Luminescence Mechanisms in Cr^{3+}-doped $(Ga_{1-x-y}In_xAl_y)_2O_3$ and $Li(Ga_{1-x-y}In_xAl_y)_5O_8$ Alloys: Insights from the Electronic Structure Calculations

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The simultaneous alloying of gallium oxide and lithium-gallium spinel crystals with In and Al oxides, is of great interest as it potentially opens greater possibilities for tailoring the physical properties of the materials [1]. When activated with Cr^{3+} ions, such compounds produce a broad and efficient near-infrared emission suitable for tunable lasers, dosimeters, pressure and temperature sensors. This report presents application of the DFT-based electronic structure calculations of $(Ga_{1-x-y}In_xAl_y)_2O_3$ and $Li(Ga_{1-x-y}In_xAl_y)_5O_8$ alloys in task of elucidation of the mechanisms of Cr^{3+}-related luminescence in such hosts. Results of the calculations are compared to experimental data on XRD structural analysis, diffuse reflectance and TSL glow curves obtained for corresponding sets of experimental samples synthesized within the same range of x and y.

The electronic structure calculations were performed using the DFT-based band-periodic pseudopotential method implemented in CASTEP program within the supercell approach. The number of In_{Ga} and Al_{Ga} substitutions were selected to maintain the x and y values as closer as possible to their values in experimental samples. For each combination of x and y, 10 structures were generated with random distributions of In_{Ga} and Al_{Ga} substitutions. All structures were subjected to geometrical optimization and the total energies were calculated for each configuration using GGA-PBE approximation. Subsequently, optical spectra were calculated only for the structures with the lowest total energy for each x and y. To overcome the underestimation of the ban gap energies by PBE functional, the band-to-band absorption spectra were calculated using the GGA + U approach.

The calculations confirmed that the tetrahedral Ga^{3+} lattice positions in the monoclinic β-$(Ga_{1-x-y}In_xAl_y)_2O_3$ are preferentially substituted by Al^{3+} ions, rather than In^{3+} ones. In turn, in the $Li(Ga_{1-x-y}In_xAl_y)_5O_8$ spinel structures the Al^{3+} ions prefer to occupy octahedral position (at least up to 50% of Al with respect to Ga), whereas larger In^{3+} cations mainly occupy Ga tetrahedral site. The calculations of the optical spectra of the lowest-energy $(Ga_{1-x-y}In_xAl_y)_2O_3$ and $Li(Ga_{1-x-y}In_xAl_y)_5O_8$ structures allowed to evaluate the behavior of the optical band gap depending on the cation composition of the compounds.

The results presented in this work clearly demonstrate the possibility of engineering the band gap and crystal structure of the Ga_2O_3 and $LiGa_5O_8$ hosts by adding Al or/and In. This in its turn allows for efficient tuning and improvement of the luminescence properties of the Cr^{3+}-doped monoclinic gallium oxide and lithium-gallium spinel phosphors.

1. L. Vasylechko, et al., "Tuning of crystal structure and electronic band gap of the monoclinic Ga_2O_3 by simultaneous alloying with Al_2O_3 and In_2O_3" *Scientific Reports* **15**, 37128 (2025).

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