Sol-gel synthesis and characterisation of (Nd, Cr) co-doped BiFeO$_3$ nanoparticles

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**ABSTRACT**

Bi$_{0.95}$Nd$_{0.05}$Fe$_{1-x}$Cr$_x$O$_3$ ($x = 0, 0.01, 0.03, 0.05$) samples are synthesised by the sol-gel method. The variation in structure, magnetisation, electrical and photocatalytic properties by Cr doping at Fe site in Bi$_{0.95}$Nd$_{0.05}$FeO$_3$ samples is analysed. X-ray diffraction pattern confirms the formation of rhombohedral structure in all the samples. The crystallite size is calculated using the Scherrer relation and found to be in nanometre range. Kubelka-Munk theory is used to determine the direct band gap of the samples from reflectance spectra. The saturation magnetisation is found to enhance with the concentration of chromium. Arrott-Belov-Kouvel plot confirms the ferromagnetic nature in the samples. The leakage mechanisms are studied to understand the influence of Cr concentration on the BFO. A good correlation exists between the leakage current and ferroelectric behaviour. Photocatalytic tests show degradation of methylene blue dye in the presence of H$_2$O$_2$. A drastic decrease in photocatalytic activity is observed with the concentration of Cr.

**KEYWORDS**
sol-gel; magnetisation; ferroelectric; leakage current density; photocatalytic

1. Introduction

BiFeO$_3$ (BFO) is a single-phase multiferroic material which possesses both ferroelectric and antiferromagnetic ordering well above the room temperature.[1] Due to these unique properties, it has attracted a lot of interest in various fields such as storage, sensors and spintronic devices.[2] However, the practical applications of BFO are hindered by its low magnetisation due to G-type antiferromagnetic nature below Neel temperature and the existence of spiral spin cycloid structure of 62 nm, which cancels the net magnetisation.[3] The ferroelectric value of BFO is also very low when compared to many standard ferroelectric samples due to its high leakage behaviour. The high leakage in BFO is attributed to the presence of defects such as oxygen vacancies, multiple states of Fe (Fe$^{2+}$ and Fe$^{3+}$), Bi vacancy and the formation of the secondary phase during synthesis.[4] Different synthesis methods like solid state,[5] sol-gel,[6] hydrothermal,[7] soft-chemistry route,[8] etc., are employed for the formation of pure BFO. The structural distortion in BFO can be induced by applying high pressure [9] or by doping,[10] which in turn influences the multiferroic properties. In order to get an improved multiferroic properties in BFO, doping is
an easiest way. In BFO, the lone pair electrons in Bi and unfilled d-shells of Fe are responsible for the ferroelectricity and magnetisation, respectively.[11] The multiferroic properties can be enhanced by doping on A- or B-site or on both sites. Alkaline or lanthanide elements are usually preferred for A-site dopants and transition metals (Co, Ni, Mn, Cu, Zr, etc.) for B-site dopants.[12–15] Yin et al. synthesised (Ca, Mn) co-doped BFO samples by solid-state reaction and showed an enhancement in ferroelectric and magnetic properties with the concentration of Mn.[16] Raghavan et al. reported improved electrical and ferroelectric properties of (Nd, Cu) co-doped thin films synthesised by chemical solution deposition method.[17] Song et al. studied magnetic and leakage current properties of (Gd, Co) co-doped samples and observed low leakage current and enhanced magnetisation in co-doped samples compared to pure BFO.[18]

Apart from its multiferroic properties, BFO is also considered as a visible light photocatalyst due to its wide band gap energy (~2.0–2.8 eV) and good chemical stability.[19] Guo et al. reported an enhanced photocatalytic activity in Gd-doped BFO nanoparticles by degrading rhodamine B (RhB) under visible light illumination.[20] Di et al. synthesised BFO samples with different morphologies by hydrothermal method and decorated BFO particles with Ag. They showed an enhancement of RhB degradation by Ag-decorated BFO compared to undecorated BFO under simulated sunlight.[21] The potential use of BFO and doped BFO for the degradation of different organic dyes like methylene blue, methyl orange [23] and congo red [24] are reported. There are a few reports on the effect of co-dopant on the photocatalytic properties. In this line of research, Nd and Cr are chosen as A- and B-site dopants, respectively.

In this article, (Nd, Cr) co-doped BFO nanoparticles are synthesised by the sol-gel method. The effect of Cr co-doping on the structural, magnetic, leakage and ferroelectric properties are investigated. Further, the photocatalytic activity of the samples is tested by degrading the methylene blue dye under visible light.

2. Experimental section

For the synthesis of Bi_{0.95}Nd_{0.05}Fe_{1−x}Cr_{x}O_{3} (x = 0, 0.01, 0.03, 0.05) samples, the sol-gel method is adapted. The starting materials used for the synthesis are bismuth nitrate (Bi(NO₃)₃·5H₂O), iron nitrate (Fe(NO₃)₃·9H₂O), neodymium nitrate (Nd(NO₃)₃·6H₂O) and chromium nitrate (Cr(NO₃)₃·9H₂O). All precursors are purchased from Alfa Aesar (GR grade) and used without further purification.

The typical procedure for the synthesis is as follows: citric acid dissolved in double distilled water is used as solvent and the ratio of citric acid to metal nitrate is 1:1. Bismuth nitrate of 4 mmol is added to the solvent and a small amount of nitric acid is used to dissolve bismuth nitrate. Subsequently, neodymium nitrate, iron nitrate and chromium nitrate are taken in the stoichiometry ratio and added to the above mixture to obtain the compound in the desired ratio. Finally, ethylene glycol is added to the solution and the weight ratio of ethylene glycol to citric acid is 40:60. The solution is stirred at 90 °C for the formation of gel. The gel is then allowed to dry at the same temperature and grinded into the smooth powder. The obtained powder is annealed at 250 °C and 600 °C for 2 h and 4 h, respectively, for the formation of (Nd, Cr) co-doped BiFeO₃.

The samples are further characterised by X-ray diffractometer in the range of 20–80°, step of 0.02° and scan rate of 2° per min using Rigaku D/Max ULTIMA III with Cu-kα
anode ($\lambda = 1.54056$ Å). Transmission electron microscope (TEM) images are obtained using JEOL JEM 1200EX II at an operating voltage of 120 kV. Diffuse reflectance spectra (DRS) are measured by Jasco UV—vis—NIR spectrometer model V670 in the range of 200—1200 nm. Vibrating sample magnetometer (VSM) Lakeshore’s Model 7404 is used to measure the room temperature magnetisation. The ferroelectric and leakage current density studies are carried out using a Precision Radiant multiferroic tester. For ferroelectric and leakage current density studies powders are formed into pellets and silver paste is applied on both sides to make electrodes. Throughout this paper, the samples Bi$_{0.95}$Nd$_{0.05}$FeO$_3$, Bi$_{0.95}$Nd$_{0.05}$Fe$_{0.99}$Cr$_{0.01}$O$_3$, Bi$_{0.95}$Nd$_{0.05}$Fe$_{0.97}$Cr$_{0.03}$O$_3$ and Bi$_{0.95}$Nd$_{0.05}$Fe$_{0.95}$Cr$_{0.05}$O$_3$ are denoted as N5, N5C1, N5C3 and N5C5, respectively.

2.1. Photocatalytic test
The photocatalytic activities of the samples are tested by studying the degradation of methylene blue. It is done in an immersion well photochemical reactor having an inlet and outlet for cooling to avoid any thermal catalytic effect. High-pressure, 150-W mercury lamp is used as a visible light source. The volume of dye used for testing is 350 mL, the initial concentration of dye is 3.2 mg/L, the pH value of the dye is adjusted to 2.24 by adding nitric acid and catalyst concentration is 100 mg. In order to attain the adsorption and desorption equilibrium, the dye solution along with catalyst is stirred in the dark for 30 minutes. After illumination, 2 mL of dye solution is taken at the regular intervals to observe the concentration of the dye. The solution is centrifuged and absorption spectra are recorded using Shimazdu UV—vis spectrometer (Model 1700). The degradation is calculated using the relation $C_t/C_0$, where $C_0$, $C_t$ is the concentration at zero minute and a time ‘$t$’, respectively, and the percentage of degradation efficiency is evaluated by $(1 - C_t/C_0) \times 100$.

3. Results and discussion
X-ray diffraction (XRD) pattern of all the samples are shown in Figure 1. The diffraction pattern confirms the formation of rhombohedral structure with space group R3c indexed using JCPDS card no. 86-1518. A small impurity peak around 28° denotes the presence of secondary phase like Bi$_2$Fe$_4$O$_9$ or Bi$_2$O$_3$ and is indicated by * in the graph. The formation of secondary phase in BFO is due to the kinetics of BFO formation in a narrow temperature region.[25] The average crystallite size of the samples calculated using Scherrer equation from the peaks (012), (104), (110), (006), (202) and (024) is presented in Table 1. There is no noticeable change observed in the crystallite size with the doping. The lattice parameters are estimated using the geometrical relation of hexagonal crystal structure [26]

$$\frac{1}{d^2} = \frac{4}{3} \left( \frac{h^2 + hk + k^2}{a^2} \right) + \frac{P^2}{c^2}$$

where $h$, $k$ and $l$ are Miller indices, $d$ is the interplanar distance and $a$, $c$ are lattice parameters.

The change in the lattice parameters is not uniform with varying values of Cr concentration.
TEM images of N5C5 sample at two different scales are shown in Figure 2(a,b). From the images, it can be concluded that the particles are irregular in shape without any definite morphology. The agglomeration of particles with various degrees is observed. The particle size distribution of N5C5 sample is shown in Figure 2(c). The maximum number of particles is found in the range of 20–60 nm.

The diffused reflectance spectra of the samples are taken in the UV–visible–NIR region and converted to absorption spectra using Kubelka-Munk theory as shown in Figure 3. There are five bands observed in this region. The bands at 250 and 380 nm correspond to charge-transfer (C-T) from O$^{2-}$ to Bi$^{3+}$. In the same way, the band around 480 nm is attributed C-T from O$^{2-}$ to Fe$^{3+}$. The band around 675 nm and broad band centred at 900 nm are assigned to d-d transitions in Fe.[27] The direct band gap of the samples is calculated using Kubelka-Munk function by plotting $[F(R)h\nu]^2$ as a function of energy.[28] The band gap is estimated by extrapolating the band tail to x-axis where y is zero and is found to be 2.12, 2.17, 2.07, 1.98 eV for N5, N5C1, N5C3 and N5C5 samples, respectively. Initially the band gap increases with 1% Cr and later it decreases for 3% and 5% Cr. The variation in the band gap is due to the different levels of defects present in the sample. The defects are lowered with 1% Cr and increase with 3% and 5% doping concentration (which is supported from leakage current density measurements).

![Figure 1. X-ray diffraction patterns of (a) N5, (b) N5C1, (c) N5C3 and (d) N5C5 samples.](image)

| Code   | Crystallite size (nm) | Lattice parameters |                  |
|--------|-----------------------|--------------------|------------------|
|        |                       | $a = b$ (Å)        | $c$ (Å)          |
| N5     | 36                    | 5.5685             | 13.8178          |
| N5C1   | 33                    | 5.5866             | 13.9269          |
| N5C3   | 35                    | 5.5769             | 13.8885          |
| N5C5   | 34                    | 5.5679             | 13.8054          |

Table 1. Crystallite size and lattice parameters of Bi$_{0.95}$Nd$_{0.05}$Fe$_{1-x}$Cr$_x$O$_3$ ($x = 0, 0.01, 0.03$ and $0.05$) samples.
The room temperature magnetisation of the samples measured in the field range of ±15,000 Oe is shown in Figure 4. It is clearly seen from the plot that with the concentration of Cr that the saturation magnetisation increases and coercivity decreases. Usually we do not observe a saturated magnetisation in BFO due to the G-type antiferromagnetic nature and the existence of spiral spin cycloid structure of 62 nm.[3] In the present case, the observation of S-type curve and enhancement of magnetisation might be due to destruction (or suppression) of spin cycloid as the particle size is less than 62 nm [2,29] and enhanced interaction between the ions in B site. The decrease in coercivity with concentration of Cr is due to reduced magnetocrystalline anisotropy and magnetoelastic energy.[30] The shape factor can be neglected, as the magnetisation is smaller than standard ferromagnets.[31] In order to confirm the ferromagnetic or antiferromagnetic behaviour, Arrott-Belov-Kouvel (ABK) plot [32] of N5 sample is shown in the inset of Figure 4. If the plot is concave it represents antiferromagnetic nature and the ferromagnetic behaviour is given by convex shape. The convex nature for N5 sample confirms the observed behaviour is ferromagnetic in nature (all other samples show convex nature).

The leakage current density ($J$) versus applied electric field ($E$) at room temperature for all the samples is shown in Figure 5(a). For N5 sample, the leakage current density is $10^{-6}$ Amp/cm$^2$ at 30 kV/cm. With the increase in Cr concentration, the change in leakage

![Figure 2. (a,b) TEM images of N5C5 sample and (c) particle size distribution.](image-url)
current density does not vary uniformly, but it varies inversely to band gap value. The conduction in the BFO samples is due to defects like oxygen vacancies or partial transfer of Fe$^{3+}$ to Fe$^{2+}$.[33] When an electric field is applied, these defects act as trap for electrons and enhance the conductivity.[4] Based on the vacancies type, different conduction mechanisms dominate.

**Figure 3.** Diffused reflectance spectra of Bi$_{0.95}$Nd$_{0.05}$Fe$_{1-x}$Cr$_x$O$_3$ ($x = 0, 0.01, 0.03$ and $0.05$) samples. (Inset shows band gap of the samples.)

**Figure 4.** Room temperature $M-H$ curves of Bi$_{0.95}$Nd$_{0.05}$Fe$_{1-x}$Cr$_x$O$_3$ ($x = 0, 0.01, 0.03$ and $0.05$) samples.
For understanding, the conduction mechanism $\log J$ as a function of $\log E$ is plotted and shown in Figure 5(b). Based on the value of slope obtained from the graph, the type of the conduction can be decided. The conduction is Ohmic for slope $\sim 1$ and it changes to space charge limited conduction (SCLC) for value approximately equal to 2. When the value is greater than 2, the conduction is due to other mechanisms like Poole-Frenkel or Schottky.\[34\] In the present case, a slope value of 1.09 is obtained for N5 sample in the entire region of measurement. It clearly denotes the presence of Ohmic conduction. By co-doping Cr, the conduction changes from the Ohmic to other mechanisms that are clearly seen from the deviation of straight line. When the concentration of Cr is 1%, two different slopes are observed in the region of low and high electric fields. At low electric fields, the slope is 0.91 and it corresponds to the grain boundary effect,\[35\] whereas at high electric fields, the slope is 1.24, which means conduction is a mixture of Ohmic and SCLC. For Cr 3% and 5% co-doping three different slopes are noticed. For 3% Cr co-doped sample, the conduction changes from grain boundary limited current (slope 0.55) to combination of Ohmic and SCLC (slope 1.36) and finally to SCLC (slope 2.16). Similarly, for 5% co-doped sample the slopes are 1.22, 1.54 and 2.04 at low, intermediate and high electric fields, respectively. With an increase in the electric field, the conduction changes from Ohmic to mixture of Ohmic and SCLC and at higher electric fields, the conduction mechanism completely switches to SCLC. SCLC conduction involves deep traps which are created by oxygen vacancies in the band gap to mobilise the activated electrons.\[36\] This confirms that the defects varied with the concentration of Cr and have an effect on conducting nature of the samples. The irregular trend in leakage current density is attributed to the different concentration of defects introduced in the system with Cr concentration.

Ferroelectric measurements carried out at room temperature at a frequency of 100 Hz are shown in Figure 6. All the samples show ferroelectric behaviour at different electric fields. The maximum polarisation ($P_{\text{max}}$) at an applied electric field of 32 kV/cm is found to be 0.27, 0.21, 0.29 and 0.43 $\mu$C/cm$^2$ for N5, N5C1, N5C3 and N5C5 samples, respectively. The changes in $P_{\text{max}}$ value are similar to variation in leakage current density. The increase in polarisation in the N5C5 sample can be related to increase in conductivity.

![Figure 5. (a) Leakage current density ($J$) as a function of electric field ($E$). (b) Log $J$ versus log $E$ for Bi$_{0.95}$Nd$_{0.05}$Fe$_{1-x}$Cr$_x$O$_3$ ($x = 0, 0.01, 0.03$ and $0.05$) samples.](image-url)
which is observed from the leakage current density measurements and vice versa for N5C1 sample. The change in coercivity with respect to Cr concentration is attributed to the different mixture of defect density in the samples.\textsuperscript{[37]} The overall contribution to coercivity observed experimentally is given by the relation $E_c = E'_c - E_{sc} + E_{\text{defect}}$, where $'E_c'$ is the internal coercivity of the domains, $'E_{sc}'$ is coercivity due to the space charge and $'E_{\text{defect}}'$ is due to bulk dipolar defect coercivity present in the sample.\textsuperscript{[38]} When compared to other samples, N5C5 samples show large coercivity due to the conducting nature arising from the defects. The low conducting nature of the N5C1 sample implies the presence of less number of defects; this reduces the contribution of defect coercivity and leads to low coercivity. Thus, the change in coercivity is mainly attributed to the defects present in the sample. The correlation of the leakage current density and ferroelectricity provides crucial information in the analysis of change in ferroelectric nature of the samples. Even though there are other effects which contribute to polarisation or coercivity, their role might be small.

Photocatalytic tests are carried out by the degradation of organic dye methylene blue (MB) at pH value 2.24 and with the addition of 0.5 mL H$_2$O$_2$ under visible light. The photocatalytic degradation performed under these conditions for all the samples is shown in Figure 7. The photolysis carried out under the similar conditions (in the presence of H$_2$O$_2$ and without catalyst) shows the degradation of MB is only 7%
The degradation of dye under visible light involves the excitation of dye (Equation (2)) and the electron transfer from excited dye molecule to Fe$^{3+}$ ion which reduces it to Fe$^{2+}$ (Equation (3)). The generated Fe$^{2+}$ reacts with H$_2$O$_2$ and form •OH radicals (Equation (4)) which will further react with MB to degrade it (Eq. (5)).

When the concentration of Cr is 1%, the degradation efficiency of MB drops to 50% compared to Nd5 sample and efficiency further reduces with the concentration of Cr. 

(Figure 7). After 90 minutes of illumination the degradation efficiency of MB is found to be 86%, 42%, 28% and 24% for N5, N5C1, N5C3 and N5C5 samples, respectively. Therefore, the photolysis plays a minimum role in the degrading the dye and hence the degradation is mainly attributed to the presence of catalyst. The mechanism for the degradation of the MB is a photo-Fenton type process [37] and an increase in separation of photo-generated charge carriers with the addition of H$_2$O$_2$, as H$_2$O$_2$ acts as a scavenger of electrons. The possible photo-Fenton process under visible light is as follows [39,40]:

\[
\begin{align*}
MB + h\nu &\rightarrow MB^+ \\
MB^+ + Fe^{3+} &\rightarrow MB^+ + Fe^{2+} \\
Fe^{2+} + H_2O_2 &\rightarrow Fe^{3+} + •OH + OH^- \\
MB^+ + •OH &\rightarrow \text{degraded or mineralised products}
\end{align*}
\]
reason for decrease in efficiency with the concentration of Cr can be explained as follows [41]:

\[
\text{Sample} + h\nu \rightarrow e_{cb}^- + h_{vb}^+
\]  

(6)

\[
\text{Cr}^{3+} + h_{vb}^+ \rightarrow \text{Cr}^{4+}
\]

(7)

\[
\text{Cr}^{4+} + \text{OH}^- (\text{ads}) \rightarrow \text{Cr}^{3+} + \bullet \text{OH}
\]

(8)

\[
\text{Cr}^{4+} + e^- \rightarrow \text{Cr}^{3+}
\]

(9)

When light illuminates on sample there will be photogeneration of electrons \((e^-)\) and holes \((h^+)\). The photogenerated holes can react with \(\text{Cr}^{3+}\) and form \(\text{Cr}^{4+}\) (Eq. 7). The \(\text{Cr}^{4+}\) can react with hydroxyl ion and generates \(\text{Cr}^{3+}\) and \(\bullet \text{OH}\) radical (Eq. 8) which will help in the enhancement of photocatalytic degradation of dye. If \(\text{Cr}^{4+}\) or trapped holes react with \(e^-\) (Eq. 9), there will be a recombination of electron and hole which is undesirable for the photocatalytic activity. In the present case, the re-combination of electron and hole dominates when compared to generation of \(\bullet \text{OH}\) radicals, because of this the degradation efficiency decreases with the concentration of Cr. Hence, a very minimum amount of Cr doping favours the photocatalytic activity when compared to high doping of Cr. In our case, even a low concentration (less than 1%) is needed for enhancing the photocatalytic activity.

4. Conclusions

Nd and Cr co-doped BiFeO3 samples are synthesised by sol-gel method. From X-ray diffraction analysis, the crystallite size of the samples is found to be in the nanometre range and the dimensionality is further confirmed using TEM. DRS confirm the bands corresponding to charge transfer and d-d transitions in UV and visible region. The variation in the band gap observed with concentration of Cr is attributed to the change in defect density. The enhancement in saturation magnetisation is due to the enhanced interaction between B-B site ions. The conduction mechanism changes from Ohmic to SCLC with the concentration of Cr. Samples with Cr 5% show high leakage current density and maximum polarisation when compared to other samples. The change in the ferroelectric nature with the concentration of Cr is attributed to the variation of defect density, which is related to the enhancement/decrement of the leakage current. Photo-Fenton type of reaction is responsible for the degradation of the methylene blue dye and the rate of recombination in Cr co-doped samples mainly depends on concentration of Cr which adverse the photocatalytic activity.

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Disclosure statement

No potential conflict of interest was reported by the authors.
References

[1] Lee J-H, Oak M-A, Choi HJ, et al. Rhombohedral-orthorhombic morphotropic phase boundary in BiFeO₃-based multiferroics: first-principles prediction. J Mater Chem. 2012;22:1667–1672.

[2] Park T-J, Papaefthymiou GC, Viescas AJ, et al. Size-dependent magnetic properties of single-crystalline multiferroic BiFeO₃ nanoparticles. Nano Lett. 2007;7:766–772.

[3] Hussain S, Khurshid Hasanain S, Hassnain Jaffari G, et al. Size and lone pair effects on the multiferroic properties of Bi₀.75A₀.25FeO₃₋₋₅ (A = Sr, Pb, and Ba) ceramics. J Am Ceram Soc. 2013;96:3141–3148.

[4] Dai H, Chen Z, Xue R, et al. Structural and electric properties of polycrystalline Bi₁₋₋ₓErₓFeO₃ ceramics. Ceram Int. 2013;39:5373–5378.

[5] Valant M, Axelsson A-K, Alford N. Peculiarities of a solid-state synthesis of multiferroic polycrystalline BiFeO₃. Chem Mater. 2007;19:5431–5436.

[6] Jiang Q-H, Nan C-W, Wang Y, et al. Synthesis and properties of BiFeO₃ ceramics. J Electro Ceram. 2008;21:690–693.

[7] Yang X, Xu G, Ren Z, et al. The hydrothermal synthesis and formation mechanism of single-crystalline perovskite BiFeO₃ microplates with dominant (012) facets. Cryst Eng Comm. 2014;16:4176–4182.

[8] Yang H, Xian T, Wei ZQ, et al. Size-controlled synthesis of BiFeO₃ nanoparticles by a soft-chemistry route. J Sol-Gel Sci Technol. 2011;58:238–243.

[9] Gavriluk AG, Struzhkin V, Lyubutin ISe, et al. Phase transition with suppression of magnetism in BiFeO₃ at high pressure. J Exp Theor Phys Lett. 2005;82:224–227.

[10] Yang C-H, Kan D, Takeuchi I, et al. Doping BiFeO₃ approaches and enhanced functionality. Phys Chem Chem Phys. 2012;14:15953–15962.

[11] Singh A, Pandey V, Kotnala R, et al. Direct evidence for multiferroic magnetoelectric coupling in 0.9BiFeO₃–0.1BaTiO₃. Phys Rev Lett. 2008;101:247602.

[12] Lan G, Jiang Y, Yang S. Magnetic properties of La and (La, Zr) doped BiFeO₃ ceramics. J Mater Sci. 2011;46:734–738.

[13] Chakrabarti K, Das K, Sarkar B, et al. Enhanced magnetic and dielectric properties of Eu and Co co-doped BiFeO₃ nanoparticles. Appl Phys Lett. 2012;101:042401.

[14] Naganuma H, Miura J, Okamura S. Ferroelectric, electrical and magnetic properties of Cr, Mn, Co, Ni, Cu added polycrystalline BiFeO₃ films. Appl Phys Lett. 2008;93:052901–052903.

[15] Bellakki M, Manivannan V. Citrate-gel synthesis and characterization of yttrium-doped multiferroic BiFeO₃. J Sol-Gel Sci Technol. 2010;53:184–192.

[16] Yin LH, Sun YP, Zhang FH, et al. Magnetic and electrical properties of Bi₀.₆Ca₀.₄Fe₁₋₋ₓMnₓO₃ (0 ≤ x ≤ 0.₅). J Alloys Compd. 2009;488:254–259.

[17] Raghavan CM, Kim JW, Kim SS. Structural and ferroelectric properties of chemical solution deposited (Nd, Cu) co-doped BiFeO₃ thin film. Ceram Int. 2013;39:3563–3568.

[18] Song GL, Su J, Ma GJ, et al. Effects of trivalent gadolinium and cobalt co-substitution on the crystal structure, electronic transport, and ferromagnetic properties of bismuth ferrite. Mater Sci Semicond Process. 2014;27:899–908.

[19] Li S, Lin Y-H, Zhang B-P, et al. Photocatalytic and magnetic behaviors observed in nanostructured BiFeO₃ particles. J Appl Phys. 2009;105:2903–2908.

[20] Guo R, Fang L, Dong W, et al. Enhanced photocatalytic activity and ferromagnetism in Gd doped BiFeO₃ nanoparticles. J Phys Chem C. 2010;114:21390–21396.
[21] Di LJ, Yang H, Hu G, et al. Enhanced photocatalytic activity of BiFeO$_3$ particles by surface decoration with Ag nanoparticles. J Mater Sci: Mater Electron. 2014;25:2463-2469.

[22] Huo Y, Jin Y, Zhang Y. Citric acid assisted solvothermal synthesis of BiFeO$_3$ microspheres with high visible-light photocatalytic activity. J Mol Catal A: Chem. 2010;331:15-20.

[23] Liu Z, Qi Y, Lu C. High efficient ultraviolet photocatalytic activity of BiFeO$_3$ nanoparticles synthesized by a chemical coprecipitation process. J Mater Sci: Mater Electron. 2010;21:380-384.

[24] Xu X, Lin Y-H, Li P, et al. Synthesis and photocatalytic behaviors of high surface area BiFeO$_3$ thin films. J Am Ceram Soc. 2011;94:2296-2299.

[25] Qian FZ, Jiang JS, Guo SZ, et al. Multiferroic properties of Bi$_{1-x}$Dy$_x$FeO$_3$ nanoparticles. J Appl Phys. 2009;106(8):084312.

[26] Cullity B. Elements of X-ray diffraction. Reading, MA: Addison-Wesley; 1978.

[27] Blessington Selvadurai AP, Pazhanivelu V, Murugaraj R. Structural, magnetic, optical and electrical properties of Ba substituted BiFeO$_3$. J Supercond Nov Magn. 2014;27:839-844.

[28] Morales AE, Mora ES, Pal U. Use of diffuse reflectance spectroscopy for optical characterization of un-supported nanostructures. Rev Mex Fis S. 2007;53:18.

[29] Dhir G, Lotey G, Uniyal P, et al. Size-dependent magnetic and dielectric properties of Tb-doped BiFeO$_3$ nanoparticles. J Mater Sci: Mater Electron. 2013;24:4386-4392.

[30] Dhir G, Uniyal P, Verma N. Effect of particle size on multiferroism of barium-doped bismuth ferrite nanoparticles. Mater Sci Semicond Process. 2014;27:611-618.

[31] Arya GS, Negi NS. Effect of In and Mn co-doping on structural, magnetic and dielectric properties of BiFeO$_3$ nanoparticles. J Phys D: Appl Phys. 2013;46:095004.

[32] Mandal S, Nath T, Karmakar D. Magnetic and optical properties of Zn$_{1-x}$Fe$_x$O ($x=0.05$ and $0.10$) diluted magnetic semiconducting nanoparticles. Philos Mag. 2008;88:265-275.

[33] Yuan GL, Or SW. Enhanced piezoelectric and pyroelectric effects in single-phase multiferroic Bi$_{1-x}$Nd$_x$FeO$_3$($x=0-0.15$) ceramics. Appl Phys Lett. 2006;88:062905.

[34] Makhdoom AR, Akhtar MJ, Rafiq MA, et al. Investigation of transport behavior in Ba doped BiFeO$_3$. Ceram Int. 2012;38:3829-3834.

[35] Chung C-F, Lin J-P, Wu J-M. Influence of Mn and Nb dopants on electric properties of chemical-solution-deposited BiFeO$_3$ films. Appl Phys Lett. 2006;88:242909.

[36] Qi X, Dho J, Tomov R, et al. Greatly reduced leakage current and conduction mechanism in aloivalent-ion-doped BiFeO$_3$. Appl Phys Lett. 2005;86:062903.

[37] Rajput SS, Katoch R, Sahoo KK, et al. Enhanced electrical insulation and ferroelectricity in La and Ni co-doped BiFeO$_3$ thin films. J Alloys Compd. 2015;621:339-344.

[38] Kim S, Gopalan V, Gruverman A. Coercive fields in ferroelectrics: A case study in lithium niobate and lithium tantalate. Appl Phys Lett. 2002;80:2740-2742.

[39] Wu K, Xie Y, Zhao J, et al. Photo-Fenton degradation of a dye under visible irradiation. J Mol Catal A: Chem. 1999;144:77-84.

[40] Vanga PR, Mangalaraja RV, Ashok M. Effect of (Nd, Ni) co-doped on the multiferroic and photocatalytic properties of BiFeO$_3$. Mater Res Bull. 2015;72:299-305.

[41] Zhu J, Deng Z, Chen F, et al. Hydrothermal doping method for preparation of Cr$^{3+}$-TiO$_2$ photocatalysts with concentration gradient distribution of Cr$^{3+}$. Appl Catal B: Environ. 2006;62:329-335.