

## Synthesis of lanthanum hexaluminate via tartarate precursor

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**Abstract:** Lanthanum hexaluminate,  $\text{LaAl}_{11}\text{O}_{18}$ , is of great importance as a material for high-temperature applications. The aim of this study was to synthesize a single-phase lanthanum hexaluminate through a technique of tartaric acid precursor. Effect of different annealing temperature on the microstructure has been studied and reported in the presented research. The annealing temperature was controlled from 900- 1300 °C. The resultant powders were investigated by Differential Thermal Analyzer (DTA), X-Ray Diffractometer (XRD), and Scanning Electron Microscopy (SEM). Despite, the annealing temperature has reached 1300 °C, a pure single phase could not be obtained. Instead, perovskite phase of  $\text{LaAlO}_3$  was observed. Moreover, random arrangement of lanthanum hexaluminate platelets were seen, which means further annealing temperature was required to achieve a single phase of lanthanum hexaluminate, using tartaric acid as precursor route.

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**Keywords:** Lanthanum hexaluminate; annealing temperature; tartaric acid.

### 1. Introduction

Recently, the development of oxides with magnetoplumbite structure becomes essential. They are very important ceramic material, and widely used for high temperature application, such as laser technology, catalysis, and thermal barrier coatings [1-5]. These materials are remarkable, due to their high melting point, high thermal expansion, low thermal conductivity, excellent longtime sintering [6, 7]. Lanthanum hexaluminate,  $\text{LaAl}_{11}\text{O}_{18}$ , is interesting material for oxide/oxide-composites [8]. It has been investigated in terms of its thermophysical properties and processing issues during air plasma spraying [9-12]. Saruhan et al., [8] indicated that the use of organic starting materials and the optimization of the sol-gel process may help to obtain pure  $\text{LaAl}_{11}\text{O}_{18}$ . Tartaric acid gel method has been used for the synthesis of alumina powders, which is relatively easy to process, energy saving and cost effective than the other sol-gel based method [13-16]. The aim of this study is to use tartaric acid gel method, in order to achieve fully crystallized  $\text{LaAl}_{11}\text{O}_{18}$  oxide at low temperature.

### 2. Material and Methods

The tartarate precursor method was applied for the synthesis of  $\text{LaAl}_{11}\text{O}_{18}$ . The tartaric acid precursor technique involves the preparation of aqueous solution of the required cation, the chelation of cations in solution by addition of tartaric acid then, raising the temperature of the solution until the precursor is formed. The tartaric acid was not only used to form stable complexes with starting metallic ions, but also used, as organic rich fuel. Pure

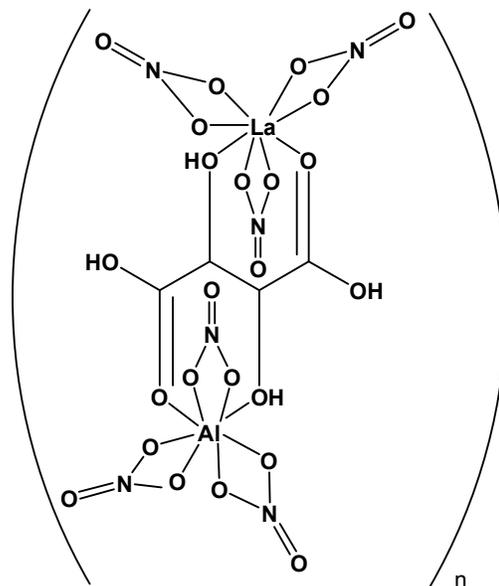
chemical grade of Aluminum nitrate, lanthanum chloride, in the presence of stoichiometric amount of tartaric acid were used as starting materials. The mixtures of La-Al solution, firstly prepared and then stirred for 15 minute on hot plate magnetic stirrer, followed with addition of an aqueous solution of tartaric acid to the mixtures with stirring. Then, the solution was evaporated to 80 °C with constant stirring until dryness, and dried in a dryer at 100 °C overnight. The dried powders obtained as aluminate precursor. Differential Thermal Analysis of the un-annealed precursor was carried out. The rate of heating was kept at 10°C/min between room temperature and 1200 °C. The measurements were carried out in a current of nitrogen atmosphere. Phase composition and structures were determined using X-ray diffraction (XRD) analysis. The analyses were performed on a Bruker axis D8 diffractometer using  $\text{Cu-K}\alpha$  ( $\lambda = 1.5406$ ) radiation and secondary monochromator in the range  $2\theta$  from 10 ° to 70 °. Identity of the phases present was determined by matching the experimental pattern with standards compiled by the Joint Committee on Powder Diffraction Standards (JCPDS). The size and morphology of the synthesized particles were directly imaged and determined using scanning electron microscopy (SEM, JSM-5400). Qualitative analysis for the different elements in the powders was used to clarify the distribution of each element of La, Al and O. These elements were semi quantitatively analyzed (spot analysis) by Energy Dispersive X-ray spectroscopy (EDX).

### 3. Results and discussions

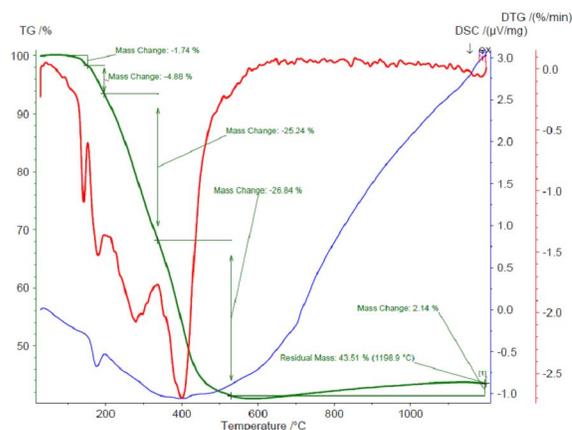
Herein in this study, thermal decomposition technique of carbonate usually is assumed to intermediate stage in between two major steps parent adduct  $[\text{La}(\text{NO}_3)_3 \cdot 11\text{Al}(\text{NO}_3)_3 \cdot x\text{C}_4\text{H}_6\text{O}_6]$  (Formula I) and lanthanum hexaaluminate,  $\text{LaAl}_{11}\text{O}_{18}$ . Figure 1 illustrates the profiles of thermal analysis (TG), differential thermal analysis (DTG) and differential scanning calorimetry (DSC) of the parent sample during the decomposition of the lanthanum-aluminum tartrate precursors at a heating rate of  $10\text{ }^\circ\text{C}\cdot\text{min}^{-1}$  in nitrogen atmosphere. The first and second decomposition steps started with a small weight loss 1.74% and 4.88% at 130 and 177  $^\circ\text{C}$ , respectively, assigned to the moisture content that still from the sample. As the temperature increase between 200 to 580  $^\circ\text{C}$  (DSC = 400  $^\circ\text{C}$ ), rapid and major weight loss of dropped in a weight loss according to the decomposition of tartrate precursor. The sample undergoes exothermic multistep weight loss between 177  $^\circ\text{C}$  and 580  $^\circ\text{C}$  due to the decomposition of carbonaceous mass of the tartrate precursor. This weight loss was reflected as broad exothermic peaks in DSC curve at around 400  $^\circ\text{C}$ . The sample weight seemed to be constant after the temperature reach to 580  $^\circ\text{C}$ . However, the total mass loss was about 58.7% at 580 $^\circ\text{C}$ . Beyond 585 $^\circ\text{C}$ , there was no significant weight loss until 1200  $^\circ\text{C}$ . The thermal decomposition steps of parent compound till reach to  $\text{LaAl}_{11}\text{O}_{18}$  can be summarized in the following equations:

- 1-  $2\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O} + 22\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O} + x\text{C}_4\text{H}_6\text{O}_6 \rightarrow [\text{La}(\text{NO}_3)_3 \cdot 11\text{Al}(\text{NO}_3)_3 \cdot x\text{C}_4\text{H}_6\text{O}_6] + x\text{H}_2\text{O}$
- 2-  $[\text{La}(\text{NO}_3)_3 \cdot 11\text{Al}(\text{NO}_3)_3 \cdot x\text{C}_4\text{H}_6\text{O}_6] \rightarrow \text{La}_2(\text{CO}_3)_3 \cdot 11\text{Al}_2(\text{CO}_3)_3$
- 3-  $\text{La}_2(\text{CO}_3)_3 \cdot 11\text{Al}_2(\text{CO}_3)_3 \rightarrow \frac{1}{2}\text{La}_2\text{O}_3 \cdot 5\frac{1}{2}\text{Al}_2\text{O}_3 + x\text{CO}_2$
- 4-  $\frac{1}{2}\text{La}_2\text{O}_3 \cdot 5\frac{1}{2}\text{Al}_2\text{O}_3 \rightarrow \text{LaAl}_{11}\text{O}_{18}$

XRD analysis was performed with several samples that had been exposed for various times, as shown in Fig. 2. The results indicated that  $\text{LaAl}_{11}\text{O}_{18}$ , and  $\text{LaAlO}_3$  were present on the samples. However, the intensities of the peaks varied. At the calcination temperature of 1000  $^\circ\text{C}$ , there were not any significant diffraction peaks detected, suggesting that there is no formation of any phase at 1000  $^\circ\text{C}$ . When the calcination temperature was raised to 1100  $^\circ\text{C}$ , the diffraction peaks of  $\text{LaAl}_{11}\text{O}_{18}$  and  $\text{LaAlO}_3$  could be observed. Typically perovskite phase of  $\text{LaAlO}_3$  appeared as the strongest peaks.



**Formula I:** Suggested structure of parent compound.

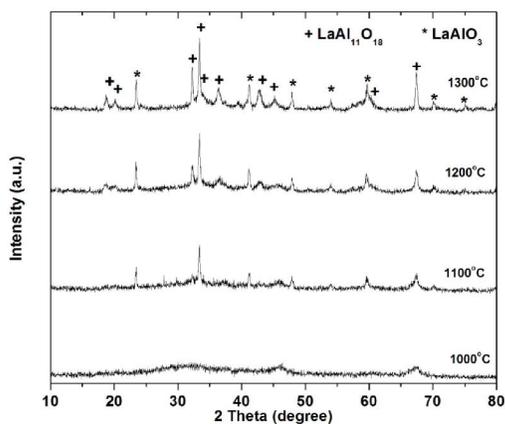


**Fig. 1:** TG, DTG and DSC curve of  $[\text{La}(\text{NO}_3)_3 \cdot 11\text{Al}(\text{NO}_3)_3 \cdot x\text{C}_4\text{H}_6\text{O}_6]$  adduct.

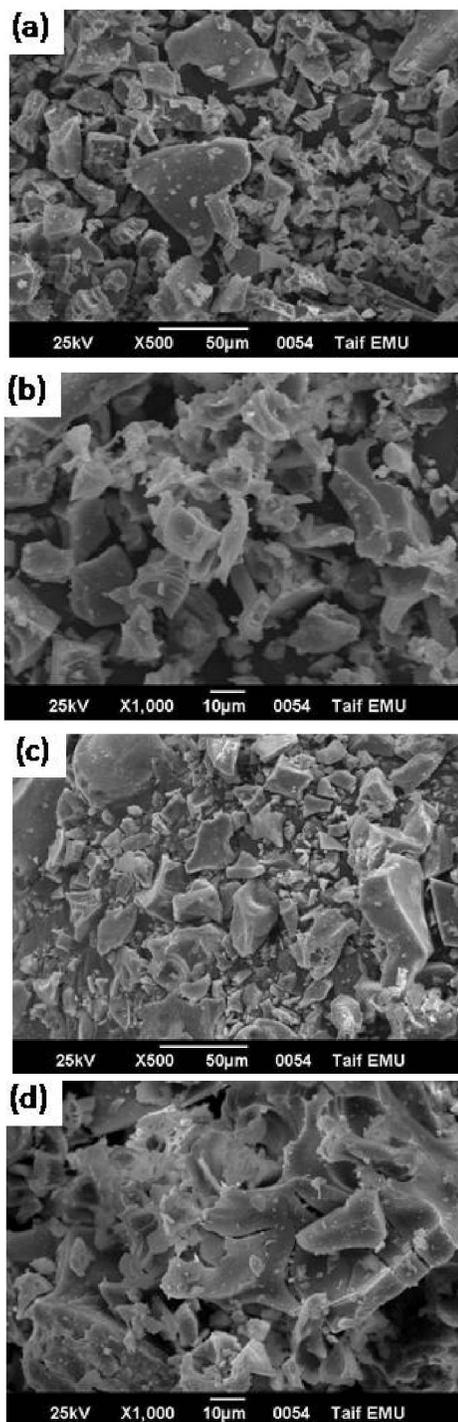
$\text{LaAl}_{11}\text{O}_{18}$  were very weak. This is suggested that the phase structure of  $\text{LaAl}_{11}\text{O}_{18}$  has started to form. The peaks of  $\text{LaAl}_{11}\text{O}_{18}$  were more intense at 1200  $^\circ\text{C}$ , which was clearly attributed to an increase in the amount of the corresponding compound. When the temperature further increased up to 1300  $^\circ\text{C}$ , the intensity of the diffraction peaks increased markedly. Moreover, it seems that heating to 1300  $^\circ\text{C}$  did not eliminate the intermediate crystallization of  $\text{LaAlO}_3$ , as its peaks appeared at 1300  $^\circ\text{C}$ . The characteristic diffraction peaks of  $\text{LaAl}_{11}\text{O}_{18}$  and  $\text{LaAlO}_3$  are 033-0699 and 03-5551 respectively.

SEM examinations of the synthesized powders in Fig.3, reveal that they were essentially, slack and porous crystals, and have many holes. The grains did not look plate-like crystals, and that is because of the short time of crystallization, which

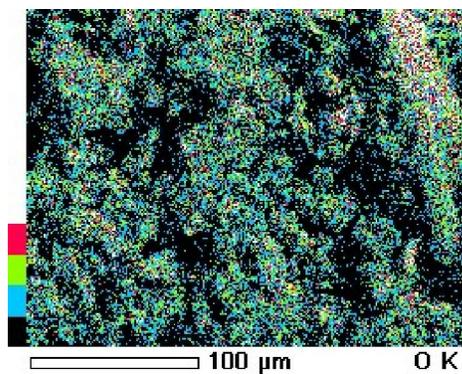
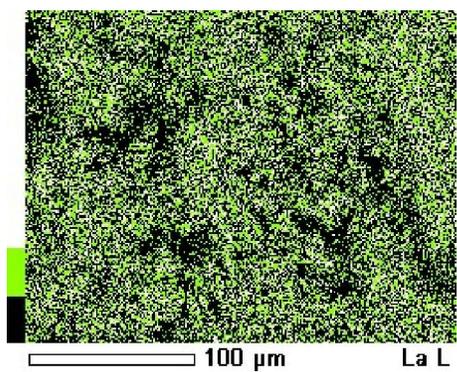
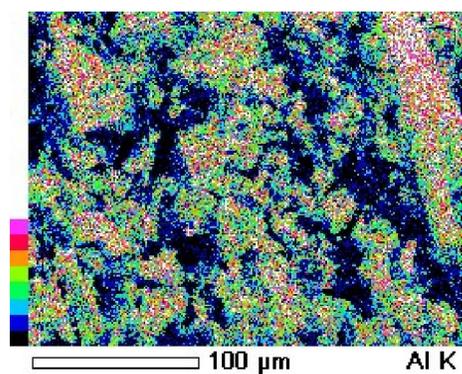
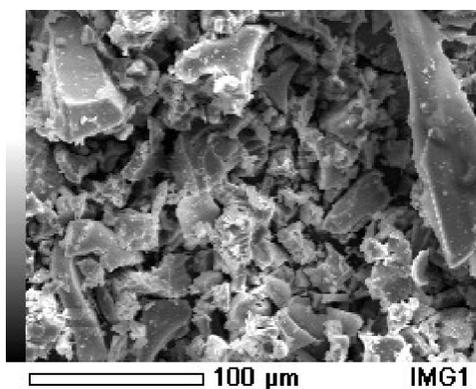
includes the formation of an intermediate  $\text{LaAlO}_3$  phase (3, 4). Moreover, the powders have a particles size of 10-25 $\mu\text{m}$ . Other important information was carried out using the elemental mapping technique, to study extensively the composition of the synthesized  $\text{LaAl}_{11}\text{O}_{18}$  powder, which was obtained from tartrate precursors annealed at 1300 °C for 2 h. The results in Fig. 4, show the distribution of La, Al and O elements was almost the same indicating excellent homogenous microstructure. Also, EDX analysis was conducted in the area, where the elemental mapping was carried out, as shown in Fig.5. The results revealed enrichment in Al and La. These results, together with other analysis using TDS and XRD, support the proposed method for synthesizing oxide with magnetoplumbite structure of the general composition,  $\text{LaAl}_{11}\text{O}_{18}$ , via tartaric acid has been successfully obtained.



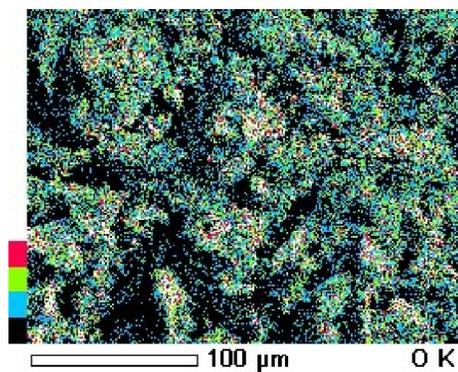
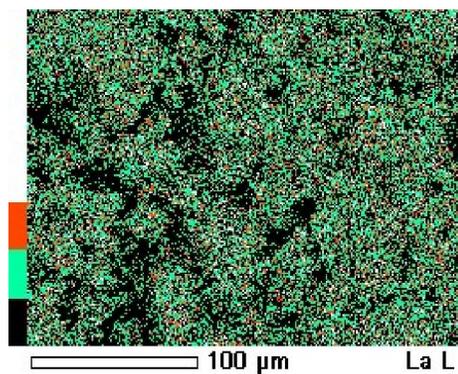
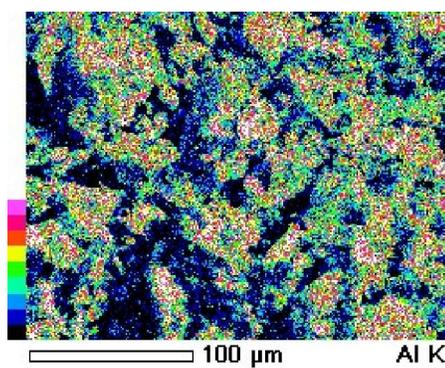
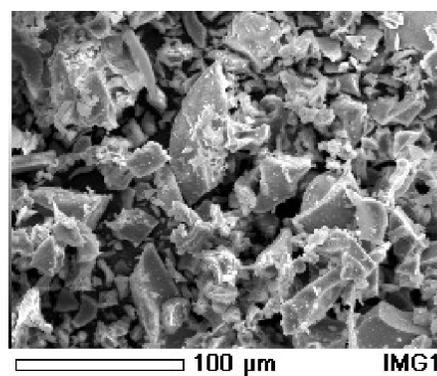
**Fig. 2:** XRD patterns of  $\text{LaAl}_{11}\text{O}_{18}$  from lanthanum-aluminum tartrate precursor treated at different temperatures (1000-1300 °C) for 2 h.



**Fig. 3:** Effect of annealing temperatures on the microstructure of synthesized  $\text{LaAl}_{11}\text{O}_{18}$  powders obtained from tartrate precursors annealed for 2h. (a & b) 1100 °C, (c & d) 1300 °C.



**Fig. 4:** Microstructure maps for constituent elements of synthesized  $\text{LaAl}_{11}\text{O}_{18}$  powders obtained from tartrate precursors annealed at 1100 °C for 2h.



**Fig. 5:** Microstructure maps for constituent elements in of synthesized  $\text{LaAl}_{11}\text{O}_{18}$  powders obtained from tartrate precursors annealed at 1300 °C for 2h.

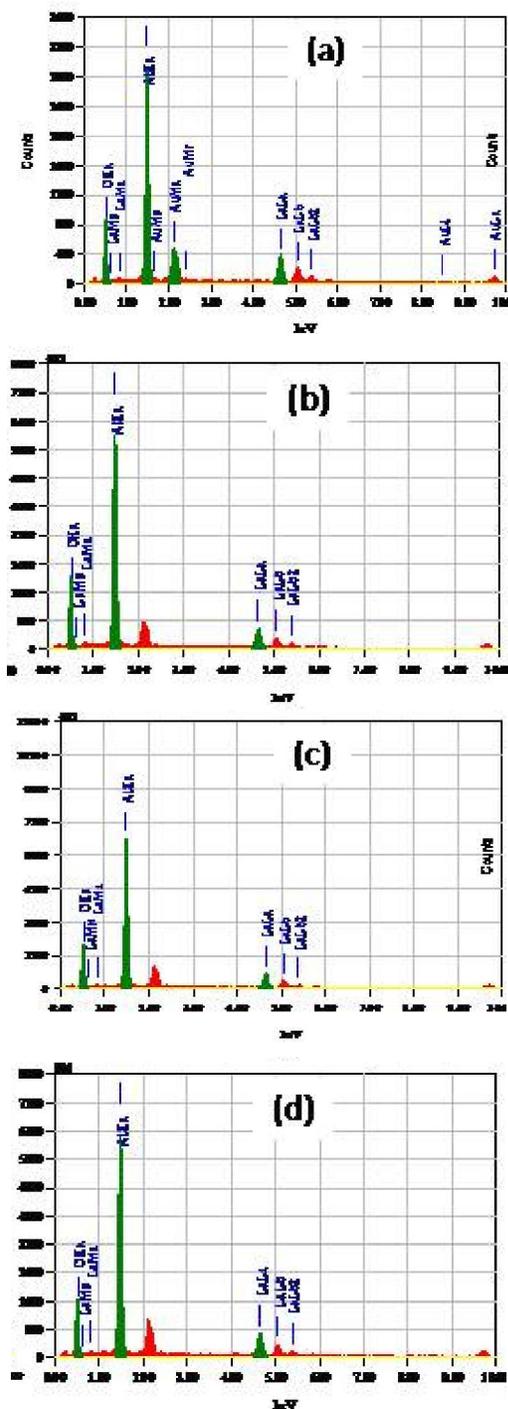


Fig. 6: EDX spectra of synthesized  $\text{LaAl}_{11}\text{O}_{18}$  powders obtained from tartrate precursors annealed for 2h. (a & b) 1100 °C, (c & d) 1300 °C

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