Effect of Fe and Bi doping on LaCoO$_3$ structural, magnetic, electric and catalytic properties

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**A B S T R A C T**

La$_{1.3}$Bi$_{0.75}$Co$_{1.3}$Fe$_{0.25}$O$_3$ perovskite was prepared by micro-emulsion method and effect of the Fe and Bi doping on the properties of perovskite was investigated. As-prepared perovskite was characterized by X-ray diffraction (XRD), Raman spectroscopy, Fourier transform infrared spectroscopy (FTIR), scanning electron microscope (SEM), Energy-dispersive X-ray (EDX) and atomic force microscopy (AFM) techniques. La$_{1.3}$Bi$_{0.75}$Co$_{1.3}$Fe$_{0.25}$O$_3$ perovskite showed distorted rhombohedral structure and particle size was in the range of 33.05-57.41 nm. Doping of perovskite with Bi and Fe enhanced the direct current (DC) resistivity. Dielectric parameters were studied in the range of 20 to 20 MHz and vibrating magnetometry revealed that the $\mu_r$ and $\varepsilon_r$ values were higher for La$_{0.75}$Bi$_{0.25}$Co$_{0.75}$Fe$_{0.25}$O$_3$, whereas LaCoO$_3$ showed higher value of $\varepsilon_r$. Photocatalytic activity (PCA) was evaluated by degrading congo red dye and Bi and Fe doped perovskite showed significantly higher activity versus LaCoO$_3$. Results revealed that the doping of LaCoO$_3$ with Bi and Fe enhanced the magnetic, dielectric and catalytic properties of LaCoO$_3$.

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1. Introduction

Nanotechnology has attained much attention due to versatile applications such as disease diagnostics, therapeutic purposes, photocatalysis, energy, environment and storage appliances. At nano-scale material exhibits ideal properties such as optical behavior, mechanical properties, high surface area to volume ratio and electrical behavior in comparison to bulk materials [1–8]. The nanoparticles based on transition metal oxides have been explored extensively and employed in different fields [9]. Perovskites [10,11] are the metal oxides represented by common formula ABO₃ [12]. Where ‘A’ represents the cation belongs to d or s block elements and B represents the small size cation of transition metals. In ABO₃ lattice, each B is located at the corner of octahedron and has octahedral coordination with oxygen as BO₆ and ‘A’ presents center of the whole body of BO₆ [13]. The perovskites are important due to their attractive optical, photochemical, ferroelectric and conducting properties [14]. The word perovskite was first used for a mineral “CaTiO₃” and Russian geologist, Count Lev Alexevich Perovski was the discoverer. The most abundant perovskite present on earth is MsiO₃ (M = Mg and Fe) [15]. The properties of the perovskites such as redox potential, geometry, catalytic activity can be changed by the replacement of A and B position in the perovskites [16].

LaCoO₃ is a fascinating materials due to its good oxidation power, thermal stability [17], super conductivity and excellent catalytic activity [18]. At low temperature, it behaves as diamagnetic and at 100 °C or above, it shows paramagnetic property due to transition in spin [19]. It has rhombohedral geometry [20] with symmetry R-3C [21] and possess applications in different fields such as energy generation, catalysis, environment, sensors [22,23], and photocatalysis [24]. The LaCoO₃ has been used as a catalyst for the removal of soot of diesel engine [25]. LaCoO₃ exhibit excellent efficiency to convert carbon monoxide to carbon dioxide even at low temperature and has been used as sensor to prevent outburst and CO leakage detection [26]. To date, perovskites are used as a photocatalyst for degradation of pollutants and generation of energy [27]. Fu et al. [28] studied the photocatalytic activity of LaCoO₃ for the degradation of neutral-red, methyl orange and methylene blue under solar light irradiation. Various methods have been adopted for the fabrication of LaCoO₃ particles, i.e., sol-gel technique, thermal decomposition [29], reflux process, co-precipitation, microwave [30] and milling [31].

In present investigation, La₁₋ₓBiₓCo₁₋ₙFe₂O₃ was prepared by micro-emulsion method and characterized by advanced techniques. Effect of Fe and Bi ions was studied on the basis of structural, magnetic, electric and catalytic properties. The photocatalytic activity (PCA) was evaluated by degrading the congo red dye under solar light irradiation.

2. Material and methods

2.1. Chemicals and reagents

All the chemicals i.e., cobalt nitrate (Co(NO₃)₂ 6H₂O, Merck, 98%), lanthanum nitrate (La(NO₃)₃ 6H₂O, Fisher, 99%), iron nitrate (Fe (NO₃)₃ 9H₂O, analar BDH, 98%), bismuth nitrate (Bi(NO₃)₃ 5H₂O, BDH, 98%), cetyltrimethylammonium-niubromide, CTAB (C₁₄H₂₉N(CH₃)₃Br, Amresco, 98%), ammonium hydroxide (NH₄OH, Merck, 32%) were of analytical grade and used as received. All the solutions were prepared in deionized water having resistivity 18.2 MΩ cm.

2.2. Fabrication of La₁₋ₓBiₓCo₁₋ₙFe₂O₃

For the fabrication of La₁₋ₓBiₓCo₁₋ₙFe₂O₃, stoichiometric amount of the metal precursors were mixed and heated at 50 °C. Then, CTAB solution was added and pH was adjusted to 10–11 using 2 M ammonia hydroxide solution. The mixture was stirred for 5 h at room temperature. The precipitates thus obtained were washed with distilled water to neutral pH. The drying was done at 80 °C followed by annealing at 950 °C (heating rate 10 °C/min) for 9 h in muffle furnace (Vulcan A-550). The powder was stored in air tight clean glass vials and subjected to characterization and PCA study.

2.3. Characterization

Crystal structure of La₁₋ₓBiₓCo₁₋ₙFe₂O₃ was determined by XRD analysis (Phillips-X pert PRO 3040/60 X-Ray Diffractometer) in 2θ range of 20–80° using CuKα as radiation source with wavelength 1.542 Å. Nexus 470 spectrophotometer was used for FTIR analysis. S-3400 scanning electron microscope (SEM) was used for morphology study. Raman spectra was recorded through T-6400 triple jobin Yvon-Atago/Bussan spectrometer in the range of 100 to 700 cm⁻¹ using excitation wavelength of 51.4 Å at 298 K having a N₂(l) cooled CCD detector. AFM analysis was done by A Nanoscope®V multimode setup equipped by Si tips in tapping mode. For dielectric measurement, 4287A RF LCR meter was used. Current voltage was measured by Kiethly-2400 m. VSM was recorded on Lakeshore-74071 vibrating sample magnetometer at room temperature. Dual beam Cary 60 (Agilent) spectrophotometer was used for UV–vis spectra and absorbance monitoring.

2.4. Photocatalytic activity and phytoxicity evaluation

The PCA was evaluated as already reported elsewhere [32]. The phytoxicity was carried out using 150 ppm dye solution before and after treatment. Phytoxicity was evaluated using Raphanus sativus plant [33]. Germination percentage of Raphanus sativus seed was calculated for degraded and non-degraded congo red dye. All experiments were performed in triplicate and data was averaged.

3. Results and discussion

3.1. Characterization

The crystal structure confirmation of La₁₋ₓBiₓCo₁₋ₙFe₂O₃ was done by powder XRD in the range of 20°–80°. The diffraction peaks at 2θ values of 23.2°, 32.81°, 33.28°, 39.86°, 40.03°, 47.62°, 52.70°, 53.66°, 59.08°, 59.93° and 68.94°, which correspond to Miller indices values of (012), (110), (104), (202), (006), (024), (122), (116), (214), (018) and (220), respectively (Fig. 1, Table 1).
La$_{1-x}$Bi$_x$Co$_{1-y}$Fe$_y$O$_3$ showed pure perovskite phases and match with JCPDS cards 25–1060 and 00-036-1392. Crystal geometry was distorted rhomboedral with R-3C space group. No extra peak were observed which confirm the purity if prepared perovskite. The lattice constants were calculated by ‘cell software’. Particle size was calculated by Debye Scherer equation (Eq. 1) [34,35].

$$D = K \lambda / \beta \cos \theta$$

(1)

Where, $D$ is the average size of particles; $K$ is a constant having value 0.9, $\lambda$ is X-ray wavelength, $\theta$ is the Bragg angle and $\beta$ is the full width at half maxima value. It was observed that by increasing the x and y concentration from 0 to 0.55, the La$_{1-x}$Bi$_x$Co$_{1-y}$Fe$_y$O$_3$ crystallite size was increased. The crystal size of perovskites increases from 33.05 nm to 57.41 nm. The unit cell volume (Fig. 2) of rhombohedral crystal was calculated using relation shown in Eq. (2).

$$V = a^2 \times c \times \cos 60^\circ$$

(2)

The x-ray density of perovskites samples was measured using relation shown in Eq. (3) [36].

$$\rho_{x-ray} = ZM / NA V$$

(3)

The observed value of x-ray density for LaCoO$_3$ was 7.4 g/cm$^3$ and in line with reported value [37]. Both crystallite volume (331.7–336.2 Å$^3$) and crystallite size (33.05–57.41 nm) values were increased by doping. The difference in ionic radius (0.001 nm) of La$^{3+}$ (0.115 nm) and Bi$^{3+}$ (0.116 nm) is very low, hence, there is no effective deformation observed due to substitution of Bi in place of La at ‘A’ sites [38]. The size increased due to larger ionic radii of Co$^{3+}$ (0.52 Å) [37] and in case of Fe$^{3+}$ (0.64 Å) [39], the difference was insignificant. The bulk density was calculated using relation shown in Eq. (4) [40].

$$\rho_{bulk} = \text{mass} / \text{volume}$$

(4)

The volume of the pallet was determined by $4\pi r^2 h$, where $r$ is the radius and $h$ is thickness of the pallets. The porosity of particles was calculated using relation shown in Eq. (5) [41].

$$\text{Porosity} = 1 - \rho_{bulk} / \rho_{x-ray}$$

(5)

The porosity was in the range of 58.5 to 64.3%. The particle size and morphological analysis of samples is done by SEM and responses are shown in Fig. 3. The samples sintered at 950 ºC shows spherical shape. The average crystallite size determined from XRD analysis is in line with SEM analysis. However, X-ray diffraction analysis reveals only the single crystallite size and the particles are in agglomeration form and in line with previous studies [30,42–44]. In order to examine the chemical composition, EDX was performed and EDX spectrum is shown in Fig. 4. The EDX analysis showed the presence of La, Co, Fe, Bi and oxygen without any impurity.
FTIR analysis of La$_{1-x}$Bi$_x$Co$_{1-y}$Fe$_y$O$_3$ perovskites was obtained in range of 400–1400 cm$^{-1}$ at room temperature by using Nexus 470 spectrometer. The typical absorption bands for O–Co–O bending and Co–O stretching vibrations of octahedral co-ordinated CoO$_6$ are observed at 420.23 cm$^{-1}$ and 600 cm$^{-1}$, respectively in the structure of LaCoO$_3$ [45–48]. The peak at 540 cm$^{-1}$ was appeared in both doped and un-doped samples due to La–O vibrations. The sharpness of bands for both doped and un-doped conform the symmetrical rhombohedral ABO$_3$ perovskites structure [45,49,50]. The peaks at 474.8 cm$^{-1}$ and 852.5 cm$^{-1}$ were due to stretching mode Fe–O and Bi–O–Bi vibrations, respectively, which was observed only in the doped material [51,52] (Fig. 5).

The Raman spectrum is shown in Fig. 6 in the range of 100–700 cm$^{-1}$. The spectra showed the presence of bands at 149 cm$^{-1}$, 220 cm$^{-1}$, 437 cm$^{-1}$ and 611 cm$^{-1}$. The bands are similar to the Raman bands of LaCoO$_3$ [18,53–55]. There was no secondary peak in the spectra which verified the single phase structure [56]. The width of the bands is related to the small grain size of the nanoparticles [57]. Further confirmation of the particle size and morphology was done by AFM. AFM image of Bi and Fe substituted LaCoO$_3$ along with their particles size

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**Fig. 3 – SEM image of Bi and Fe substituted LaCoO$_3$ perovskites.**

**Fig. 4 – EDX spectrum of Bi and Fe substituted LaCoO$_3$ perovskites.**

**Fig. 5 – FTIR spectrum of Bi and Fe substituted LaCoO$_3$ perovskites.**

**Fig. 6 – Raman spectra of Bi and Fe substituted LaCoO$_3$ perovskites.**
distribution is shown in Fig. 7. Different heights of groove show that the particles size was slightly variable; however majority of the particles lies in the size range of 58.6 nm. The nanoparticles are not separated well and possess compact distribution [58].

The magnetic measurements of annealed samples for \(x, y=0.0, 0.25, 0.35, 0.45\) and 0.55 were carried out by VSM at room temperature (298 K) and responses are shown in Figs. 8 and 9. The samples exhibited ferromagnetic behavior. The magnetic parameters such as (Ms) magnetization saturation, (Hc) coercivity and (Mr) remanance are calculated from the hysteresis cycle and values are mentioned in Table 2. It is clear that the values of Mr and Ms were maximum for \(\text{La}_{0.75}\text{Bi}_{0.25}\text{Co}_{0.75}\text{Fe}_{0.25}\text{O}_3\) \((x, y=0.25)\) and minimum for \(\text{La}_{0.55}\text{Bi}_{0.45}\text{Co}_{0.55}\text{Fe}_{0.45}\text{O}_3\) \((x, y=0.45)\). The magnetic parameters (Ms and Mr) values were decreased by doping with Bi and Fe when \(x, y \geq 0.35\). The coercivity \((Hc)\) was maximum for \(x, y=0.0\) and minimum for \(x, y=0.45\) (50.61 G). The most probable valence state for La, Bi, Fe and Co was +3. So for, the substitution of Bi and Fe did not alter the oxidation state in LaCoO$_3$ perovskites [59,60]. The increase in Ms and Mr value from \(x, y=0.0\) to 0.25 was due to increase in Fe contents and interaction of \(\text{Fe}^{3+}–\text{O}–\text{Co}^{3+}\) and destruction of \(\text{Co}^{3+}–\text{O}–\text{Co}^{3+}\) and contribution of \(\text{Fe}^{3+}/\text{Co}^{3+}\) leads to net magnetization. In \(\text{La}_{0.75}\text{Bi}_{0.25}\text{Co}_{0.75}\text{Fe}_{0.25}\text{O}_3\) 25% of Co is replaced by Fe and La is replaced by Bi leads to larger Mr value [61]. The replacement of Bi with La decreased the ferromagnetic nature of \(\text{La}_{0.65}\text{Bi}_{0.35}\text{Co}_{0.65}\text{Fe}_{0.35}\text{O}_3\) and \(\text{La}_{0.55}\text{Bi}_{0.45}\text{Co}_{0.55}\text{Fe}_{0.45}\text{O}_3\) due to diamagnetic nature of Bi than La [59,62]. The DC resistivity of Bi and Fe doped LaCoO$_3$ shown in Figs. 10–13. The IV measurements were done at room temperature. The value of resistance \(R'\) of pure LaCoO$_3$ and doped LaCoO$_3$ with varying concentration of Bi and Co was calculated from the graphs. The specific resistance or resistivity \(\rho\) was calculated using relation shown in Eq. (6).

\[
\text{Resistivity}(\rho) = \frac{RA}{L} \quad (6)
\]

Whereas \(R'\) and \(L'\) are the resistance and thickness of pallets, respectively and \(A'\) is the area calculated by equation \(A = \pi r^2\), where \(r\) is the radius. The value of \(\rho\) depends upon the concentration of doped element and crystalline phase of the particles since specific resistance may change by varying the dopant substitution [63–66]. Results revealed that resistivity
increased by increasing the concentration of dopant at A and B site in ABO₃ type LaₓBiₙ₋ₓCo₁₋₂FeₙO₃ perovskite. The resistivity of lanthanum (54 × 10⁻⁸ ohmm at 4.7 K) and cobalt (9 × 10⁻⁸ ohmm) is less than that of iron (9.7 × 10⁻⁸ ohmm) and bismuth (115 × 10⁻⁸ ohmm). So far, overall an increasing trend in resistivity was observed by doping from 1.16 × 10¹¹ Ωcm to 4.08 × 10¹² Ωcm [67]. The increasing resistivity with Bi and Fe substitution is advantageous for their utilization in microwave appliances because such devices need extremely resistive materials. The dielectric study of LaₓBiₓCo₁₋₂FeₙO₃ was done using wayneker (WK6500B) LCR meter at room temperature. The frequency range was kept from 20Hz to
Table 2 – The magnetic parameters; magnetization saturation (Ms), coercivity (Hc) and remanence (Mr) of Bi and Fe substituted LaCoO$_3$ perovskites.

<table>
<thead>
<tr>
<th>Dopant concentration</th>
<th>0.00</th>
<th>0.25</th>
<th>0.35</th>
<th>0.45</th>
<th>0.55</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mr (emu/g)</td>
<td>0.00167</td>
<td>0.00827</td>
<td>0.00175</td>
<td>0.00143</td>
<td>0.00153</td>
</tr>
<tr>
<td>Ms (emu/g)</td>
<td>0.222</td>
<td>0.224</td>
<td>0.07</td>
<td>0.127</td>
<td>0.127</td>
</tr>
<tr>
<td>Hc (G)</td>
<td>161.36</td>
<td>152.08</td>
<td>119.07</td>
<td>50.61</td>
<td>158.17</td>
</tr>
</tbody>
</table>

20 MHz. The dielectric constant or relative permittivity ($\varepsilon$) is the ratio of the permittivity of a substance to the permittivity of free space. Dielectric constant is the measure of the polarity of a medium [68]. It is an expression of the extent to which a material concentrates electric flux, and is the electrical equivalent of relative magnetic permeability. Dielectric behavior is an important property of materials and it depends on the particle size, method of formation, sintering temperature and composition of materials [36]. The dielectric constant was calculated using relation shown in Eq. (7) [69].

$$\varepsilon = \frac{C \times d}{\varepsilon_0 \times A}$$  \hspace{1cm} (7)

Where, $\varepsilon$ is dielectric constant, $C$ is capacitance, $A$ is area of pallets, $d$ is pallet's thickness and $\varepsilon_0$ is permittivity of free space. The dielectric loss or tangent loss ($\tan \delta$) is the inherent dissipation of electromagnetic energy by dielectric material. The tangent loss value is actually ratio between the imaginary ($\varepsilon''$) and real part ($\varepsilon'$) of dielectric constant as shown in Eq. (8) [70].

$$\tan \delta = \frac{\varepsilon''}{\varepsilon'}$$  \hspace{1cm} (8)

The trend of Bi and Fe substitution on dielectric parameters are shown in Figs. 14 and 15 and the values of dielectric parameters at the frequencies 20 Hz, 80 Hz, 495.41 Hz...
grain boundaries. Due to resistance of grain boundaries the polarization is produced as hopping electrons pile up at the grain boundaries. The possibility of electrons to arrive at the grain boundaries is decreased by increasing frequency. Actually, the polarons not follow the alternating electric field and all other polarizations except electronic polarization become negligible at higher frequency. So far, the value of dielectric constant decreased with frequency \([73,74]\). Similar trend was observed for decreasing value of dielectric loss and tangential loss with frequency, which was due to decrease electron hopping.

### 3.2. Photocatalytic activity

Photocatalysts convert organic pollutants such as complex dye materials into less harmful forms by oxidation and reduction processes under irradiation. In order to study the PCA of La\(_{1-x}\)Bi\(_x\)Co\(_{1-y}\)Fe\(_y\)O\(_3\), congo red dye was used. In 200 mg/L of dye solution, 15 mg La\(_{1-x}\)Bi\(_x\)Co\(_{1-y}\)Fe\(_y\)O\(_3\) was suspended and degradation activity was performed under visible light as already reported elsewhere \([32]\). The absorbance was monitored by UV–vis spectrophotometer at 500 nm and percentage degradation was estimated. The UV–vis spectra of congo red dye is shown in Fig. 16. The La\(_{1-x}\)Bi\(_x\)Co\(_{1-y}\)Fe\(_y\)O\(_3\) showed excellent PCA for dye degradation. The peak in the visible region at 498 nm shows the degradation of (N≡N–) bond and peaks lies in the UV range at 241 nm specify the degradation of benzene ring and 342 nm indicate the degradation of naphthalene ring. A 95% of dye was degraded by the system in 1 h (Figs. 17 and 18). The degradation of congo red dye increased with time and reached 95% after 1 h irradiation under solar light irradiation. Under irradiation, electrons are transfer from valance band to conduction band and establishment of electron-hole pair occurred \([75,76]\). The proposed mechanism of photo-catalyzed degradation of congo red dye is shown in relations (Eqs. 9–16) and Fig. 19.

\[
\text{La}_{0.65}\text{Bi}_{0.35}\text{Co}_{0.65}\text{Fe}_{0.35}\text{O}_3 \overset{\text{Irradiation}}{\rightarrow} \text{La}_{0.65}\text{Bi}_{0.35}\text{Co}_{0.65}\text{Fe}_{0.35}\text{O}_3(e^-_{cb} + h^+_{vb})
\]

(Eq. 9)
The discharge of dyes in effluents from the textile industry is serious ecological and health issues since dyes are toxic [77–83]. Therefore, the toxicity of treated and untreated dye solution was also evaluated. The relative toxicity of Congo red was studied by exposing the seeds of *Raphanus sativus* to untreated and treated dye solution and responses are shown in Fig. 20. Results clearly indicated that seeds of *Raphanus sativus* shows 0 germination index and 100 percent germination inhibition in untreated dye solution, whereas seeds of *Raphanus sativus* germinated 100% in treated solution of dongo red dye, which indicates that in case of treated dye, photo-toxicity reduced 100% with respect to original dye solution. Toxicity results revealed that La$_{1-x}$Bi$_x$Co$_{1-y}$Fe$_y$O$_3$ detoxify the dye as a result of dye degradation. Previous studies also showed that photocatalytic treatment is best to degrade and detoxify the dye and textile wastewater, which is a serious threat to the environment [84–96].

### 4. Conclusions

La$_{1-x}$Bi$_x$Co$_{1-y}$Fe$_y$O$_3$ was successfully synthesized by microemulsion method. The formation of synthesized material was confirmed by X-ray diffraction, Raman spectroscopy, Fourier transform infrared spectroscopy (FTIR), scanning electron microscope (SEM), Energy-dispersive X-ray (EDX) and atomic force microscopy (AFM) techniques. The La$_{1-x}$Bi$_x$Co$_{1-y}$Fe$_y$O$_3$ size was in the range of 33.05–57.41 nm. Doping of LaCoO$_3$ with Bi and Fe significant changed the DC resistivity, dielectric parameters and magnetic properties. Photocatalytic activity was evaluated by degrading Congo red dye and Bi and Fe doped LaCoO$_3$ (perovskite) showed excellent PCA versus LaCoO$_3$. Results revealed that the doping could possibly be used to enhance the perovskite magnetic, dielectric properties and catalytic activity.
Conflicts of interest

The authors declare no conflicts of interest.

REFERENCES


[20] Weidenkaff A, Ebbinghaus SG, Lippert T. Ln1−xA4CoO3 [Ln = Er, La; A = Ca, Sr]/carbon nanotube composite materials


[36] Ali R, Khan MA, Mahmood A, Chughtai AH, Sultan A, Shahid M, et al. Structural, magnetic and dielectric behavior of Mg$_{0.5}$Ca$_{0.5}$Ni$_{0.5}$Fe$_{2.5}$O$_4$ nano-ferrites synthesized by the micro-emulsion method. Ceram Int 2014;40:3841–6.


[61] Zhang D, Huang W, Chen Z, Zhao W, Feng L, Li M, et al. structure evolution multi ferroic properties cobalt doped Bi$_2$NiNdTi$_2$Fe$_{1.5}$Ti$_{0.5}$O$_6$ - Bi$_2$NiNdTi$_2$Fe$_{1.5}$Ti$_{0.5}$O$_6$ – b intergrowth Aurivillius. Comp Sci Report 2017:7.


[94] Ibisi NE, Etsolu CA. Use of agro waste (Musa paradisiaca peele) as a sustainable bio sorbent for toxic metal ions removal from contaminated water. Chem Int 2018;4:52–9.