

## Synthesis and Applications of Silver Doped Bismuth Ferrite (BiFeO<sub>3</sub>) Nanoparticles

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### Abstract

In this research, silver doped bismuth ferrite (BiFeO<sub>3</sub>) nanoparticles were synthesized by the sol-gel and co-precipitation methods. In the sol-gel method, bismuth ferrite and silver nitrate were used as starting materials with different ratios of 5:0.1, 5:0.2, 5:0.3, and 5:0.4 (AgBFO-1<sub>s</sub>, AgBFO-2<sub>s</sub>, AgBFO-3<sub>s</sub>, and AgBFO-4<sub>s</sub>, respectively). In the co-precipitation method, bismuth nitrate pentahydrate, ferric nitrate nanohydrate, and silver nitrate were mixed with different mole ratios: 1:1:0.125, 1:1:0.25, 1:1:0.5, and 1:1:1 (AgBFO-1<sub>c</sub>, AgBFO-2<sub>c</sub>, AgBFO-3<sub>c</sub>, and AgBFO-4<sub>c</sub>, respectively). The prepared samples were characterized by XRD and EDXRF techniques. According to the resulting data, AgBFO-3<sub>s</sub> and AgBFO-4<sub>c</sub> were chosen as selected samples for electrical application. An LCR meter (frequency range of 20–100 MHz at 2 V) was used to measure the electrical properties of selected samples. In accordance with the electrical properties, selected samples showed semiconducting properties and higher conductivity values (> 10 kcm<sup>-1</sup>), which were well consistent with the literature. Based on the results of their electrical properties, selected samples could be used as cathode electrode in an electrochemical cell.

**Keywords:** BiFeO<sub>3</sub>, nanoparticles, electrical properties, conductivity values, electrochemical cell

### 1. Introduction

Bismuth ferrite (BiFeO<sub>3</sub>) is one kind of ferrite, a magnetic material that has combined electrical and magnetic properties. Recently, there has been renewed interest because of its possible novel applications in the fields of radio, television, microwave and satellite communications, audio-video, digital recording, and permanent magnets (Mallahi *et al.*, 2014). BiFeO<sub>3</sub> is a well-known multiferroic at room temperature, having a para- to ferro-electric transition temperature (T<sub>C</sub> ~ 1103K) and a G-type antiferromagnetic transition at T<sub>N</sub> ~ 643K (Ibrahim *et al.*, 2017). Multiferroic BiFeO<sub>3</sub> nanostructures exhibit interesting magnetic and optical properties because of nanoscale size effects (Freitas, 2013). BiFeO<sub>3</sub> exhibits photocatalytic activities under visible light irradiation for water splitting and degradation of pollutants because of its narrow band gap and excellent chemical stability (Ghosh *et al.*, 2005). In fact, doping BiFeO<sub>3</sub> with a foreign atom at either the A or B site of the ABO<sub>3</sub> lattice has been proven to be a valuable route to enhancing its properties. Demonstrated substitution of Bi<sup>3+</sup> with Ag resulted in a remarkable improvement of the photocatalytic activity of BiFeO<sub>3</sub> under visible light (Albino *et al.*, 2014).

Many researchers have attempted to synthesize nanostructured BiFeO<sub>3</sub>, such as spheres, nanorods, nanowires, and plates, using different methods. Several techniques have been utilized to prepare BiFeO<sub>3</sub> nanostructures, ball-milling technique, co-precipitation, polymeric assisted route, hydrothermal, reverse micelles, etc. Choosing proper synthesis techniques plays an important role in controlling the size and surface area, and hence the properties, of materials

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(Johari, 2011). Among all used techniques, the sol-gel method has many advantages, such as low temperature, low cost, simplicity, energy savings, relatively low impurity content resulting from the easy formation of the bismutite phase during calcination, and uniform-sized BiFeO<sub>3</sub> nanoparticles (Muneeswaran *et al.*, 2013).

Studying silver doped bismuth ferrite (BiFeO<sub>3</sub>) nanoparticles that were made using the co-precipitation and sol-gel processes is the goal of the current investigation. On the structural, elemental, and electrical characteristics of silver, the impact of doping has been investigated.

## 2. Materials and Methods

### Preparation of Silver Doped Bismuth Ferrite Powder by Sol-gel Method

The chemical reduction procedure was used to produce the powdered silver doped bismuth ferrite. A reductant called PVP (polyvinyl pyrrolidone) was employed to create silver doped bismuth ferrite powder. 20 mL of distilled water and 1.88 g of PVP were combined, and the liquid was then heated to 60 °C in the air while being stirred magnetically until the PVP was completely dissolved. In varying mole ratios of 5:0.1, 5:0.2, 5:0.3, and 5:0.4, the bismuth ferrite powder and silver nitrate (AgNO<sub>3</sub>) were combined and dissolved in distilled water. The PVP solution was then added to the resulting mixture, which was then heated at 80 °C for 2 hours while being magnetically stirred. The product was extracted by centrifugation, cleaned with distilled water, and then dried in a 100 °C oven. Bismuth ferrite powder that has been doped with silver was eventually made. They were designated as AgBFO-1<sub>s</sub>, AgBFO-2<sub>s</sub>, AgBFO-3<sub>s</sub>, and AgBFO-4<sub>s</sub>, respectively.

### Preparation of Silver Doped Bismuth Ferrite Powder by Co-precipitation Method

Ferric nanohydrate (Fe(NO<sub>3</sub>)<sub>3</sub>.9H<sub>2</sub>O) and bismuth pentahydrate (Bi(NO<sub>3</sub>)<sub>3</sub>.5H<sub>2</sub>O) were dissolved in 2-methoxy ethanol in a mole ratio of 1:1. At room temperature, the solution was constantly agitated for an hour until it turned translucent. Citric acid (C<sub>6</sub>H<sub>8</sub>O<sub>7</sub>) was added as a chelating agent, and the mixture was heated and stirred at 80 °C for 2 hours. The mixture that resulted was then clear, translucent, and reddish-black. In addition, the mixture was heated to 80 °C while being continuously stirred for 5 hours, or until all the liquid evaporated. Many brown vapours were rapidly evaporating. Near the end of the reaction, a fluffy brown substance (gel) was found in the bottom of the beaker. The resultant gel was then heated to 550 °C for 4 hours.

Polyvinyl pyrrolidone (PVP) was used as a reductant in the chemical reduction method to produce BiFeO<sub>3</sub> powder that was doped with silver. 1.88 g of PVP was dissolved in 20 mL of distilled water, and the mixture was then heated to 60 °C in the air while being magnetically agitated. Silver nitrate (AgNO<sub>3</sub>), BiFeO<sub>3</sub> powder, and distilled water were combined in a mole ratio of 5:0.3 before the PVP solution was added. The resulting mixture was then heated for two hours at 80 °C while being constantly stirred. The material was separated using centrifugation, and then it was washed with distilled water and baked in an oven at 100 °C to produce silver doped bismuth ferrite powder. AgBFO-1<sub>c</sub>, AgBFO-2<sub>c</sub>, AgBFO-3<sub>c</sub>, and AgBFO-4<sub>c</sub> were used to identify them.

### **Characterization**

By employing an X-ray diffractometer (Rigaku, Japan), X-ray diffraction analysis was used to confirm that the samples were silver doped bismuth ferrite. Using an energy dispersive X-ray fluorescence spectrometer (Shimadzu EDX-700, Japan), the relative abundance of the elements in these samples was also determined.

### **Preparation of Pellets**

Using a MAEKAWA Testing machine, the chosen samples (AgBFO-3<sub>s</sub> and AgBFO-4<sub>c</sub>) were prepared into pellets measuring 1.5 cm in diameter and 0.16 cm in thickness.

### **Determination of the Electrical Properties of AgBFO-3<sub>s</sub> and AgBFO-4<sub>c</sub>**

LCR-8110G meter was used to measure the electrical characteristics of AgBFO-3<sub>s</sub> and AgBFO-4<sub>c</sub> pellets (Inductance, capacitance and resistance meter, GwInstek, DC 20-10 MHz). The measurement of electrical conductivity was done at room temperature.

### **Using AgBFO-3<sub>s</sub> or AgBFO-4<sub>c</sub> as Cathode Electrode in an Electrochemical Cell**

The beaker was filled with 50 mL of pure water, and 5.8 g of sodium chloride was added. With a glass rod, the salt solution was gently swirled. Graphite served as the anode and an AgBFO-3<sub>s</sub> or AgBFO-4<sub>c</sub> electrode used as the cathode was submerged in the salt solution. With a black connecting wire, the AgBFO-3<sub>s</sub> or AgBFO-4<sub>c</sub> cathode was linked to the battery's negative terminal. A red connecting wire was used to attach the graphite anode to the battery's positive end. The electrolysis of a sodium chloride (NaCl) solution has started and will last for two to three minutes. The two clips were taken out of the battery and connected to the LED. So, the LED lights up brightly.

## **3. Results and Discussion**

### **XRD Analysis**

XRD diffractograms of prepared samples were shown in Figures 1 (a, b, c, d) and 2 (a, b, c, d) (AgBFO-1<sub>s</sub> to AgBFO-4<sub>s</sub> and AgBFO-1<sub>c</sub> to AgBFO-4<sub>c</sub>). It has been found that as the amount of silver doping increases, the size of the crystallites grows, which may be the result of particle growth. AgBFO-3<sub>s</sub> (sol-gel method) and AgBFO-4<sub>c</sub> (co-precipitation method) were chosen as the best samples among them because they have high crystallinity and average crystallite sizes that, according to the Debye-Scherrer equation, are 32.10 nm and 33.06 nm, respectively.

### **EDXRF Analysis**

Figures 3(a, b, c, d), and Figures 4 (a, b, c, d) demonstrated the EDXRF spectra of the prepared samples (AgBFO-1<sub>s</sub> to AgBFO-4<sub>s</sub> and AgBFO-1<sub>c</sub> to AgBFO-4<sub>c</sub>). In silver doped bismuth ferrite powder, Bi, Fe, and Ag are the primary elements. According to the EDXRF analysis data, AgBFO-4<sub>c</sub> was found to have 37.2% of Bi, 11.2% of Fe, and 2.22% of Ag and AgBFO-3<sub>s</sub> was also found to have 26.9% of Bi, 9.98% of Fe, and 2.74% of Ag, respectively. Based on the percentage of silver doping, AgBFO-3<sub>s</sub> (sol-gel method) and AgBFO-4<sub>c</sub> (co-precipitation method) were chosen as selected samples.

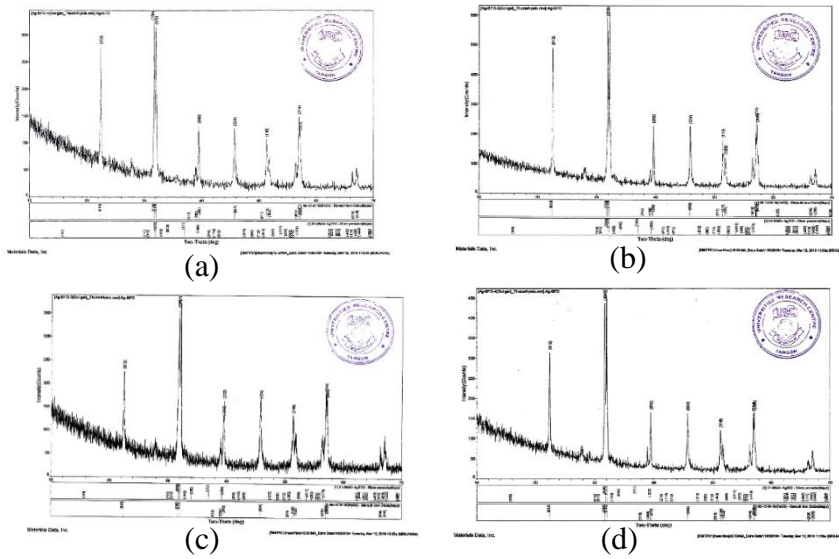


Figure 1. XRD patterns of (a) AgBFO-1s, (b) AgBFO-2s, (c) AgBFO-3s and (d) AgBFO-4s powder samples

Table 1. Average Crystallite Sizes of AgBFO Samples Synthesized by Sol-gel Method

Sample	Average crystallite sizes (nm)
AgBFO-1s	27.18
AgBFO-2s	40.01
AgBFO-3s	32.10
AgBFO-4s	31.71

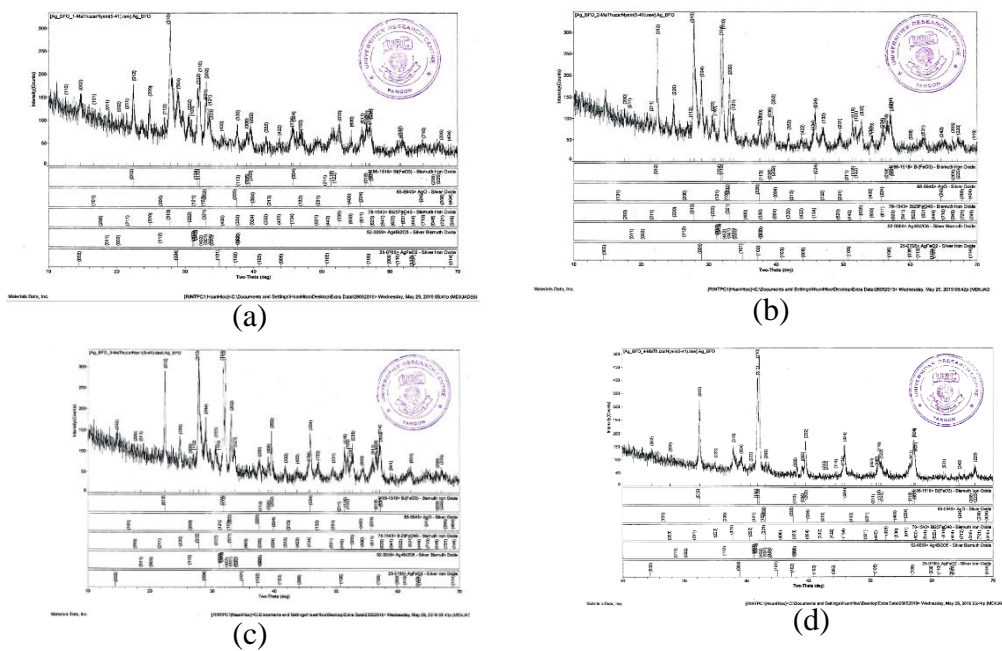


Figure 2. XRD patterns of (a) AgBFO-1c, (b) AgBFO-2c, (c) AgBFO-3c and (d) AgBFO-4c powder samples

Table 2. Average Crystallite Sizes of AgBFO Samples Synthesized by Co-precipitation Method

Samples	Average crystallite sizes (nm)
AgBFO-1c	23.29
AgBFO-2c	26.44
AgBFO-3c	30.88
AgBFO-4c	33.06

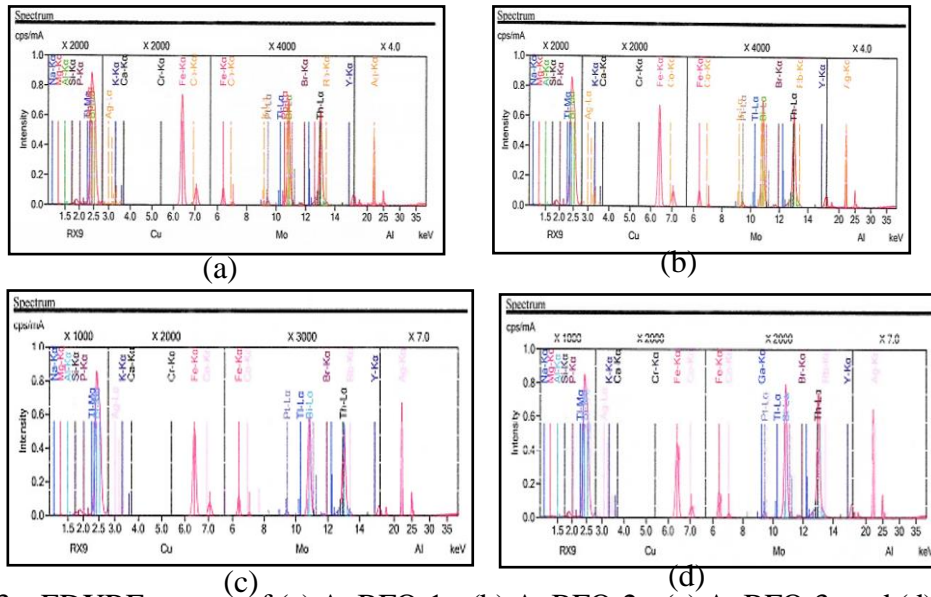


Figure 3. EDXRF spectra of (a) AgBFO-1s, (b) AgBFO-2s, (c) AgBFO-3s and (d) AgBFO-4s powder

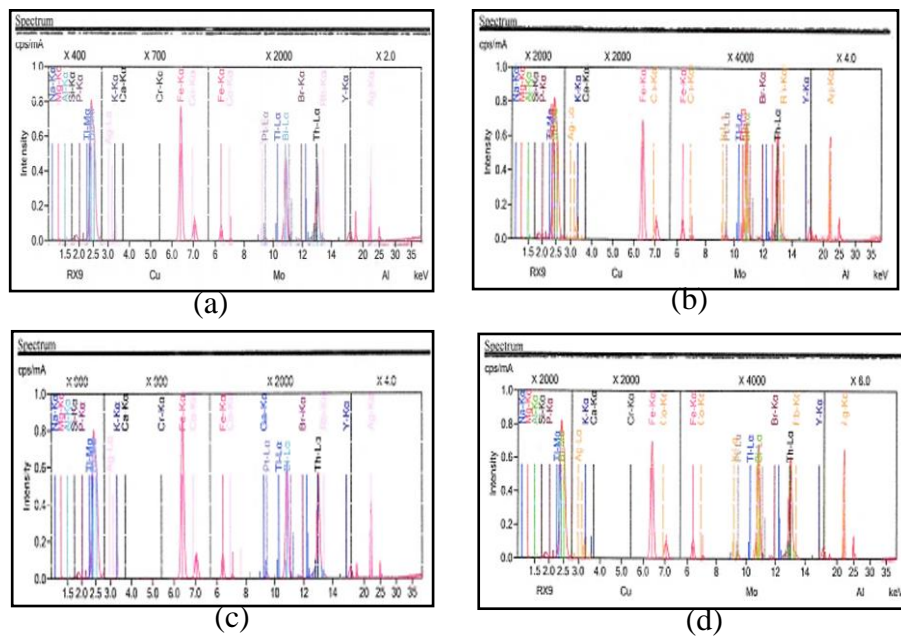


Figure 4. EDXRF spectra of (a) AgBFO-1c, (b) AgBFO-2c, (c) AgBFO-3c and (d) AgBFO-4c powder

**Evaluation on the Electrical Properties of Selected (AgBFO-3s and AgBFO-4c) Samples AC and DC Conductivities**

AC and DC conductivities of AgBFO-3s and AgBFO-4c samples were measured using an LCR meter at 2 V over a frequency range of 20 to 100 kHz. It showed that AgBFO-3s had considerably greater AC and DC conductivities than the AgBFO-4c sample. Hence, as demonstrated in Figures 5 (a) and (b), the metal conduction behavior for both samples rises with increasing frequency. Also, as the applied alternating electric field's frequency increased, the values of the AC conductivity gradually increased since the higher frequency allowed electron migration easier. (Mubarak *et al.*, 2014).

Table 3. AC Conductivity of AgBFO-3s and AgBFO-4c Samples at Different Frequencies

Samples	AC conductivity ( $k\Omega\text{ cm}^{-1}$ )				
	20 kHz	40 kHz	60 kHz	80 kHz	100 kHz
AgBFO-3s	4.164	6.848	8.948	11.049	13.157
AgBFO-4c	3.513	5.954	7.905	9.824	11.355

Table 4. DC Conductivity of AgBFO-3s and AgBFO-4c Samples at Different Frequencies

Samples	DC conductivity ( $k\Omega\text{ cm}^{-1}$ )				
	20 kHz	40 kHz	60 kHz	80 kHz	100 kHz
AgBFO-3s	27.241	43.323	59.126	73.201	86.065
AgBFO-4c	23.085	39.346	53.341	65.066	75.392

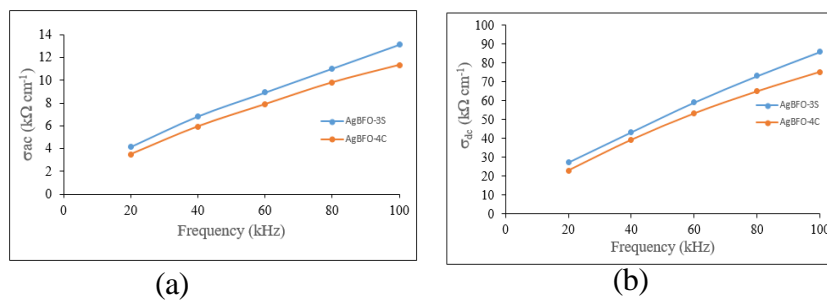


Figure 5. Plots of (a) AC conductivity and (b) DC conductivity of AgBFO-3s and AgBFO-4c Samples

**Resistivity**

With semiconductor materials, the conductivity values are inversely associated with the resistance. Table 5 and Figure 6 depict the variations in electrical resistivity of the chosen samples. As a result, the resistivity values of particular samples (AgBFO-3s and AgBFO-4c) reduce when DC conductivity rises.

Table 5. Resistivity of AgBFO-3<sub>s</sub> and AgBFO-4<sub>c</sub> Samples at Different Frequencies

Samples	Resistivity (MΩcm)				
	20 kHz	40 kHz	60 kHz	80 kHz	100 kHz
AgBFO-3 <sub>s</sub>	36.709	23.082	16.913	13.661	11.619
AgBFO-4 <sub>c</sub>	43.318	25.415	18.747	15.369	13.264

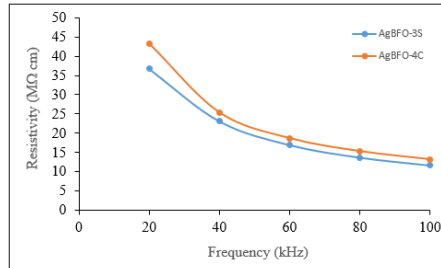
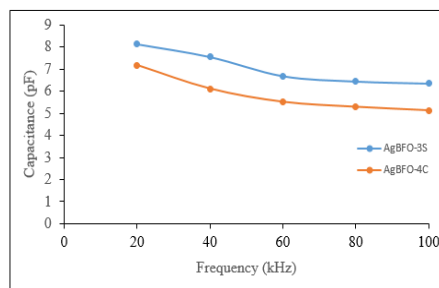
Figure 6. Plots of resistivity of AgBFO-3<sub>s</sub> and AgBFO-4<sub>c</sub> samples vs frequency

Table 6 and Figure 7 display the frequency-dependent resistivity and capacitance of the AgBFO-3<sub>s</sub> and AgBFO-4<sub>c</sub> samples, respectively. It was also discovered that the capacitance decreased out when the frequency increased. At the lowest frequency, the maximum capacitance value was displayed. Moreover, the capacitances of both samples fell within the range of Pico farads. This result demonstrated that both samples have the capacity for conducting electrical energy-based charging and recharging operations.

Table 6. Capacitance of AgBFO-3<sub>s</sub> and AgBFO-4<sub>c</sub> Samples at Different Frequencies

Samples	Capacitance (pF)				
	20 kHz	40 kHz	60 kHz	80 kHz	100 kHz
AgBFO-3 <sub>s</sub>	8.121	7.546	6.687	6.447	6.354
AgBFO-4 <sub>c</sub>	7.170	6.108	5.511	5.285	5.125

Figure 7. Plots of Capacitance of AgBFO-3<sub>s</sub> and AgBFO-4<sub>c</sub> samples vs frequency

### Generating Electricity in Electrochemical Cell using AgBFO-3<sub>s</sub> and AgBFO-4<sub>c</sub> as Electrode

AgBFO-3<sub>s</sub> or AgBFO-4<sub>c</sub> were used as the cathode electrode for generating electricity in the electrochemical cell. Graphite was also used as an anode electrode. The output voltages of the selected samples were also recorded by increasing the charging time. The variation of their output voltages, as shown in Table 7, reveals that the output voltage value is not significantly different between the selected AgBFO-3<sub>s</sub> and AgBFO-4<sub>c</sub>. Moreover, these samples have the

ability to store energy. According to the experimental results, these samples had promising applications in electrochemical cells. It is expected that this research will aid in the generation of electricity for optical-electronic devices.

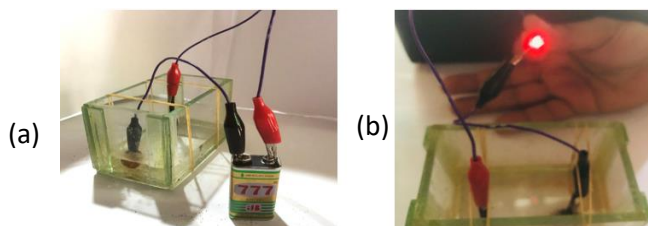


Figure 8. (a) Charging of electrochemical cell by electrolyte of 2 M NaCl solution for 2-3 min by using selected AgBFO-3s cathode and graphite anode, (b) Photo showing as the use of charged electrochemical cell to light LED

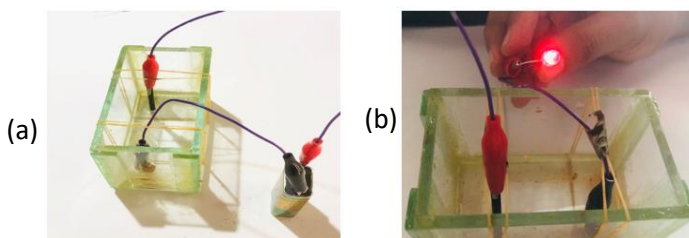


Figure 9. (a) Charging of electrochemical cell by electrolyte of 2 M NaCl solution for 2-3 min by using selected AgBFO-4c cathode and graphite anode, (b) Photo showing as the use of charged electrochemical cell to light LED

Table 7. Output Voltage of Silver Doped Bismuth Ferrite with Increasing Charging Time

Samples	Output voltages (V)				
	Charging time (min)				
	2	3	4	5	6
AgBFO-3s	2.21	2.26	2.48	2.49	2.54
AgBFO-4c	2.17	2.24	2.29	2.32	2.35

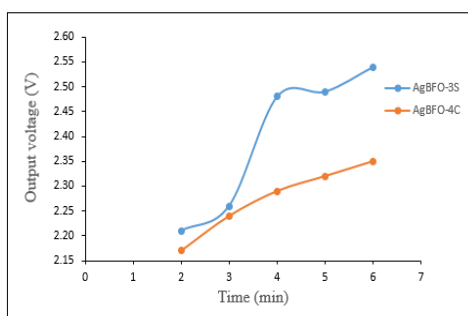


Figure 10. Plots of the output voltage vs charging time of AgBFO-3s and AgBFO-4c used as cathodes

#### 4. Conclusion

Silver doped bismuth ferrite (BiFeO<sub>3</sub>) nanoparticles were successfully synthesized by the sol-gel and co-precipitation methods. According to XRD and EDXRF analyses, AgBFO-3s and AgBFO-4c were chosen as selected samples due to their high crystallinity and silver doping



percent. The electrical conductivity values of both samples gradually increased with an increase in frequency. The maximum values of AC and DC conductivity were 13.157 and 86.065  $\text{k}\Omega\text{cm}^{-1}$  for AgBFO-3s, and also 11.355 and 75.392  $\text{k}\Omega\text{cm}^{-1}$  for AgBFO-4c. These results indicated that the AC and DC conductivity values of these samples were higher than 10  $\text{k}\Omega\text{cm}^{-1}$  (literature value). Moreover, the conductivity values of AgBFO-3s prepared by the sol-gel method were higher than those of the others. These samples have the ability of a capacitor to store energy. It can be concluded that the semiconducting properties of these samples were found through investigation of their results. The selected AgBFO-3s and AgBFO-4c nanoparticles have very similar output voltage values. So, these two nanoparticles could be applied by two different methods as a potential electronic device for electrochemical cells as well as fuel cell technology. From the point of view of conductivity, it is obvious that the selected nanoparticles can be used as a good electronic conductor (electrode) instead of a platinum or silver cathode electrode in an electrochemical cell.

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### References

- Albino, G. M., O. P. Perez, B. R. Beleno and Y. C. Mattei. (2014). "Effect of Ca and Ag Doping on the Functional Properties of BiFeO<sub>3</sub> Nanocrystalline Powders and Films". *Mater. Res. Soc. Symp. Proc.*, vol. 1675, pp. 104-111
- Freitas, V. F. (2013). "Structural Phase Relations in Perovskite-structured BiFeO<sub>3</sub> Based Multiferroic Compounds". *J. Adv. Ceram.*, vol. 2(2), pp. 103-111
- Ghosh, A., S. Dasgupta, A. Sen and H. Shekhar. (2005). "Low Temperature Synthesis of Nanosized Bismuth Ferrite by Wet Chemical Route". *J. Am. Ceram. Soc.*, vol. 88, pp. 1349-1352
- Ibrahim, E. M. M., G. Farghal, M. Khalaf and H. M. A. EL-Lateef. (2017). "Effect of Calcination Temperature on Magnetic and Electrical Properties of BiFeO<sub>3</sub> Nanoparticles Prepared by Sol-Gel Method". *J. Nano. Adv. Mat.*, vol. 5(1), pp. 33-39
- Johari, A. (2011). "Synthesis and Characterization of Bismuth Ferrite Nanoparticles". *AKGEC. J. Technol.*, vol. 2(2), pp. 17-20
- Mallahi, M., A. Shokuhfar, M. R. Vaezi, A. Esmailirad. and V. Mazinani. (2014). "Synthesis and Characterization of Bismuth Oxide Nanoparticles via Sol-Gel Method". *ISSN: 2320-0936, American Journal of Engineering Research*, vol. 3(4), pp. 162-165
- Mubarak, T., B. Azhdar, K. Hassan and C. Kareem. (2014). "Effect of Temperature on Structural and Electrical Properties of Bismuth Ferrite Nanoparticles Prepared by Sol-Gel Method". *International Journal of Innovative Research in Science, Engineering and Technology*, vol. 3(10), pp. 17034-17041
- Muneeswaran, M., P. Jegatheesan and N. V. Giridharan. (2013). "Synthesis of Nanosized Bismuth Ferrite Powders by Co-precipitation Method". *J. Experimental Nanoscience*, vol. 8(3), pp. 341-346