Synthesis, processing, and electron paramagnetic resonance response of $Y_{1.98}Eu_{0.02}O_3$ micro rods

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Innovating dosimetric materials, which includes design and development of new dosimetric materials based on rare earth oxides, is challenging. Yttrium oxide (Y_2O_3) is one of the most important sesquioxides and presents crystal characteristics that enable doping with rare earth ions, making it a promising material for radiation dosimetry. This paper reports on the development and measurement of Electron Paramagnetic Resonance (EPR) signal response for $Y_{1.98}Eu_{0.02}O_3$ micro rods that have undergone facile low-pressure hydrothermal synthesis and bio-prototyping. As-synthesized powders with narrow sub-micrometer particle size distribution with d_{50} of 584 nm exhibited a reactive surface, which led to the formation of stable aqueous suspensions by controlling the surface charge density of particles through alkaline pH adjustment. Ceramic samples with dense microstructure were formed by sintering at 1600 °C for 4h at ambient atmosphere. $Y_{1.98}Eu_{0.02}O_3$ micro rods were irradiated using a ^{60}Co source with doses from 1 to 100 kGy, and EPR spectra were measured at room temperature in X-band microwave frequencies. Sintered samples exhibited linearity of the main EPR signal response from 10 Gy to 10 kGy. Supralinearity was observed for higher doses, which is possibly ascribed to formation of more defects. Using europium as a dopant enhanced the EPR signal of yttrium rods remarkably, due to 4f–4f transitions of the Eu^{3+} ion. These innovative findings make europium-doped yttrium oxide a promising material for radiation dosimetry.

Keywords: Synthesis; yttrium oxide; bio-prototyping; EPR; dosimetry; ceramic processing.

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1. Introduction

Rare earth elements (REs) present unique chemical and physical proprieties, which are very useful for such applications as semiconductors, luminescent devices, capacitors, special alloys, and radiation dosimetry.¹⁻⁵ Dysprosium doped calcium sulphate ($\text{CaSO}_4\text{:Dy}$) is used as a thermoluminescent dosimeter, which is applied for beta,⁶ gamma,⁷ X,⁸ electrons,⁹ photons,¹⁰ UV,¹¹ and laser dosimetry.¹² The $\text{CaSO}_4\text{:Dy}$ dosimeter exhibits excellent reproducibility and high sensitivity (40 times higher than LiF:Mg,Ti),¹³ as well as AO¹⁴ and RPE¹⁵ properties.

The development of new dosimetric materials with luminescent and spectrometric/paramagnetic response that is higher than established dosimeters is a great challenge for innovation of materials. Among REs, yttrium oxide (Y_2O_3) is a promising material for radiation dosimetry due to its intrinsic chemical and physical properties, such as melting point of 2400°C, refractive index of 1.9, and thermal and chemical stability. Besides, Y_2O_3 is also used for enhancement of sintering,¹⁶ catalysis,¹⁷ luminescence,¹⁸ electrical,¹⁹ electronic,²⁰ mechanical,²¹ and thermal²² behavior of many advanced materials. Yar *et al.*²³ synthesized highly uniform nano-sized yttrium-doped tungsten oxide particles ($\text{WO}_2\text{:Y}_2\text{O}_3$) by chemical reaction. Samples sintered at 1400°C showed higher relative density ($R_D=95\%$) and finer grain size as compared to those sintered at 1500°C and 1600°C. Li *et al.*²⁴ produced yttrium-doped zinc oxide nanofibers ($\text{ZnO:Y}_2\text{O}_3$) by using electrospinning method, followed by calcination. The resultant particles featured a uniform morphology and higher specific surface area (40.2 m²/g) than ZnO. Europium doped yttrium oxide ($\text{Y}_2\text{O}_3\text{:Eu}^{3+}$) is noted for its excellent luminescence.²⁵ Zhang *et al.*²⁶ reported the synthesis of single-layer yttrium oxide nanosheets doped with Eu^{3+} and Tb^{3+} by the exfoliation method.

Using a facile hydrothermal synthesis to produce europium doped yttrium oxide nanoparticles, the dopant content which is 2 at% Eu ($\text{Y}_{1.98}\text{Eu}_{0.02}\text{O}_3$), the present paper aims to develop ceramic micro rods by bio-prototyping, followed by EPR evaluation.

2. Experimental

2.1. Starting materials

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).

2.2. Hydrothermal synthesis

Synthesis of $\text{Y}_2\text{O}_3\text{:Eu}$ powders with 2 at% Eu was performed by a facile hydrothermal process using environmental pressure and a temperature of 60°C. Aqueous solutions of yttrium nitrate ($\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$) and europium nitrate ($\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$) were prepared by the dissolution of rare earth powders in HNO_3 . These solutions were stirred together, followed by the addition of NH_4OH to adjust the pH of the final solution. As a result, a

precursor gel suspension was formed at pH 10, corresponding to europium–yttrium hydroxide. The present gel was stirred at 60°C for 6 h using a condenser system to maintain a constant volume of suspension. The precursor gel was dried at 70°C for 24 h, followed by a thermal treatment up to 1200 °C in ambient atmosphere using a box furnace (Lindberg Blue, Haake).

2.3. Powder characterization

Powder characterization consisted of determining the mean particle size (d_{50}) by means of (1) Photon Correlation Spectroscopy (PCS, ZetaPALS Analyzer, Brookhaven Instruments) and using a hydrodynamic diameter model;²⁷ (2) X-ray diffraction (XRD, Rigaku Multiflex, Japan) with an angular range (2θ) from 15 to 70°, scanning of 0.5°/min, and a $K\alpha$ source; (3) helium pycnometry (Pycnometer Micrometrics 1330); and (4) Scanning Electron Microscopy (SEM, INCAx-act, Oxford Instruments).

2.4. Processing of ceramic rods

Processing of ceramic rods $Y_{1.98}Eu_{0.02}O_3$ rods were formed by bio-prototyping using suspensions with 20 vol% of solids prepared at pH 10 through a tetramethylammonium hydroxide solution (TMAH, 25 wt% in water, Sigma Aldrich). Parameters for stabilization of yttrium oxide-based suspensions are reported in our previous study.²⁸ The homogenization of ceramic suspensions was performed with a ball mill for 24 h using alumina spheres ($\phi_{spheres}=10$ mm). Ceramic samples (4.35 x 2.27 mm, height x diameter) were shaped as microrods by casting using organic templates on a plaster plate. Thermal treatment of as shaped samples was performed in a vertical furnace (Lindberg Blue) at a temperature of 1600°C for 4 h at ambient atmosphere.

2.5. Characterization of rods

The crystalline structure of as-sintered rods was evaluated by XRD (Rigaku Multiflex) scanning at 1°/min, $\Delta\theta = 10\text{--}80^\circ$ (2θ), with Cu- $K\alpha$ radiation, and identified according to powder diffraction files (PDF).

$Y_{1.98}Eu_{0.02}O_3$ rods were irradiated with a gamma source with doses from 1 Gy to 100 kGy in ambient temperature. Microstructural evaluation of irradiated samples was performed by SEM (Incact-X Oxford). Crystal defects and radicals induced by ionizing radiation were characterized by EPR at ambient temperature and atmosphere using an X-band EPR spectrometer (Bruker EMX PLUS). The EPR spectra of samples were recorded using the following parameters: 100 kHz field modulation frequency, 0.6325 mW microwave power, 320 mT center field, 600 mT sweep width, 4 G modulation amplitude, 0.01 ms time constant, and 10 scans. The EPR spectra of irradiated samples were determined as a mean of each batch normalized by the mean mass of samples. The EPR dose response and time decay curves were plotted considering the mean of peak–peak amplitudes of irradiated samples.

3. Results

Conditions to obtain crystalline yttrium oxide vary according to starting materials, synthesis route, and thermal treatment of precursor. Shivaramu *et al.*²⁹ produced yttrium oxide nanoparticles by combustion route and thermal treatment of precursor at 600°C for 2 h. In this work, thermal treatment at 800°C for 2 h in ambient atmosphere provides formation of europium doped yttrium oxide powders in a cubic C-type lattice, including no formation of secondary phase peaks in the interval ($\Delta_{2\theta}$) between 10–70° (Fig. 1a). Thus, doping with 2 at% Eu was effective.

Yttrium oxide exhibits Y^{3+} ions located at the C_2 and (C_{3i}, S_6) axis in its crystal lattice, surrounded by six oxygen atoms (Fig. 1a). Since europium and yttrium ions exhibit similar size, doping is characteristically substitutional. Europium ions tend to occupy C_2 and (C_{3i}, S_6) to form energy levels as illustrated in Fig. 1b.

Fig. 1. XRD curves of powders: (a) as synthesized and (b) after thermal treatment at 800°C for 2 h at ambient atmosphere.

Figure 2a illustrates particle size distribution of powders. Based on results, yttrium powders exhibited sub-micrometric particle size distribution, with a mean diameter (d_{50}) around 576.3 nm, dispersion of 16.6 nm and relative dispersion of 0.03. From SEM (Fig. 2b), it is seen that powders are composed by agglomerates of rounded particles.

Thermal treatment aims to enhance the physical particle–particle bond by means of mass transfer, forming a microstructure that is responsible for whole characteristics of the final component. Sintering samples at 1600°C for 4 h was effective to produce dense rods with handle strength (Fig. 3a). As-sintered rods exhibited (1) homogeneous shape and size with mean height h_m of $3.335 \text{ mm} \pm 0.011 \text{ mm}$, mean diameter ϕ_m of $2.271 \text{ mm} \pm 0.014$, and mean mass m_m of $63.7 \text{ mg} \pm 0.0021 \text{ mg}$; (2) dense surface microstructure (Fig. 3b); and (3) internal microstructure showing cleavage planes as shown in Fig. 3c.

Fig. 2. Powder characterization of $Y_2O_3:Eu$ from thermal treatment of precursor at $800^\circ C$ for 2h at ambient atmosphere: (a) particle size distribution by PCS and (b) SEM image of powders.

Fig. 3. SEM images of $Y_2O_3:Eu$ rods formed by sintering at $1600^\circ C$ for 4 h: (a) ceramic rod, (b) surface microstructure, and (c) internal surface of a transgranular fracture showing cleavage planes.

Rare earth ions (RE) such as Eu^{3+} , Tb^{3+} , Dy^{3+} , and Yb^{3+} are often incorporated into a crystal structure host in order to enhance host material characteristics such as mechanical–chemical strength, density, refractive index, and spectroscopy response (e.g., luminescence, EPR). As crystalline yttrium oxide exhibits an intrinsic and suitable number of vacancies, as well as a similar ionic radius like other REs, it is one of the most promising materials to form new dosimetric materials.

Figure 4 shows EPR dose response behavior, where values were normalized by the median mass of samples and the log–log scale was used in order to improve the view of curves. Yttrium oxide presented linear behavior from 0.1 up to 10 kGy. $Y_2O_3:Eu$ samples exhibited linear behavior from 0.01 to 10 kGy. From 50 to 150 kGy, linearity was no longer established. Based on results, $Y_2O_3:Eu$ is a promising material for clinical dosimetry ($1 \text{ Gy} < \text{dose} < 1 \text{ kGy}$), as well as industrial application ($1 \text{ kGy} < \text{dose} < 50 \text{ kGy}$).

In addition, doping with 2 at% Eu remarkably improved the sensitivity of yttrium oxide rods for a wide dose range.

Fig. 4. Dose response curves as a function of the absorbed dose for Y_2O_3 and $\text{Y}_2\text{O}_3\text{:Eu}$ up to 150 kGy at ambient atmosphere.

Doping yttrium oxide with europium led to enhancement of EPR signal response due to formation of new defects, which in turn enable energy transfer from europium ions to the yttrium oxide host material. Figure 5 illustrates EPR fading of rods as a function of time. It is observed that whole samples showed variation of the EPR signal during the first 168 h. After this time, the EPR signal became constant. Relative EPR fading of yttrium oxide was around 30%, whereas Y:Eu was around 13%. Based on these conditions, it is observed that doping yttrium oxide with 2 at% of europium provided higher EPR signal in samples.

Fig. 5. Fading of EPR signal of as irradiated $\text{Y}_2\text{O}_3\text{:Eu}$ rods during 168 h.

Fig. 6. Decrease of EPR signal of Y₂O₃:Eu rods as a function of temperature.

Figure 6 illustrates the effect of thermal treatment on the decreasing EPR signal of rods irradiated with 150 kGy. It is observed that for temperatures up to 650°C, the EPR signal is still high, around 75%. A significant decrease in EPR signal was achieved at a temperature of 800°C, which corresponded to 30%. Full signal cleaning was achieved at 1000°C, in which the EPR signal was 0. It is believed that irradiation with 150 kGy promoted deep traps that are cleaned only in high temperatures.

4. Conclusion

Europium-doped yttrium oxide microrods were produced from a facile-low pressure hydrothermal method followed by bio-prototyping. As-synthesized powders with a mean diameter of 576 nm were useful to prepare stable suspensions. Bio-prototyping and sintering at 1600°C for 4 h led to formation of rods with dense microstructures. Micro ceramic rods exhibited a linear dose response behavior of the main EPR signal for doses from 0.001 to 10 kGy. Thermal fading of the EPR signal was less than 20% during 162 h for all samples. Complete cleaning of the EPR signal was achieved by thermal treatment at 1000°C for 2 h in air. Doping with europium significantly improved the dose sensitivity of the yttrium oxide host.

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