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Zinc gallium oxide nanocrystals doped with Cr^{3+} and Yb^{3+} for persistent luminescence bioimaging

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

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

Zinc gallium oxide ($ZnGa_2O_4$, ZGO) is a cubic spinel-structured oxide that has recently attracted considerable interest for various photonic applications [1]. Owing to its chemical stability, resistance to oxidation and humidity, and biocompatibility, ZGO is a promising phosphor material for bioimaging applications [2]. In the ZGO lattice, Zn^{2+} ions occupy tetrahedral sites, while Ga^{3+} ions occupy octahedral sites. During the synthesis, partial cation inversion may occur. In this case, a fraction of Zn^{2+} ions occupy octahedral sites, while a fraction of Ga^{3+} ions occupy tetrahedral sites, leading to the formation of antisite defects [3]. Antisite defects act as charge traps, storing excitation energy from hours to days and enabling delayed emission known as persistent luminescence (PersL). Persistent luminescence is particularly advantageous for *in vivo* bioimaging because the material can be pre-charged *ex vivo* and subsequently injected into an organism. This allows imaging without continuous laser excitation, reducing tissue autofluorescence, minimizing phototoxicity and thermal damage. Additional doping with Cr^{3+} and Yb^{3+} can tune ZGO emission to the first (700-900 nm) and second (1000-1700 nm) biological windows, which are characterized by low tissue absorption and scattering, enabling deep-tissue imaging.

In the current study, Cr^{3+}- and Yb^{3+}-doped and Cr^{3+}/Yb^{3+} co-doped $ZnGa_2O_4$ nanoparticles (NPs) were synthesized hydrothermally from metal nitrate precursors at pH 8 and 200 °C for 24 h. The NPs were collected via ultracentrifugation, washed, dried, and annealed at 200–900 °C for 3 h. The structural and optical properties of ZGO:Cr^{3+} were investigated using X-ray diffraction (XRD), steady-state and time-resolved photoluminescence (PL), thermoluminescence, and diffuse reflectance spectroscopy.

XRD analysis confirmed the formation of the cubic spinel structure in the synthesized $ZnGa_2O_4$ materials. With increasing annealing temperature, the diffraction peaks became narrower, indicating improved crystallinity, crystallite growth, and reduced microstrain or defect-related broadening up to 800 °C. At 800 °C, the XRD pattern closely matched that of the pre-annealed sample, suggesting a structural phase transformation or significant crystallinity improvement. The highest steady-state PL intensity was observed for the 1.00 mol% Cr^{3+}-doped ZGO. In contrast, the longest persistent-luminescence decay was obtained for the 0.25 mol% Cr^{3+}-doped sample, indicating that the optimal Cr^{3+} concentration for steady-state emission intensity does not necessarily coincide with the optimal concentration for persistent luminescence.

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