# Photo and radioluminescent $Eu^{3+}$-doped gadolinium hafnates nanoparticles: a candidate to be applied in radiotherapy and X-PDT

Caio Faim Lima [1], Fernanda Hediger Borges [1], Nancy Gabriela Chicango Arcos[2], Éder Guidelli[2] and Rogéria Rocha Gonçalves [1]

[1]*Laboratório de Materiais Luminescentes Micro e Nanoestruturados – Mater Lumen, Departamento de Química, FFCLRP, Universidade de São Paulo, 14040-900, SP, Brazil.*
[2] *Departamento de Física, FFCLRP, Universidade de São Paulo, SP, Brazil.*
*E-mail:* caiofaim@usp.br, rrgoncalves@ffclrp.usp,br

**Thematic Area**: Rare Earths

**Keywords**: Spectroscopy, Radioluminescence, Rare earth.

Recently, $HfO_2$ nanoparticles have emerged as potential candidates for cancer radiotherapy, to decrease the radiation dose used during the treatment [1]. Rare earth (RE) hafnates, however, have received less attention, despite their notable features as excellent thermal conductivity, chemical stability, high melting temperatures, and also high transparency, density (8.92 g/cm³), and effective atomic number, making them potential candidates for scintillator hosts. In this work, we report the synthesis of $Eu^{3+}$ doped $Gd_2Hf_2O_7$ by sol-gel assisted by hydrothermal process (S1) and a polyol mediated methodology (S2) [2] starting from $HfOCl_2.8\ H_2O$ and RE nitrates as precursor, followed by annealing at 900 and 1100°C. The $Eu^{3+}$ content was varied from 0.1 to 5 mol%, while Gd:Hf molar ratio was fixed at 1:1. The crystalline structure was attested by X-ray diffraction, FTIR, and Raman spectroscopies. The stabilization of cubic defect fluorite $Ln_2Hf_2O_7$, belonging to the $Fm\overline{3}m$, was observed for S1, which is also the major crystalline phase in the S2 samples. Monoclinic hafnium oxide and tetragonal rare earth stabilized hafnia was evidenced only as minor secondaries phases. High resolution transmission electron microscopy shows nanoparticles, with cube shape ranging from 10 nm and 20 nm for polyol (S1) and hydrothermal synthesis (S2) respectively (Figure 1). The excitation spectra depict the $Eu^{3+}$ characteristic *f-f* transitions, as well as broadband in the UV range ascribed to the $O^{2-}\rightarrow Eu^{3+}$ charge transfer band. Emission bands in the red region ($^5D_0\rightarrow{}^7F_{0,1,2,3\text{ and }4}$) were observed upon excitation at CT band and intraconfigurational f-f transitions. Intense radioluminescence was observed suggesting potential application for theranostics.

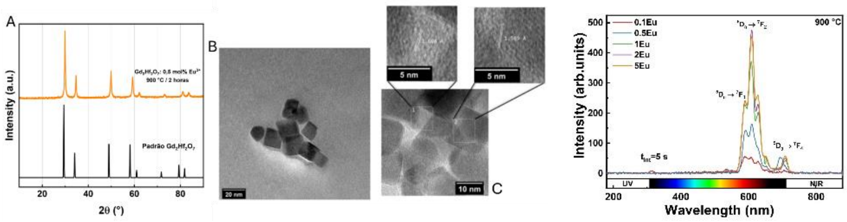


**Fig. 1. (A)** XRD diffractogram for the $Eu^{3+}$ doped gadolinium hafnate by S1. **(B)** HR-TEM for the $Gd_2Hf_2O_7$ sample synthesized by S2 (D) radioluminescence.

**Acknowledgments:** We would like to acknowledge FAPESP, CAPS, CNPQ, and Photonics National Institute for Science and Technology (INFO) for financial support.

## References

[1] Maggiorella, L., Barouch, G., Devaux, C., Pottier, A., Deutsch, E., Bourhis, J., … Levy, L. (2012). Nanoscale Radiotherapy with Hafnium Oxide Nanoparticles. Future Oncology, 8(9), 1167–1181
[2] Martin Nikl 2006 Meas. Sci. Technol. **17** R37