

# Combustion synthesis and photoluminescence of Tb<sup>3+</sup> doped LaAlO<sub>3</sub> nanophosphors

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## ABSTRACT

Terbium doped lanthanum aluminate (LaAlO<sub>3</sub>) nanophosphors were successfully synthesized by a combustion process using concentrated solution of lanthanum nitrates and aluminate as oxidiser, and glycine acid as fuel. The powders were characterized by infrared spectroscopy (IR), X-ray diffraction (XRD), Rietveld refinement, scanning electron microscopy (SEM), transmission electron microscopy (TEM) and fluorescence spectroscopy. Pure LaAlO<sub>3</sub> phase was obtained at 800 °C heated for 4 h, without formation of any intermediate phase, with an average crystal size, as determined by TEM, of 60 nm. Intense green emission is reported at 542 nm, from the <sup>5</sup>D<sub>4</sub> level, which intensity depends on Tb concentration.

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## 1. Introduction

Lanthanum aluminate (LaAlO<sub>3</sub>) with a perovskite-type structure presents good thermal stability with high melting point at 2180 °C, which can minimize interfacial dislocations [1]. Typically, LaAlO<sub>3</sub> has been prepared by conventional solid-state reaction of Al<sub>2</sub>O<sub>3</sub> and La<sub>2</sub>O<sub>3</sub> in the temperature range of 1500–1700 °C [2,3,4]. But this method suffers from many inherent shortcomings, such as the high-temperature heat treatment which have a detrimental effect of the grain size, limited chemical homogeneity and low sintering temperature.

Recently LaAlO<sub>3</sub> have been successfully prepared by microwave irradiation [5]. Moreover, various wet and soft chemical methods including polymerized complex method using citric acid and ethylene glycol route have been reported [6]. Several low temperature (750–900 °C) chemical routes are used for preparing finer and homogeneous powders of LaAlO<sub>3</sub> like Poly Vinyl Alcohol (PVA) with metal nitrate synthesis [7], sol–gel process [8–10], EDTA gel route [11,12], co-precipitation method [13,14], pyrolysis using triethanolamine [15] and combustion synthesis with urea and hydrazine as fuel [16–19].

This paper presents the synthesis and characterization of LaAlO<sub>3</sub>:Tb<sup>3+</sup> phosphors, prepared by combustion synthesis [20], which has the advantage of being simple, fast and economical in doping. The structural details and optical properties of the synthe-

sized phosphor have been investigated by X-ray diffraction (XRD), Rietveld refinement, transmission electron microscopy (TEM), scanning electron microscopy (SEM), infrared spectrometry (IR) studies, and fluorescence spectroscopy.

## 2. Experimental procedure

The starting materials were lanthanum nitrate hexahydrate [La(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O] (98%), aluminum nitrate nonahydrate [Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O] (99%), europium(III) nitrate pentahydrate [Tb(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O], and glycine [H<sub>2</sub>NCH<sub>2</sub>COOH] (99%). La(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O and Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O Tb(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O and H<sub>2</sub>NCH<sub>2</sub>COOH were dissolved in distilled water. Tb<sup>3+</sup> ions doped Lanthanum aluminate with general formula (La<sub>1-x</sub>Tb<sub>x</sub>)AlO<sub>3</sub> were prepared with different concentration of Tb ( $x = 2\%$ , 5%, 10%, 15%, 20%). During the process, the molar ratio of glycine to total metal cations concentration G/M was 2 and the cation ratio of La:Al was 1:1. Glycine was used as a fuel. The resulting solution was magnetically stirred at 85 °C to get a clear and uniform solution. The solution slowly turned viscous on continued heating for about 1.5 h, it turned into a highly viscous gel. Throughout the process, no signs of precipitation or turbidity were observed. The gel was put into a vacuum oven and kept at 110 °C for 24 h, undergoing rapid dehydration and foaming followed by decomposition and generating combustible gases. These volatile combustible gases ignite and burn with a flame yielding voluminous solid. Finally this solid was ground to fine powders and was calcined at 600 °C, 700 °C and finally at 800 °C for 4 h to obtain pure LaAlO<sub>3</sub>.

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### 3. Experimental

The X-ray powder diffraction (XRD) patterns of all samples were recorded on a Philips X'Pert system (PW3020 vertical goniometer and PW3710 MPD control unit) with Cu K $\alpha$  1, 2 radiation ( $\lambda_1 = 1.54059 \text{ \AA}$  and  $\lambda_2 = 1.54442 \text{ \AA}$ ). In order to improve the signal to noise ratio, at least three runs (collected with 10 s/step and 0.05°/step) were measured.

The quantitative phase analysis for samples composed of one crystal and one amorphous phase (CGXXC series) was performed on XRPD data by applying the Rietveld method (DBWS9600 computer program written by Sakthivel and Young modified by Riello et al. (1995, 1998), using  $\alpha\text{-Al}_2\text{O}_3$  as the internal standard (IS).

Infrared spectra were recorded on a NICOLET 560 spectrometer using KBr pellets in the region of 4000–400  $\text{cm}^{-1}$ . The scanning electron images of samples were recorded with scanning electron microscope (SEM) JEOL JSM-5600LV, operated at 20 kV equipped with an Oxford Instruments ISIS series 300 EDS detector.

The morphology of products was characterized by transmission electronic microscopy (TEM) (Tecnai G2 ultra Twin). TEM images were taken at 300 kV with a JEOL JEM-3010 instrument, with an ultra-high resolution pole-piece (0.17 nm point resolution), equipped with a Gatan multi-scan CCD camera (Mod. 794) and an oxford EDS microanalysis detector. The powdered samples were dispersed in ethanol by sonication for approximately 5 min and deposited onto a holey carbon film grid.

Photoluminescence measurements were performed with a Fluorolog3-21 system (Horiba Jobin Yvon). A 450 W xenon arc lamp was used as a broadband excitation source and a double Czerny–Turner monochromator was used to select the excitation wavelength for photoluminescence excitation.

The analysis of the emitted luminescence signal from the samples was obtained by using a iHR320 single grating monochromator and a R928 Hamamatsu photomultiplier tube detector. Time resolved characterization was obtained by exciting the sample with a SpectraLED-03 laser diode, providing 377 nm excitation with 12 nm spectral bandwidth. The excitation pulse duration was set at 5 ms and the photoluminescence decay was acquired for about 20 ms, which was sufficient to allow the signal going to zero. These measurements were obtained by working in multi channel single photon counting (MCSPC) mode. All emission spectra are obtained using the same amount of powder, measured at room temperature and recorded under the same conditions.

The particle size was estimated from the X-ray line broadening of the (110) diffraction peak using the Scherrer formula [21].

$$D = 0.9\lambda/\beta \cos \theta, \quad (1)$$

where  $D$  is the particle size in nm,  $\lambda$  the radiation wavelength,  $\theta$  the diffraction peak angle and  $\beta$  is the corrected line width at half-peak intensity. The correction for instrumental peak broadening was made using the Warren formula:  $\beta = (b_{\text{obs}}^2 - b^2)^{1/2}$ , where  $b_{\text{obs}}$  is the line width at half-peak intensity related to  $\text{LaAlO}_3$  powder and  $b$  is the line width of the (110) diffraction peak of the  $\text{LaAlO}_3$ .

### 4. Results and discussion

#### 4.1. X-ray diffraction

The X-ray diffraction patterns of  $\text{LaAlO}_3:\text{Tb}^{3+}$  are shown in Fig. 1. According to observed and calculated XRD analysis (Fig. 1a), the structural analysis of  $\text{LaAlO}_3$  obtained at 800 °C is carried by Rietveld refinement program. It crystallizes in a pure rhombohedral perovskite structure with space group R-3c (No. 167). The reliability factors obtained from the refinement are  $R_{\text{wp}} = 8.02$ ,  $R_{\text{p}} = 5.82$ ,  $R_{\text{exp}} = 3.58$ , with unit cell dimensions  $a = 5.37 \text{ \AA}$  and

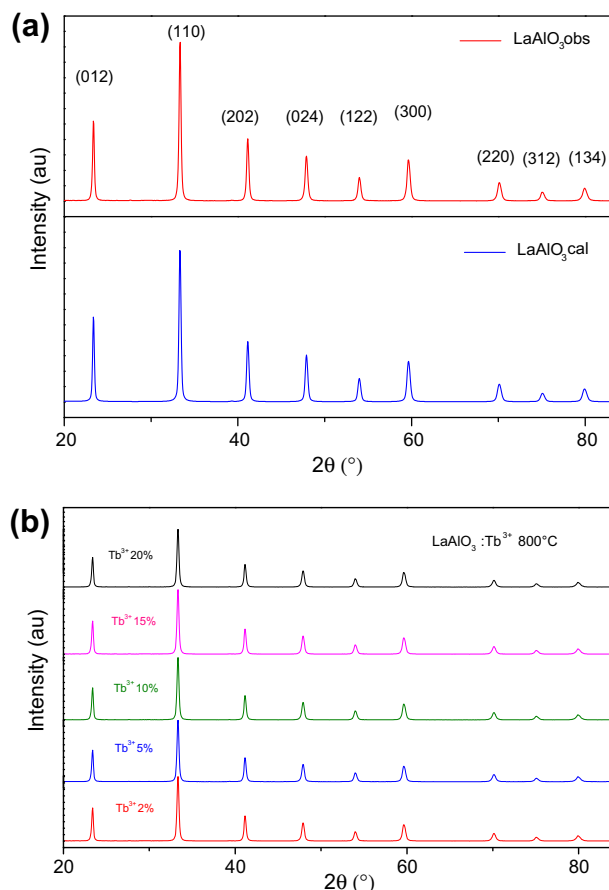


Fig. 1. X-ray diffraction patterns of  $\text{LaAlO}_3:\text{Tb}^{3+}$  (a) observed and calculated, and (b) doping concentration variation.

$c = 13.10 \text{ \AA}$ . Which are close to the reported values (JCPDS no. 01-082-0478). The atomic coordinates of  $\text{LaAlO}_3$  obtained from the Rietveld analysis are given in Table 1.

Fig. 1b shows that the doping concentration does not influence the crystalline phase formation. So all diffraction peaks in these XRD patterns could be attributed to the rhombohedral perovskite crystal structure of  $\text{LaAlO}_3$ . The particles size of  $\text{LaAlO}_3$  powder calcined at 800 °C for 4 h calculated from the Scherrer formula is about 60 nm.

#### 4.2. IR spectra

Fig. 2 shows IR spectra of the samples containing different doping concentrations obtained at 800 °C. All spectral profiles are identical; the two frequencies at 660 and 445  $\text{cm}^{-1}$  are typical for the M–O (possibly La–O and Al–O stretching frequencies) vibrations for the perovskite structure compounds [22].

#### 4.3. TEM and SEM analysis

Fig. 3a presents TEM micrographs of  $\text{LaAlO}_3$  powders calcined at 800 °C, showing that the powders are composed by monocrystal-

Table 1  
Atomic coordinates of  $\text{LaAlO}_3$ .

Element	Wyckoff position	Site occupancy	x	y	z
La	6a	1/6	0	0	0.25
Al	6b	1/6	0	0	0
O	18e	1/2	0.528	0	0.25

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