PREPARATION AND CHARACTERIZATION OF SILVER DOPED BISMUTH FERRITE NANOPARTICLES BY CO-PRECIPITATION METHOD

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Abstract

The main aim of the research work is to study the preparation and characterization of silver doped bismuth ferrite, Ag-$BiFeO_3$ by co-precipitation method. In this method, Ag-$BiFeO_3$ nanoparticles were prepared by using bismuth nitrate, ferrite nitrate and silver nitrate as starting materials with different ratios (1:1:0.125, 1:1:0.25, 1:1:0.5 and 1:1:1) and the prepared silver doped samples were noted as S-1, S-2, S-3, S-4 respectively. The precursor powder was calcined at 500 °C for 4 h. The prepared samples were characterized by XRD, SEM and EDXRF techniques. The ratio (1:1:1) of bismuth nitrate, ferrite nitrate and silver nitrate was selected as optimum ratio due to its high crystallinity and average crystallite size. Some physicochemical properties and optical properties of prepared Ag-$BiFeO_3$ powder samples were also determined.

Keywords: Ag-$BiFeO_3$ powder, Co-precipitation method, XRD, SEM, EDXRF techniques

Introduction

Among all the perovskite materials with ABO_3 structure studied, $BiFeO_3$ shows ferroelectric properties with a high Curie temperature (T_C ~ 830 °C) and G-type antiferromagnetic properties below the Neel temperature (T_N ~ 370 °C) (Selbach *et al*., 2007). Therefore, it has been widely used in magnetic and ferroelectric devices. Apart from ferroelectric properties, $BiFeO_3$ is one of the materials with the largest known electric polarizations and has a small (≈ 3 eV) band gap for which it is likely applied in conducting domain walls, catalyst and fuel and/or solar cells (Fischer and Polomska, 1980). $BiFeO_3$ exhibits photocatalytic activities under visible light irradiation for water splitting and degradation of pollutants because of its narrow band gap and excellent chemical stability (Erenstein *et al*., 2007). In fact, doping of $BiFeO_3$ with a foreign atom at either A or B site of the ABO_3 lattice has been proven to be a valuable route to enhancing its properties. Demonstrated substitution of Bi^{3+} with Ag resulted in remarkable improvement of the photocatalytic activity of $BiFeO_3$ under visible light (Freitas, 2013).

Many researches have attempted to synthesis nanostructured $BiFeO_3$, such as spherical, nanorods, nanowires and plates with different methods. Several techniques have been utilized to prepare $BiFeO_3$ nanostructures, ball-milling technique, co-precipitation, polymeric assisted route, hydrothermal, reverse micelles etc. Choosing proper synthesis techniques play an important role in controlling the size and surface area and hence the properties of materials (Johari, 2011). Among all used techniques, the co-precipitation method has many advantages such as the use of low temperature, low cost, simplicity, energy saving, relatively low impurity content resulting from the easy formation of bismutite phase during calcination and uniform-sized $BiFeO_3$ nanoparticles (Muneeswaran *et al*., 2013).

In this present work, $BiFeO_3$ nanoparticles were synthesized using co-precipitation method. The effect of calcination temperature on its structural, morphological, optical and electrical properties has been studied.

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Materials and Methods

Materials and Methods

Ferric nitrate nanohydrate ($Fe(NO_3)_3.9H_2O$) with 98 % purity, bismuth nitratepentahydrate ($Bi(NO_3)_3.5H_2O$) with 98 % purity, silver nitrate with 98 % purity and other reagents were purchased from commercial sources with analytical purity and used as received. Laboratory equipment was used at Chemistry Laboratory of Yangon University and also at the Maubin University and Universities' Research Center, Lower Myanmar, Yangon Region. Instruments employed were hot plate, magnetic stirrer, oven, furnace and spectrophotometer. The methodologies and techniques used were carried out according to the procedures given in the recommended texts and literatures.

Preparation of Silver Doped Bismuth Ferrite Nanoparticles

Bismuth nitrate pentahydrate [$Bi(NO_3)_3.5H_2O$], ferric nitrate nanohydrate [$Fe(NO_3)_3.9H_2O$] and silver nitrate [$AgNO_3$] were mixed with different mole ratios (1:1:0.125, 1:1:0.25, 1:1:0.5 and 1:1:1) respectively and dissolved in distilled water and stirred for about 20 min at room temperature to form a clear solution. The mixture of 10 mL of 2.5 M ammonia and 10 mL of distilled water were added in this clear solution to get the reaction product. These precipitates were kept at room temperature for about 24 h and were washed several times with distilled water to remove unreacted products and then filtered. Final products were dried in the oven at 100 °C for about 5 h. The obtained powder was calcined at 500 °C for 4 h.

Characterization

The average crystallite sizes of prepared silver doped bismuth ferrite (Ag-$BiFeO_3$) nanoparticles were calculated from XRD pattern by using Scherrer equation. XRD model was Regaku, X-ray Diffractometer, RINT 2000 P/C software at no. 9240 J 101, Japan. The surface morphology of prepared silver doped bismuth ferrite (Ag-$BiFeO_3$) nanoparticles was examined by a JSM 5610 LV scanning microscope, JEOL Ltd., Japan. The relative abundance of elements of silver doped bismuth ferrite (Ag-$BiFeO_3$) nanoparticles were analyzed by using EDXRF (Energy Dispersive X-ray Fluorescence) Spectrometer Shimadzu EDX-700, Japan. The optical properties of the prepared silver doped bismuth ferrite (Ag-$BiFeO_3$) nanoparticles were determined by using UV-1800 SHIMADZU UV spectrophotometer (Amtt Customer Support & Analytical Laboratory).

Determination of Some Physicochemical Properties

pH

1 g of (Ag-$BiFeO_3$) sample was placed into a Pyrex 200 mL beaker and 100 mL of distilled water was added. The content of the beaker was heated at 80 ˚C for 10 min. The beaker and content were gently shaken and the sample was filtered. The filtrate was cooled at room temperature and pH of the sample was determined by using a pH meter.

Moisture content

Moisture content (%) was determined by the oven method at 110 ± 5 ˚C. An accurately weighed sample (about 1 g) was added to a pre-dried and cooled dish with a cover. The uncovered dish is placed in the electric oven, and dried at 110 ± 5 ˚C for 2 h. After heating, the cover was placed in position and in desiccator for cooling. And weighing which was repeated until a constant weight was obtained. The moisture percent is represented by the loss in weight.

Bulk density

A clean dry 10 mL graduated cylinder was weighed. It was then filled with the dry sample to the 10 mL mark and reweighed. The graduated cylinder was placed in a tapping box and the cylinder was gently tapped until there was no more reduction in volume. The minimum volume was recorded and the bulk density was calculated.

Porosity

The porosity of sample was measured by dry-wet method. About 1 g of the dry sample was placed in a beaker and 0.8 mL of distilled water was added. The sample was equilibrated with distilled water for 24 h and then was determined by dividing the amount of water adsorbed (mL) with the amount of the dry sample (mL).

Surface area by methylene blue adsorption test

A stock solution of methylene blue was prepared by dissolving 0.1 g of methylene blue in 1 L distilled water. By serial dilution, the methylene blue solutions within the concentration ranges from 10 ppm to 100 ppm were prepared. Analyses were carried out spectrometrically by using Cary 60 UV-Visible spectrophotometer. Different concentrations of dye solutions and 0.1 g of sample were determined and the surface area was calculated.

Results and Discussion

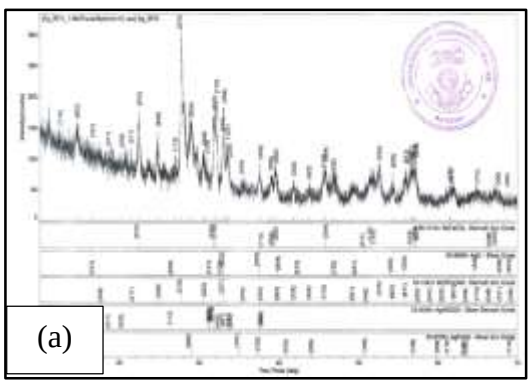
Preparation of Silver Doped Bismuth Ferrite (Ag-$BiFeO_3$) Nanoparticles

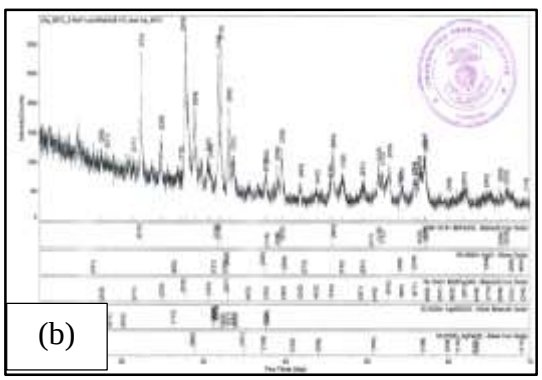
Different molar ratios (1:1:0.125, 1:1:0.25, 1:1:0.5 and 1:1:1) of bismuth nitrate pentahydrate, ferrite nitrate nanohydrate and silver nitrate were mixed respectively and dissolved in distilled water, and then stirred for about 20 min at room temperature to obtain a clear solution. Various pH levels were obtained by dropping of the mixture of 10 mL of 2.5 M ammonia and 10 mL of distilled water. This solution was kept at room temperature for about 24 h. The resulting precipitates were washed several times with distilled water and then filtered. Final products (precipitates) were dried in the oven at 100 °C for about 5 h and calcined at 500 °C for 4 h.

Characterization

XRD Analysis

The average crystallite sizes of prepared samples (S-1, S-2, S-3, S-4) were calculated by using Debye-Scherrer equation. It was observed that the crystallite size increases with increasing silver doping levels which may be due to the growth of particles size. Among them, the sample S-4 has high crystallinity and average crystallite size was found to be 33.06 nm from calculating. Based on the XRD results, S-4 was chosen for selected sample.


(a)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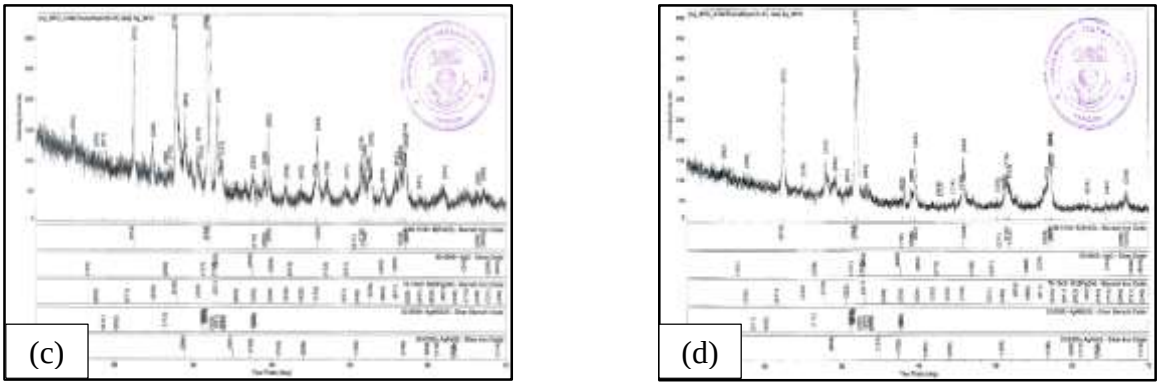

Figure 1 XRD diffractograms of (a) S-1 (b) S-2 (c) S-3 (d) S-4 nanoparticles

Table 1 Average Crystallite Sizes of Prepared Ag-$BiFeO_3$ Nanoparticles

Samples	Average crystallite sizes (nm)		Lattice Parameters (A°)			Crystal system
	XRD data	using Debye Scherrer equation	a	b	c	
S-1	31.72	23.29	9.9546	9.9546	9.9546	Cubic
S-2	31.48	26.44	10.0292	10.0292	10.0292	Cubic
S-3	39.20	30.88	9.7967	9.7967	9.7967	Cubic
S-4	39.44	33.06	9.5300	9.5300	12.2496	Hexagonal

SEM Analysis

SEM micrographs of prepared silver doped bismuth ferrite (S-1 to S-4) were indicated in Figures 2 (a) to 2 (d). Figure 2 (d) showed the SEM image of selected sample S-4 and it can be seen that the spherical shape and agglomeration nature increases with increasing silver doping levels.

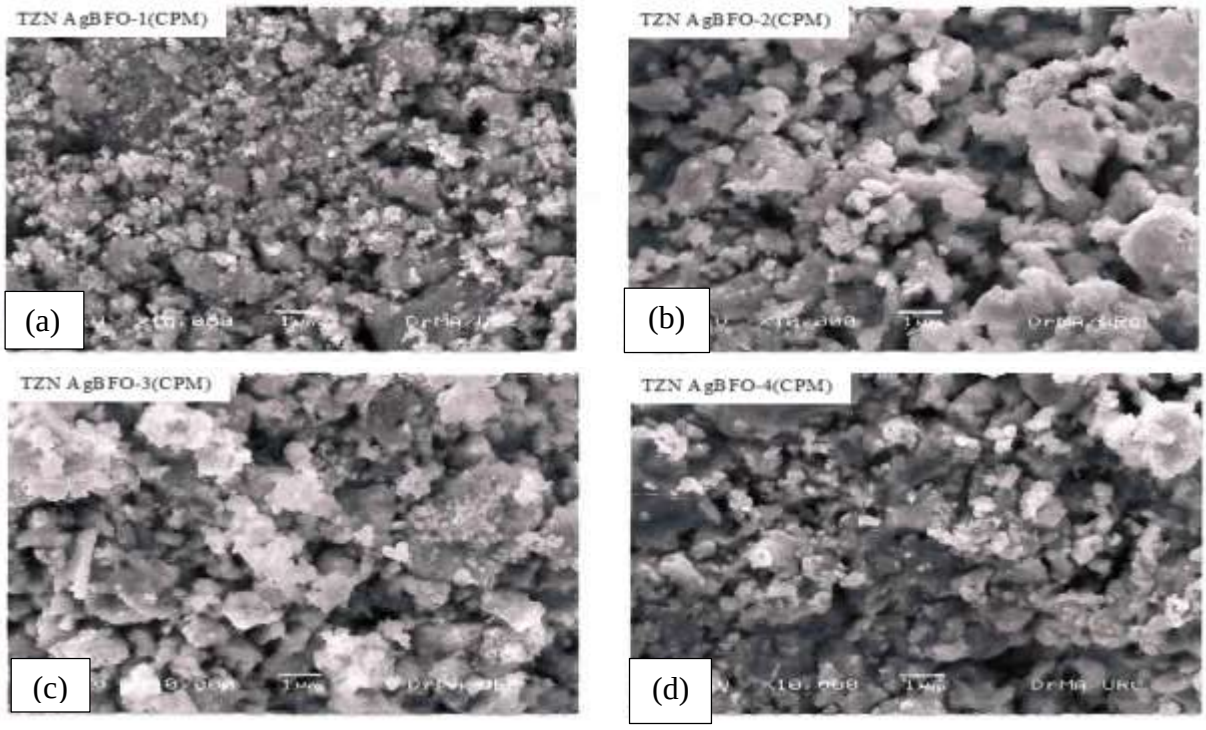

Figure 2 SEM micrographs of (a) S-1 (b) S-2 (c) S-3 (d) S-4 nanoparticles

EDXRF Analysis

The EDXRF spectra of prepared samples with different ratios showed that the silver content was increased with increasing the silver doping levels. Therefore, the sample S-4 was chosen for selected sample due to the silver doping percent.

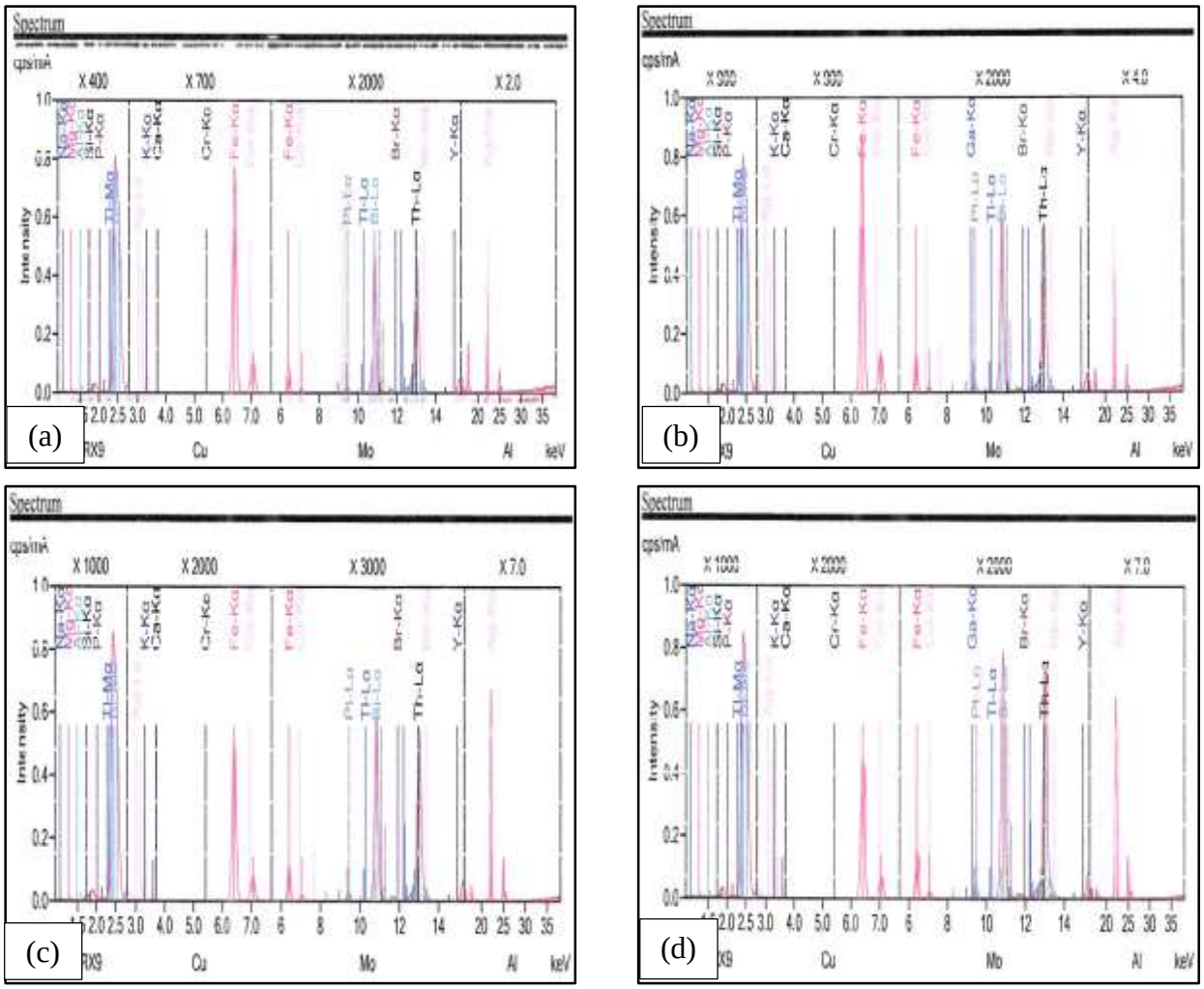

Figure 3 EDXRF spectra of (a) S-1 (b) S-2 (c) S-3 (d) S-4 nanoparticles

Table 2 Relative Abundance of Elements in Prepared Ag-$BiFeO_3$ Nanoparticles

Samples	Relative Abundance of Elements (%)		
	Bi	Fe	Ag
S-1	22.1	8.29	0.631
S-2	30.9	11.8	1.68
S-3	26.9	9.98	2.74
S-4	29.0	10.9	3.26

Physicochemical Properties

The physicochemical properties of selected sample (S-4) by co-precipitation method were such as pH, moisture, bulk density, porosity and surface area. The sample showed neutral (pH-7) and the moisture percent and bulk density were 0.11 % and 1.25 g cm^{-3} respectively. Therefore, it was found that the lesser the moisture percent the better the crystallinity. The porosity and surface area of the sample indicated 80 % and 571 m^2 g^{-1}. Thus, the large surface area and porosity revealed

the good nanoparticles for photodegradation, electrical application (semiconductors), optical devices and electrochemical cells.

Table 3 Physicochemical Properties of S-4 Nanoparticles

Sample	pH	Moisture (%)	Bulk density (g cm^{-3})	Porosity (%)	Surface area (m^2 g^{-1})
S-4	7.0	0.11	1.25	80	571

Optical Properties

The optical properties of selected sample (S-4) were studied by UV-visible absorption spectroscopy in the spectral range (200-400 nm). The absorption coefficient (α) was calculated from the observed absorption spectra and the optical band gap of S-4 sample was calculated from the Tauc's plot of $(\alpha h\upsilon)^2$ vs hυ. The optical band gap of S-4 sample was found to be 2.25 eV. According to the band gap value, the perovskite S-4 sample found within the semiconductor band-gap range.

Tauc's plot

$$(\alpha h\upsilon)^n = K\,(h\upsilon - E_g)$$

Where α = absorption coefficient
hυ = incident photon energy
K = constant
E_g = optical band gap energy
n = nature of transition

Table 4 Band Gap Value of Prepared Silver Doped Bismuth Ferrite (S-4) Nanoparticles

Sample	Band gap value (eV)
S-4	2.25

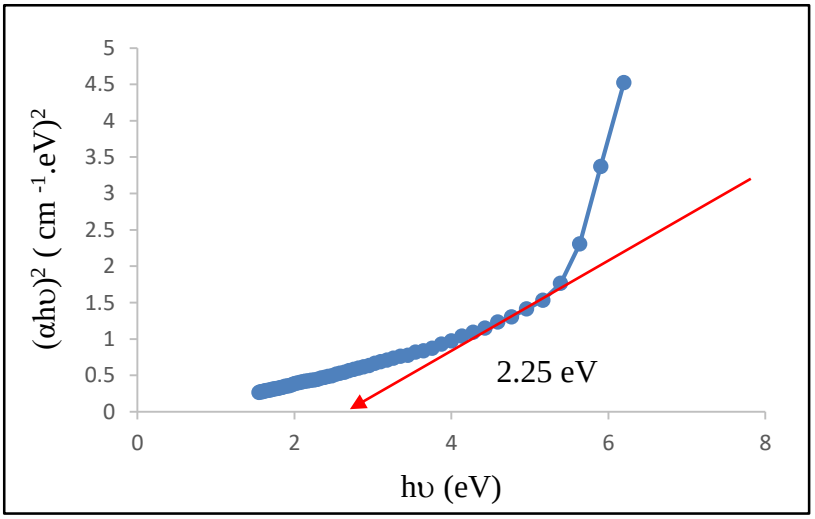

Figure 4 Plot of $(\alpha h\upsilon)^2$ against hυ for prepared silver doped bismuth ferrite (S-4) nanoparticles

Conclusion

Silver doped bismuth ferrite (Ag-$BiFeO_3$) nanoparticles were successfully prepared by co-precipitation method at different ratios. The resulting nanoparticles were characterized by XRD, SEM and EDXRF techniques. According to physicochemical properties (porosity and surface area), optical properties (Band Gap Value) and other characterization studies (XRD, SEM, EDXRF), the selected S-4 nanoparticles may be used as good adsorbent for photo degradation, semiconductor for electrical application and sensor for optical properties.

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