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Improvement in Multiferroic and Photocatalytic Properties of Bismuth Ferrite Nanoparticles: A Review

Adil Hamid, Mohit Sahni* and Aarti Gupta
Department of Physics, School of Basic Sciences and Research, Sharda University, Greater Noida, Uttar Pradesh, India
*Corresponding Author: mohit.sahni@sharda.ac.in

Abstract: $BiFeO_3$ (BFO) is the most promising of this rare ABO_3-type perovskite multiferroic materials because it exhibits in bulk BFO's with high ferroelectric Curie temperatures (T_C = 1103 K) and G-type antiferromagnetic Neels (T_N = 643 K), multiferroic behavior can be observed at room temperature. It is lead-free, possesses fascinating multiferroic and optical properties, and is environmentally benign. Recent investigations on BFO have shown that it forms an excellent visible light-responsive photo-catalytic material due to its band gap of 2 eV and the remarkable stability of chemicals. In this manuscript we have tried to explain the improvement in the multiferric and photocatalytic properties of BFO by substitution on A and B site. The various synthesis processes along with their impact, the types of doping and their impact on the structural changes and thereafter these impact results in the improvement in the properties has been explored in the manuscript.

Keywords: ABO_3, Degradation, Doping, Multiferroic materials, Photocatalytic.

I. INTRODUCTION

Scientific and industry interest in multiferroic materials having two or more co-existing order parameters is high. These materials offer a wide range of possible uses in photocatalysis, sensors, transducers, optoelectronics, telecommunications, information storage, and other fields. These materials are, however, uncommon in perovskite materials of the ABO_3 class. From the perspective of practical applications, $BiFeO_3$ (BFO) is the most promising of this rare ABO_3-type perovskite multiferroic materials because it exhibits in bulk BFO's with high ferroelectric Curie temperatures (T_c = 1103 K) and G-type antiferromagnetic Neels (T_N = 643 K), multiferroic behavior can be observed at room temperature [1, 2]. The distorted rhombohedral structure of space group R3c, which best describes the BFO crystal structure and is ideally suited for multifunctional devices, exhibits multiferroic behavior at room temperature. It is lead-free, possesses fascinating multiferroic and optical properties, and is environmentally benign. Recent investigations on BFO have shown that it forms an excellent visible light-responsive photo-catalytic material due to its band gap of 2 eV and the remarkable stability of chemicals [1, 2].

We are well aware that environmental degradation is one of the major issues facing the globe today. Water contamination is one of them that deserves attention. After use, dangerous chemical dyes used in various sectors: such as clothing, the printing process, leather products, and rubber-based products, are thrown into rivers. As a result, river's water quality has considerably declined. It has major ramifications because our rivers are crucial as a supply of water for agriculture and drinking. The government has issued directions to various industries to develop effluent treatment plants (ETP) to prevent this pollution. These ETP's use mechanical, electrochemical, and biological techniques to remove contaminants from contaminated water and render it usable. The breakdown of organic dyes through photocatalysis is one of the most significant techniques used by ETP's. The photocatalytic components are crucial to this approach.

The advanced oxidation process is one of the effective methods utilized globally to solve this problem that has been addressed by many countries. Different kinds of semiconductor photocatalysts are used in the advanced oxidation process. TiO_2 was a promising semiconductor photo-catalyst due to its distinctive qualities, including large capacity for oxidation, chemical inertness, affordability, as well as significant durability. Nevertheless, it can only utilize UV light, which only accounts for 4% of the overall solar light spectrum, because of its high band gap (3.2 eV). In comparison to TiO_2, Multiferroic BFO nanoparticles' photocatalytic activity has lately attracted attention because it can utilize the visible portion of the solar spectrum and has a reduced band gap (2.2 eV). BFO nanoparticles have a further advantage because of their multiferroic features (ferroelectric and weakly ferromagnetic in nature), which make it easy to remove them from the water and prevent them from polluting it on their own [9]. To address these issues, a chemical alteration replacement with adequate rare earth ion ionic radius is created at the BFO site A, this can be found in the BFO crystal lattice at the Bi^{3+} locations [3, 4]. By modifying the symmetry, These dopant substitutions result in morphological deformation that significantly improves magnetization as well as ferroelectric characteristics. For instance, when the size of the nanoparticle is lower than the period of the spin helical ordering structure (62 nm). The spin helical ordering structure can be broken down by the size effect, which dramatically increases the magnetization of BFO nanoparticles. Additionally, recent thorough research has concentrated on the substitution of the A, B, or A-B sites of $BiFeO_3$ by rare-earth or alkaline earth elements [5]. The lone pair of Bi $^6s_2$ could become unbalanced and the lattice structure could clearly be affected by replacement at the A-site. Bismuth Ferrite ferroelectric behaviors are impacted, and magnetism is also somewhat impacted. The exchange interaction between the host Fe^{3+} ion and the dopant ions or the dissolution of the spin cycloid, On the other hand, are two mechanisms by which its magnetic behaviors might be directly impacted by replacement at the B-site [6, 7]. Alkali elements as a dopant to replace the A or B-site of BFO, however, have been the subject of a few studies that have been published. $BiFeO_3$ has undergone several recent inspections that have attempted to enhance its magnetic characteristics by suppressing its spiral spin structure, which has improved its multiferroic capabilities. The techniques based on the lanthanide series of rare earth metal ions and the reduction of particle size for nano crystalline materials (Pr, Er, Dy, and Gd) [5, 14, 22], transition metal ions, and the ferroelectric, magnetic, optical, and magneto-electric characteristics of $BiFeO_3$ are significantly affected by the presence of 2-divalent cations (Calcium, Strontium, Lead and Barium) [7, 9, 15, 18].

II. METHODOLOGY

In the pursuit of modifying the multiferroic and photocatalytic properties of Bismuth Ferrite ($BiFeO_3$) nanoparticles, researchers have investigated a variety of synthesis strategies, each offering an effort in tailoring nanoparticle characteristics. These are Sol-Gel Method, solid chemical route, and hydrothermal method.

The Sol-Gel Method stands out as one particularly popular renowned method known for its versatility and precise control over nanoparticle morphology [8, 13]. This process typically commences with the dissolution of high-purity precursor chemicals, such as bismuth nitrate and iron nitrate, alongside possible dopants like samarium nitrate or nickel nitrate, in deionized water. The kinetics of the process can be accelerated by adding a catalyst, most commonly nitric acid [16]. Afterwards, a chelating agent like tartaric acid is added to facilitate the formation of a homogenous sol. Controlled heating, usually around 70 °C, induces gelation, yielding a gel that is then subjected to control drying to remove excess solvent. The gel is further calcined, usually for several hours at temperatures of about 500 °C in an oxygen-rich environment, to produce crystalline $BiFeO_3$ nanoparticles with specific characteristics [19, 20].

The Solid Chemical Route offers an alternative pathway for nanoparticle synthesis, which starts chemical reactions between precursor chemicals immediately instead of going through the solution phase. This process usually entails the careful blending of stoichiometric amounts of precursor chemicals, such as bismuth nitrate and iron nitrate, sometimes enhanced with dopants like samarium nitrate or nickel nitrate, however particular procedures may differ which makes it easier for BFO nanoparticles to develop. This uncomplicated method is highly valued for its simplicity and scalability, making it suitable for large-scale production projects.

Moreover, the Hydrothermal Method offers an alternative strategy that utilizes high temperature and pressure in an aqueous environment. A standard process is dissolving precursor compounds in a solvent, like water, then surrounding the solution inside a high-pressure vessel, however the specifics may differ. After that, the vessel is heated to high temperatures—often beyond 100 °C—which trigger chemical reactions and start the formation of $BiFeO_3$ nanoparticles. Applications requiring precisely tailored nanostructures are ideally suited for this approach because it provides exquisite control over nanoparticle size, shape, and crystallinity.

To sum up, the Sol-Gel technique, Solid Chemical Route, and Hydrothermal method are essential resources for synthesizing $BiFeO_3$ nanoparticles. They each have unique benefits when it comes to dressing up the properties of the nanoparticles to improve multiferroic and photocatalytic performance. Significant progress in comprehending and utilizing $BiFeO_3$ nanoparticles over a wide range of technical boundaries is supported by these approaches.

III. CONCLUSION

The XRD patterns were Rietveld refined in the first research; we noticed that the clean stage development of $Bi_{0\cdot85}Ba_{0.15}FeO_3$& $Bi_{0.85}Mn_{0.15}FeO_3$ [2], the experimental investigation of nanoparticles and substitution-induced phase change. When Ba doping was used instead of Mn doping in BFO samples, the magnetic tests showed room-temperature ferromagnetic behavior and an improvement in the remnant magnetization. The uncompensated spin moments of the nanoparticles' surfaces and the structural deformation are responsible for these outcomes. Future paper TEM findings show that as the Ca-Ni content increases, the particle size of $BiFeO_3$ decreases. Additionally, EPR experiments have demonstrated that co-doped materials with the greatest net magnetizations of 0.11, 0.37, and 2.95 emu/g for x = 0.0-0.10, respectively, at 300 K, are also the most stable, and have dramatically improved magnetic properties.

The remnant magnetization (2Mr) in BFO samples increased with increasing Mn content, reaching between 0.08 and 0.51 emu/g for BM-5 and BM-15 due to the dissolution of the spiral spin structure. Dielectric anomalies near Neel temperature, a marker of magneto-electric coupling, were found in every sample of Mn-doped BFO. The improvement in multiferroic characteristics of Mn-doped BFO samples is indicated by the rise in magneto-electric coupling from 1.46% for BM-5 to 2.6% for BM-15 samples. The potential for employing Mn-doped BFO nanoparticles in optoelectronic devices has increased due to their enhanced multiferroic and magneto-electric properties as well as their fascinating optical characteristics.

XRD patterns supported the deformed rhombohedral structure of Bismuth Ferrite nanoparticles. The rhombohedral form of BFO nanoparticles was further validated by Raman spectroscopy. The enhanced visible light absorption of the BFO nanoparticles showed large absorption bands (400-650 nm) and a 2.17 eV energy band gap. Pure-phase BFO nanoparticles with enhanced optical and ferromagnetic characteristics in the visible range may be advantageous for optoelectronic devices [3].

The distortion in the BFO lattice generated was identified using the change in lattice parameters and the Fe-O-Fe bond angle by Dy replacement in the fifth through eighth studies. Dy^{3+} and Fe^{3+} ions' ferromagnetic interaction and deformation, which partially suppress the modulated spiral spin structure, are thought to be the cause of the rise in magnetism. In the sixth work, $BiFeO_3$ ceramics with pristine phase Pr and Zr co-doped were made, and their multiferroic characteristics were enhanced [4].

Strong visible light absorption was observed in BPFZ ceramics with energy band gaps of 2.16, 2.0, and 2.0 eV, respectively. The improved dielectric, optical, and magnetic characteristics could have significant use in multiferroic and optical systems. The specimen contains a single-phase rhombohedral structure with the (R3c) space group, according to XRD. Chemical substitution caused the sample's structure to shift from rhombohedral (R3c) to orthorhombic (Pbnm). The magnetic properties of the samples get better as Sm^{3+} dopant is added to BFO. In the eighth publication, XRD patterns and Raman spectra were used to demonstrate that BFO nanoparticles with Ho and Ho-Co doping include an orthorhombic phase. Ho and Ho-Co-doped samples both exhibited ferromagnetism [7].

According to papers from the ninth to the twelfth grades, the band-gap of $Bi_{0\cdot96}Sm_{0.04}Fe_{0\cdot96}Ni_{0\cdot04}O_3$ nanoparticles is 2 eV, and it rises to 2.35 eV in the $Bi_{0\cdot96}Sm_{0.04}Fe_{0\cdot96}Ni_{0\cdot04}O_3$ @ZnO nano combination [9-12]. Due to more active catalyst sites, this shift in band gap might have made MB's photocatalytic degradation process more effective. Sm and Ni are switched out for Ni in $BiFeO_3$ and combined with ZnO, which causes molecular orbital rearrangement and deformation in FeO_6 octahedral structure. FeO_6 may also be the cause of the rise in MB's photocatalytic degradation efficiency.

In the eleventh work, the Sm- and Ni-doped, a tartaric acid-based sol-gel technique was used to create Bismuth ferrite nanoparticles. All of the synthesized nanoparticles were found to have an energy band gap between 2.2 and 2.0 eV, and as Sm and Ni are used in place of Bismuth ferrite, the band gap reduces. When more BFO is loaded with Sm and Ni, the dielectric constant and dielectric loss (tan) rise. As Sm and Ni co-doping levels rise, the saturation magnetization of BFO rises from 0.014 to 0.726 emu/g. $Bi_{(1-x)}Sm_xFe_{(1-x)}Ni_xO_3$ ($x = 0.06$) nanoparticles were demonstrated to completely break down MB, demonstrating that the efficiency caused by Sm and Ni co-doping in BFO encourages decomposition [11].

In the eleventh work, using the sol-gel technique, cobalt-doped bismuth ferrite nanoparticles were created in a single phase. The size of the crystallite decreased due to the dopant's presence at the bismuth ferrite's Fe site. The tauc equation was used to get the band gap energy as well as with the aid of numerous characterization techniques, the structural, optical, and photocatalytic properties of the generated samples are successfully evaluated. Cobalt doping concentration was increased to improve band gap energy. According to XRD patterns, all of the produced samples have crystallized, and Ni doping boosts crystallinity. The Ni-doping-induced changes in the XRD peaks show how the structure of BFO has changed. UV-vis spectroscopy has demonstrated that Ni doping has decreased the optical band gap. The deformed rhombohedral structure of the Ni-doped BFO in the R3c space group is also revealed by Raman spectroscopy. The greater reduction of MB dye as a result of Ni doping illustrates how Ni doping has improved the photocatalytic properties of BFO.

From the twelfth through sixteenth research, it was deduced that Yb^{3+} and Co^{2+} replaced Bismuth ferrite nanoparticles could be synthesized effectively we investigated the photocatalytic behavior. The outcomes of the XRD sample displayed that the nanoparticles had solid crystalline structures. Unit cell characteristics and volume decreased as the concentration of Yb/Co substitution increased [12].

Two phonon modes' intensity decreases from $x = 0.02$ to 0.06 but increases for $x = 0.08$. Samples, according to a Raman spectroscopy investigation, Co^{2+} and Co^{3+} ions will coexist in Yb/Co substituted samples with Co^{2+} / Co^{3+} ratios of 3.4 and 2.6 for samples with $x = 0.04$ and 0.06, respectively, according to X-ray photoelectron spectroscopy analysis. Additionally, The BFO nanoparticles substituent (Yb/Co) has a specific electrical interaction that causes the Bi, Fe, O, Yb, and Co X-ray photoelectron spectroscopy spectra to alter. By swapping Yb^{3+} and Co^{2+}, the band gap of the visible range detected $BiFeO_3$ nanoparticles can be adjusted to 2.3 eV.

After 100 minutes of radiation exposure, it was discovered that 76% of the MB dye had degraded for pure BFO and 99% for $Bi_{0\cdot94}Yb_{0\cdot06}Fe_{0\cdot94}Co_{0.06}O_3$ nanoparticles. The structural change from the rhombohedral to the orthorhombic phase is made easier by the co-substitution of rare earth Sm and transition metal Cr in BFO, and this has been shown to have a considerable effect on optical bandgap energy.

The optical bandgap energy of Co-doped BSFCO-5 drops from 2.29 eV to 1.89 eV. The research described now offers novel techniques for changing optical bandgap BFO doped nanoparticles, which could be used as UV, visible, and photocatalysts as well as photovoltaic devices [17].

In the fifteenth study, the structural, dielectric, magnetic, and optical characteristics of bismuth ferrite nanoparticles Co-doped with Gd and Zr were thoroughly investigated. Raman investigations reveal that some active modes are merging and dissipating, which suggests that the samples have structural distortion. A rise in the strength of the E-9 mode with increasing Zr concentration serves as a sign of the distortion in FeO_6 octahedra [15].

The Rietveld examination of the XRD data shows the structural distortion in $BiFeO_3$ brought on by the Na substitution. The results of FESEM and TEM investigation showed that the size of the Bismuth ferrite nanoparticles ranged from 50 to 125 nanometers and decreased with increasing Na concentration. Along with X-ray diffraction & TEM data investigation, single-crystalline Na-substituted $BiFeO_3$ samples, which have the deformed R3c phase was further demonstrated by a drop in Raman intensity and an expansion of the Raman modes. The apparent bandgap of 2.16 eV in $BiFeO_3$ nanoparticles may be modified by the Na substitution. Furthermore, a viable photocatalytic mechanism for the Na-substituted $BiFeO_3$ nanocrystalline photocatalyst was anticipated [15].

The XRD characterization data from publications 17 through 20 indicate that the bismuth ferrite nanoparticles have a rhomboid-centered structure. The calcination temperature causes an increase in the BFO nanoparticle's diameter.

According to the results of the analysis. The EDAX data provide confirmation of the BFO nano particle's elemental makeup and the presence of Bi. The bismuth nanoparticle has shown to be very beneficial in the treatment of cancer based on antibacterial investigations.

Furthermore, in our 18th publication, we investigated the effects of Co-doping with Sm and Co on the crystalline structure, electric behavior, ferroelectric behavior, and ferromagnetic behavior of BFO nanoparticles. $Bi_{0.9}Sm_{0.1}Fe_{1-y}Co_yO_3$ ($y = 0.05$, 0.1, or 0.15), rhombohedral nanoparticles showed structural conversion to orthorhombic regularity that was comparable to clean Bismuth Ferrite. Along with a corresponding notable reduction in crystallite sizes. $Bi_{0.9}Sm_{0.1}Fe_{1-y}Co_yO_3$ composite's electric resistance, reactance, and resistivity all significantly decrease with increasing Co concentration at low frequency (1 kHz). $Bi_{0.9}Sm_{0.1}Fe_{0.85}Co_{0.15}O_3$ when measured at 107 Hz, has an AC conductivity that is almost 3.5 times larger than that of the parent BFO [18].

Sm and Co co-doped BFO's improved conductivity and decreased resistance may make it acceptable for solar applications. At 15 kV/cm, the Pr of$Bi_{0.9}Sm_{0.1}Fe_{0.85}Co_{0\cdot15}O_3$ is about 9.5 times more abundant than pure Bismuth Ferrite. $Bi_{0.9}Sm_{0.1}Fe_{0.85}Co_{0\cdot15}O_3$ nanoparticles displayed a remarkable rise in Ms that was nearly five times greater compared to pure Bismuth ferrite [17].

Due to uncompensated spins at the surface and the suppression of the spin helical ordering structure both contribute, M-H tests reveal that nanoparticles have a weak ferromagnetic nature. For Na-doped BFO samples, the core (AFM)-shell (FM) structure is responsible for the isolated exchange bias phenomenon (EB) that is observed without field cooling. Additionally, as the Na concentration increases, the samples' band gap and leakage current both significantly decrease with the 3% Na doped BFO recording the lowest leakage current density (10^{-7} A cm^{-2}) [15]. The Ohmic behavior brought on by the thermal emission of electrons is enhanced as the concentration of Na ions increases, and the SCLC linked to oxygen vacancies of the samples weakens ever-increasingly. While magnetization studies at room temperature show that changing the size of the nanoparticles can vary their magnetic properties from antiferromagnetic to weakly ferromagnetic, structural characterization of NPs reveals that they have a distorted rhombohedral crystal structure. Using the FORC technique, we were able to deconvolute the magnetic influences in the Nanoparticles. Based on the total operation of the individual coercivity provision intensities, we think that each contribution has a distinct origin that may be connected to a core-shell structure. Magnetometry and FORC measurements substantiate this.

We can observe that Cr-doping was discovered to significantly improve the dielectric characteristics in publications 21 through 24. In the low-frequency range, 1% of Cr-doped Bismuth Ferrite NPs have a reduced dielectric constant and decreased dielectric loss [21]. Unlike past investigations on the doping of Cr in bulk and nano-BFO, the results. Both pure and doped NPs showed distinct dielectric loss peaks. These Cr-doped BFO NPs are advantageous for photocatalytic processes that employ sunlight because they have tunable visible spectrum absorption. The crystallite diameters in the 22nd article ranged from 5.8 nm to 13.7 nm. The calculated grain sizes fell between 8-30 nm. For each of these samples, the dielectric loss was below unity, indicating the potential of the $La_{0.1}Bi_{0\cdot9}Fe_{0.80}Cr_{0\cdot20}O_3$ composition for applications involving high-frequency/microwave devices. The investigation indicated that adding La/Cr to bismuth ferrite enhanced its dielectric and impedance properties. In order to develop applications for multifunctional devices, it would be preferable to investigate the properties of thin films with similar compositions. It was the 23rd paper. The structural and multiferroic characteristics of ceramic samples were examined in this work formed of $Bi_{1-x}Gd_xFeO_3$ using the hydro-evaporation manufacturing method were examined in relation to the effects of gadolinium doping. $Bi_{1-x}Gd_xFeO_3$ (x = 0.0625, 0.075, and 0.09) ceramic samples displayed decreased electric conductivity as a result of a decrease in the number of defects. $Bi_{1-x}Gd_xFeO_3$ ceramic samples were shown to exhibit a discernible development of mild ferromagnetism and a significant rise. Magnetic investigations show a constant increase in Gd concentration and a steady increase in net magnetization.

For all of the $Bi_{1-x}Gd_xFeO_3$ ceramic samples, the calculated Fe-O-Fe bond angles, which are used to determine how strong the antiferromagnetic super exchange interaction is, and the rise in weak ferromagnetic moments that have been observed are in good alignment. The weakening of antiferromagnetic coupling created by the distortion of the rhombohedral lattice and an increase in the orthorhombic phase in $Bi_{1-x}Gd_xFeO_3$ is what causes the Neel temperature to drop with Gd doping.

The structural, morphological, and multiferroic characteristics of these nanofibers have been studied in the 24th investigation. Perovskite and spinel structures are present in the CFO @ BCT Sn NFs, according to XRD and SAED studies. Core-shell connectivity has been supported by SEM and TEM pictures that display the geometry of the core-shell nanofibers. The piezoelectric response d_{33eff} was roughly 6 pm V^{-1} whereas the Ms and Mr values were 11.63 $emu.g^{-1}$ and 1.43 $emu.g^{-1}$, respectively, under a magnetic field of 25 kOe [22-23].

IV. Scope for Future Work

Multiferroic $BiFeO_3$ materials may prove to be very beneficial from an application standpoint since they can couple both the ferroelectric and ferromagnetic order characteristics and so give an additional level of functionality. As a result, a thorough analysis and synthesis of several doped and codoped $BiFeO_3$ systems have been done in the current work.

V. Conclusion

Nanoscale samples show better magnetic, dielectric, and optical properties. Improvement in magnetization is anticipated as the size of the synthesized nanoparticles decreases below 62 nm due to the suppression of the 62 nm spiral spin structure. These samples' better magnetism, decreased dielectric loss, and improved magnetoelectric coupling give designers and developers of novel devices new inspiration, including memory devices, resistive switching, and synchronous multi-harmonic imaging for tissue nanoparticles, solar cells, oxygen photocatalysis, gas sensors, and electromagnetic wave attenuation.

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