Effect of titanium substitution on the structural and optical properties of lanthanum orthoferrite nanoparticles

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Abstract. A series of LaFe$_x$Ti$_{3-x}$O$_9$ (x = 0.4, 0.5 and 0.6) nanoparticles was successfully synthesized via sol–gel method. All samples were characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), and ultraviolet-visible (UV-vis) spectrophotometry. XRD characterization revealed an orthorhombic crystal structure with the $\text{Pnma}$ space group. In the FTIR spectra, the vibrational modes of tilting, bending, and symmetric stretching of the Fe/TiO$_6$ octahedra were observed. UV-Vis analysis showed the increasing of the energy gap with Ti content.

Keywords: La(Fe,Ti)O$_3$, crystal structure, vibrational mode, energy gap

1. Introduction

Perovskite orthoferrite represents an interesting class of materials and is used for a variety of applications, including electrode materials for high-temperature solid oxide fuel cells, catalysts for the complex oxidation of hydrocarbons, and sensor materials for humidity, alcohol, and oxygen detection [1]. Among the various perovskite orthoferrite compounds, the LaFeO$_3$–based one is an attractive research topic because of its significance contributions to advanced technological applications, such as multilayer capacitors, photocatalyst, gas sensors, and magnetic storage devices [2]. As reported by Tang et al. [3], pure perovskite LaFeO$_3$, with $\text{Pnma}$ space group and orthorhombic structure, has a strong visible absorption and an optical bandgap (E$_g$) of 2.36 eV.

Several studies reported changes in LaFeO$_3$’s structural and optical properties, which were caused by substitutions on the La and/or Fe sites [1,4–5] such as Ca doping. This resulted a decreased crystallite size in La$_{1-x}$Ca$_x$FeO$_3$ with increased Ca content [1]. Janbutrach et al. [4] reported that Al substitution on La sites, resulting in La$_{1-x}$Al$_x$FeO$_3$ nanopowders, decreases crystallite size and the calculated bandgap in the 2.05–2.09 eV range with increasing Al content. Swatisiant et al. [5] observed that Sm doping on La sites leads to decreased lattice parameters, crystallite size, and E, (from 2.218 to 1.880 eV) with increasing the Sm content. Several researchers focused on the Ti substitution in LaFeO$_3$. Sasikala et al. [2] reported that Ti doping (0–80 mol %) on the Fe sites of LaFeO$_3$, synthesized by co precipitation, increases E, in the 2.05–2.61 eV range with increasing Ti content. Łańcucki et al. [6] observed that, in three-dimensionally ordered (3DOM) materials based on LaFe$_{1-x}$Ti$_x$O$_3$ with different Ti amounts (0–20 mol %) using polystyrene nanospheres as a template agent, increasing Ti content leads to higher phase stability followed by a decreased crystallite size.

Based on previous research, Ti substitution on the Fe sites of LaFeO$_3$ induces unexpected properties compared to its parent compounds. In addition; the synthesis method also affects the materials’ physical properties. Hence, by using the sol–gel method for synthesis, we aim to investigate, in detail, the structural and optical properties of La(Fe,Ti)O$_3$, analyzed by X-ray diffraction (XRD), Fourier
### Table 1. Structural parameters of LaFe$_{1-x}$Ti$_x$O$_3$ (x = 0.4, 0.5, and 0.6) nanoparticle

| Parameter                      | x = 0.4 | LaFe$_{1-x}$Ti$_x$O$_3$ x = 0.5 | x = 0.6 |
|--------------------------------|---------|---------------------------------|---------|
| **Crystallography parameters** |         |                                 |         |
| Lattice parameters             |         |                                 |         |
| a (Å)                          | 5.584   | 5.565                           | 5.563   |
| b (Å)                          | 7.863   | 7.836                           | 7.816   |
| c (Å)                          | 5.548   | 5.572                           | 5.557   |
| Volume (Å$^3$)                 | 243.5   | 242.9                           | 241.6   |
| Crystallite size (nm)          | 18.50   | 23.82                           | 19.26   |
| Crystallite strain             | 0.177   | 0.137                           | 0.077   |
| Density g/cm$^3$               | 6.631   | 6.635                           | 6.667   |
| **Atomic Position**           |         |                                 |         |
| La (x,y,z)                     | (0.470, 0.250, 0.007) | (0.470, 0.250, 0.007) | (0.470, 0.250, 0.007) |
| Fe/Ti (x,y,z)                  | (0.000, 0.000, 0.000) | (0.000, 0.000, 0.000) | (0.000, 0.000, 0.000) |
| O1 (x,y,z)                     | (0.198, 0.029, 0.281) | (0.198, 0.029, 0.281) | (0.198, 0.029, 0.281) |
| O2 (x,y,z)                     | (0.515, 0.250, 0.580) | (0.515, 0.250, 0.580) | (0.515, 0.250, 0.580) |
| Wyckoff Factor                 |         |                                 |         |
| La                             | 4c      | 4c                              | 4c      |
| Fe/Ti                          | 4a      | 4a                              | 4a      |
| O(1)                           | 4c      | 4c                              | 4c      |
| O(2)                           | 8d      | 8d                              | 8d      |
| **Geometrical parameters**     |         |                                 |         |
| Bond length (Å)                |         |                                 |         |
| Fe/Ti-O1 (s)                   | 1.923   | 1.929                           | 1.924   |
| Fe/Ti-O1 (l)                   | 2.089   | 2.089                           | 2.087   |
| Fe/Ti-O2 (m)                   | 2.018   | 2.010                           | 2.006   |
| <Fe/Ti-O>                      | 2.010   | 2.009                           | 2.006   |
| Bond angle (°)                 |         |                                 |         |
| Fe/Ti – O1 – Fe/Ti             | 157.06  | 157.11                          | 157.12  |
| Fe/Ti – O2 – Fe/Ti             | 154.14  | 153.91                          | 153.93  |
| Tilt angle (°)                 | 14.91   | 14.95                           | 14.94   |
| Tolerance factor <t>           | 0.8577  | 0.8597                          | 0.8611  |

transform infrared spectroscopy (FTIR), and ultraviolet–visible (UV–Vis) spectrophotometry, and compare the results to those obtained in previous studies.

### 2. Experimental details

All samples were synthesized by the sol–gel method. The stoichiometric amounts of lanthanum (III) oxide, titanium (IV) oxide, iron (III) nitrate nonahydrate, and citric acid monohydrate were mixed and stirred into solution until the gel phase was obtained. Then, the gel was dried to remove water, citric acid, and other organic compounds and successively calcined until the nanoparticles were formed. The details of the sample preparation have been explained in a previous work [7].

The nanoparticles’ XRD patterns were recorded using a PANalytical X’Pert PRO diffractometer with a Cu Kα radiation ($\lambda = 1.5405$ Å), 2θ between 20° and 90°, and a step size of 0.02°/s. The Rietveld refinement of the XRD results was performed via GSAS/EXPGUI software. The molecular and metal oxide bonds were analyzed in the 400–4000 cm$^{-1}$ range with a Perkin Elmer Spectrum Two FTIR spectrometer. The E$_g$ values were determined by using an Agilent Cary 100/300 UV–Vis spectrophotometer.

### 3. Results and discussion

#### 3.1. XRD analysis

XRD patterns of LaFe$_{1-x}$Ti$_x$O$_3$ (x= 0.4, 0.5, and 0.6) nanoparticles are shown in figure 1. The refinement confirmed that all samples have orthorhombic crystal phase without secondary phase. The structural parameters derived from the XRD patterns are summarized in table 1; there was no change in
Table 2. Fourier transform infrared spectra (FTIR) band assignment for some specific absorption modes of the LaFe$_{1-x}$Ti$_x$O$_3$ (x = 0.4, 0.5, and 0.6) nanoparticles

| LaFe$_{1-x}$Ti$_x$O$_3$ | FTIR band positions |
|-------------------------|---------------------|
|                         | Fe/Ti–O–Fe/Ti       |
|                         | Bending             |
| x = 0.4                 | 455                 |
| x = 0.5                 | 434                 |
| x = 0.6                 | 435                 |
|                         | Fe/Ti–O             |
|                         | Stretching          |
| x = 0.4                 | 537                 |
| x = 0.5                 | 539                 |
| x = 0.6                 | 542                 |
|                         | O–Fe/Ti–O           |
|                         | Bending             |
| x = 0.4                 | 758                 |
| x = 0.5                 | 757                 |
| x = 0.6                 | 757                 |

Figure 1. The XRD patterns of LaFe$_{1-x}$Ti$_x$O$_3$ (x = 0.4, 0.5, and 0.6) nanoparticles

structural symmetry (orthorhombic) with the $P_{nma}$ space group, similar to the results reported by Sasikala et al. [2] and Pokha et al. [8] for LaFe$_{1-x}$Ti$_x$O$_3$ compounds, and the crystallite size ranged between 18 and 24 nm. The lattice parameters and/or the unit cell volume slightly decreased with increasing Ti content. This might be caused by the Ti$^{4+}$ (ionic radii: 0.610 Å) ions substitution on the Fe$^{3+}$ (ionic radii: 0.645 Å) sites of La$^{3+}$Fe$^{3+}$O$_3$2–, introducing Fe$^{4+}$ (ionic radii: 0.580 Å) ions in the lattice for electric charge compensation. Since the ionic radii of Ti$^{4+}$ and Fe$^{3+}$ are smaller than that of Fe$^{3+}$, the Ti substitution decreased lattice parameters, as reported by Pokha et al. [8]. However, the difference among these ionic radii is not significant and, hence, no significant changes were observed in the geometrical parameters (table 1). The Fe/Ti–O bond length slightly decreased with increasing Ti content. The tolerance factor (t) describes the crystal structure stability [2]. Its value was below 0.96, indicating that all samples had stable orthorhombic crystal structures, as confirmed by XRD in a previous study [2].

3.2. FTIR analysis

Figure 2 shows the FTIR spectra of the LaFe$_{1-x}$Ti$_x$O$_3$ nanoparticles; they were consistent with those previously reported for LaFeO$_3$, La(Fe,Ti)O$_3$, and (La, K)FeO$_3$ [2,9,10]. The specific FTIR modes are summarized in table 2. The absorption bands around 400–500 cm$^{-1}$, attributed to the metal–oxygen (M–O) bond vibration, confirmed the typical perovskite structure (ABO$_3$) had formed [10].

According to previous reports, the absorption bands in 400–500 cm$^{-1}$ were due to the asymmetric stretching and bending vibration of the Fe/Ti–O–Fe/Ti bond, leading to the Fe/TiO$_6$ octahedra.
Fourier transform infrared spectra of the LaFe$_{1-x}$Ti$_x$O$_3$ (x = 0.4, 0.5, and 0.6) nanoparticles. The dash lines indicate the vibration of symmetry bonding in the lattice.

Diffuse reflectance spectra of LaFe$_{1-x}$Ti$_x$O$_3$ (x = 0.4, 0.5, and 0.6) nanoparticles.

deformation and changes in the corresponding bond angle. The bands in 530–560 cm$^{-1}$ were identified as the stretching vibration modes of the Fe/Ti–O bond, involving the internal motion of a change in the corresponding bond length. The band around 750 cm$^{-1}$ was assigned to the O–Fe/Ti–O bonds in the lattice, leading to changes in the corresponding bond angle. The bending modes of the O–H bond were observed around 1500 cm$^{-1}$. Other absorption bands, observed around 3600 cm$^{-1}$, were assigned to the water molecules' symmetric and asymmetric stretching modes.

As shown in table 2, the Fe/Ti–O band position increased with increasing Ti content, which might be due to the reduced mass of samples at the perovskite structure’s B sites [10]. However, the
positions of all the bands observed remained almost unchanged, indicating that the bond angle and length did not change (table 1).

3.3. UV–Vis analysis

Figure 3 shows the diffuse reflectance spectra of the LaFe$_{1-x}$Ti$_x$O$_3$ ($x = 0.4, 0.5, 0.6$) nanoparticles in the UV–Vis–near infrared (NIR) range. The Kubelka–Munk function $F(R)$ was used to calculate the absorption coefficient ($\alpha$) based on the diffuse reflectance ($R$) as follows $[9,10]$:

$$F(R) = \frac{a}{s} = \frac{(1 - R)^2}{2R}$$

where $s$ is the scattering coefficient. Then, the energy dependence of the UV–Vis–NIR range was further described.

Figure 4 shows the plots of $(F(R)E)^2$ vs. $h\nu$ for the LaFe$_{1-x}$Ti$_x$O$_3$ nanoparticles. Extrapolating the linear parts of the curves toward absorption equal to zero gives $E_g$ for direct transition. The $E_g$ values were in the 2.1–2.2 eV range, which is consistent with those in a previous work for LaFe$_{1-x}$Ti$_x$O$_3$ ($x = 0.2, 0.4, 0.6, \text{and } 0.8$) $[2]$. However, the $E_g$ obtained was smaller than those previously reported $[2]$, possibly because there was no secondary phase in this experiment. Its increasing with the Ti content suggests a decreased conduction response, which is related to the release of space charge carriers for balancing the columbic interactions in the substitution sites.

The effect of Ti substitution on the Fe sites of LaFeO$_3$ could be explained based on the experimental results. The crystal structure (orthorhombic) and symmetry ($Pnma$ space group) remained unchanged. The existence of the Fe/Ti–O vibration was confirmed by the FTIR analysis. The UV–Vis analysis confirmed the increasing of the optical bandgap with the Ti content. The decreased lattice parameters and Fe/Ti–O bond length might be due to the strengthened atomic bonding, which
makes charge carriers’ (electrons, holes, etc.) movement to other sites in the lattice more difficult. Hence, the energy needed to move to another site, i.e., $E_g$, tends to increase.

4. Conclusions
LaFe$_{1-x}$Ti$_x$O$_3$ (x = 0.4, 0.5, and 0.6) nanoparticles were successfully synthesized via the sol–gel method. The structural and optical analysis confirmed the orthorhombic crystal structure. When Ti content increased, the lattice parameters and/or cell volumes decreased and the optical band gap increased.

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