Influence of Lanthanum Doping on the Structural and Optical Properties of Hematite Nanopowders

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Abstract

Rare-earth elements are an attractive class of dopant elements, as they give easily trivalent cations that possibly altering the structure and other properties of the parent nanoparticles and creating multifunctional materials because of their f-electronic configurations. Herein, experimental evidence has been given for a better understanding of the factors that dictate the interactions of La doping on the structure and optical properties of iron oxide nanoparticles. For that, lanthanum doped hematite (α-Fe₂O₃) nanoparticles were prepared by a facile solution method using iron (III) chloride (FeCl₃) as starting precursor and sodium hydroxide (NaOH) as reducing agent without templates at low temperature. As-prepared powders were subsequently calcined in air for 3 hr at 800 °C. X-ray diffraction (XRD) technique was used to study the nanocrystal formation of α-Fe₂O₃ and Fourier Transform Raman (FT-Raman) spectral information identified the chemical bond structure of the nanoparticles. Morphology study of the nanoparticles was identified using Scanning Electron Microscope (SEM) and the incorporated La content was recognized from the Energy Dispersive X-ray Spectroscopy (EDS) analysis. The optical absorption spectrum was recorded in the wavelength range of 200-2000 nm and the optical parameters such as absorption coefficient and optical band gap energy of pure and doped Fe₂O₃ nanoparticles were determined. Obtained results are interpreted by considering the impregnation of trivalent La cations that replaced Fe cations of the host structure.

Keywords: Sol-gel precipitation, nanopowder, XRD, FT-Raman, SEM, Optical

1. Introduction

Nanosized iron oxides have wide applications in catalysis, magnetic recording, catalysis, field emission devices, spin electronic devices and rechargeable lithium batteries due to its special optical, magnetic and electrical properties [1-6]. Rare earth ions having large magnetic moments and luminescent properties greatly influence the crystal properties [7]. They are used in magnetic resonance imaging (MRI) as contrasting agents [8]. Lanthanum ions are also an interesting candidate possessing unique chemical and physical properties. Mixed oxides having perovskite structure shows interesting properties [9, 10]. Melo et al. have synthesized lanthanum doped Fe₂O₃ pigments from polymeric precursors using Pechini method [11]. Francesca et al. [12] and Gaurav Goyal et al. [13] have studied the modification of magnetic properties of α-Fe₂O₃ on doping Eu and Nd respectively. Here we report a facile solution approach for the synthesis of pure and La doped hematite nanoparticles by simply adjusting the pH of the solution for the first time. The influence of dopant on its structural, surface morphological and optical characterization was systematically presented in this paper.

2. Experimental Procedure

2.1. Synthesis

For the synthesis of pure and lanthanum doped hematite nanoparticles, ferric chloride (AR grade) and ethylene glycol were used as the starting chemicals. Initially, Iron (III) chloride was dissolved in a mixture of deionized water and ethylene glycol at room temperature for a concentration of 0.1M. The obtained solution was reduced using NaOH solution (0.1 M) to get a dark reddish brown clear solution. The pH of this solution was adjusted to be 3 by adding ammonia solution and stirred for 1h at 100°C and then allowed to precipitate. The obtained precipitates were repeatedly washed with ethanol and distilled water and dried in air at 80°C. This as-prepared sample was then annealed at 800°C for 3 hrs. Thus pure hematite nanopowders were obtained. For preparing lanthanum doped hematite nanopowders, 1% of Lanthanum nitrate was dissolved in the mixture of deionized water and ethylene glycol.

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2.2. Characterization

X-ray powder diffraction (XRD) patterns of pure and doped α-Fe₂O₃ powder samples were obtained using PANalytical-X’pert Pro X-ray diffractometer with Cu kα radiation at room temperature (λ = 1.5460 Å). Fourier Transform Raman spectra were measured by BRUKER RFS 27 FT-Raman spectrometer with Nd:YAG laser source. Morphological studies of pure sample was carried out using JEOL JSM-6390 SEM operated at an accelerating voltage of 20 kV and that of doped sample was done by using JEOL JSM-7600F FESEM operated at an accelerating voltage of 5 kV. The optical absorption spectra were taken on a Varian Cary 5000 UV–visible spectrometer.

3. Results and Discussion
3.1. X-Ray diffraction Analysis

![XRD patterns of the prepared hematite nanopowders](image)

**Table 1 Structural parameters of hematite nanopowders**

<table>
<thead>
<tr>
<th>Sample Details</th>
<th>2θ Position</th>
<th>Lattice Parameter</th>
<th>Unit cell volume x10⁶ pm³</th>
<th>Density g/cm³</th>
<th>Crystallite Size nm</th>
<th>Dislocation density x10¹⁶ lines/m²</th>
<th>Micro strain</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard value</td>
<td>33.198</td>
<td>(a = 5.0285 \text{ Å} ) (c = 13.7360 \text{ Å} )</td>
<td>300.79</td>
<td>5.29</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Pure</td>
<td>33.2374</td>
<td>(a = 5.0345 \text{ Å} ) (c = 13.7313 \text{ Å} )</td>
<td>301.402</td>
<td>5.277</td>
<td>50</td>
<td>0.4072</td>
<td>0.0024</td>
</tr>
<tr>
<td>Doped</td>
<td>33.2571</td>
<td>(a = 5.0310 \text{ Å} ) (c = 13.7204 \text{ Å} )</td>
<td>300.743</td>
<td>5.2886</td>
<td>36</td>
<td>0.7511</td>
<td>0.0033</td>
</tr>
</tbody>
</table>

The XRD patterns of the pure and La doped α-Fe₂O₃ samples prepared using starting precursors maintained at pH=3 are shown in Fig. 1. All the peaks obtained at the specified locations in the 2θ axis can be indexed as α-Fe₂O₃ based on the JCPDS standards (PDF file no. 01-079-0007) and they are in good agreement with the standard values [14-16]. No peaks of impurities were detected, indicating the purity of the synthesized α-Fe₂O₃. The strong and sharp diffraction peaks of the XRD patterns suggested that the prepared samples are well crystalline and has nano sized grains. The most intense peaks observed at about 2θ=33.2° correspond to the (104) plane. There is a small shift in this peak to the higher angle side in the doped sample and it validates the perfect incorporation of La ions in the α-Fe₂O₃ lattice by replacing Fe ions. Moreover, the present level of doping does not modify the hexagonal unit cell.
The unit cell of $\alpha$-Fe$_2$O$_3$ is hexagonal and contains only octahedrally coordinated Fe$^{3+}$ ions in the pure sample (corundum structure) [17, 18]. Based on the hkl values, the structural parameters were calculated for its hexagonal structure and are listed in Table 1. The lattice parameters of the pure $\alpha$-Fe$_2$O$_3$ sample are very close to the standard values and the incorporated dopant ions modify the cell edge that is compressed along both the a and c axes. Therefore, the unit cell volume is reduced and hence there is an increase in density. Since the dopant cation diameter is not similar to the native cation, the dislocation density and microstrain values increase. The crystallite size also reduces on doping.

3.2. FT-Raman spectroscopy

$\alpha$-Fe$_2$O$_3$ belongs to D$^{6h}_{3d}$ point symmetry group and there exists seven Raman active modes, two vibrations of A$_{1g}$ and five E$_g$ [19]. The mode at 225 cm$^{-1}$ in the bulk material has A$_{1g}$(1) symmetry, the 245 cm$^{-1}$ is an E$_g$(2), the 290 cm$^{-1}$ is an E$_g$ (3) + E$_g$(4), the 409 cm$^{-1}$ mode is E$_g$(5), the mode at 500 cm$^{-1}$ is A$_{1g}$(6) and the mode at 612 cm$^{-1}$ is E$_g$(7). The existence of a mode at 1295 cm$^{-1}$ has been assigned to a two magnon mode.

Fig. 2 FT-Raman spectra of the hematite nanopowders (a) pure (b) La doped

The Raman active modes in the pure sample (Fig. 2a) can be assigned as: A$_{1g}$ (223, 501 cm$^{-1}$), E$_g$ (293, 412, 614 cm$^{-1}$). For doped sample (Fig. 2b), the modes can be assigned as A$_{1g}$ (229, 499 cm$^{-1}$), E$_g$ (293, 413, 613 cm$^{-1}$). The peak at 1280 cm$^{-1}$ is originated from a two-magnon scattering [20]. The observed Raman modes are in good agreement with the reported values [21-23]. The magnon mode is shifted from 1295 cm$^{-1}$ in the bulk material to 1280 cm$^{-1}$ and broadened in the nanomaterial suggesting the effect of phonon confinement on the mode. The resonance in the nanomaterial is more intense. The phonon confinement relaxes the K=0 selection rule in Raman spectroscopy [23]. Raman spectral analysis once again supports the results obtained through XRD that the synthesized product is nanocrystalline Fe$_2$O$_3$.

3.3. SEM Analysis

Fig. 3 SEM images of the hematite nanopowders: (a) pure (b) La doped
The morphologies of the prepared samples were studied by SEM and Fig. 3 shows the SEM images of the pure and doped hematite nanopowders. The particles of the pure sample are fine and uniform, forming nearly spherical shape. The size distribution is almost uniform and the calculated average particle size is about 155 nm. In the case of doped sample, the average particle size is 74 nm and the particles are spherical in shape. Obtained particle size values are higher than that obtained through XRD studies, however the size reduction is clearly seen through the SEM images. The composition of the samples was identified from the EDAX spectrum shown as an inset. Pure \( \alpha-Fe_2O_3 \) nanoparticle has x-ray absorption peaks corresponding to the elements Fe and O. However in the doped sample, additional peaks corresponding to the element La is visible along with Fe and O. The study further confirms the impregnation of the dopant ion into the \( Fe_2O_3 \) lattice.

3.4. UV-Vis spectroscopy

![Fig. 4 UV-vis absorption spectra of the hematite nanopowders (a) pure (b) La doped](image)

![Fig. 5 Variation of \((\alpha h\nu)^2 \) vs. photon energy](image)

Fig. 4 shows the optical absorption spectra at room temperature of the pure and lanthanum doped samples. The specific absorption located at 270 nm can be assigned to metal to ligand charge transfer interactions and partly due to the \( Fe^{3+} \) ligand field transitions \( 6A_1 \rightarrow 4T_1(4P) \). This absorption intensity of the La doped hematite nanoparticles is higher than that of the pure sample. The absorption peak at 540 nm is mainly due to the \( 6A_1 \rightarrow 4T_1(4G) + 4T_1(4G) \) excitation of an \( Fe^{3+} – Fe^{3+} \) pair, overlapped with the contributions of \( 6A_1 \rightarrow 4E, 4A_1 (4G) \) ligand field transition and the charge-transfer band tail [15]. It has already been reported that \( \alpha-Fe_2O_3 \) exhibits both direct and indirect band gaps [24, 25]. The direct and indirect band gap energy \( (E_g) \) is estimated using the Tauc equation, \((\alpha h\nu)^{1/n} = B (h\nu-E_g)\), where \( h\nu \) is the incident photon energy, \( \alpha \) is the absorption coefficient, \( B \) is a material-dependent constant and \( E_g \) is the optical band gap. The value of \( n \) depends on the nature of transition. For direct allowed transition, \( n=1/2 \) and for indirect allowed transition \( n=2 \). Tauc plots drawn by taking \((\alpha h\nu)^{1/n}\) along the y-axis and \( h\nu \) along the x-axis is shown in Fig. 5 and 6.

<table>
<thead>
<tr>
<th>Nature of transition</th>
<th>Literature value [26]</th>
<th>Pure</th>
<th>Doped</th>
</tr>
</thead>
<tbody>
<tr>
<td>Direct</td>
<td>2.6 eV</td>
<td>2.47 eV</td>
<td>2.51 eV</td>
</tr>
<tr>
<td>Indirect</td>
<td>1.9 eV</td>
<td>1.22 eV</td>
<td>1.18 eV</td>
</tr>
</tbody>
</table>

Table 2 Band gap values of the hematite nanopowders

The average optical band gap is found by extrapolating the linear portion of the curve. The average band gap of the bulk \( \alpha-Fe_2O_3 \) is 2.1 eV [15]. The literature values and the calculated values of direct and indirect optical band gap energy of pure and doped hematite nanopowders are listed in Table 2. The calculated values of band gap are found to be in agreement with the literature values. Since the crystallite sizes are different, the band gap values for the pure and doped sample are different.
4. Conclusion

Pure and lanthanum doped $\alpha$-Fe$_2$O$_3$ nanoparticles were prepared by a facile solution method by simply controlling the pH value of the starting precursor solution. Prepared Fe$_2$O$_3$ nanoparticles are phase pure and the present level of La doping has not altered the crystalline structure. Incorporation of the dopant ion into the lattice was identified from the XRD studies and confirmed through FT-Raman and EDAX studies. These results showed the perfect replacement of Fe ions by La ions and the La ions are not seated in the interstitial sites. The phonon confinement of both the samples is evidenced from the FT-Raman studies. Surface morphological studies confirmed the induced alteration in shape, size and distribution of the crystallites due to the dopant ion. Both the direct and indirect band gap changes on replacing the native Fe ions with La ions.

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References


