

SHORT COMMUNICATION.

# Formation and EPR response of europium-yttria micro rods

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## Abstract

Designing new materials with suitable dose-response efficiency is a great challenge in radiation dosimetry search. Yttria ( $Y_2O_3$ ) has excellent optical, mechanical, chemical, and thermal properties. Besides, yttria exhibits crystal characteristics that provide insertion of other rare earths, forming innovative materials. Nevertheless, there are quite few studies on formation, microstructural and EPR response evaluation of yttria. This work reports the formation and EPR characterization of europium-yttria micro rods for radiation dosimetry. Ceramic rods obtained by sintering at 1600°C/4h in air were exposed to gamma radiation with doses from 1Gy to 150kGy. Particle, microstructural and dosimetry characterizations were performed by PCS, XRD, SEM, OM, and EPR techniques. As sintered europium-yttrium rods exhibited dense microstructure (90% theoretical density) and linear EPR dose response behavior up to 10kGy. These results show that europium-yttria is a promising material for radiation dosimetry.

**Keywords:** bio-prototyping, dosimetry, EPR, yttria, rare earths

## 1. Introduction

Rare earth elements (REs) present unique proprieties, being considered critical materials by American Government and European Union, whose applicability varies from semiconductors to radiation dosimetry<sup>[1-5]</sup>. Innovation in dosimetry materials with spectrometric/paramagnetic response higher than established dosimeters is a great challenge. Yttria ( $Y_2O_3$ ) is a promising material for radiation dosimetry due to its intrinsic chemical and physical properties, including great number of oxygen vacancies that enable insertion of other RE into its structure. Besides, yttria applicability includes sintering,<sup>[6]</sup> catalysis,<sup>[7]</sup> luminescence,<sup>[8]</sup> electrical,<sup>[9]</sup> electronic,<sup>[10]</sup> mechanical,<sup>[11]</sup> and thermal<sup>[12]</sup> behaviour of many advanced materials. Europium-yttria ( $Y_2O_3:Eu^{3+}$ ) is noted for its excellent luminescence.<sup>[13]</sup> Zhang *et al.*<sup>[14]</sup> reported the synthesis of single-layer yttrium oxide nanosheets doped with  $Eu^{3+}$  and  $Tb^{3+}$  by the exfoliation method with transparency and strong red and green emissions. These promising results show that nano sheets have potential to be used as building.

This paper aims to evaluate EPR (Electron Paramagnetic Resonance) response as a function of absorbed dose of europium-yttria micro rods produced by colloidal processing, which includes hydrothermal synthesis, followed by bio prototyping, and sintering.

## 2. Material and Methods

The following starting materials were used: yttrium oxide ( $Y_2O_3$ , 99.99%, Alfa Aesar GmbH), europium oxide ( $Eu_2O_3$ , 99.999%, Alfa Aesar GmbH), nitric acid ( $HNO_3$ , Synth), and ammonium hydroxide ( $NH_4OH$ , Casa Americana). Synthesis of  $Y_2O_3:Eu$  powders was performed by hydrothermal process reported previously<sup>[15]</sup>. As synthesized nanoparticles were characterized by Photon Correlation Spectroscopy (PCS, ZetaPALS Analyzer, Brookhaven Instruments)<sup>[16]</sup>; x-ray diffraction (XRD, Rigaku Multiflex, Japan); and helium pycnometry (Pycnometer Micrometrics 1330. Ceramic rods (4.35 x 2.27mm, height x diameter) formed by bio-prototyping<sup>[15]</sup> were characterized by XRD, SEM (Incact-X Oxford) and optical microscopy (OM, Nikon SMZ1270). Ceramic rods were irradiated with a gamma source with doses from 1Gy to 150kGy in ambient temperature. Crystal defects and radicals induced by ionizing radiation were characterized by EPR using an X-band EPR spectrometer (Bruker EMX PLUS).

## 3. Results and Discussion

The proposed synthesis method provided formation of europium-yttria particles with cubic C-type structure in agreement with Powder Diffraction File (P.D.F. 25101), mean diameter ( $d_{50}$ ) of 580nm, and pycnometric density of  $4.93 \text{ g}\cdot\text{cm}^{-3}$ . In addition, as sintered rods exhibited homogeneous shape and size, as mean diameter ( $2.271\text{mm} \pm 0.014$ ) Fig. 1a, mean height ( $3.335\text{mm} \pm 0.011\text{mm}$ ) - Fig. 1b, mean mass ( $63.7\text{mg} \pm 0.0021\text{mg}$ ), dense surface microstructure - Fig. 1c.

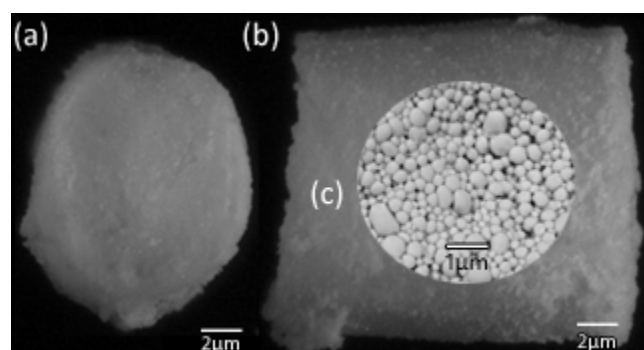


Figure 1. Europium-yttria rod obtained by bio-prototyping and sintering at  $1600^\circ\text{C}$  for 4h. Optical images of (a) superior view and (b) lateral view; (c) microstructure of rod surface by SEM.

As crystalline yttria exhibits intrinsically great number of vacancies, as well as chemical and physical similarity with RE group, the insertion of RE into its structure is facilitated and lead to form the most promising materials for dosimetry materials. EPR dose response curves normalized by the median mass of samples in log-log scale are illustrated in Figure 2.

Yttria EPR response exhibits linearity from 0.1 up to 10 kGy, whereas europium-yttria presents from 0.01 to 10 kGy. Above 50kGy this linearity was no longer established. Considering this remarkable results europium-yttria seems a promising material for clinical dosimetry ( $1\text{Gy} < \text{dose} < 1\text{kGy}$ ), as well as industrial application ( $1\text{kGy} < \text{dose} < 50\text{kGy}$ ). Moreover, europium as activator improved the sensitivity of yttria.

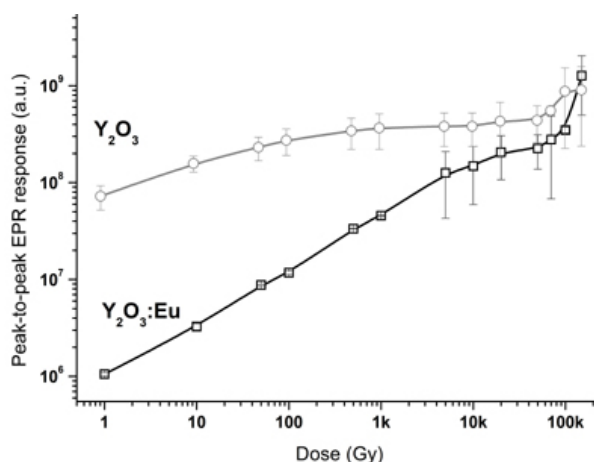


Figure 2. Dose response curves of yttria and europium-yttria rods from 0.01 up to 150kGy at room atmosphere

#### 4. Conclusions

Europium-yttria rods obtained by hydrothermal synthesis, followed by bio-prototyping and sintering at 1600°C for 4h exhibited linear dose response behaviour of the main EPR signal within dose range from 0.001 to 10 kGy. Using europium as dopant of yttria improved substantially the dose sensitivity of this ceramic material.

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