

Belo Horizonte, September 12 - 15th 2024

Advances in the development of special glasses containing rare-earth ions for luminescence thermometry and sensing of volatile organic compounds

<u>Danilo Manzani ¹</u>, Ricardo Baltieri^{1,2}, Renato G. Capelo^{1,3,4}, Henrique F. Fazan¹, Lothar Wondraczek², Frederic Smektala³, Guillermo Orellana⁴, Fernando Maturi⁵, Luís D. Carlos⁵

¹São Carlos Institute of Chemistry (IQSC), University of São Paulo (USP), São Carlos, Brazil ²Friedrich-Schiller Universität Jena, Jena, Germany ³Laboratoire Interdisciplinaire Carnot de Bourgogne, Université de Bourgogne, Dijon, France ⁴GSOLFA, Universidad Complutense de Madrid, Madrid, Spain ⁵Phantom-g, Department of Physics, University of Aveiro, Aveiro, Portugal E-mail:<u>dmanzani@usp.br</u>

Thematic Area: Material Chemistry

Keywords: special glasses, optical sensors, luminescence

Recent advancements in the development of optical glasses co-doped with lanthanide ions (Ln) have opened new avenues for luminescence thermometry and sensing of volatile organic compounds (VOCs). In this work, we studied the unique tunable properties of different oxyfluoride glasses, focusing on compositions co-doped with Er³⁺/Yb³⁺ (NaPO₃-AIF₃-BaF₂-CaF₂) and Pr³⁺/Yb³⁺ (LiPO₃-YF₃-SrF₂-CaF₂). These materials exhibited high performance as luminescent primary thermometers relying on the thermally coupled levels of Er^{3+} and Pr^{3+} , with relative thermal sensitivity between 0.3-1.5 % K^{-1} and temperature uncertainty around 0.5 K at a given temperature, making them competitive with existing luminescent thermometers and promising for cost-effective, accurate temperature probes. The prepared glasses demonstrated excellent resistance to crystallization and possess a broad transparency window extending from the UV to the infrared range (300 to 4000 nm). We also explored the influence of Ln concentration, particularly at higher Yb³⁺ content in the NaPO₃-AlF₃-BaF₂-CaF₂ composition, showing the potential to tune Er^{3+} emission wavelengths and temperature responses. Additionally, to design multifunctional glass platforms, we combined Ln-MOF with tellurite and fluorotellurite glass compositions for VOCs sensing. The glasses were prepared by conventional meltquenching method, while the Ln-MOFs were synthesized via microwave-assisted hydrothermal methods, with EuCl₃ and 1,3,5-benzene tricarboxylic or 1,2,4,5-benzene tetracarboxylic acids as precursors. The glass pieces were immersed in the reactive medium inside the reactor chamber. This process was also used to functionalize the end of a single-index tellurite optical fiber. The glass@Ln-MOF composites and Ln-MOFs ($[Eu(BTC)]_n$ and $[Eu(B_4C)]_n$) were characterized by XRD, SEM, and photoluminescence (PL). The TZN@[Eu(BTC)] composite and fiber were exposed to different VOCs carried by N_2 , with PL measurements acquired in real-time at varying concentrations. Notably, in the presence of acetone and dimethylformamide, a 15-fold luminescence enhancement was observed for the ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition of Eu³⁺, exhibiting intense luminescence under UV light and high sensitivity to acetone, hydrocarbons, and dimethylformamide. In summary, this work highlights significant advances in integrating Ln into optical glasses, enhancing luminescence thermometry and chemical sensing. The development of these materials contributes to photonic technologies and sensing applications, offering high stability, tunable optical properties, and straightforward synthesis procedures.

Acknowledgments: These works were developed within the scope of the projects FAPESP (2023/05594-6, 2023/02179-0, 2023/16047-8, 2022/15958-4, 2020/12280-1), CNPq 405048/2021-1.