Optical properties of La$_{0.9}$Sr$_{0.1}$Fe$_{1-x}$Mo$_x$O$_3$ (x = 0.1, 0.2, and 0.3) perovskite material prepared by sol-gel method

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Abstract. The perovskite-type oxide La$_{0.9}$Sr$_{0.1}$Fe$_{1-x}$Mo$_x$O$_3$ (LSFMO) with x = 0.1, 0.2, and 0.3 were successfully prepared by sol-gel method. The synthesized perovskite has been characterized by Fourier transformed infrared spectroscopy (FTIR) and UV-Vis spectroscopy for further studies. FTIR spectra confirm the presence of Fe/Mo−O stretching and Fe/Mo−O−Fe/Mo bending vibration s in lattice. UV-Vis analysis displayed the optical band gap increase with increasing of Mo-content.

1. Introduction
Perovskite with general formula ABO$_3$ have been paid attention for twenty century due to the unique dielectric, electronic conductivity, multiferroics behaviour, magnetic ordering, and optical properties [1-2]. LaFeO$_3$ is the one of the perovskite materials which is widely studied for various potential application such as solid oxide fuel cells (SOFC), batteries, dan photocatalysis [2]. The semiconducting perovskite LaFeO$_3$ nanostructure has potential in photocatalyst application due to the lower direct bandgap energy in the range of visible light [1]. Based on theoretical model using ab initio pseudopotential method, Shein et al. [3] calculated the band gap energy of LaFeO$_3$ and found to be 2.52 eV. Meanwhile, Arima et al. [4] calculated the band gap energy of LaFeO$_3$ based on the atomic ionization potential and found to be 2.10 eV. Subramaniam et al. [5] studied the effect of experimental condition and molar concentration in LaFeO$_3$ and found that these parameters could be used to controlled the morphology, surface area, particle size, and band gap energy of LaFeO$_3$. Murade et al. [6] reported the appearance of Sr−O and Fe−O stretching modes due to the Sr-substitution on La$_{0.7}$Sr$_{0.3}$FeO$_3$ samples. Based on several research above, we study the effect Mo-substitution on La$_{0.9}$Sr$_{0.1}$Fe$_{1-x}$Mo$_x$O$_3$ (LSFMO) with x = 0.1, 0.2, and 0.3. The samples were prepared by sol-gel method. The LSFMO materials were characterized by Fourier transformed infrared spectroscopy (FTIR) to investigate the Sr/La−O and Mo/Fe−O vibration modes in lattice and UV-Visible spectrophotometer to reveal the bandgap energy. From this, the effect of Mo-doped on LSFMO perovskite materials could be explained.

2. Experimental Methods
Perovskite LSFMO was synthesized by sol-gel method of La$_2$O$_3$, Sr(NO$_3$)$_2$, Fe(NO$_3$)$_3$.9H$_2$O, MoO$_3$, citric acid, and aqua distillation as a precursor. The solution was converted to gel phase with stirring and heating process. Then, the drying process was applied to remove water, citric acid and another organic compounds. The powder phase was obtained after calcined process. The details of the sample preparation have been explained in previous work [7].

The FTIR spectrum was recorded using PerkinElmer type SpectrumTwo to confirm the structural information. The spectrum was collected in the mid-IR range from 4000 to 250 cm$^{-1}$ at room
temperature. Optical reflectance spectrum was recorded in the range of 200 – 800 nm by using UV-VIS (Agilent Cary 100/300).

3. Results and Discussion

3.1. Fourier transform infrared spectroscopy
Vibrational spectroscopy measurements were performed to investigate further on the structure of different compositions prepared. The FTIR spectra of La$_{0.9}$Sr$_{0.1}$Fe$_{1-x}$Mo$_x$O$_3$ (x=0.1, 0.2, 0.3) nanoparticles is shown in figure 1. The small shift is observed to the lower wavenumber due to the Mo-substitution.

![Figure 1. The IR spectra of LSFMO LSFMO (x=0.1, 0.2, 0.3) nanoparticles.](image)

The two important bands with the wavenumber around 540 cm$^{-1}$ and 400 cm$^{-1}$ confirm the formation of perovskite structure (ABO$_3$) [2]. The detailed of some specific bands for all samples are shown in table 1. The band around 400 cm$^{-1}$ is assigned to Fe/Mo−O−Fe/Mo bending vibration. Wavenumber in the range 500−550 cm$^{-1}$ is attributed to the Fe/Mo−O stretching vibration. The vibration Fe/Mo−O shifts toward higher wavenumber which probably related to changes in bond distances [2,8]. A small peak in the range of 700−800 cm$^{-1}$ reveals the presence of metal-oxide (M-O) bonds which caused by increasing Mo-substituted on Fe-site [8]. The effect of substitution Sr on La-site causes the broadening of band around 800 cm$^{-1}$ which was identified as Sr−O stretching mode [6]. Band around 900 cm$^{-1}$ was identified as La−O stretching vibration [9]. The exposure of environmental humidity in perovskite caused the appearance of O−H bond around 2000 cm$^{-1}$. The Fe/MoO$_6$ vibrational bands trend to shift towards higher wavenumber with increasing of Mo-substitution. It might be due to the changes in reduce mass of the variation of Mo-content in lattice [2].
Table 1. The band position of some specific vibration modes in infrared spectrum of LSFMO nanoparticles

| x     | Sr—O stretching (cm⁻¹) | Fe/Mo—O stretching (cm⁻¹) | Fe/Mo—O— Fe/Mo bending (cm⁻¹) |
|-------|------------------------|---------------------------|-------------------------------|
| 0.1   | 818.2                  | 537.3                     | 464.1                         |
| 0.2   | 815.1                  | 536.3                     | 469.1                         |
| 0.3   | 815.9                  | 540.1                     | 473.1                         |

3.2. UV-Vis analysis

Optical band gap energy of LSFMO was obtained based on diffuse reflectance spectrum mode with UV-Vis spectroscopy. Figure 2 presents the reflectance spectrum of La₀.₉Sr₀.₁FeₓMo₀.₁₋ₓO₃ (x=0.1, 0.2, 0.3) nanoparticles. The higher percentage of reflectance spectrum along with increasing of Mo-content indicates the decrease in absorption. It might be due to the replacing of Mo-ions in Fe-site inside the lanthanum orthoferrite lattice.

![Figure 2. Recorded reflectance spectrum of LSFMO (x=0.1, 0.2, 0.3) nanoparticles](image)

In order to estimate the bandgap energy of LSFMO, the diffuse reflectance data is used to obtain the coefficient absorption based on the Kubelka-Monk (KM) function [10].

\[
F(R) = \frac{\alpha}{s} = \frac{(1 - R)^2}{2R} \tag{1}
\]

where \(F(R)\) is the KM function, \(\alpha\) is absorption coefficient, \(s\) is the scattering coefficient, and \(R\) is the diffuse reflectance recorded.

Figure 3 shows the bandgap energy \(E_g\) which was estimated by using Tauc’s plot. The band gap energy is found in the range of 2.0 – 2.2 eV. The band gap energy increases with increasing of Mo-doped. It is possible caused by the Mo⁶⁺ substituted in Fe³⁺-site in lattice introducing the mixed valence cation of Mo⁴⁺/Mo⁶⁺ and/or Fe²⁺/Fe³⁺ which has smaller ionic radii that leads to the increase the atomic bonding in lattice. Accordingly, the movement of charger carriers become more difficult, so the energy that needed to facilitate the movement of carriers, i.e., gap energy tends to increase.
Figure 4 shows bandgap energy as a function of Mo-concentration. The increasing of band gap energy indicates the decreasing of conduction response in the samples. Similar trend has been reported by Yutana et al. [11] that substitution of Al on A-sites in LaFeO$_3$ increases band gap energy with rise Al-substitution.

**Figure 3.** Tauc’s plot of LSFMO (x=0.1, 0.2, 0.3) nanoparticles

**Figure 4.** The plot of band gap energy as a function of Mo-content of LSFMO (x=0.1, 0.2, 0.3) nanoparticles
4. Conclusion

La_{0.9}Sr_{0.1}Fe_{1-x}Mo_xO_3 (x = 0.1, 0.2, and 0.3) nanoparticle has been successfully synthesized by sol-gel method. FTIR spectra confirmed deformation of perovskite structure which was evidenced by the existence of the stretching and deformation of Fe−O and Fe−O−Fe of FeO_6 vibrational modes. Mo-substitution caused the vibrational bands occurring in Fe/MoO_6 octahedra shifts towards higher wavenumber. The presence of Sr-ions in La-site has also displayed by the appearance of the Sr−O stretching mode in lattice. The band gap energy increases with Mo-substitution.

5. Acknowledgments

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6. References

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