Available online at www.SciMedJournal.org

SciMedicine Journal

Vol. 1, No. 3, September, 2019

Preparation, Characterization and Optical Property of $LaFeO_3$ Nanoparticles via Sol-Gel Combustion Method

Mya Theingi [a*], Kay Thi Tun [b], Nwe Nwe Aung [a]

[a] *Department of Chemistry, University of Yangon, Myanmar.*

[b] *Department of Chemistry, East Yangon University, Myanmar.*

Received 06 June 2019; Accepted 27 August 2019

Abstract

Perovskite $LaFeO_3$ is one of the most useful materials for the application in a catalyst, gas sensors, and fuel cells, etc. $LaFeO_3$ nanoparticles were synthesized by the citrate sol-gel method. According to the TG-DTA analysis on $LaFeO_3$ xerogel powder, the proper crystallization temperature was found to be at 450 °C. The TEM images also show clear crystal formation was started at 450 °C. The $LaFeO_3$ nanocrystalline particles were obtained by sintering the calcined powders at different temperatures (800 °C, 900 °C, and 1000 °C) for 4 hours. The resulting particles were characterized by XRD, EDXRF, FT IR, and SEM analysis. At 900 °C, the XRD pattern of LaFeO3 shows an orthorhombic crystal structure. The average crystallite sizes vary between 30-60 nm and the increase in crystallite size with increasing sintering temperatures and it may be due to the increase in grain growth. FT IR analysis shows strong La-O and Fe-O vibrations. Based on the XRD and FT IR data, the optimum sintering temperature was chosen at 900 °C. The SEM micrographs show that the morphology of $LaFeO_3$ has small-sized grains with round shape. The optical properties were determined by UV-visible spectroscopy in the wavelength range of 300 nm-700 nm. The optical band gap energy values of $LaFeO_3$ using Tauc's plot were found to be about 2.45 eV. These results indicate that the LaFeO3 prepared by the sol-gel method has a relatively lower band gap value and so it can have the potential for photocatalytic applications.

Keywords: Perovskite; $LaFeO_3$; Citrate Sol-Gel Method; Optical Properties.

---

1. Introduction

Perovskite-type oxides of general formula ABO_3 (A = rare or alkali earth metals, B = transition metals) have become one of the most promising candidates due to their wide range of physical and technological properties, such as ferroelectricity, piezoelectricity, pyroelectricity, high-temperature superconductivity, magnetic behavior, and catalytic activity [1, 2]. These properties determine the use of such materials in many applications such as gas transducers, catalysts, solid electrolyte batteries and magnetic sensors [3, 4]. Among perovskite-type oxides, LaFeO3 is of interest because of its low price, non-toxicity, abundant reserve, and excellent electrochemical capacity [5]. There are several methods for the synthesis of perovskite-type oxide LaFeO3 such as solid-state reaction, sol-gel method, co-precipitation, and hydrothermal process. The sol-gel method is widely used for the preparation of inorganic ceramic and composite materials, with controlled properties for several applications. This is a novel way with a combination of the chemical sol-gel process and the combustion process. The advantages of the sol-gel method are inexpensive precursors; a simple preparation method; and a resulting nano-sized, homogeneous, highly reactive powder. Therefore, the sol-gel auto combustion method has been considered as an attractive and quality technique for the preparation of oxide materials [6-8]. In this work, therefore, we focus on the synthesis of LaFeO3 by sol-gel method followed

---

* Corresponding author: mya.tt.chem@gmail.com

http://dx.doi.org/10.28991/SciMedJ-2019-0103-5

calcination and sintering at different temperatures. The synthesized LaFeO3 powder also was characterized by TG-DTA, XRD, FT IR, SEM, TEM, and UV–Vis spectrophotometer.

2. Materials and Methods

2.1. Materials

Analytical grade lanthanum nitrate hexahydrate ($La(NO_3)_3$*.$6H_2O$), iron nitrate nonahydrate ($Fe(NO_3)_3.9H_2O$), citric acid monohydrate ($C_6H_8O_7$*.$6H_2O$) and ethylene glycol (CH_2OHCH_2OH) were used as reagents for synthesis. All the reagents are Analar grade and used as received.

2.2. Preparation of LFO Nanocrystalline Particals

$LaFeO_3$ particles were prepared by the sol-gel combustion method. Firstly, lanthanum nitrate hexahydrate and iron nitrate nonahydrate were weighted in stoichiometric proportions (1:1 molar ratio) and were dissolved in distilled water by a magnetic stirrer. Subsequently, when the metal salts were completely dissolved in the solution, citric acid and ethylene glycol were added to the precursor solution. The molar amount of citric acid and 5 mL of ethylene glycol were equal to a total molar amount of metal nitrates in the solution. The molar amount of citric acid was equal to a total molar amount of metal nitrates in the solution. This solution was heated to 70-80 °C on a heating plate with stirring for several hours using a magnetic stirrer to achieve the gel formation. For the gel formation was put rapidly into the electrical oven at a temperature of 110 °C for 5 hours to obtain dry powders, known as xerogel powders. These powders were ground and calcined at 400, 450, 500 °C for 5 hours in a muffle furnace. According to XRD analysis, the optimal calcined temperature is 450 °C and the selected sample was sintered at 800, 900 and 1000 °C for 4 hours.

2.3. Characterization

TG-DTA was carried out on the xero-gel powder to characterize thermal behavior and estimate crystallization temperatures. The crystal structure of $LaFeO_3$ nanoparticles was determined using XRD measurements using a Cu-Kα (λ = 1.5406 Å) radiation operated at 30 kV and 20 mA in the range of 2θ 10° to 70°. FT IR was carried out to determine possible functional groups and EDXRF analysis was also carried out to examine composition elements of the prepared $LaFeO_3$ particles. SEM and TEM were used to determine morphology and average particle sizes. Optical bandgap energy of $LaFeO_3$ sintered at 900°C was calculated by Tauc plot by the use of UV-vis spectroscopy data.

3. Results and discussion

3.1. TG-DTA Analysis

TG-DTA curves of $LaFeO_3$ xerogel powder are shown in Figure 1. The three sharp exothermic peaks at 261, 365 and 408 °C were observed. The small endothermic peak about 100 °C with 5.20 % weight loss has corresponded to the elimination of adsorbed water, the other endothermic peaks at ~ 231 °C with 30.55 % is corresponded to decomposition and the burn out of organic species in the powder, the peak at ~ 358 °C with 27.66 % corresponds to decomposition of remaining nitrate and the peak at ~ 544 °C with 17.30 % is corresponded to the formation of the expected perovskite phase of $LaFeO_3$.

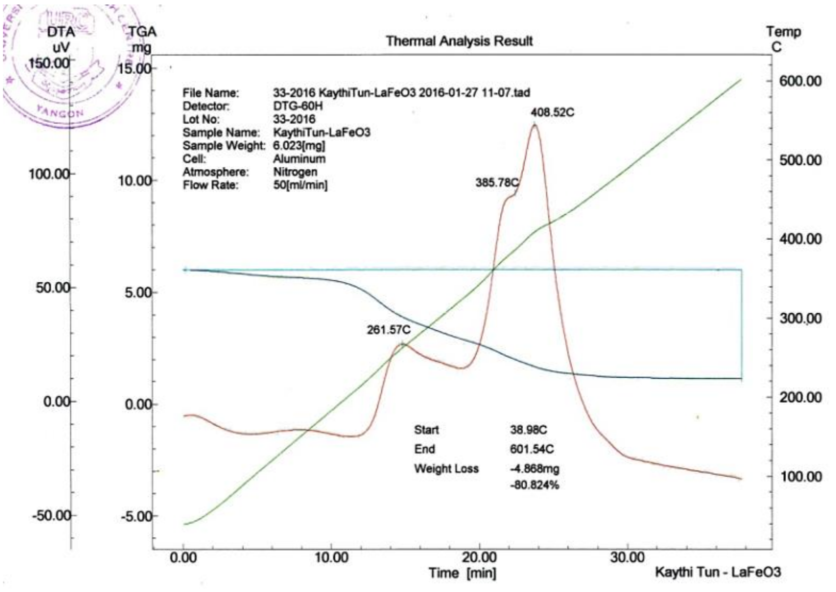


Figure 1. TG-DTA curves of the thermal decomposition of $LaFeO_3$ xero-gel powder

3.2. XRD Analysis

Room temperature X-ray powder diffraction patterns of $LaFeO_3$ xerogel powder and $LaFeO_3$ particles calcined at 400, 450 and 500 °C are shown in Figure 2 and 3. Any diffraction peak is not observed in the XRD pattern of xerogel powder which indicates the prepared gel is mainly amorphous. X-ray diffraction pattern of $LaFeO_3$ powder calcined at 400 ˚C also show amorphous nature and which is difficult to index according to the JCPDS data indicating the insufficient calcination temperature. XRD pattern of $LaFeO_3$ calcined at 450 and 500 °C indicates that the prepared samples have the perovskite structure and all peaks are well defined and it indicates that synthesized particles are well crystallized. The strongest peak and characteristic planes (110) were observed and it has a cubic crystal structure with Pm-3m space group. The XRD patterns of $LaFeO_3$ particles sintered at 800 ˚C, 900 °C and 1000 ˚C are shown in Figure 4 and It was found that crystal structure was a change into orthorhombic due to high-temperature sintering and It has Pbmn space group. The crystallite sizes of prepared samples calcined at 450 and 500 °C were calculated by equation $D = 0.9\lambda/\beta\cos\theta$, where D is the average size of the particles, λ is wavelength of X-ray radiation, β the full width at half maximum of the diffracted peak and θ is the angle of diffraction [9]. The crystallite sizes of the prepared samples calcined at 450 and 500 °C are 27.68 and 27.97 respectively. The crystallite size of the samples, sintered at 800, 900 and 1000°C, are 51.27, 49.75 and 66.70 nm respectively.

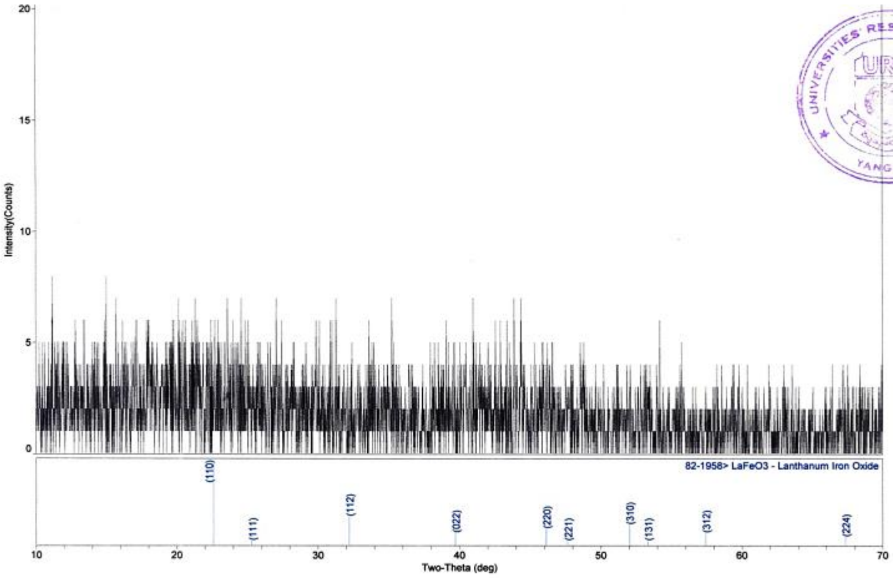


Figure 2. XRD pattern of $LaFeO_3$ xerogel powder

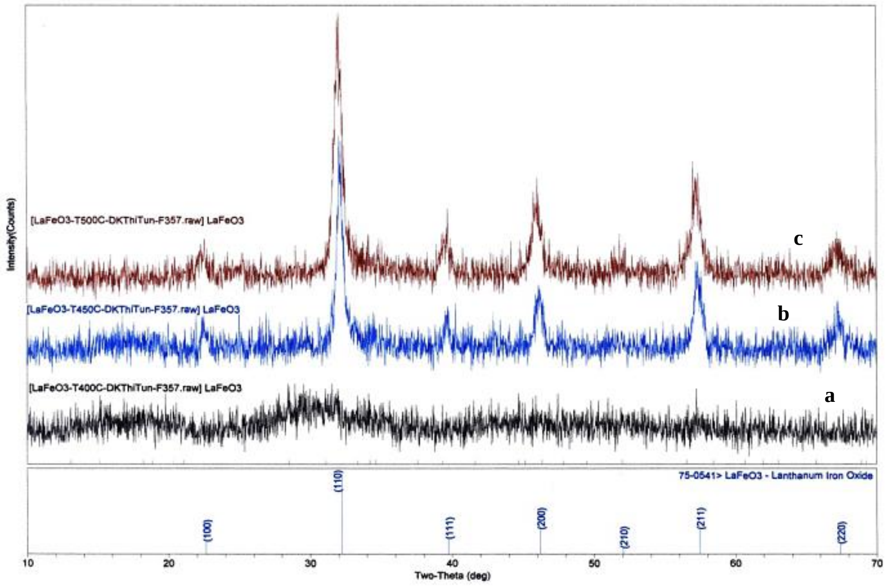


Figure 3. XRD patterns of $LaFeO_3$ particles calcined at (a) 400 °C (b) 450 °C (c) 500 °C

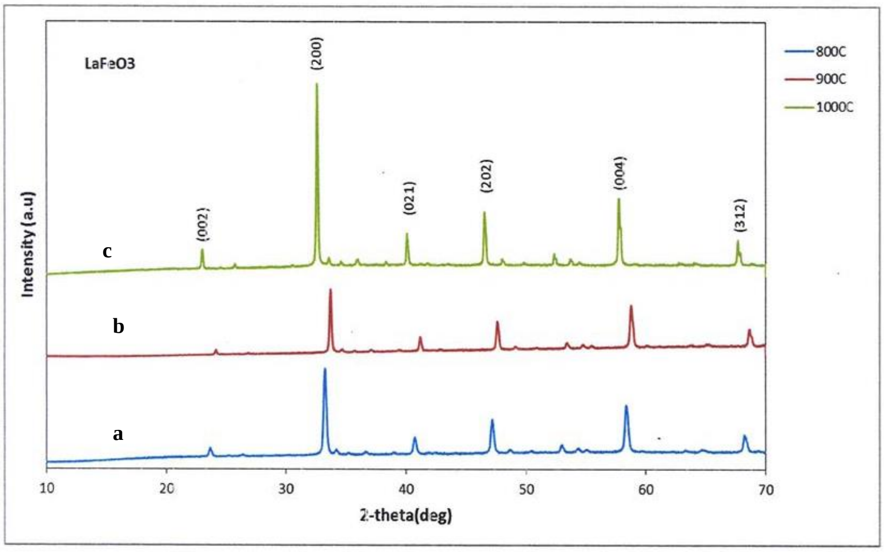
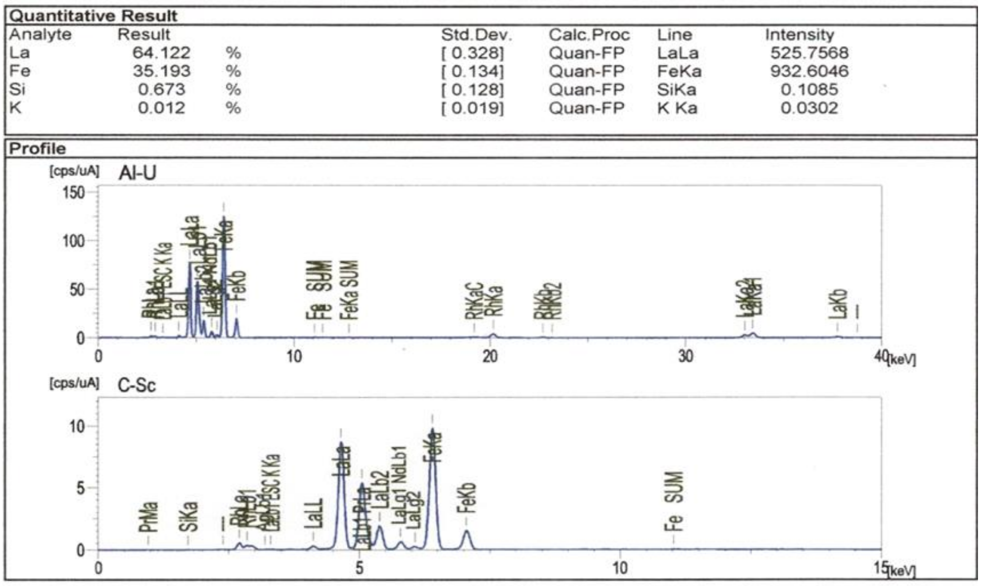


Figure 4. XRD patterns of $LaFeO_3$ samples sintered at (a) 800 ˚C, (b) 900 °C and (c) 1000 ˚C

3.3. EDXRF Analysis

EDXRF analysis was used to confirm the elemental composition of prepared $LaFeO_3$ sample calcined at 450 °C. From EDXRF analysis, La and Fe are main constituent elements samples as shown in Figure 5. The elements present are La, Fe and O with a mole ratio of 1:1:3 corresponding to the stoichiometric composition of $LaFeO_3$.



Quantitative Result

Analyte	Result		Std.Dev.	Calc.Proc	Line	Intensity
La	64.122	%	[0.328]	Quan-FP	LaLa	525.7568
Fe	35.193	%	[0.134]	Quan-FP	FeKa	932.6046
Si	0.673	%	[0.128]	Quan-FP	SiKa	0.1085
K	0.012	%	[0.019]	Quan-FP	K Ka	0.0302

Profile

Figure 5. EDXRF spectra of $LaFeO_3$ nanocrystalline particles calcined at 450 °C

3.4. FT IR Analysis

The FT IR spectrum of the prepared $LaFeO_3$ particles calcined at 450 °C is shown in Figure 6. The FT IR spectrum of the prepared sample exhibit absorption bands between 3400-3000 cm^{-1} due to the O-H stretching vibration, a band between 1400-1500 cm^{-1} which represent the C-O stretching vibration from residual carbon, the band at 800-900 cm^{-1} shows C-H bending vibration from residual carbon and the bands between 400-750 cm^{-1} show stretching vibration of metal-oxygen bond. The FT IR spectra of the prepared $LaFeO_3$ particles sintered at 800, 900 and 1000 °C are shown in Figures 7(a), 7(b) and 7(c). The bands observe between 400-750 cm^{-1} are stronger and prominent and it may be due to the increasing of metal oxygen stretching vibration and no carbon residue because of high temperature processing. FT IR data of the prepared $LaFeO_3$ samples were consistent with literature values [10, 11].

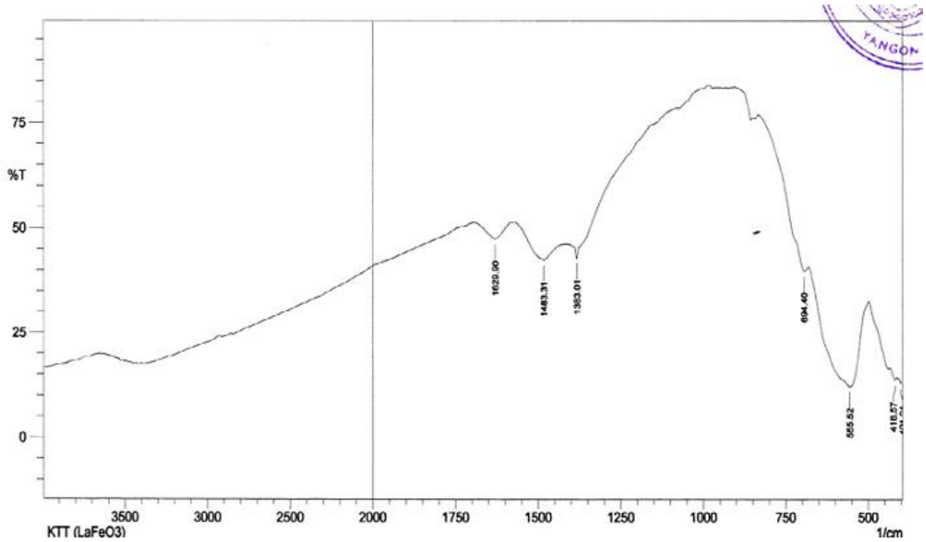


Figure 6. FT IR spectrum of $LaFeO_3$ nanocrystalline particle calcined at 450 °C

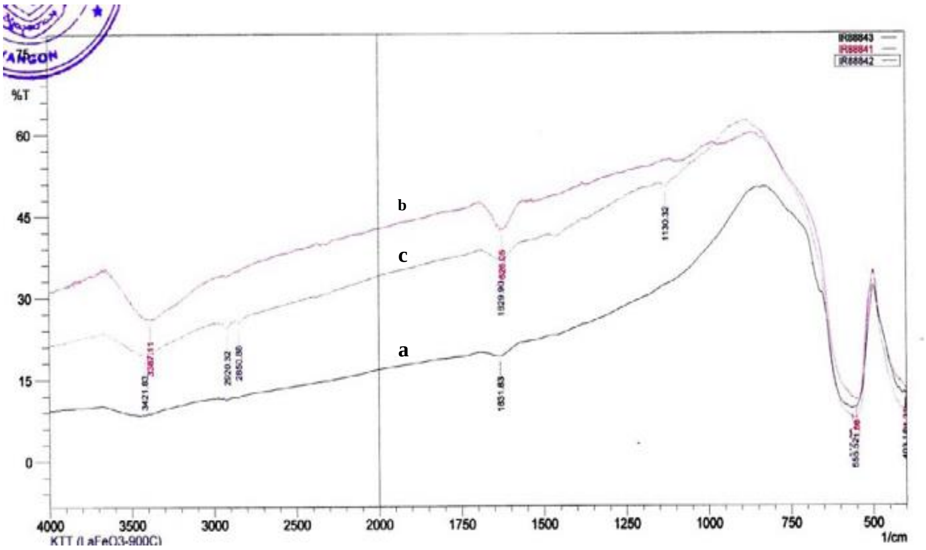


Figure 7. FT IR spectra of $LaFeO_3$ nanocrystalline particles sintered at (a) 800 ˚C, (b) 900 ˚C and (c) 1000 ˚C

3.5. SEM Analysis

Figures 8 and 9 show the SEM images of the particles prepared calcined at 450 ˚C and 900 ˚C. The surface of the $LaFeO_3$ calcined at 450 ˚C has porous surface nature and agglomerations also occur. The $LaFeO_3$ nanoparticles sintered at 900 ˚C has porous nature but particles are compact and uniform distribution.

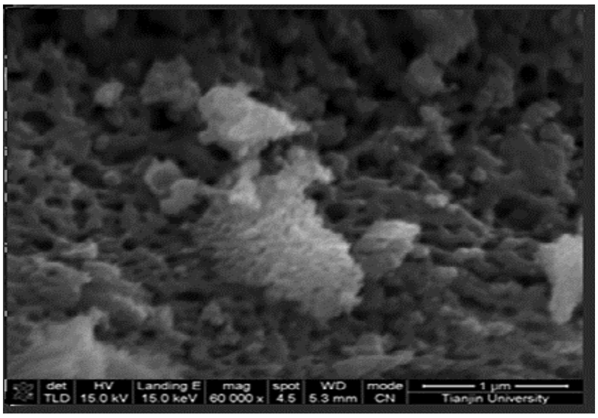


Figure 8. EM micrographs of $LaFeO_3$ nanocrystalline particles calcined at 450 °C

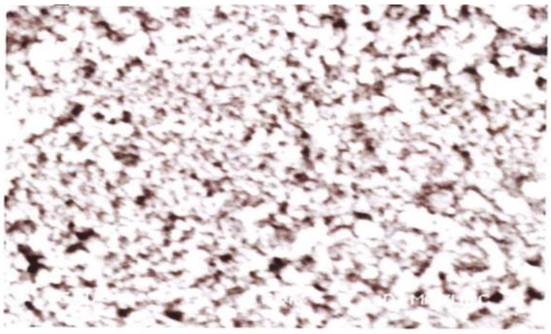
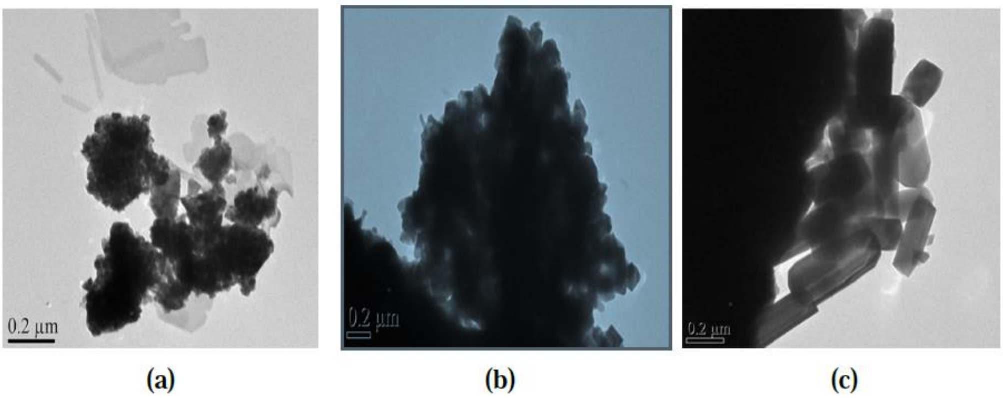


Figure 9. SEM micrographs $LaFeO_3$ nanocrystalline particles sintered at 900 °C

3.6. TEM Analysis

Figures 10(a), 10(b) and 10(c) show TEM images of $LaFeO_3$ powders calcined at 400 °C, 450 °C and 500 °C. Cubic liked crystallite structure was found at 450 °C. It was found that crystal growth and agglomeration increase with increase in calcination temperature. The rod shape crystals are found at 500 °C, which can be seen in Figure 10 (c). TEM images of $LaFeO_3$ powders were measured by transmission electron microscope (JEM- 2100F, Japan) from Tianjin Beiyang University, China.



(a) (b) (c)

Figure 10. TEM images of $LaFeO_3$ nanoparticles calcined at (a) 400 °C (b) 450 °C (c) 500 °C

3.7. UV-vis Spectroscopy

The optical property of $LaFeO_3$ nanocrystalline powder was studied by calculating bandgap energy from tauc plot that was drawn by UV-vis absorption spectrum data in the spectral range (300- 700 nm). The absorption coefficient (α) was calculated from the observed absorption spectra and the optical band gap of $LaFeO_3$ samples was calculated from the Tauc's plot of $(\alpha h\nu)^2$ vs $h\nu$. Figure 11 shows the optical band gap of $LaFeO_3$ and it was found to be the bandgap values of $LaFeO_3$ sintered at 900 °C is 2.45 eV. According to the band gap values, the perovskite $LaFeO_3$ samples found within the semiconductor bandgap range.

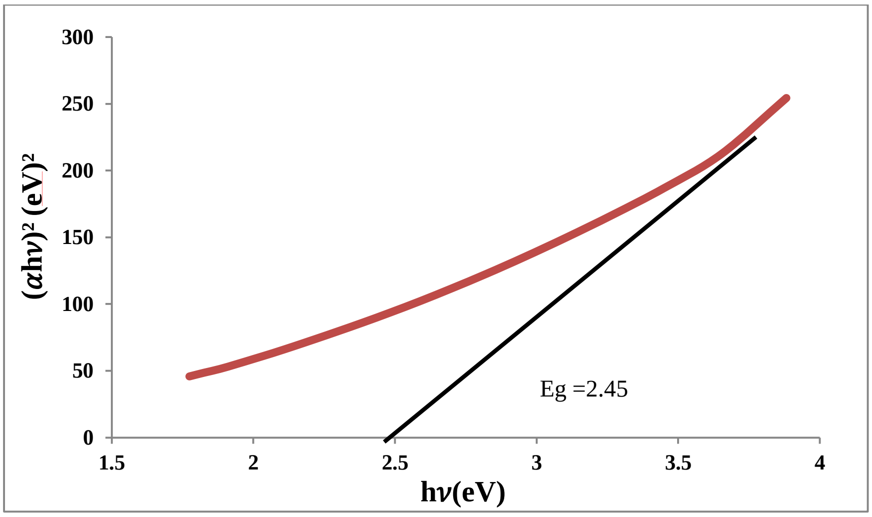


Figure 11. Plot of $(\alpha h\nu)^2$ against $h\nu$ for $LaFeO_3$ prepared by sol-gel method sintered at 900 °C

4. Conclusion

$LaFeO_3$ nanocrystalline particles had been prepared by the sol-gel combustion method. The major advantage of this method is that at relativity low temperature (450 °C), the xerogel precursor is directly transformed into a cubic perovskite structure. On sintering at high temperatures, it was found that cubic perovskite transforms into an orthorhombic perovskite structure. The optical bandgap of the $LaFeO_3$ nanocrystalline particles was found to be 2.45 eV. This bandgap energy value is reliable for the semiconductor device such as photocatalyst, solar cell, solid oxide fuel cell, sensor, and other electronic devices.

5. Acknowledgements

The authors would like to express their profound gratitude to the Department of Higher Education, Ministry of Education, Yangon, Myanmar, for the provision of opportunity to do this research and ICPAC/ ISAPM 2019, Yangon, Myanmar, for allowing to present this paper.

6. Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

7. Ethical Approval

All procedures performed in studies involving human participants were in accordance with the ethical standards of the institutional and/or national research committee and with the 1964 Helsinki declaration and its later amendments or comparable ethical standards.

8. References

[1] Huang, X., Zhao, G., Wang, G., & Irvine, J. T. S. (2018). Synthesis and applications of nanoporous perovskite metal oxides. Chemical Science, 9(15), 3623–3637. doi:10.1039/c7sc03920d.

[2] Benali, A., Bejar, M., Dhahri, E., Sajieddine, M., Graça, M. P. F., & Valente, M. A. (2015). Magnetic, Raman and Mössbauer properties of double-doping LaFeO3 perovskite oxides. Materials Chemistry and Physics, 149-150, 467–472. doi:10.1016/j.matchemphys.2014.10.047.

[3] Köferstein, R., Jäger, L., & Ebbinghaus, S. G. (2013). Magnetic and optical investigations on LaFeO3 powders with different particle sizes and corresponding ceramics. Solid State Ionics, 249-250, 1–5. doi:10.1016/j.ssi.2013.07.001.

[4] Thirumalairajan, S., Girija, K., Mastelaro, V. R., & Ponpandian, N. (2015). Investigation on magnetic and electric properties of morphologically different perovskite LaFeO3 nanostructures. Journal of Materials Science: Materials in Electronics, 26(11), 8652–8662. doi:10.1007/s10854-015-3540-z.

[5] Zafar, N., & Khan, M. N. (2015). Structural, Electric and Thermoelectric Studies of CaFeO3 System. Nucleus, 52(1), 25-28.

[6] Shabbir, G., Qureshi, A. H., & Saeed, K. (2006). Nano-crystalline LaFeO3 powders synthesized by the citrate–gel method. Materials Letters, 60(29-30), 3706–3709. doi:10.1016/j.matlet.2006.03.093.

[7] Liu, T., & Xu, Y. (2011). Synthesis of nanocrystalline LaFeO3 powders via glucose sol–gel route. Materials Chemistry and Physics, 129(3), 1047–1050. doi:10.1016/j.matchemphys.2011.05.054.

[8] Haron, W., Wisitsoraat, A., Sirimahachai, U., & Wongnawa, S. (2018). A simple synthesis and characterization of LaMO 3 (M= Al, Co, Fe, Gd) perovskites via chemical co-precipitation method. Songklanakarin Journal of Science & Technology, 40(3), 484-491.

[9] Swatsitang, E., Karaphun, A., Phokha, S., Hunpratub, S., & Putjuso, T. (2016). Investigation of structural, morphological, optical, and magnetic properties of Sm-doped LaFeO3 nanopowders prepared by sol–gel method. Journal of Sol-Gel Science and Technology, 81(2), 483–492. doi:10.1007/s10971-016-4212-z.

[10] Nakamoto, K. (1970). Infrared spectra of inorganic and coordination compounds. New York: 2nd Edition, Wiley Interscience Publication, 436-445.

[11] Liu, Q., You, Z., Zeng, S. J., & Guo, H. (2016). Infrared properties of Mg-doped LaFeO3 prepared by sol–gel method. Journal of Sol-Gel Science and Technology, 80(3), 860–866. doi:10.1007/s10971-016-4141-x.