosphere. Structure analysis and phase transformation were carried out using X-ray diffraction. The results show that not only BiFeO$_3$ phase is formed but also other phases as secondary phases on all variation temperatures. The secondary phases, i.e. Bi$_{25}$FeO$_{40}$ and Bi$_2$Fe$_4$O$_9$, have different molar or weight percentage at that variation. BiFeO$_3$ has a perovskite structure and considering as R3c space group, for all secondary phases consist of cubic structure. The results showed that increasing calcination temperature decrease the amount of BiFeO$_3$ phases and increase the secondary phases. The highest percentage of BiFeO$_3$ phases (91.69%) is obtained at 800ºC.

1. Introduction

Multiferroics are materials that can behave as ferroelectric, ferromagnetic, and often ferroelastic on single or composite structure. This material is getting more attention due to those properties and their potential for various applications. Multiferroics are the combination of ferroelectric and ferromagnetic, the interaction between magnetic and electric fields correspond the magneto electric (ME) effect in their materials [1]. ME effect provides the possibility of controlling magnetic properties using electrical fields (E) and electrical properties using magnetic fields (H). Some practical applications of multiferroic materials are transducers, magnetic fields sensor, memory device, and photovoltaic devices.

BiFeO$_3$ (BFO) is one of the materials that can exhibit as ferroelectric and antiferomagnetic properties at room temperature in the same phase [2]. BFO, a rhombohedra ferroelectric with perovskite structure (ABO$_3$), has high ferroelectric Curie temperature (Tc \~ 830°C) and G-type antiferomagnetic below Néel temperature (T_N\~370°C) [3]. BFO is very difficult to synthesize in a pure single phase; it is often on polycrystalline condition and other secondary phases, such as Bi$_2$Fe$_4$O$_8$ and Bi$_{25}$FeO$_{39}$. Liu et al reported on their paper that secondary phase is formed in all their variation temperatures from 650– 850°C[4]. Golci et al by using different method also confirmed that during temperature 620– 770°C the secondary phase is appears together with BFO phases[5]. The synthesis process of BFO can be done by various methods, such as solid solution [6], sol gel [7], and auto-combustion methods [8].
In this work, we studied the phases during the heating process at various temperatures in air atmosphere. The change of phase’s percentage are further examined and presented, thus it may provide some useful experimental guidance for the preparation of pure phase of BFO.

2. Experimental
In this work, Bi$_2$O$_3$ (99%) and Fe$_2$O$_3$ (99%) were used to prepare BFO’s precursor by conventional mixed oxide methods. The chemical reaction for this synthesis is given as follow:

\[ \text{Bi}_2\text{O}_3 + \text{Fe}_2\text{O}_3 \rightarrow 2\text{BiFeO}_3 \]  \hspace{1cm} (1)

The mixtures of powder are milled by planetary ball mill with speed of 150 rpm for 5 hours. The process is carried out in ethanol media using ZrO$_2$ balls, then dried and homogenized using evaporator. The calcination process is completed with various temperatures, 800, 840, 860, and 880$^\circ$C with holding time of 4 hours. The temperature variation is selected based on the phase diagram of Bi$_2$O$_3$ - Fe$_2$O$_3$ systems that stable of BFO in the stoichiometric of Bi:Fe = 1:1 at the temperature range of 800-900$^\circ$C, at higher than 900$^\circ$C it will disappears [9]. Furthermore Cheng reported by in-situ XRD, the BFO formation located at temperature higher than 600$^\circ$C [10].

The calcined powders are characterized by XRD (Philips X’Pert MPD) using CuKα1 radiation then analyzed using Match program for phase identification. Crystal structure and percentage of phases are characterized using Rietveld methods by Rietica software.

3. Result and discussion
X-ray diffraction of BFO samples with various temperatures are presented in figure 1. It shows that all samples not only distinguished the presence of BFO, but also other secondary phases. The secondary phases, Bi$_3$Fe$_4$O$_9$ and Bi$_{25}$FeO$_{39}$, appear with different intensity and compositions. The peak positions on XRD pattern of all various samples can be considered similar. The increasing of temperatures induces the changes on the number of phases. The BFO phases became decrease while the secondary phases increase as the calcination temperature increase.

The lattice parameter and percentage of phases of samples were quantitatively calculated by using Rietica with Rietveld methods. The results are summarized in table 1. All samples variation and phases indicated having similar lattice parameters. It means that the increasing temperatures, within 800 – 880$^\circ$C, not significantly influence into the lattice parameter of materials.

Figure 1. XRD pattern of BFO at various temperature; 800, 840, 860, and 880 $^\circ$C.
Table 1 Lattice parameter of BFO samples.

| Phase      | Calcination temperature (°C) | 800       | 840       | 860       | 880       |
|------------|------------------------------|-----------|-----------|-----------|-----------|
|            | a = 5.581(7)                 | a = 5.574(4) | a = 5.574(1) | a = 5.552(8) |
|            | c = 13.876(3)                | c = 13.856(2) | c = 13.858(6) | c = 13.939(6) |
| BFO        | a = 90°                      | α = 90°    | α = 90°    | α = 90°    |
|            | β = 120°                     | β = 120°   | β = 120°   | β = 120°   |
| Bi₂Fe₄O₉   | a = 7.891(4)                 | a = 7.956(4) | a = 7.953(6) | a = 7.972(1) |
|            | b = 8.482(9)                 | b = 8.441(8) | b = 8.434(6) | b = 8.455(4) |
|            | c = 5.988(4)                 | c = 5.996(7) | c = 5.993(4) | c = 6.039(1) |
| Bi₂5FeO₃₉ | α = β = γ = 90°              | α = β = γ = 90° | α = β = γ = 90° | α = β = γ = 90° |

The percentage of BFO and the secondary phases, Bi₂Fe₄O₉ and Bi₂5FeO₃₉, are shown on figure 2 and 3. From figure 2, during temperature of 800 – 880°C, the graph simultaneously showed the decreasing of molar percentage of BFO phase and increasing of molar percentage of Bi₂Fe₄O₉. Figure 3, the graph showed some different result; in the similar temperature condition both molar percentage of BFO and Bi₂5FeO₃₉ are decrease. In here, the decreasing of Bi₂5FeO₃₉ phases shows significantly lower than other phases.

The chemical reaction of bismuth – ferrite is ideally formed as indicated in equation (1), where it should be only BFO single phase. However, XRD pattern showed not only the BFO phase but also other phases, i.e.Bi₂Fe₄O₉ and Bi₂5FeO₃₉ phases, as qualitatively and quantitatively identified. However, other possibilities of reaction also can be considered, as follow:

\[
\begin{align*}
Bi₂O₃ + Fe₂O₃ & \rightarrow Bi₂Fe₄O₉ \quad (2) \\
25Bi₂O₃ + Fe₂O₃ & \rightarrow 2Bi₂₅FeO₃₉ \quad (3)
\end{align*}
\]

As shown in figure 2 and 3, the increasing temperature effects on the decreasing of BFO and Bi₂5FeO₃₉ phases, and on the contrary increasing Bi₂Fe₄O₉ phase. These phenomena were also reported by Cheng, et al. [10]: at above 840°C the secondary phase, Bi₂Fe₄O₉, is more stable than Bi₂5FeO₃₉. Furthermore, both those secondary phases, Bi₂5FeO₃₉ and Bi₂Fe₄O₉, actually still can be further transformed become pure BFO by addition of Bi₂O₃ and Fe₂O₃, due to the following equations:

\[
\begin{align*}
Bi₂Fe₄O₉ + Bi₂O₃ & \rightarrow 4BiFeO₃ \quad (4) \\
2Bi₂₅FeO₃₉ + 24Fe₂O₃ & \rightarrow 50BiFeO₃ \quad (5)
\end{align*}
\]

Indeed, the results of this study were not in line with as indicated in the phase diagram, in which BFO phase will become better formed at higher temperature. This can be explained due to the phenomena of the volatility of Bismuth (Bi) [11]. So that, the Bi ions became deficit to react with Fe and resulting on fewer of pure BFO phase is formed. As reported on [11], the volatility of Bi can be minimized by an addition of bismuth up to 5-10 wt.%
4. Conclusion
BiFeO$_3$ (BFO) is formed as polymorph and perovskite structure at range of temperature of 800-880 °C, including Bi$_2$Fe$_4$O$_9$ and Bi$_{25}$FeO$_{39}$ as secondary phases. The molar percentage of BFO decreased and Bi$_2$Fe$_4$O$_9$ increases. This is due to the volatility of Bismuth (Bi) that evaporates at increasing temperature. Decreasing of Bi atoms is causing greater of Fe numbers, as a consequent Bi$_2$Fe$_4$O$_9$ dominantly to be formed.

Acknowledgement
The first author acknowledges Department of Physics, Institute of Technology Sepuluh Nopember (ITS) to support this work.
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