

Luminescence and Scintillation Properties of Nonstoichiometrically Engineered YAG:Pr Transparent Ceramics

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YAG:Pr crystals are commonly used scintillators in radiation detection due to their good light yield typically around 18 000 photons/MeV and a fast scintillation response on the order of 20-30 ns [1]. Ceramic scintillators offer lower cost, higher homogeneity, and greater compositional flexibility, including nonstoichiometric tuning, compared to single crystals. A key advantage of ceramic processing is the possibility of nonstoichiometric engineering, enabling intentional deviation from the stoichiometric $Y_3Al_5O_{12}$ garnet composition. Upon yttrium excess (Y-rich condition), antisite defects form (Y in Al coordination, Y_{Al}^x). Under yttrium-deficient (Al-rich condition), YAG tends to form Al in Y coordination, (Al_Y^x) and Y vacancies ($V_Y^{\prime\prime}$) [2]. Nonstoichiometry allows control over the local coordination environments of activator ions, directly influencing luminescence mechanism. As demonstrated by Wang et al, nonstoichiometry can switch the emission color by modifying coordination environments – $Y_{3.2}Al_{4.8}O_{12}$ doped with Yb^{3+} and Er^{3+} emits green light compared to the red emission of stoichiometric $Y_3Al_5O_{12}$ with the same dopants [3]. Furthermore, certain nonstoichiometric garnets exhibit improved thermal stability and enhanced luminous efficacy, making them attractive for high-temperature applications. For instance, nonstoichiometric $Y_{2.955}Ce_{0.03}Nd_{0.0135}Al_5O_{12}$ demonstrated a luminous efficacy of approximately 200 lm/W with thermal stability up to 680 K, exceeding ~130 lm/W and 380 K of the stoichiometric YAG:Ce [4].

Nonstoichiometric Y deficiency introduces Y-site vacancies that distort the local crystal field and increase lattice disorder, reshaping Pr^{3+} 5d¹ levels and broadening trap-depth distributions. The associated Pr^{3+} segregation and reduced local symmetry suppress self-absorption while strengthening charge trapping, improving energy delivery to Pr^{3+} centers and enabling higher scintillation light yield with tailored decay kinetics.

In this work, the strategy of nonstoichiometric engineering was applied to $Y_{3-x}Al_5O_{12}:Pr^{3+}$ (x = 1, 3, 5, 7, and 10%) transparent garnet ceramics. It was shown that the photoluminescence excitation and emission spectra of Pr^{3+} ions were slightly affected by nonstoichiometric engineering. In contrast, scintillation performance showed pronounced improvement: the light yield increased by approximately 42%, and the slow decay component accelerated from ~780 ns to ~340 ns compared with stoichiometric YAG:Pr ceramics.

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3. W. Cao *et al.*, “Highly nonstoichiometric YAG ceramics with modified luminescence properties,” *Advanced Functional Materials*, **33**, 10.1002/adfm.202213418 (2023).
4. K. Bartosiewicz *et al.*, “Energy-Transfer Processes in Nonstoichiometric and Stoichiometric Er^{3+} , Ho^{3+} , Nd^{3+} , Pr^{3+} , and Cr^{3+} -Codoped Ce:YAG Transparent Ceramics: Toward High-Power and Warm-White Laser Diodes and LEDs,” *Phys. Rev. Applied*, **20**, 014047 (2023).