Synthesis of Bismuth Ferrite BiFeO$_3$ by solution combustion method

J Peñalva$^1$ and A Lazo$^2$

$^1$ National University of Engineering, Faculty of Sciences, Lima 25, Peru
$^2$ National University of Engineering, Faculty of Geological, Mining and Metallurgical Engineering, Av. Túpac Amaru, Lima 25, Peru

Email: jpenalvas@uni.pe

Abstract: In this work we describe the synthesis of bismuth ferrite BiFeO$_3$ (BFO) by the method of combustion in solution. Using the techniques of X-ray diffraction (XRD) together with its refinement Rietveld reveals the existence of a distorted rhombohedral perovskite structure (Space group-R3c). The average size of the BFO crystallite was estimated from the half-height width of the X-ray diffraction peaks using the Scherrer’s equation. The morphology of the prepared sample was determined by scanning electron microscopy (SEM) and stoichiometry ratio of BFO was determined by energy dispersive spectroscopy (EDS).

Keywords: Combustion synthesis, BFO, Multiferroics, X-Ray Diffraction (XRD)

1. Introduction

Multiferroic materials, with simultaneous coexistence of electrical and magnetic order, are currently the subject of intense research not only due to promising applications of multifunctional devices, but also to the interesting physics taking place in this class of materials.

Multiferroic material BiFeO$_3$ (BFO) has ABO$_3$ distorted perovskite structure and it is known as magneto-electric material. Due to this magneto-electric coupling at room temperature, BFO can be used to develop novel applications in the field of information storage, spintronics, sensors and photovoltaic devices [1,2,3]. In addition to potential magneto-electric applications, the photovoltaic activity of BFO has attracted considerable attention because of its small band gap which is used to the absorption between visible light ranges, making it a promising candidate for a visible light photocatalyst [4]. Bismuth ferrite exhibits simultaneous ferroelectric order at Curie temperature ($T_C\approx 830$ ºC) and antiferromagnetic at Neel temperature ($T_N\approx 370$ ºC) [5]. However, antiferromagnetic order shows modulated spin spiral structure of periodicity 62nm whereby it show very low magnetization in BFO [6].

BFO has been synthesized by different methods: nitrate combustion methods with several fuel as Glycine [7,8], Tartaric Acid [8,9] and Sucarose [10]; Sol-Gel method [11] and Pechini method [12]. However, each of these methods has its own advantages and limitations. The development of simpler and efficient process to obtain BFO nanoparticles with regular morphology and a homogeneous chemical composition is still an active area of research. The combustion method is found to be a rapid process, simple and effective to get very fine and homogeneous nanopowders. This method is one of the most-convenient methods for the preparation of oxides materials, which allows effective synthesis of a variety of nanosize materials.

In this work we have synthesized the BFO nanoparticles prepared by the combustion method using metallic nitrates with mixture fuel between glycine and urea, in which we have used the ratio of fuels recommended by Ianos et al [13]. The structure of the crystal and morphology are studied by X-ray diffraction (XRD) and scanning electron microscopy (SEM), stoichiometry ratio of BFO was determined by energy dispersive spectroscopy (EDS).
2. Experimental procedure

The reagents used in this synthesis were bismuth nitrate pentahydrate Bi (NO₃)₃·5H₂O (Aldrich > 99.99%), iron nitrate nanohydrate Fe (NO₃)₃·9H₂O (Merck > 99.99%), diluted nitric acid HNO₃, glycine C₂H₅NO₂ and urea CH₄N₂O. The mixture of the total solution was prepared by mixing the solution of Bi (NO₃)₃·5H₂O (dissolved in deionized water and in nitric acid HNO₃) and Fe (NO₃)₃·9H₂O (dissolved in deionized water) under magnetic stirring at room temperature until a clear solution was obtained, then the glycine and urea fuels were added to the mixture in the required stoichiometry:

\[
6 \text{Bi(NO}_3\text{)}_3 \cdot 5\text{H}_2\text{O} + 6 \text{Fe(NO}_3\text{)}_3 \cdot 9\text{H}_2\text{O} + 10\text{C}_2\text{H}_5\text{NO}_2 + 15 \text{CH}_4\text{N}_2\text{O} \rightarrow 6 \text{BiFeO}_3 + 35\text{CO}_2 + 38\text{N}_2 + 139\text{H}_2\text{O} \quad (1)
\]

The total mixture in a porcelain dish was taken to a heating mantle where the temperature was gradually raised to 400 °C. The mixture was heated until all the solvent was evaporated, then a combustion reaction was observed with a large amount of gas released. The brown powder obtained was taken to a muffle furnace for a thermal treatment at a temperature of 500 °C (1h) with a ramp of 2 °C / min. The powder obtained with thermal treatment was taken to its respective characterization.

The crystal structure of BiFeO₃ crystal was determined by and X-ray diffractometer with a Co source (Kα, λ = 1.7889Å), its morphology was studied by a scanning electron microscopy (SEM) of model EVO MA10 and stoichiometry ratio of BFO was determined by energy dispersive spectroscopy (EDS).

3. Results and discussions

3.1. X-ray powder diffraction

The powder X-ray pattern (XRD) of the BiFeO₃ obtained using a mixture of urea and glycine is shown in Figure 1. In Figure 1a, the powder obtained from the synthesis presents an amorphous phase which can be due to incomplete combustion and that there is probably deficient oxygen in BFO due to the release of gases in the combustion [8]. When the sample was heated to 500 °C for one hour, the peaks corresponding to the BFO phase appear in the DRX pattern in Figure 1b. The result of the DRX is in accordance with PDF # 01-071-2494 and reveals that the sample has a rhombohedral perovskite crystal structure, with space group R3c.

The average crystallite size of BFO were estimated using Debye-Scherrer equation:

\[
D = \frac{0.9\lambda}{\beta\cos\theta}
\]

where D is the average the crystallite size, λ = 1, 7889 Å (X-ray wavelength) and β is width of diffraction peak at half maximum for the angle 2θ. The average crystallite size of BFO was 27nm calculated by the half-height width of the peaks (012) and (024).
Figure 1. (a) Diffraction pattern of BFO without heat treatment and (b) with thermal treatment at 500ºC for 1h.

The X-ray pattern of the BFO has been refined by the Free Full Suit software [14] and is shown in Figure 2. The diffraction XRD has been used in the refinement by the Rietveld method [15]. This method determines structural parameters and atomic positions of the BFO from the construction of a theoretical model that is able to predict the experimental diffraction pattern. The BFO DRX pattern shows fit with the rhombohedral phase model (group space R3c). Structural, atomic position and R-factor parameters obtained from the refinement are observed in Table 1.

Figure 2. XRD pattern after structural refinement procedure using Rietveld’s method.
Table 1. Structural parameters, atomic position and R factor of the DRX refinement for the BFO.

| Sample     | Lattices parameters(A) | Atomic position | X     | Y     | Z     | R factor  |
|------------|------------------------|-----------------|-------|-------|-------|-----------|
| BiFeO₃     | a=b=5.5972, c=13.9155, v=377.5540 | Bi 6a           | 0.0000 | 0.0000 | 0.0000 | R_{wp}=18.7%  |
|            |                        | Fe 6a           | 0.0000 | 0.0000 | 0.2219 | R_{exp}=16.5% |
|            |                        | O 18b           | 0.4481 | 0.0171 | 0.9488 | $\chi^2=1.29$ |

The structure simulation based on XRD pattern was carried out on Rietveld crystal structure refinement. The data of the lattice parameters and atomic positions were placed in the input file of the VESTA software [16], which allowed us to visualize the crystal structure of the BiFeO₃ in the hexagonal cell unit including six formula units and rhombohedral cell unit including two formula unit. In addition, we have visualized the Fe³⁺ cations located inside an octahedron of oxygen atoms (FeO₆).

![Figure 3](image-url)

**Figure 3.** (a) Hexagonal cell unit of BFO with lattice parameters a=b=5.5972 Å, c=13.9155 Å, (b) Rhombohedral cell unit of BFO with parameters a=b=c=5.5972 Å.

3.2. Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS)

The morphology of the prepared sample was determined by SEM at different magnification and is shown in figure 4. The SEM images clearly reveals that BFO powder show pores or voids with different size and shape (Figure 4 a), in addition to the presence of an agglomerate and non-homogenous particles (Figure 4b). The presence of pores in the sample are attributed by the release of a large amount of gases (NO, NO₂, CO, NH₃ and H₂O) during the reaction between fuels and nitrates in the combustion process [8,13].
Figure 4. SEM image of the BFO powder with (a) a scale of 2μm and 10kx magnifications, (b) at a scale of 1μm and 30.83kx magnifications.

The stoichiometry ratio of BFO was determined by the SEM-EDS technique. The theoretical values for the atomic percentage between Bi, Fe and O in BiFeO₃ are 20, 20 and 60, respectively. The values obtained for Bi, Fe, O were 18.1%, 22.9%, 59%, these values obtained experimentally by SEM-EDS are close to the theoretical.
4. Conclusions

In this study, nanocrystalline BiFeO$_3$ is successfully prepared by solution combustion synthesis. The BFO phase was formed after heat treatment at 500°C for only 1h, in which the diffraction peaks are highly compatible with the presence of the BFO phase with a rhombohedral structure and space group R3C. The average crystallite size of about 27 nm by Scherrer’s equation. Scanning electron microscopy analysis confirmed the presence of pores or avoids and agglomerate of particles. Dispersive energy spectroscopy (EDS) reveals the proportion of Bi, Fe, O are close to the nominal 1: 1: 3 ratio for BiFeO$_3$.

Acknowledgments

This work was possible thanks to CONCyTEC within the Master's program in Physical Sciences of the National University of Engineering (UNI). We thank the company Ingenieros SAC for the measures of X-ray diffraction and the Physical Sciences laboratory for the measurements with their Scanning Electron Microscope.

References

[1] Cheong S and Mostovoy M 2007 Nat. Mater. 6 13-20.
[2] Anar S, Vibhav P, Kotnala R and Dhananjai P 2008 Phys. Rev. Lett. 101 247602.
[3] Wang J, Neaton J , Zheng H, Nagarajan V, Ogale S, Liu B, Viehland D, Vaithyanathan V, Schlom D, Waghmare U, Spaldin A, Rabe K, Wuttig M and Ramesh R 2003 Science 209 1719-22.
[4] Feng G, Xinyi C, Kuobo Y, Shuai D, Zhifeng R, F Y, Tao Y, Zhigang Z and Jun-Min L 2007 Adv. Mater. 19 2889-92.
[5] Erenstein W, Mathur N and Scott J 2006 Nature 442 759-65.
[6] Sosnowska L, Peterlin-Neumaier T and Steichele E 1982 J. Phys. C: Solid State Phys. 15 4835-46.
[7] Vijayanad S, Potdar H and Pattayil J 2009 Appl. Phys. Lett. 94 182507.
[8] José O, David D, Inti Z, Humberto A, Israel B, Patricia S and Noel N 2013 Inorg. Chem. 52 10306-10317.
[9] Xuelian Y and Xiaoqiang A 2009 Solid Stat. Comm. 149 711.

[10] Farhadi S, Zaidi M and J Mol 2009 Catal. A-Chem. 299 18.

[11] Ting L, Yebin X and Jingyuan Z 2010 J. Am. Ceram. Soc. 93, 3637-3641.

[12] Elidia A, Vetter F, Ivair A, Eduardo R, Rafaelle B and Emerson G 2008 J. Braz. Chem. Soc. 19 1153-57.

[13] Robert I, Radu L, Silvana B and Roxana B 2015 J. Mater. Sci. 50 6382-87.

[14] Rodriguez C 1993 Phys. B. 192 55-69.

[15] Hugo R 1969 J. Appl. Cryst. 2 65-71.

[16] Koichi M and Fujio I 2008 J. Appl. Cryst. 41 653-58.