$GdAlO_3:Er^{3+},Yb^{3+}$ upconversion phosphor: a photonic approach to anti-counterfeiting inks

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Photonic materials have emerged as promising luminescent inks to combat counterfeiting, which affects various sectors of society, including industries, governments, and consumers. Traditional downshifting phosphors excited by UV radiation exhibit limitations, including potential health risks. A safer alternative involves upconversion (UC) phosphors doped with Ln^{3+} ions, excited by infrared (IR) radiation. The materials emit tunable colors and are harder to replicate [1]. In this context, the perovskite-type phosphor $Gd_{1-0.01-x}AlO_3$ (GAP):$Er_{0.01}Yb_x$ (x = 0.01, 0.03, 0.05, and 0.10) was synthesized via urea combustion [2] to assess the effect of Yb^{3+} sensitizer ion concentration for use application in luminescent inks. A urea solution (metal:urea molar ratio of 1:0.85) was added to metal nitrates solution and heated at 80 °C until forming a transparent fluid. This was heated at 600 °C for 12 min, producing a white foam, then calcined at 1100 °C for 3 h. XRD and Rietveld refinement confirmed all samples exhibited the orthorhombic $GdAlO_3$ phase. FTIR spectra showed ν_{M-O} and δ_{M-O} vibrational modes (450–700 cm^{-1}), and a ν_{Al-O} band (750–850 cm^{-1}). The absence of $\nu_{OC=O}$ band at 1635 cm^{-1} confirmed complete combustion. Emission spectra under 980 nm laser (1.5 W) excitation displayed characteristic Er^{3+} bands: 412 nm (violet, $^2P_{3/2}\rightarrow{}^4I_{13/2}$); 488 (blue, $^2P_{3/2}\rightarrow{}^4I_{11/2}$); 529,544 nm (green, $^2H_{11/2}$,$^4S_{3/2}\rightarrow{}^4I_{15/2}$); and 658 nm (red, $^4F_{9/2}\rightarrow{}^4I_{15/2}$). Kinetic measurements showed that increasing Yb^{3+} concentration reduced lifetimes from ~0.30 to 0.10 ms throughout the series, with red emissions consistently displaying shorter values among the others. GAP:$Er_{0.01}Yb_{0.03}$ exhibited the highest green-to-red emission ratio and intermediate lifetimes (0.21–0.25 ms), indicating efficient energy transfer and making it the most promising composition for polymer-based upconversion inks in anti-counterfeiting applications.

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References

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