Structural, magnetic and photocatalytic characterization of $\text{Bi}_{1-x}\text{La}_x\text{FeO}_3$ nanoparticles synthesized by thermal decomposition method

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Abstract. Single-phase La-substituted bismuth ferrite ($\text{Bi}_{1-x}\text{La}_x\text{FeO}_3$) nanoparticles have been synthesized by thermal decomposition of a glyoxylate precursor. The crystal structure transition of BiFeO_3 from the rhombohedral ($R3c$) to the cubic $Pm\bar{3}m$ structure by La addition was confirmed by X-ray diffraction and infrared spectroscopy methods. Furthermore, the $\text{Bi}_{1-x}\text{La}_x\text{FeO}_3$ nanoparticles showed a weak ferrimagnetism behaviour, while the magnetization increased from 0.18 to 0.48 emu g^{-1} with La substitution. The $\text{Bi}_{1-x}\text{La}_x\text{FeO}_3$ nanoparticles exhibited strong absorption in the visible region with the optical band gap calculated from Tauc's plot in the range of 2.19–2.15 eV. Furthermore, the effects of La substitution on the photodegradation of the methylene blue (MB) under visible light were also studied. The photodegradation of MB dye was enhanced from 64 to ~99% with increasing La substitution from $x = 0$ to 0.1 and then decreased to 8% for $x = 0.15$.

Keywords. BiFeO_3 ; lanthanum; magnetic property; photocatalytic activity.

1. Introduction

Discharge of organic dyes used in textile, paper and rubber industries causes water pollution such as an increase in toxicity and chemical/biological oxygen demand, which leads to serious environmental problems [1]. Photocatalytic degradation is considered as an effective way for the removal of dye contaminants from water [2]. TiO_2 -based photocatalysts have been applied widely for the remediation of hazardous wastes, contaminated groundwater and toxic air [3]. However, the band gap of TiO_2 (3.0–3.2 eV for anatase) is so wide that it can absorb only ultraviolet (UV) light, which is only 5% in the sun source, and it leads to low light utilization efficiency [4]. Hence, another class of oxides such as ferrites with narrow band gap functioning in the visible light region has gained much interest in recent years as potential visible catalysts for different processes [5]. Among ferrites, bismuth ferrite (BiFeO_3) is an efficient visible-light photocatalyst for degradation of organic pollutants and water splitting applications, due to its narrow band gap energy (<2.8 eV) and excellent chemical stability [6]. Bismuth ferrite (BiFeO_3) with a rhombohedrally distorted perovskite structure (space group of $R3c$) is famous as a room-temperature single-phase multiferroic material. It is ferroelectric below the Curie temperature of 830°C and is antiferromagnetic with a Neel temperature of 370°C [7]. Bulk BiFeO_3 is G-type antiferromagnetic with a spin cycloid arrangement of 62 nm, which does not allow net magnetization [8]. However, BiFeO_3

exhibits a weak ferrimagnetic (FM) behaviour when the particle size is less than 62 nm or by suppression of spin cycloid arrangement due to doping of rare-earth or alkaline-earth elements in Bi-site [9,10]. Moreover, BiFeO_3 thin films are also a promising material for non-volatile memory devices and photovoltaic applications [11].

A variety of low-temperature chemical methods such as hydrothermal [12], coprecipitation [13], sol-gel [14], thermal decomposition [15], sonochemical [2] and microemulsion method [16] have been employed for synthesis of pure BiFeO_3 nanoparticles. Furthermore, strategies such as the surface modification [17] and composite with other semiconductors [18] etc. have been adopted to promote photocatalytic properties of BiFeO_3 nanoparticles. However, there are only a few reports on the influence of dopant-modified BiFeO_3 on the photocatalytic degradation of organic dyes [19]. On the other hand, the most effective way of improving the multiferroic properties of BiFeO_3 is lattice site substitution in BiFeO_3 with appropriate element/ion [20,21]. Doping at A-site of the BiFeO_3 with rare earth like Eu, La, Nd, Sm, Tb and Gd is one of the effective ways to eliminate the impurity phases and improve ferroelectric properties as well as to release the latent magnetization locked within the spiral spin structure [22–24]. Recently, Dhanalakshmi *et al* [23] and Sakar *et al* [24] observed an enhancement in photocatalytic behaviour by the substitution of La^{3+} and Dy^{3+} ions, respectively, in BiFeO_3 .

In this study, the structural, magnetic and photocatalytic properties of $\text{Bi}_{1-x}\text{La}_x\text{FeO}_3$ ($x = 0, 0.05, 0.1$ and 0.15) nanoparticles synthesized by thermal decomposition method have been investigated.

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2. Experimental

Analytical grade $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, ethylene glycol ($\text{OH}(\text{CH}_2)_2\text{OH}$) and nitric acid (68 wt%) were provided from Merk Co.

The precursor was prepared by dissolving $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in 100 mmol ethylene glycol and then added into 15 ml of 3 mol l^{-1} nitric acid solution containing $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ under magnetic stirring at 70°C . The molar ratio of ethylene glycol: NO_3^- was 2.5:1. On increasing the temperature up to 100°C , the redox reaction between the NO_3^- anions and the OH groups of the diol was initiated with the evolving of brown nitrogen oxides (NO_x) [25]. Finally, in order to obtain pure $\text{Bi}_{1-x}\text{La}_x\text{FeO}_3$ ($x = 0, 0.05, 0.1$ and 0.15) nanoparticles, the dried precursor was decomposed at 600°C for 1 h in air.

The phase evolution was investigated using an X'pert Pro prefix X-ray diffractometer with monochromatic $\text{CuK}\alpha$ radiation. The crystal structure, crystallite size and lattice parameters of the samples were evaluated by the Rietveld method using Highscore plus software. Infrared spectra were recorded on a Shimadzu-84005 system in the range of $400\text{--}700 \text{ cm}^{-1}$ using KBr pellets. The morphology and microstructure of the particles were observed by TESCAN Vega II field emission scanning electron microscopy (FESEM). A vibrating sample magnetometer (Meghnatis Daghigh Kavir Kashan Co., Iran) with maximum field of 12 kOe was employed to measure the magnetic properties of the samples at room temperature. The UV-vis absorption spectra were recorded on a Shimadzu UV-vis-52550 spectrophotometer with the wavelength range of $200\text{--}700 \text{ nm}$.

Photocatalytic activity of the synthesized $\text{Bi}_{1-x}\text{La}_x\text{FeO}_3$ nanoparticles was evaluated by the degradation of methylene blue (MB) in aqueous solution under visible light radiation. A 100 W Xenon lamp with ultraviolet filter was employed as

the visible light source. In each experiment, 0.1 g of photocatalyst was added into 100 ml MB solution with a concentration of 15 mg l^{-1} . Furthermore, pH of the solution was adjusted to 2 by adding HCl. The suspension was magnetically stirred in dark for 60 min to establish the adsorption/desorption equilibrium; then the solution was irradiated using visible radiation. At appropriate time intervals, about 5 ml of suspension was sampled and the solid phase was separated from the solution with centrifugation at 4000 rpm for 30 min. The change in the concentration of each degraded solution was monitored on a PG Instruments Ltd T80-UV/vis spectrophotometer.

3. Results and discussion

Figure 1 shows the X-ray diffraction (XRD) patterns of the $\text{Bi}_{1-x}\text{La}_x\text{FeO}_3$ ($x = 0, 0.05, 0.1$ and 0.15) nanoparticles synthesized by thermal decomposition method. The unsubstituted sample was composed of a mixture of BiFeO_3 and a few impurity $\text{Bi}_2\text{Fe}_4\text{O}_9$ phases. However, the impurity $\text{Bi}_2\text{Fe}_4\text{O}_9$ phase disappeared with La substitution in which the single-phase BiFeO_3 was formed. The elimination of impurity phase by La substitution can be attributed to the stabilization of the perovskite structure, because the rare earths typically exhibit a significantly higher bond enthalpy with oxygen than bismuth [26]. The bond energy of La-O is higher than that of Bi-O , which may lead to a reduction in the enthalpy and the free energy of formation ΔH_f and ΔG_f of La-substituted bismuth ferrite in comparison with the unsubstituted BiFeO_3 , making the former more stable [27]. $\text{Bi}_{0.95}\text{La}_{0.05}\text{FeO}_3$ and $\text{Bi}_{0.90}\text{La}_{0.10}\text{FeO}_3$ nanoparticles are crystallized in rhombohedrally distorted perovskite structure with $R3c$ space group. Furthermore, the peaks can also be indexed as (012), (104), (110), (202), (024), etc.,

Figure 1. XRD patterns of the $\text{Bi}_{1-x}\text{La}_x\text{FeO}_3$ nanoparticles as a function of lanthanum content. (Enlarged view of the (104) and (110) reflections ($\square$: $\text{Bi}_2\text{Fe}_4\text{O}_9$)).

Figure 2. XRD patterns and Rietveld refinement results of the Bi_{1-x}La_xFeO₃ ($x = 0.05, 0.1$ and 0.15) nanoparticles (I_{obs} showing observed intensity, I_{calc} showing calculated intensity and $I_{\text{obs}} - I_{\text{calc}}$ showing the residue).

Table 1. Crystallite size and structural parameters of Bi_{1-x}La_xFeO₃ nanoparticles.

Composition (x)	0	0.05	0.10	0.15
Crystallite size (nm)	67	68	39	24
Space group	R3c	R3c	R3c	R3c $Pm\bar{3}m$
$a = b$ (Å)	5.5820	5.5816	5.5815	5.5818
c (Å)	13.8789	13.8501	13.8220	13.7864
V (Å ³)	374.5	373.6	372.9	371.9
Fe–O (Å)	1.946	1.945	1.937	1.931
La/Bi–O (Å)	2.661	2.266	2.270	2.273
Fe–O–Fe (deg)	157.06	157.02	156.1	155.7
χ^2	1.3	1.4	1.7	1.5

which are characteristics of single-phase perovskite-type BiFeO₃ (JCPDS card no. 01-071-2494). However, the double split reflections like (104) and (110) are partially merged into a single peak with increasing of La additions, as shown in enlarged view of XRD pattern for $31^\circ < 2\theta < 33^\circ$. The other twin peaks, such as (006) and (202), (116) and (122) and (018) and (214), are also merged together to form a single peak. The gradual structural phase transition from the distorted rhombohedral R3c to cubic $Pm\bar{3}m$ resulted in the merging of the double splitting reflections [28].

The Rietveld refinement results of the Bi_{1-x}La_xFeO₃ ($x = 0.05, 0.1$ and 0.15) nanoparticles are presented in figure 2. The fitting qualities of the patterns, R_{exp} , R_{wp} and χ^2 , are about 17.4, 27.3 and 1.7%, respectively, showing a good refinement. Table 1 also gives the crystallite size and the structural parameters. The crystallite size decreases from 67 to 24 nm with increase of La³⁺ substitution. The bond energy of La–O is higher than that of Bi–O, which results in more activation energy for La³⁺ to enter Bi³⁺ sites, which suppresses the crystallization of bismuth ferrites [26]. On the basis of the best agreement between the observed and calculated XRD patterns, the structure of the BiFeO₃, Bi_{0.95}La_{0.05}FeO₃ and Bi_{0.90}La_{0.10}FeO₃ nanoparticles is rhombohedral with the R3c space group, while the cubic $Pm\bar{3}m$ structure should also be considered for the Bi_{0.85}La_{0.15}FeO₃ nanoparticle. The lattice parameters and unit cell volume decrease with an increase of La substitution, due to the smaller ionic radius of La³⁺ (1.03 Å) than that of Bi³⁺ (1.17 Å) [29]. The tolerance factor (t) of the perovskite (ABO₃) structure evaluates the degree of matching between A-site and B-site ions:

$$t = \frac{r_A + r_O}{\sqrt{2}(r_B + r_O)}, \quad (1)$$

where t is the tolerance factor, r_A and r_B are the average ionic radii of, respectively, the A and B sites and r_O is the oxygen ion radius. The La³⁺ substitution results in the reduction of the tolerance factor from 0.889 to 0.879, and in the increase of the octahedron tilting to relieve lattice strain, which stretched the Bi/La–O bond and compressed

Figure 3. (a) FTIR spectra of the Bi_{1-x}La_xFeO₃ ($x = 0.05, 0.1$ and 0.15) nanoparticles and (b) the deconvoluted spectra of the Bi_{0.90}La_{0.1}FeO₃ nanoparticles (+: experimental data).

Table 2. IR bands of $\text{Bi}_{1-x}\text{La}_x\text{FeO}_3$ nanoparticles.

Composition (x)	Assignment		
	E(TO8)	E(TO9)	A1(TO4)
0	449	547	573
0.05	445	543	574
0.1	443	549	575
0.15	441	555	579

the Fe–O bond (table 1). Consequently, the BiFeO_3 structure transforms from the rhombohedral $R3c$ to the cubic $Pm\bar{3}m$ structure when the distortion is beyond the limit of the rhombohedral structure [30].

FTIR spectra of the $\text{Bi}_{1-x}\text{La}_x\text{FeO}_3$ nanoparticles in the range of $400\text{--}700\text{ cm}^{-1}$ are shown in figure 3. The absorption band in the range of $440\text{--}450\text{ cm}^{-1}$ defined as transverse optic of E vibrational mode (E(TO8)) is attributed to the bending vibration of the O–Fe–O bond in the FeO_6

Figure 4. SEM micrograph of (a) BiFeO_3 , (b) $\text{Bi}_{0.95}\text{La}_{0.05}\text{FeO}_3$, (c) $\text{Bi}_{0.90}\text{La}_{0.10}\text{FeO}_3$ and (d) $\text{Bi}_{0.85}\text{La}_{0.15}\text{FeO}_3$ nanoparticles.

octahedral unit [31]. However, the most important as well as complex part of the spectra in the region from 480 to 680 cm⁻¹ was deconvoluted with the Gaussian type function. The spectra are resolved into two bands, E(TO9) and A₁(TO4) vibrational modes, as shown typically for the Bi_{0.90}La_{0.1}FeO₃ nanoparticles in figure 3b. The absorption band (A₁(TO4) mode) at 575 cm⁻¹ is assigned to the stretching vibration of the Fe–O bond in the FeO₆ octahedral unit, while the vibration mode (E(TO9) mode) of Bi/La–O bond in the Bi/LaO₆ octahedral unit resulted in the absorption band at around 550 cm⁻¹ [32]. A shift of the absorption bands to higher wavenumber can also be observed with the increasing of the La substitution (table 2), which can be attributed to the smaller atomic number of La³⁺ as compared with Bi³⁺. Moreover, the blue-shift indicates that the bending of Fe–O and Bi–O bonds has been increased on account of the distortion of the octahedron with the La substitution [33].

SEM images of the Bi_{1-x}La_xFeO₃ nanoparticles are shown in figure 4. The particles have quasi-spherical shapes.

Figure 5. Magnetization hysteresis loops of the Bi_{1-x}La_xFeO₃ nanoparticles.

The average particle size decreases from 130 to 75 nm and the particle size distribution becomes rather uniform with the increasing of La substitution. The particle size reduction may be attributed to the inhibiting of grain growth by smaller La³⁺ ions [34].

Figure 5 shows the room-temperature magnetization hysteresis loops for the Bi_{1-x}La_xFeO₃ nanoparticles as a function of composition. The BiFeO₃ nanoparticles exhibit a FM response with the magnetization of 0.18 emu g⁻¹ at 13 kOe. However, the magnetization increases up to 0.48 emu g⁻¹ with La addition. Bulk BiFeO₃ is known to show a G-type antiferromagnetic ordering with linear field dependence of magnetization, while the BiFeO₃ nanoparticles exhibit weak ferrimagnetism due to the interruption of the long-range antiferromagnetic order at the particle surface. Furthermore, the intrinsic spiral spin structure with the period length of ~62 nm is also partially suppressed for the nanoparticles smaller than ~62 nm, leading to the observed weak magnetization [8]. With the La substitution, the structural transition from rhombohedral to cubic structure can destroy the spin cycloid and release the latent magnetization locked within the cycloid by the uncompensated spins [10]. The more uncompensated spins from the surface also induce magnetization enhancement due to a high surface-to-volume ratio in the smaller-La-substituted nanoparticles. The larger magnetic contribution of La³⁺ ions compared with that of Bi³⁺ ions can also lead to an increase in the magnetization [35]. The FM behaviour of the samples can be exploited for magnetic separation of photocatalyst after degradation of the aqueous dye solution.

The UV-vis absorption spectra of the Bi_{1-x}La_xFeO₃ nanoparticles are shown in figure 6a. The Bi_{1-x}La_xFeO₃ nanoparticles can absorb considerable amounts of visible light, suggesting their potential applications as visible-light photocatalysts. The optical direct band gap, E_g , can be determined by the equation $(\alpha h\nu)^2 = A(h\nu - E_g)$, where $h\nu$ is the photon energy in eV, α is the absorption coefficient and A is a material-dependent constant [36]. The measured band gap of the Bi_{1-x}La_xFeO₃ nanoparticles is 2.19, 2.18, 2.16 and 2.15 eV for $x = 0, 0.05, 0.1$ and 0.15 , respectively (figure 7b). The direct band gap values are consistent with

Figure 6. (a) UV-vis absorption spectra and (b) Tauc's plots $((\alpha h\nu)^2$ vs. $h\nu$) of the Bi_{1-x}La_xFeO₃ nanoparticles.

those reported for BiFeO₃ nanostructures (1.8–2.5 eV), which are smaller than that of bulk or thin films (2.66–2.81 eV) [37]. The absorption band is attributed to the electronic transition from the valence band to conduction band ($O_{2p}^{2-} \rightarrow Fe_{3d}^{3+}$) in the bismuth ferrite lattice [38]. However, the La substitution effects on the Fe–O bond length (table 1), which in turn distorts the Fe–O octahedral structure and rearranges the molecular orbitals of BiFeO₃, leading to a negligible change in band gap. Furthermore, the blue-shifting of the absorption edges may come from the electronic transition from the dopant energy level to the energy bands of BiFeO₃ [39].

The UV–vis spectra of MB solution after different irradiation times in the presence of BiFeO₃ and Bi_{0.9}La_{0.1}FeO₃ nanoparticles are given in figure 7a and b, respectively. The main absorption peaks of MB molecules at 664 nm almost completely disappeared after about 90 min, suggesting the excellent photocatalytic activity of the Bi_{0.9}La_{0.1}FeO₃ nanoparticles. The photodegradation results of MB dye by Bi_{1-x}La_xFeO₃ nanoparticles as a function of irradiation time are summarized in figure 7c. A blank test is evaluated for MB and it exhibits very less photolysis (3%), which clearly shows that MB was hardly degraded without the catalyst upon irradiation. The MB degradation rates can reach about 64, 89 and ~99% for $x = 0, 0.05$ and 0.1 , respectively, indicating that the photodegradation of MB dye by Bi_{1-x}La_xFeO₃ photocatalysts increases with the increase of La³⁺ substitution. However, the improvement of the photocatalytic activity does not increase further for

more La substitution (80% for $x = 0.15$). Furthermore, the photodegradation rate constant of MB dye can be calculated by the modified Langmuir–Hinshelwood equation as below [40]:

$$\ln\left(\frac{C}{C_0}\right) = -kt, \quad (2)$$

where k (min⁻¹) could be obtained from the plot of $\ln(C/C_0)$ vs. the irradiation time. MB photodegradation follows the first-order reaction kinetics as shown in figure 7d. The values of rate constant are 0.0113, 0.0224, 0.0481 and 0.0161 min⁻¹ for $x = 0, 0.05, 0.1$ and 0.15 , respectively.

The photocatalytic performance depends strongly on the energy band configuration and the nature of surface/interface chemistry of Bi_{1-x}La_xFeO₃ nanoparticles. The slight reduction of band gap energy from 2.19 to 2.15 eV cannot be applied for explaining the higher photocatalytic efficiency of La-substituted BiFeO₃ nanoparticles.

It has been known that the contact between a semiconductor and another phase (i.e., liquid, gas or metal) generally involves a redistribution of electric charges and the formation of a double layer [41]. The semiconductor contains a uniform distribution of charge in the absence of a space-charge layer, while the existence of positive charges on the interface increases the majority carrier concentration of electrons near the surface within the region of the space-charge layer (figure 8). The electrons or holes in the space-charge region were separated to the surface and participated in the surface

Figure 7. UV–vis spectra of MB solution in the presence of (a) BiFeO₃ and (b) Bi_{0.9}La_{0.1}FeO₃, and (c) C/C_0 and (d) $\ln(C/C_0)$ vs. irradiation time for photodegradation of MB dye under visible light irradiation by the Bi_{1-x}La_xFeO₃ nanoparticles.

Figure 8. Space-charge layer formation and the photodegradation mechanism of MB.

reactions. The wider space-charge region results in the higher separated carriers and thus the higher photochemical activity. The width of the space-charge region is proportional to the Debye length L_D , which is a function of dielectric constant [42]:

$$L_D = \left(\frac{\epsilon_r \epsilon_0 k T}{e^2 N_D} \right)^{1/2},$$

where ϵ_0 is the permittivity of free space, ϵ_r is the dielectric constant of the material and N_D is the donor density. According to the above equation, we can see that an increase in the dielectric constant increases the Debye length and then the width of the space-charge region. The dielectric constant of the Bi_{1-x}La_xFeO₃ nanoparticles reaches the maximum value at the composition near $x = 0.1$, due to the structural transition from rhombohedral to cubic structure [33], which resulted in the wide space-charge region and hence the maximum photocatalytic activity for the Bi_{0.9}La_{0.1}FeO₃ nanoparticles. In other words, the wider space-charge region on Bi_{0.9}La_{0.1}FeO₃ nanoparticles reduced the probability of electron-hole recombination. The electron can react with molecular oxygen to produce $O_2^{\bullet-}$, which is a precursor for $OH^{\bullet}$ on protonation. Similarly, the holes can attract electrons from water and hydroxyl ions to generate $OH^{\bullet}$ through an oxidative process [43]. Bhardwaj *et al* [44] also investigated the composition dependence of photochemical activity of Ba_{1-x}Sr_xTiO₃. They observed a maximum in the photochemical reactivity at $x = 0.26$, which is near the tetragonal-cubic phase boundary, due to the anomalously high dielectric constant and hence the wider space-charge region. Furthermore, the reduction of particle size by La substitution (as shown in figure 4) can contribute to the photocatalytic enhancement.

In spite of the reduced photocatalytic performance for further La addition ($x = 0.15$), due to the decreasing of dielectric constant and then the narrow space-charge region

the photodegradation of MB dye in the presence of the Bi_{0.85}La_{0.15}FeO₃ nanoparticles is still higher than that of the unsubstituted BiFeO₃ nanoparticles, which may be due to the smaller particle size (figure 4) and hence the larger specific surface area and reactive sites [45].

4. Conclusions

Single-phase La-substituted bismuth ferrite (Bi_{1-x}La_xFeO₃) nanoparticles have been synthesized by thermal decomposition of a glyoxylate precursor. The crystal structure of BiFeO₃ transitioned from the rhombohedral (R3c) to the cubic $Pm\bar{3}m$ structure by La³⁺ substitution, as confirmed by X-ray diffraction and infrared spectrometry methods. Furthermore, the crystal distortion and the reduction of particle size increased the magnetization from 0.18 to 0.48 emu g⁻¹ with the increasing of La substitution. However, the optical band gap energy slightly decreased from 2.19 to 2.15 eV with La addition. The photodegradation of MB by Bi_{1-x}La_xFeO₃ nanoparticles enhanced from 64 to ~99% for $x = 0$ to 0.1, respectively, and then decreased to 8% for $x = 0.15$. The high photocatalytic efficiency for $x = 0.1$ may be attributed to an anomalously high dielectric constant at the rhombohedral-cubic phase boundary, which enlarged the space-charge region on the interface of the particle and solution and prevented the recombination of electrons and holes.

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