

# COMPARATIVE STUDIES ON THE PREPARATION AND CHARACTERIZATION OF $\text{LaFeO}_3$ NANOCRYSTALLITE POWDER BY CITRATE SOL- GEL METHOD AND CO-PRECIPIATION METHOD

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## Abstract

Lanthanum ferrite ( $\text{LaFeO}_3$ ) nanocrystalline material is a promising material for its interesting electrical, magnetic, catalytic and thermoelectric properties. In this study, the nanocrystalline  $\text{LaFeO}_3$  powder was prepared by citrate sol-gel method and co-precipitation method. In the citrate sol gel method, a modified Pechini method based on the polyesterification of citric acid and ethylene glycol for the synthesis of the  $\text{LaFeO}_3$ . The precursor for  $\text{LaFeO}_3$  will be synthesized by co-precipitation from metal nitrate and carbonate salts. The properties of the  $\text{LaFeO}_3$  powders were studied by TG-DTA, XRD, SEM, FT IR and EDXRF. The results showed that  $\text{LaFeO}_3$  was formed at the lower temperature in the citrate sol-gel method compared to co-precipitation method. The size of spherical  $\text{LaFeO}_3$  synthesized by sol-gel was 20-25nm, whereas the sample prepared by co-precipitation yielded nearly tetragonal and flake like powder with particle size of 20-35nm. The difference in preparation methods results in the difference in the structure and morphology of prepared materials.

**Keywords:** Perovskite,  $\text{LaFeO}_3$ , citrate sol-gel method, co-precipitation method

## Introduction

Perovskite materials exhibit many interesting and intriguing properties from both theoretical and application point of view. Colossal magneto resistance, ferroelectricity, superconductivity, charge ordering, spin dependent transport, high thermo power the interplay of structural, magnetic and transport properties are commonly observed features in this family. These perovskite compounds are used as sensors and catalyst electrodes in certain type of fuel cells, memory devices and spintronic applications (Kanta and Kumar, 2014). The general formula of perovskite is  $\text{ABO}_3$  (where A is rare earth, alkaline earth or an alkali metal cation and B is 3d transition metal). A large ionic radius have 12 fold coordination with oxygen atoms, occupying A-

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sites and cations with a smaller ionic radius have 6 fold coordination occupying B-sites. The LaFeO<sub>3</sub> materials have been prepared by several techniques such as hydrothermal synthesis, micro emulsion, co-precipitation method, sol-gel method, solid state reaction, flame hydrolysis and electrochemical oxidation method (Unikoth *et al.*, 2014). For achieving optimum performances and functional properties well defined microstructures are desirable, which in fact strongly depend on the method of synthesis. In this paper, we examined the preparation of LaFeO<sub>3</sub> nanocrystals via the citrate sol-gel and co-precipitation method and investigated the comparative study of their calcination temperatures, crystal structure, surface morphology and elemental composition by modern techniques. In addition, the structural and morphological difference of LaFeO<sub>3</sub> prepared by different methods was investigated.

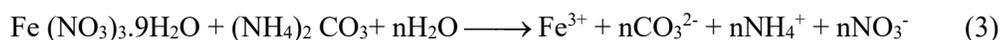
## Materials and Methods

### Synthesis of Perovskite LaFeO<sub>3</sub> Powder

Perovskite LaFeO<sub>3</sub> nanocrystallite powder were prepared by two methods i.e. citrate sol-gel method and co-precipitation method. All AR-grade chemicals were used in the preparation of nanocrystallite powder. In the first method, LaFeO<sub>3</sub> was prepared by citrate sol-gel method in which the aqueous solution of La(NO<sub>3</sub>)<sub>3</sub> .6H<sub>2</sub>O and Fe(NO<sub>3</sub>)<sub>3</sub> .9H<sub>2</sub>O were mixed with citric acid that was equivalent in gram mole with that of the total cations (La<sup>3+</sup>, Fe<sup>3+</sup>) (Anupama and Prasad, 2015). Subsequently 5 mL of ethylene glycol was added to the mixture solution. Resulting yellow coloured solution was heated at 80 °C under continuous stirring. After being heated for about 6 h, the resulting solution became highly viscous and the reddish brown transparent gel was formed. Finally, the xerogel was obtained after the gel was dried completely in an oven at 120 °C for 6 h. The xerogel was ground in the mortar and pestle. The dried powder was calcined at 400°C, 450 °C and 500 °C for 4 h. The citrate sol-gel synthesis occurs according to the following overall reaction (1) which gives rise to a perovskite powder and gaseous species.



In the second method, LaFeO<sub>3</sub> was prepared by co-precipitation method in which nitrate precursors La (NO<sub>3</sub>)<sub>3</sub> .6H<sub>2</sub>O and Fe (NO<sub>3</sub>)<sub>3</sub>.9H<sub>2</sub>O were mixed in the required stoichiometric ratio (i.e. La/ Fe= 1/1) to make aqueous solution. Then (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> solutions was added rapidly with continuous stirring. The precipitate was formed immediately by adding ammonium carbonate solution in nitrate solution, which was continuously stirred for 30 minutes at room temperature. After centrifuging, the precipitate was filtered and washed with deionized water, until pH 7. The prepared precipitate was dried at 110 °C for 6 hours and further calcined separately at 500 °C, 550 °C and 600 °C for 4 hours. The precipitation and calcination reactions may be represented by equations (2), (3) and (4) respectively.



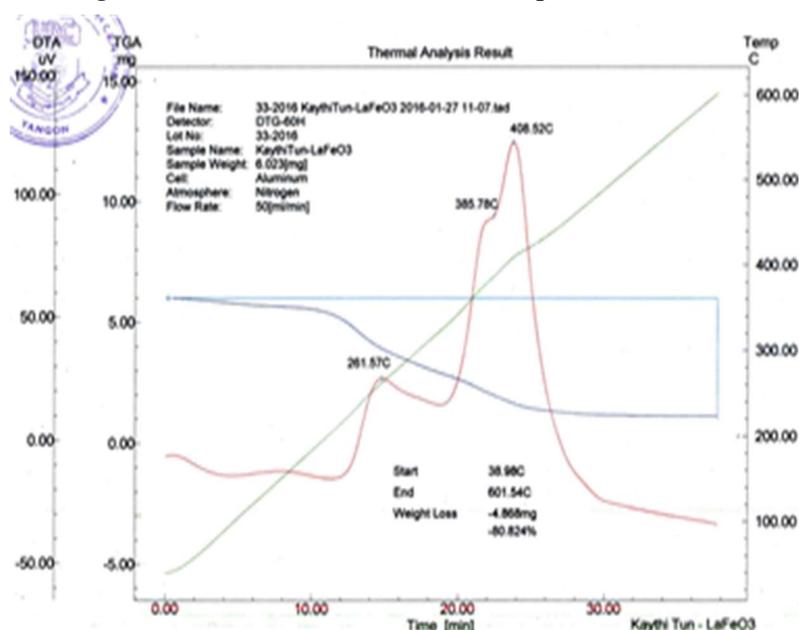
### Characterizations of the sample

The thermal decomposition behaviors of the powder prepared by two different methods were characterized by thermogravimetric and differential thermal analysis (TG-DTA) at a heating rate of 10°C/min in nitrogen. The phase identification of the as-prepared powder was performed using X-ray diffractometer with CuK<sub>α</sub> radiation (λ=1.5405Å). The lattice parameters and the average crystallite size were calculated using PDXL-software. The morphology of the as-prepared powder was characterized by scanning electron microscopy (SEM). The FTIR measurements have been performed in the KBr mode the region from 400- 4000 cm<sup>-1</sup> was measured using 8400 SHIMADZU, Japan FTIR spectrometer. The elemental compositions of LaFeO<sub>3</sub> perovskite oxides prepared by two different methods were detected by using energy dispersive X-ray spectrometer (EDXRF).

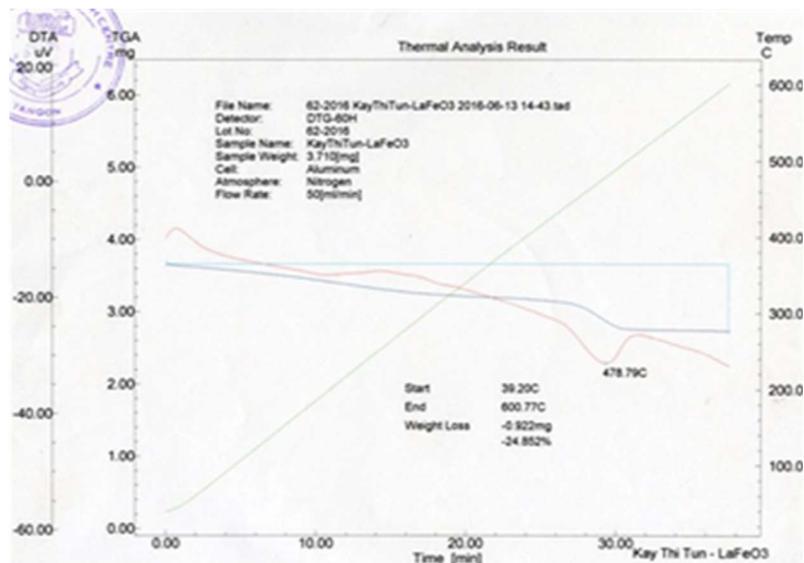
## Results and Discussion

### Thermal Analyses

Thermogravimetric and differential thermal analysis (TG-DTA) was performed to study the thermal analysis behavior of the nanocrystallite powder obtained by two different methods. The respective thermograms are shown in Figure 1 and 2. During the citrate sol-gel synthesis, the process of oxides formation involves liberation of gaseous products, which is accompanied by a decrease of mass. The three sharp exothermic peaks (261, 365 and 408°C) were observed. The three broad exothermic lines might relate to the elimination of adsorbed water, the decomposition of nitrates and the combustion of organic residues due to the formation of expected perovskite  $\text{LaFeO}_3$ . Thermal decomposition of lanthanum ferrite prepared by coprecipitation method was investigated TG-DTA. The rate of weight loss takes place above 100 °C with slow rate up to 400 °C; there is no prominent weight loss above 400 °C. The DTA curve indicate small exothermic peak at 329°C which confirms the presence of phase transition behavior. There is no detectable change in both DTA and TGA curves up to 100 °C.



**Figure 1:** TG-DTA curve for the xerogel  $\text{LaFeO}_3$  powder prepared by citrate sol-gel method



**Figure 2:** TG-DTA curve for the precursor  $\text{LaFeO}_3$  powder prepared by co-precipitation method

### XRD analysis

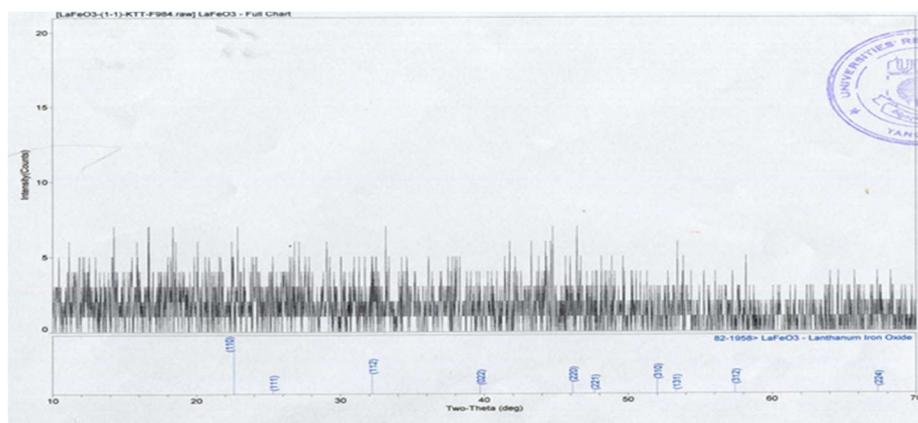
Phase confirmation and crystal structure of the compounds were investigated by X-ray diffractometer (XRD) at room temperature in the diffraction angle range of  $2\theta$  value  $10\text{--}70^\circ\text{C}$ . XRD pattern of  $\text{LaFeO}_3$  xerogel powder prepared by citrate sol-gel method are shown in Figure 3. Any diffraction peak is not observed in XRD pattern which indicates the prepared gel is mainly amorphous. Figure 4 shows diffraction patterns of  $\text{LaFeO}_3$  powder calcined at  $400^\circ\text{C}$ ,  $450^\circ\text{C}$  and  $500^\circ\text{C}$  for 4 hours. At  $400^\circ\text{C}$  for the citrate sol-gel sample, which is difficult to index according to the JCPDS data indicating that the powder is possibly in amorphous form. The strongest peak and characteristic planes (110) of cubic crystalline structure observed at temperature  $450^\circ\text{C}$  and  $500^\circ\text{C}$ .

Furthermore, the XRD pattern of  $\text{LaFeO}_3$  powder prepared by co-precipitation method before calcination is shown in Figure 5. Figure 6 shows the X-ray diffraction patterns of  $\text{LaFeO}_3$  powder calcined at  $500^\circ\text{C}$ ,  $550^\circ\text{C}$  and  $600^\circ\text{C}$  for 4 hours in co-precipitation method. The XRD patterns at all calcination temperature that the intensities of three basic peaks of (103) plane

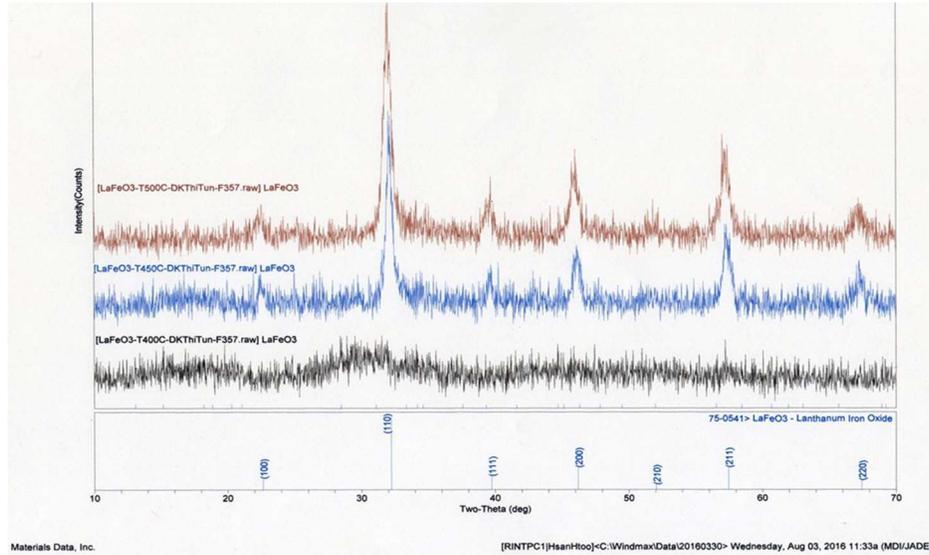
are more than the other peaks. The crystallite size of the sample prepared by different method was in the range of 20-35nm respectively. The difference in crystallite size was due to different preparation conditions for ferrite synthesis.  $\text{LaFeO}_3$  prepared by the citrate sol-gel method displayed the most intense XRD peak, indicating their highest crystallinity. The XRD diagram of  $\text{LaFeO}_3$  obtained by co-precipitation method show some diffraction peaks and this may be due to the phase purity is not completely achieved. The crystallite size of synthesized compounds obtained by different methods was calculated by the X-ray line broadening method using the Scherrer formula,

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

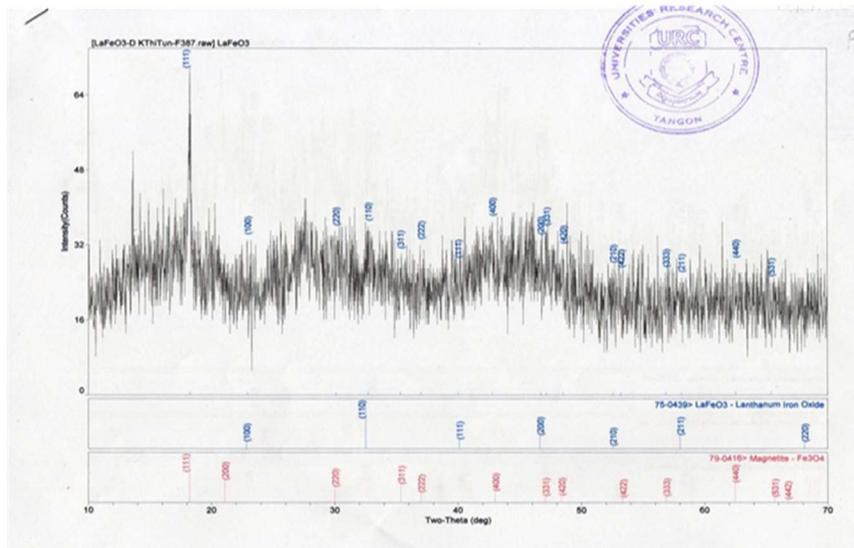
where D is the average crystallite size (nm),  $\lambda$  is the X-ray radiation wavelength (nm) and  $\beta$  is the X-ray diffraction full width peak at half maximum (rad) and  $\theta$  is the Bragg's angle (degree). It shows a trend that the average crystallite size is larger at higher calcination temperature, which is related to the grain growth (Theingi, 2013). The resultant data are presented in Table 1.



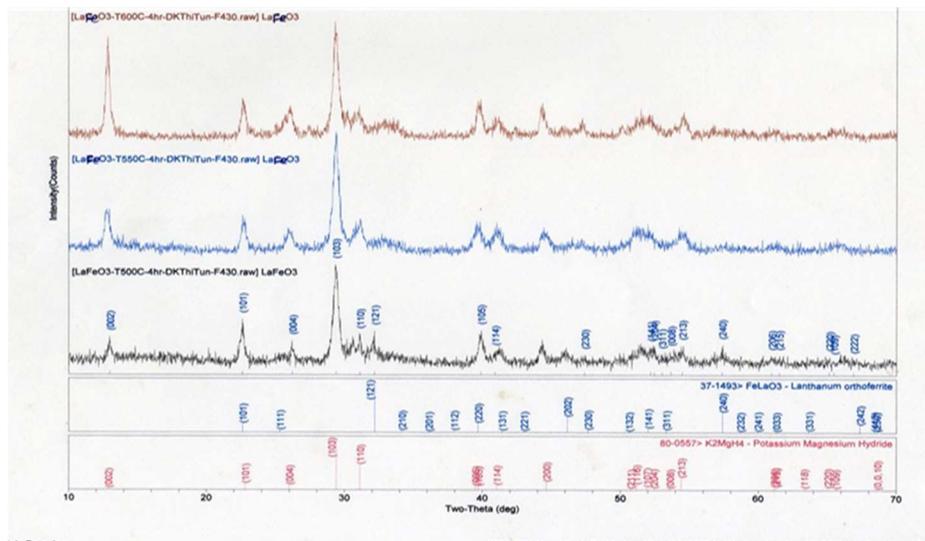
**Figure 3:** XRD diffraction pattern of xerogel  $\text{LaFeO}_3$  powder obtained by citrate sol-gel method



**Figure 4:** XRD diffraction patterns method of LaFeO<sub>3</sub> nanopowder at different calcined temperatures (a) 400 °C (b) 450 °C (c) 500 °C



**Figure 5:** XRD diffraction pattern of LaFeO<sub>3</sub> precursor powder obtained by co-precipitation method



**Figure 6:** XRD diffraction patterns of  $\text{LaFeO}_3$  nanopowder at different calcined temperature (a)  $500^\circ\text{C}$  (b)  $550^\circ\text{C}$  (c)  $600^\circ\text{C}$

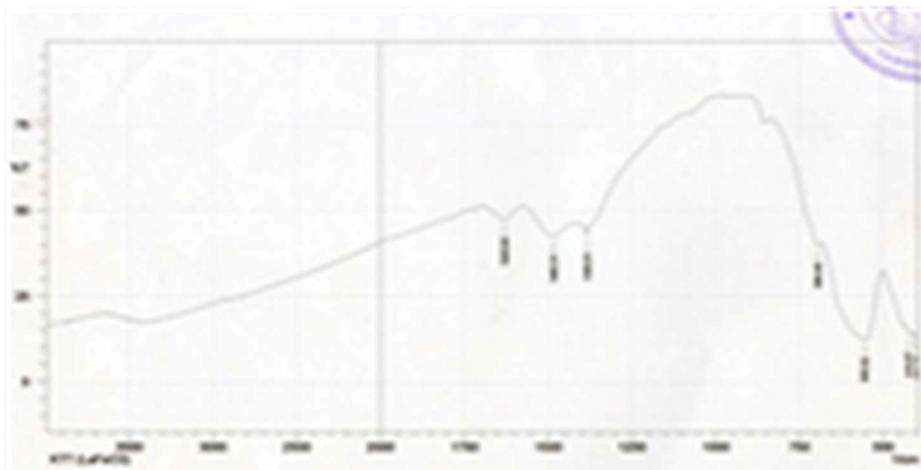
**Table 1:** Crystallite size of  $\text{LaFeO}_3$  Nanoparticle Prepared by Different Methods

| Method           | Calcination temperature ( $^\circ\text{C}$ ) | Crystallite size/D (nm) |
|------------------|--|-------------------------|
| Citrate sol-gel  | 450  | 23.26                   |
|                  | 500  | 24.01                   |
| Co-precipitation | 500  | 23.01                   |
|                  | 550  | 29.80                   |
|                  | 600  | 34.06                   |

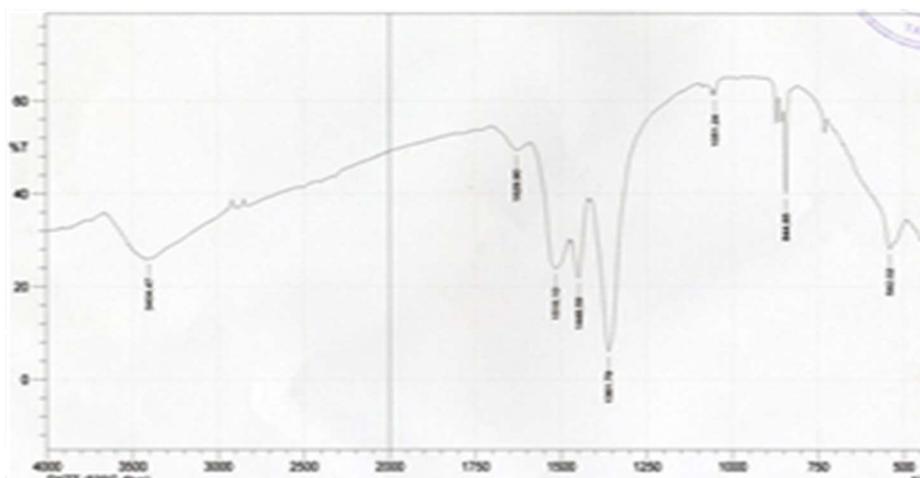
### FTIR Analysis

FTIR spectra with wave number ranges from  $400 - 4000\text{ cm}^{-1}$  are shown in Figures 7 and 8 for  $\text{LaFeO}_3$  prepared by citrate sol-gel method and co-precipitation method respectively. Both methods showed an intense band around  $1629\text{ cm}^{-1}$  are assigned to asymmetric carbonyl group and  $545\text{ cm}^{-1}$  around the peak corresponds to Fe- O stretching vibration mode. The  $\text{LaFeO}_3$  prepared by co-precipitation method, showed the absorption band appearing at  $3404\text{ cm}^{-1}$  is due to the stretching vibration of hydroxyl group, whereas for

that prepared by citrate sol-gel method has not strong intense peak of the hydroxyl group band. The low intense peak observed in citrate sol-gel at  $1483\text{ cm}^{-1}$  and  $1383\text{ cm}^{-1}$  are due to the asymmetric stretching of metal carbonates. The absorption bands at around  $1361, 1448$  and  $1516\text{ cm}^{-1}$  as strong intense peak shown in  $\text{LaFeO}_3$  prepared by co-precipitation are indicated the symmetric and asymmetric stretching vibration mode of  $\text{NO}_2$  (Ghosh *et al.*, 2010).



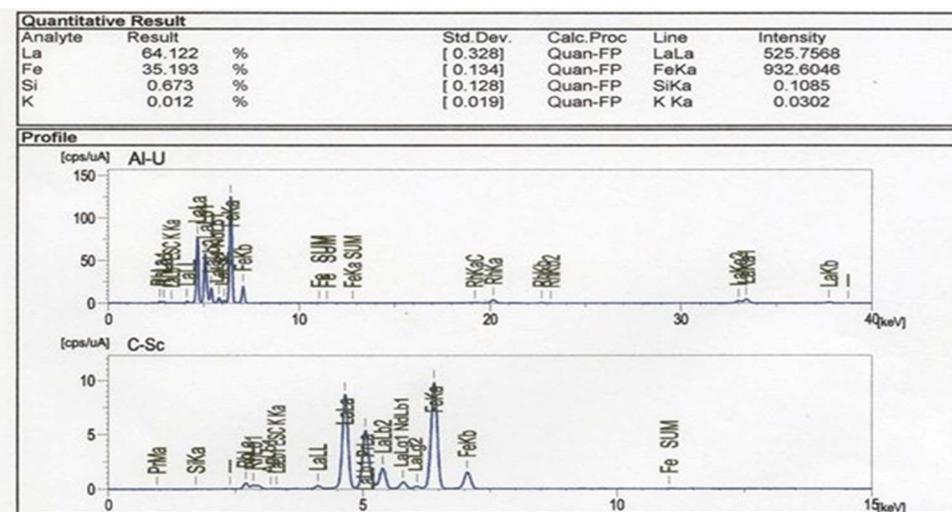
**Figure 7:** FT IR spectrum of  $\text{LaFeO}_3$  nanopowder prepared by citrate sol-gel method calcined at  $450^\circ\text{C}$  for 4 hours



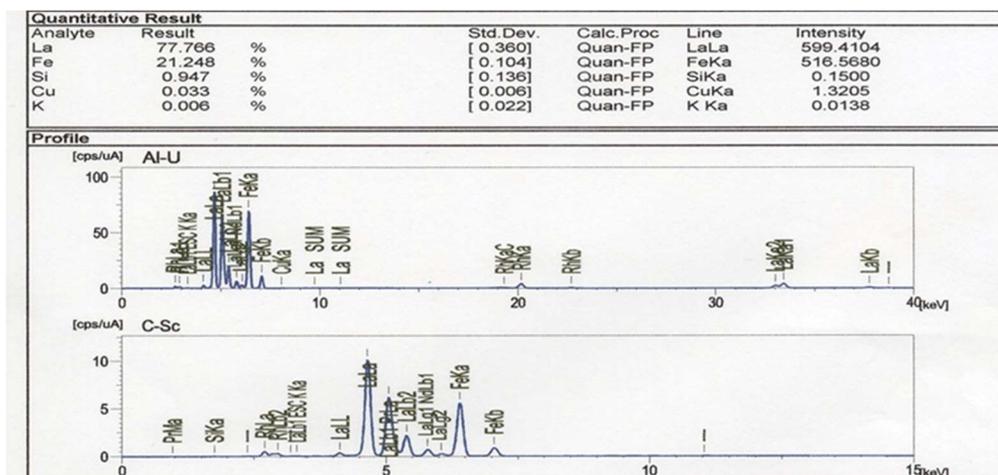
**Figure 8:** FT IR spectrum of  $\text{LaFeO}_3$  nanopowder prepared co-precipitation method calcined at  $500^\circ\text{C}$  for 4 hours

### EDXRF analysis

For more details, the EDXRF which has higher sensitivity was used to confirm the elemental composition of perovskite  $\text{LaFeO}_3$  samples synthesised by the two methods. From EDXRF analysis, La and Fe are main constituents elements prepared by two different methods as shown in Figures 9 and 10. The elements present are La, Fe and O with a mole ratio of 1:1:3 corresponding to the stoichiometric composition of  $\text{LaFeO}_3$  obtained by citrate sol-gel method. It was found that the relative abundance of the  $\text{LaFeO}_3$  prepared by citrate sol-gel method are match with the molecular formula of  $\text{LaFeO}_3$ .



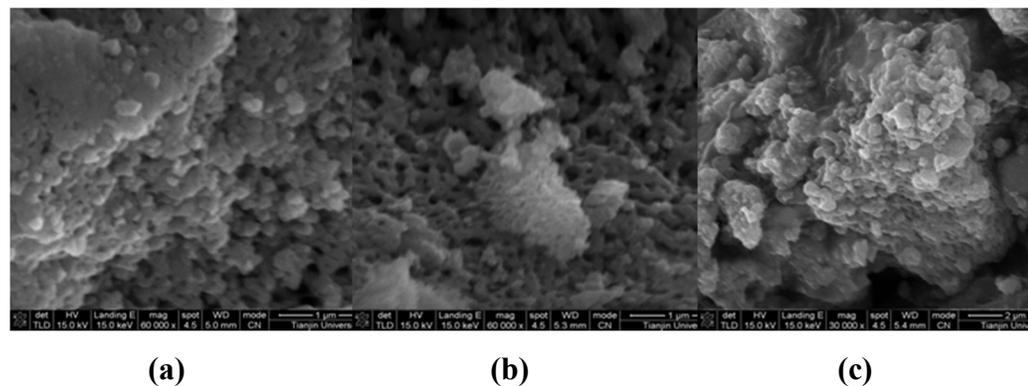
**Figure 9:** EDXRF spectrum of  $\text{LaFeO}_3$  nanopowder synthesized by citrate sol-gel method calcined at  $450^\circ\text{C}$  for 4 h



**Figure 10:** EDXRF spectrum of  $\text{LaFeO}_3$  nanopowder prepared by co-precipitation method calcined at  $500^\circ\text{C}$  for 4 hours

**SEM analysis**

Figures 11 and 12 show the SEM images of the particles synthesized by citrate sol-gel and co-precipitation methods. The citrate sol-gel particles have porous surface with uniform distribution unlike the strong agglomeration with varied size of the sample. The  $\text{LaFeO}_3$  nanoparticles synthesized by co-precipitation method have different shapes with the size of 30-40 nm such as tetragonal or flake like structure, whereas citrate sol-gel  $\text{LaFeO}_3$  nanoparticles are more spherical with uniform structure having the size distribution of 20-30 nm.



**Figure 11:** SEM micrographs of  $\text{LaFeO}_3$  nanopowder prepared by citrate sol-gel method calcined at (a)  $400^\circ\text{C}$  (b)  $450^\circ\text{C}$  (c)  $500^\circ\text{C}$  for 4 h



(a) (b) (c)

**Figure 12.** SEM micrographs of  $\text{LaFeO}_3$  nanopowder prepared by co-precipitation method at (a)  $500^\circ\text{C}$  (b)  $550^\circ\text{C}$  and (c)  $600^\circ\text{C}$  for 4 hours

### Conclusion

On the basis of the above systematical investigations, the following conclusions can be drawn.  $\text{LaFeO}_3$  perovskite nanocrystallites were prepared by citrate sol-gel and co-precipitation methods. From XRD showed that not only existence of  $\text{LaFeO}_3$  phase but also the present of impurity secondary phases for co-precipitation method. On the other hand only single perovskite phase  $\text{LaFeO}_3$  was successfully prepared by citrate sol-gel method at low temperature ( $\sim 450^\circ\text{C}$ ). The crystallite structure of  $\text{LaFeO}_3$  with cubic crystal structure was obtained in citrate sol-gel method at  $450^\circ\text{C}$  and the tetragonal crystallite structure was obtained via the co-precipitation method at  $500^\circ\text{C}$ . The SEM micrographs of  $\text{LaFeO}_3$  prepared by two methods shown that the morphologies of  $\text{LaFeO}_3$  were quite different. It was found that the particle size of the  $\text{LaFeO}_3$  powder varies from 20 to 40 nm depending on the preparation method. According to FT IR data, the absorption band of metal-oxygen band of  $\text{LaFeO}_3$  observed at citrate sol-gel method and many absorption bands appear in co-precipitation method. The EDXRF result has a little different these two methods. The major advantage of the citrate sol-gel method is that even at relatively low calcined temperature ( $450^\circ\text{C}$ ) xerogel precursors are directly transformed into a single perovskite phase without intermediate step. These results are comparable to those for  $\text{LaFeO}_3$  powder and bulk samples synthesized by co-precipitation methods.

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