PREPARATION AND CHARACTERIZATION OF BISMUTH FERRITE ($BiFeO_3$) NANOPARTICLES BY SOL-GEL METHOD

Thuzar Nyein[1], Zaw Naing[2], Khin Than Yee[3], Cho Cho[4]

Abstract

This research work was concerned with the preparation and characterization of bismuth ferrite ($BiFeO_3$), a trigonal or rhombohedral distorted perovskite structure, by sol-gel method. In this method, $BiFeO_3$ powder was prepared by using bismuth(III) nitrate and iron(III) nitrate as starting materials. The precursor powders were calcined at different temperatures (450, 550, 650 and 750 °C) for 4 h. The prepared samples were characterized by XRD, TG-DTA and FT IR and SEM techniques. The calcined temperature of 550 °C was selected as optimum temperature due to high crystallinity and average nanocrystallite size. Some physicochemical properties (pH, moisture, bulk density, porosity and surface area) of the prepared $BiFeO_3$ powder sample calcined at 550 °C were also determined.

Keywords: $BiFeO_3$ powder, Sol-gel method, XRD, TG-DTA, FT IR, SEM techniques

Introduction

Multiferroic materials are of particular interest due to the co-existence of ferromagnetic and ferroelectric properties (Awan and Bhatti, 2009). Among varies multiferroics, bismuth iron oxide ($BiFeO_3$/BFO) is the only material that shows both ferroelectric and antiferromagnetic properties at room temperature. There is an increasing need for magnetic nanoparticles for different applications that could be solved through high performance technique production large quantities of nanoparticles (Dwita and Wijaya, 2016). In particular, bismuth nanoparticles are expected to play important role in a variety of relevant applications like an enhancing spontaneous magnetization, high super conductivity, high tech magnetic tape, photovoltaics, spintronics and field of magnetism (Selbach *et al*., 2007). This ferroic material can be synthesized by different methods such as co-precipitation method, sol-gel method, microwave assisted method, hydrothermal method, solvothermal method and micro emulsion method (Freitas, 2013).

Among these methods, sol-gel method is one of the methods to synthesize nanoparticles are very simple and relatively clean materials. $BiFeO_3$ nanoparticle was prepared by sol-gel method using bismuth nitrate and ferric nitrate are dissolved with 2-methoxy ethanol, citric acid and acetic acid. The synthesized bismuth ferrite ($BiFeO_3$) nanoparticle was characterized by XRD, TG-DTA, FT IR and SEM techniques (Chunlin *et al.*, 2012). Unit cell of $BiFeO_3$ can be described by hexagonal, trigonal, rhombohedral and cubic structures. From a structural point of view, the room temperature structure of $BiFeO_3$ is a highly rhombohedrally distorted perovskite or trigonal structure with space group R_3c (Johari, 2011). The aim of the present research work is to study the role of the prepared bismuth ferrite ($BiFeO_3$) nanoparticle powder by sol-gel method and its characterization.

[1] Assistant Lecturer, Department of Chemistry, Maubin University
[2] Dr, Associate Professor, Department of Chemistry, Dagon University
[3] Dr, Lecturer, Department of Chemistry, Myeik University
[4] Dr, Professor, Department of Chemistry, University of Yangon

Materials and Methods

Materials and Methods of Analysis

Ferric nitrate nanohydrate ($Fe(NO_3)_3.9H_2O$) with 98 % purity, bismuth nitrate pentahydrate ($Bi(NO_3)_3.5H_2O$) with 98% purity and other reagents were purchased from commercial sources with analytical grade and used as received. Labwares and glasswares facilities were 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 Bismuth Ferrite ($BiFeO_3$) Powder by Sol-Gel Method

Bismuth nitrate pentahydrate [$Bi(NO_3)_3.5H_2O$] and ferric nitrate nanohydrate [$Fe(NO_3)_3.9H_2O$] were mixed with mole ratio of 1:1 and dissolved in 2-methoxy ethanol. After the solution became transparent it was continued to stir one hour at room temperature. Citric acid ($C_6H_8O_7$) as a chelating agent and acetic acid were added. Then the resulting solution was transparent, blackish red and clear. Furthermore, solution was heated at temperature 80 °C on a hot plate under continuous stirring condition until all the liquid evaporated. There was an immense evolution of brown fumes, towards the end of the reaction a fluffy brown mass (gel) was obtained at the base of the beaker. The obtained gel was calcined at 450, 550, 650 and 750 °C for 4 h.

Characterization of the Prepared Bismuth Ferrite ($BiFeO_3$) Powder

The average crystallite size of prepared bismuth ferrite ($BiFeO_3$) nanoparticles were determined from XRD pattern by using Scherrer equation. XRD model was Rigaku X-ray diffractometer, RINT 2000 P/C software at no. 9240 J 101, Japan. Thermal stability of prepared bismuth ferrite ($BiFeO_3$) nanoparticles was examined by Shimadzu DTG 60 H operated under nitrogen and oxygen atmosphere. The FT IR spectra of prepared bismuth ferrite ($BiFeO_3$) nanoparticles were recorded by using Shimadzu, IR Prestige-21, (Japan) FT IR spectrophotometer at Department of Chemistry, University of Yangon. The surface morphology of the prepared bismuth ferrite ($BiFeO_3$) nanoparticles were observed on a JSM 5610 LV scanning microscope, JEOL Ltd., Japan.

Determination of Some Physicochemical Properties of the Prepared Bismuth Ferrite ($BiFeO_3$) Powder

Determination of pH

The sample (about 1 g) 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.

Determination of free 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 an 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

Determination of 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 tapped gently until there was no more reduction in volume. The minimum volume was recorded and the bulk density was calculated.

Determination of 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 with the amount of the dry sample.

Determination of 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 ranged from 10 ppm to 100 ppm were prepared. Analyses were carried out spectrometrically by using Cary 60 UV-visible spectrophotometer. Different concentrations of dye solution were prepared and accurate weight (0.1 g) of sample was equilibrated with an appropriate concentration of the test solution and the surface area was calculated.

Results and Discussion

Preparation of Bismuth Ferrite ($BiFeO_3$) Powder by Sol-Gel Method

Molar ratio (1:1) of bismuth nitrate pentahydrate and ferric nitrate nanohydrate were mixed. The mixture was dissolved in 2-methoxy ethanol and then citric acid (a chelating agent) and acetic acid were added after stirring 1 h at room temperature. After continuous stirring, all the liquid were evaporated. At the end of the reaction a fluffy brown mass (gel) was obtained and calcined at 450, 550, 650 and 750 °C for 4 h.

Characterization of Prepared Bismuth Ferrite ($BiFeO_3$) Powder by Sol-Gel Method

XRD analysis

The XRD diffractograms of prepared bismuth ferrite ($BiFeO_3$) powder by sol-gel method are illustrated in Figure 1. The average crystallite sizes of prepared sample calcined at different temperatures were calculated using XRD spectra and Debye-Scherrer equation. It was observed that the crystallite size increases with increasing temperature which may be due to the growth of particles size but the sample calcined at 550 °C was selected as optimum temperature because the sample $BiFeO_3$ has high crystallinity and average crystallite size 42.21 nm from XRD result and 41.05 nm by using Debye Scherrer equation (Table 1).

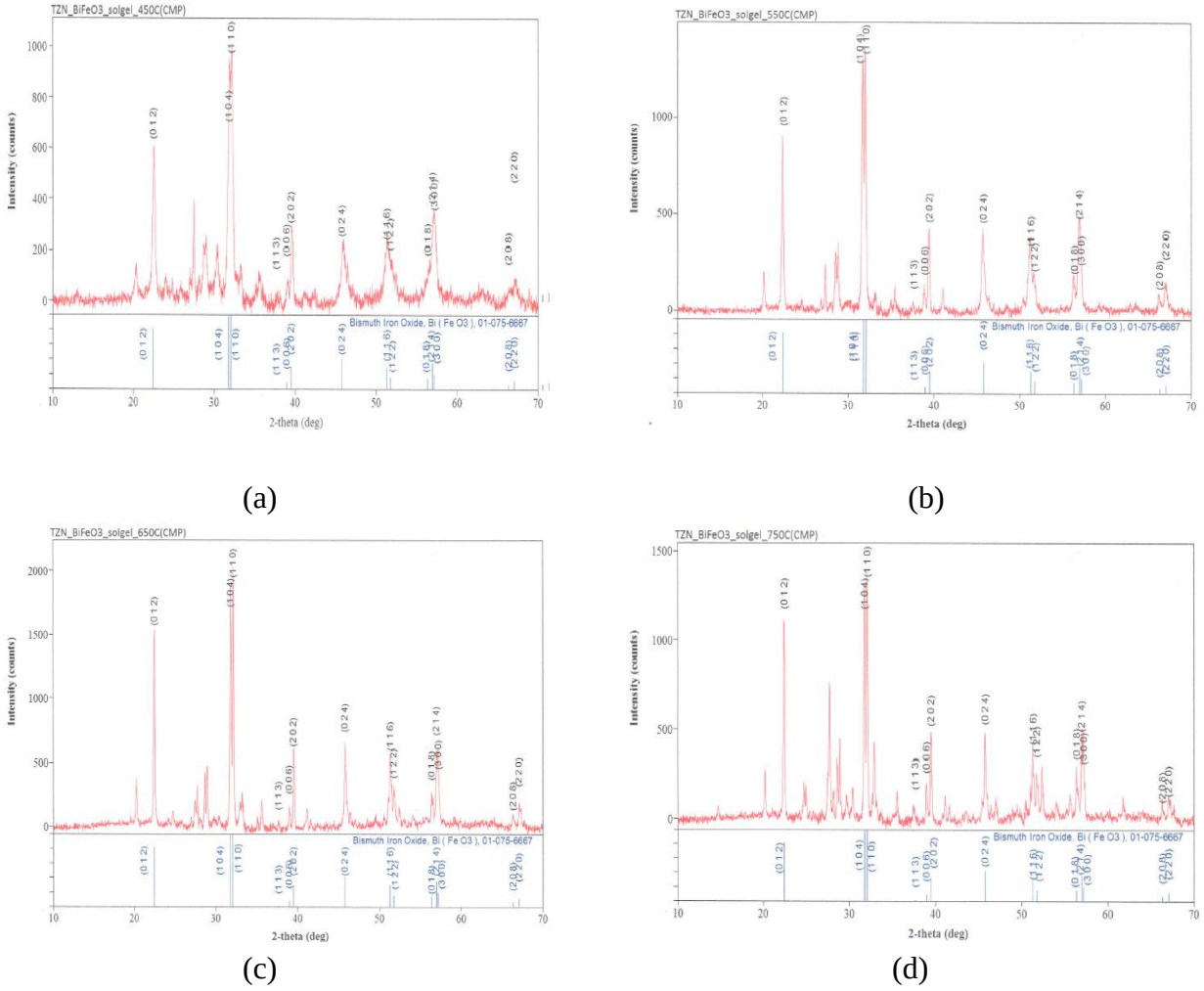

Figure 1 X-ray diffractograms of prepared $BiFeO_3$ powder calcined at (a) 450 °C (b) 550 °C (c) 650 °C (d) 750 °C for 4 h

Table 1 Average Crystallite Sizes of the Prepared $BiFeO_3$ Powder Calcined at Different Temperatures for 4 h

Temperature (°C)	Average crystallite size (nm)		Lattice Parameters (A)			Crystal System
	XRD data	Debye Scherrer Equation	a	b	c	
450	59.31	65.34	5.5474	5.5474	13.7895	Trigonal
550	42.21	41.05	5.5770	5.5770	13.8694	Trigonal
650	61.48	56.79	5.5756	5.5756	13.8621	Trigonal
750	65.34	59.78	5.5729	5.5729	13.8573	Trigonal

Thermal analysis

The TG-DTA thermograms of prepared $BiFeO_3$ powder by sol-gel method are illustrated in Figure 2. The weight loss percent of prepared samples at different temperatures was very low. Thermal stability of all prepared samples was observed above the temperature of 550 °C (Table 2).

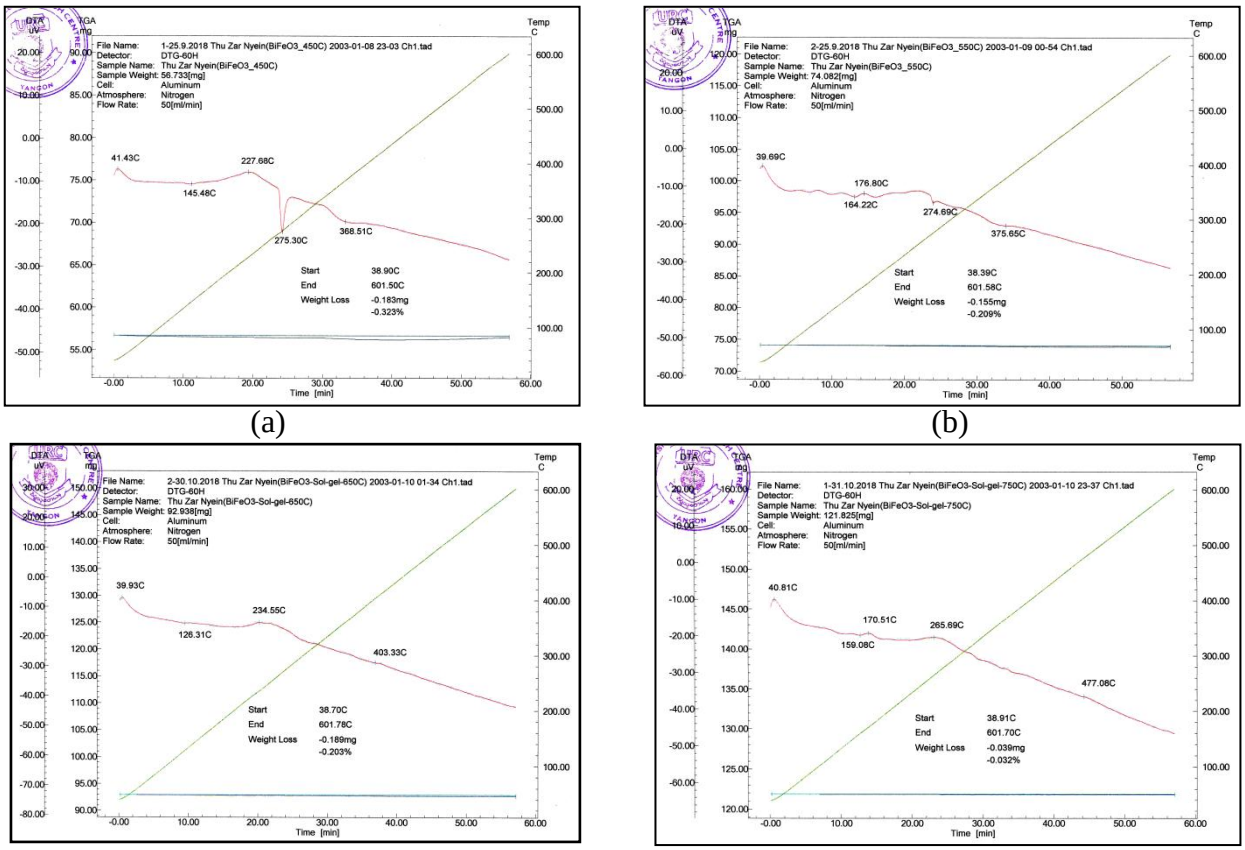

Figure 2 TG-DTA thermograms of prepared $BiFeO_3$ powder calcined at (a) 450 °C (b) 550 °C (c) 650 °C (d) 750 °C for 4 h

Table 2 Thermal Analysis of Prepared $BiFeO_3$ Powder Calcined at Different Temperatures for 4 h

Temperature (°C)	Weight loss (%)
450	0.323
550	0.209
650	0.203
750	0.032

FT IR spectral analysis

The FT IR spectra of prepared bismuth ferrite ($BiFeO_3$) powder by sol-gel method are illustrated in Figure 3. Stretching vibration of Bi-O and Fe-O chemical bonds of prepared sample at 550 °C was observed in wave number 527 and 845 cm^{-1}. There is no O-C-O symmetric stretching in the sample (Table 3).

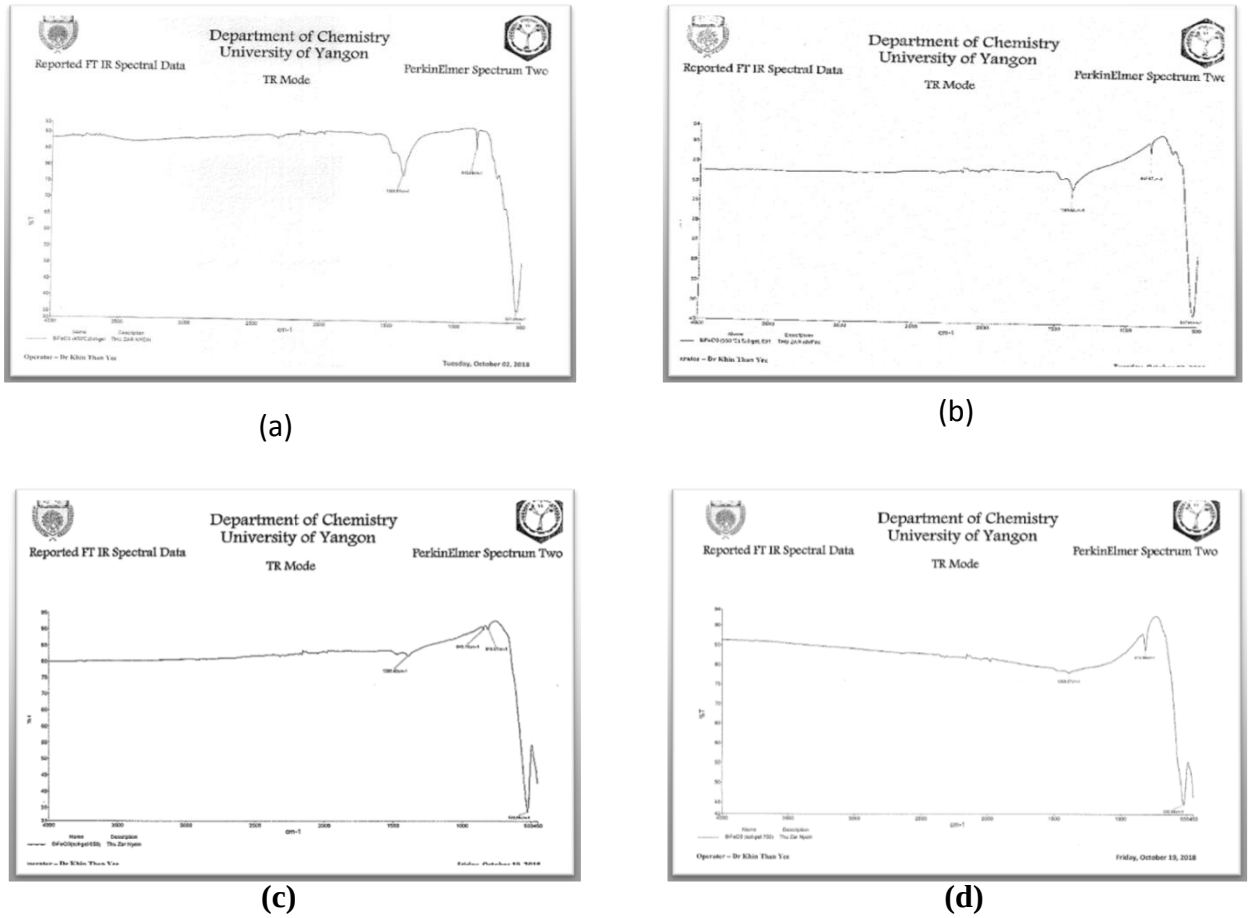

Figure 3 FT IR spectra of the prepared $BiFeO_3$ powder calcined at (a) 450 °C (b) 550 °C (c) 650 °C (d) 750 °C for 4 h

Table 3 FT IR Spectral Data of Prepared $BiFeO_3$ Powder Calcined at Different Temperatures for 4 h

Observed Wavenumber (cm^{-1})					
Temperatures (**°C**)				Literature Wavenumber (cm^{-1})	Band Assignment
450	550	650	750		
531	527	522	522	*970 - 450	Bi–O & Fe–O stretching
845	845	846	813		
1390	-	-	-	**1450 - 1350	O – C – O symmetric stretching

*(Silverstein, 2003 and ** Nakamoto, 1970)

SEM analysis

The SEM micrograph of prepared $BiFeO_3$ powder calcined at 550 °C (optimum temperature) indicated that the continuous distribution of spherical shapes with clear grain boundaries and the formation of well defined pores in the sample.

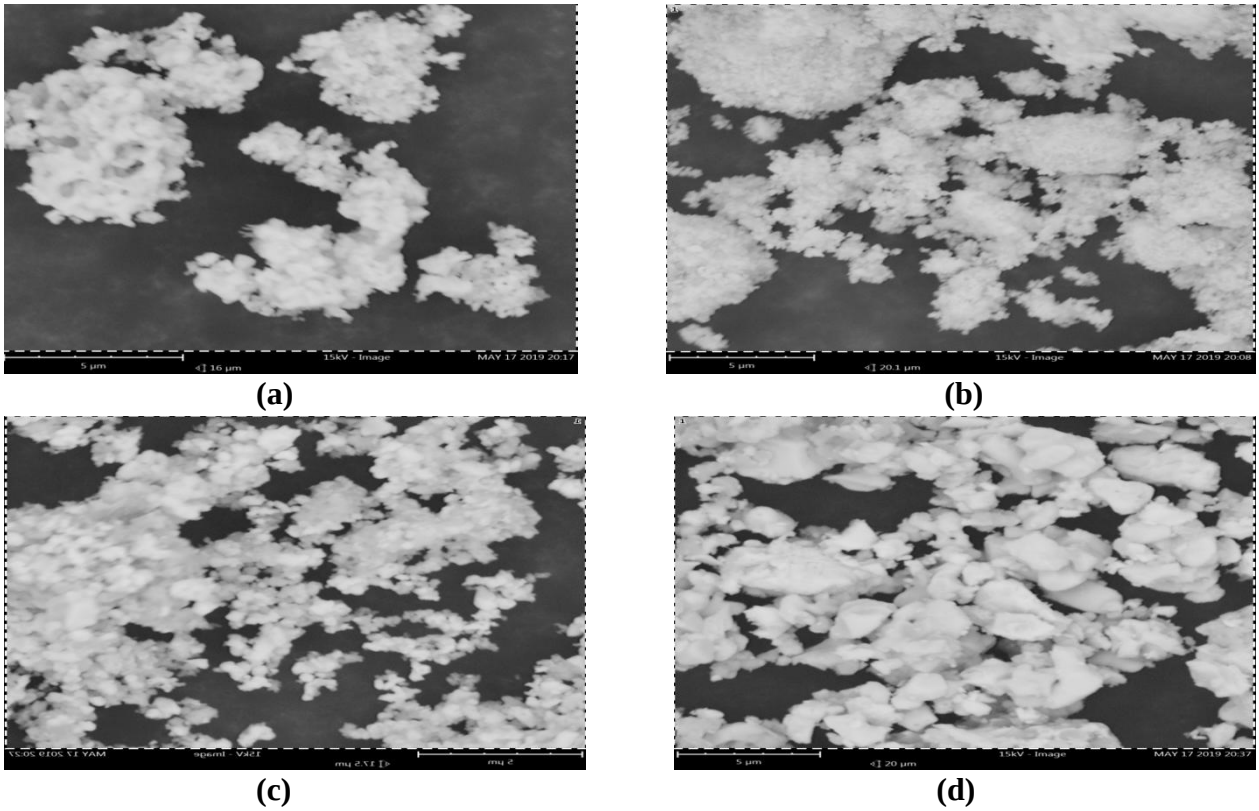

Figure 4 SEM micrographs of prepared $BiFeO_3$ powder calcined at (a) 450 °C (b) 550 °C (c) 650 °C (d) 750 °C for 4 h

Aspect of Physicochemical Measurement of the Prepared $BiFeO_3$ Powder Calcined at 550 °C for 4 h by Sol-gel Method

The physicochemical properties of prepared $BiFeO_3$ powder calcined at 550 °C for 4 h by sol-gel method were pH, moisture, bulk density, porosity and surface area (Table 4). The sample showed nearly neutral (pH~ 6.80) and the moisture percent and bulk density were 0.11 % and 1.25 g cm^{-3}. So, it was found that the lesser the moisture percent the better the crystallinity. The porosity and surface area of the sample indicated 85 % and 342 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 4 Physicochemical Properties of Prepared $BiFeO_3$ Powder Calcined at 550 °C for 4 h by Sol-gel Method

Sample	pH	Moisture (%)	Bulk density (g cm^{-3})	Porosity (%)	Surface area (m^2 g^{-1})
$BiFeO_3$	6.80	0.11	1.25	85	342

Conclusion

Bismuth ferrite ($BiFeO_3$) nanoparticles was successfully prepared by sol-gel method at different temperatures. The resulting nanoparticles were characterized by XRD, TG-DTA, FT IR and SEM techniques. From the characterization studies, it can be concluded that the prepared bismuth ferrite ($BiFeO_3$) nanoparticles may be useful as good adsorbent for photodegradation, semiconductor for electrical application and sensor for optical properties.

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