Study of the optical and photovoltaic properties in nanoparticles of BiFeO$_3$

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Abstract: Bismuth ferrite ceramic powders (BiFeO$_3$) were synthesized by a combustion reaction in solution, using the mixture of urea and glycine as fuels, whose objectives were to improve their optical, electrical and photovoltaic response properties. X-ray diffraction analysis indicated the formation of the single phase BiFeO$_3$. Transmission electron microscopy (TEM) shows images of uniform nanoparticles of 70 nm on average. Through diffuse reflectance we obtain a band gap with a direct electronic transition of 2.14 eV, this value presents an improvement compared to that reported by other authors in BiFeO$_3$ ceramic powders. The value of the resistivity obtained by the 4-pointed method was $\rho = 0.486 \times 10^6 \ \Omega \cdot cm$, checking that our material is a semiconductor. Finally, by building a prototype of Ag/BiFeO$_3$/Ag, with visible light ($\lambda = 405 \ \text{nm}$), a photovoltaic response of 0.2 nA at room temperature was achieved.

Keyword: Band gap BiFeO$_3$, Resistivity, Photovoltaic effect.

1. Introduction

Among the multiferroic materials the BiFeO$_3$ has attracted great attention for the scientific community because it has a narrow prohibited band between 2.2 - 2.7 eV, simultaneous ferroelectric and ferromagnetic properties at room temperature, these allow the development of a new generation of memory devices [1].

Recently, BiFeO$_3$ research has been reactivated by having a great photovoltaic effect because these materials have a spontaneous polarization with an electric field capable of separating the charge carriers [2], that is the photocurrent and photovoltage can be observed in pure homogeneous crystals. The biggest problem is the obtaining of the pure or single phase material, this affects its structural, morphological, optical and electrical properties, which prevents the material from functioning properly when used in various devices.

What is intended to be done in this study is to synthesize the material through the combustion method using urea and glycine as fuels, this will have a great boost in obtaining the pure material and will influence the improvement of its optical, electrical and photovoltaic response properties under illumination with visible light, for application to solar cells. The combustion method was used because it is an ideal technique that allows the BiFeO$_3$ to be synthesized with a quick, simple and effective process to obtain nanoparticles of different sizes and cigars. Finally, in this work, a prototype was constructed to measure the correlation between the photovoltaic responses and the intensity of the lighting in the Ag/BiFeO$_3$/Ag configuration.
2. Experimental procedure

This section describes the materials, the experimental procedure and the description of the equipment used for the characterizations of bismuth ferrite.

The bismuth ferrite nanoparticles were synthesized by the combustion method in solution using bismuth nitrate pentahydrate Bi(NO$_3)_3.5$H$_2$O (Solutest - 98.5%), iron nitrate nonahydrate (Solutest - 98.5%), diluted nitric acid HNO$_3$ (Panreac - 65%), glycine (C$_2$H$_4$NO$_2$) and urea (CH$_4$N$_2$O) as fuels. For the synthesis of BiFeO$_3$ was used 1.550 g of Bi(NO$_3$)$_3$.5H$_2$O, 1.291 g of Fe(NO$_3$)$_3$.9H$_2$O, 0.399 g of glycine and 0.479 g of urea, each dissolved in deionized water separately. In the process, 4 ml of HNO$_3$ was added to Bi(NO$_3$)$_3$.5H$_2$O under magnetic stirring at room temperature to obtain a homogeneous solution and thus avoid precipitates, then Fe(NO$_3$)$_3$.9H$_2$O solutions, glycine and urea fuels were added to the solution of Bi(NO$_3$)$_3$.5H$_2$O, respectively. The total solution was kept under magnetic stirring for 1 hour at room temperature until a completely clear solution was obtained. Finally, the total solution was poured into a 200 ml porcelain crucible and then brought to a heating mantle where the temperature gradually increased from 30 °C to 390 °C with a duration of approximately 48 minutes. In this process, the propagation of self-sustained exothermic reactions throughout the aqueous medium is observed, which evaporates, producing a large gas release, as a result, ceramic powder was formed. The cinnamon-colored powder obtained was taken to a muffle furnace for a heat treatment at a temperature of 600 °C for one hour with a ramp of 2 °C/min. By means of X-ray diffraction (DRX) at room temperature, its phase, crystalline structure and crystallite size in BiFeO$_3$ powders were identified. The data was collected using 0.02 ° steps for 0.3 seconds per step in the range of 5° to 110° for angle 2θ, using a Bruker D8 Discover brand diffractometer with Cu-Kα radiation of 0.154 nm wavelength. The morphology and structure of the samples was observed using a transmission electron microscope (TEM) (JEM2010 FEG, JEOL) operated at 200KV. The average size distributions and standard deviations were calculated for each nanoparticle sample of the TEM images using ImageJ software. The diffuse reflectance spectra (DRS) of the samples were recorded using a UV-Vis spectrophotometer with an integrating sphere (Cary 5000 UV-Vis). To determine the band gap (Eg), the Kubelka-Munk F(R) theory [3] and the Tauc equation [4] were used. The BiFeO$_3$ powder sample was compacted with a pressure of 2.5 Mpa in the form of 13 mm diameter discs and the base of the contacts was made by depositing Ag by sputtering for 10 minutes. The resistivity of the material was calculated for the 4-point method using the Van der Pauw technique, supplying current in the range of -1 μA to 1 μA with a Keithley 6220 DC source and the output voltage was measured with a Keithley 2701 multimeter. In the Van der Pauw equation, resistivity was calculated [5]. For photovoltaic measurements, a 405 nm wavelength laser (hν = 3.06 eV) was used as the excitation source, varying the intensity of the laser illumination on the surface of the sample, these intensities were measured with a digital solar radiometer. Current measurements were made with a source and unit of measurement Keithley 2400.

3. Results and discussions

Figure 1 shows the X-ray diffraction pattern of the powder sample, the positions of the diffraction peaks indicate the formation of a rhombohedral structure with hexagonal lattice parameters (a = b = 5.578 Å, c = 13,862 Å) of the BiFeO$_3$, when compared with reference diffractograms; powder diffraction file (PDF): 01-71-2494.

The average crystallite size of BiFeO$_3$ was calculated by the Scherrer equation using the DRX peaks. The average size calculated was 40 nm using the crystalline planes (012), (020) and (024). Manjula et al. [6] synthesized BiFeO$_3$ powders using the chemical coprecipitation method and reported an average crystallite size of 63nm, for BiFeO$_3$ powders with heat treatment at 600 °C (2h). Köferstein [7] using a combustion-like method using starch as a complexing agent, synthesized BiFeO$_3$ powders, calculating a crystallite size of 41 nm for BiFeO$_3$ with a heat treatment at 600 °C (1h).
Figure 1. X-ray diffraction of BiFeO₃: a) BiFeO₃ with heat treatment at 600 °C.

Representative results by transmission electron microscopy (TEM) are shown in Figure 2 (a), the images shown are irregular, relatively elliptical nanoparticles of 70 nm on average. Figure 2 (b) presents the analysis of a high resolution image (HR-TEM) of a BiFeO₃ nanoparticle with an average size of 36 x 42 nm. Figure 2 (c) shows the family of planes (110) with inter-planar distances of 2.64 Å. Figure 2 (d) shows the analysis of the fast Fourier transform (FFT) which confirms the presence of corresponding planes with the R3c symmetry.

Figure 2. BiFeO₃ at 600 °C heat treatment: a) TEM image, b) HRTEM image of a single BiFeO₃ nanoparticle, c) Inter-planar distances and d) FFT analysis.
Making a comparison between the size of crystallite calculus in DRX and particle size measured by TEM, it shows us that a particle can be made up of several different crystallites [8]. Layek & Verma [9] synthesized BiFeO$_3$ powders by the combustion method with citric acid and by characterization by TEM they measured nanoparticles of sizes between 35 to 65 nm, for BiFeO$_3$ with heat treatment at 600 °C (2h).

The diffuse reflectance spectrum for BiFeO$_3$ powder nanoparticles has been studied. Figure 3 shows the percentage of diffuse reflectance as a function of the wavelength of the incident light, showing a large decay between 525-580 nm corresponding to the electronic transitions that involve the transfer of charge from the O (2p) states of the valence band at the Fe (3d) states of the conduction band [10], a strong absorption in the UV-Vis region between 400-525 nm and slight absorption between 525-800 nm.

The value of the calculated band gap, using the ratio of Tauc [F (R) hυ] n ∝ (hυ - Eg) with n = 2 for direct prohibited band, is presented graphically in Figure 4. The band gap is obtained by taking the part that allows a linear adjustment, the same that is extrapolated to the abscissa axis [11], giving a value of 2.14 eV. This band gap is relatively narrow compared to other multiferroic perovskites such as BaTiO$_3$ (3.28 eV) and LiNbO$_3$ (3.78 eV), indicating the possibility of being used for photovoltaic systems, given that light absorption and concentrations Bearer depend on the bandwidth range prohibited [12]. Köferstein et al. [7] by the combustion method using starch as a complexing agent reported an Eg = 2.27 eV (at 600 °C for 1h), Manjula et al. [6] using the chemical coprecipitation method reported an Eg = 2.2 eV (at 600 ° for 2h) and Xu et al. [13] by sol gel and tartaric acid reported Eg = 2.21 eV (at 600 °C for 2h).

The decrease in the prohibited band value may be due to the existence of energy levels induced by defects between the conduction and valence bands, more specifically the energy levels close to the conduction band [10]. It should be noted that, by obtaining a narrower prohibited band, the passage of electrons between the valence band and the conduction band will be more optimal. In our case, one of the contributions made was to use urea and glycine as fuels to obtain a narrow energy band.
Figure 4. \([F(R) \cdot h\nu]^2\) vs \(h\nu\) of BiFeO\(_3\) nanoparticles. The intersection of the extrapolated absorption edge on the energy scale (x-axis) gives the prohibited band interval of the sample.

In Figure 5, the I-V curves show us the ohmic characteristic of the material, checking the passage of electrons and that the resistance is the same at any of the measuring points. With these values, the resistivity of the material was calculated, which resulted \(\rho = 0.486 \times 10^6 \, \Omega\,\text{cm}\), this value is in the semiconductor range. Between the results of the prohibited band and the resistivity a proportional dependence is observed, as the resistivity decreases the prohibited band as well. This is because the gap between the valence band and the conduction band is reduced, resulting in the faster electron jump, the particle size also influences these results since it is tending to grow due to its crystallization by the heat treatment performed [14].

Figure 5. I-V measurements on BiFeO3 tablets at 600 °C heat treatment.

Not many references have been found regarding resistivity measurements, however Safari & Akdogan [15] reported a measured resistivity achievement of \(\rho = 3 \times 10^9 \, \Omega\,\text{cm}\), which is a direct consequence of the suppression of oxygen vacancies synthesized by sol-gel, thermal analysis
was performed for BiFeO$_3$ powders with heat treatment at 500 °C, highly crystalline and well formed of a size of approximately 50 nm.

Figure 6 shows the response of the photovoltaic measurement, the graph tends to an increasing exponential function. The current flow measured in the range of 350-560 W/m$^2$ tends to saturation and this stabilizes as the light intensity is greater, as we can see in the graph inserted in Figure 6, the incident photons of the lasers with energies greater than the prohibited band of BiFeO$_3$, manage to excite the electrons of the material generating electric current flow. On the other hand, the photocurrent measured between 0 - 350 W/m$^2$ is very weak, because the photons of the incident laser fail to excite the electrons of the material. The maximum current measured at the maximum light intensity of the laser was 0.2 nA and one of the necessary conditions for the appearance of the photovoltaic effect is the availability of empty states at the levels within the valence band where photons with an energy greater than the band interval can produce electric current.

![Figure 6. Light intensity vs. current in BiFeO$_3$ samples with heat treatment at 600 °C](image-url)

4. Conclusion

Bismuth ferrite was synthesized by the combustion method using urea and glycine as fuels, the addition of nitric acid allowed us to obtain the solution completely in pure phase, thus controlling the problems in obtaining the pure material (without impurities) and improving its optical, electrical and photovoltaic response properties. The results by X-ray diffraction, both qualitatively and analytically, reveal the rhombohedral structure with hexagonal network parameters. The measurements (TEM) show images of relatively elliptical nanoparticles, the inter-planar distances of one of the samples are 2.64 Å belonging to the family of planes (110) corresponding to the R3c symmetry, general nanoparticles of average size 70nm could be observed. We found an optimal band prohibited with a direct electronic transition of 2.14 eV was found, it is an improvement in the values reported by other authors that are in the range of 2.2 - 2.7 eV, the method of synthesis, heat treatment and purity in the phase influence in this
value. The resistivity was measured by the 4-pointed method applying the Van der Pauw technique, obtaining as a best result $\rho = 0.486 \times 10^6 \ \Omega \cdot \text{cm}$, this value is in the range of semiconductors $10^8$ and $10^3 \ \Omega \cdot \text{cm}$. The photovoltaic effect was measured by acquiring the light intensity characteristics of a laser with a wavelength of 405 nm. ($\hbar \nu = 3.06 \text{ eV}$) resulting in a current of 0.2 nA at its maximum intensity, this characteristic makes it a promising candidate for photovoltaic systems.

References

[1] Liu, K., Fan, H., Ren, P., & Yang, C. (2011). Structural, electronic and optical properties of BiFeO$_3$ studied by first-principles. Journal of Alloys and Compounds, 509(5), 1901–1905.

[2] Young S M and Rappe, A M, (2012) First principles calculation of the shift current photovoltaic effect in ferroelectrics. Physical Review Letters, 109 (11).

[3] Lazo, A. (2014). Síntesis y propiedades ópticas y magnéticas del YCrO$_3$ preparado por los métodos precursor polimérico y reacción de combustión (tesis doctoral). Universidad Federal de Goiás, Goiani, Brasil.

[4] Abdullahi, S. S., Güner, S., Koseoglu, Y., Murtala, I., Adamu, B. I., & Abdulhamid, M. I. (2016). Simple Method For The Determination of Band Gap of a Nanopowdered Sample Using Kubelka Munk Theory. Journal of the Nigerian Association of Mathematical Physics (NAMP), 35(May), 241–246.

[5] Estrella, J. (2016). Electrical measurements by the four-pointed method in thin films of photovoltaic interest (master's thesis). National Polytechnic Institute, Tamaulipas, Mexico.

[6] Manjula, N., Ramu, S., Kumar, K. S., Reddy, D. A., & Vijayalakshmi, R. P. (2015). Magnetic and dielectric properties of BiFeO$_3$ nanoparticles. Journal of Advances in Chemistry, 10(1), 2146–2161.

[7] Köferstein, R. (2014). Synthesis, phase evolution and properties of phase-pure nanocrystalline BiFeO$_3$ prepared by a starch-based combustion method. Journal of Alloys and Compounds, 590, 324–330. https://doi.org/10.1016/j.jallcom.2013.12.120.

[8] Colonía, R. (2012). Análisis estructural por el refinamiento de Rietveld del peróxido de zinc (ZnO 2 ) sintetizado y sometido a diferentes temperaturas.

[9] Layek, S., & Verma, H. C. (2012). Magnetic and dielectric properties of multiferroic BiFeO3 nanoparticles synthesized by a novel citrate combustion method. Advanced Materials Letters, 3(6), 533–538. https://doi.org/10.5185/amlett.2012.icnano.242.

[10] Mocherla, P. S. V., Karthik, C., Ubic, R., Ramachandra Rao, M. S., & Sudakar, C. (2013). Tunable bandgap in BiFeO3 nanoparticles: The role of microstrain and oxygen defects. Applied Physics Letters, 103(2). https://doi.org/10.1063/1.4813539

[11] Moyano, M. (2015). Processing, structural characterization and study of the electrical conductivity of the ceramic material Bi$_{0.7}$La$_{0.3}$Fe$_{0.9}$Ti$_{0.1}$O$_{3.05}$ (undergraduate thesis). National Polytechnic School, Quito, Ecuador.

[12] Zhang, G., Wu, H., Li, G., Huang, Q., Yang, C., Huang, F., … Lin, J. (2013). New high Tc multiferroics KBiFe$_2$O$_5$ with narrow band gap and promising photovoltaic effect. Scientific Reports, 3, 1–8. https://doi.org/10.1038/srep01265.

[13] Xu, Q., Zheng, X., Wen, Z., Yang, Y., Wu, D., & Xu, M. (2011). Enhanced room temperature ferromagnetism in porous BiFeO$_3$ prepared using cotton templates. 151, 624–627. https://doi.org/10.1016/j.ssc.2011.01.029.

[14] Gao, T., Chen, Z., Zhu, Y., Niu, F., Huang, Q., Qin, L., … Huang, Y. (2014). Synthesis of BiFeO3 nanoparticles for the visible-light induced photocatalytic property. Materials Research Bulletin, 59, 6–12.

[15] Safari, A., & Akdogan, E. K. (2008). Piezoelectric and Acoustic Materials for Transducer Applications (1st ed.; Libgen librarian, Ed.). Springer US.