



EPR dosimetry of yttria micro rods

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ABSTRACT

The use of rare earths (RE) as dopant of materials has led the development of advanced materials for many applications such as optical tracers, special alloys, semiconductors, as well as radiation dosimeters. The development of new dosimetric materials based on REs is a great challenge in innovation of materials. Yttria (Y_2O_3) presents luminescent proprieties and is a promising material for radiation dosimetry. The present paper aims to evaluate paramagnetic defects of Y_2O_3 rods obtained via bio-prototyping by using Electron Paramagnetic Resonance (EPR) technique at room temperature. Ceramic rods were irradiated with gamma doses from 0.001 to 150 kGy and evaluated by EPR at room temperature with X-band EPR. According to EPR results, as sintered samples exhibited an EPR signal with principal g tensor of 2.020 and maximum line width around 2.3 mT, which is ascribed to interstitial oxygen ion. Dose response behaviour exhibited two distinct dose ranges, one is from 1 to 100Gy and the second is from 0.1 to 70 kGy. Thermal annealing approaches reveal that defect centres of yttria decay significantly at high temperature. These innovative results make Y_2O_3 a promising material for radiation dosimetry.

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1. Introduction

Electron Paramagnetic Resonance (EPR) is a powerful, versatile, non-destructive and nonintrusive characterization technique, which yields meaningful structural and dynamical information from chemical and physical processes. EPR applications include polymerization reactions [1], spin trapping [2], catalysis [3], defects in crystals i.e. colour centres [4], laser [5], radiation effects and damage [6], free radicals in living tissues and fluids [7], drug detection [8], hybrid supercapacitors [9], semiconductors [10]. Therefore, EPR is a powerful tool for solid state dosimetry.

Rare earth elements (RE) present unique chemical and physical proprieties, which are very useful for applications as semiconductors, luminescent devices, capacitors, special alloys and also in radiation dosimetry [11–15]. Dysprosium doped calcium sulphate ($CaSO_4:Dy$) is used as thermoluminescent dosimeter, which is applied for beta [16], gamma [17], X [18], electrons [19], photons [20], UV [21] and laser dosimetry [22]. $CaSO_4:Dy$ dosimeter exhibits excellent reproducibility, high sensitivity (40 times higher than $LiF:Mg,Ti$) [23], AO [24] and RPE [25] properties.

The development of new dosimetric materials with luminescent and paramagnetic response higher than commercial dosimeters is a

challenge in innovation of materials. Among RE, yttria (Y_2O_3) is a promising material for radiation dosimetry due to unique proprieties as melting point of 2400 °C, refractive index of 1.9, specific heat capacity of 0.45 J g⁻¹ K⁻¹, and Dielectric strength of 11 kV mm⁻¹ [26]. Besides, Y_2O_3 is used for improving characteristics of many advanced materials such as, sintering [27], catalysis [28], luminescence [29], electrical [30], electronic [31], mechanical [32] and thermal [33]. Yar et al. [34] synthesized highly uniform nano-sized yttrium doped tungsten oxide particles ($WO_3:Y_2O_3$) by chemical reaction. Samples sintered at 1400 °C showed higher relative density (R_D of 95%) and finer grain size as compared to ones sintered at 1500 °C and 1600 °C. Li et al. [35] produced yttrium doped zinc oxide nanofibers ($ZnO:Y_2O_3$) by electrospinning method followed by calcination. As a result, doping with yttrium was useful to form particles with uniform morphology, higher specific surface area (40.2 m² g⁻¹) and gas sensing as compared to ones ZnO. Europium doped yttria ($Y_2O_3:Eu^{3+}$) is noted for its excellence in luminescence [36]. ZHANG et al. [37] reported the synthesis of single-layer yttria nanosheets doped with Eu^{3+} and Tb^{3+} by the exfoliation method. The promising results such as transparency, strong red and green emissions show that nano sheets have potential to be used as building blocks and other functional materials.

Based on Y_2O_3 potentiality, the present work reports an EPR characterization of yttria rods formed by colloidal processing as an approach to evaluate this promising rare earth at room temperature for radiation dosimetry.

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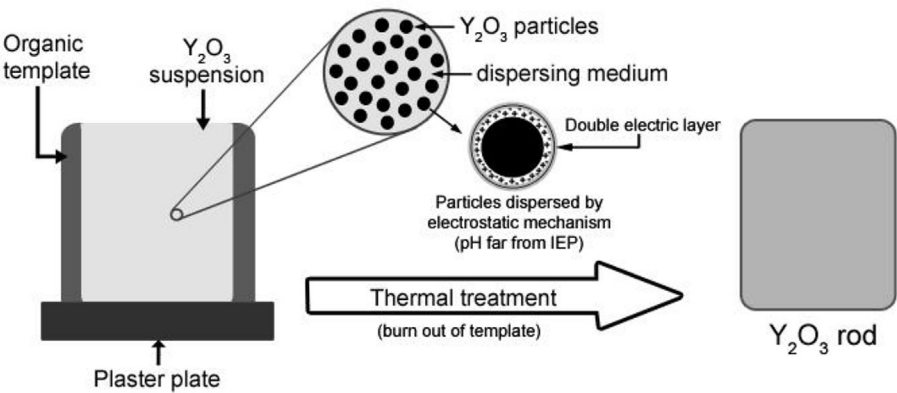


Fig. 1. Formation of yttria rods by bio-prototyping.

Table 1
Processing parameters to form yttria micro rods by bio-prototyping.

Particle characteristics	d_{50} (nm)	d_c (nm)	ρ (g.cm ⁻³)	C_s
	410.0	4.42	4.94	Cubic type-C
Suspension	Solids (%vol) 20.0	pH 10.0	η (mPa.s) 210.0	Binder (wt.%) 0.40
Sintering	H_R (°C.min ⁻¹) 5	Temp (°C) 1600	Slope (h) 4	Atmosphere Air

d_{50} : mean particle size; d_c : crystallite size; ρ : pycnometric density; C_s : crystalline structure; η : apparent viscosity at 10s⁻¹; H_R : heating rate; Temp: temperature.

2. Experimental

Yttria rods were produced by bio-prototyping according our recent study [38] as illustrated in Fig. 1. The morphology and size evaluation of yttria rods were performed by optical microscopy (OM, Nikon SMZ1270). Besides, microstructure formation was observed by scanning electron microscopy (SEM, Oxford Instruments).

Batches of four yttria rods were irradiated with gamma source with dose range from 0,001–100 kGy in electronic equilibrium conditions and room temperature (20 °C). Crystal defects and radicals induced by ionizing radiation were characterized by electron paramagnetic resonance at room temperature (20 °C) and room atmosphere (air) using X-band EPR spectrometer (Bruker EMX PLUS).

EPR spectra of samples were recorded using the following

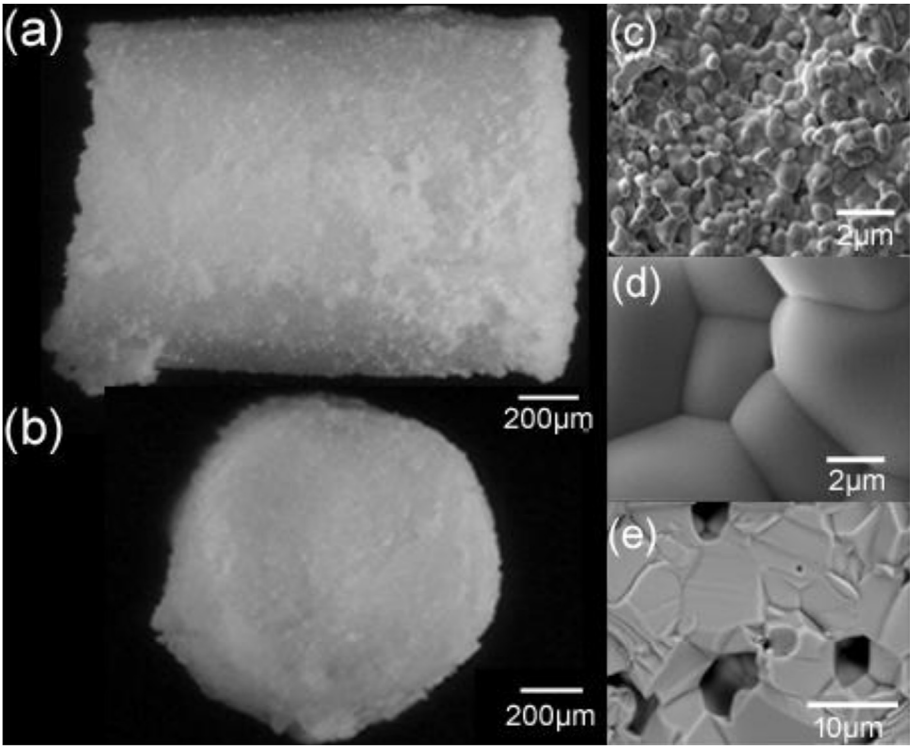


Fig. 2. Yttria micro rod produced by bio-prototyping: OM images of rod in (a) side view; (b) top view; SEM images of microstructure of (c) external surface; (d) zoom in on external surface exhibiting grains with size higher than 2 µm; and (e) inner surface showing cleavage planes characteristic of fragile fracture.

parameters: field frequency modulation of 100 kHz, microwave power of 0.6325 mW, centre field at 320 mT, sweep width of 600 mT, modulation amplitude of 4 G, 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-peak amplitudes of irradiated samples.

3. Results and discussion

Nowadays, dosimetric materials are inorganic crystalline materials nominally addressed as phosphors ascribe to their characteristic luminescence as suitably excited. These materials are usually in the form of discs, square chips, rods, films, pellets, single crystals or nano/micro powders. For this work, micro rods of yttria were produced by bio-prototyping. Table 1 lists processing

parameters for bio-prototyping of ceramic samples according to our recent work [38].

As can be seen, yttria micro rods exhibit rough surface, diameter and height of $3.335 \times 2,271$ mm, respectively (Fig. 2a and Fig. 2b). Besides, the control of stability of particles in suspension enables the conformation of ceramic samples by many shaping process such as casting, tape casting, extrusion, dip coating, bio-prototyping. Furthermore, stable suspensions lead to formation of higher packing of particles, avoiding voids during shaping and drying. As a consequence, samples with suitable mechanical strength and dense microstructure are usually formed after sintering as shown in Fig. 2d. As fractured rods exhibited dense-homogeneous microstructure, containing grains which size is higher than $1 \mu\text{m}$.

Crystalline structure of yttria rods was confirmed by XRD curves as shown in Fig. 3a. All XRD peaks coincided to PDF 70-603, which describes that Y_2O_3 has cubic C-type type (Fig. 3b) [39], Ia3 space

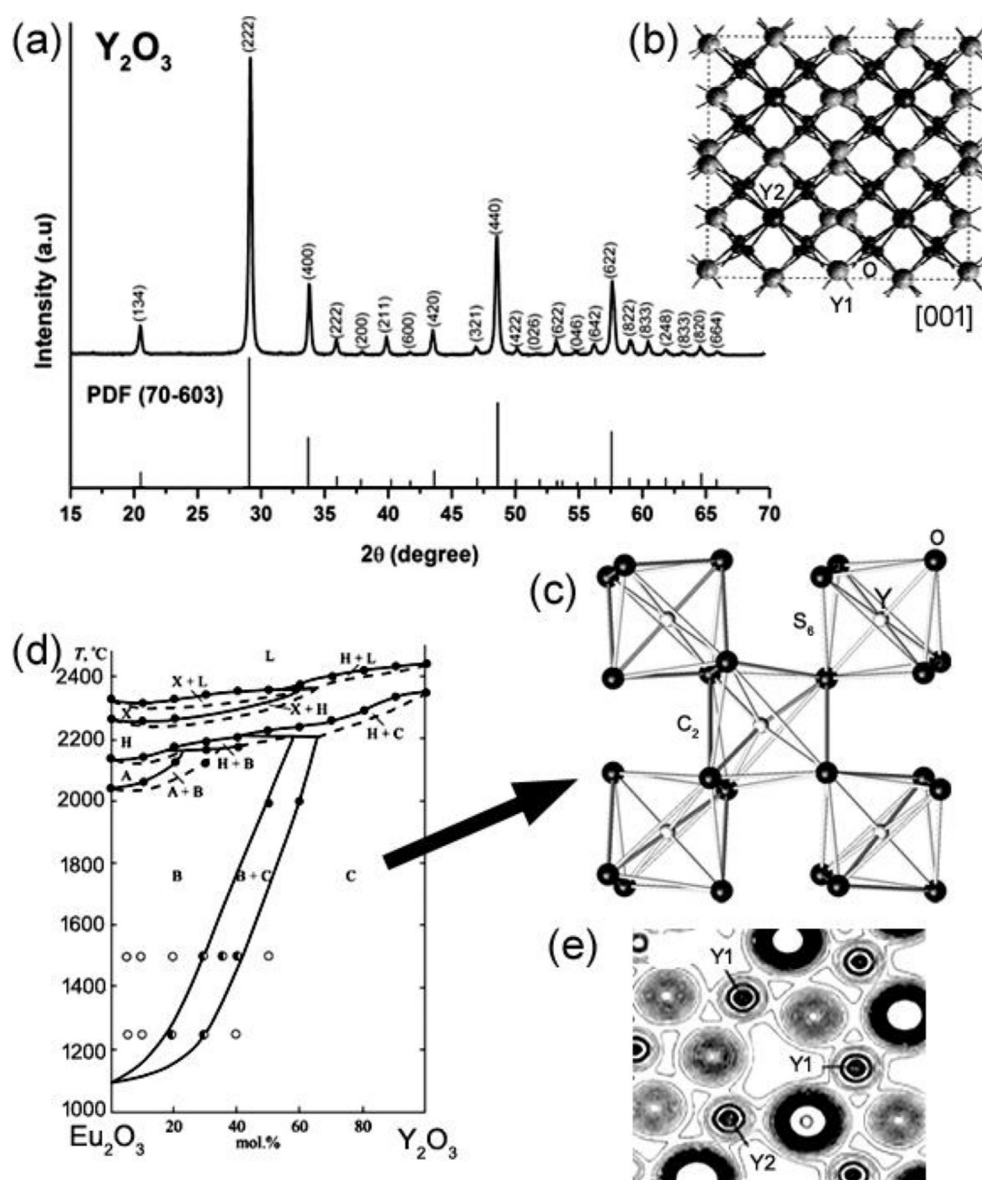


Fig. 3. Crystal characterization of yttria rods: (a) XRD curves of Y_2O_3 cubic C-type; (b) crystal lattice along [001] direction; (c) cation sites C_2 and S_6 in cubic C-type structure; (d) phase equilibria diagram of Y_2O_3 - Eu_2O_3 system exhibiting all field of composition of yttria, in which cubic C-type is the most predominant structure; (e) valence charge diagram in a plane exhibiting Y1-O-Y2 bonding and void spaces.

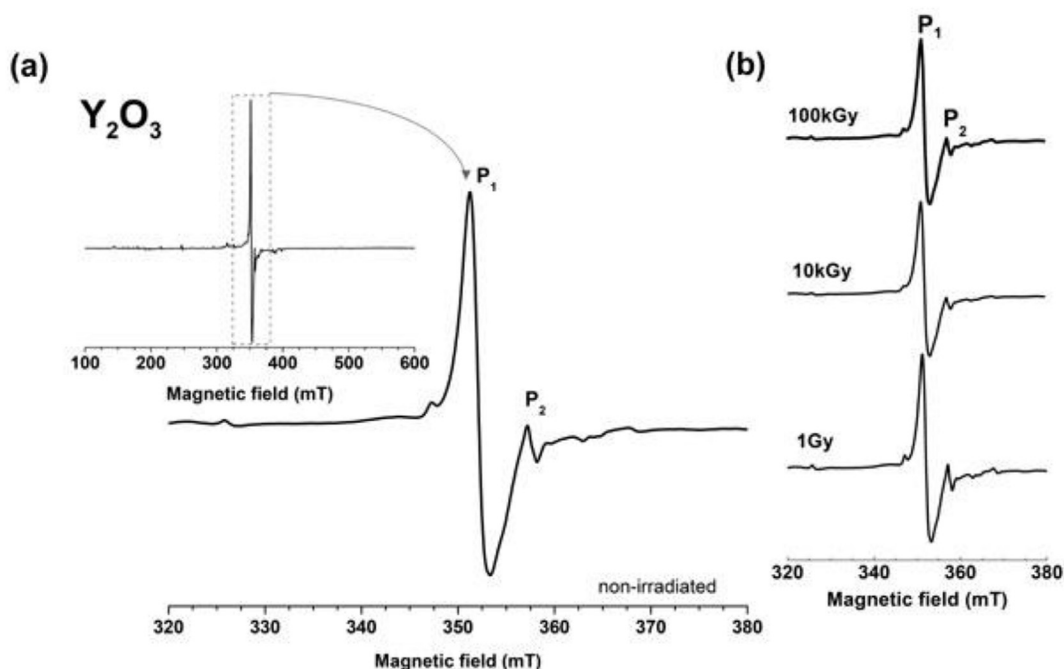


Fig. 4. EPR spectra recorded at room temperature and atmosphere for Y_2O_3 rods irradiated with doses from 0 to 100 kGy.

group, sixteen formula units per unit cell, coordination number (N) of 6 and two points symmetry S_6 , C_{3i} and C_2 (Fig. 3c) [40]. Among 32 ions, 24 ions occupy sites with C_2 symmetry, whereas 8 ions occupy S_6 . The local axes of the S_6 sites are in the $[111]$, $[\bar{1}11]$, $[1\bar{1}1]$, and $[11\bar{1}]$ directions. The C_2 axes are parallel to $[100]$, $[010]$, or $[001]$. The S_6 site has small crystal field and inversion centre, in which electron-dipole transitions are not allowed. However, thermal fluctuations of crystal lattice destroy the S_6 symmetry locally,

which provides the possibility of electron-dipole transition occur [41]. In addition, C_2 symmetry has no centre of inversion, which enables electron-dipole transitions and consequently luminescent emissions as doped with RE ions.

All sesquioxides as Dy_2O_3 , Th_2O_3 , Ga_2O_3 and Ln_2O_3 exhibit C-type structure [42]. Nevertheless, monoclinic [43], fluorite and hexagonal [44,45] structures were also reported for yttria. Based on phase equilibria diagram of $Eu_2O_3 - Y_2O_3$ system (Fig. 3d) [46] yttria exhibits large range of compatibility in which cubic C-type is

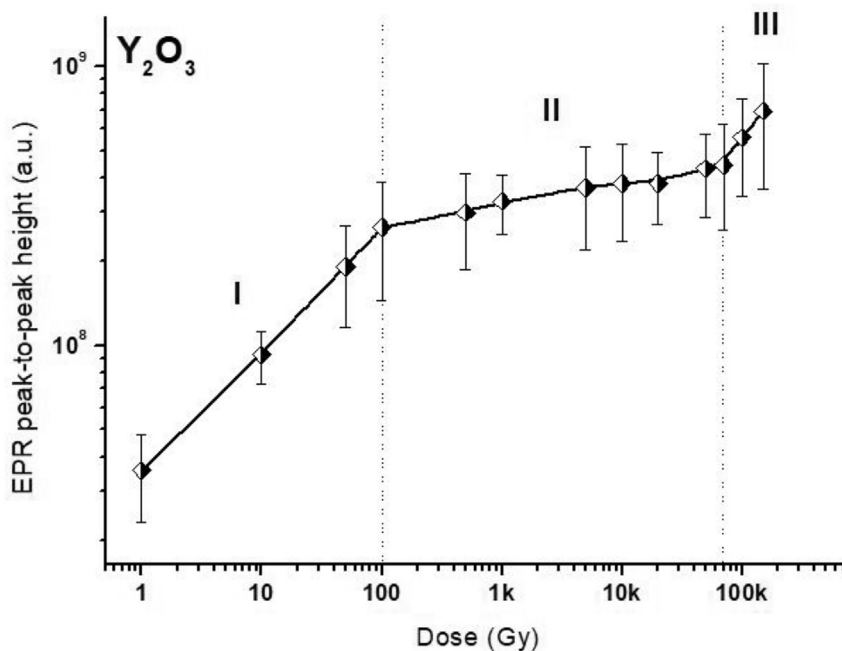


Fig. 5. EPR dose response of Y_2O_3 rods as a function of absorbed irradiation dose from 0.001 up to 150 kGy at ambient temperature and atmosphere.

formed. This range increases as a function of yttria content e.g. 10 mol.% Y_2O_3 provides C-type phase stability up to 1100 °C, whereas 100 mol.% up to 2300 °C.

Some investigations reported that the nature of bonding between Y-O is not completely ionic [47]. Nian Xu et al. [39] reported a theoretical study on the bond order of Y_2O_3 , which means a quantitative measure of the strength of the bond for Y and O in crystal lattice of Y_2O_3 (Fig. 3e) [39]. From this study, the chemical bond of Y_2O_3 is far from fully ionic and the bonding between Y and O is significantly covalent. Using valence charge density maps authors reported that the cubic structure of Y_2O_3 is less closed packed, exhibiting large vacancies for Y and O planes. These vacancies enable RE ions incorporation and formulation of luminescent yttria based materials ($Y_2O_3:RE$).

EPR spectrum of unirradiated Y_2O_3 rods at room atmosphere

and temperature is shown in Fig. 4a. As can be see, ceramic rods exhibited EPR a signal P_1 with principal g tensor of 2.020 and line width around 2.3 mT, and a lower intensity signal P_2 with principal g tensor of 2.040 and line width around 2.3 mT. Irradiation of samples with dose range up to 100 kGy created no new defect centres, as illustrated in Fig. 5b. Indeed, it led to increase of the main EPR signal (P_1), which means that more trapped electrons at anionic vacancies were produced. In addition, two very low intensity signals on the left side of spectra with g tensor values of 2.1604 and 2.0296 respectively, and may be ascribed to impurities of yttria. Considering that rare earths are found in nature with others rare earths and their extraction, which means their purification is a process extremely complex, the presence of impurities even in very low concentration can be observed. The investigation of these two very small signals is beyond the aim of the present study.

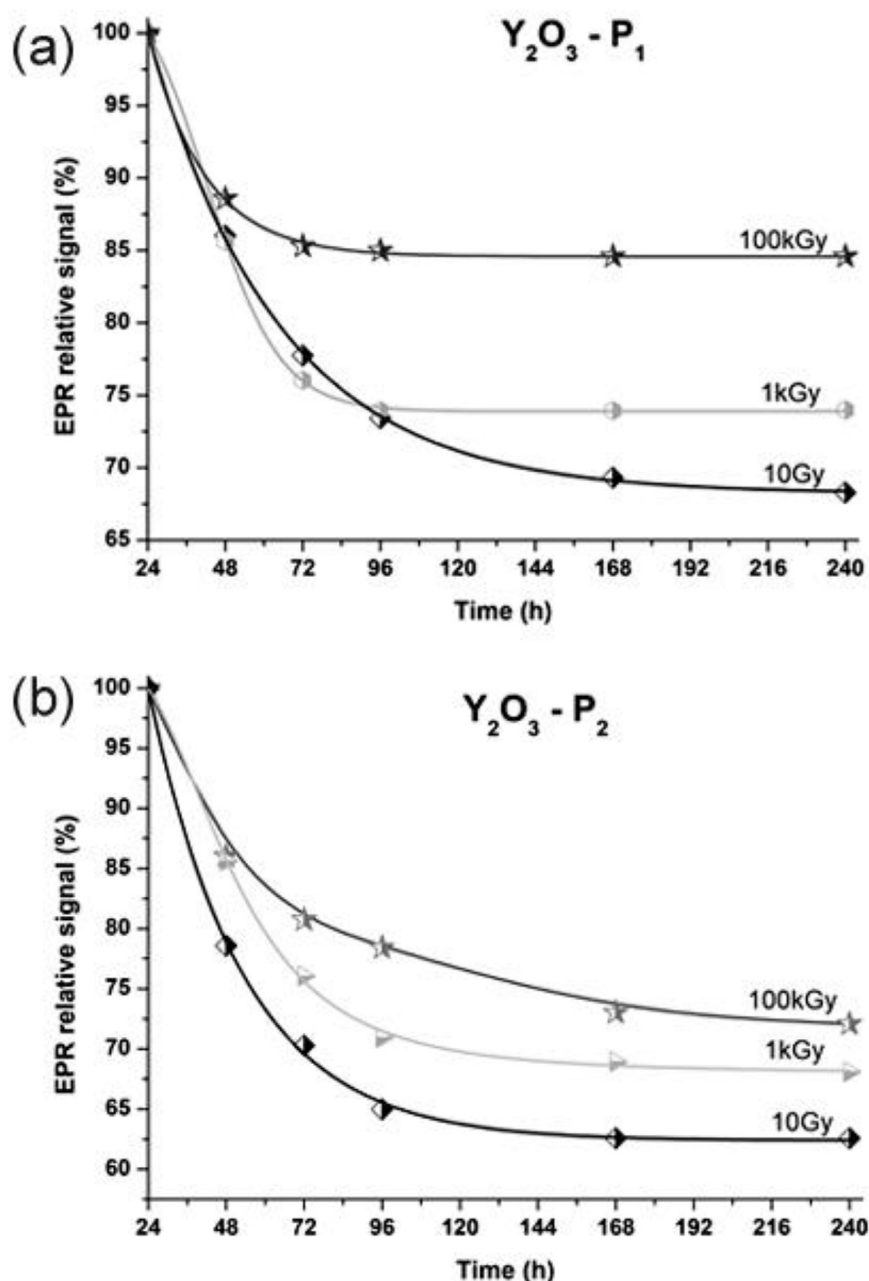


Fig. 6. EPR signal fading of centres (a) P_1 and (b) P_2 of Y_2O_3 rods evaluated at room temperature during 240 h.

The observed defect addressed as P_1 is ascribed to interstitial O^{2-} ion, nominally addressed as superoxide ion, which is generated by adsorption of molecular oxygen as observed by Lunsford [48]. In addition, oxygen can be either removed from the bulk of material with subsequent diffusion to surface or from surface by means of electron irradiation, annealing, sputtering, exposure to x-rays, or chemical reaction [49–54]. Osada et al. [55] reported that 10mol% Y_2O_3 -CaO powders annealed at oxygen atmosphere exhibited g values of 2.070 and 2.040, respectively. On the other hand, none of these signals was observed at vacuum. Singh et al. [56] observed for $Y_2O_3:Er$, in which the main signal was nominally addressed as centre I, exhibiting as characteristic g values of 2.0415 and 2.0056, respectively. In addition, it was reported that even though centre I signal was intense, it presented significant decay at low temperature around 160 °C.

Upon no irradiated sample (Fig. 4a), the low intensity centre (P_2) exhibited line width around of 13G and g tensor of 1.969. This centre is assigned to F^+ centre charged vacancy oxygen having one remaining electron. Besides, C-type crystal lattice of Y_2O_3 presents intrinsic oxygen vacancies that can produce F centres close to P_2 . For irradiated samples no significant change in c_2 shape and intensity was observed.

The effect of the P_2 on luminescence of Y_2O_3 thin was discussed previously by Bourdun [57]. Thermal treatment of Y_2O_3 samples in air atmosphere leads to the filling the oxygen vacancies by oxygen atoms from air into Y_2O_3 and as a result, additional weak bonds with oxygen ions are formed. On irradiation a radiative recombination between these new centres and those intrinsic centres occurs, resulting in an increase of the luminescence near 2.9eV. Costantini et al. [58] reported the characteristic centre P_2 with principal g values of 1.966 and 1.972 as investigating yttria stabilized zirconia (YSZ). Singh et al. [56] evaluated the stability of c_2 as a function of temperature and observed that this centre decays at low temperature around 180 °C.

The dose dependence of any material is the fundamental basis of its application as a dosimetric material. Within the dose range of interest defined the response is expected to be reproducible as a function of dose and preferably linear. Linearity describes

proportionality between EPR signal and absorbed dose. Usually, the dose response behaviour of most dosimetric materials exhibits linear, supralinear and saturating response.

In this work, the EPR signal as a function of gamma radiation absorbed dose, determined as peak height of the main centre (P_1), exhibited two distinct dose response behaviours (Fig. 5). The first linear range (I) with expressive EPR peak-to-peak increase was from 1 to 100Gy, which means the sensitiveness of yttria for low doses. The second range (II) from 0.1 to 70 kGy exhibited small increase of EPR peak-to-peak, which reveals that higher doses were not effective to provide significant defects in yttria. A new slope is formed apart from 70 kGy which might correspond to formation of new defects and a third range. Considering that a dose of 150 kGy is extremely high for dosimetry application, higher doses were not evaluated in this work.

Fading of Y_2O_3 rods irradiated with doses up to 150 kGy at room temperature was evaluated considering EPR relative signal during eleven days (Fig. 6). It is observed that the centre P_1 (Fig. 6a) decays relatively moderated, wherein samples irradiated with 10Gy exhibited fading of 32% and samples irradiated with 1 and 100 kGy presented lower fading around of 25 and 15%, respectively. Apart from 168 h (seven days) P_1 maintained at least 70% of its original signal. On the other hand, it is seen that centre P_2 (Fig. 6b) which is ascribed to new centres formed during irradiation, exhibited fading behaviour like centre P_1 . Even though oxygen from air form weak bond into Y_2O_3 , the new electronic defects are quite stable over 240 h with fading around of 37%.

The stability of centres P_1 and P_2 were measured by means of annealing approach up to 1200 °C and at environmental atmosphere. The thermal annealing behaviour of centre P_1 is illustrated in Fig. 7a. According to results, P_1 EPR relative response decays significantly at high temperature ($T > 600$ °C). Singh et al. [56] reported low temperature decay around of 160 °C for $Y_2O_3:Er$ samples irradiated with 5ky. In addition, centre P_2 (Fig. 7b) exhibited similar annealing behaviour. Considering that yttria lattice exhibits a large number of vacancies, one of the most probable defects is F^+ centre, which means an electron trapped at an anion vacancy. Such defect were observed by Singh [56] and Hutchison [59].

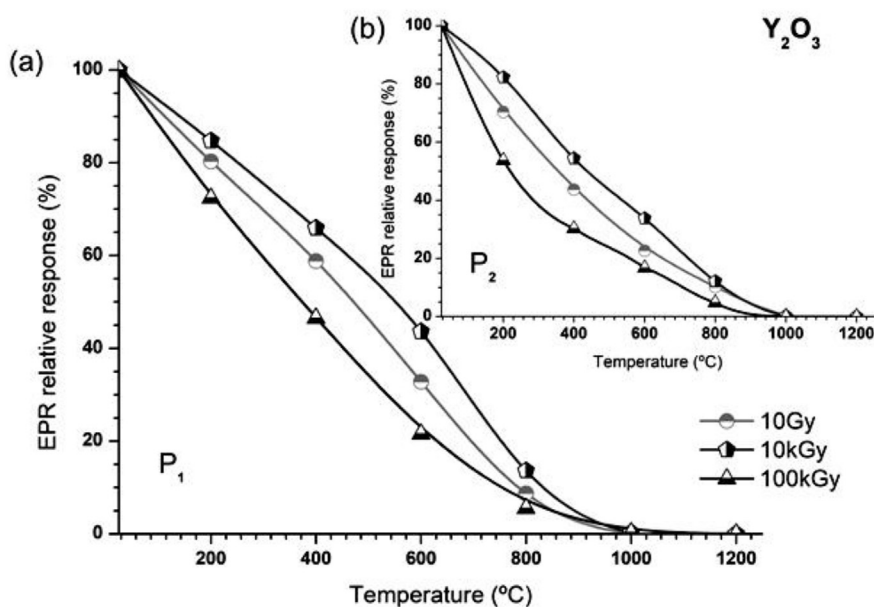


Fig. 7. Thermal annealing behaviour of centres (a) P_1 and (b) P_2 of Y_2O_3 rods.

4. Conclusion

Yttria rods with dense microstructure were produced by bio-prototyping and followed by sintering at 1600 °C for 4 h at room atmosphere. Ceramic samples exhibited an EPR signal with principal g tensor of 2.020 and maximum line width around 2.3 mT is ascribed to interstitial oxygen ion. Dose response behaviour exhibited two distinct dose ranges, one is from 1 to 100Gy and the second is from 0.1 to 70 kGy. Irradiated samples exhibited fading stability from 96 h. Thermal annealing approaches reveal that defect centres of yttria decay significantly at high temperature. According to results, yttria is a promising material to be used for radiation dosimetry.

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