The experimental investigation on the crystalline structure, lattice vibration, and optical energy of La$_{1-x}$Bi$_x$FeO$_3$ nanoparticles

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Abstract. Lanthanum-bismuth orthoferrite (La$_{1-x}$Bi$_x$FeO$_3$ with $x=0.1$, 0.2, 0.3, 0.4 and 0.5) nanoparticles have been successfully prepared using sol-gel method. The crystalline structure, lattice vibration, and optical energy analysis have been characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), Raman scattering spectroscopy, and UV-Vis spectroscopy. The XRD revealed the single phase orthorhombic structure with $Pnma$ space group. The crystallite size tends to decrease in the range of 130 − 298 nm with increasing Bi-content. The existence of Fe−O stretching and bending modes were investigated by FTIR spectra and also confirmed by Raman scattering analysis. The optical bandgap was investigated by UV-Vis spectroscopy concluding the decrease of gap energy with Bi-content.

1. Introduction
Perovskite material has the chemical formula ABX$_3$, where A is rare earth ion and usually a large cation, B is transition metal ion and usually a medium-sized cation and X is anion [1]. Several researches have been reported and developed not only related to the structure, electricity, magnetism but also the optical properties [1-6]. Lanthanum orthoferrite (LaFeO$_3$) is the one of orthorhombic crystal perovskite structure which have the high structural stability at room temperature [2]. The LaFeO$_3$ have been reported improving the degradation of various organic pollutants [3]. Atma and Awalendra [4], reported that substitution of monovalent ion Li in site-A and trivalent ion Mn in site-B (La$_{1-x}$Li$_x$Fe$_{1-y}$Mn$_y$O$_3$ with $x = y = 0.00$, 0.05, 0.10, 0.15 and 0.20) using Pechini route improved the dielectric, optical, magnetic and conduction properties. Sasikala et al [5], reported that Ti-substitution on LaFeO$_3$ (LaFe$_{1-x}$Ti$_x$O$_3$ with x 0.2, 0.4, 0.6 and 0.8) decreased the crystallite size and increased the gap energy in the range of 2.05 – 2.61 eV. Also, couplings of ZnO/Bi-doped on LaFeO$_3$ significantly extended visible light absorption activities [6].

This work will focus on the experimental investigation on the structure, vibration, and optical band gap energy of La$_{1-x}$Bi$_x$FeO$_3$. The samples were synthesized by sol-gel method with variation of Bi-content. By using the structure and optical characterization explained below, the investigation on the crystalline structure, lattice vibration, and optical energy of La$_{1-x}$Bi$_x$FeO$_3$ have been systematically studied.
2. Experimental Details
The preparation of La$_{1-x}$Bi$_x$FeO$_3$ (x=0.1, 0.2, 0.3, 0.4 and 0.5) by sol-gel method were used La$_2$O$_3$, BiN$_2$O$_5$.5H$_2$O, Fe(NO$_3$)$_3$.9H$_2$O, citric acid as a precursor and aquades as raw materials. All chemical compounds were mixed using magnetic stirrer to create the gel-phase. The gel was heated with the certain heating condition to remove the acid and form the nanoparticles. The details of synthesize process have been explained in previous work [7].

The crystalline structure of La$_{1-x}$Bi$_x$FeO$_3$ nanoparticles have been checked by XRD characterization using the X-Ray diffractometer PANalytical:X'pert Pro. The Raman scattering spectra were measured with Thermo SCIENTIFIC: DXR2 Raman Microscope in range from 100-1600 cm$^{-1}$. The chemical bounding were investigate by Fourier transform infrared spectroscopy (FTIR) (PerkinElmer type Spectrum Two). The UV-Vis reflectance spectra were measured by UV-Vis Agilent Cary 100/300, to determine the optical bandgap.

3. Result and Discussions
3.1. X-ray diffraction (XRD) analysis
The XRD pattern were fitted by the LaFeO$_3$ (No.COD 96-152-6451) in the refinement of full pattern in Highscore Plus program. The result of the fitting XRD patterns La$_{1-x}$Bi$_x$FeO$_3$ (x= 0.2 and 0.4) nanoparticles are shown in figure 1 (a). The XRD patterns of La$_{1-x}$Bi$_x$FeO$_3$ (x= 0.1, 0.3 and 0.5) nanoparticles have been reported in previous work [7].

The refinement results is acceptable with the orthorhombic structure with Pnma space group without any trace of secondary or impurity phase detected. The detailing about the crystalline structure parameters are tabulated in table 1. Figure 1 (b) shows the magnification of peak (200). The peak shown that shift to the higher degree with increasing the Bi-content and the peak become smoother suggesting that the structure parameters were changed. The lattice parameters increase with increasing of Bi-content, it may be due to the difference of ionic radii La$^{3+}$ and Bi$^{3+}$, whose value is 1.16Å and 1.17Å [7,8]. The increase in the volume of unit cell confirm the fact that Bi$^{3+}$ ions have been incorporated into the lanthanum orthoferrite lattice. The crystallite size decreases with Bi-content indicating the existence of Bi-ions in lattice becomes the inhibitor for crystal growth process [9]. The tolerance factor, bond length, and bond angle increase suggesting the lattice distortion is reduced with increasing of Bi-content [7].
Figure 1. (a) XRD pattern of $\text{La}_{1-x}\text{Bi}_x\text{FeO}_3$ materials. (b) The magnification peak (200) in the range of $30 < 2\theta < 35$
Table 1. The crystalline structure parameters of La$_{1-x}$Bi$_x$FeO$_3$ (x = 0.2 and 0.4) nanoparticles

| Parameter                     | La$_{1-x}$Bi$_x$FeO$_3$  |
|-------------------------------|--------------------------|
| Crystalline Parameter         |                          |
| Lattice Parameters            |                          |
| a                             | 5.5696                   |
| b                             | 7.8548                   |
| c                             | 5.5457                   |
| $\chi^2$                      | 1.0164                   |
| Crystallite size (nm)          | 298.0                    |
| Density (g/cm$^3$)             | 6.631                    |
| Volume (V/10$^6$ pm$^3$)       | 242.61                   |
| R factor (%)                  |                          |
| Re                            | 5.8379                   |
| Rp                            | 6.6648                   |
| Rwp                           | 8.5097                   |
| Geometrical parameters        |                          |
| Bond length (Å)               |                          |
| La/Bi–O1                      | 2.6925                   |
| La/B–O2                       | 2.3813                   |
| <La/Bi–O>                     | 2.5369                   |
| Fe–O1                         | 2.0872                   |
| Fe–O2                         | 2.0150                   |
| <Fe–O>                        | 2.0511                   |
| Bond angle (°)                |                          |
| La/Bi–O1–La/Bi                | 163.53                   |
| La/Bi–O2–La/Bi                | 106.82                   |
| Fe–O1–Fe                      | 157.06                   |
| Fe–O2–Fe                      | 154.11                   |
| Tolerance Factor              | 0.8299                   |

3.2. Raman scattering analysis
Raman spectroscopy has a shorter length of scale than X-ray diffraction (XRD) and very useful for identifying structural transition phases, the movement of oxygen from perovskite material, and studying the effect of order-disorder on the lattice [11]. Raman spectrum of La$_{1-x}$Bi$_x$FeO$_3$ (x = 0.1, 0.2, 0.3, 0.4 and 0.5) nanoparticles are shown in figure 2. The raman scattering spectrum are similar with the previous work [11, 12].

According to the previous work [11, 12], the modes observed below 200 cm$^{-1}$ are assigned to the vibration of La-cation with $A_g$ symmetry. Mode around 200 – 300 cm$^{-1}$ are related to FeO$_6$ octahedra tilt modes with $A_g$ symmetry. Oxygen octahedral bending vibration mode is observed in the frequency range of 400 – 500 cm$^{-1}$ with $A_g$ symmetry. The mode in the frequency range of 500 – 600 cm$^{-1}$ is attributed to oxygen stretching vibration with $B_{1g}$ symmetry. The mode in the frequency range of 600 – 700 cm$^{-1}$ is related to Jahn-Teller distortion with $B_{1g}$ symmetry. The additional modes above 900 cm$^{-1}$ are related with the multi phonon processes [14].

The some specific Raman modes are tabulated in table 2. The Raman modes shift toward higher frequency with increasing of Bi-content suggesting the changes in geometrical parameters, i.e., bond length, bond angle, lattice distortion, etc, which has been confirmed by XRD refinement results (Table 1) [12].
Figure 2. Raman scattering spectra of La$_{1-x}$Bi$_x$FeO$_3$ (x = 0.1, 0.2, 0.3, 0.4 and 0.5) nanoparticles. The Raman spectra were fitted using standard Lorentzian profile. The dash line described the fitting results of raman scattering spectra.
Table 2. The some specific Raman modes of La$_{1-x}$Bi$_x$FeO$_3$ (x=0.1, 0.2, 0.3, 0.4 and 0.5) nanoparticles

| x      | ω1 (cm$^{-1}$) | ω2 (cm$^{-1}$) | ω3 (cm$^{-1}$) | ω4 (cm$^{-1}$) | ω5 (cm$^{-1}$) | ω6 (cm$^{-1}$) | ω7 (cm$^{-1}$) | ω8 (cm$^{-1}$) | ω9 (cm$^{-1}$) | ω10 (cm$^{-1}$) | Mode          |
|--------|---------------|---------------|---------------|---------------|---------------|---------------|---------------|---------------|---------------|---------------|--------------|
| x=0.1  | 104           | 141           | 245           | 295           | 427           | 521           | 656           | 1053          | 1173          | 1300          | A$_g$        |
| x=0.2  | 105           | 145           | 247           | 310           | 430           | 532           | 657           | 1054          | 1175          | 1302          | A$_g$        |
| x=0.3  | 106           | 147           | 250           | 311           | 430           | 532           | 659           | 1056          | 1179          | 1303          | A$_g$        |
| x=0.4  | 107           | 150           | 251           | 314           | 435           | 532           | 659           | 1057          | 1180          | 1305          | A$_g$        |
| x=0.5  | 108           | 161           | 252           | 315           | 436           | 536           | 664           | 1057          | 1180          | 1308          | A$_g$        |

Table 3. Fourier transform infrared spectra of La$_{1-x}$Bi$_x$FeO$_3$ (x=0.1, 0.2, 0.3, 0.4 and 0.5) nanoparticles

| x      | FTIR band position (cm$^{-1}$) |
|--------|--------------------------------|
|        | Fe−O vibration                | C=O        | C=O        | Bending Vibration Water Molecules and nitrate groups |
| x=0.1  | 534                            | 1219       | 1358       | 1736          |
| x=0.2  | 540                            | 1220       | 1359       | 1737          |
| x=0.3  | 541                            | 1222       | 1367       | 1739          |
| x=0.4  | 543                            | 1224       | 1368       | 1740          |
| x=0.5  | 547                            | 1226       | 1370       | 1743          |

3.3. Fourier transform infrared spectra (FT-IR) analysis

Fourier transform infrared spectra of La$_{1-x}$Bi$_x$FeO$_3$ (x=0.1, 0.2, 0.3, 0.4 and 0.5) nanoparticles are presented in figure 3.

![Figure 3. FTIR spectra of La$_{1-x}$Bi$_x$FeO$_3$ (x=0.1, 0.2, 0.3, 0.4 and 0.5) nanoparticles](image)

The band around 530 cm$^{-1}$ is corresponded to Fe−O stretching vibration [15]. The band around 1200 cm$^{-1}$ are attributed to the presence of C−O vibration. The band around 1300 cm$^{-1}$ and 1700 cm$^{-1}$ are attributed to the C=O and bending vibrations of the water molecules and nitrate groups, respectively [16]. The vibrational modes tend to shift toward higher frequency suggesting the changes in Fe−O−Fe bond angle and decrease in the asymmetry Fe−O−Fe bond inside lattice with increase of Bi-content [17].

3.4. UV-Visible
The UV-Vis reflectance spectra of La$_{1-x}$Bi$_x$FeO$_3$ (x=0.1, 0.2, 0.3, 0.4 and 0.5) are shown in figure 4. The strong reflectance peak is observed in wavelength around 550 – 650 nm and centered at approximately 614 nm. The UV-vis spectrum can be used to determine the band gap of the material using this equation [18],

$$a h v = k (h v - E_g)^{1/n}$$

Where $a$ is the optical absorption coefficient, $h v$ is the photon energy, $k$ is an energy-independent constant and $E_g$ is the optical bandgap. The optical bandgap can be described by extrapolating the slope of plots of $(a h v)^2$ vs. $h v$ as shown in figure 5a.

The band gap energy as a function of Bi-content is shown in figure 5(b). The optical bandgap decreases with increasing the Bi-content in the range of 1.98 – 2.08 eV. It might be due to the incorporation of charge carriers inside lattice induces localized states near the conduction band and/or valence band [19]. Furthermore, the localized of charge carrier is strongly dependent on the particle size, structure distortion, and ionic vacancy [12, 20]. The study of band gap is useful in photocatalytic application [2].

![Figure 4](image1.png)

**Figure 4.** The UV-Vis spectra of La$_{1-x}$Bi$_x$FeO$_3$ (x=0.1, 0.2, 0.3, 0.4 and 0.5) nanoparticles

![Figure 5](image2.png)

**Figure 5.** (a) Plots of $(F(R)E)^2$ vs. $h v$ for La$_{1-x}$Bi$_x$FeO$_3$ with x = 0.1 and (b) The gap energy as a function of Bi-content
4. Conclusion
The La$_{1.3}$Bi$_x$FeO$_{3.5}$ (x = 0.1, 0.2, 0.3, 0.4 and 0.5) nanoparticles have been successfully prepared by sol-gel method. Crystalline structure analysis disclosed the orthorhombic perovskite structure with $Pmna$ space group. The lattice vibrational investigation revealed the shifting of metal-oxygen vibration modes to higher frequency with increase of Bi-content. Additionally, the band gap energy decreases with increasing Bi-content.

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References
[1] Tilley R J D 2016 Perovskite Structure-Property Relationships (United Kingdom: Wiley) p 10
[2] Thirimalairajan S, Girija K, Ganesh J, Mangalaraj D, Viswanathan C, Balamurugan A and Ponpdian N 2012 Chem. Eng. J 209 420-28
[3] Shen H, Tong X, Yanmin W, Guozhong C, Youju L and Guoli F 2016 Mater. Res. Bull 84 15-24
[4] Atma R and Awalendra K. Thakur 2017 Ceram. Int 43 13828-38
[5] Sasikala C, Durairaj N, Baskaran I, Sathyaseelan B, Henini M and ManiKandan E 2017 J. Alloys Compd 712 870-77
[6] Humayyun M, Ning S, Fazal R, Xuliang Z, Rui Y, Zhijun L, Yang Q and Liqiang J 2018 Appl. Catal., B: Environmental 231 23-33
[7] Fitria S N and Triyono D 2018 Structural analysis and dielectric properties of La$_{1.3}$Bi$_x$FeO$_{3.5}$ perovskite material Conf. August 14th 2018 Solo
[8] Ahmed M A, Azab A A and El-Khawas E H 2015 J. Mater. Sci.- Mater. Electron 26 8765-73
[9] Cao E, Yanrong Q, Tingting C, Lin S, Wentao H and Yongjia Z 2017 Ceram. Int 43 7922-8
[10] Oroosa S, Chris R B, Malik M M and Rajnish K 2016 J. Alloy. Compd 688 27-36
[11] Yaru W, Yongping P, Xin L, Hanyu Z and Ziyang G 2016 Mater. Chem. Phys 183 247-53
[12] Preet S, Tejwant S K and Randhawa B S 2015 J. Alloys. Compd 625 336-45
[13] Blanck D, Anke S, Anne-Sopjie M, Crtistophe D, Jean-Philippe, Pascal G, Jean F P, and Elise B 2017 Catal. Today 283 151-7
[14] Jaouali I, Hayfa H, Noomen M, Mohamed F N, Miguel A C, Anna B, Giovanni N and Salvatore G L 2018 Ceram. Int 44 4183-9
[15] Abazari R and Soheila S 2013 Superlattices Microstruct 64 148-157
[16] Yadav, Avadhesh K, Rajneesh K S and Prabhakar S 2016 Sens. Actuators, B: Chemical 229 25-30
[17] Basiri M H, Shokrollahi H and Isapour. Gh 2014 J. Magn. Magn. Matt 354 184-89
[18] Kofestern, Roberto, Lothar J and Stefan G E 2013 Solid State Ionics 249-250 1-5
[19] Akbar, A, Saira R, Shahid A and Shahzad N 2013 Advances in Nano, Biomechanics, Robotics, and Energy Research 883-91
[20] Kumar, Kotesh M, Bhavani K, Srinivas B, Naveen K S, Sudhakar M, Naresh G, and Venugopal A 2016 Appl. Catal., A: General 515 91-100