$ZnGa_2O_4$ SPINEL NANOPHOSPHORS WITH PERSISTENT LUMINESCENCE FOR BIOIMAGING

Vilius Čirgelis[1,2], Simona Streckaitė[1], Vitalii Boiko[3], Lena Golubewa[1], Vidas Pakštas[1], Mariusz Stefanski[3], Dariusz Hreniak[3], Vidmantas Gulbinas[1]

[1]Center for Physical Sciences and Technology, Sauletekio Ave. 3, 10257 Vilnius, Lithuania
[2]Vilnius University, Faculty of Physics, Sauletekio Ave. 9, 10222 Vilnius, Lithuania
[3]Polish Academy of Sciences, Institute of Low Temperature and Structure Research, Okolna 2, 5-422 Wroclaw, Poland
vilius.cirgelis@ftmc.lt

Zinc gallium oxide ($ZnGa_2O_4$, ZGO) is a cubic spinel-structured oxide that has attracted interest for applications in optoelectronics [1], plasmonics [2] and biomedicine [3]. ZGO is chemically stable, inert to oxygen and humidity, and biocompatible, making it promising phosphor for applications, like bio-imaging and theranostic [4]. In ZGO lattice, Zn2+ occupies tetrahedral sites and Ga3+ occupies octahedral sites. Since chemical synthesis is entropy driven process, partial cation inversion can occur, where a fraction of Zn2+ occupies octahedral and a fraction of Ga3+ occupies tetrahedral positions, forming antisite defects. Antisites introduce trap states that capture charge carriers and hinder their recombination, enabling long-lived energy storage of excitation energy on timescales from hours to days [5]. The delayed photon emission, occurring from exciton recombination is called persistent luminescence (PersL). PersL is advantageous for in vivo bioimaging because the material can be pre-charged ex vivo and subsequently injected into organism, allowing imaging without continious excitation, thereby reducing tissue autofluorescence and minimizing phototoxicity and thermal damage [6]. ZGO optical properties can be altered by introduction of rare-earth ions into the lattice. Emission from Cr^{3+} and Yb^{3+} overlaps with the first and second biological windows—spectral ranges where tissue absorption and scattering are relatively low—enabling efficient deep-tissue imaging.

In this study, Cr^{3+} doped $ZnGa_2O_4$ was synthesized hydrothermally from aqueous solutions of $Zn(NO_3)_2$, $Ga(NO_3)_3$, and $Cr(NO_3)_3$. Stoichiometric amounts of the metal-nitrate precursors were combined and the pH was adjusted to 8 using NH_4OH. The mixture was transferred to a Teflon-lined vessel and sealed in a stainless-steel autoclave for hydrothermal treatment at 200 °C for 24 h. The resulting powder was washed with water and ethanol, dried for 24 h, and annealed at temperatures between 200 °C and 900 °C for 3 hours. The structural and optical properties of ZGO:Cr^{3+} were characterized by X-ray diffraction (XRD), steady-state and time-resolved photoluminescence (PL), thermoluminescence, and diffuse reflectance spectroscopy.

XRD measurements confirm that the synthesized $ZnGa_2O_4$ materials crystallize in the cubic spinel structure. With increasing annealing temperature, the diffraction peaks become narrower, indicating improved crystallinity and crystallite growth (i.e., reduced microstrain/defect-related broadening) over the range from 0 to 800 °C. At 800 °C, the XRD pattern matches that of the pre-annealed sample, indicating phase transition. The highest steady-state PL intensity is observed for ZGO:Cr^{3+} with 1.00 mol% Cr^{3+}, whereas the longest persistent-luminescence decay is obtained for the 0.25 mol% Cr^{3+}-doped sample. As ongoing work, ZGO:Yb^{3+} samples will be characterized using the same set of techniques.

Acknowledgements
This research was funded by Polish-Lithuanian research project DAINA-3, agreement No [S-LL-24-11].

Keywords: Spinels, persistent luminescence

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