



Research article

Formation of dysprosium doped yttria (YDy) powders with EPR response

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ABSTRACT

From rare-earth (RE) based oxides, yttria (Y_2O_3) has unique solid-state characteristics, and as doped with RE-ions, exhibits excellent spectroscopic properties. However, its potentiality in radiation dosimetry field has been rarely explored. Based on this context, the present paper reports an alternative hydrothermal synthesis based on low temperature and environmental pressure to form dysprosium doped yttria (YDy) nanoparticles with potential application in radiation dosimetry. According to the results, YDy compositions with up to 2 at%Dy exhibited cubic C-type form, rounded-like shape, and narrow particle size distribution with the average size inferior to 700 nm. In addition, by Electron Paramagnetic Resonance (EPR), it was seen that the EPR response of the YDy nanoparticles relied on the content of dysprosium, while the YDy composition containing 0.1 at%Dy exhibited the maximum spin concentration $23.10^{27} \text{ s.mm}^{-3}$ among all compositions. These innovative findings are useful processing parameters to advance toward the formation of shaped bodies by additive manufacturing, and use in solid state dosimetry.

1. Introduction

Rare-earths (REs) form a select group of seventeen elements from La to Lu, including Y and Sc, with remarkable chemistry and physical properties, which in turn, input high strategic value to this elements [1–11]. Calcium sulfate (CaSO_4) as doped with dysprosium (Dy), thulium (Tm), terbium (Tb), and erbium (Er) becomes highly sensitive to ionizing radiation, and exhibits linear dose response behaviour from microgray (μGy) up to tens of grays (Gy). However, it is energy dependent, very sensitive to light exposure, and presents some fading particularly from a low-temperature thermoluminescent (TL) peak at room temperature [12–14].

Yttria (Y_2O_3), also known as yttrium oxide, is one of the most used rare-earth (RE) oxides due to its intrinsic properties as high melting point (2400°C), high chemical strength, and high structural stability, where cubic C-type form is the most predominant. Moreover, its lattice features make it an excellent host for RE-ions, forming new materials ($\text{RE:Y}_2\text{O}_3$) with outstanding response and wide range of applicability as thin films, catalysts, scaffolds, heavy alloys, quantum-dots, capacitors, magnets, solar cells, and batteries. Recently, our group has explored the potential use of yttria in radiation dosimetry field by colloidal processing studies based on Electron Paramagnetic Resonance (EPR) characterization. It has been observed that the radiation sensitivity of yttria is enhanced significantly when it is doped with RE-ions as europium (Eu),

and thulium (Tm). Therefore, studies on RE-doped yttria and its potential application in radiation dosimetry are worth of investigation [12–23].

Powder synthesis is an important strategy in ceramic processing to obtain powders with controlled characteristics such as shape, size, density, and surface area. Hydrothermal synthesis is a traditional synthesis method that provides particles in nano-sized range, with stoichiometry composition and high surface area. However, it demands high pressure (200–300 MPa), temperature ($450\text{--}750^\circ\text{C}$), and energy by using an autoclave system [24]. On the other hand, our research group has succeeded in producing rare-earth based nanoparticles such as β -yttrium disilicate ($\beta\text{-Y}_2\text{Si}_2\text{O}_7$), dysprosium doped yttrium disilicate ($\text{Y}_2\text{Si}_2\text{O}_7\text{:Dy}$), europium doped yttria ($\text{Y}_2\text{O}_3\text{:Eu}$), and thulium doped yttria ($\text{Y}_2\text{O}_3\text{:Tm}$), by an alternative hydrothermal approach based on low temperature and environmental pressure. The great advantage of this method consists in processing the precursor powder under room pressure and temperature around 70°C [13,21,22].

With regard to yttria properties and applicability, this work reports a synthesis approach based on a low temperature hydrothermal method to form dysprosium doped yttria powders (YDy) with controlled characteristics and potential applicability in radiation dosimetry. The findings reported here are useful processing parameters to advance toward the formation of shaped bodies by additive manufacturing. Afterwards, the dosimetric characteristics of the final components will be evaluated to

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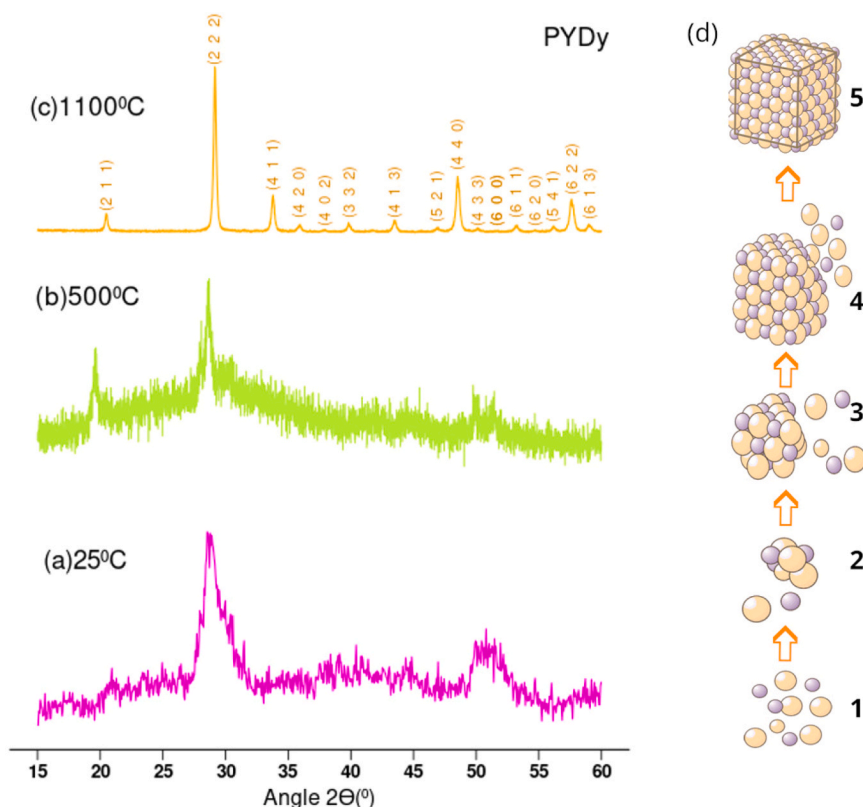


Fig. 1. Formation of crystalline YDy powders: (a–c) XRD curves of the PYDy as a function of temperature; (d) stages of crystal formation and evolution from (1) atoms, (2) nucleation, (3) growth, (4) crystal face, and (5) unit cell.

confirm their applicability as high dose dosimeters.

2. Experimental

2.1. Starting materials

In this work dysprosium doped yttria powders (YDy) with controlled features as surface area, density, morphology, chemical composition, and size were stoichiometrically synthesized by using the following starting materials: yttria (Y_2O_3 , 99.99 %, Alfa Aesar GmbH), dysprosium oxide (Dy_2O_3 , 99.999 %, Alfa Aesar GmbH), distilled water, nitric acid (HNO_3 , Synth), ammonium hydroxide (NH_4OH , Casa Americana), and ethanol ($\text{CH}_3\text{CH}_2\text{OH}$, Labsynth). The acronym YDy is based on the rare-earth sesquioxides (RE_2O_3), Y as yttria (Y_2O_3) and Dy as dysprosium oxide (Dy_2O_3).

2.2. Powder synthesis

YDy powders were obtained by an alternative hydrothermal synthesis method based on the previous study of the group [25]. The formation of the YDy powdered compositions was performed by stoichiometric calculations, in which Dy content was estimated in atomic percentage (at%), ranging from 0.1 % up to 2.0 at% of Dy, and considering Y as the host material.

The precursor powders (PYDy) were obtained by processing a stock solution at 60°C for 6 h in a condenser system, followed by a washing cycle using deionized water. Finally, the powders were formed by thermal treatment up to 1500°C for 2 h in air atmosphere using a box furnace (Lindberg Blue, Haake).

2.3. Powder characterization

With the aim to define a compatible thermal treatment condition to

succeed in forming YDy powders with controlled size, morphology, and density, an evaluation of thermal decomposition of PYDy powders was performed. Using a box furnace (Lindberg Blue, Haake) a PYDy powdered sample of 5 mg was heated from 25°C up to 1400°C in air atmosphere, where its mass was measured in each 100°C, using an analytical balance (Mettler Toledo, AB204-S). In this way, a curve between mass loss (m , mg) and temperature (T , °C) was established. Besides, the first derivative of the mass loss curve as a function of temperature was calculated to determine the temperature at which the maximum decomposition of sample occurred. Therefore, the conditions of thermal treatment of PYDy powders to form YDy powders with controlled features were proposed taking in account the results achieved during this step.

The evolution and formation of the crystalline structure of the YDy powders as a function of the thermal treatment was followed by X-ray diffraction (XRD, Rigaku Multiflex, Japan), considering an angular range (2θ) from 15 to 70°, step size of 0.5°.min⁻¹, and $\text{K}\alpha$ source. The identification of the crystalline structure was performed by taking as reference the Crystallography Open Database (COD) [26] and BGMN source [27]. While Rietveld refinement, crystallite size (d_c), crystalline density (ρ_{XRD}) and lattice parameter (a), and electron density map based on the maximum entropy method (MEM) [28] were succeeded by PROFEX [29] software. Moreover, ball-and-stick and polyhedral representations of the unit cell of a YDy powdered compositions were created by Vesta [30] software.

The as-synthesized YDy powders were characterized by Photon Correlation Spectroscopy (PCS, Litesizer500, Anton Paar) in order to determine the particle size distribution (d_{10} , d_{50} , and d_{90}), where the hydrodynamic diameter of particles (d_h) was calculated based on the hydrodynamic diameter model [31]. Besides, to carry out the particle size characterization the following parameters were used: diluted aqueous suspensions (0.05 %vol particles), equilibration time 10 s, number of runs 5, evaluation time 20 s, and temperature 25°C. In addition, the solid density [32] (ρ_s) was evaluated by using a helium gas

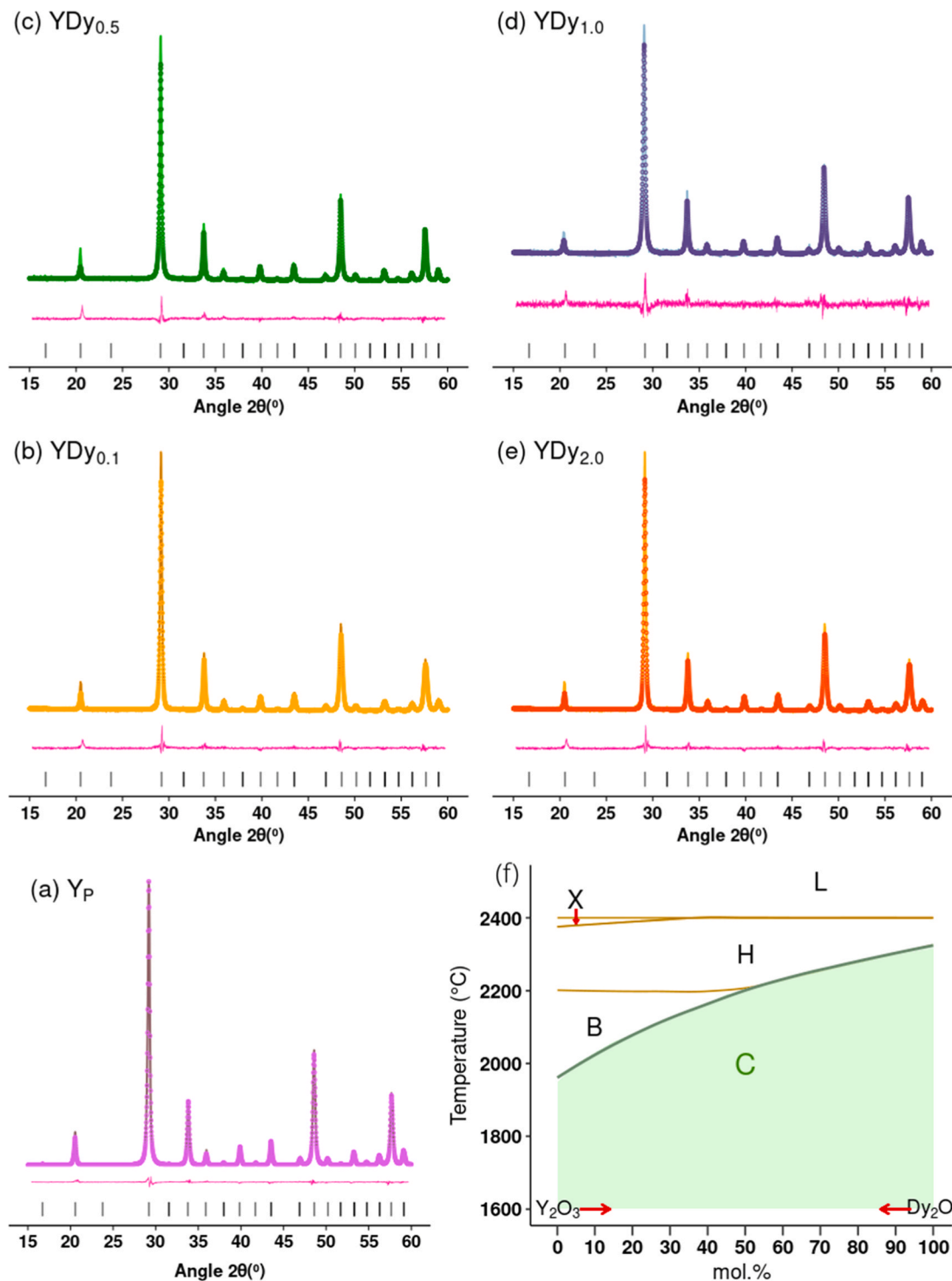


Fig. 2. Rietveld refinement of the XRD pattern observed of YDy powders as a function of Dy content: (a) Y_p – “pure yttria”; (b – e) YDy from 0.1 up to 2at%Dy, where solid lines represent the experimental data, while points are the simulated pattern; pink solid line is the difference pattern (experimental – simulated), and straight gray lines are the indexed peaks according to BGMN/COD structure file 1539587. At (f) phase equilibrium diagram of the Y_2O_3 - Dy_2O_3 system, where the cubic C-type form is the most predominant crystal structure in the system.

pycnometer (Micrometrics 1330), while the specific surface area (S_{SA}) was determined by gas adsorption method [33], using a surface analyser (ASAP2010, Micrometrics). Considering the SSA result, particle shape, and theoretical density, the particle size (d_{BET}) was calculated.

The agglomeration factor (F_{ag}) of particles is the ratio of the mean particle diameter (d_{50}) measured by PCS and the particle size calculated directly by BET method (d_{BET}). As F_{ag} is 1.0, this value indicates that

particles are uniform and dispersed, while F_{ag} is inferior to 1.0, this condition suggests that there are differences of shape (length/ radius) among particles. However, as F_{ag} value is higher than 1.0, it means that particles are agglomerated. The shape and size of the YDy powders were observed by Scanning Electron Microscopy (SEM, INCAx-act, Oxford Instruments).

The Paramagnetic response of YDy powdered compositions were

Table 1

Rietveld refinement results of the YDy powdered compositions.

YDy (at%Dy)	R _{wp} (%)	R _{exp} (%)	χ^2	GoF	BGMN/COD file
0.0	12.69	11.41	1.24	1.11	1539587
0.1	13.28	11.88	1.25	1.12	
0.5	12.69	11.55	1.21	1.10	
1.0	11.69	11.59	1.01	1.01	
2.0	13.28	11.88	1.25	1.12	

evaluated by Electron Paramagnetic Resonance (EPR), using an X-band EPR spectrometer (Bruker EMX PLUS), under room temperature and atmosphere. Based on the previous study of the group [34], the following EPR protocol was used: EPR spectra was recorded in field modulation frequency of 100 kHz, microwave power of 2.5 mW, center field of 300mT, sweep width of 300mT, modulation amplitude of 0.4mT, time constant of 0.01 ms, 10 scans, temperature of 20°C, room atmosphere, under controlled humidity, and using DPPH (2, 2-Diphenyl-1-picrylhydrazyl, Bruker) as EPR reference.

3. Results and discussion

The XRD curves of the precursor powders (PYDy) as a function of temperature are illustrated in Fig. 1. It is evidenced that as-synthesized powders (Fig. 1a) exhibited amorphous phase, with two wide peaks recorded around 29.5° and 51°. After thermal treatment at 500°C (Fig. 1b), it is observed a tendency of crystalline phase formation, where two peaks at 18.5° and 29.5° with sharper form were recorded. Finally, the crystalline form of the powders corresponding to cubic C-type was succeed at 1100°C (Fig. 1c), wherein a highly intensity peak was recorded at 29.5° (222). This result is in agreement with the

BGMN/COD file (1539587).

Even though thermal treatment using high temperature is effective in the formation of crystalline powders, its limitation is essential to avoid the development of larger particles, or aggregates that can be detrimental for further powder processing. In recent studies of the group, nano-sized rare-earth based powders as RE-doped/undoped yttrium disilicate [35,36] and RE-co/doped yttria [25,37] were produced successfully under thermal treatment up to 1100°C in room atmosphere. The XRD results illustrated in Fig. 1 make evident that the proposed synthesis method based on an alternative hydrothermal synthesis using low temperature of processing and environmental pressure, followed by thermal treatment at 1100°C provided the formation of highly crystalline ceramic powders.

Rietveld refinement of YDy spectra powdered compositions with Dy content varying from 0.1 at% up to 2 at% is shown in Fig. 2. Considering “pure” yttria as the reference spectra (Fig. 2a), it is seen that Dy content (Fig. 2b–Fig. 2e) did not induce the formation of second phases, neither changed yttria crystalline form (from cubic C-type to A, B, H, X). Additionally, this finding is in agreement with the phase equilibrium diagram of the system $\text{Dy}_2\text{O}_3 - \text{Y}_2\text{O}_3$ illustrated in Fig. 2f. Taking in account the chemical form $\text{Y}_{2-x}\text{Dy}_x\text{O}_3$, where x is the Dy content, the following crystalline forms can be achieved as C, B, H, and X. The liquid phase (L) is achieved over 2400°C, which corresponds to the fusion temperature. Among all crystalline forms, the C-type form (highlighted in light green) is the most predominant form, while the X-type presents the narrowest field of formation. In addition, the stability of type C form changes as a function of Dy content, varying from 2200°C as Y is 100 % to 2000°C as Dy is 100 %. Besides, the polymorphic forms B, H, and X can be succeeded by rising the temperature above C-type line, and taking in account the phase composition. Moreover, using high pressure combined with high temperature lead to transform cubic-C type to B, X,

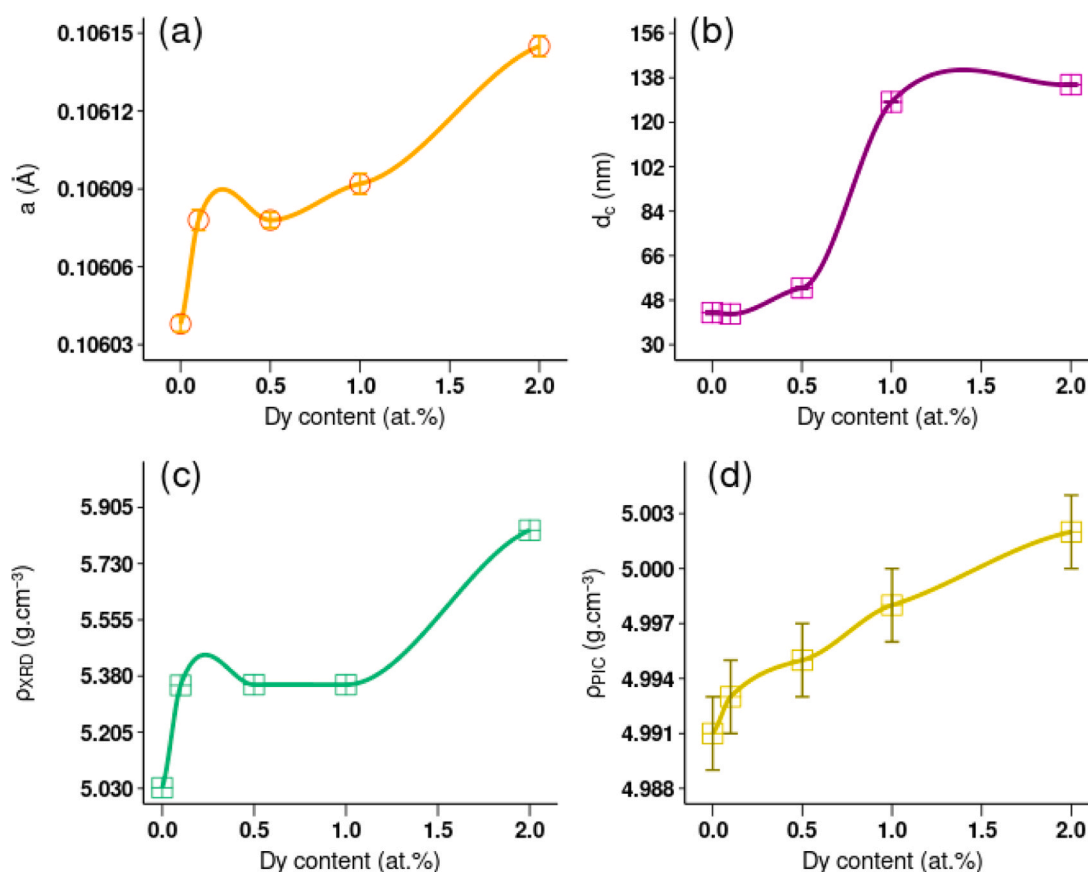


Fig. 3. Crystal features achieved by processing XRD data of samples: (a) lattice parameter – a ; (b) diameter of crystallite (d_c); (c) density (ρ_{XRD}), while (d) density (ρ_{PIC}) was resulted from helium pycnometry.

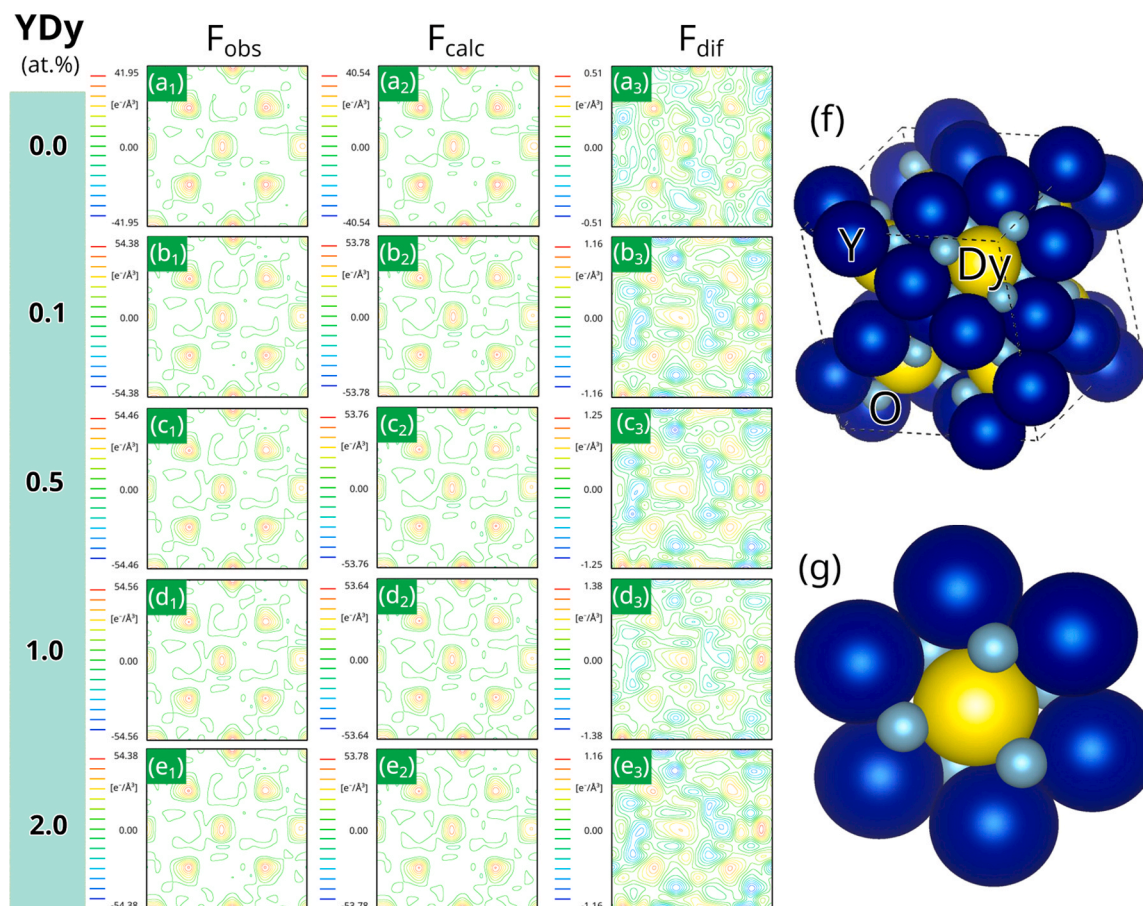


Fig. 4. Crystal characterization of YDy powders from Rietveld refinement data (a–d) electron density map as a function of Dy content from 0, 0.1, 0.5, 1.5, and 2 at% respectively; and (f) ball-filling model of cubic C-type, and (g) ball-filling cluster, which highlights (1) Dy atom surrounded by (03) O atoms, and followed by (06) Y atoms.

or H.

The Rietveld results of YDy powdered compositions reported in Table 1 assure that the refinement was successfully performed due to low values of R-factors, the acceptance limit (χ) was inferior to 1.5, and all spectra fit the BGMN/COD standard file 1539587. Therefore, the proposed hydrothermal synthesis was effective for doping yttria with up to 2 at%Dy. Forming a material with a composition stoichiometrically defined is essential to enhance its radiation sensitiveness, which relies on the formation of electron defects, paramagnetic radicals, new energy levels, and traps in the lattice.

Ranson et al [38], reported that the excessive content of RE-ion in yttria lattice tend to be located at its S_6 symmetry axis, which results in poor luminescence response. While, using small content of RE-ion, these ions tend to be located at C_{3i} axis of the lattice, providing higher luminescence emission. Therefore, doping content is a very important parameter in colloidal processing and the formation of new materials for radiation dosimetry.

The control of synthesis parameters as stoichiometry of rare-earth starting solutions, temperature, digestion time of solution, refining, and thermal treatment impact directly on the crystal features of the free powders. This issue has been extensively reported in literature. Moskovskikh et al [39], observed that the synthesis temperature, holding time, excess of reducing agent, method of compacting a charge, and conditions of hydrometallurgical treatment affect the composition, purity, and phase of LaNi_5 powders formed by calciothermic process. Zhu et al [34], highlighted that synthesis conditions such as concentration, temperature, and stoichiometry are a challenge and critical factors that control large-scale synthesis of high-performance TiN powders.

YDy powders characteristics as lattice parameter (a), crystallite size

(dc), picnometric density (ρ_{PIC}), and lattice density (ρ_{XRD}) as a function of Dy content are represented in Fig. 3. It is clearly evidenced that the small difference (0.011 Å) of ionic radius of the host material yttria (0.901 Å) and the dopant Dy (0.912 Å) did not induce any relevant changes in crystal lattice of yttria, where the lattice parameter (a) illustrated in Fig. 3a enlarged only 0.00011 Å. In addition, it is observed that the crystallite size (dc) presented in Fig. 3b exhibited significant increase from 42.96 to 135.20 nm due to mass diffusion and grain growth induced by thermal treatment of as-synthesized powders. Many approaches have been proposed to control the crystallite size of advanced ceramic powders as variation of heating temperature [40], type of dopant [41], milling time [42], and pH condition of the precursor solution [43]. The crystal density (ρ_{XRD}) shown in Fig. 3c rose from 5.032 to 5.834 $\text{g}\cdot\text{cm}^{-3}$, while the pycnometric density (ρ_{PIC}) increased from 4.991 to 5.002 $\text{g}\cdot\text{cm}^{-3}$ due to increasing molecular weight with Dy doping.

By Rietveld refinement of YDy spectra powdered compositions a Fourier series concerning (1) observed spectra (F_{obs}), (2) calculated one (F_{calc}), and (3) the difference $F_{\text{obs}} - F_{\text{calc}}$ (F_{dif}), was calculated to build up electron density maps [44], that illustrate the variation in the local concentration of electrons in the crystal and is colored in units of volume ($\text{e}\cdot\text{\AA}^{-3}$) as shown in the color representation from Fig. 4a to Fig. 4e. Taking in account that yttrium (Y) has 39 electrons, while dysprosium (Dy) has 66 electrons, Dy doping gives rise to increase the concentration of electrons in yttria lattice. As X-rays are scattered by electrons (core electrons and valence electrons), the presence of Dy is evidenced by the distribution of color with contour lines, ranging from 0 at% to 2 at%Dy. Furthermore, the similarity of F_{obs} and F_{calc} density maps, which in turn results in low intensity distribution F_{dif} maps, is an additional

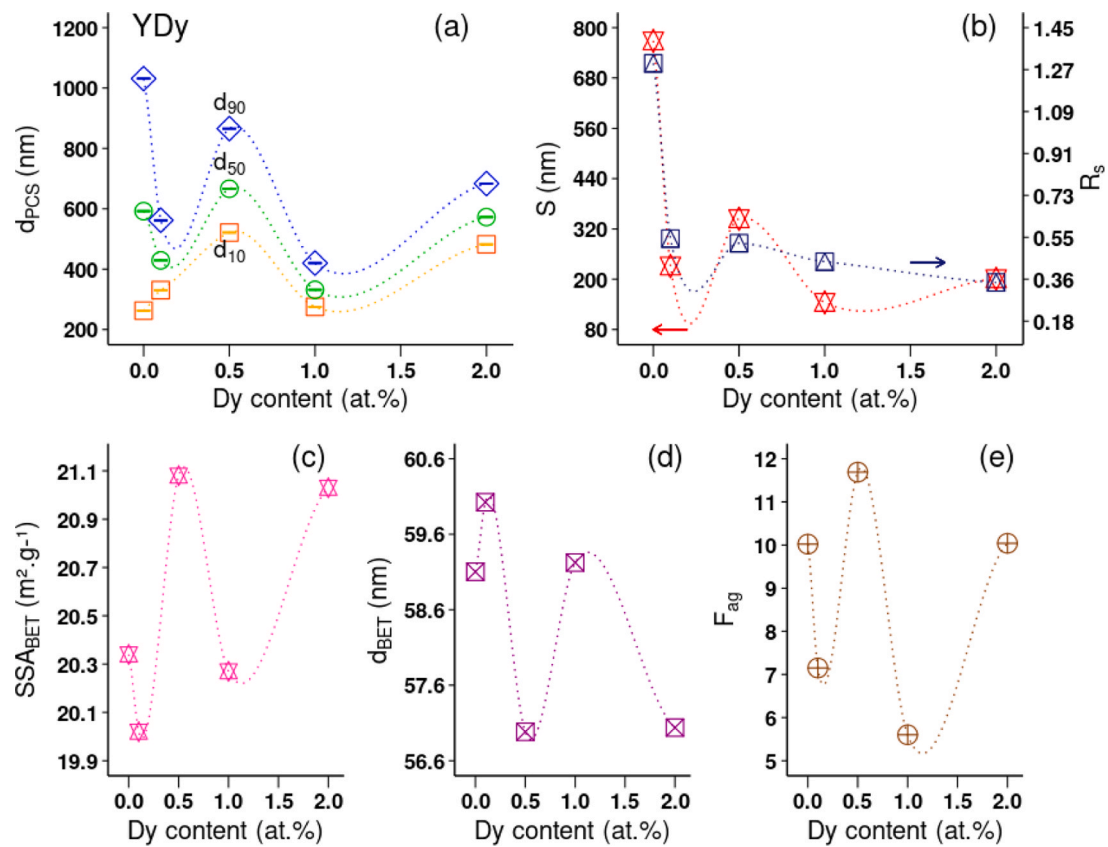


Fig. 5. YDy powders characteristics achieved from (a) particle size distribution by PCS; (b) Span (S) and Relative Span (R_s) of particle size distribution; (c) specific surface area by BET method; (d) particle size ($dBET$) by BET method; and (e) agglomeration factor (F_{ag}) of particles.

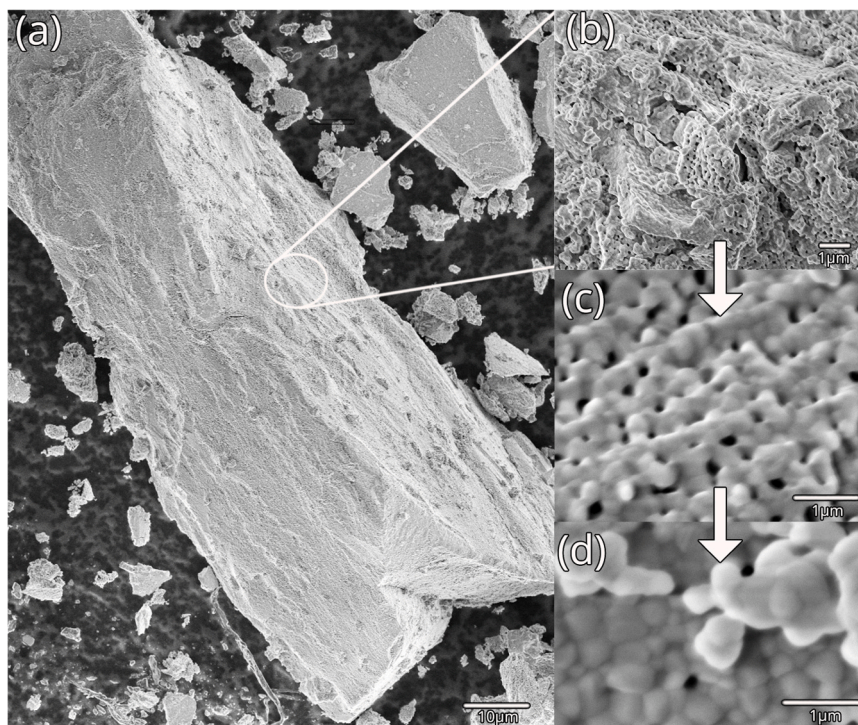


Fig. 6. SEM images of YDy powders: (a) general view on agglomerates of particles; (b) area magnification of an agglomerate surface constituted by porous structure; (c, d) porous surface microstructure which reveals rounded particles bonded together (neck effect).

parameter to guarantee that the Rietveld refinement was performed successfully.

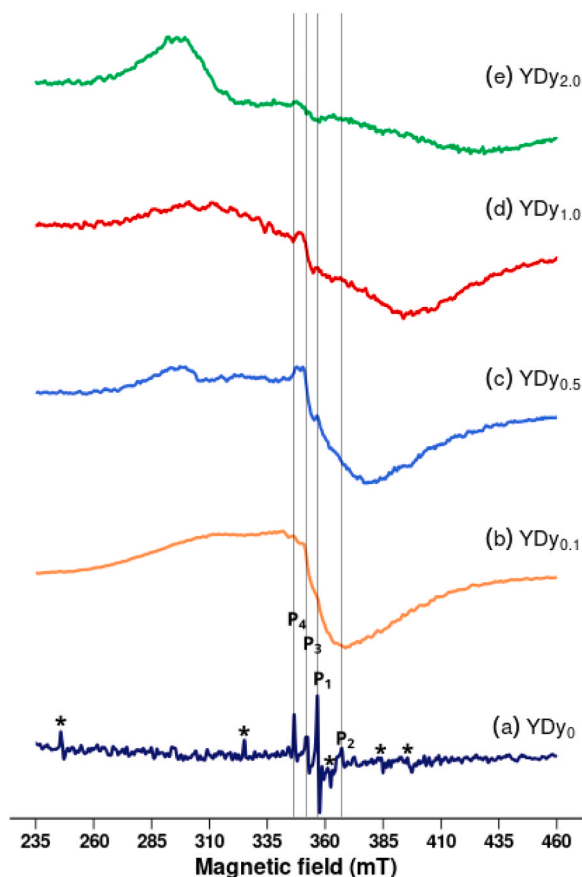


Fig. 7. (a-e) EPR spectra of YDy powders as a function of Dy content up to 2.0 at%.

Additional particle characterization results of YDy powdered compositions are illustrated in Fig. 5. Based on the particle size distribution by PCS (Fig. 5a) is observed that all synthesized compositions exhibited a mean particle size (d_{50}) inferior to 700 nm (light green curve). The broad fraction corresponding to d_{90} (blue curve) ranged from 1020 nm to 410 nm, while the narrowest fractions (d_{10}) ranged from 240 to 570 nm. Moreover, the span (S), which is the difference between d_{90} and

d_{10} fractions and the relative span (Rs), which is the ratio between S and d_{50} , represented in Fig. 5b make evident that Dy doping induced a significant reduction in S (blue curve) of particles, ranging from 780 nm (0 at%Dy) to 200 nm (2.0 at%Dy). Furthermore, this behavior was also achieved for R_s (red curve), which a decrease was observed from 790 nm to 200 nm.

With concern to specific surface area (SSA_{BET}) of YDy powdered compositions (Fig. 6c), it is seen that Dy doping did not change significantly SSA of particles, which ranged from 20 to 21.1 nm. Additionally, the diameter size calculated from BET data (d_{BET}) and illustrated in Fig. 6d varied only from 59.3 nm to 57.1 nm. These findings reveal that YDy compositions are formed by particles in nano-sized range with high S, which in turn lead particles to form agglomerates as evidenced in Fig. 6e. Particles with Fag near to 1.0 are considered to be very dispersed and as “single particle”, while higher values of Fag suggest that particles are in hard agglomerate state. According to the results, Fag reached this maximum value with 0.5 at%Dy (11.8) and this minimum value with 1.0 at%Dy (5.5). Therefore, the proposed synthesis method provided YDy particles in nano-sized range, even though they are in agglomerate state due to high S values.

Synthesis method and its parameters drive the powder characteristics with the aim to reach their utmost condition for technological application. Robakowska et al [45], successfully synthesized LaMnO₃ and LaFeO₃ powders by mechanochemical [46] and sol-gel methods [47]. While mechanochemical synthesis provided for both compounds powders with orthorhombic structures, sol-gel synthesis resulted powders in an orthorhombic structure for LaFeO₃ and trigonal structure for LaMnO₃. Strizhak et al [48], observed that the size of hydrate powder aggregates, associated with carbon nanotubes and surfactants concentration make influence on the kinetics of synthesis and dissociation of gas hydrates. According to the results, the minimum average aggregate size of the methane hydrate powder corresponds to a nanotube concentration of 0.1 wt%. Sun et al [49], succeeded in forming by hydrothermal spherical α -Al₂O₃ powders with uniform particle size and d_{50} of 815 nm.

SEM images of YDy powders are illustrated in Fig. 6. It is evidenced that the hydrothermal synthesis provided narrow particles that agglomerate easily (Fig. 6a) due to their size in nanoscale range. Further, nanosized particles are subject of surface forces such as electrostatic and van Der Waals and tend to form agglomerates. From Fig. 6b to Fig. 6d it is seen that the powder agglomerates are constituted of thin rounded-like particles with size inferior to 1 μ m, in agreement with the particle

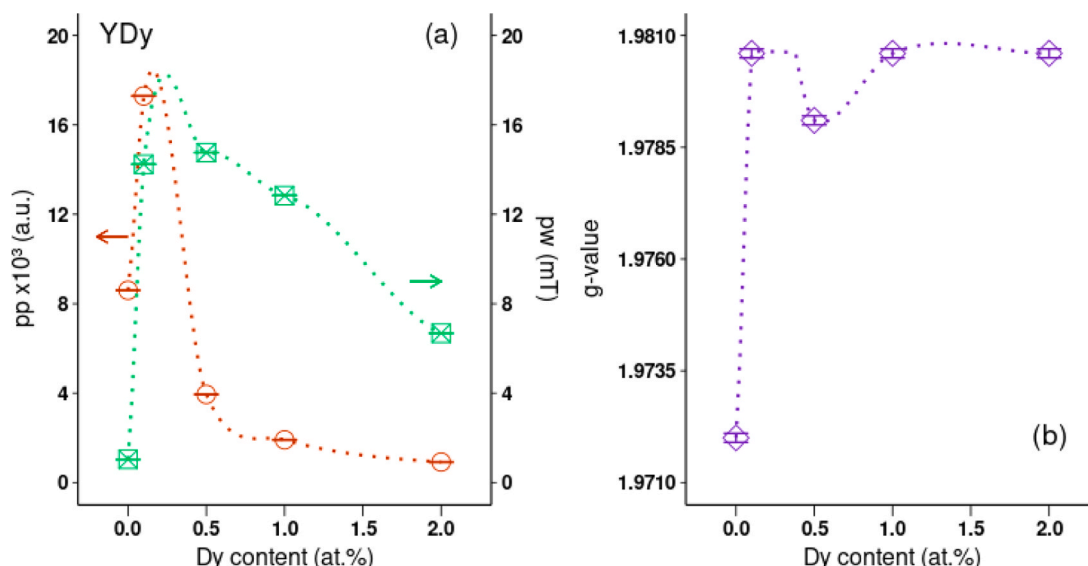


Fig. 8. EPR spectra characteristics of YDy powders as a function of Dy content by (a) peak-to-peak amplitude (pp) and peak width (pw), and (b) g-value.

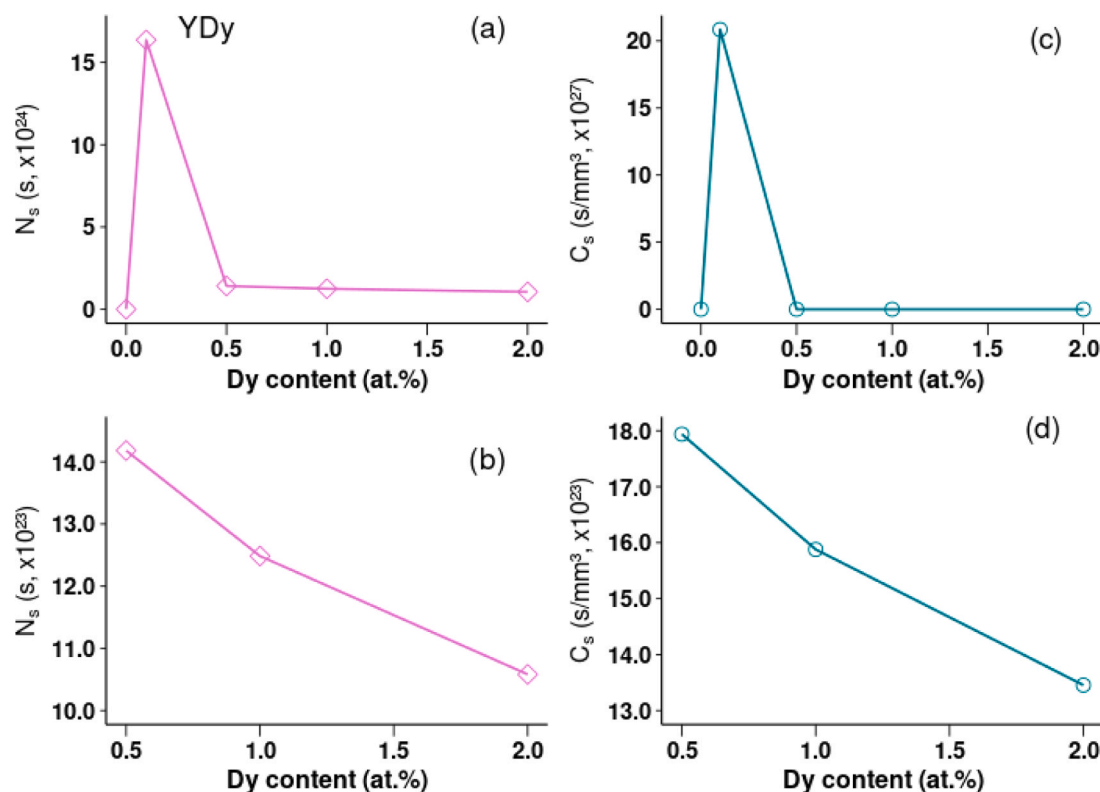


Fig. 9. Determination of (a, b) spin number (N_s), and (c, d) spin concentration (C_s) of YDy powders as a function of Dy content.

characteristics results shown in Fig. 5a. Moreover, the agglomerated state of particles was predicted in Fig. 5d, in which the Fag values ranged from 7 to almost 12.

Particle size and shape have great effect on the colloidal processing and the final characteristics of functional materials [50–54]. Particles in nanoscale range can form powder compacts with high green density [55], and under highly controlled sintering they usually succeed in forming ceramic components with dense microstructure, symmetric geometry, free of cracks, and uniform grain size [56]. A recent study of the group [25] on development of new materials for radiation dosimetry, micro rods of europium doped yttria with pycnometric density of 4.98 g.cm^{-3} were obtained by colloidal processing of particles with average size of 430 nm and rounded-like shape.

Doping yttria with Dy ions is performed by replacing Y^{3+} ions for Dy^{3+} ions on yttria sites C_2 and C_{3i} , which can give rise to new electron defects and enhance spectroscopic characteristics of yttria. The doping effect is illustrated by EPR spectra of the YDy powdered compositions in Fig. 7. It is seen that YDy₀ “pure yttria” represented in Fig. 7a exhibited four EPR peaks assigned to P_1 , P_2 , P_3 , and P_4 , and recorded at 358, 365, 355, and 340mT, respectively. While the peak P_1 is due to interstitial oxygen ions from environmental atmosphere, peak P_2 is attributed to F^+ centre charged vacancy oxygen, where an electron remains. These peaks were also observed by Bourdun[57], and Ivanova et al. [58]. Besides, comparing this achievement with those reported in previous studies of the group on EPR characterization of yttria particles [59–62], it is evidenced the relevance of the chemical composition of the powders on EPR spectra. Based on those findings reported in [60], high-purity yttria nanoparticles exhibited only two EPR peaks recorded in a magnetic field range between 345 and 360mT, and g-values around of 2.0000 and 1.9690, respectively. The additional EPR peaks assigned to P_3 , and P_4 recorded at 347 and 356mT, including those low intensity peaks indicated as (*) are due to impurities of yttria. It is important to consider that rare earths are found in nature with others rare earth metals and their extraction, including their purification process is very complex. Moreover, the EPR technique is extremely sensitive, where even low

concentration of impurities can be observed in a spectra. On the other hand, adding Dy into yttria lattice gave rise to rearrange of the electron defects, once Dy^{3+} ions filled yttria sites, forming new traps as shown in the sequence of EPR spectra from Fig. 7b to Fig. 7e. It is clearly seen that using only 0.1 at%Dy led to promote significantly the intensity of P_3 peak, where P_1 , P_2 , and P_4 peaks were nearly suppressed. Therefore, using lower concentration of Dy^{3+} ions led to enhance the number of electron defects into yttria lattice, which means, more paramagnetic radicals. Moreover, P_3 peak exhibited a very low intensity for YDy_{2.0} samples, while a tendency of new electron defects was observed in a range of magnetic field from 270 to 300mT due to increase of oxygen species.

The effect of Dy content on yttria EPR response is illustrated in Fig. 8. According to the results, the peak-to-peak amplitude (pp) represented in Fig. 8a increased remarkably as adding 0.1 at%Dy, ranging from 8.3 a. u.–17.4 a.u., while higher contents of Dy led to an expressive decrease of pp values from 17.4 a.u. (0.1 at%Dy) to almost 1 a.u. (2.0 at%Dy). Similar behaviour was observed for peak width (pw) results, where pw reached its maximum value 17.5mT at 0.1 at%Dy, but a tendency of reduction was observed for higher Dy content. These results can be associated with the recombination effect of Dy electrons into yttria lattice, including the excess of Dy ions into yttria lattice sites, which induce to electron/holes recombination, formation of deep traps, annihilation of electron defects and other detrimental effects in solid state characteristics of yttria. Even though higher Dy content was not effective in providing higher EPR response of yttria considering pp values, the Dy doping effectiveness has to be evaluated by irradiating YDy powdered samples with ionizing radiation, which is the scope of a future investigation. Upon g-values, it is seen in Fig. 8 that a slight shift of the central peak from 355mT to 350mT occurred, and as a consequence g-values exhibited a very narrow shift as illustrated in Fig. 8b, from 1.9725 (“pure yttria”) to 1.9798 (2.0 at%Dy). Besides, all Dy content resulted in g-values into the range between 1.9785 and 1.9810, which indicates that all Dy content did not provide any structural change of yttria host [63].

Using Dy as a dopant had the aim to enhance the quantity of electron

defects in yttria, and such defects as paramagnetic radicals could be quantified in the form of spin number (N_s) and spin concentration (C_s) as illustrated in Fig. 9. As observed previously on pp results, the N_s (Fig. 9a and Fig. 9b) and C_s (Fig. 9c and Fig. 9d) achieved their maximum values with Dy content of 0.1 at%Dy. Apart from this minimum Dy content, both N_s and C_s expressively decreased, and these results corroborate with the previous results (Fig. 9). The present findings suggest that the doping yttria with Dy^{3+} ions should be performed with a maximum limit of 0.1 at%Dy, and lower Dy content compositions should be considered for future EPR characterization studies. Even though only the composition of YDy powders containing 0.1 at%Dy exhibited the highest C_s and N_s values, all compositions have to be evaluated as irradiated with ionizing radiation with the aim to confirm effectiveness of Dy in promoting yttria dose-response and its possible applicability in radiation dosimetry.

4. Conclusion

Dysprosium doped yttria (YDy) powdered compositions with up to 2 at%Dy content, with average particle size (d_{50}) inferior to 700 nm and cubic C-type form were successfully obtained by an innovative hydrothermal synthesis based on room pressure and temperature around 60°C, being more feasible to conduct than the conventional hydrothermal synthesis. Among all YDy compositions obtained, those prepared with 0.1 at%Dy exhibited the most significant Electron Paramagnetic Resonance (EPR) response, with the peak-to-peak amplitude (pp) of $17.5 \cdot 10^3$ a.u., and spin concentration (C_s) over $20 \cdot 10^{27}$ s.m $^{-3}$. The next step of the study is to evaluate the dose-response behavior of this composition as exposed to distinct ionizing radiation sources e.g. X-rays, gamma, beta, neutrons, etc. The findings reported here are useful processing parameters to advance toward the formation of shaped bodies by additive manufacturing. Afterwards, the dosimetric characteristics of the final components will be evaluated to confirm their applicability as high dose dosimeters.

Consent for publication

We authors declare our consent for publication.

Ethics and consent to participate

No human or animal were used in the study

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

We cannot share any data today due to a hacker attack to our server. The data will be available as soon as this issue is solved.

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