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Thermally stable photoluminescence and long persistent luminescence of Ca₃Ga₄O₉:Tb³⁺/Zn²⁺

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Abstract: A green long persistent luminescence (LPL) phosphor $Ca_3Ga_4O_9:Tb^{3+}/Zn^{2+}$ was prepared. $Ca_3Ga_4O_9$ matrix exhibits blue self-activated LPL due to the creation of intrinsic traps. When Tb^{3+} is doped, the photoluminescence (PL) and LPL colors change from blue to green with their intensities significantly enhanced. The doping of Zn^{2+} evidently improve the PL and LPL performances of the $Ca_3Ga_4O_9$ matrix and $Ca_3Ga_4O_9:Tb^{3+}$. The thermoluminescence (TL) spectra show that a successive trap distribution is formed by multiple intrinsic traps with different depths in the $Ca_3Ga_4O_9$ matrix, and the incorporation of Tb^{3+} and Zn^{2+} effectively increases the densities of these intrinsic traps. The existence of a successive trap distribution makes the $Ca_3Ga_4O_9:Tb^{3+}/Zn^{2+}$ phosphor exhibit thermally stable PL and LPL. It is indicated that this phosphor shows great promise for the application such as high-temperature LPL phosphor.

Keywords: self-activated; long persistent luminescence; successive trap distribution; thermal stability; rare earths

1. Introduction

As typical optical-storage materials, long persistent luminescence (LPL) phosphors can store charge carriers (electrons and holes) under the excitation at UV or sunlight and then subsequently release at room temperature (~ 25-27 °C), owing to the suitable trapping depth. They have attracted extensive attention in multiple fields because of their broad applications, such as safety signage, night-vision surveillance, and decoration ^[1–8]. Especially, after the SrAl₂O₄:Eu²⁺/Dy³⁺ phosphor was discovered in 1996, the enthusiasm of the researchers has been greatly stimulated ^[9,10]. However, the process in developing excellent LPL phosphors is quite tortuous due to the lack of effective strategy. Up to now, the trial and error method is still dominant ^[11,12], which leads to much consumption in the time. Hence, the use of more effective methods is necessary and meaningful. Because the LPL property is strictly dependent on the generation of suitable traps, simplifying the design with self-activated LPL phosphor as a matrix to effectively realize LPL property seems feasible and meaningful. Recently, alkaline earth metal gallate compounds have received great attention because of low synthesis temperature and high stability^[13]. Besides, such compounds tend to exhibit self-activated LPL behavior owing to their special structure and semiconducting properties^[14]. Hence, alkaline earth metal gallate compounds are definitely ideal candidates as LPL phosphor matrix.

Moreover, considering the high sensitivity of the human eye to green light ^[15], the development of green LPPs is exceedingly meaningful for practical applications. As a rare earth ion, Tb^{3+} usually presents excellent green luminescence due to the 4f inter-transition ${}^{5}\text{D}_{4} \rightarrow {}^{7}\text{F}_{J}$ (J = 6, 5, 4, 3)^[16-18]. More importantly, the radius and ionization potential of Tb^{3+} are also appropriate for matching the alkaline earth metal ions. It implies that Tb^{3+} is easily introduced into the lattice to replace alkaline earth ions

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