Available online at www.sciencedirect.com

ScienceDirect

Ceramics International 40 (2014) 16209–16212

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Laser sintering and radioluminescence emission of pure and doped Y_2O_3 ceramics

Tiago Cordeiro de Oliveira, Marcelo Souza da Silva, Lilian Menezes de Jesus, David Vieira Sampaio, Jerre Cristiano Alves dos Santos, Natalilian Roberta da Silva Souza, Ronaldo Santos da Silva*

Department of Physics, Federal University of Sergipe, CEP 49100 São Cristóvão, Sergipe, Brazil

Received 21 March 2014; received in revised form 9 July 2014; accepted 10 July 2014
Available online 18 July 2014

Abstract

In this study, pure and Ca-, Mn-, and Zn-doped Y_2O_3 powders, synthesized by the polymeric precursor method, are sintered by a new laser sintering technique in which a CO_2 laser, in continuous mode, is employed as the main heating source. The laser-sintered ceramics show a single crystalline phase and have high relative density (~98% Y_2O_3:Ca), with a homogeneous and crack-free microstructure. When excited with X-rays, the samples present identical radioluminescence (RL) emission spectra, with a band centered at 495 nm. This emission is thought due to the presence of self-trapped excitons (STE).

Keywords: Laser sintering; CO_2 laser; Yttria; Radioluminescence

1. Introduction

Scintillators are luminescent materials that absorb high-energy photons or particles and subsequently emit visible light. Oxide scintillator materials are characterized by their high thermal, chemical, and radiation stability. When compared with single crystals, ceramics are lower in cost, more easily produced, and have the potential for being produced in predefined formats [1], so it is important to study the production and luminescent emissions of ceramic scintillators. Yttria (Y_2O_3) has a cubic crystalline structure with a lattice parameter of 10.604 Å. Its unit cell contains two inequivalent cation sites, Y1 at the 8*a* site and Y2 at the 24*d* site, and one type of O at the 48*e* site [2]. Yttrium oxide is an essential material in current technological applications due to the development of ceramic oxide purification processes, and also due to its excellent physicochemical characteristics such as its high refractive index (~1.9); high thermal conductivity in a state of high purity; high melting point (2400 °C); high corrosion resistance; thermal stability; transparency from violet to infrared; high density (5.04 g/cm^3); and high effective atomic number (36.7) [3–5]. The latter two features are required in X-ray scintillators that increase the number of interactions between high energy photons and the material involved [6].

To optimize yttrium's ceramic properties, high density ceramic bodies must be obtained. Several different yttria sintering methods have been employed to this end [3–10]. High-density Y_2O_3 ceramic has been obtained by long sintering periods [6], at temperatures of 2000 °C with no pressure application [7] or at 1500 °C under high pressure [8] and with addition of ThO_2, La_2O_3, HfO_2, or LiF, to promote densification [9]. In addition, Kodo et al. [10] found that the sintering temperature required for Y_2O_3 complete sample densification was reduced between 100 and 400 °C when doped with 1 mol% of the divalent cations Ca^{2+}, Mg^{2+}, Mn^{2+}, Ni^{2+}, Sr^{2+}, and Zn^{2+}.

Recently a new laser sintering method to produce bulk ceramics has been proposed. The authors have observed changes in the microstructure, structure, optics, and electric properties in laser

*Corresponding author.
E-mail address: rsilvafisica@gmail.com (R.S.d. Silva).

http://dx.doi.org/10.1016/j.ceramint.2014.07.056
0272-8842/

sintered ceramic materials such as Ta_2O_5 [11], $Ka_{0.5}Na_{0.5}NbO_3$ [12], and $Bi_4Ge_3O_{12}$ [13] when compared to that produced by the conventional sintering method using an electric oven. In this method, a CO_2 laser, in continuous mode, is employed as the main heating source during the sintering. The main advantages of this method are the rapid processing, the potential for using high heating and cooling rates (about 2000 °C/min) without crucibles, thereby reducing the risk of contamination, and the potential for sintering materials with high melting points. Therefore, in this study we use the laser technique in order to produce dense, pure, Ca-, Mn-, and Zn-doped Y_2O_3 ceramics.

2. Experimental procedure

Pure and doped Y_2O_3 powders were produced by the Pechini method using the precursors $Y(NO_3)_3$ (99.9%, Sigma), $Mn(NO_3)_2 \cdot 4H_2O$ (99%, Merck), $Ca(NO_3)_2 \cdot 4H_2O$ (99%, Synth), and $Zn(NO_3)_2 \cdot 4H_2O$ (99%, Synth). Initially citric acid (CA – 99.5%, Vetec) was dissolved in distilled water (0.6 g/ml) and, after complete homogenization, $Y(NO_3)_3$ and the dopants were added in the molar ratio of citric acid:metalic ion = 3:1. The resultant solution was stirred and heated until the complete dissolution of the cation (70–80 °C). Next, ethylene glycol (EG – 99%, Synth) was added in a mass ratio of 3:2 (AC:EG), and the temperature was raised to approximately 120 °C [14]. To produce the powders, this resultant solution was calcined at 600 °C for 4 h at a heating rate of 2 °C/min. The doped samples were produced with addition of 1 mol% of Ca, Mn, and Zn.

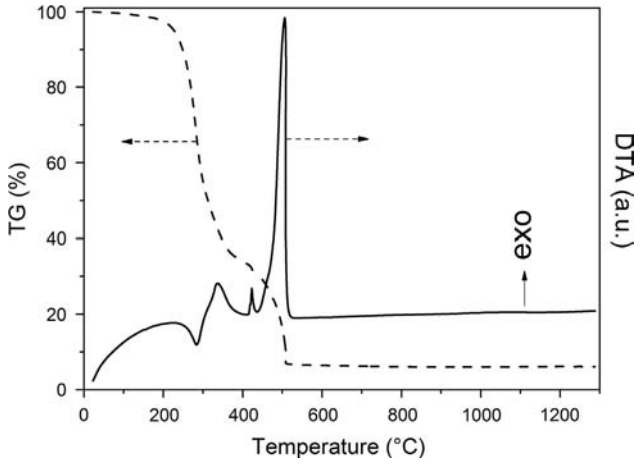

Fig. 1. DTA and TG curves of the Y_2O_3 precursor solution after drying at 100 °C/24 h.

Differential thermal analysis (DTA) and thermogravimetry (TG) measurements were performed simultaneously (Nerzsch STA 409) in a temperature range from 25 °C to 1300 °C at a heating rate of 10 °C/min in an atmosphere of synthetic air (O_2/N_2 – 1/4), using alumina as the reference material. X-ray diffraction (XRD) was performed using a Rigaku diffractometer RINT 2000/PC using Cu Kα radiation in the 2θ range between 20° and 80° in continuous scan mode in steps of 0.02°.

For sintering, the calcined powders were uniaxially pressed (10 MPa pressure) into disks with diameter of 4 mm and thickness of 1 mm. Laser sintering was accomplished by keeping a laser beam fixed in the center of the sample throughout the sintering process. Before irradiation, the samples were heated to 300 °C at a heating rate of 50 °C/min and kept at this temperature during the laser sintering process. After this pre-heating, laser power was raised at a linear rate of 0.05 W/mm^2 s up to 2.1 W/mm^2 and maintained at this value for 60 s. After irradiating the first face of the sample, this process was repeated on the other side. The microstructural surface of the sintered samples was then analyzed with no pre-treatment, using scanning electron microscopy (SEM) (model JSM-6510LV). The average grain size was estimated from the SEM images according to the well-known intercept length method [15]. The relative density of the ceramics was determined using the Archimedes principle. The radioluminescence (RL) of the laser sintered ceramics was measured under X-ray excitation (Rigaku diffractometer RINT 2000/PC) with a voltage of 40 kV and current of 40 mA. The luminescence was obtained using an Ocean Optics HR2000 spectrometer in the range of 300–1000 nm.

3. Results and discussion

Fig. 1 presents the DTA/TG curves of the pure Y_2O_3 precursor solution after drying at 100 °C/24 h. Four peaks are clearly

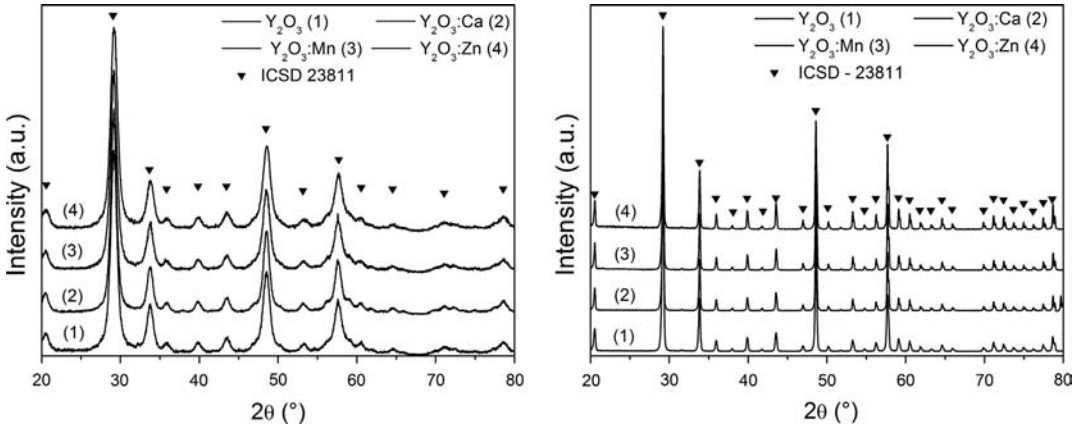

Fig. 2. X-ray diffraction (XRD) patterns of the pure and 1 mol% Ca-, Mn-, and Zn-doped Y_2O_3 samples. (a) Calcined powder at 600 °C for 5 h; and (b) laser-sintered ceramics at a power density of 2.1 W/mm^2 for 60 s.