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SYNTHESIS, CHARACTERIZATION AND PHOTOLUMINESCENCE BEHAVIOUR OF BISMUTH FERRITES

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Abstract:

Ultrapure Bismuth ferrites (BFO) has been synthesized successfully using ascorbic acid as promoter followed by annealing at 500ºC. The structural morphology of the samples has been investigated by UV-Vis., IR, XRD, SEM, PL, and Cyclic voltammetry. These studies confirmed that there is no impurities such as Bi_2O_3 and $Bi_2Fe_4O_9$ (stoichiometry and non – stoichiometry) in BFO NPs and the high crystalline size of BFO was proved by XRD. The average size of BFO nanoparticles is 83 nm and the direct electron transition of 1.75 eV was confirmed by Tauc's plot. The increased crystallite size of BFO at 500ºC was confirmed by photoluminescence (PL) studies showed a doublet peak at 420 - 440 nm. Electrochemical studies indicates that the synthesized BFO Nps exhibit good cyclic property at 1 mol lit^{-1} NaOH aqueous solution and specific capacitance was found to be 165 Fg^{-1} at a scan rate of 10 mVs^{-1}.

Key Words: Bismuth Ferrites, Ascorbic Acid, Annealing, Electron Microscopy, Luminescence & Capacitance

1. Introduction:

Bismuth ferrites [BFO] are one of the new classes of metal oxides have anti-ferromagnetic with a high Neel temperature T_N ~ 643K and ferroelectric with high curie temperature T_C ~ 1103K[1]. This is used in wide range of applications such as spintronics, data storage and magnetic sensor devices owing to their ferroelectric and ferromagnetic behaviour[2-4]. In recent years, BFO NPs successfully tested for the degradation of triphenyl methane dyes and azo dyes due to their photocatalytic behaviour[5-7]. Jose Luis et.al.[8] reported that the formation of single phase BFO nano particles using tartaric acid / glycine as promoters with high purity and enhanced magnetic behaviour.

Silva et.al.[9] observed that the formation of secondary phases ($Bi_{25}Fe_2O_{39}$, $Bi_{25}FeO_{40}$, $Bi_2Fe_4O_9$, $Bi_{46}Fe_2O_{72}$, $Bi_{36}Fe_{24}O_{57}$) as byproducts in the synthesis of $BiFeO_3$ or doped $BiFeO_3$ NPs by a conventional solid state reaction or sol-gel methods. Lebeugle et.al.[10] pointed out that $Bi_{25}Fe_2O_{39}$ impurity is responsible for weak ferromagnetism at low temperature in polycrystalline $BiFeO_3$. In recent survey of literatures, BFO NPs have been synthesized using tartaric acid, citric acid, succinic acid and glycine as supporters[11]. Though the different supporters have been used in the preparation of pure, single phase BFO NPs is a difficult task. Using ascorbic acid as supporter, synthesis of BFO has been found to produce high pure, improved size BFO NPs. The synthesized BFO single phase materials showed the luminescence behaviour with direct electron transition band gap near 1.7 eV proved by Tauc's plot and the theoretical calculation is well correlated with direct electron transition band gap and nanoparicle size[8].

In our present work, BFO nano particles have been synthesized using ascorbic acid as promoter and the characterization was done by UV-Visible, IR, XRD, SEM, Photoluminescence (PL) and cyclic voltammetric studies for morphology, band gap, absorption, trapping of electron holes and surface capacitive behaviour of synthesized BFO.

2. Experimental Section:

2.1 Materials and Methods:

Bismuth nitrate [Bi $(NO_3)_3.5H_2O$], Iron nitrate [Fe $(NO_3)_3.9H_2O$], Ascorbic acid (AA), Benzoic acid (BA), salicylic acid (SA) from Merck have been used as such without further purification. Nitric acid and acetic acid from Merck of Analar grade reagent (A.R) were used without purification and de-ionized water was used for the sample preparation.

2.2 Preparation of BFO:

Equimolar bismuth nitrate and iron nitrate was mixed with ascorbic acid (0.001M) and dissolved in 40 mL of deionized water and nitric acid (1.2 mL, 99.5%) in magnetic stirrer at room temperature for 30 min. and the dark green coloured solution was obtained. The mixture was heated until all the solvent evaporated and combustion reaction took place. The brown powder obtained was heated at 500ºC in Muffle furnace for 1 h, washed with water followed by acetic acid and then dried at about 65ºC to remove Bi_2O_3.

2.3 Characterization of Materials:

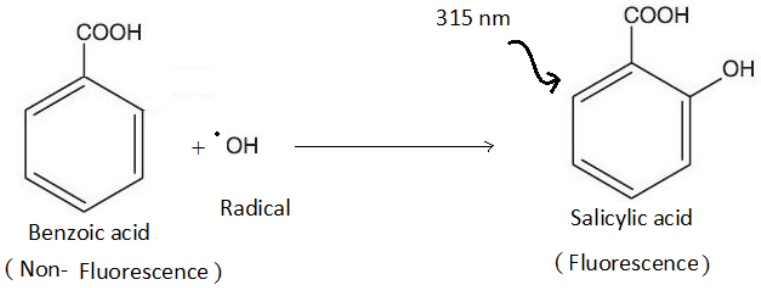
UV–Visible absorption spectrum of the compound was recorded by using UV- Visible spectrometer (UV-1800, Shimadzu, Japan). FT-IR spectrometer of the type IR Prestige-21, Shimadzu, used to record IR spectrum using KBr pellets. The crystalline structure was identified by X-ray diffraction instrument (XRD,

Shimadzu labX-6000), Samples morphology and size were examined using Scanning electron microscope (SEM, Jeol JSM-6390). The photoluminescence emission spectra of the samples were recorded with fluorescence spectrophotometer (PL, Horiba Jobin Yvon Flurolog-3). Cyclic Voltammetic studies have been done in an electrochemical work station using CH Instruments, Inc., CH1660C, USA.

2.4 Estimation of Hydroxyl Radicals:

The efficiency of production of hydroxyl radical by BFO nanoparticles was estimated using Photoluminescence technique, in which benzoic acid (BA) was used as probe molecules. This mechanism involves the conversion of benzoic acid into a fluorescent molecule, salicylic acid (SA) via their reaction with OH radicals that produced by the photocatalyst as shown in Figure 5 (b).

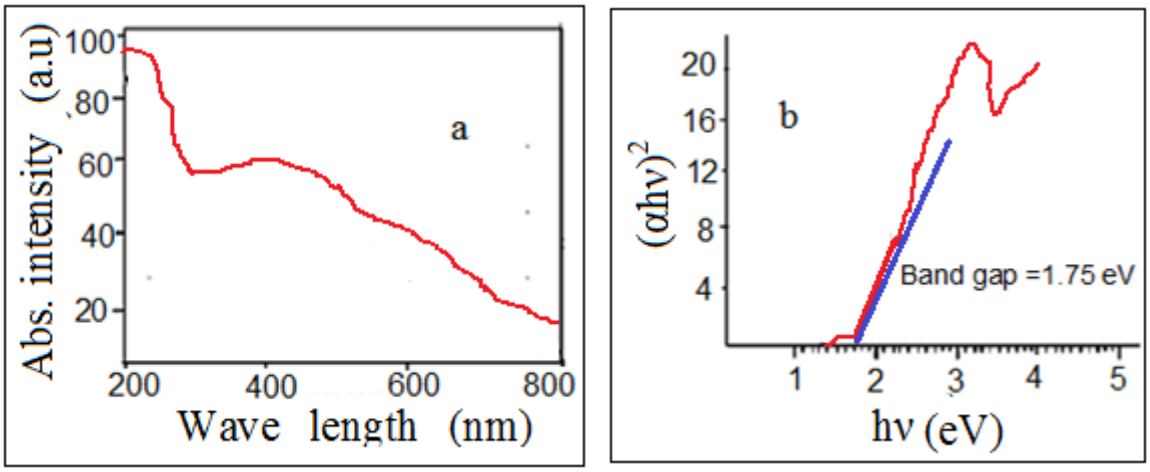
In the typical procedure, 0.1 mole of BA was dissolved in 100 ml of hot aqueous solution, equal mole of ethanol was added as scavenger[12] and then 1g of photocatalyst was added to 100 ml of BA solution. The solution was exposed under sunlight. The reacted solution was centrifuged to separate the catalyst and performed the PL measurement using fluorescence spectrometer with the excitation wave length of 315 nm.



3. Results and Discussion:

3.1 UV – Visible Spectra:

The UV − Visible absorption spectra of $BiFeO_3$ NPs at 500ºC are shown in Figure 1(a). The optical absorption edge is relevant to photocatalytic activity of BFO. The synthesized BFO absorbs visible light in the wavelength of 400 − 650nm. The band gap energy was calculated using Tauc's equation[13] by extrapolating the linear portion of $(\alpha h\nu)^2$ against hν plot to the point α = 0 and was shown in Figure 1(b).The band gap was estimated at about 1.75 eV compared with previous results[14-17]. The smaller band gap of BFO nanoparticles indicates a possibility of utilizing more visible light for photo catalysis.



(a) (b)

Figure 1: (a) UV – Visible spectrum of BFO nanoparticles (b) Band gap calculation of BFO Nps

3.2 XRD Studies:

Usually, bismuth oxide impurities were removed with HNO_3, a strong acid[18], which could dissolve $BiFeO_3$. José Luis et.al.[8] has been reported that the acetic acid was used first time for the removal of impurities such as $Bi_{24}Fe_2O_{39}$. Figure.2 shows XRD pattern obtained for BFO NPs after washing with AcOH to remove the bismuth oxide impurities. The average crystallite size of BFO was 83 nm, determined using Scherrer equation with high intensity peak at 2θ = 31.93°. It is obvious from the XRD studies that BFO nanoparticles are highly crystallized and exhibit a single-phase perovskite structure. Non-perovskite phases such as $Bi_2Fe_4O_9$ and Bi_2O_3/Fe_2O_3 are not detected in XRD analysis[17,18]. The commonly observed byproducts like $Bi_2Fe_4O_9$, $Bi_{24}Fe_2O_{39}$ located at 2θ =27.97° and α- and β-Bi_2O_3 formed by polynuclear species[19] are removed shown in figure 2 and hence XRD studies proved the synthesized $BiFeO_3$ is highly crystalline and high purity.

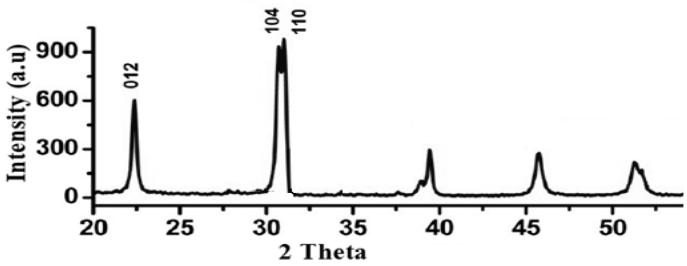


Figure 2: XRD pattern of BFO nanoparticles

3.3 Morphological Analysis:

The morphological studies of BFO was done by Scanning Electron Microscope, showing agglomerated particles with mean size of about 81 nm was observed. The agglomeration of BFO nanoparticles formed due to evaporation and has highly interconnected, agglomerated particles with less than 100nm[20]. Sol-gel techniques are adopted by Gautam et.al.[21] gave agglomerated clusters of spherical particles. Also, Feng[22] found that solid state route provides polyhedral particles with reduction in particle size when doping concentration increases. Thus, the literature survey indicates that the agglomeration of BFO nanoparticles leads to decrease in particle size, which observed in our present work also.

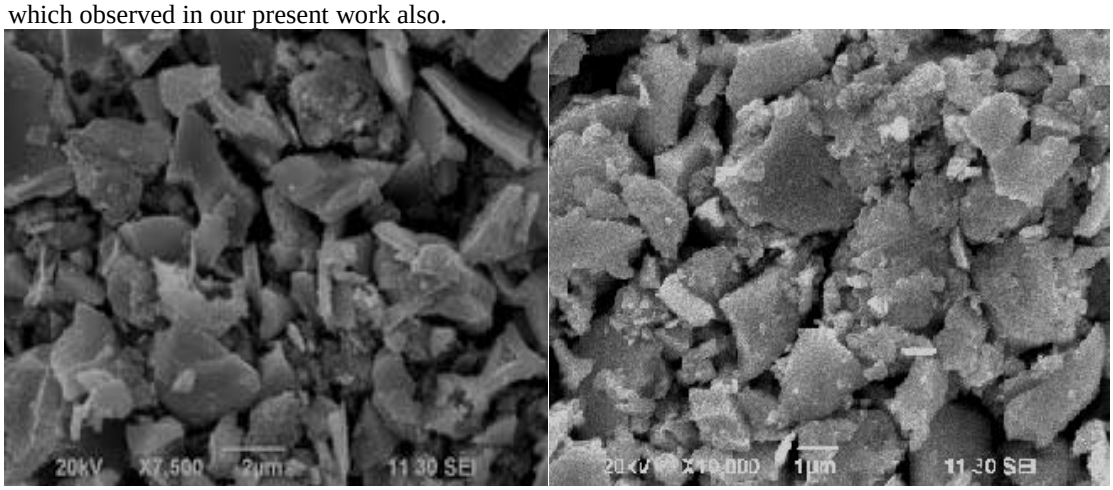


Figure 3: SEM images of BFO nanoparticles

3.4 FT – IR Spectra:

The strong absorption IR peaks together with some weak peaks appeared for BFO precursor using ascorbic acid, shown in Figure 4. BFO NPs have wide IR peaks, corresponding to stretching vibrations of –OH. The IR peak obtained at 3425 cm^{-1} was assigned to stretching vibrations of structural hydroxyl group. The IR peaks below 1000 cm^{-1} such as 879 and 810 cm^{-1} corresponding to the vibration of Bi– O and a strong peak at 555 cm^{-1} was attributed to Fe–O stretching and bending vibrations[23]. The band disappeared around 1380 cm^{-1} in this spectrum indicates that nitrates were not entrapped[24] in BFO due to calcination at 500˚C.

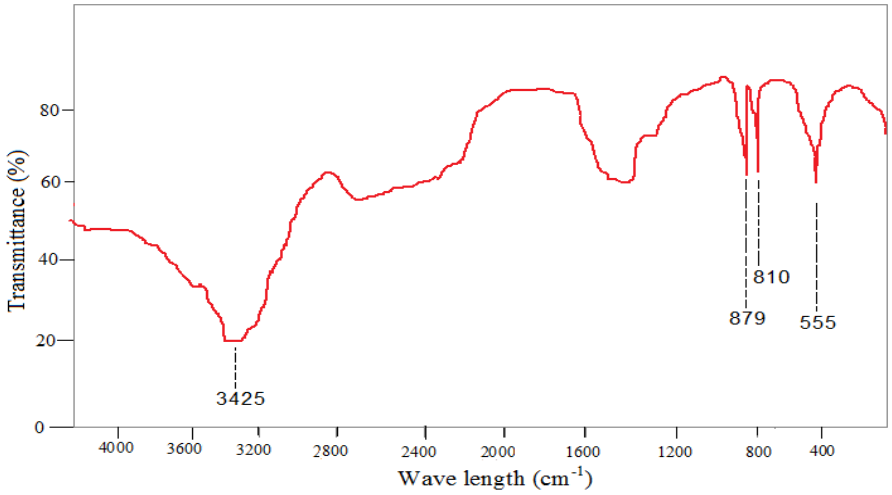


Figure 4: FT-IR spectrum of BFO nanoparticles

3.5 PL Spectra:

$BiFeO_3$ is a fascinating optical material, which shows promising application in photocatalyst and photoconductive devices. Thus, photoluminescence spectroscopy is used to study the optical property of $BiFeO_3$ nanoparticles. Figure 5(a) shows the photoluminescence of $BiFeO_3$ which gave broad emission spectrum at about 410 – 440 nm. Xin Wang et.al.[25] was observed that the enhanced luminescence is due to increased annealing temperature. The values of band gaps of the crystalline films are higher than those reported by F. Gao et.al.[26] (~ 2.5eV) and those reported by Y. Xu et.al.[27] (~ 2.7eV). The difference of band gap energies between the well crystallized films and the bulk sample has been attributed to the existence of the grain boundaries in the crystallized film. Pure nano structured $BiFeO_3$ exhibits a characteristic luminescence spectrum with two maxima around 3.0 and 2.81 eV might have been attributed to the near band edge transition of free electrons and abundance of oxygen vacancies. The electrons from the oxygen vacancies are able to be emitted in the conduction band more easily than those from the valence band since $BiFeO_3$ shows a larger band gap[28]. This confirms the pure crystalline nature of nano structured BFO.

Figure 5(b) shows that the PL spectra of salicylate solution after reacted with BFO nanoparticles for 2 h under direct sunlight irradiation. The peak at about 455nm shows the presence of SA obtained by conversion of BA upon its reaction with OH radical produced by BFO photocatalyst. The observed peak is attributed for the efficiency of OH radical production[29,30].

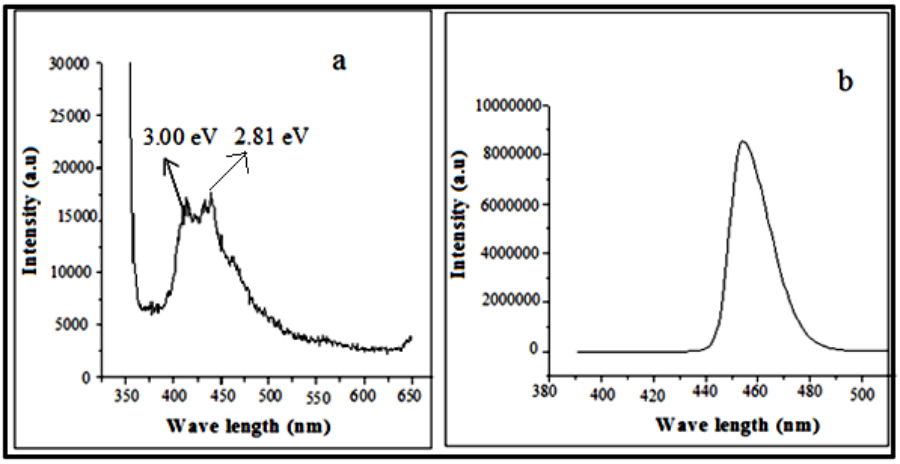


Figure 5: (a) Photoluminescence of BFO nanoparticles (b) PL of SA solution reacted with BFO

3.6 Cyclic Voltammetry:

Perovskite type $BiFeO_3$ nanocrystalline electrode is exploited as an efficient material for supercapacitor applications[31,32]. It is expected that the combined oxide of transition metal oxides, $BiFeO_3$ has to show the better performance. The bismuth iron oxide material may sustain the charges in its phases during electrochemical changes. The nanocrystalline $BiFeO_3$ electrodes were electrodeposited at room temperature, showed good performance in NaOH electrolyte[31].

A typical cyclic voltammograms of BFO at different scan rate of 10 – 50 mV s^{-1} between + 0.3 and – 0.8 V in aqueous solution of 1M NaOH are shown in Fig. 6. The specific capacitance of $BiFeO_3$ found to be 165 F g^{-1} and this is comparable with other commonly used ruthenium based oxide perovskite formed in powder or pellet forms. Park[33] has been obtained the specific capacitance for lead Ruthenate pyrochlore pellets upto 160 F g^{-1}. This value certainly better than those obtained from a perovskite $SrRuO_3$ (Specific capacitance = 8 F g^{-1}) by Mehrens[34]. The large value of specific capacitance can be attributed to the nanostructure of BFO and the cycle life of $BiFeO_3$ electrode exhibited the stable nature.

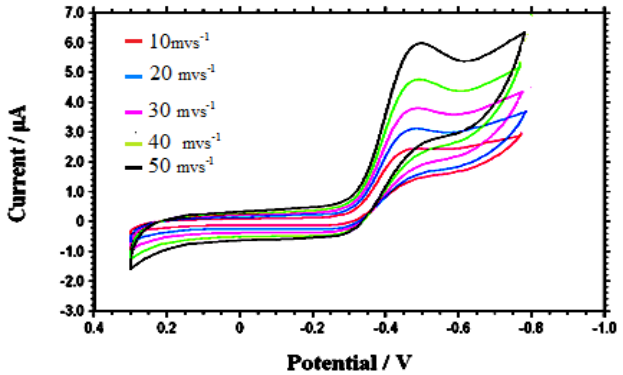


Figure 6: Cyclic Voltammograms of $BiFeO_3$ in NaOH at different scan rate.

4. Conclusion:

In the present work, pure BFO nanoparticles were prepared successfully by sol-gel method using ascorbic acid promoter at room temperature. BFO nanoparticles with measured band gap of 1.75eV exhibited high crystallization, smaller crystallite size. The average crystallite size of $BiFeO_3$ nanostructure was found to be 83 nm for (110) plane by XRD studies. The smaller crystallite size of BFO indicates that the agglomeration occurs due to evaporation. From the FT – IR analysis, it was confirmed that the nitrates were not trapped by BFO even though nitrates used to prepare BFO Nps. PL studies showed that the enhanced luminescence observed with increased annealing temperature and hence crystalline size increased. The specific capacitance of BFO is found to be 165 F g^{-1} and this large value of specific capacitance is attributed to the nano structured and the stability of BFO Nps.

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