

# Photoluminescence enhancement of Mn<sup>2+</sup> via Ti<sup>4+</sup> co-doping in calcium hexaaluminate phosphor

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Mn<sup>2+</sup>-doped green phosphors are gaining attention as a sustainable and cost-effective alternative to rare-earth-based materials for applications such as white LEDs (W-LEDs), optical temperature sensing, and persistent luminescence (PersL) materials. Typically, achieving strong Mn<sup>2+</sup> luminescence requires either synthesis under a reducing atmosphere or sensitization using rare-earth ions.

In this study, we investigate the effect of co-doping CaAl<sub>12</sub>O<sub>19</sub>:Mn phosphor with tetravalent Ti<sup>4+</sup> on its optical properties. Our results demonstrate that such co-doping strategy significantly enhances the intensity of green Mn<sup>2+</sup> emission.

Spectroscopic analysis shows that CaAl<sub>12</sub>O<sub>19</sub>:Mn synthesized under ambient air exhibits green Mn<sup>2+</sup> emission at 520 nm and red Mn<sup>4+</sup> emission at 655 nm under visible-light excitation. Co-doping with Ti<sup>4+</sup> significantly enhances the Mn<sup>2+</sup> green emission intensity, leading to more than a tenfold enhancement. Ti<sup>4+</sup> co-doping completely suppresses Mn<sup>4+</sup> emission, resulting in a bright green phosphor with a single emission band and PLQY of 65%, achieved without the need for reducing synthesis conditions. The enhanced emission is primarily attributed to the suppression of non-radiative energy transfer from Mn<sup>2+</sup> to Mn<sup>3+</sup>/Mn<sup>4+</sup> quenching centers. The reduction of Mn<sup>3+</sup> and Mn<sup>4+</sup> to Mn<sup>2+</sup> oxidation state has been confirmed by the diffuse reflectance spectroscopy. EPR studies have demonstrated that Mn<sup>2+</sup> occupies single tetrahedral site and its concentration increases upon co-doping with Ti<sup>4+</sup>.

Overall, this study establishes co-doping with Ti<sup>4+</sup> as a viable approach for controlling manganese oxidation states in CaAl<sub>12</sub>O<sub>19</sub> to achieve bright green photoluminescence.

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