Wide band long persistent luminescence of $Ca_3Ga_2Ge_3O_{12}$: Tb^{3+}, Tm^{3+} phosphor with synergistic effect of different traps

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ABSTRACT

The as-prepared $Ca_{3-x-y}Ga_2Ge_3O_{12}$ (CGGO): xTb^{3+}, yTm^{3+} phosphors exhibit a color-tunable long persistent luminescence (LPL) after the near-ultraviolet irradiation. Our results indicate that the shallow traps act as not only the trapping centers but also the bridge that contributes to the release of the carriers from deeper traps at room-temperature (RT), improving the LPL properties significantly. Moreover, the CGGO: xTb^{3+}, yTm^{3+} phosphors exhibit an advantageous LPL performance at high-temperature because of the existence of deeper defect states.

1. Introduction

When electron trapping materials (ETMs) are exposed to the ultraviolet (UV) or visible light, the charge carriers, such as holes and electrons, captured by traps, could be subsequently released by thermal, optical, or physical stimulations to achieve the stimulated emissions by the recombination process. Long persistent luminescence (LPL) phosphor is regard as a special case of ETMs, in which the carriers are captured and then released by thermal energy available at the room temperature (RT) [1]. LPL phosphors have drawn a wide range of interest for the advanced scientific application, such as safety signage, night-vision surveillances, vivo biomedicine, and energy and environmental engineering [2–4].

In LPL phosphor, emitting and trapping centers play vital roles in the persistent luminescence properties, determining the color and lasting time of LPL, respectively [5,6]. The most suitable trap depth for an excellent LPL phosphor is about 0.65 eV, of which the carriers captured can be released by the thermal energy of RT. If the trap depth is too shallow, the carriers are released quickly and the phosphor exhibits a poor LPL performance [7,8]. On the other hand, the carriers cannot acquire enough energy to escape from the trap if the trap depth is too deep, which suggests the energy captured in deep traps cannot contribute to the LPL process. Furthermore, the various types of traps might contribute to different energy transitions, influencing the performance of LPL. Therefore, designing and exploring suitable trap distribution to optimize the performance of LPL with increasing the deep trap concentration and creating suitable shallow trap as the bridge to release the

trapped carriers are attractive and challenging targets.

At present, germanate of $Ca_3Ga_2Ge_3O_{12}$ has been synthesized as the host matrix of LPL phosphors due to the tenability of the luminescence properties and excellent crystallinity [7,9,10]. Also, the persistent luminescence phosphor doped with two different rare earth ions have been studied, showing excellent properties of LPL [11–13].

In previous work, Tb^{3+}-doped phosphors produced excellent green emission and blue emission derived from the transition of $^5D_4–^7F_J$ and $^5D_3–^7F_J$ (J = 3–6), respectively [14–16]. In this paper, we devoted to develop a series of Tb^{3+}/Tm^{3+} co-doped CGGO phosphors with two kinds of traps. The as-prepared phosphors show color tunable long persistent luminescence (LPL) after the near-ultraviolet irradiation. The capture and release process of the carriers in the deeper traps through the shallow traps which act as the bridge was studied. Moreover, the CGGO: xTb^{3+}, yTm^{3+} phosphors exhibit a favorable LPL performance at high-temperature due to the existence of deeper defect states. The as-prepared phosphors have a potential application in certain environment where temperature is higher than RT, such as in biological yield (approximately 38 °C in most living biological tissues).

2. Materials and methods

A series of phosphors of CGGO: xTb^{3+}, yTm^{3+} (x = 0, 0.005, 0.01, 0.015, 0.02, and 0.025, y = 0, 0.0025, 0.01, and 0.0125) were synthesized by a high-temperature solid-state reaction. The original materials were $CaCO_3$ (99.99%), Ga_2O_3 (99.99%), GeO_2 (99.999%), Tb_4O_7 (99.99%), Tm_2O_3 (99.99%) and H_3BO_3 (A.R) at 5% of the reactant was
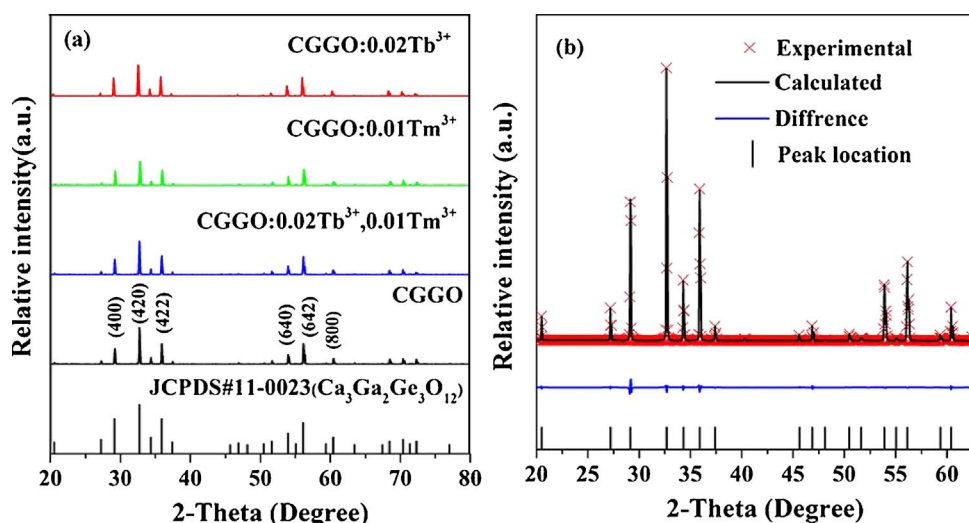
Fig. 1. (a) XRD patterns of CGGO, CGGO:0.02Tb^{3+}, CGGO:0.01Tm^{3+}, and CGGO:0.02Tb^{3+}, 0.01Tm^{3+} and the JCPDS#11-0023 of CGGO; (b) XRD refinement of CGGO:0.02Tb^{3+}, 0.01Tm^{3+}.
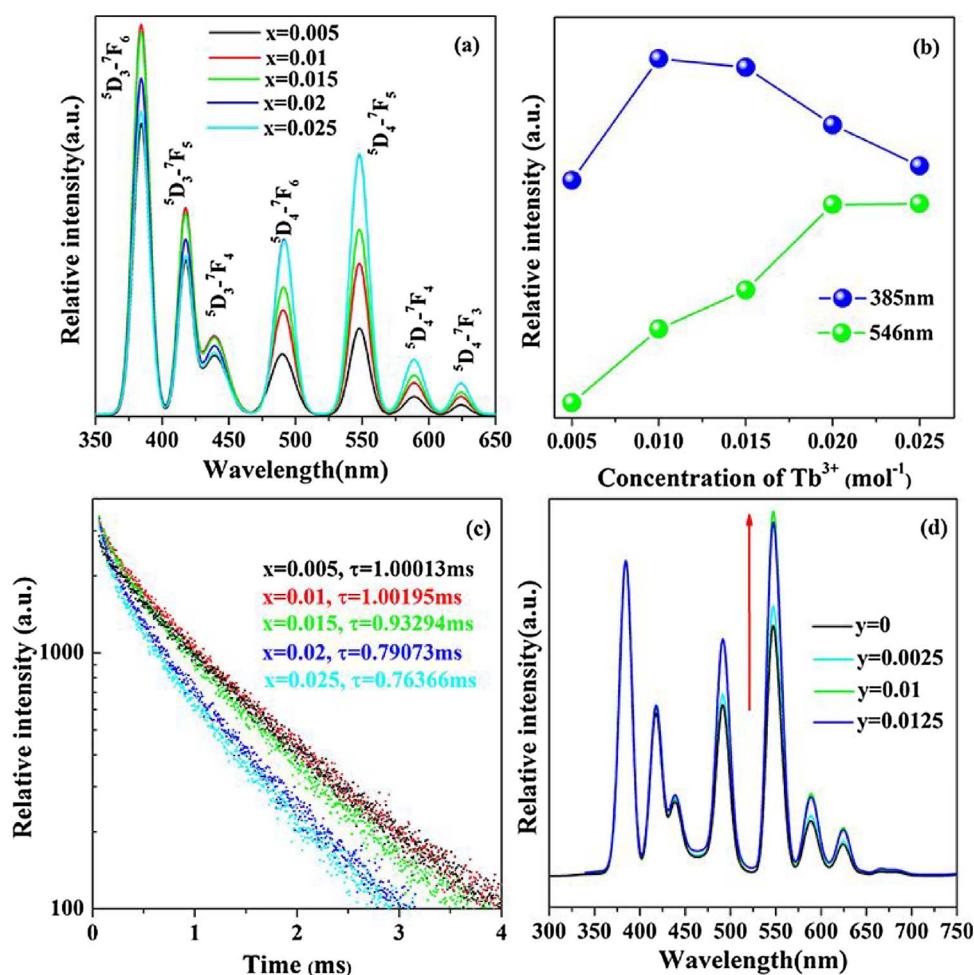

Fig. 2. (a) PL spectra of CGGO: xTb^{3+} (x = 0.005–0.025); (b) The relative emission intensity change of the blue (385 nm) and green (546 nm) peaks as a function of Tb^{3+} concentration; (c) Decay curves of CGGO: xTb^{3+} (x = 0.005, 0.01, 0015, 0.02, and 0.025) phosphors (λ_{em} = 385 nm, λ_{ex} = 265 nm); (d) PL spectra of CGGO: 0.02Tb^{3+}, yTm^{3+} (y = 0, 0.0025, 0.01, and 0.0125) with normalized intensity of 385 nm emission. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.).

used as flux. The stoichiometric amounts of the starting materials were mixed homogeneously in an agate mortar with proper amounts of ethanol (A.R) for about 30 min. The mixed powder was sintered at 1200 °C for 3 h in alumina crucibles with heating rate of 3 °C/min. Subsequently, the powder was collected at room temperature and finely grounded to obtain the final products.

The phases of the samples were identified by X-ray powder diffraction (XRD) (D8ADVANCE/Germany Bruker X-ray diffractometer), using CuK$_\alpha$ at a scanning step of 0.02° in the 2θ range from 10–90°. The

XRD data was refined by the Rietveld method using the MAUD refinement program. A Hitachi F-7000 fluorescence spectrophotometer was used to record the PL, PLE, and LPL spectra. The decay curves of Tb^{3+} emission at 385 nm were recorded by using a time-resolved fluorescence spectrophotometer (FLS980; Edinburgh Instrument Ltd., Edinburgh, UK). The thermoluminescence (TL) curves were measured with a FJ-427A TL meter (Beijing Nuclear Instrument Factory) with heating rate of 60 °C/min after the samples were exposed to the radiation from UV light (254 and 365 nm) for 15 min, the weights of the