Preparation, Characterization and Optical Property of LaFeO$_3$ Nanoparticles via Sol-Gel Combustion Method

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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 LaFeO$_3$ shows an orthorhombic crystal structure. The average crystallite sizes vary between 30-60 nm and the increase in crystal 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 was found to be about 2.45 eV. These results indicate that the LaFeO$_3$ 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, LaFeO$_3$ 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 LaFeO$_3$ 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 LaFeO$_3$ by sol-gel method followed
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(NO₃)₃·6H₂O), iron nitrate nonahydrate (Fe(NO₃)₃·9H₂O), citric acid monohydrate (C₆H₈O₇·6H₂O) and ethylene glycol (CH₂OHCH₂OH) were used as reagents for synthesis. All the reagents are Analar grade and used as received.

2.2. Preparation of LFO Nanocrystalline Particles

LaFeO₃ 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 LaFeO₃ 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 20° 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 LaFeO₃ particles. SEM and TEM were used to determine morphology and average particle sizes. Optical bandgap energy of LaFeO₃ 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 LaFeO₃ 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 LaFeO₃.

![Figure 1. TG-DTA curves of the thermal decomposition of LaFeO₃ xero-gel powder](image-url)
3.2. XRD Analysis

Room temperature X-ray powder diffraction patterns of LaFeO₃ xerogel powder and LaFeO₃ 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 LaFeO₃ 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 LaFeO₃ 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 LaFeO₃ 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 = 0.9λ/βcosθ, 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 LaFeO₃ xerogel powder

Figure 3. XRD patterns of LaFeO₃ particles calcined at (a) 400 °C (b) 450 °C (c) 500 °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$_3$.

3.4. FT IR Analysis

The FTIR spectrum of the prepared LaFeO$_3$ particles calcined at 450 °C is shown in Figure 6. The FTIR 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 FTIR 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. FTIR data of the prepared LaFeO$_3$ samples were consistent with literature values [10, 11].
Figure 6. FTIR spectrum of LaFeO$_3$ nanocrystalline particle calcined at 450 °C

Figure 7. FTIR 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
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 like 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.

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 ($\alpha$) was calculated from the observed absorption spectra and the optical band gap of LaFeO$_3$ samples was calculated from the Tauc’s plot of $(\alpha \nu)^2$ vs $\nu$. 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.
4. Conclusion

LaFeO$_3$ nanocrystalline particles had been prepared by the sol-gel combustion method. The major advantage of this method is that at relatively 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.

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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

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