Structural and vibrational analysis of LaFe$_{1-x}$Mn$_x$O$_3$ (x = 0.05, 0.10, 0.15 and 0.20) perovskite materials

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Abstract. Lanthanum orthoferrite (LaFeO$_3$) and lanthanum manganite (LaMnO$_3$) are the important family of perovskite compound which intensively studied and explored due to its applications as functional materials, such as a fuel cell electrode, photocatalytic and gas sensor. The performance of functional materials is strongly depended on their structural properties. Here, we investigated the structure and vibrational of LaFe$_{1-x}$Mn$_x$O$_3$ (x = 0.05, 0.10, 0.15 and 0.20) perovskite materials prepared by sol-gel method. The structural and optical properties of the materials were characterized by X-Ray diffraction (XRD) spectroscopy, Fourier Transform Infra-red (FTIR) spectroscopy, Raman spectroscopy, and Ultraviolet-Visible (UV-Vis) spectroscopy. The analysis of the XRD pattern confirmed the single-phase orthorhombic structure (space group: Pnma) following by the decreasing of lattice parameters, crystallite size, and Fe/Mn–O bond distance with the increasing of Mn-content. The presence of the Fe/Mn–O bending and Fe/Mn–O stretching modes has been confirmed by FTIR and Raman investigation. The optical band gap energy was measured by UV-Vis DRS spectroscopy, which obtained in the range of 1.99–2.14 eV. The band gap energy decreases with the increase of Mn-content.

Keywords: Perovskite, sol-gel method; La(Fe, Mn)O$_3$; structure; band gap energy

1. Introduction
Lanthanum orthoferrite and manganite (chemical formula: LaFeO$_3$ and LaMnO$_3$, respectively) are one of the widely studied and explored materials due to its structural stability and multiferroics behavior [1]. The chemical substitution on La- or Fe-/Mn-sites has been reported to change its physical properties, especially the structural and optical properties which can be useful for improving its performance in applications [2-5]. Kamarkar et al. reported Fe-substitution Mn-sites on LaMn$_{1-x}$Fe$_x$O$_3$ (0 ≤ x ≤ 1) revealed the structure transition from rhombohedral to orthorhombic [2]. Y. Janbutrach et al. reported that the band gap energy of LaFeO$_3$ is about 2.05 eV; Al- substitution in LaFeO$_3$ decreases the lattice parameters and crystallite size together with the increase of magnetization and band gap energy [3]. Atma Rai et al. reported that double substitution of Ca and Mn on La$_{1-x}$Ca$_{x}$Fe$_{1-x}$Mn$_x$O$_3$ increases the lattice parameters and crystallite size together with the increase of magnetization and band gap energy [4]. The substitution of Li and Mn in La$_{1-x}$Li$_x$Fe$_{1-x}$Mn$_x$O$_3$ has also been reported by Thakur et al. that band gap energy decreases as compared to the LaFeO$_3$ parent in the range value of 2.11–1.61 eV that is useful in various electronics like photo-catalyst [5]. The substitution by Li and Mn...
improved dielectric, optical, and magnetic properties with maximum enhancement at 20% concentration.

Following the previous reported work [1-5], a systematic study of structural and optical properties of LaFe1-xMnxO3 (x = 0.05, 0.10, 0.15 and 0.20) perovskite materials has been carried out in this work. The LaFe1-xMnxO3 perovskite materials were prepared by the sol-gel method. The structural and optical properties investigations were characterized by using X-Ray Diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), DXR2 Raman microscope and UV-VIS spectroscopy.

2. Materials and method

The LaFe1-xMnxO3 (x = 0.05, 0.10, 0.15 and 0.20) perovskite materials were synthesized by the sol-gel method by using the Lanthanum oxide, manganese chloride tetrahydrate, iron nitrate monohydrate, and citric acid monohydrate as a precursor. The precursors were weighed and dissolved with distilled water. Then, the stirring and heating processes were accomplished in the solution until the gel-phase was composed. Then, the gel-obtained was heated with a heating treatment to form the nanoparticle in powder-form. The detailed about the synthesizing process have been explained in our previous work [6].

The lattice structure was investigated by using X-Ray Diffraction (XRD) type PANalytical-X’Pert PRO with source radiation Cu Kα (λ = 1.5418 Å) in the 2θ range of 20–80°. The lattice vibration was examined by Fourier-transform infrared spectroscopy (FTIR) PerkinElmer type Spectrum Two. Raman scattering studied using Thermo SCIENTIFIC DXR2 Raman microscope with an infrared wavelength rate of 538 nm. The band gap energy was measured by UV-VIS (Agilent Cary 100/300) to estimate band gap energy.

3. Results and discussion

3.1. Structural analysis

Figure 1 presents the XRD pattern of LaFe1-xMnxO3 nanoparticles plotted from JCPDS Number COD 96-152-6451. The spherical symbol shows the intensity of observations (Iobs) obtained from the results of the XRD characterization test. The red line shows the intensity of fitting results (Ical), and the green line is the difference between the intensity of observation and the intensity of fitting results (Iobs - Ical). The goodness of fit (χ2) in table 1 from refinement results is closed to 1 which indicates the good agreement between the observed and fitting results [5]. From the Rietveld refinement, the peak shows the hkl as follows: (101), (121), (022), (202), (123), (242) and (161). All peaks have been recognized and suggested the conformation of single-phase LaFe1-xMnxO3 (x = 0.05, 0.10, 0.15 and 0.20). There is no secondary phase indicating that Mn2+ has successfully occupied Fe3+ in B-sites.

The structural data obtained from XRD have been refined by using the High Score and VESTA software. The whole pattern refinement results conclude the orthorhombic crystal structure with the Pnma space group. The changes in structural parameters caused by the variation of Mn-substitution have been tabulated in table 1. Though the results suggest the changes in the lattice structure, such as a decrease in lattice parameters and/or volume unit cells, bond distance, and crystallite size. This might be associated with the substitution of Mn2+ (0.84 Å) for Fe3+ (0.64 Å) to make a change in the new valence states of Mn and/or Fe ions because of electric charge compensation, which makes an impact on the lattice volume decrement. This phenomenon can be also caused by the compensation of charge imbalance [4]. The tolerance factor decreases with Mn-substitution indicating the lattice becomes more distorted due to the Mn-substitution. The lattice parameters decreased with the increasing of Mn content. From the table 1, the calculated tolerance factor, t value decreased, indicating that the lattice becomes more distorted with the increasing of Mn content. The Fe/Mn–O bond distance is slightly decreased, indicating an escalating distortion of the Fe/MnO6 octahedra and reduced symmetry to reach stability.
3.2. Fourier transform infrared (FTIR) analysis

Fourier transform infrared (FTIR) spectrums of LaFe$_{1-x}$Mn$_x$O$_3$ (x = 0.05, 0.10, 0.15 and 0.20) have been characterized in region 400–4000 cm$^{-1}$. The FTIR spectrums of the samples reveal the presence of metal oxide bonds which shown in figure 2. The mode position depends on the composition and structure crystal of samples. This spectrum is like the previous report by Yutana et al. The strong modes are clearly observed around 400 cm$^{-1}$ and 500 cm$^{-1}$ [3]. The modes around 400 cm$^{-1}$ and 500 cm$^{-1}$ are assigned to Fe/Mn–O–Fe/Mn bending and Fe/Mn–O stretching vibrations. Each vibration correlates with the internal motion of bond angle and distance in Fe/MnO$_6$ octahedra, respectively [3, 4]. The metal-oxide stretching mode position increases at a higher wavenumber side with decreasing lattice parameters and Fe/Mn-O bond distance from 2.013 Å to 2.008 Å as shown in table 1. The decreasing metal-oxide bending mode position maybe due to the increasing Fe/Mn-O–Fe/Mn bond angle from 154.0° to 153.9°. A similar phenomenon is shown by Rai A [4]. The O–H bending mode was identified in the range of 1485–1635 cm$^{-1}$ suggesting the absorbing and trapping of water from the atmosphere. It is also supported by the modes around 3000 cm$^{-1}$ attributing to the stretching modes of water molecules [3, 7-8].

Some specific modes observed are tabulated in table 2. The changes in metal-oxide stretching and bending vibrations modes might be related to the change in the reduced mass of chemical environment due to the Mn-substitution [5]. Nonetheless, the slight changes in mode position indicate the insignificant changes in bond angle and distance. The presence of Fe/Mn-O-Fe/Mn bending, and Fe/Mn-O stretching confirms the Fe/Mn-O-Fe/Mn bond angle and Fe/Mn-O bond distance in XRD refinement results (table 1).

3.3. Raman spectroscopy analysis

Raman spectroscopy is an effective method to identify and explain the structural phase transition, oxygen motion of perovskite-type samples, and the presence of order-disorder effects in the lattice [9].

Figure 3 describes the Raman spectra of LaFe$_{1-x}$Mn$_x$O$_3$ (x = 0.05, 0.10, 0.15 and 0.20). The identical Raman spectrum confirms the unchanging crystal structure for all samples which is consistent with the XRD refinement results (table 1). The Raman spectra of LaFe$_{1-x}$Mn$_x$O$_3$ are similar to the previously reported for the orthorhombic structure of perovskite compounds [10, 11]. Some specific Raman modes are collected in table 3. In accordance with previous reports [10, 11], the modes $\omega_1$, $\omega_2$, and $\omega_3$ are assigned to La vibrations, tilting of the oxygen octahedral (Fe/MnO$_6$), and asymmetric stretching corresponding to Jahn-Teller distortion with Ag symmetry, respectively. The mode $\omega_4$ is related to the symmetric stretching of Fe/MnO$_6$ octahedra with B1g symmetry. Another phonon mode

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**Figure 1.** XRD pattern of LaFe$_{1-x}$Mn$_x$O$_3$ (x = 0.05, 0.10, 0.15, and 0.20) perovskite materials.
Table 1. Structural parameters from refinement results and calculated the tolerance factor of LaFe$_{1-x}$Mn$_x$O$_3$ ($x = 0.05$, $0.10$, $0.15$ and $0.20$) perovskite materials.

| Lattice parameters | LaFe$_{1-x}$Mn$_x$O$_3$ | $x = 0.05$ | $x = 0.10$ | $x = 0.15$ | $x = 0.20$ |
|--------------------|-------------------------|-----------|-----------|-----------|-----------|
| $a$ (Å)            | 5.562                   | 5.559     | 5.554     | 5.552     |
| $b$ (Å)            | 7.850                   | 7.845     | 7.830     | 7.826     |
| $c$ (Å)            | 5.554                   | 5.554     | 5.557     | 5.554     |
| Volume (Å$^3$)     | 242.5320                | 242.2878  | 241.6958  | 241.3832  |
| Bond Angles        |                         |           |           |           |
| Fe/Mn–O1–Fe/Mn     | 157.0748                | 157.0782  | 157.0901  | 157.0910  |
| Fe/Mn–O2–Fe/Mn     | 154.0550                | 154.0370  | 153.9800  | 153.9800  |
| Bond Distance      |                         |           |           |           |
| Fe/Mn–O1 x 2 (Å)   | 1.92372                 | 1.92353   | 1.92334   | 1.92241   |
| Fe/Mn–O1 x 2(Å)    | 2.08648                 | 2.08590   | 2.08470   | 2.08380   |
| Fe/Mn–O2 x 2(Å)    | 2.01392                 | 2.01274   | 2.00915   | 2.00805   |
| $\chi^2$           | 1.0689                  | 1.11067   | 1.25113   | 1.24851   |
| Crystallite Size (Å)| 795.6                   | 765.7     | 670.1     | 587.8     |
| Crystallite Strain (%)| 4.1 x 10$^{-2}$       | 4.3 x 10$^{-2}$ | 4.9 x 10$^{-2}$ | 2.2 x 10$^{-2}$ |
| Tolerance factor $<\sigma>$ | 0.917654               | 0.913268  | 0.908924  | 0.904621  |

Figure 2. The FTIR patterns of LaFe$_{1-x}$Mn$_x$O$_3$ ($x = 0.05$, $0.10$, $0.15$ and $0.20$) perovskite materials.

Table 2. FTIR modes assignment measured from transmittance spectrum for LaFe$_{1-x}$Mn$_x$O$_3$ ($x = 0.05$, $0.10$, $0.15$ and $0.20$) perovskite materials.

| LaFe$_{1-x}$Mn$_x$O$_3$ | FT-IR band positions |
|--------------------------|-----------------------|
| $x = 0.05$               | 477                   |
| $x = 0.10$               | 470                   |
| $x = 0.15$               | 463                   |
| $x = 0.20$               | 470                   |

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observed for $\omega_5$ and $\omega_6$ are associated with one-phonon and two-phonon scattering, respectively [12]. The Raman modes shift toward a higher wavenumber with the increasing of Mn-content. This might be affected by the change of crystallite size, lattice strain, and defects in lattice [11].

3.4. *Uv-vis spectroscopy analysis*

The Kubelka Munk function is used to calculate the absorption coefficient from the reflectance data. The formula is [13]:

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

where $F(R)$ is Kubelka-Munk function, $\alpha$ is the absorption coefficient, $s$ is the scattering coefficient, and $R$ is the diffused reflectance. Figure 4a shows the plot of $(F(R)E)^2$ vs. $h\nu$ for LaFe$_{1-x}$Mn$_x$O$_3$ for $x = 0.05$. The band gap energy is found in the range of 1.99–2.14 eV. This result is compatible with the previously reported for the LaFeO$_3$ compound [3]. Figure 4b describes the band gap energy as a function of Mn-content. The band gap energy decreases with the increasing substitution of Mn-substitution.

![Figure 3. The Raman spectra of LaFe$_{1-x}$Mn$_x$O$_3$ (x = 0.05, 0.10, 0.15 and 0.20) perovskite materials. Raman spectra were fitted using the standard Lorentzian profile.](image-url)
Table 3. Raman shift (cm\(^{-1}\)) and mode of LaFe\(_{1-x}\)Mn\(_x\)O\(_3\) (x = 0.05, 0.10, 0.15, 0.20) perovskite materials

| x   | \(\omega_1\) | \(\omega_2\) | \(\omega_3\) | \(\omega_4\) | \(\omega_5\) | \(\omega_6\) | Mode            |
|-----|---------------|---------------|---------------|---------------|---------------|---------------|-----------------|
| 0.05| 167           | 313           | 501           | 647           | 1154          | 1319          | \(A_g\)        |
| 0.10| 170           | 316           | 502           | 648           | 1148          | 1316          | \(A_g\)        |
| 0.15| 161           | 310           | 515           | 649           | 1150          | 1309          | \(A_g\)        |
| 0.20| 176           | 313           | 517           | 649           | 1148          | 1312          | \(B_{1g}\)     |

Figure 4. (a) The plot of \((F(R)E)^2\) vs. \(h\) for LaFe\(_{1-x}\)Mn\(_x\)O\(_3\) (x = 0.05) and (b) band gap energy as a function of Mn-content.

This might be due to the decrease in lattice parameters and/or bond distance as confirmed in table 1 [13]. The decrease of bond distance makes the atomic bonding more bound which causes the increasing band gap in the sample. It can be explained by the Burstein-Moss effect [14]. The Mn-substitution on lattice leads to the exceeding of free carrier concentration in the edge density of the conduction band. Accordingly, the Fermi level moves towards the conduction band, i.e., the increase of band gap energy [14].

The effect of Mn-substitution in Fe-site (has greater ionic radii than Fe-ions) induces the decrease in the lattice parameters and bond distance Fe/Mn–O as presented in table 1. The decrease in lattice parameters and bond distance is confirmed by the shifting in vibrational modes position towards a higher wavenumber as shown in Raman and FTIR. The decrease in the bond distance with Mn-substitution causes the atomic bond to become stronger. It is also confirmed by the band gap analysis that increases with the increasing of Mn substitution.

4. Conclusion
The single-phase LaFe\(_{1-x}\)Mn\(_x\)O\(_3\) (x = 0.05, 0.10, 0.15 and 0.20) nanoparticle studied have been successfully synthesized by sol-gel method. The X-Ray diffraction (XRD) pattern revealed the orthorhombic structure with the \(Pnma\) space group which is also confirmed by the identical FTIR and Raman scattering spectrums for all samples. The decrease in lattice parameters and bond distance with Mn-content could be interpreted as the consequence of the different ionic radii and valence state
The presence of metal-oxygen bonds, i.e., Fe/Mn – O – Fe/Mn bending and Fe/Mn – O stretching confirmed the formation of the oxide perovskite structure. The band gap energy decreases with increasing of Mn-content.

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