Structural and optical properties of La$_{1-x}$Pb$_x$Fe$_{3}$Ti$_{2}$O$_{12}$, (x = 0.1, 0.2, and 0.3) perovskite material prepared by sol-gel method

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Abstract. A series of La$_x$Pb$_{1-x}$Fe$_3$Ti$_2$O$_{12}$ (x = 0.1, 0.2, and 0.3) nanoparticles have been successfully synthesized by sol-gel method. All prepared samples were characterized by X-ray diffraction (XRD), Raman scattering, Fourier Transform Infrared spectroscopy (FTIR), and UV-Vis spectrophotometry. The X-ray diffraction pattern revealed the orthorhombic crystal structure and the increase of crystallite size with Pb content. The Raman scattering exhibited the similar Raman spectrum indicating the crystal structure remain unchanged due to the Pb substitution; indeed, the difference in lattice vibration phonon modes confirmed the variation in structural parameters with Pb-substitution which is also supported by FT-IR analysis. By using UV-Vis characterization, the optical band gap is found in the range of 2.1 – 2.2 eV.

Keywords: (La,Pb)(Fe,Ti)O$_3$, crystal structure, symmetry, energy gap

1. Introduction

Oxide perovskite has general formula ABO$_3$. [1]. Substitution in A- and B-site of oxide perovskite structure caused the modification in its properties and useful in electrode material, photocatalytic, and chemical sensor application [1–6]. This paper will focus on the modification of perovskite structure with LaFeO$_3$ as a parent compound. LaFeO$_3$ has been considered due to its complex physical behavior, which is strongly related with spin, charge and defects, and orbital state [2]. Several researches have been reported about pure- and doped- LaFeO$_3$ [2–5]. LaFeO$_3$ has strong visible-light absorption with the optical band gap 2.36 eV [3–4]. Pb-doped on LaFeO$_3$ introduced the colossal dielectric permittivity with multiple relaxations [2]. Ti-doped on LaFeO$_3$ have been reported to cause the decrease of crystallite size, increase the band gap, and introducing the weak ferromagnetic behavior [5]. Based on the previous works [2–5], it is interesting to study the double substitution on La and Fe site of LaFeO$_3$. To the best our knowledge, substitution of Pb- and Ti-ions on the structure and optical properties of La$_{1-x}$Pb$_x$Fe$_{3}$Ti$_{2}$O$_{12}$ have not been reported and paid attention on yet. The materials were setup by sol-gel method and investigated by X-Ray Diffraction (XRD), Raman scattering spectroscopy, Fourier Transform Infrared (FTIR) and UV-Vis.

2. Experimental details

Sol-gel method was used to synthesize the La$_{1-x}$Pb$_x$Fe$_{3}$Ti$_{2}$O$_{12}$ with x = 0.1, 0.2, 0.3. The precursors that used were lanthanum oxide (La$_2$O$_3$), lead oxide (PbO), iron nitrate (Fe(NO$_3$)$_3$·9H$_2$O), titanium oxide (TiO$_2$), and citric acid as solvent (all analytically grade). The prepared precursors were dissolved in citric acid solution and stirred at 120 °C. To obtain sponge phase, the drying process was applied in certain condition. Then, the sponge phase was calcined to form the powder-phase of La$_{1-x}$Pb$_x$Fe$_{3}$Ti$_{2}$O$_{12}$.
Table 1. Structural parameters of La$_{1-x}$Pb$_x$Fe$_{0.5}$Ti$_{0.5}$O$_3$ (x = 0.1, 0.2, and 0.3) as obtained from HighScore Plus software.

|       | Crystallographic Parameters | Geometrical Parameters |
|-------|-----------------------------|------------------------|
|       | a (Å)           | b (Å)     | c (Å)     | volume (Å$^3$) | crystallite size (nm) | density (gr/cm$^3$) | <Fe/Ti-O> (Å) | bond angle (°) | B = Fe/Ti | tilt angle (°) | tolerance factor |
| x = 0.1 | 5.566           | 7.872     | 5.533     | 242.5         | 23.3                 | 6.77                | 2.007       | 157.014     | 154.219     | 14.883               | 0.8317          |
| x = 0.2 | 5.557           | 7.841     | 5.680     | 242.6         | 24.4                 | 6.91                | 2.008       | 157.109     | 153.966     | 14.937               | 0.8304          |
| x = 0.3 | 5.578           | 7.860     | 5.554     | 243.5         | 27.2                 | 7.07                | 2.011       | 157.075     | 154.085     | 14.912               | 0.8301          |

Figure 1. The XRD patterns of La$_{1-x}$Pb$_x$Fe$_{0.5}$Ti$_{0.5}$O$_3$ (x = 0.1, 0.2, and 0.3) calcined at 900 °C.

The structural properties were investigated by using X-Ray Diffractometer with Cu Kα radiation source. Optical properties were studied by using Raman scattering spectra (experimental conditions: laser source of 532 nm, power 2.0 mW), FTIR spectrometer (Perkin Elmer type Spectrum Two), and UV-vis spectrophotometer (Agilent Cary 100/300).

3. Results and discussion

3.1. X-ray diffraction analysis

Figure 1 shows the XRD patterns of La$_{1-x}$Pb$_x$Fe$_{0.5}$Ti$_{0.5}$O$_3$ (x = 0.1, 0.2, and 0.3). It confirms that all compounds are single phase with no measurable secondary phase. The refinement of XRD patterns using HighScore Plus software displays that all samples crystallize in the orthorhombic crystal structure. The details of refinement results are summarized in table 1. As can be seen, there are no significant changes in lattice and geometrical parameters. However, the crystallite size increases with Pb content. The tolerance factor decreases indicating the increase of lattice distortion due to the Pb content.


Table 2. FT-IR mode assignment of La$_{1-x}$Pb$_x$Fe$_{0.5}$Ti$_{0.5}$O$_3$ (x = 0.1, 0.2, 0.3) compounds.

| x  | FT-IR band position |
|----|---------------------|
|    | O–Fe/Ti–O Bending  | Fe/Ti–O–Fe/Ti Bending | Fe/Ti–O Stretching | O–H Bending |
| 0.1 | 459               | 761                  | 535            | 1477         |
| 0.2 | 459               | 760                  | 537            | 1482         |
| 0.3 | 458               | 754                  | 538            | 1476         |

Figure 2. The Raman scattering spectra of La$_{1-x}$Pb$_x$Fe$_{0.5}$Ti$_{0.5}$O$_3$ (x = 0.1, 0.2, and 0.3) compounds. The certain region describing in the dash line is related with vibrational modes occurring in samples.

3.2. Raman scattering spectra

In order to confirm the stability of phase and crystal structure, the Raman scattering was applied [6]. Figure 2 shows the Raman scattering spectra of La$_{1-x}$Pb$_x$Fe$_{0.5}$Ti$_{0.5}$O$_3$ (x = 0.1, 0.2, and 0.3) compounds. All samples show similar Raman spectra indicating the crystal structure remain unchanged due to the variation of Pb content. The spectra are also consistent with previously reported for the undoped and doped of LaFeO$_3$ [6–8]. According to the previous reports [6–8], the modes inside the region I are described as vibrational occurring in La/Pb-site; the modes inside the region II are related with the vibrational in Fe/Ti site; the modes inside the region III should be assigned to multi-phonon processes. The increase of Pb content causes the lowering of frequency phonon modes, broadening of peaks, and reducing of intensity indicating the lattice becomes more distorted as confirmed by XRD analysis.

3.3. FTIR analysis

The vibrational modes occurring in samples are also confirmed by FT-IR analysis. Figure 3 shows the FT-IR analysis of La$_{1-x}$Pb$_x$Fe$_{0.5}$Ti$_{0.5}$O$_3$ (x = 0.1, 0.2, and 0.3) compounds. This result is consistent with previous work for the doped and un-doped LaFeO$_3$ [4, 9]. Some specific vibrational modes are listed in table 2. As can be seen, the vibrational modes of metal oxide appear in the range of 400 – 800 cm$^{-1}$ for all samples. The slightly change in modes wavenumber with Pb substitution confirms the difference in metal oxide bond angle and bond length (table 1).

3.4. UV-Vis analysis

Figure 4 shows the UV-Vis spectra of La$_{1-x}$Pb$_x$Fe$_{0.5}$Ti$_{0.5}$O$_3$ (x = 0.1, 0.2, and 0.3) compounds. As shown in figure 4, the linear parts extrapolation against the absorption which equal to zero describes the direct band gap energy, $E_g$, for all samples. The $E_g$ is found in the range of 2.1 – 2.2 eV for all samples. These results are consistent with the previous report for direct band gap energy of LaFeO$_3$ [3–4].
Figure 3. The FT-IR spectra of La$_{1-x}$Pb$_x$Fe$_{0.5}$Ti$_{0.5}$O$_3$ (x = 0.1, 0.2, and 0.3) compounds.

Figure 4. UV-Vis spectra of La$_{1-x}$Pb$_x$Fe$_{0.5}$Ti$_{0.5}$O$_3$ for x = (a) 0.1, (b) 0.2, and (c) 0.3 compounds.
4. Conclusions
The series of La$_{1-x}$Pb$_x$Fe$_{0.5}$Ti$_{0.5}$O$_3$ ($x = 0.1, 0.2$, and 0.3) have been synthesized by sol-gel method. The structural analysis revealed the orthorhombic crystal structure, which is also confirmed by the identical Raman scattering spectra for all samples. The crystallite size increased with the increase of Pb content. The Raman scattering analysis revealed the presence of metal-oxide vibrational modes in lattice, which also confirmed by FT-IR analysis. The optical band gap for all samples is found in the range of 2.1 – 2.2 eV.

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