Materials Chemistry and Physics 199 (2017) 557–566

Contents lists available at ScienceDirect

Materials Chemistry and Physics

journal homepage: www.elsevier.com/locate/matchemphys

Bio-prototyping of europium-yttria based rods for radiation dosimetry

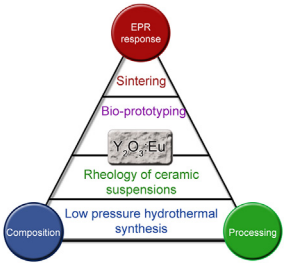
S.C. Santos*, O. Rodrigues Jr., L.L. Campos

Instituto de Pesquisas Energeticas e Nucleares – IPEN, Av. Prof. Lineu Prestes 2242, Cidade Universitaria, Sao Paulo, Brazil

HIGHLIGHTS

- Alternative hydrothermal synthesis of powders is demonstrated.
- Bio-prototyping of europium-yttria rods is reported.
- Microstructure evolution of as sintered rods is evaluated.
- The effect of Eu^{3+} on paramagnetic response of yttria host is discussed.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 28 March 2017
Received in revised form
26 June 2017
Accepted 15 July 2017
Available online 17 July 2017

Keywords:
Yttria
Rare earths
Radiation dosimetry
Bio-prototyping
Ceramic processing

ABSTRACT

The application of solid state dosimeters in radiation protection has grown significantly as consequence of advances in the development of dosimetric materials using rare earths. The conception of new dosimetric materials concerns synthesis methods, which control the evolution of material structure, including further processing steps as, shaping, drying, and sintering. The present study reports a full bio-prototyping approach to produce europium doped yttria rods with potential application in radiation dosimetry. Ceramic particles synthesized by hydrothermal route were characterized by Photon Correlation Spectroscopy (PCS), X-ray diffraction (XRD), and Scanning Electron Microscopy (SEM). The effect of europium on promoting electronic defects in yttria host was evaluated by Electron Paramagnetic Resonance (EPR). Low pressure hydrothermal synthesis led to formation of rounded particles with mean diameter of 410 nm. Aqueous suspensions with 20 vol% of particles prepared at pH 10, and 0.2 wt% binder exhibited apparent viscosity of 213 mPa s, being suitable for bio-prototyping of rods. Sintering of shaped samples at 1600°C for 4 h provided formation of dense ceramic rods. Europium-yttria rods containing 5 at.% Eu exhibited the most intense EPR response.

1. Introduction

A basic feature of dosimeter material is the ability to absorb radiation energy and release it in form of visible light as photon or thermally stimulated. The mechanism that converts absorbed radiation energy into visible light output depends on material characteristics such as chemical composition and crystal structure. Besides, these characteristics are consequence of synthesis route, including the nature of starting materials and further processing steps.

The structure of material, including its defects (intrinsic and extrinsic) can be controlled by synthesis methods such as evaporation [1], Pechini [2], chemical vapour deposition (CVD) [3], spray pyrolysis [4], sol-gel [5], co-precipitation [6], hydrothermal [7], and combined synthesis methods [8]. Usually these routes lead to formation of powder materials, in which further processing steps are required to produce the desired product. Recently our group presented a facile hydrothermal synthesis using environmental

* Corresponding author.
E-mail address: silas.cardoso@alumni.usp.br (S.C. Santos).

http://dx.doi.org/10.1016/j.matchemphys.2017.07.063
0254-0584/

pressure and temperature around of 60 °C to obtain submicrometer yttrium disilicate powders, with mono modal particle size distribution, rounded shape, high specific surface area and pycnometric density similar to theoretical one [9,10].

Nowadays our research group has reported approaches on development of advanced materials by bio-prototyping using renewable materials [9,11–15]. Yttria nettings with homogeneous void shape were produced using wood based netting as template [12]. Biomorphic burners with thermoluminescence response based on dysprosium doped yttrium disilicate were formed from Luffa Cylindrica vegetable sponge [14]. Yttria micro rods with dense microstructure and electron paramagnetic response were shaped from wheat starch templates [11].

Bella et al. [16–18] employed carboxymethyl cellulose (CMC) and micro fibrillated cellulose (MFC) as bio-sourced materials to produce quasi-solid electrolytes for polymeric dye-sensitized solar cells (DSSCs). Nishiyama et al. [19] using alginate hydrogel and inkjet printing produced 3D biological structures composed of living cells in vitro, which procedure was termed as 3D printer. Zolin et al. [20] proposed a new solid Li-ion cell structural design based for LiFePO4/graphite electrodes using carbonised cellulose nanofibrils.

Colloidal processing consists in a full procedure to obtain advanced materials since manipulation of molecular structures (colloids), including the control of inter-particle forces, followed by consolidation of colloidal particles into a desired shape and finally, the enhancement of interparticle bonds by means of thermal treatment. Recently our research group has published some contributions addressing colloidal processing and bio-prototyping of rare earth ceramics such as, yttria nettings [12]; bio-prototyping rare earth doped yttria ceramics [15], yttrium disilicate microcellular ceramics [9] and, biomorphic dysprosium doped yttrium disilicate burners [14].

Yttria (Y_2O_3) is a promising material for radiation dosimetry due to its intrinsic chemical and physical proprieties as melting point of 2400 °C, refractive index of 1.9, thermal and chemical stability. Besides, Y_2O_3 is used for enhancement of sintering [21], catalysis [22], luminescence [23], electrical [24], electronic [25], mechanical [26] and thermal [27] behavior of many advanced materials. Europium doped yttrium oxide (Y_2O_3:Eu^{3+}) is noted for its excellence in luminescence [28]. ZHANG et al. [29] reported the synthesis of single-layer yttrium oxide nanosheets doped with Eu^{3+} and Tb^{3+} by the exfoliation method. As synthesized nano sheets exhibited transparency, strong red and green emissions, these results rise it as potential to be used as building blocks and other functional materials.

Considering yttria potential for radiation dosimetry and our experience on processing of rare earth powders, this work reports a full colloidal processing of europium doped yttria rods as following: stoichiometric composition of material, powders synthesis, rheology of suspensions, bio-template evaluation, bio-prototyping, microstructural evolution of rods as a function of sintering parameters, and effect of europium on EPR response of yttria rods.

2. Experimental

For development of europium-yttria powders (Y_2O_3:Eu) with controlled size, shape and stoichiometry the following starting materials were used: yttria (Y_2O_3, 99.99%, Alfa Aesar GmbH), europium oxide (Eu_2O_3, 99.999%, Alfa Aesar GmbH), nitric acid (HNO_3, Synth), ammonium hydroxide (NH_4OH, Casa Americana).

Synthesis of Y_2O_3:Eu powders with up to 10 at%. Eu^{3+} was performed by a facile hydrothermal process, based on environmental pressure and temperature of 60 °C. Aqueous solutions of yttrium nitrate ($Y(NO_3)_3 \cdot 6H_2O$) and europium nitrate ($Eu(NO_3)_3 \cdot 6H_2O$) were prepared by dissolution of rare earth powders in HNO_3. Considering the stoichiometry of final powders, aqueous solutions based on yttrium and europium nitrates were stirred together, followed by addition of NH_4OH to adjust pH of final solution. The precursor gel suspension was formed at pH 10, corresponding to europium-yttrium hydroxide (Eq. (1)). The present gel was stirred at 60 °C for 6 h, using a condenser system to maintain constant the volume of suspension.

$$(2-a)Y(NO_3)_{3(aq)} + (a)Eu(NO_3)_{3(aq)} + NH_4OH_{(aq)} \xrightarrow{60^{\circ}C} Y_{(2-a)}Eu_a(OH)_{3(s)} + 3NH_4(NO_3)_{(aq)} \quad (1)$$

The precursor gel was dried at 70 °C for 24 h, followed by thermal treatment up to 1200 °C in air atmosphere using a box furnace (Lindberg Blue, Haake) as shown in Fig. 1. Thermal treatment of precursor powders (YE) was based on thermal decomposition assay of powders. A sample of 10 mg was heating up to 1400 °C in air atmosphere (Lindberg Blue, Haake), in which its mass was measured in each 100 °C, using an analytical balance (Mettler Toledo, AB204-S). The first derivate of mass loss curve as a function of temperature was calculated in order to determine in which temperature the maximum decomposition peak of sample takes place.

Powder characterization consisted in determining the mean particle size (d_{50}) by means of Photon Correlation Spectroscopy (PCS, ZetaPALS Analyzer, Brookhaven Instruments) and using hydrodynamic diameter model [30] as shown in (Eq. (2)); X-ray diffraction (XRD, Rigaku Multiflex, Japan), with an angular range (2θ) from 15 to 70°, scanning of 0.5°.min^{-1} and Kα source, in which crystallite size was calculate from Scherrer formula [31] (Eq. (3)), and based on the measurement of full-width at half-maximum (FWHM) values in the corresponding XRD pattern; helium pycnometric (Pycnometer Micrometrics 1330), and Scanning Electron Microscopy (SEM, INCAx-act, Oxford Instruments).

$$d_{50} = \left(\frac{K_{BT}}{3\pi\eta(T)D_t}\right) [\text{nm}] \quad (2)$$

Where, K_{BT} is Boltzmann constant ($1.38064852.10^{-23}$ m^2. kg S^{-2}. K^{-1}), T is temperature (K), η(T) is viscosity of the suspending liquid and, D_t is particle diffusion coefficient.

$$d_c = \left(\frac{0.9\lambda}{\beta cos\theta}\right) [\text{nm}] \quad (3)$$

Suspensions with 20 vol% Y_2O_3:Eu content were prepared at pH 10 from tetramethylammonium hydroxide (TMAH, 30 wt%, Sigma Aldrich), 0.2 wt% corn starch as binder (CS, Maizena), and followed by homogenization in a ball mill for 24 h using alumina spheres ($Ø_{spheres}$ of 10 mm).

Rheological characterization of Y_2O_3:Eu suspensions was performed with a rheometer (Haake RS600, Thermo Scientific). The sensor system consists in a double-cone rotor and a stationary plate (DC60/1°). The flow behavior of the suspensions was characterized in the control rate mode (CR) and compared with rheological models available in rheometer database (Haake Rheowin Data Manager v. 3.61.0.1). All measurements were evaluated at 25° by increasing the shear rate ($\dot{\gamma}$) from 0 to 1000 s^{-1} in 5 min, holding for 2 min at 1000 s^{-1} and returning to 0s^{-1} in 5 min. For each CR step 200 points were measured.

Organic tubes based on wheat starch were used as biotemplates (BM) for replica method. BMs are abundant, renewable, low cost, and exhibit suitable inner void shape, in which filling with suspension (casting) lead to the formation of ceramic rods as shown in Fig. 1. Shape and microstructure features of BMs were