

## Characterization of yttria nano structured material for radiation dosimetry

Santos, S. C<sup>a</sup>, Campos, L.L<sup>b</sup>, Mello-Castanho, S.R.H<sup>c</sup>.

<sup>a-c</sup>*Instituto de Pesquisas Energeticas e Nucleares – IPEN,  
Av. Prof. Lineu Prestes 2242, Cidade Universitaria, Sao Paulo, Brazil*

<sup>a</sup>*silas.cardoso@usp.br*

The use of rare earths (RE) as dopant of materials has supplied the development of advanced materials for many applications such as optical markers, special alloys, semiconductors, as well as radiation dosimetry. The development of new dosimetric materials is a great challenge in innovation of materials. Yttria (Y<sub>2</sub>O<sub>3</sub>) presents luminescent proprieties and can be considered a potential material for radiation dosimetry. In this study Y<sub>2</sub>O<sub>3</sub> nanoparticles were characterized by Photon Correlation Spectroscopy (PCS), Specific Surface Area by BET method (SSA), X ray diffraction pattern (XRD) and Scanning Electron Microscopy (SEM) and Thermally Stimulated Luminescence (TL). According results yttria powders with mean particle size of d<sub>50</sub>=304nm, pycnometric density of ρ=4.84g.cm<sup>-3</sup>, specific surface area SSA=13.5m<sup>2</sup>.g<sup>-1</sup> presents TL signal response at 150°C and λ=550nm when exposed to <sup>60</sup>Co gamma radiation.

Key words: yttria, rare earths, thermoluminescence, radiation dosimetry.

### 1.INTRODUCTION

The development of new dosimetric materials with luminescent and spectrometric/paramagnetic response higher than established dosimeters is a great challenge in innovation of materials. From RE, yttria (Y<sub>2</sub>O<sub>3</sub>) is a promising material for radiation dosimetry due to its intrinsic chemical and physical proprieties as melting point of 2400°C, refractive index of 1.9, thermal and chemical stability. Y<sub>2</sub>O<sub>3</sub> is used for enhancement of sintering<sup>[1]</sup>, catalysis<sup>[2]</sup>, luminescence<sup>[3]</sup>, electrical<sup>[4]</sup>, electronic<sup>[5]</sup>, mechanical<sup>[6]</sup> and thermal<sup>[7]</sup> behavior of many advanced materials. YAR et al.<sup>[8]</sup> by chemical reaction highly uniform nano-sized yttrium doped tungsten oxide particles (WO<sub>2</sub>:Y<sub>2</sub>O<sub>3</sub>) were synthesized. Samples sintered at 1400°C showed higher relative density (R<sub>D</sub>=95%) and finer grain size as compared to those sintered at 1500°C and 1600°C. LI et al.<sup>[9]</sup> produced yttrium doped zinc oxide nanofibers (ZnO: Y<sub>2</sub>O<sub>3</sub>) by electrospinning method followed by calcination. As a result, doping with yttrium was useful to form particles with uniform morphology, higher specific surface area (40.2m<sup>2</sup>.g<sup>-1</sup>) and gas sensing as compared to those ZnO. Europium doped yttria (Y<sub>2</sub>O<sub>3</sub>:Eu<sup>3+</sup>) is noted for its excellence in luminescence<sup>[10]</sup>. ZHANG et al.<sup>[11]</sup> reported the synthesis of single-layer yttrium oxide nanosheets doped with Eu<sup>3+</sup> and Tb<sup>3+</sup> by the exfoliation method. The promising results such as transparency, strong red and green emissions show that nanosheets have potential to be used as building blocks and other functional materials. Based on yttrium oxide proprieties and its promising applications the present work aims to characterize yttrium oxide powders as a first step for future application in radiation dosimetry.

## 2. EXPERIMENTAL

In this work yttria powder ( $Y_2O_3$ ; Johnson Matthey) was used as raw material. Powder characterization was performed as follow: X-ray diffraction (XRD; Rigaku Multiflex), scanning at  $1^\circ \cdot \text{min}^{-1}$ ,  $\Delta\theta = 10-80^\circ(2\theta)$  and radiation Cu- $k\alpha$ ; scanning electron microscopy (SEM, Oxford); X-ray fluorescence (XRF, Rigaku RIX 3000); photon correlation spectroscopy (PCS, ZetaPALS Analyzer, BrookhavenInstruments); specific surface area by BET method (SSA, Micrometrics ASAP 2010); determination of the theoretical particle size ( $d_{\text{BET}}$ ) from BET model<sup>[12]</sup> and agglomeration factor ( $F_{AG}$ ); helium pycnometry (Pycnometer Micrometrics 1330). Thermoluminescence response (TL) was carried out after irradiating the samples with  $\gamma$  dose of 10KGy from a  $^{60}\text{Co}$  source and using the TL reader Risø (TL/OSL-DA-20) and the spectrometer Ocean Optics (QE65 Pro) with spectral sensibility from 200 to 950 nm. The samples were heated at a heating rate of  $10^\circ\text{C}\cdot\text{s}^{-1}$  up to  $400^\circ\text{C}$ .

## 3. RESULTS AND DISCUSSION

Figure 1 shows XRD pattern of  $Y_2O_3$  powders. According to result is observed that diffraction peaks corresponded to body-centered cubic yttria (C-type) fitting PDF (70-603) and a peak of high intensity in  $29^\circ$  which is related with the crystallographic plane (222). HOEKSTRA et al.<sup>[13]</sup> reported that the rare earths sesquioxides belong to C-type as  $Dy_2O_3$ ,  $Th_2O_3$ ,  $Ga_2O_3$  and  $In_2O_3$ . In addition, literature has shown that  $Y_2O_3$  can present other polymorphs. GOURLAOUEN et al.<sup>[14]</sup> reported the monoclinic structure (B-type) at  $997^\circ\text{C}$  under 2.0 GPa during plasma spray coating. NAVROTSKY et al.<sup>[15]</sup> showed that the C-type becomes fluorite type at  $2308^\circ\text{C}$  and hexagonal A-type at  $2325^\circ\text{C}$ . QUIN et al.<sup>[16]</sup> observed structural changes from C-type to B-type for particles smaller than 10 nm.

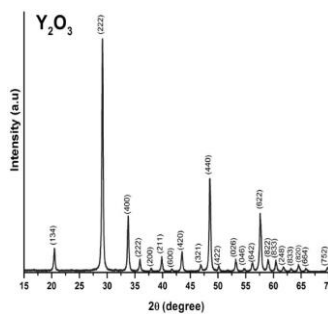


Figure 1. XDR curve of  $Y_2O_3$  powders according to PDF 70-603.

Powder characterization of  $Y_2O_3$  by PCS and SEM is shown in Figure 2. From results,  $Y_2O_3$  presents narrow particle size distribution with a mean particle diameter  $d_{50} = 304\text{nm}$  (Figure 2a). Besides, the difference of size (span) between minor ( $d_{10}$ ) and major ( $d_{90}$ ) distributions was less than 7nm, which confirms the uniformity of particle size distribution, and the relative span was only 0.02. Therefore,  $Y_2O_3$  showed a monomial particle size distribution.

Particles of nano sized scale are ruled by surface forces and as a consequence tend to agglomerate easily as shown in Figure 2b. From SEM image is observed that  $Y_2O_3$  powders are composed of agglomerates of particles in which size is smaller than  $1\mu\text{m}$ . Furthermore, specific surface area by BET method  $SSA = 13.59 \text{ m}^2\text{g}^{-1}$ , pycnometric density  $\rho = 4.84\text{g}\cdot\text{cm}^{-3}$  and as comparing theoretical particle diameter ( $d_{\text{BET}}$ ) from BET equation with experimental result from

PCS ( $d_{50}$ ) the difference of size is 214nm and agglomeration factor ( $F_{ag}$ ) was very small 3.33, which means that particles were weakly agglomerated. For radiation dosimetry the configuration of particle size plays an important role. GUIDELLI et al.<sup>[17]</sup> reported that radiation sensitivity of silver-alanine nanocomposites increases as a function of particle size. FEOFILOV<sup>[18]</sup> showed that life time of excited trivalent rare earth ions tend to enhance as a function of decreasing of particle size. BOLSHUKHIN<sup>[19]</sup> reported that the luminescent behavior and light persistent of  $\text{Sr}_4\text{Al}_2\text{O}_3:\text{Eu}^{3+}$  is longer for particles of nano scale size.

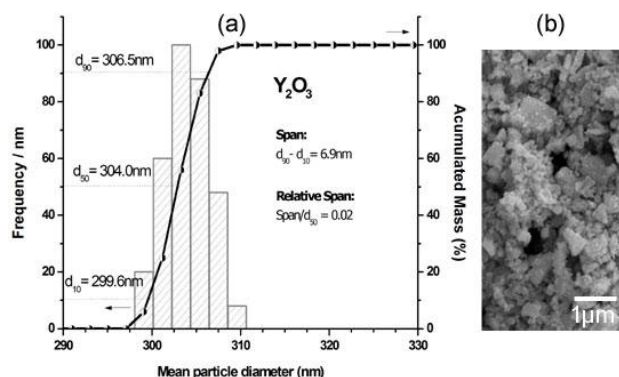


Figure 2. Size and shape characterization of  $\text{Y}_2\text{O}_3$  powders (a) particle size distribution by PCS and (b) SEM micrograph.

The thermoluminescence (TL) response of yttrium oxide nanoparticles is shown in Figure 3. From the figure, yttrium oxide exhibited a TL peak at  $150^\circ\text{C}$  and with light emission quanta at  $\lambda=550\text{nm}$ . For yttrium oxide nanoparticles evaluated in this study the light emission at  $\lambda=550\text{nm}$  (green light) is new in literature. The TL response may be due to particle characteristics as chemical composition, crystalline and surface defects. These factors can produce charge transport vacancies and luminescence centers. Many contributions on rare earth luminescence response have presented yttrium oxide as matrix for formation of phosphors<sup>[20-25]</sup>. RAUSKAS et al.<sup>[26]</sup> reported that yttrium oxide nanoparticles exhibited white light luminescence at  $\lambda=330\text{nm}$  like  $\text{Y}_2\text{O}_3:\text{Ce}^{3+}$ .

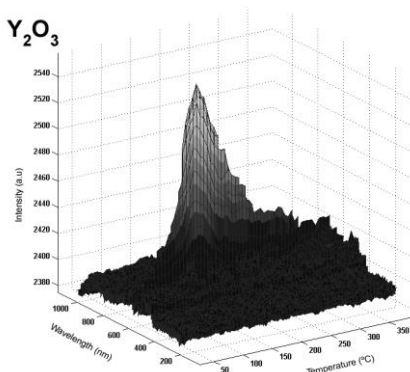


Figure 3. Thermally stimulated luminescence response of  $\text{Y}_2\text{O}_3$  powders in which TL peak was observed at  $150^\circ\text{C}$  and  $\lambda=550\text{nm}$ .

#### 4. CONCLUSION

Characterization of yttria powders for future application in radiation dosimetry was performed. Body-centered yttria powders exhibited uniform particle size distribution, mean diameter  $d_{50}=304\text{nm}$ , specific surface area around  $6.4\text{m}^2.\text{g}^{-1}$ , pycnometric density  $\rho=4.84\text{g}.\text{cm}^{-3}$ . Thermally stimulated luminescence response of yttria was observed at temperature around  $150^\circ\text{C}$  and wavelength  $\lambda=550\text{nm}$ . The emission of light in visible spectra is new in literature, considering that yttria has been used as matrix for others rare earth activator ions which exhibit visible luminescence. Therefore, complementary characterizations will be performed in order to understand this behavior.

#### 5. ACKNOWLEDGMENTS

We authors are deeply grateful to Dr. Wilson Acchar, Dr. Francisco Braga, Dr. Thomaz Augusto Restivo, Dr. Linda Caldas, Dr. Maira Tiemi Yoshizumi, MSc. Douglas Will Leite, and MSc. William Naville. In addition, grant #2014/23621-3, São Paulo Research Foundation (FAPESP), National Council for Scientific and Technological Development (CNPq), and Coordination for Improvement of High Degree People (CAPES).

#### 6. REFERENCES

- [1] M. Marina, M. Z. M. Zamzuri, M. N. Derman, M. A. Selamat, and Z. Nooraizedfiza, "Comparison Study in Consolidation of Yttria Reinforced Iron-Chromium Composites using Conventional and Microwave Sintering Technique," *Advanced Materials Engineering and Technology Ii*, vol. 594-595, pp. 832-836, 2014.
- [2] F. Hayashi, M. Tanaka, D. M. Lin, and M. Iwamoto, "Surface structure of yttrium-modified ceria catalysts and reaction pathways from ethanol to propene," *Journal of Catalysis*, vol. 316, pp. 112-120, Jul 2014.
- [3] X. M. Han, X. Feng, X. W. Qi, X. Q. Wang, and M. Y. Li, "The Photoluminescent Properties of  $\text{Y}_2\text{O}_3:\text{Bi}^{3+}$ ,  $\text{Eu}^{3+}$ ,  $\text{Dy}^{3+}$  Phosphors for White-Light-Emitting Diodes," *Journal of Nanoscience and Nanotechnology*, vol. 14, pp. 3387-3390, May 2014.
- [4] A. Jyotsana, G. S. Maurya, A. K. Srivastava, A. K. Rai, and B. K. Ghosh, "Synthesis and electrical properties of  $\text{Y}_2\text{O}_3:\text{Dy}^{3+}$  &  $\text{Eu}^{3+}$  nanoparticles," *Applied Physics a-Materials Science & Processing*, vol. 117, pp. 1269-1274, Nov 2014.
- [5] T. Mongstad, A. Thogersen, A. Subrahmanyam, and S. Karazhanov, "The electronic state of thin films of yttrium, yttrium hydrides and yttrium oxide," *Solar Energy Materials and Solar Cells*, vol. 128, pp. 270-274, Sep 2014.
- [6] M. A. Auger, V. de Castro, T. Leguey, J. Tarcisio-Costa, M. A. Monge, A. Munoz, *et al.*, "Effect of yttrium addition on the microstructure and mechanical properties of ODS RAF steels," *Journal of Nuclear Materials*, vol. 455, pp. 600-604, Dec 2014.

- [7] J. Hostasa, J. Matejcek, B. Nait-Ali, D. S. Smith, W. Pabst, and L. Esposito, "Thermal Properties of Transparent Yb-Doped YAG Ceramics at Elevated Temperatures," *Journal of the American Ceramic Society*, vol. 97, pp. 2602-2606, Aug 2014.
- [8] M. A. Yar, S. Wahlberg, M. O. Abuelnaga, M. Johnsson, and M. Muhammed, "Processing and sintering of yttrium-doped tungsten oxide nanopowders to tungsten-based composites," *Journal of Materials Science*, vol. 49, pp. 5703-5713, Aug 2014.
- [9] X. B. Li, Q. Q. Zhang, S. Y. Ma, G. X. Wan, F. M. Li, and X. L. Xu, "Microstructure optimization and gas sensing improvement of ZnO spherical structure through yttrium doping," *Sensors and Actuators B-Chemical*, vol. 195, pp. 526-533, May 2014.
- [10] F. B. Vetrone, J.-C.; Capobianco, J. A., *Luminescence, Optical Spectroscopy and Applications of Rare Earth Doped Y2O3 Nanocrystals*. vol. 2: Inorganic Display Materials. Stevenson Ranch, CA: American Scientific Publishers, 2003.
- [11] L. Zhang, D. Y. Jiang, J. F. Xia, C. X. Li, N. Zhang, and Q. Li, "Novel luminescent yttrium oxide nanosheets doped with Eu<sup>3+</sup> and Tb<sup>3+</sup>," *Rsc Advances*, vol. 4, pp. 17648-17652, 2014.
- [12] J. Reed, *Principles of Ceramics Processing*, 2 ed. vol. 1. New York: John Wiley & Sons, 1995.
- [13] H. R. Hoekstra and K. A. Gingerich, "High-Pressure B-Type Polymorphs of Some Rare-Earth Sesquioxides," *Science*, vol. 146, pp. 1163-&, 1964.
- [14] V. Gourlaouen, G. Schnedecker, A. M. Lejus, M. Boncoeur, and R. Collongues, "Metastable Phases in Yttrium-Oxide Plasma Spray Deposits and Their Effect on Coating Properties," *Materials Research Bulletin*, vol. 28, pp. 415-425, May 1993.
- [15] A. Navrotsky, L. Benoist, and H. Lefebvre, "Direct calorimetric measurement of enthalpies of phase transitions at 2000 degrees-2400 degrees C in yttria and zirconia," *Journal of the American Ceramic Society*, vol. 88, pp. 2942-2944, Oct 2005.
- [16] X. Qin, Y. G. Ju, S. Bernhard, and N. Yao, "Flame synthesis of Y2O3 : Eu nanophosphors using ethanol as precursor solvents," *Journal of Materials Research*, vol. 20, pp. 2960-2968, Nov 2005.
- [17] E. J. Guidelli and O. Baffa, "Influence of photon beam energy on the dose enhancement factor caused by gold and silver nanoparticles: An experimental approach," *Medical Physics*, vol. 41, Mar 2014.
- [18] R. S. Meltzer, W. M. Yen, H. R. Zheng, S. P. Feofilov, and M. J. Dejneka, "Relaxation between closely spaced electronic levels of rare-earth ions doped in nanocrystals embedded in glass," *Physical Review B*, vol. 66, Dec 1 2002.
- [19] V. A. Bolshukhin, N. P. Soshchin, V. N. Lichmanova, and A. D. Azarov, "Effect of dispersion on optical-physical parameters of luminescence," in *Proceedings of the International Conference on Nanotechnology*, 2004, pp. 202-206.
- [20] V. Dubey, R. Tiwari, R. K. Tamrakar, G. S. Rathore, C. Sharma, and N. Tiwari, "Infrared spectroscopy and upconversion luminescence behaviour of erbium doped yttrium (III) oxide phosphor," *Infrared Physics & Technology*, vol. 67, pp. 537-541, Nov 2014.
- [21] Q. Z. Duan, Q. H. Yang, S. Z. Lu, C. Jiang, Q. Lu, and B. Lu, "Fabrication and properties of Er/Tm/Pr tri-doped yttrium lanthanum oxide transparent ceramics," *Journal of Alloys and Compounds*, vol. 612, pp. 239-242, Nov 5 2014.
- [22] C. de Mayrinck, D. P. Santos, S. J. L. Ribeiro, M. A. Schiavon, and J. L. Ferrari, "Reassessment of the potential applications of Eu<sup>3+</sup>-doped Y2O3 photoluminescent material in ceramic powder form," *Ceramics International*, vol. 40, pp. 15965-15971, Dec 2014.
- [23] R. Balderas-Xicohtencatl, R. Martinez-Martinez, Z. Rivera-Alvarez, J. Santoyo-Salazar, and C. Falcony, "Photo and cathodoluminescence characteristics of dysprosium doped yttrium oxide nanoparticles prepared by Polyol method," *Journal of Luminescence*, vol. 146, pp. 497-501, Feb 2014.

- [24] G. Alarcon-Flores, M. Garcia-Hipolito, M. Aguilar-Frutis, S. Carmona-Tellez, R. Martinez-Martinez, M. P. Campos-Arias, *et al.*, "Luminescent and Structural Characteristics of Y<sub>2</sub>O<sub>3</sub>:Tb<sup>3+</sup> Thin Films as a Function of Substrate Temperature," *Ecs Journal of Solid State Science and Technology*, vol. 3, pp. R189-R194, 2014.
- [25] S. Abe, Y. Hamba, A. Hyono, S. Yamagata, M. Uo, J. Iida, *et al.*, "Preparation and biocompatibilities of luminescent europium-doped yttria and titania nanoparticles," *Journal of the Ceramic Society of Japan*, vol. 122, pp. 216-221, Mar 2014.
- [26] M. Raukas, A. Konrad, and K. C. Mishra, "Luminescence in nano-size Y<sub>2</sub>O<sub>3</sub>:Ce," *Journal of Luminescence*, vol. 122–123, pp. 773-775, 2007.