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## Structural and Optical Investigations of $\text{Tm}^{3+}/\text{Yb}^{3+}$ Doped Yttrium Pyrogermanate for Blue and NIR Upconversion

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The rare-earth germanates has attracted significant attention due to their remarkable thermal stability, low phonon energy, and structural flexibility, making them promising hosts for rare-earth ion doping in photonic and optoelectronic applications. Yttrium pyrogermanate ( $\text{Y}_{20}\text{Ge}_2\text{O}_{72}$ ) phosphors were synthesized via the solid-state reaction method and doped with  $\text{Tm}^{3+}$  and  $\text{Yb}^{3+}$  ions to investigate their structural and optical properties for potential upconversion (UC) applications. The focus was on evaluating how co-doping with  $\text{Yb}^{3+}$  enhances the blue/NIR emission of  $\text{Tm}^{3+}$  under near-infrared 980 nm excitation.

Powder X-ray diffraction confirmed the formation of the tetragonal  $\text{P4}_1\text{2}_1$  phase for both undoped and doped samples, with no secondary phases detected. Field emission scanning electron microscopy revealed irregularly shaped particles with average grain sizes of around 1  $\mu\text{m}$ , forming agglomerated clusters typical of solid-state reaction prepared materials. The diffuse reflectance revealed absorption bands around 452 nm ( $\text{H}_{6\text{H}} \rightarrow \text{G}_{4\text{H}}$ ), 684 nm ( $\text{H}_{6\text{H}} \rightarrow \text{F}_{3\text{H}}$ ) and 797 nm ( $\text{H}_{6\text{H}} \rightarrow \text{H}_{4\text{H}}$ ) of  $\text{Tm}^{3+}$  ions, as well as and 980 nm ( $\text{F}_{7/2} \rightarrow \text{F}_{5/2}$ ) of  $\text{Yb}^{3+}$  ions, confirming successful doping. A notable red-shift in the absorption edge was observed in the co-doped sample.

The photoluminescence measurements excited at 355 nm exhibited characteristic blue emission at ~453 nm ( $\text{D}_{2\text{H}} \rightarrow \text{F}_{4\text{H}}$ ) and weaker red and NIR bands at 650 nm ( $\text{G}_{4\text{H}} \rightarrow \text{F}_{4\text{H}}$ ) and 792 nm ( $\text{H}_{4\text{H}} \rightarrow \text{H}_{6\text{H}}$ ) of  $\text{Tm}^{3+}$  ions. Upconversion studies under 980 nm excitation showed weak blue emission at ~475 nm ( $\text{G}_{4\text{H}} \rightarrow \text{H}_{6\text{H}}$ ) and a strong NIR emission at ~797 nm ( $\text{H}_{4\text{H}} \rightarrow \text{H}_{6\text{H}}$ ). Notably, co-doping with 2%  $\text{Yb}^{3+}$  enhanced the UC emission intensity considerably compared to the singly doped sample, confirming efficient energy transfer from  $\text{Yb}^{3+}$  to  $\text{Tm}^{3+}$  ions. This enhancement is attributed to two-photon and three-photon energy transfer upconversion (ETU) mechanisms responsible for NIR and blue emissions, respectively, with  $\text{Yb}^{3+}$  ions acting as effective sensitizer. These findings demonstrate the potential of rare-earth doped pyrogermanate phosphors as promising candidates for UC-based applications.

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