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Effect of Na^+ co-doping concentration on the luminescence and crystalline phase in Eu^{3+} doped gadolinium niobates

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Rare earth niobate compounds are renowned for their properties, including low phonon frequencies, higher dielectric constants, self-activating luminescence, and nonlinear optical characteristics. When doped with Eu^{3+} ions, they have been highlighted in the literature as promising nanoprobes for multimodal bioimaging and photodynamic therapy [1]. This study focuses on the synthesis of Na^+ and Eu^{3+} co-doped gadolinium niobate nanoparticles by a classical sol gel route and a polyol mediated methodology [2], starting from niobium ethoxide and rare earth nitrate as precursor followed by thermal annealing at 900 and 1100 °C. The Na^+ content was varied from 0.5 mol% to 5 mol%, while Eu^{3+} was fixed a 0.5 mol%. The influence of Na^+ ion co-doping on both the structural and luminescent properties of these compounds was systematically evaluated, as well as the synthetic routes. Crystallization of Gd_3NbO_7 and $GdNbO_4$ was observed by X-ray diffraction (XRD), with cubic and monoclinic phases respectively, depending on the dopant concentration and annealing temperature. By classical sol-gel route, in most of samples, both phases crystallize. However, the stabilization of pure cubic Gd_3NbO_7 phase at 900 °C at lower Na^+ concentration (0.1 to 0.5 mol%) occurs, while pure monoclinic $GdNbO_4$ phase is formed when the temperature and concentration increase to 1100 °C and 5.0 mol% Na^+. Transmission electron microscopy (TEM) evidenced a nanostructured material with presence of aggregates. On the other hand, Na^+ and Eu^{3+}-co-doped Gd_3NbO_7 nanoparticles were synthesized by refluxing the precursors in ethyleneglycol (EG), followed by annealing at 900 °C and 1000 °C. Phase purity and stabilization were observed by X-ray diffraction (XRD) analysis, affording the cubic Gd_3NbO_7 crystalline phase, even increasing the Na^+ concentration from 2 to 7 mol% and Eu^{3+} from 0.5 to 1.0 mol%. Photoluminescence spectroscopy was investigated using Eu^{3+} as a structural probe. Through selective excitation (in the CT band or f-f transitions), an inhomogeneous broadening is observed in the emission spectra for the Eu^{3+} in the cubic fluorite-related Gd_3NbO_7 lattice, due to the structural disorder, whereas better-resolved emission profile appears when Eu^{3+} in GdNbO4 is excited. Apart from the emission from $^5D_0$, samples show contribution from the ^5D_J (J = 1, 2, and 3) manifolds, attesting to the low phonon energy of the gadolinium niobate host. This structural and spectroscopic investigation will serve as the foundation for preparing materials doped with Pr^{3+} ions as well as understanding the effect of Na^+ ions on their structure and persistent luminescence features.

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