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Investigations on multiferroic, optical and photocatalytic properties of lanthanum doped bismuth ferrite nanoparticles

Manpreet Kaur¹, K. L. Yadav², Poonam Uniyal^{1*}

¹School of Physics and Materials Science, Thapar University, Patiala 147004, Punjab, India ²Smart Material Research Laboratory, Department of Physics, Indian Institute of Technology, Roorkee 247667, India

*Corresponding author. Tel: (+91) 8559083113; E-mail: poonam.uniyal@thapar.edu

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ABSTRACT

Single phase $Bi_{1-x}La_xFeO_3$ nanoparticles have been successfully synthesized with varied concentration $(0.0 \le x \le 0.2)$ for the photocatalytic degradation of an industrial dye. The room temperature X-ray diffraction (XRD) pattern of La^{3+} doped BiFeO₃ nanoparticles reveals the structural phase transition from rhombohedral (R3c) to orthorhombic (Pnma) at x=0.1, which is further analyzed via Rietveld refinement. The La^{3+} doped BiFeO₃ nanoparticles have much negative enthalpy of formation (ΔH_f) than undoped BiFeO₃. The particle size gradually decreases from ~132 to ~68 nm with La^{3+} doping. Magnetic and ferroelectric transition temperatures are found to be slightly shifted towards room temperature upto x= 0.1 and then higher temperature side which could be attribute to the particle size effect. All compositions presented weak ferromagnetic ordering, which indicates that the La^{3+} substitution in the BiFeO₃ matrix released the latent magnetization. The increase in the energy band gap from 2.045 to 2.658 eV with cutoff wavelengths 639.58 and 513.061 nm for x=0.0 and 0.2 respectively, increases the visible light efficiency of photocatalytic activity in La^{3+} doped BiFeO₃ samples. The photodegradation efficiency of La^{3+} doped BiFeO₃ for azo-dye RB-5 is observed to be ~27% higher as compared to the undoped BiFeO₃ (43% photodegradation efficiency), which makes it suitable for visible-light responsive photocatalysis for photocatalytic applications. Copyright © 2015 VBRI Press.

Keywords: Nanoparticles; multiferroic properties; optical properties; photocatalytic activity.

Introduction

The growth of industry worldwide has tremendously increased the generation and accumulation of waste byproducts. This problem is of global concern as conventional water treatment technologies such as solvent extraction, activated carbon adsorption, and chemical treatment process often produce hazardous by-products and generate large amount of solid wastes, which require costly disposal or regeneration method [1, 2]. One important technique for removing industrial waste is the use of light energy (electromagnetic radiation) and particles sensitive to this energy to mineralized waste which aids in its removal from solution. Multifunctional oxides have shown to be promising participants for photocatalytic applications, and accordingly, water insoluble TiO2 is one of the most efficient photocatalytic semiconductor due to its high quantum yield [3]. The recent research conveys the information at that stage where the large energy band gap (i.e. $\sim 3.2 \text{ eV}$) restricts the TiO₂, the narrow band gap (i.e. ~2.1 eV) of multifunctional BiFeO₃ and its excellent chemical stability makes it suitable for visible- light responsive photo-catalysis for water splitting and degradation of organic-inorganic pollutants [4, 5]. Researchers also revealed its applications in solar cells and

optoelectronic devices in the visible region [5]. In addition, BiFeO₃ also raises the possibility of potential devices in information storage, spintronics, actuators, sensor devices, etc. due to the existence of both the ferroelectric and antiferromagnetic ordering with its ferroelectric transition temperature, T_C of ~830 °C and a high G-type canted antiferromagnetic ordering temperature, T_N of ~380 °C simultaneously are well above the room temperature [4, 6]. Despite these important applications, its photocatalytic abilities as well as multifunctional properties are hampered due to the presence of impurity phases and structural instability. It is very challenging to synthesize the single phase bismuth ferrite as the number of competing phases such as $Bi_2Fe_4O_9$, $Bi_{12}(Bi_{0.5}Fe_{0.5})O_{19.5}$ and $Bi_{25}Fe_1O_{39}$ prevent the formation of single phase material [7]. Nanoparticles of partial substituted lanthanides at A-site for Bi³⁺ ions have essentially raised the numerous studies for improving the structural and multiferroic properties. The lanthanide content shows the mixed behavior at the Bi³⁺ site in BiFeO₃. At lower lanthanide content level, enhancement in the ferroelectric and magnetic properties has been reported [8, 9]. However, at higher content, the Bi³⁺ lone pair activity becomes diluted and a structural transition from the polar R3c symmetry to the centrosymmetric orthorhombic Pnma space group of LaFeO₃ is observed [10, 11].

Though, effect of rare earth doping (La, Gd, Dy etc.) has been studied widely for multiferroic properties [**12-17**], limited work is done on the photocatalytic properties. Z. Zhang *et al* [**5**] synthesized $Bi_{1-x}La_xFeO_3$ nanofibres and subsequently reported little influence of La doping on the optical and photocatalytic properties via degradation of Congo red dye. To the best of our knowledge its potential to reduce the toxicity of a very common azo-dye RB-5((tetrasodium-4-amino-5-hydroxy-3,6(bis(4-(2-

(sulfonatooxi)ethylsulfonyl)phenyl)azo)-naphthalene-2,7disulfonate)) used at large scale in the textile industry has not been reported in literature. In the present report, the effect of La^{3+} doping on the structural, multiferroic and optical properties as well as photocatalytic degradation of azo-dye RB-5 is studied.

Experimental

Material synthesis /chemicals detail

The reagents Bi(NO₃)₃'5H₂O, Fe(NO₃)₃'9H₂O, and La(NO₃)₃'3H₂O of analytical grade in appropriate amounts were used to prepare the Bi_{1-x}La_xFeO₃ nanoparticles ($0.0 \le x \le 0.2$) by sol gel auto-combustion method. Bi(NO₃)₃'5H₂O in nitric acid (HNO₃), and Fe(NO₃)₃'9H₂O in deionized water were then added in turn with constant stirring at 60–70 °C to obtain a homogeneous solution and to avoid any possible precipitation. Glycine is used as a fuel in the procedure. The viscous sol was heated at 70-150 °C on a hot plate. A rapid and vigor auto-ignition was completed within a few minutes. The brownish color ash obtained after combustion occurred. The obtained ash was then dried at 100 °C for 1 h in a hot air oven. The fine powder obtained after drying was calcined at 500 °C for 4 h.

Fuel nitrate ratio/reaction

To synthesize the BiFeO₃ nanoparticles, the reagents were combined in a molar proportion of 1:1:3.33 of $Bi(NO_3)_3$;5H₂O, Fe(NO₃)₃;9H₂O and Glycine (C₂H₅NO₂) respectively.

The calculation of the stoichiometric composition of combustion reaction has been conducted by balancing the total oxidizing and reducing vacancies of the oxidizer and fuel using the thermochemical concepts from propellant chemistry. This leads to the release of maximum energy for a particular reaction. In the reaction, the elements C, H, Bi and Fe, were considered as reducing agent and O played the role of oxidizing agent with the corresponding valances of +4, +1, +3, +3 and -2 respectively. The valency of the N was taken as zero. Thus, for glycine-nitrate combustion, the total valences of Fe(NO₃)₃·9H₂O add up to Bi(NO₃)₃·5H₂O was -30 that should be balanced by the total valencies in the fuel, which add up to +9. Hence, the stoichiometric composition of the glycine-nitrate redox mixture in order to release the maximum energy for the reaction, requires that -30 + 9n = 0 or n = 3.33 moles of glycine [18]. CO₂, H₂O and N2 may be evolved as the gaseous products in combustion synthesis can be expressed as,

 $Bi(NO_3)_3 \cdot 5H_2O \ + \ Fe(NO_3)_3 \cdot 9H_2O \ + \ 3.33C_2H_3NO_2 \ = \ BiFeO_3 \ + \ 6.66CO_2 \ + \ 22.33H_2O \ + \ 4.66N_2$

Characterizations

The phase formation of nanoparticles was investigated by the XRD technique and further analyzed via the Rietveld refinement using FULLPROF tool. The morphology and size were determined by TEM CM 200. DTA measurements were recorded on NETZSCH STA449-F3 Jupiter, while heating the sample in a nitrogen environment. The dielectric constant (ϵ) and dielectric loss (tan δ) were measured using an automated HIOKI 3532-50 Hi-Tester LCR Meter in the temperature range 30 °C-500 °C at different frequencies. The room temperature magnetization data were taken using vibrating sample magnetometer in the field range of 10 to 10 kOe. FTIR was recorded on Perkin Elmer-Spectrum with a resolution of 1 cm⁻¹ and scan range of 400–700 cm⁻¹ using KBr powder. Photoluminescence (PL) spectroscopy was performed on Cary eclipse. The absorption optical properties of the resultant doped BiFeO₃ samples were characterized using a Hitachi U-3900H spectrophotometer.

Photocatalytic activity

The photocatalytic activity of $Bi_{1-x}La_xFeO_3$ nanoparticles; (x=0.0 and 0.1) were performed for the degradation of azodye; Reactive black-5 (RB-5) in aqueous solution under visible light irradiation. The reaction was performed with initial concentration 200 ml of RB-5 (10 mgL⁻¹) solution and 0.2 g of the catalyst $Bi_{1-x}La_xFeO_3$; (x=0.0 and 0.1). The photodegradation efficiency of azo-dye RB-5 was estimated by measuring absorbance at 597 nm using a UV-Vis spectrophotometer.

Results and discussion

Structural analysis

Fig. 1(a) shows the room temperature X-ray diffraction (XRD) patterns of Bi_{1-x}La_xFeO₃ nanoparticles with the systematic increase in concentration, $0.0 \le x \le 0.2$ calcined at 500 °C. Undoped BiFeO₃ is found to crystallize in rhombohedrally distorted perovskite structure (R3c space group) without any impurity peaks, in accordance with the standard ICSD-Code 08-2614 of the crystal BiFeO₃. In fact, for samples upto x=0.1, the rhombohedral phase was evident and with further increase in La³⁺ doping content, samples only reflect the orthorhombic phase similar as LaFeO₃ (ICSD-Code 08-4941). This structural phase transformation from rhombohedral to orthorhombic at x=0.1, is evidenced by the merging of the split diffraction peaks into one peak indexed as (104) (110), (006) (202) and (116) (122) around the angle $2\theta=32^\circ$, $2\theta=39^\circ$ and $2\theta=51^{\circ}$ in the pattern of x=0.0. Magnified view of the characteristic peak of all the samples is shown in Fig. 1(b). Structure phase transformation is further confirmed by rietveld refinement. The refinement of the XRD pattern for undoped BiFeO₃ nanoparticles was carried out using the rhombohedral crystal symmetry with R3c space group in a hexagonal lattice. Best fits between the observed and calculated diffraction patterns or good R-factors are obtained for undoped BiFeO3 with this structural model confirm the formation of rhombohedrally distorted BiFeO₃ nanoparticles [19]. But the same model could not fit to the observed XRD patterns for La³⁺ doped BiFeO₃ BiFeO₃. Therefore, the refinement of XRD patterns for doped BiFeO₃ nanoparticles were performed with an orthorhombic structural model (space group: Pnma). The Rietveld fit between the observed and calculated profiles of the all the samples are shown in **Fig. 1(c)**, while the refine parameters are given in **Table 1**. The extracted values of Fe–O bond lengths and of, Fe–O–Fe bond angles are also listed in **Table 1**.



Fig. 1. (a) XRD pattern with La³⁺ doping content varying from $0.0 \le x \le 0.2$, (b) enlarged view of the characteristic peak and (c) Rietveld refinement of the XRD patterns of Bi_{1-x}La_xFeO₃ nanoparticles, (x=0.0, 0.1, and 0.2).

Table. 1. Structural parameters for $Bi_{1-x}La_xFeO_3$ nanoparticles, x=0.0, 0.1, and 0.2 obtained by Rietveld refinement of the XRD patterns at room temperature.

Composition of	Atom	Fractional coordinates			Lattice	Bond angle	Bond	R-factor
Bi _{1-x} La _x FeO ₃		x	у	z	Parameter [Å]	[°]	Length [Å]	[%]
x-0.0	Bi	0.0000	0.0000	0.0000	a=5.5770	Fe-O-Fe	Bi-O=2.166	$R_{p}=3.72$
space group-R3c	Fe	0.0000	0.0000	0.2212	c=13.8463	=156.662	Fe-O=2.171	Rwp=4.85
V=372.9568(Å ³)	0	0.4748	0.0178	-0.0563				$R_{exp}=3.41$ $\chi^2=2.02$
x-0.1	Bi/La	0.0357	0.2500	0.9946	a=5.5847	Fe-O1-Fe	Bi-O1= 2.101	$R_{\rm p} = 4.38$
space group-Pnma	Fe	0.0000	0.0000	0.5000	b=7.8713	=139.190	Bi-O2=3.108	Rwp=5.76
V=245.8880(Å ³)	01	0.5111	0.2500	0.1303	c= 5.5937	Fe-O2-Fe	Fe-O1=2.099	$R_{exp}=3.98$
	02	0.2677	0.5291	0.2174		=166.204	Fe-O2=2.188	χ ² =2.09
x-0.2	Bi/La	0.0393	0.2500	0.9953	a=5.5840	Fe-O1-Fe	Bi-O1=2.368	Rp=3.57
space group-Pnma	Fe	0.0000	0.0000	0.5000	b=7.8897	=153.690	Bi-O2=2.761	Rwp=4.79
$V = 245.8443(Å^3)$	01	0.5170	0.2500	0.0808	c=5.5803	Fe-O2-Fe	Fe-O1=2.025	$R_{exp} = 3.09$
	02	0.2067	0.5445	0.2034		=151.621	Fe-O2=2.048	$\chi^2 = 2.41$

All these resultant parameters suggested a distortion which involves Fe^{3+} or Bi^{3+} ion displacement with structural phase transformation in $BiFeO_3$ with the effect of La^{3+} doping. Thermodynamic analysis based on Pauling's equation can endorse this distortion/variation in $BiFeO_3$ due to the doping of La^{3+} . The Pauling's equation relates the ionic bond strength and ions electronegativity is written as,

$$l_{AB} = 1 - exp \frac{-|x_A - x_B|}{|x_B|}$$
(1)

Here **Las** is the ionic bond strength of ions, **La** is electronegativity of cation and **La** is electronegativity of anion [**20**]. The obtained results reveal that the La-O bond has more ionic strength, $I_{La-O}=0.442$ over the Bi-O bond, IBi-O= 0.319 by using electronegativity values 1.9, 1.10 and 3.44 for Bi³⁺, La³⁺ and O²⁻ ions respectively in the above mentioned equation (1). The much negative enthalpy of formation (ΔH_f) is observed in La³⁺ doped BiFeO₃ nanoparticles as the enthalpy of formation is the function of bond strength. Therefore, this negative enthalpy of formation (ΔG_f) will enhance the more stability in the perovskite phase of La³⁺ doped nanoparticles [**21**].

Debye-Scherrer equation is used to calculate the crystalline size of $Bi_{1-x}La_xFeO_3$ nanoparticles [22]. The obtained crystalline size of the undoped BiFeO₃ sample is ~24.69 nm. Moreover, the crystalline size gradually decreases from 24.69 nm to 20.09 nm with an increase the strain effect from 0.0054 to 0.0060. Fig. 2 exhibits the TEM morphology and particle size of Bi_{1-x}La_xFeO₃ nanoparticles at the scale of 100 nm using a carbon coated grid. Agglomerate particles are acquired due to the high surface energy of uniform particles with fairly narrow size. The mean particle size of the undoped BiFeO₃ sample is ~132 nm as can be observed in Fig. 2(a) which further decreases with increase the La^{3+} doping content, from ~132 nm for undoped BiFeO₃ to \sim 68 nm for x= 0.2. The SAED pattern taken for undoped BiFeO₃ nanoparticles exhibits the discrete rings indicating well developed polycrystalline nature as shown in Fig. 2(d). The observed lattice spacing is measured to be 2.84 Å, 2.28 Å, 1.96 Å and 1.79 Å which correspond to (104), (202), (024) and (116) lattice planes of BiFeO₃, respectively.



Fig. 2. TEM micrographs of $Bi_{1-x}La_xFeO_3$ nanoparticles, (x=0.0, 0.1, and 0.2).

Thermal analysis

Thermal analysis of $Bi_{1-x}La_xFeO_3$ nanoparticles has been investigated to study the doping effect on the magnetic and ferroelectric transition temperatures of $BiFeO_3$. The DTA curve of single phase $BiFeO_3$ is shown in **Fig. 3(a)**. The small endothermic peak in the DTA trace at 380 °C can be ascribed to antiferromagnetic transition temperature (T_N) and another peak around 825 °C is evident which indicates the transition temperature (T_C) from ferro- to paraelectric phase. Both the peaks are found to shift towards the lower temperature due to the increase of pressure with the decrease in cell volume [**10**, **23**] shown in the inset of **Fig. 3(a)**. This shift towards the room temperature also assigned to reduce particle size in La³⁺ doped nanoparticles as reported in literature [**24**], is quite desirable for obtaining room temperature magneto electric coupling. The presence of two endothermic peaks in all the compositions at 100 ± 5 °C and 130 ± 5 °C is due to the evaporation of surface and locked-in water molecules.



Fig. 3. (a) DSC curves of $Bi_{1-x}La_xFeO_3$ nanoparticles, (x=0.0, 0.1, and 0.2), (b) Variation in ε , and (c) tan δ for undoped BiFeO₃ at various frequencies as a function of temperature. Doping Effect on the samples shown in the inset.

Dielectric analysis

The temperature dependence of the dielectric constant (ε) and dielectric loss (tanb) for BiFeO3 sample at different frequencies (10 kHz, 100 kHz and 1 MHz) is shown in Fig. **3(b)** and (c) respectively. The observed dielectric constant is found to increase with increase in temperature upto 380 °C and then it decreases with further increase in temperature for all the applied frequencies. This peak corresponds to an antiferromagnetic Neél temperature (T_N). The effect of La³⁺ doping is observed in the inset of **Fig.** 3(b), which indicates a decrease in T_N value from 380 to 330 °C at 1 MHz is in agreement with the explanation of thermal analysis. In this context a dielectric anomaly has been observed. This anomaly with the increase in temperature, obtained here may be ascribed to reflect the change in electric dipole order state from one to another because of antiferromagnetic transitions/possible magnetoelectric coupling effects which was predicted by the Landau-Devonshire theory of phase transition in magnetoelectrically ordered systems [25, 26]. However, this type of anomaly has not been observed in the dielectric loss for $Bi_{1,x}La_xFeO_3$ nanoparticles shown in Fig. 3(c),

indicating that the observed anomaly is not a cause of ferroelectric-paraelectric phase transition, but it arises due to a change of magnetic ordering in nanoparticles.

Magnetic analysis

Room temperature magnetic hysteresis plots of Bi1-_xLa_xFeO₃ nanoparticles are shown in **Fig. 4**. The magnetic moments of Fe³⁺ cations associated with ferromagnetically in pseudo cubic (111) planes and antiferromagnetically between adjacent planes, which are surrounded by six O^2 ions in the common vertex of two adjacent FeO₆ octahedral [27]. At an applied field of 10 kOe, undoped and La^{3+} doped BiFeO₃ nanoparticles show a weak ferromagnetic hysteresis loop because of the lattice strain-induced spin canting [28]. The regular Fe-Fe interaction in BiFeO₃ is clubbed with new magnetic interactions by adding small amounts of La³⁺ doping ions such as La-La and La-Fe. The disturbance introduced by these new magnetic interactions leads to a dramatic change in the M-H loops. It is observed that the enhanced hysteresis loop of nanoparticles with composition x = 0.2 exhibits larger magnetization over the other compositions. But the obtained curves of magnetization are not well saturated with the applied field. These unsaturated hysteresis loops and presence of small remnant magnetization reveals the of presence antiferromagnetic associated with weak ferromagnetism. Many possible conditions have been reported in the literature to increase the magnetization. This may be attributed to modification of the spin spiral structure into linear [29] caused by change in bond angle Fe-O-Fe in La³⁺ doped BFO nanoparticles associates with the large distortion due to the considerable ionic mismatches between Bi³⁺ ions and La³⁺ ions. The coupling between La-La and La-Fe may also lead to the higher values of the magnetization [30]. Additionally, La^{3+} doped BFO nanoparticles required charge compensation, which can be achieved by formation of Fe^{4+} or oxygen vacancies. If Fe^{4+} exists, the statistical distribution of Fe³⁺ and Fe⁴⁺ ion breaking down the balance between the antiparallel sublattice magnetization may also be a responsible for this phenomenon.

A magnified view of magnetic hysteresis loops is shown in the Fig. 4 (b)-(d). A ferromagnetic hysteresis loop with coercivity, 2Hc of 2.8 kOe and a remnant magnetization, 2 Mr of 0.135 emu/g at the maximum field of 10 kOe are observed in case of the undoped BFO nanoparticles. For x=0.1 coercivity increases to 3.5 kOe with decrease in remnant magnetization, 2 Mr 0.114 emu/g but further decrease to 3.2 kOe with the maximum increase in 2Mr to 0.271 emu/g for x= 0.2. The increase in the coercivity could be attributed to decrease in the particle size from 132 nm for x = 0.0 to 91.37 nm for x = 0.1 because of lattice strain-induced spin canting or ferromagnetism in nanoscale [28]. From the XRD analysis a structural transformation is evident for x = 0.2. This structure change could lead to fall in coercivity [31]. Other contributing factor towards the change in coercivity is anisotropy (magnetocrystalline anisotropy, magnetoelastic anisotropy, shape anisotropy). Out of these, contribution of shape anisotropy could be excluded because of the spherical nature of nanoparticles as evidenced form TEM. It is clear from the figures that there is a vertical as well as horizontal asymmetry in all the

samples which could be ascribed to the presence of exchange coupling between ferromagnetic surfaces and also, from the cores of antiferromagnetism [**32**].



Fig. 4. Magnetic loops of $Bi_{1-x}La_xFeO_3$ nanoparticles, (x=0.0, 0.1, and 0.2).

Optical analysis

FTIR spectra of Bi_{1-x}La_xFeO₃ nanoparticles are shown in Fig. 5(a) in the wave number range of 700–400 cm⁻¹. The characteristic peaks at 565 and 454 cm^{-1} in x= 0.0 is attributed to the overlapping of Fe-O bending and stretching mode in FeO₆ octrahedra and BiO₆ octahedral structure unit. The presence of this metal-oxide band directly indicates the formation of highly crystalline BiFeO₃ perovskite phase [33]. With the increase in La^{3+} content, peaks slightly shifted towards the lower wave number which can be attributed to two reasons. Firstly, the reduction in particle size with increased doping content leads to more surface area and grain boundaries [24]. Secondly, lattice strain relaxes with the presence of orthorhombic crystal symmetry fraction in samples [34]. The obtained results are consistent with the quantitative crystallographic phase of rietveld analysis. To look into the active site properties of the metal oxide surface, photoluminescence (PL) spectra for Bi_{1-x}La_xFeO₃ nanoparticles an excitation wavelength of 380 nm has been studied at room temperature. It is well known that, the undoped BiFeO₃ represented only one strong blue emission around 454 nm in the PL spectra which corresponds to the self-activated center. A blue emission nearly 488 nm is observed in the PL spectra of undoped BiFeO3 as shown in Fig. 5(b). The strong influence of La^{3+} doping in Bi₁₋ _xLa_xFeO₃ nanoparticles is evident from the shifting of the blue emission band towards lower wavelength. This shifting of peak from 488.02 to 481.95 nm wavelength could be ascribed to the increase in band gap due to the small crystalline size of La^{3+} doped samples [35]. Another high intensity peak is seen in the PL spectra, besides 488.02 nm wavelength. This green band emission around 528 nm can be attributed to the transition of $5p^6$ electrons in La³⁺. La³⁺ content in BiFeO₃ affect the green band emission by

shifting the position of the band towards lower wavelength in few nm.



Fig. 5. (a) FTIR spectra and (b) Photoluminescence spectra of $Bi_{1-x}La_xFeO_3$ nanoparticle, (x=0.0, 0.1 and 0.2).



Fig. 6. Optical absorption spectra of the $Bi_{1-x}La_xFeO_3$ nanoparticles (a) x=0.0 (b) x=0.1 (c) x=0.2 with band gap values shown in the inset and (d) Photodegradation efficiency of $Bi_{1-x}La_xFeO_3$ nanoparticles; (x=0.0 and 0.1) as a function of irradiation time.

Fig. 6(a)-(c) shows the UV-Vis absorption spectra of $Bi_{1-x}La_xFeO_3$ nanoparticles where the absorption cutoff wavelengths are seen at 638.58 nm, 627.82 nm and 513.061 nm respectively as shown in the inset of **Fig. 6(a)-(c)**. This decrease in cutoff wavelength indicates the disturbance in electronic structure of BiFeO₃ with the addition of La³⁺ ions and an obvious blue shift towards the lower wavelength due to the oxygen vacancies. The Optical band gap of the nanoparticles calculated using Tauc's relationship,

$$ahv = A(hv - E_g)^n \tag{2}$$

using $n = \frac{1}{2}$. The observed band gap values of the nanoparticles increases from 2.0450, 2.134 to 2.658 eV with increase in La³⁺ content from x=0.0 to 0.2 respectively. Therefore increase in the band gap of the samples, increases the efficiency of photo catalytic activity in Bi_{1-x}La_xFeO₃ nanoparticles [**36**]. To further investigate the photocatalytic properties of Bi_{1-x}La_xFeO₃ nanoparticles, azo-dye RB-5 with a major absorption peak at ~597±5nm

was chosen as a model organic pollutant for photocatalytic applications. The complex structure of RB-5 ((tetrasodium-4-amino-5-hydroxy-3, 6(bis (4- (2 sulfonatooxi) ethylsulfonyl) phenyl) azo) -naphthalene-2, 7-disulfonate)) is very hard to decompose as its intermediate bonds (--N=N--) absorb in the range of 200-400 nm. The photodegradation efficiency of azo-dye RB-5 at 597 nm was calculated with the following formula as a function of irradiation time in the normal environmental medium under visible light during the photodegradation process.

$$\eta = \frac{Ao - A}{Ao} \times 100\% \tag{3}$$

where, Ao is the absorbance of RB-5 solution before the illumination, A is the absorbance of RB-5 solutions in suspension after time t. With La^{3+} content in $Bi_{1-x}La_xFeO_3$ nanoparticles (x=0.1), approximately 27% higher degradation of the RB-5 is observed after 100 minutes, showing better photocatalytic activity than the undoped BiFeO₃ nanoparticles as shown in the inset of **Fig. 6(d)**.

Conclusion

In summary, the effects of La^{3+} doping on multiferroic, optical and photocatalytic properties have been investigated for various concentrations and compared with those of decrease undoped BiFeO₃. Considerable in antiferromagnetic Neél temperature (TN) from 380 to 330 $^{\circ}$ C is observed with increase in La³⁺ doping. La³⁺ ions decreased the mean particle size, while the energy band gap was found to be increased as calculated from absorption coefficient spectra. The undoped BiFeO₃ nanoparticles exhibited the less photocatalytic ability toward azo-dye RB-5 in visible-light but considerably enhanced photocatalytic activity was obtained by adding La³⁺ doping content in BiFeO₃ nanoparticles, which could be ascribed to the increased absorption of RB-5 on the catalyst surface. Thus we conclude that Bi_{1-x}La_xFeO₃ nanoparticles are "efficient photocatalytic semiconductor" for degradation of organic pollutants.

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