ISSN: 0973-0583

# Synthesis and Characterisation of Bismuth Iron Oxide (BFO) by Sol-Gel Method towards Photocatalytic Degradation of Organic Pollutants

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*ABSTRACT*

The toxic organic pollutant present in the environment is a serious anxiety to human and other living organism. Now a day, many nanomaterials are discovered by researchers which show photocatalytic activity. Among them the perovskite type Bismuth Ferrite, BiFeO3 (BFO) has been greatly investigated as photocatalyst due to its multiferroic behaviour at room temperature which promote the separation of charge carrier, narrow band gap and chemical stability. The perovskite type Bismuth Ferrite, $BiFeO_3$ (BFO) has been greatly investigated as photocatalyst due to its multiferroic behaviour at room temperature which promote the separation of charge carrier, narrow band gap and chemical stability. The Pure-phase bismuth iron oxide ($BiFeO_3$) nanoparticles is synthesised by Sol-Gel method from bismuth nitrate and iron nitrate. The prepared sample is calcined at 550oC for 2.5 hrs in furnace. The synthesized sample is characterized by the X-ray diffraction (XRD) studies show that there are gradual shift in the position of the X- ray diffraction peaks. Transmission Electron microscopy (TEM) and High Resolution Transmission Electron Microscopy (HRTEM) which is used to imaging the crystal structure sample at atomic level.

**Keywords:** Nanoparticle, Bismuth nitrate, Iron nitrate, XRD, TEM, HRTEM

**Introduction:**

Escalated development of industrial activities, agricultural activities and continuously tremendous growth in world population continuously damage our environment by spreading pollutant in the environment. These pollutants contaminate air, soil and aquatic ecosystem cause serious threat to environment and harmful for human health along with another species especially aquatic species who survive in polluted environment. In aquatic ecosystem, water contamination problem is affected by many industrial effluents such as pharmacy, textile, rubber industries, pesticide, paint, paper industries. Specially food processing factories and textile industries widely used dyes which affect water quality and made it dangerous for aquatic life such as fish. To overcome these problems, a new group material is used now days which have perovskite structure having general formula $ABO_3$ [1]. The structure of $ABO_3$ semiconductor material is described in fig.1.

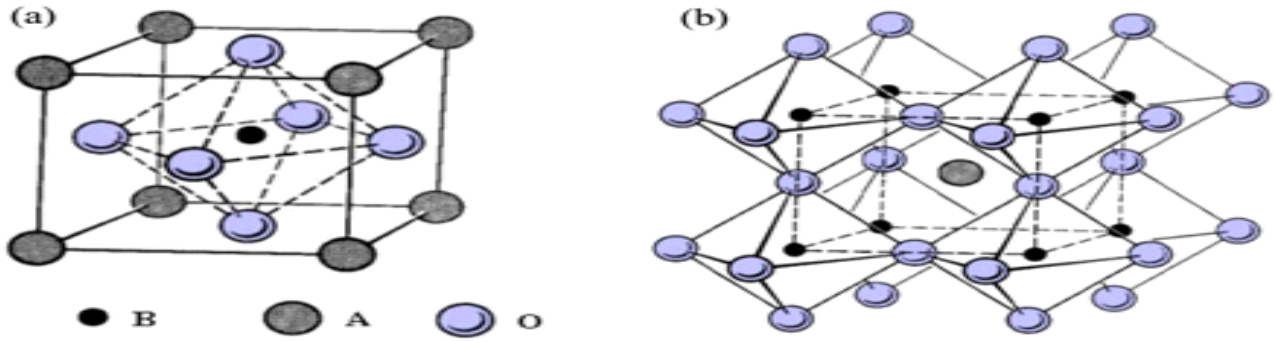

Fig. 1: Two typical views of ideal cubic $ABO_3$ perovskite structure unit cell. (a) The A atom located at the corner of the cube (0,0,0), and B atom located at the centre position of the cube (½ , ½ , ½ ), while oxygen atom sits at the face centre positions ( ½ , ½, 0); (b) $ABO_3$ structure in terms of $BO_6$ octahedral networks.

$BiFeO_3$ is a special single phase magnetoelectric multiferroic material. It shows ferroelectric properties, ferromagnetic properties, and antiferromagnetic properties at or above room temperature with Neel temperature of TN=647K for antiferromagnetic and a ferroelectric Curie temperature of TC=1103K. BFO ferrielectric behaviour is due to presence of 6s lone pair of electrons of Bi and its magnetic properties is attributed to presence of partially filled 3d orbital of the Fe. At room temperature BFO has rhombohedral distorted perovskite structure with space group $R_3c$ [2]. The unit cell of BFO has lattice constant of a=5.63 Å, and the rhombohedral angle Y h of 89.45° at room temperature. In cubic type unit cell, Bi-ion present on corners of cube and Fe-ion present at body centre position and oxygen atom present at the centre of each face position as shown in Fig.2. This cubic structure is three-dimensional network formed by the corner sharing of $FeO_6$ octahedral

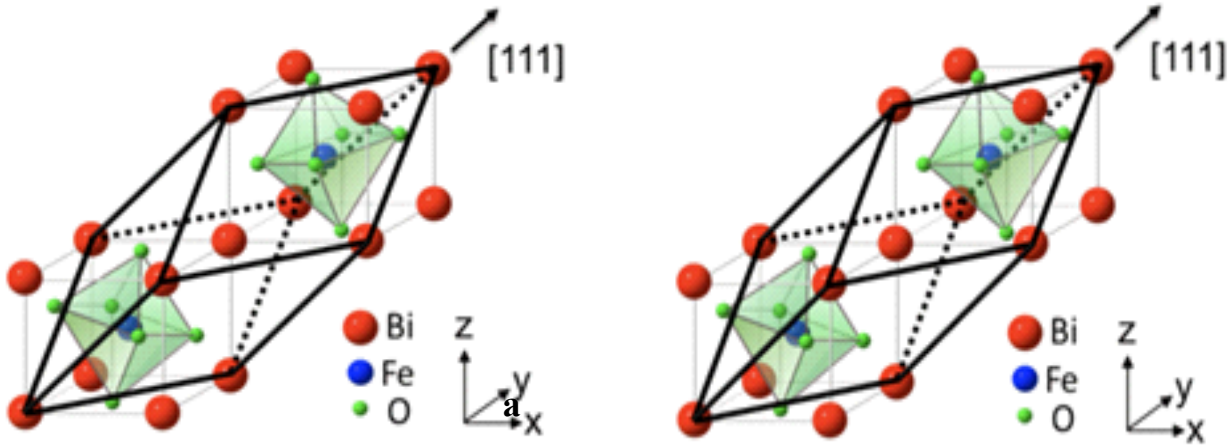


Fig.2 (a) Schematic diagrams of a distorted rhombohedral perovskite structure of the $BiFeO_3$ (b)Hexagonal structure of $BiFeO_3$ having R3cspace group symmetry.

Some researchers support a pseudo cubic structure of BFO. It is formed by connection of two distorted unit cell along their body diagonal[111]pseudocubic(c) to form rhombohedral unit cell as shown in Fig. 2a. Another view of description of unit cell of BFO is hexagonal structure where the C-axis parallel to diagonal of cube such as [001]hexagonal parallel to [111]pseudo cubic. This structure is formed by transformation of rhombohedral unit cell structure to an equivalent hexagonal representation in which pseudo cubic direction [111]c correspondsto direction hexagonal [001]hex. The hexagonal lattice parameters are $\alpha$ h =5.58Å and ch =13.90 Å at room temperature [3].

At room temperature BFO polarises due to stereo chemically active lone pair of $Bi^{3}$+ due to which BFO show ferroelectric properties. The direction of this polarisation is along the rhombohedral C-axis i.e., along the diagonal of perovskite unit cell due to dislocation of $Bi^{3}$+ ion relative to $FeO_6$ octahedral. Ferromagnetic and antiferromagnetic properties of BFO is due to $Fe_3$+ ion. The magnetic moment of $Fe^{3}$+ aligned ferromagnetically along [111]c plane i.e., within plane and aligned antiferromagnetically between adjacent plane, which leads to G-type antiferromagnetic order. On structural point of view angle of rotation of oxygen octahedral play, a very critical role in structural parameter. For cubic perovskite the rotation angle of oxygen octahedral is 0o. Gold Schmidt in 1926 gave a parameter tolerance factor 't' which define the stability and distortion of perovskite unit cell. It is defined as t =(rBi +rO)/ √ 2 (rFe + rO), where r is the ionic radius of respective ions [4]. For $BiFeO_3$, t is 0.88 (catlalan

and scott 2009). Value of t is changed when changes take place in $Bi^{3+}$ and $Fe^{3+}$ atomic species. This is done by doping or co-doping, which effect the crystallographic symmetry which change to monoclinic, tetragonal or orthorhombic in various perovskite.

## 2. Experimental Procedure:

Synthesis method for $BiFeO_3$ Nano particle

For synthesis of BFO nanostructure, bismuth nitrates Bi $(NO_3)_3.5H_2O$ and ferric nitrate Fe $(NO_3)_3.9H_2O$ are used as metal source propylene glycols are used as chelating agent. After adding chelating agent chelation reaction starts which facilitate the gelation process. The chelating agents effect the phase and morphology of final product, which is controlled by molecular structure of the chelating agents. Hence the selection of chelating agent is important for fabrication of $BiFeO_3$ with specific morphology. Appropriate chelating agent is added under constant stirring and heating at about 100oC. After 2-3-hour liquid changes to fluffy gel which gives a brown-coloured fine $BiFeO_3$ nanoparticles. The as-prepared bismuth ferrite is calcined at 400-550oC for 2-3 hour to obtained the $BiFeO_3$ nanoparticle. In calcinations process the volatile matters such moisture and other unwanted components were removed and finally get the pure phase of the $BiFeO_3$ nano particle. [5]

**Table 1**

**Summary of chelating agent and result in sol -gel synthesis of $BiFeO_3$**

| Chelating Agent | Solvent | Calcination Temperature(oC) | Particlesize (nm) | Ref. |
|---|---|---|---|---|
| Tartaric acid | DI water, nitric acid | 600 | 16 | [6] |
| Tartaric acid | EG/ nitric acid | 500 | 60 -19 | [7] |
| Citric acid | EG | 600 | 11 | [8] |
| Citric acid<br>tartaric acid | DI water nitric acid | 300 | 4 (C.A.)<br>12 (T.A.) | [9]<br>[9] |
| Succinic acid | DI water, nitric acid | 600 | 60 - 70 | [10] |
| EDTA | DI water, nitric acid | 600 | 110 | [11] |
| Propylene glycol | DIwater, nitric acid | 415 | 35 | [12] |
| Malonic acid | DI water | 600 | 60 to 70 | [13] |

## 3. Results and Discussion:

### X-ray Diffraction (XRD)

To identify the phase, crystal structure, and lattice parameters of material XRD techniques is used. In this technique the diffracted X-ray intensity is measured as a function of diffraction angle 2?. Powdered X-ray diffraction (PXRD) used for the identification of phase for the crystalline materials (BFO) which explore the morphology & structure of crystals of BFO nanoparticles. It also informs the pure-phase and highly crystalline form of BFO at room temperature. XRD yields separate peaks of BFO in well indexed form and shows that the crystal structure is rhombohedral with R3c symmetry. In the characterisation of BFO with X-ray diffraction, the diffraction peak appears for the reflection from (012), (104), (113), (110), (006), (202), (024), (116), (122), (018) and (214) planes for diffraction angle 2θ between $20^o$ and $60^o$. By analysis of XRD pattern, different lattice parameters for $BiFeO_3$ as a = b = 5.57, c = 13.86, and V = 373 Å [14].

The prominent peaks in the XRD plots of your Bismuth Ferrite Nanoparticles are confirming the synthesis of pure phase Bismuth Iron Oxide. The Debye-Scherer formula is commonly used to estimate the average grain size of nanocrystalline materials from their XRD patterns. The average grain size (D) was calculated using the formula the Full Width at Half Maxima (FWHM) of the high intense peak from XRD data.

The Formula is, $D = \frac{K \lambda}{\beta Cos\theta}$

Where, D = Size of crystallite

K = Scherre's constant

$\lambda$ = Wavelength of X-Ray

$\beta$ = Full width at half maximum

Theta = Peak position or Bragg angle in degrees.

Thus, Sherre's Formula is very useful to predict the crystalline size of nanoparticles of nano size materials [15,16].

The high-intensity peak at 2q= 31.93 corresponds to the (104) and (110) planes of a rhombohedral crystal structure, which is consistent with BiFeO3. XRD studies showed that the nanoparticles are highly crystallized and exhibit a single-phase perovskite structure, which indicates that the synthesized BiFeO3 is of high purity and highly crystalline. The perovskite structure is a common crystal structure for many metal oxides, and it consists of a cubic unit cell with a metal cation in the center, surrounded by oxygen ions

**B. Transmission Electron Microscopy (TEM):**

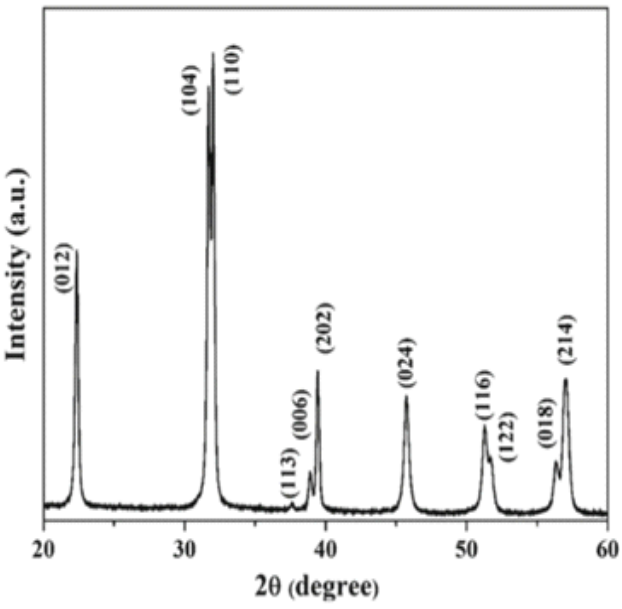


**Fig.3** XRD pattern of $BiFeO_3$ nanoparticles.

This technology is used for the characterisation of shape, size, morphology, crystallinity, and crystal structure of $BiFeO_3$ nanoparticles. Selected area electron diffraction (SAED) patterns are obtained by diffracting the electron beam from selected area of the sample by using Bragg's law which provide a way to determine the Bravais lattices and lattice parameters of the nanomaterials. High Resolution Transmission Electron Microscopy (HRTEM) which is used to imaging the crystal structure sample at atomic level. It gives information about grain boundaries, interface formation, defects, stacking faults, and precipitates. Srivastav et al. synthesized $BiFeO_3$ nanoparticles by sol -gel method and found TEM images in different condition which is shown in fig. 4. [6]

Fig. 4 (a) shows the TEM image for

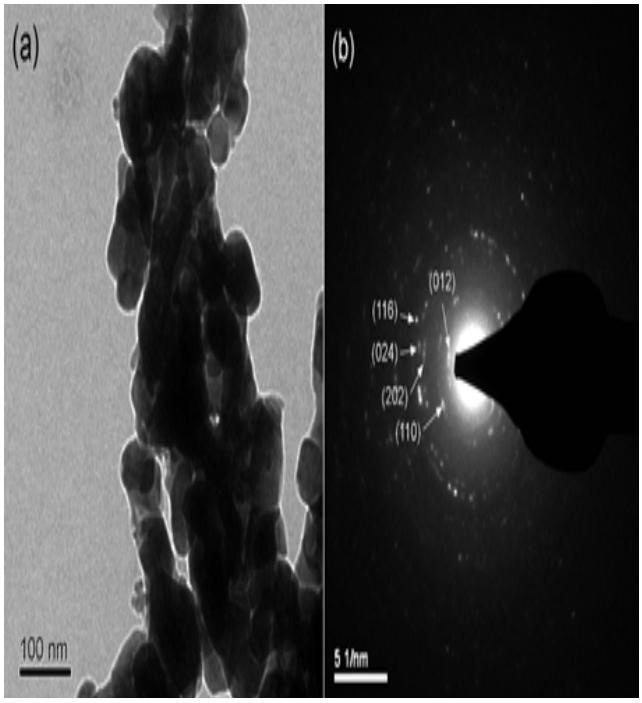


Fig.4 (a) TEM image of $BiFeO_3$ (b) indexed SAED pattern of individual $BiFeO_3$ nanoparticle.

perovskite-type BiFeO3 nanoparticles which has spherical shaped morphology having particle sizes of 10-45 nm. Fig. 4 (b) shows the SAED pattern of BiFeO3 nanoparticles having ring pattern which is characteristic of polycrystalline samples. These diffraction rings are indexed as (012), (110), (202), (024), and (116) planes of rhombohedral distorted perovskite phase of $BiFeO_3$ nanoparticle which is in well agreement with the XRD results.

## Conclusion:

Bismuth Ferrite Oxide ($BiFeO_3$) was prepared using Sol-Gel Method. The XRD data analysis the prominent peaks in the XRD plots of Bismuth Ferrite Nanoparticles are confirming the synthesis of pure phase Bismuth Iron Oxide. TEM and HRTEM confirm that the synthesized sample is nanoparticles of bismuth ferrite oxide and the size of the particles is found to be 10-45 nm which is the range of nanometre.

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