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EPR response of yttria micro rods activated by europium

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ABSTRACT

Rare earth (RE) materials present excellent properties, which importance is recognized worldwide. Innovation approaches in energy, medicine, communication, transportation, militarism, and radiation dosimetry consist in RE based materials. As yttrium oxide (Y_2O_3) exhibits intrinsic lattice characteristics that enable doping with others RE elements (Y_2O_3:RE), new materials with promising characteristics can be developed. This work aims to evaluate EPR response of europium-yttria (Y_2O_3:Eu) rods obtained by bio-prototyping. Ceramic rods containing up to 10 at.%Eu were irradiated with gamma doses from 0.001 to 150 kGy and evaluated by Electron Paramagnetic Resonance (EPR) at room temperature with X-band EPR. Based on results, Y_2O_3:Eu rods with 2 at.%Eu exhibited the most significant response, in which linear behavior arose from 0.001 up to 50 kGy. Fading and thermal annealing evaluations revealed that 2 at%.Eu improved dosimetric characteristics of yttria remarkably. These innovative findings afford that Y_2O_3:Eu is a promising material for radiation dosimetry.

1. Introduction

The Fourth Industrial Revolution characterized as global transformation in which digital, physical, chemical, and biological sciences converge, is in progress due to materials development [1–3]. Development of new dosimetric materials is inserted into mission-oriented innovation policy agenda, which means identifying and articulating new approaches to galvanize research-development, production, distribution, and consumption patterns trough sectors [4].

As rare earths (REs) exhibit expressive properties their use even if in low concentration (atomic percentage) lead to improvement of materials proprieties. These new materials become suitable for application in highly advanced technologies as dosimetry materials. Dysprosium doped calcium sulphate ($CaSO_4$:Dy) used as thermoluminescent dosimeter is applied for beta [5], gamma [6], X [7], electrons [8], photons [9], UV [10] and laser dosimetry [11]. The $CaSO_4$:Dy dosimeter exhibits excellent reproducibility, high sensitivity [12], AO [13] and EPR [14] response. Therefore, the use of rare earths as materials for dosimetry applications is on frontier knowledge.

Yttria (Y_2O_3) is a promising material for radiation dosimetry due to its unique proprieties as, density of 5.02 g cm^{-3}, refractive index over 1.9, melting point of 2400 °C, band gap of 1.6eV, Young's modulus of 160 GPa, and cubic C-type lattice composed by Ia_3 space group, sixteen formula units per unit cell, coordination number (N) of 6, and two points symmetry (S_6, C_{3i}) and C_2 [15,16]. Nian Xu et al. [17] reported that cubic structure of Y_2O_3 is less closely packed, exhibiting large vacancies of Y and O planes. These vacancies enable incorporation of RE ions into yttria host and formation of highly luminescent materials (Y_2O_3:RE) can be achieved.

Spectroscopic characteristics of yttria are improved according to processing parameters such as, RE dopant concentration [18], synthesis method [18], microstructure [19], crystallite-particle size [20], and shaping [21]. Upon applications yttria is used as, thermal coatings [22], catalysts [23], special alloys, biomaterials [24], scintillators [25], luminescent devices [26], membranes [27], gas burners [28], sintering aid [29], capacitors [30], nanocomposites [31], and reinforcement [32]. In addition, yttria is a promising material for dosimetry [33]. Even though yttria presents reliable proprieties, being used in many applications, few studies on massive processing of this promising rare earth have been carried out.

Recently, our group reported approaches on bio-prototyping of rare earth based ceramics [19,28,34–37], including yttria based rods with potential application in radiation dosimetry. Ceramic

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rods of yttria and europium-yttria with dense microstructure and homogeneous shape-size were obtained by sintering at 1600 °C for 4 h in air atmosphere [38,39]. As a step forward to obtain a new dosimeter material, the present study purposes to evaluate EPR response of europium-yttria rods as a function of ionizing irradiation dose, in which dosimetry parameters as EPR spectra, dose-response, fading, and thermal annealing are analyzed and discussed.

2. Experimental

Europium-yttria rods (Y_2O_3:Eu) were produced by bio-prototyping according our recent study [38], which process is illustrated in Fig. 1. Europium content was from 0.5 up to 10 at.%. The morphology and size evaluation of ceramic rods were performed by optical microscopy (OM, Nikon SMZ1270). Besides, microstructure formation was observed by scanning electron microscopy (SEM, Oxford Instruments).

Batches of four ceramic rods were irradiated with gamma source with dose range from 0.001 to 150 kGy in electronic equilibrium conditions and room temperature. Crystal defects and radicals induced by ionizing radiation were characterized by electron paramagnetic resonance at room temperature and atmosphere using X-band EPR spectrometer (Bruker EMX PLUS).

EPR spectra of samples were recorded using the following parameters: field frequency modulation of 100 kHz, microwave power of 2.5 mW, centre field at 320 mT, sweep width of 600 mT, modulation amplitude of 4G, time constant of 0.01 ms and, 10 scans. The EPR response of irradiated samples was determined as a mean of each batch normalized by mean mass of containing samples. EPR dose response and time decay curves were plotted considering the mean of peak-to-peak amplitudes of irradiated samples.

3. Results and discussion

Formation of crystalline europium-yttria micro rods for radiation dosimetry depends on processing parameters as, synthesis route, dispersion of powders, viscosity of suspension, shaping, as well as sintering of green compacts. Bio-prototyping is an environmental friendly shaping method, in which renewable materials are used as preform to shape suspension of nano particles [38]. Stable suspensions provide green compacts constituted by high packing of particles, which avoids formation of voids during drying stage. These green compacts as sintered on suitable sintering conditions exhibit dense microstructure and substantial mechanical strength [40].

An optical image of europium-yttria micro rod (2 at.%Eu) with size of 3.335 × 2.271 mm (diameter x height) sintered at 1600 °C for 4 h is shown in Fig. 2a. The ceramic rod exhibits rough surface, and surface microstructure with grains like shape-rounded, which size is higher than 2 μm (Fig. 2b). As fractured europium-yttria micro rod presented transgranular fracture (Fig. 2c), dense-homogeneous microstructure, and containing grains with size higher than 2 μm. In our recent paper [39], in which yttria based micro rods were also produced by bio-prototyping, similar microstructural characteristics were observed. Moreover, the addition of 2 at.% europium into yttria host did not provide any substantial effect on sintering of samples.

The incorporation of europium ions into yttria gives rise to soft rearrangement of yttria crystal lattice. Since the size of ionic radius of Eu and Y is quite similar 0.098 nm and 0.092 nm, respectively, the character of incorporation is substitutive. Eu ion replaces Y ion in C_2 and S_6 sites with no significant distortion of crystal lattice, bonds to oxygen ion and, provides an oxygen vacancy, as shown in Eq. (1). However, europium excess can lead to formation of second phases, change of crystal structure and, decrease of spectroscopic characteristics as luminescence. Ranson et al. [41] reported that excess of europium into yttria provided low luminescence emission due to europium ions are located at S_6 symmetry axis of yttria host. On the other hand, using suitable concentration of doping, europium ions tend to be located at C_{3i} axis and, as a consequence provide highly luminescence emission of samples.

$$\boldsymbol{Eu_2O_3} \xrightarrow{\boldsymbol{Y_2O_3}} \boldsymbol{Eu_Y} + \boldsymbol{O_O^x} + \boldsymbol{V_O^{\cdot\cdot}} \quad (1)$$

Cubic C-type yttria is composed by YO_6 unit cells, which exhibit two oxygen vacancies located at the corners. The cell arrangement forms the structure of the YO radical situated in the outer surface of cell and bounded to crystal lattice by yttrium ion as illustrated in Fig. 3a. The interaction of YO radical with its environment is determinant on luminescence of the material. Moreover, particle size and shape is effective on YO radical behavior. As the size of particle increases, its flat surface also increases and leads to weak the interaction of YO radical with environment. Osipov et al. [42] reported that yttria powders with particle size smaller than 3 μm exhibited a broad cathode luminescence band at λ around of 437 nm. On the other hand, particles with size higher than 5 μm exhibited emission bands in blue, orange, red and infrared series.

Yttria exhibits intrinsically considerable number of vacancies,

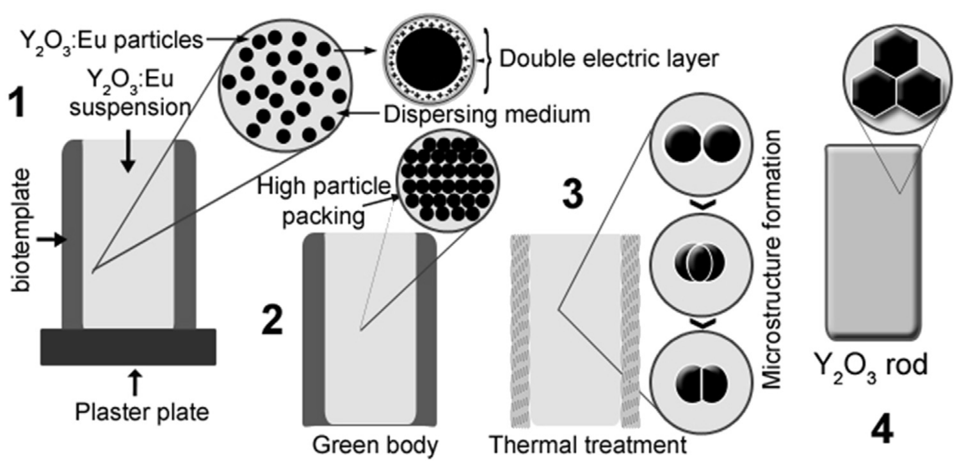

Fig. 1. Bio-prototyping of europium-yttria rods performed in this work.