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The Synthesis and Characterization of Metal Oxide Photocatalysts By Sol-Gel Method for Degradation of Organic Dyes

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Abstract

As metal oxide, Bismuth ferrite ($BiFeO_3$) is a good semiconductor photocatalyst for environmental remediation due to its eccentric properties such as a multiferroic material, and ferroelectric properties. BiFeO3 has a visible-light band-gap, which makes it convenient for photocatalytic use. The sol-gel method is an extensively used synthesis method for BiFeO3 because it controls shape, size and morphology of the materials. Sol-Gel method provides many advantages, including the ability to easily incorporate dopants and the potential for large-scale production. To improve the photocatalytic properties of BiFeO3, various techniques such as doping and surface morphology control have been used to enhance its photocatalytic activity. Doping of metal in BFO improves its photocatalytic performance by reducing the band gap, which enhances visible light absorption, and reducing electron-hole pair recombination sites, which increases the number of participating electrons and holes in photocatalytic reactions. X-ray diffraction (XRD) studies are used to identify the crystal structure of the sample and to determine its purity. The shifting of X-ray diffraction peaks indicates that the sample has undergone structural changes during synthesis and calcination. The UV-visible spectra show a gradual decrease in the band gap, which is attributed to the doping of metals in $BiFeO_3$. The decrease in the band gap enhances the visible light absorption of $BiFeO_3$, making it more efficient in photocatalytic reactions.

Keywords: **Keywords**: Photocatalytic, X-ray diffraction (XRD), UV-visible, dopants, Doping

1. Introduction:

The synthesis and characterization of metal oxides for the purpose of photocatalytic degradation of dyes is an area of active research in materials science and environmental engineering. The objective of this research is to develop efficient and effective photocatalysts that can be used to degrade organic pollutants in water. Metal oxide photocatalysts, such as Bismuth Ferrite ($BiFeO_3$), titanium dioxide (TiO_2), zinc oxide (ZnO), and iron oxide (Fe_2O_3), have attracted significant attention due to their unique properties, including high surface area, strong redox activity, and excellent stability under a wide range of conditions. These properties make them excellent candidates for use in photocatalytic degradation of dyes. Bismuth Iron Oxide ($BiFeO_3$ or BFO) is a well-known example of a multiferroic material that exhibits both ferroelectric and antiferromagnetic properties at room temperature. It is a complex oxide that crystallizes in a rhombohedral distorted perovskite ABO_3 structure with space group R3c, where A represents bismuth and B represents iron. The lattice parameters of $BiFeO_3$ are a = 5.58 Å and c = 13.87 Å, which reflect the distorted perovskite structure of the material [1, 2]. The ferroelectric properties of $BiFeO_3$ arise due to the displacement of the Bi and Fe ions from their ideal positions in the perovskite lattice, leading to a net polarization along the crystallographic c-axis. The antiferromagnetic properties of $BiFeO_3$ arise due to the alignment of the magnetic moments of the Fe ions in an antiparallel manner in adjacent unit cells. The transition temperatures for ferroelectricity (TC) and antiferromagnetism (TN) in $BiFeO_3$ are about 1103 K and 643 K, respectively [3]. Due to its multiferroic and small size properties, $BiFeO_3$ has attracted significant attention from researchers in recent years, with potential. BFO also has a smaller bandgap, which makes it a visible-light-driven photocatalyst. This property is useful in the degradation of organic pollutants and dyes.

Synthesizing pure phase BiFeO3 can be challenging due to the formation of various impurity phases. [4] due to the formation of impurity phases such as Bi2Fe4O9, Bi36Fe24O57, and Bi25FeO40 is still a challenge. The formation of these impurity phases can occur due to various reasons such as improper stoichiometry, inadequate synthesis conditions, and impurities present in the starting materials. To minimize the formation of these impurity phases, it is essential to carefully control the synthesis conditions such as temperature, pressure, and atmosphere. It is also important to use high-purity starting materials and to optimize the synthesis parameters and possible to obtain pure phase BiFeO3[5]. Bismuth Ferrite (BFO) is multiferroic properties arise from the arrangement of the 'A' site Bi ions and the 'B' site Fe ions respectively, and any imbalance in the stoichiometric ratio between Bi, Fe and O ions can affect its multiferroic properties [6-7]. BFO has a spiral modulated spin structure (SMSS) with a long-wavelength period of 62 nm. To destroy the SMSS in BFO, substitution of cation or doping is the easiest way [8]. Another way is to synthesize nanoparticles of $BiFeO_3$. In this research, we are interested is to prepare $BiFeO_3$ nanoparticles by the simple wet chemical method, sol-gel method to reduce the wavelength of BFO. The sol-gel method to prepare BiFeO3 nanoparticles should allow for precise control over the size, shape, and composition of the particles, as well as enable the production of homogeneous material. By reducing the wavelength of BFO, the nanoparticles may exhibit new or improved optical, electrical, or magnetic properties that could be useful for various applications. The characterization of the synthesized photocatalyst is also important to understand its properties and its potential as a photocatalyst. X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and Fourier transform infrared spectroscopy (FTIR) can be used to characterize the morphology, crystal structure, and surface properties of the photocatalyst. The photocatalytic degradation of dyes is typically measured by monitoring the change in the concentration of the dye over time using techniques such as UV-Vis spectroscopy. Factors affect the photocatalytic activity of the metal oxide photocatalysts include the type of dye, the concentration of the photocatalyst, and the intensity of the UV light [9-10].

2. Materials and Methods

A. Synthesis Procedure of $BiFeO_3$ Nanoparticle (Sol-Gel Method):

- The considered quantity of Bismuth nitrates Bi $(NO_3)_3.5H_2O$ and ferric nitrate $Fe(NO_3)_3.9H_2O$ separately were taken into a beaker with about 200-250 ml. Bismuth nitrate is not soluble in water hence it dissolve with nitric acid (HNO_3).
- Then the solution was magnetically stirred by adding propylene glycol (2ml) as chelating agent. (Figure 1b)
- After that the solution was heated at a constant temperature at about 100°C -110°C with continuous magnetic stirring for about 3-4 hours. (Fig. 1a)
- At last, about all the solvent got evaporated and the solution got thicker. And finally gel-like layer of dark brown colour appeared. (Fig 1b)
- The prepared sample is grinding into mol tar and keeps into furnace for calcinations at temperate 450°C for 3 hours to get nanoparticles of $BiFeO_3$. (Fig. 1c)

Fig. 1(a) Fig. 1(b) Fig. 1(c)

Fig.1: Synthesis steps (a) formation of gel (b) precursor of xerogel (c) $BiFeO_3$ Nanoparticles

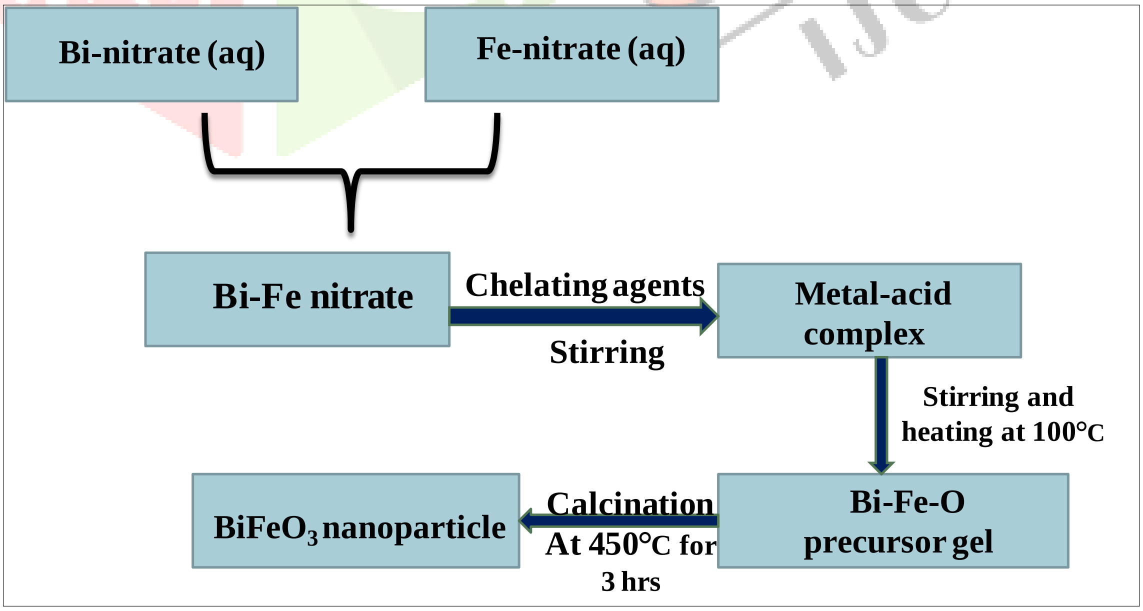

Fig.2: Flow diagram for Sol-Gel synthesis Procedure $BiFeO_3$ Nanoparticls

3. Results and Discussion-

A. X-ray Diffraction (XRD):

X-ray diffraction (XRD) is a powerful technique for analyzing the crystal structure and phase purity of materials. The prominent peaks in the XRD pattern can confirm the synthesis of a pure phase of Bismuth Iron Oxide. The Debye-Scherer formula is commonly used to estimate the average grain size of nanocrystalline materials from their XRD patterns. This formula relates the average crystalline size (D) of a nanocrystalline material to the Full Width at Half Maxima (FWHM) of the XRD peak using the following equation:

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

Where K is a constant, λ is the wavelength of the X-ray used, β is the FWHM of the peak, and θ is the diffraction angle. The Debye-Scherer formula is useful for predicting the crystalline size of nanoparticles and nanocrystalline materials. [11-12]

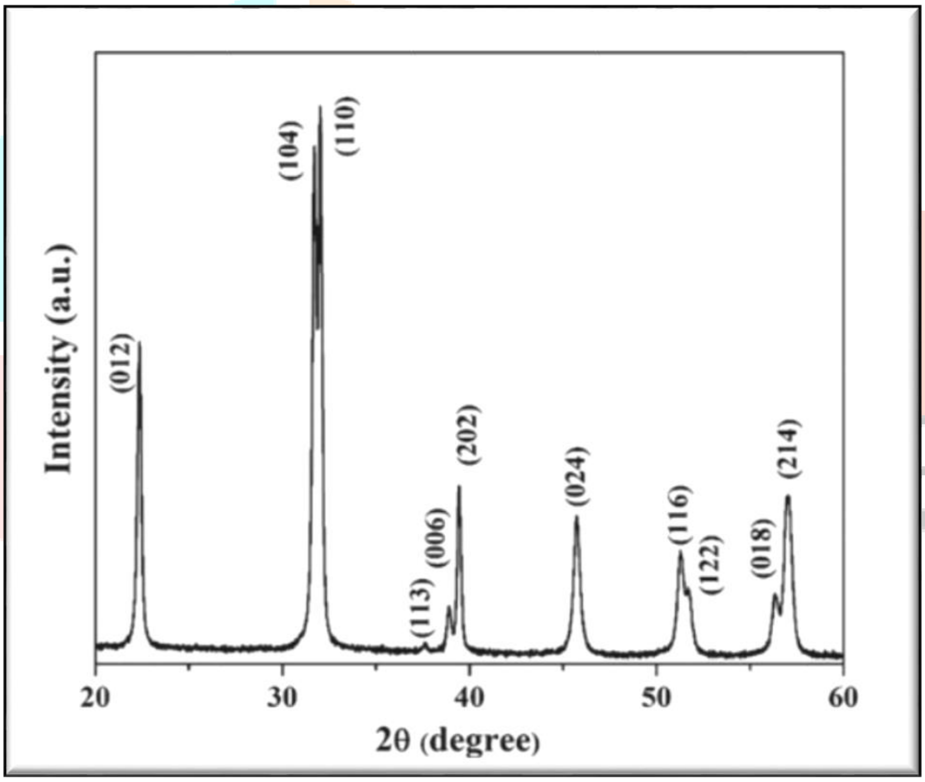

Fig.3 shifting of peak showing in XRD image of $BiFeO_3$ nanoparticles.

B. High-resolution transmission electron microscopy (HRTEM):

High-resolution transmission electron microscopy (HRTEM) is a powerful tool for studying the crystal structure of materials at the atomic scale. It uses a beam of high-energy electrons to interact with the sample, which causes the electrons to scatter and form an image on a detector. HRTEM reveal information about the arrangement of atoms in the sample, including grain boundaries, interface formation, defects, stacking faults, and precipitates. This information is important for understanding the properties and behavior of materials, as well as for designing new materials with specific properties. Srivastav et al. Synthesized

$BiFeO_3$ nanoparticles by sol -gel method and found TEM images in different condition. Fig.4 shows the TEM image for perovskite-type $BiFeO_3$ nanoparticles which has spherical shaped morphology having particle sizes of 10–45 nm [13].

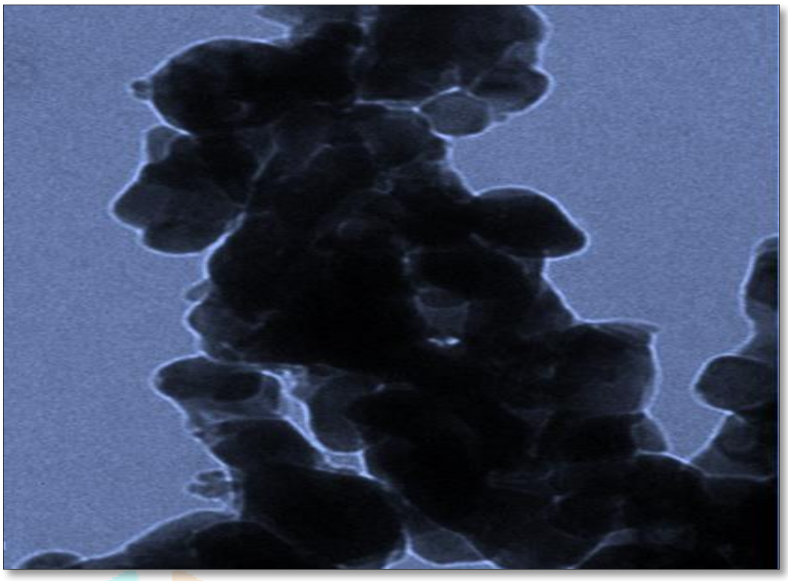

Fig.4 TEM image of $BiFeO_3$ (at 450°C)

Table-1: Synthesis Methods, Criterion, Photo-degrade organic Pollutant/dyes and characterisation properties of $BiFeO_3$ nanoparticles

Sl No.	Perovskite Structure /type	Method	Morphology	Calcinations Temperature	Degrade dyes/org. pollutant	Characterisation	Ref.
1	$BiFe_2O_3$, BFO	Sol-gel	Nanoparticles	500^0C 2hrs.	Decomposition of organic contaminants, such as Methyl orange (MO)	XRD, SEM, TEM and UV-vis are used for the characterisation. MO absorption measured by using UV-vis.	[14]
2	$BiFeO_3$	Sol-gel	Nanoparticles	Calcined at 500°C for 4 hr.	Degradation of RB dyes	Morphology of crystal find out by using XRD (1.54 A° wavelength),	[15]
3	$BiFe_2O_3$, BFO	Sol-gel	Nanoparticles	600^0C 2hrs.	Decomposition of organic compounds	XRD is used to determine the crystalline size of phases.	[16]
4	$BiFe_2O_3$, BFO	Sol-gel	Nanoparticles	400^0C-600^0C 2hrs.	Decomposition of organic compounds	FESEM is used to see the images of the synthesized powder.	[17]
5	$BiFe_2O_3$, BFO	Sol-gel	Nanoparticles	550^0C 2hrs.	Decomposition of organic compounds	XRD used for crystal observation, TEM used to observe morphology of the particles	[18]

4. Conclusion:

X-ray diffraction (XRD) is a widely used technique to determine the crystal structure of a material. When X-rays are incident on a crystal, they interact with the atoms in the crystal lattice and get diffracted. The resulting diffraction pattern contains information about the arrangement of atoms in the crystal lattice. By analyzing the diffraction pattern, it is possible to determine the crystal structure of the material, as well as its lattice parameters, grain size, and other structural properties. For BiFeO3 nanoparticles, the presence of prominent peaks in the XRD plot indicates that the nanoparticles are in a pure phase and have a well-defined crystal structure without any impurities. From the HRTEM image in Fig.4 it seems that the particles should not be agglomerated and should have a heterogeneous size distribution, with an average particle size in the range of 10-45 nm which is common requirement in nanoparticle synthesis. As agglomeration can lead to reduced surface area and reactivity, while a narrow size distribution can limit the properties and applications of the nanoparticles.

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