



# High-temperature long persistent and photo-stimulated luminescence in Tb<sup>3+</sup> doped gallate phosphor



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## ABSTRACT

The formation of suitable defects levels is crucial to the optical performance of the electron trapping materials which provide a wide range of applications from the initial civil uses to life sciences, energy and environmental engineering. SrGa<sub>2</sub>O<sub>4</sub>, possessing a one-dimensional chain structure of cations along a crystal direction, exhibits a self-activated blue long persistent luminescence (LPL) related to the intrinsic defects. Different trap depths are generated forming a successive defect structure in this three-dimensional framework of SrGa<sub>2</sub>O<sub>4</sub> containing channels occupied by Sr<sup>2+</sup> when Tb<sup>3+</sup> ions are introduced. The captured carriers in shallow traps are spontaneously released at room temperature and recombine in the luminescence center of Tb<sup>3+</sup>, eventually causing characteristic emission of Tb<sup>3+</sup>. The deeper traps are critically important to prevent the thermal fading of carriers at room temperature, therefore, LPL is achieved in SrGa<sub>2</sub>O<sub>4</sub>:Tb<sup>3+</sup> phosphor at 328 K. Furthermore, a photo-stimulated luminescence (PSL) originated from Tb<sup>3+</sup> ions is realized in SrGa<sub>2</sub>O<sub>4</sub>:Tb<sup>3+</sup> phosphor induced by 980 nm laser diode with the releasing of the carriers trapped in the deeper traps at room temperature. Our results infer that the existence of a successive defect structure with multiple traps for the incorporation of the shallow and deep ones is conducive to the thermal stability of SrGa<sub>2</sub>O<sub>4</sub>:Tb<sup>3+</sup> phosphor, which could provide a potential application in a rigorous environment with a higher thermal energy than the room temperature, such as solar energy utilization, and in vivo-imaging.

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## 1. Introduction

Manipulating and tuning the charge carrier transport in photoactive materials has attracted much attention in the fields of photodetector, photovoltaics and photocatalysis, since it plays an important role in enhancing the photoconversion efficiency [1–5]. Considerable research efforts have been devoted to the amplify photon energy absorption as well as enhance charge separation and hinder the charge recombination to optimize the photo-related device performance by engineering the architecture of the corresponding counterparts [6–8]. Electron trapping materials (ETMs), possessing appropriate trap centers to capture charge carriers

(electrons or holes) which can be subsequently released by thermal, optical, or physical stimulations, resulting in stimulated emissions from the emitting centers, has been also thoroughly investigated for their important applications, like biomedicine, clinical medicine, or energy and environmental engineering [9]. Therefore, the trapping and de-trapping processes of electrons and holes is of current interest due to the necessity to understand the mechanism of long persistent luminescence and optical storage phenomena, as well as to improve the performance of ETMs [10].

Via so-called “defect engineering”, such as type, distribution, depth of the defects could be managed by the introduction of lanthanum ions and size/morphology/homogeneity/bonding control [11–15]. Tremendous progresses have been achieved. Specifically, rather than employing doping to engineer defects, designed energy band structure [16–20] to modulate the charge carrier generation is an efficient approach which has been drawn

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considerable theoretical and experimental efforts nowadays.

Now that the optical properties of ETMs are critically rely on the crystal structure of host matrixes and the properties of defects, simplify the study with a specific structure of the host to determine the nature and origin of the defects seems feasible and necessary. Recently, the host matrix of luminescence materials with a unique low-dimensional chain crystal structure has attracted great research interest [21–23]. The host possesses an unusual one dimensional chain structure of cations along a certain crystal direction, which could be beneficial to the formation of the trap level and excited state level, and especially could provide an effective transmission path in one direction between luminescent and trapping centers for efficient transportation of majority carriers [24]. Hence, in this work, the gallates of  $\text{SrGa}_2\text{O}_4$  has been chosen as host lattice, the structure of which is characterized by layers of six-membered rings of  $\text{GaO}_4$  tetrahedra perpendicular to the  $a$  axis, and the stacking of the layers parallel to the  $a$  axis results in a three-dimensional framework containing channels that are occupied by the Sr cations [25]. Furthermore, low-dimensional structural materials are easy to use to implant rare earth ions into the host lattice and create traps located at suitable depths [24].  $\text{Tb}^{3+}$  ions are introduced to  $\text{SrGa}_2\text{O}_4$  due to its excellent green emission derived from the transition of  $^5\text{D}_4$ – $^7\text{F}_5$ . Traps with different depth are generated and a successive defect structure is formed in  $\text{SrGa}_2\text{O}_4:\text{Tb}^{3+}$  phosphors. The roles of these traps, especially the deeper ones which contributes to prevent the thermal fading of carries and stabilize them at room temperature, are investigated. The thermally stimulated LPL and photo-stimulated luminescence (PSL) process in  $\text{SrGa}_2\text{O}_4:\text{Tb}^{3+}$  phosphor is studied. The high-temperature-resistance LPL ability of  $\text{SrGa}_2\text{O}_4:\text{Tb}^{3+}$  phosphor provides a potential application in vivo bio-imaging or a harsh environment where the thermal energy is much higher than the room temperature. The aim of our work is to get a deeper understanding on the possibility to shape the spectroscopic properties of phosphors based on the unique low-dimensional host structure and the effective trapping centers.

## 2. Experimental procedure

$\text{Sr}_{1-x}\text{Ga}_2\text{O}_4:\text{xTb}^{3+}$  ( $x = 0, 0.005, 0.01, 0.03, 0.05$  and  $0.07$ ) samples were synthesized by the conventional high-temperature solid state reaction. Stoichiometric amounts of  $\text{Sr}_2\text{CO}_3$ (A.R),  $\text{Ga}_2\text{O}_3$ (A.R), and  $\text{Tb}_4\text{O}_7$  (99.99%) were mixed in an agate mortar with ethanol. After being fully ground, the mixtures were put into crucibles and calcined at  $1200^\circ\text{C}$  for 6 h in a reducing atmosphere (95:5  $\text{N}_2:\text{H}_2$ ). After cooling to room temperature naturally, the as-obtained samples were ground into powder for the following measurements.

The crystalline structures of the prepared powders were investigated by X-ray diffraction (XRD) with Ni-filter  $\text{Cu K}\alpha$  radiation ( $\lambda = 0.154056$  nm) at a scanning step of  $0.02^\circ$ . The XRD data were collected in the range of  $10$ – $40^\circ$  by applying a D8ADVANCE/Germany Bruker X ray diffractometer. The photoluminescence excitation (PLE), photoluminescence (PL), LPL, and PSL spectra were recorded by using a Hitachi F-7000 fluorescence spectrophotometer. The LPL lifetime curves were measured with a PR305 long afterglow instrument (Zhejiang University Sensing Instruments Co., Ltd., China) after the sample had been irradiated with UV light (254 nm and 365 nm) for 20min. When the sample vessel was heated to the corresponding temperature through the DC power, the decay curves of  $\text{Sr}_{0.995}\text{Ga}_2\text{O}_4:0.005\text{Tb}^{3+}$  at different ambient temperature were recorded subsequently after ceasing the excitation of UV light for 20min. The thermo-luminescence (TL) curves were measured with a FJ-427A TL meter (Beijing Nuclear Instrument Factory). The weight of the measured samples was constant

(0.002 g). Prior to the TL measure, the samples were first exposed to the radiation from the UV light for 20min and then heated from room temperature to 550 K at a rate of 1 K/s. Before the PSL had been measured ( $\lambda_{\text{ex}} = 980$  nm), the samples were pre-irradiated with UV light for 20 min and then placed in the dark for 20 h. A 980 nm laser diode is used as a stimulating source.

## 3. Results and discussion

The purity of all the prepared samples was systematically checked by XRD measurements. Fig. 1 shows the typical XRD patterns of  $\text{Sr}_{1-x}\text{Ga}_2\text{O}_4:\text{xTb}^{3+}$  ( $x = 0, 0.005, 0.01$  and  $0.03$ ) samples. Clearly, all the diffraction peaks could be indexed to the phase of  $\text{SrGa}_2\text{O}_4$  registered in JCPDF file No. 22-0905, which indicates that all the samples are identified as  $\text{SrGa}_2\text{O}_4$  phase. No significant impure phases are observed when  $\text{Tb}^{3+}$  ions are doped, demonstrating the pure phase is synthesized in this work. Based on the effective ionic radius ( $r$ ) of cations with different coordination number (CN) [26], the radii of  $\text{Tb}^{3+}$  (0.0995 nm) is closer to that of  $\text{Sr}^{2+}$  (0.1130 nm). Since both four-coordinated  $\text{Ga}^{3+}$  (0.0470 nm) sites are too small for  $\text{Tb}^{3+}$  ions to occupy, therefore, we conclude that  $\text{Tb}^{3+}$  ions tend to prefer the  $\text{Sr}^{2+}$  sites due to size consideration. As shown in the inset of Fig. 1, the structure of  $\text{SrGa}_2\text{O}_4$  phase possesses a distinct open structure with tunnel-like cavities ( $a$  crystal direction) running throughout the host lattice [25,27].

Fig. 2 presents the PL spectra of  $\text{Sr}_{1-x}\text{Ga}_2\text{O}_4:\text{xTb}^{3+}$  ( $x = 0, 0.001, 0.003, 0.005, 0.01$  and  $0.03$ ) samples under the excitation of 252 nm. As shown in Fig. 2,  $\text{Ga}^{3+}$  is the luminescence center of  $\text{SrGa}_2\text{O}_4$  phosphor, and the emission wavelength is 407 nm, which is referred to the  $^4\text{T}_1 \rightarrow ^4\text{A}_2$  transition of electrons in d orbits  $\text{Ga}^{3+}$  [27,28]. Whereas, the PL intensity of the transition of  $\text{Ga}^{3+}$  drastically decreased when  $\text{Tb}^{3+}$  ions are introduced. Under 252 nm excitation, the emission spectra yield from blue to green emissions in the region of 380–460 and 480–650 nm, which are due to the  $^5\text{D}_3 \rightarrow ^7\text{F}_j$  ( $J = 6, 5, 4, 3$ ) and  $^5\text{D}_4 \rightarrow ^7\text{F}_j$  ( $J = 6, 5, 4, 3$ ) transitions of  $\text{Tb}^{3+}$  ions [29] in  $\text{Sr}_{1-x}\text{Ga}_2\text{O}_4:\text{xTb}^{3+}$  samples, respectively. In addition, the emission intensity of  $\text{Tb}^{3+}$  ions at 547 nm increases firstly, of which reaches the maximum when the doped concentration of  $\text{Tb}^{3+}$  is up to 0.005, and then decreases due to the concentration quenching. The inset of Fig. 2 exhibit the PLE spectra of  $\text{SrGa}_2\text{O}_4$  and  $\text{Sr}_{0.995}\text{Ga}_2\text{O}_4:0.005\text{Tb}^{3+}$ , respectively. The PLE spectrum of  $\text{SrGa}_2\text{O}_4$

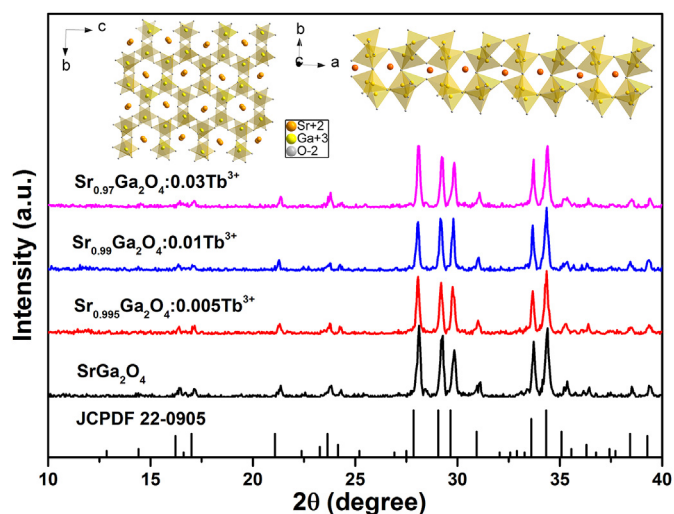


Fig. 1. XRD patterns of  $\text{Sr}_{1-x}\text{Ga}_2\text{O}_4:\text{xTb}^{3+}$  ( $x = 0, 0.005, 0.01$  and  $0.03$ ) samples and the JCPDF No.22-0905 of  $\text{SrGa}_2\text{O}_4$ , respectively. The inset is the crystal structure of the  $\text{SrGa}_2\text{O}_4$  seen from  $a$  axis and  $c$  axis, respectively.

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