

Combustion synthesis and photoluminescence of Eu^{3+} doped LaAlO_3 nanophosphors

A. Dhahri^a, K. Horchani-Naifer^{a,*}, A. Benedetti^b, F. Enrichi^c, M. Ferid^a

^a Laboratoire de Physico-chimie des Matériaux Minéraux et leurs Applications, Centre National des Recherches en Sciences des Matériaux, Technopole de Borj Cedria, B.P. 73, 8027 Soliman, Tunisia

^b Dipartimento di Chimica Fisica, Università Ca' Foscari Venezia e INSTM, via Torino 155/b, 30170 Mestre (VE), Italy

^c CIVEN (Coordinamento Interuniversitario Veneto per le Nanotecnologie), via delle Industrie 5, 30175 Marghera (VE), Italy

ARTICLE INFO

Article history:

Received 28 January 2012

Received in revised form 21 March 2012

Accepted 9 April 2012

Available online 17 May 2012

Keywords:

Combustion process

Lanthanum aluminate

Europium

Nanoparticle

Photoluminescence

ABSTRACT

Eu^{3+} doped LaAlO_3 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), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and fluorescence spectroscopy. Pure LaAlO_3 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 photoluminescence emission is reported at 616 nm, allowing the use of this material as red phosphor.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

Lanthanum aluminate (LaAlO_3) with a perovskite-type structure has attracted great attention in recent years for many applications because of its properties. Indeed, this material presents good thermal stability with high melting point at 2180 °C, which can minimize interfacial dislocations [1], good dielectric properties, high relative permittivity ($\epsilon_r = 23$), high quality factor ($Q \times f \approx 68,000$; $Q = 1/\tan \delta$; f : measuring frequency and $\tan \delta$: dissipation factor) and very small temperature coefficient of resonant frequency ($\tau_f = -44$ ppm/K) [2]. Traditionally, LaAlO_3 has been prepared by conventional solid-state reaction of Al_2O_3 and La_2O_3 in the temperature range of 1500–1700 °C [3,4]. But this typical 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.

Several low temperature (750–900 °C) chemical routes are used for preparing finer and homogeneous powders of LaAlO_3 like Poly Vinyl Alcohol (PVA) with metal nitrate synthesis [5], sol–gel process [6–8], EDTA gel route [9,10], co-precipitation method [11,12], pyrolysis using triethanolamine [13] and combustion synthesis with urea as fuel [14,15].

Moreover, various wet and soft chemical methods including polymerized complex method using citric acid and ethylene glycol

route have been reported [16]. Recently LaAlO_3 have been successfully prepared by microwave irradiation [17].

This paper presents the synthesis and characterization of $\text{LaAlO}_3:\text{Eu}^{3+}$ phosphors, prepared by combustion synthesis, which has the advantage of being simple, fast and economical in doping. The structural details and optical properties of the synthesized phosphor have been investigated by X-ray diffraction (XRD), 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 [$\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$] (98%), aluminum nitrate nonahydrate [$\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$] (99%), europium(III) nitrate pentahydrate [$\text{Eu}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$], and glycine [$\text{H}_2\text{NCH}_2\text{COOH}$] (99%). $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ $\text{Eu}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and $\text{H}_2\text{NCH}_2\text{COOH}$ were dissolved in distilled water. Eu^{3+} ions doped Lanthanum aluminate with general formula ($\text{La}_{1-x}\text{Eu}_x$) AlO_3 were prepared with different concentration of Eu ($x = 2\%$, 5%, 10%). 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

* Corresponding author. Fax: +216 79 325 314.

E-mail address: karima_horchani@yahoo.com (K. Horchani-Naifer).

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_3 .

3. Experimental

The X-ray powder diffraction (XRD) patterns of all samples were recorded on a X'PERT Pro PANAnalytical diffractometer with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$). Infrared spectra were recorded on a NICO-LET 560 spectrometer using KBr pellets in the region of 4000–400 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 (1 1 0) diffraction peak using the Scherrer formula [18].

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

where D is the particle size in nm, λ the radiation wavelength, θ the diffraction peak angle and β 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_{obs} is the line width at half-peak intensity related to LaAlO_3 powder and b is the line width of the (1 1 0) diffraction peak of the LaAlO_3 .

4. Results and discussion

4.1. X-ray diffraction

The X-ray diffraction patterns of $\text{LaAlO}_3:\text{Eu}^{3+}$ are shown in Fig. 1. According to XRD analysis (Fig. 1a), a pure rhombohedral phase of LaAlO_3 (JCPDS no. 01-082-0478) with a perovskite structure could be obtained at 800 °C. 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 LaAlO_3 with space group R-3c, with unit cell dimensions $a = 5.369 \text{ \AA}$ and

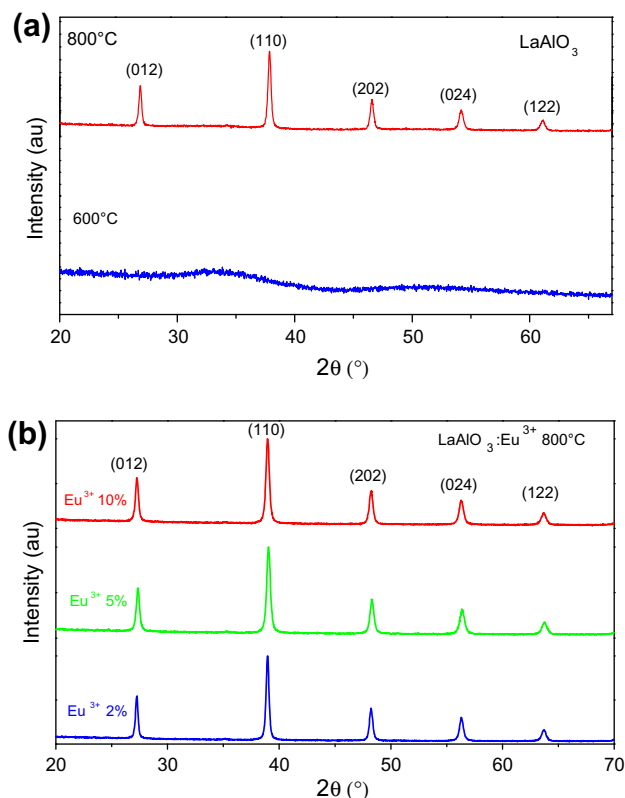


Fig. 1. X-ray diffraction patterns of $\text{LaAlO}_3:\text{Eu}^{3+}$ (a) temperature variation and (b) doping concentration variation.

$c = 13.11 \text{ \AA}$. The particles size of 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 cm^{-1} are typical for the M–O (possibly La–O and Al–O stretching frequencies) vibrations for the perovskite structure compounds [19].

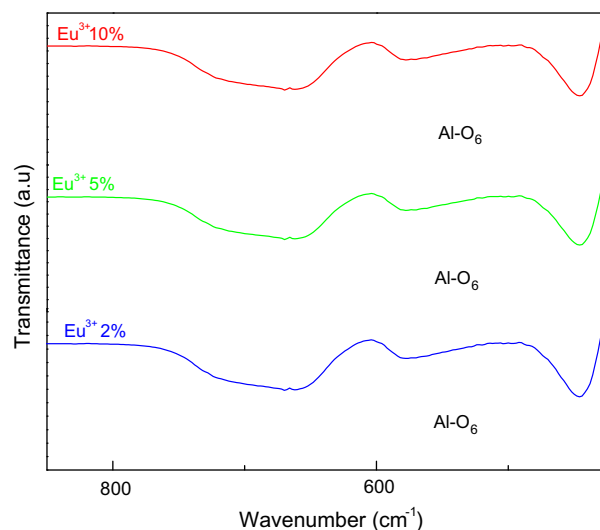


Fig. 2. FT-IR spectra of $\text{LaAlO}_3:\text{Eu}^{3+}$ doping concentration variation.

Download English Version:

<https://daneshyari.com/en/article/1495447>

Download Persian Version:

<https://daneshyari.com/article/1495447>

[Daneshyari.com](https://daneshyari.com)