Structural and Spectroscopic Studies of Nanostructured Alumina Doped LaFeO$_3$ a Photo catalyst Ceramics Synthesized Through an Auto Igniting Combustion Synthesis.

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LaFeO$_3$ with an orthorhombic phase of the ABO$_3$ type perovskite structure has become a currently attractive research topic because it is proposed for various applications in several advanced technologies such as catalysts, various kinds of chemical and gas sensors and electrode materials in solid oxide fuel cells. In the present work La$_{1-x}$Al$_x$FeO$_3$ ($x = 0.01$) nanopowder was prepared through an auto ignited combustion technique. In order to study the phase stability, the structural, vibrational and optical properties, the as prepared material was heat treated at 600$^0$C. The phase purity of the powder was examined using X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR) studies. XRD studies show that the powder possesses an orthorhombic structure with lattice constants a=5.55, b=7.85 and c=5.55. The transmission electron microscopic study confirmed the ultrafine nanocrystallite nature of the powder. The thermal stability of the nanopowder studied using thermo gravimetric analysis (TGA) and differential thermal analysis (DTA) shows that the nanopowder has ~7% weight loss in the temperature range 100-600$^0$C. The UV-Visible diffuse reflectance spectroscopy study carried out on the alumina doped LaFeO$_3$ ceramics indicate that the sample has narrow optical band gap of ~2.08 eV. These results show the strong visible-light absorption characteristics of the sample and it perfectly satisfies the band gap requirements of an ideal visible light active photo catalyst.

**Keywords:** Combustion synthesis, bandgap, Photocatalyst.

1. Introduction

Photocatalysis has long been studied for clean energy and environmental applications. Over the past two decades, the number of applications based on photocatalysis has
increased sharply, while a wide range of material systems have been developed\textsuperscript{1-3}. Photocatalysis has been of particular interest in the production of hydrogen from water using solar energy\textsuperscript{4}. Further, conversion of carbon dioxide to hydrocarbons (fuels) is also of significant interest, as it is a solution to reduce carbon dioxide emissions across the globe\textsuperscript{5}. Apart from the clean energy generation, photocatalysis has several promising applications in the environmental field. Some of the applications include degradation of volatile organic compounds (VOC) for water treatment\textsuperscript{6}, germicide and antimicrobial action\textsuperscript{7}, de-coloration of industrial dyes\textsuperscript{8}, nitrogen fixation in agriculture\textsuperscript{9} and removal of NO\textsubscript{x}/SO\textsubscript{x} air pollutants\textsuperscript{10}. Perovskite based photocatalysts are of significant interest in the field of photocatalysis. Titanates, tantalates, niobates, vanadates and ferrites are promising photocatalytic materials in visible light driven photoreactions\textsuperscript{11}.

The visible light activity still remains a challenge in the field of photocatalysis since most of the active photo catalysts have a wide intrinsic band gap greater than 3 eV. This allows such photo catalysts to absorb only UV light. Extending the band gap of photo catalysts into the wide visible light region is an important branch of research. Transition metal ion doping and rare-earth metal ion doping have been extensively investigated for enhancing photocatalytic activities of photo catalyst under visible light.

As a kind of important functional material, LaFeO\textsubscript{3} with a typical ABO\textsubscript{3}-type perovskite structure has many applications, such as catalytic oxidation, electrode materials and chemical sensors for the humidity and alcohols, and it is also an ideal potential semiconductor material for visible light photocatalyst because of its small band gap energy\textsuperscript{12}. A number of fabrication methods such as hydrothermal synthesis\textsuperscript{13}, combustion synthesis\textsuperscript{14,15}, sol–gel\textsuperscript{16} and precipitation\textsuperscript{17} have been developed successfully so far to synthesize ultrafine nanostructured ceramic powder LaFeO\textsubscript{3}. Among them combustion synthesis evolved as the economic and efficient method in terms of the cost, time and the complexities in the synthesis of nanomaterials.

In the present work a single step auto igniting modified combustion method is used to synthesize nanostructured ceramic powder La\textsubscript{0.99}Al\textsubscript{0.01}FeO\textsubscript{3}. The modified combustion technique used in the present study is a relatively simple method through the omission of high temperature calcinations for prolonged duration, we could obtain phase pure nano particles of extremely small size. However, there are no reports on the synthesis of nanocrystalline LaFeO\textsubscript{3} with this method up to now. The structure, vibrational spectra, surface morphology, optical properties, thermal stability and weight loss are recorded and
analysed. The effect of Aluminium doping on the optical properties of nanostructured LaFeO$_3$ for their application as photocatalytic material is studied.

2. Experimental Details

Stoichiometric amount of high purity Al (NO$_3$)$_3$.9H$_2$O, La$_2$O$_3$ and Fe(NO$_3$)$_3$.9H$_2$O was dissolved in double distilled water to make a clear solution. Citric acid was then added to the solutions taken in separate beakers as complexing agent. Amount of citric acid was calculated based on total valence of the oxidizing and reducing agents for maximum release of energy during combustion$^{18}$. Oxidant to fuel ratio of the system was adjusted to unity (~1) by adding concentrated nitric acid which serves as oxidizer and ammonium hydroxide solution as fuel. The precursor solution of pH ~7.0 was stirred well for uniform mixing without any precipitation or sedimentation. The solution was then heated using a hot plate kept at ~250$^0$C in a ventilated fume hood. The solution boils on continuous heating and undergoes dehydration accompanied by foam. On persistent heating the foam gets auto-ignited giving a voluminous fluffy powder of nano La$_{0.99}$Al$_{0.01}$FeO$_3$. The sample is then heated at 600 $^0$C.

The prepared nanopowder obtained from the combustion process are characterized by different powder characterization techniques. The prepared samples are characterized by X-ray diffractometer (Xpert-pro) with Cu Kα radiation for the determination of crystalline structure and phase of the nanomaterials. The average crystallite size is estimated for the sample from Scherrer’s equation. The absorption spectrum of prepared sample is recorded using a UV-Visible spectrophotometer (Perkin Elmer lambda-35). The uv-vis spectra are recorded to resolve the correlation between the grain size and absorption edge of the nanoparticles. Additional information regarding the phase purity and the presence of any inorganic impurity are obtained using FTIR spectroscopy using Fourier Transform Infrared spectrometer (FTIR, Perkin elmerspectrum 2) in the range 350-4000 cm$^{-1}$ using ATR mode.

Particulate properties of the combustion product are examined using high resolution transmission electron microscopy (TEM, Model-Hitachi H600 Japan) operating at 200 kV. The samples for Transmission Electron Microscope (TEM) are prepared by ultrasonically dispersing the powder in methanol and allowing a drop of this to dry on a carbon-coated copper grid. The thermal stability of the nanopowder La$_{0.99}$Al$_{0.01}$FeO$_3$
studied using thermal gravimetric analysis (TGA) and differential thermal analysis (DTA).

3. Results and Discussion

The powder XRD patterns of the synthesized LaFeO$_3$ and La$_{0.99}$Al$_{0.01}$FeO$_3$ with 2θ values between 10$^0$ and 90$^0$ are shown in the Figures 1 (a) and (b) respectively. XRD studies show that the powders possess an orthorhombic structure of space group Pnma (62) with lattice constants $a=5.55$, $b=7.82$ and $c=5.53$ for LaFeO$_3$ and $a=5.55$, $b=7.85$ and $c=5.55$ for La$_{0.99}$Al$_{0.01}$FeO$_3$ which agrees well with the XRD data reported in JCPDS file number 88-0641. The average crystallite size was calculated using the Scherrer formula

$$D = \frac{0.9\lambda}{\beta \cos \theta}$$

where $\lambda$ is the wavelength of CuK$\alpha$ radiation, $\beta$ is the full width at half maximum and $\theta$ is the Bragg’s diffraction angle. The average crystallite size of LaFeO$_3$ and La$_{0.99}$Al$_{0.01}$FeO$_3$ estimated by the Scherrer’s equation are 35 nm and 32 nm respectively.

![Figure 1. XRD pattern of (a) LaFeO$_3$(b) La$_{0.99}$Al$_{0.01}$FeO$_3$](image)

The description about the structure, crystallite size and lattice parameters of the nanopowders LaFeO$_3$ and La$_{0.99}$Al$_{0.01}$FeO$_3$ are enclosed in Table 1.
Table 1: Crystal structure, Lattice parameter and Crystallite size of samples

| Compound     | Crystal structure | Lattice Parameter | Crystallite size (nm) |
|--------------|-------------------|-------------------|-----------------------|
|              |                   | Standard (Å³)     | Calculated (Å³)       |                        |
|              |                   | a   | b   | c   | a   | b   | c   |                        |
| LaFeO₃       | Orthorhombic      | 5.56| 7.85| 5.55| 7.82| 5.55| 35   |
| La₀.₉₉Al₀.₀₁FeO₃ | Orthorhombic      | 5.56| 7.85| 5.55| 7.85| 5.55| 32   |

Though the XRD pattern of the sample LaFeO₃ when it is doped with 0.01% of Aluminium shows no detectable change in their peak positions, their particle size decreases which in turn increases their photocatalytic activity.

The extent of line broadening in the diffraction pattern due to the strain, which is caused by the non-displacement of the atoms with respect to their reference lattice position, could be identified by Williamson-Hall (W-H) method\(^{20}\). In this method, reciprocal peak width $\beta \cos \theta / \lambda$ are plotted versus the reciprocal lattice distance $\sin \theta / \lambda$ and the resulting plot is linearly fit.

Figure 2 shows the Williamson-Hall plot for La₀.₉₉Al₀.₀₁FeO₃ nanoparticles. The reciprocal of y intercept, a measure of particle size obtained from this plot was 39 nm. The lattice strain constant $\eta$, proportional to the slope of the line estimated as 2.8039 x10⁻⁴. The negative slope
of the line indicates that strain is compressive and the broadening of peaks due to the strain is very small.

Figure 3 shows the TGA/DTA curve of $\text{La}_{0.99}\text{Al}_{0.01}\text{FeO}_3$ powder in the temperature range from 30 $^\circ\text{C}$ to 950 $^\circ\text{C}$ at a heating rate of 10 $^\circ\text{C}$ in nitrogen atmosphere. It was observed that the nanopowder $\text{La}_{0.99}\text{Al}_{0.01}\text{FeO}_3$ has approximately 7% weight loss in the temperature range 100-600 $^\circ\text{C}$ after which there is no considerable weight loss in the TG curve. The fractional decrease in weight below 600 $^\circ\text{C}$ is due to liberation of the adsorbed moisture present in the combustion synthesised sample.

![Figure 3. TGA and DTA curve of $\text{La}_{0.99}\text{Al}_{0.01}\text{FeO}_3$](image)

No abrupt changes are observed in the DTA curve in the higher temperature range which indicate that no phase transitions are occurring and the $\text{La}_{0.99}\text{Al}_{0.01}\text{FeO}_3$ ceramics synthesised by the modified combustion synthesis is stable at elevated temperature ranges.

Absorption spectrum of $\text{La}_{0.99}\text{Al}_{0.01}\text{FeO}_3$ was shown in the Figure 4. It is observed that the sample $\text{La}_{0.99}\text{Al}_{0.01}\text{FeO}_3$ shows maximum absorption at 607 nm. The property of high absorption in the visible region makes the material a good candidate as photocatalytic material. It has been found that $\text{La}_{0.99}\text{Al}_{0.01}\text{FeO}_3$ is visible light photocatalytic active due to its unique optoelectronic properties and narrow bandgap$^{21}$. The strong absorption can generally be related to the electronic transition from the valence band to conduction band ($\text{O}_{2p}\rightarrow\text{Fe}_{3d}$). Consequently, this indicates that the $\text{La}_{0.99}\text{Al}_{0.01}\text{FeO}_3$ nanoparticles prepared by this method could be a kind of photocatalytic material. In otherwords, due to their optical properties, these nanoparticles may find valuable applications in photocatalysis and magneto-optical devices$^{22}$. 


A semiconductor is characterized by its electronic band structure. In the high-energy absorption region, the dependence on the photon energy is expressed by Tauc’s equation. According to this relation, the absorption coefficient $\alpha$ is related to the band gap of a material by the relation, $\alpha h\nu = \beta (h\nu - E_g)^m$. where $\beta$ is an energy independent constant, $\alpha$ is the optical absorption coefficient, $h$ is the Planck’s constant, $\nu$ is the frequency of incident photon, $E_g$ is the optical band gap and $m$ is a constant which characterize the nature of band transition. $m=1/2$ and 3/2 corresponds to direct allowed and direct forbidden transitions while $m=2$ and 3 corresponds to indirect allowed and indirect forbidden transitions, respectively. The optical band gap can be obtained from extrapolation of the straight-line portion of the $(\alpha h\nu)^{1/m}$ vs $h\nu$ plot to $h\nu =0$. The obtained value of band gap is 2.08 eV for La$_{0.99}$Al$_{0.01}$FeO$_3$, which was shown in the Figure 5.

![Figure 4](image1.png)

**Figure 4. Absorption Spectrum of La$_{0.99}$Al$_{0.01}$FeO$_3$**

![Figure 5](image2.png)

**Figure 5. Tauc’s plot of La$_{0.99}$Al$_{0.01}$FeO$_3$**
Figure.6 shows the IR spectra of La$_{0.99}$Al$_{0.01}$FeO$_3$ recorded at room temperature, over the range 350-1000 cm$^{-1}$. The peak at 372 cm$^{-1}$ corresponds to O-Fe-O bending mode. The peaks ranging from 400 cm$^{-1}$ to 450 cm$^{-1}$ corresponds to deformation of FeO$_6$ octahedra. Broad band ranging from about 500 cm$^{-1}$ to 650 cm$^{-1}$ corresponds to asymmetrical stretching vibration of Fe-O-Fe bonds$^{23-26}$.

![Figure. 6 IR Spectra of La$_{0.99}$Al$_{0.01}$FeO$_3$](image)

Figure.7 shows the TEM and HRTEM images of the prepared powder sample La$_{0.99}$Al$_{0.01}$FeO$_3$. From the distinctly visible grain in Figure.7(a), the average grain size was calculated as 32 nm. From the Figure.7(b) and (c), the interfacial spacing was calculated as 0.395 nm and 0.273 nm for [0 2 0] and [0 0 2] planes respectively. From XRD, it is calculated as 0.393 nm and 0.277 for [0 2 0] and [0 0 2] planes respectively.
Figure 7. (a) TEM image of $\text{La}_{0.99}\text{Al}_{0.01}\text{FeO}_3$ (b) HRTEM image of $\text{La}_{0.99}\text{Al}_{0.01}\text{FeO}_3$ (c) HRTEM image of $\text{La}_{0.99}\text{Al}_{0.01}\text{FeO}_3$

Hence it is concluded that the average particle size and interfacial spacing from the HRTEM result was found to be in well agreement with result obtained from XRD analysis. These results indicated that $\text{La}_{0.99}\text{Al}_{0.01}\text{FeO}_3$ nanoparticles are efficient photocatalyst under visible light. In general, the photocatalyst with a smaller particle size has more active surface sites and exhibits high efficiency of surface charge carrier transfer in photocatalysis. In otherwords, higher surface to volume ratio of the catalyst enhances the photocatalytic activity. Consequently, it is anticipated that $\text{La}_{0.99}\text{Al}_{0.01}\text{FeO}_3$ nanoparticles has promising applications in the optoelectronic devices and photocatalysis. It is also
expected that the nanoparticles produced in this system might show other interesting physical properties relevant to potential applications.

4. Conclusion

A single step modified combustion synthesis is used to prepare nano structured ceramic powder $\text{La}_{0.99}\text{Al}_{0.01}\text{FeO}_3$. This synthesis route is an economic and efficient method in terms of the cost, time and the complexities in the synthesis of nanomaterials. It does not require expensive high temperature calcination process. X-ray diffraction (XRD) analysis of the prepared powders confirms the formation of phase pure orthorhombic structured nanoparticles. All the peaks in the XRD of the sample was indexed to an orthorhombic structure of space group Pnma (62) with calculated lattice parameters agreeing well with the XRD data reported in Joint Committee on Powder Diffraction Standards (JCPDS) file no.88-0641. The XRD analysis, TEM and HRTEM studies reveal that the average crystallite size is approximately 32 nm for $\text{La}_{0.99}\text{Al}_{0.01}\text{FeO}_3$ and the lattice planes are well defined. From the W-H plot, lattice strain constant $\eta$ is proportional to the slope of the line and the estimated value of $\eta$ is -0.00028039. The vibrational spectroscopic studies confirm the structure of the sample. In IR spectra, most of the fundamental bands are indexed and interpreted. The absorption spectrum of $\text{La}_{0.99}\text{Al}_{0.01}\text{FeO}_3$ was recorded and the maximum absorption is at 607 nm for $\text{La}_{0.99}\text{Al}_{0.01}\text{FeO}_3$. The obtained band gap of $\text{La}_{0.99}\text{Al}_{0.01}\text{FeO}_3$ are direct band gap of $E_g$ value 2.08 eV. The TGA and DTA curve shows that the nanopowder $\text{La}_{0.99}\text{Al}_{0.01}\text{FeO}_3$ has approximately 7% weight loss in the temperature range of 100-600°C which is due to the presence of adsorbed moisture in the samples. The results clearly indicate that the ultra-fine nanopowder $\text{La}_{0.99}\text{Al}_{0.01}\text{FeO}_3$ synthesised by the modified auto-igniting combustion technique can be used effectively as a photocatalytic material. Aluminium doping in the nanostructured $\text{LaFeO}_3$ reduces the particle size and increases the bandgap. It is hoped that this study will represent a useful material in the field of photocatalysis, particularly as a photocatalyst for industrial applications.

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