



A long persistent phosphor based on recombination centers originating from Zn imperfections



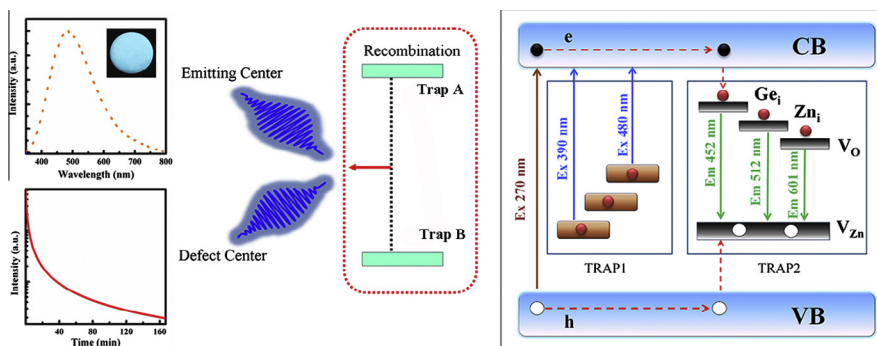
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HIGHLIGHTS

- A blue-white long persistent phosphor.
- Zn imperfections as emitting centers without any rare-earth doping.
- An energy transfer and remission process is proposed.

GRAPHICAL ABSTRACT



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ABSTRACT

The recombination luminescence from Zn imperfections has been extensively investigated; however, there have been few reports on the long persistent luminescence of Zn imperfections as emitting centers. Here, we observed a long persistent luminescence in blue-white visible region from 6 ZnO:3 GeO₂:Al₂O₃ phosphor with Zn imperfections as emitting centers. Persistent luminescence could be observed beyond 2 h with naked eyes. The properties of traps were also elaborated by the measurements of thermo-luminescence spectra and photo-stimulated luminescence decay curves. Furthermore, a long persistent phosphor with warm white color was developed by doping Cr³⁺ into 6 ZnO:3 GeO₂:Al₂O₃ phosphor.

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Introduction

Long persistent phosphors (LPPs) have been widely used in various areas, including safety indications and emergency lighting etc. [1]. Generally, long persistent phosphors require materials have abilities to form electrons reservoir, as well as accommodate suitable emitting centers. The emission wavelength of the long persistent phosphors is mainly determined by the emitters, while the persistence luminescence intensity and time are restricted by the defects [2]. Up to now, emitting centers in long persistent phosphors

have been focused on the discrete luminescent centers, e.g. rare earth ions [3]. Except the discrete luminescent centers, it is well known that recombination centers are also a kind of important emitting centers, and defects usually act not only as the traps centers, but also as the emitting centers. However, there have been few reports on the long persistent luminescence from defects as emitting centers.

The recombination photo-luminescence of Zn imperfections has been extensively investigated [4,5], but long persistent luminescence from Zn imperfections as emitting centers was rare. Herein, we observed a long persistent luminescence in blue-white visible region from 6 ZnO:3 GeO₂:Al₂O₃ phosphor with Zn imperfections as emitting centers. The persistent luminescence could be

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observed beyond 2 h with naked eyes. The properties of the related traps were also elaborated by the thermo-luminescence (TL) spectra and photo-stimulated luminescence (PSL) decay curves. In addition, a long persistent phosphor with warm white color was obtained by doping Cr^{3+} ion into $6 \text{ ZnO}:3 \text{ GeO}_2:\text{Al}_2\text{O}_3$ phosphor.

Experimental

Phosphors with the compositions of $6 \text{ ZnO}:3 \text{ GeO}_2:\text{Al}_2\text{O}_3$ (GZA), $6 \text{ ZnO}:3 \text{ GeO}_2:\text{Al}_2\text{O}_3:0.02 \text{ mol}\% \text{ Cr}^{3+}$ (GZA1) were prepared with solid state reaction method. The 4 N pure GeO_2 , ZnO , Al_2O_3 , and Cr_2O_3 , were used as the raw materials, and mixed homogeneously in an agate mortar. The mixed powders were pre-fired at 1000°C in air for 4 h, and were then ground to fine powders. The prepared powders were pressed into discs with diameters of $\sim 10 \text{ mm}$ using a hydraulic press with the pressure of 10 MPa for 10 min. The discs were sintered again at 1400°C in air for 4 h. X-ray diffraction (XRD) measurements were performed on a D8 advance Bruker diffract meter (Cu $K\alpha$ radiation) equipped with a Vantec-1 linear detector. The data were collected between 10° and 130° (2θ) with a 0.0164° step size at room temperature, confirming the presence of ZnGe_2O_4 (JCPDS no 11-0687) as the sole crystalline phase (Fig. s1). A FEI Quanta 400, field emission environmental SEM fitted with an oxford energy dispersive spectrometry (EDS) analyzer was employed for surface investigation and features detection, further confirming the presence of the sole crystalline phase (Fig. s2). All of the luminescence spectra were measured with Edinburgh instrument FLS 920 using a R928P photomultiplier as the signal collector and equipped with a 500 W xenon lamp. Thermo-luminescence (TL) glow curves were measured with a FJ-427A TL meter. Photographs were taken by a Canon digital camera un-irradiated or irradiated by the 4 W 254 nm UV lamp.

Results and discussion

Photoluminescence properties

Fig. 1 shows the excitation and emission spectra of GZA phosphor. Two excitation bands were observed around 270 and 310 nm when monitored the emission at 488 nm. Under the excitation at 270 nm, GZA phosphor exhibits a bluish-white broad

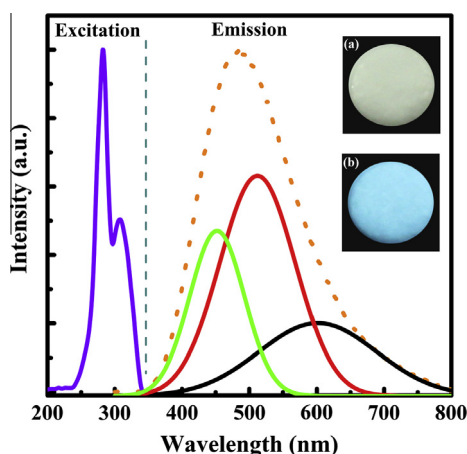


Fig. 1. Emission spectrum (excited at 270 nm) and excitation spectrum by monitoring emission at 488 nm of GZA phosphor. The emission is Gaussian-resolved into three bands located at 452 (green solid line curve), 512 (red solid line curve), and 601 nm (black solid line curve), respectively. The inset shows the photographs un-irradiated (a) or irradiated (b) by a 254 nm UV lamp. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

emission band at 488 nm (Inset. b), which can be readily Gaussian-resolved into three bands located at 452, 512, 601 nm. The same photoluminescence has been observed in ZnO powders, ZnO nano-particles, and other compounds [5–7]. The broad emission band should be assigned to the transitions associated with Zn imperfections [8]. Atomic and electronic structures of native Zn imperfections have also been extensively investigated both theoretically and experimentally [9,10]. The emitting centers of blue, green, and orange bands are considered to be the intrinsic defects [10], including O vacancy (V_{O}), Zn vacancy (V_{Zn}), Zn interstitial (Zn_i), O interstitial (O_i), and so on. [11]. Fan et al. suggested that radiative recombination transition between the shallow traps and deep acceptors (V_{O} or V_{Zn}) gives rise to emission bands at 2.51, and 2.36 eV, respectively [12]. Wang et al. assigned the emissions at 2.9 and 2.38 eV to the transitions from Zn interstitial (Zn_i) to valence band, and from conduction band to O_{Zn} defect in ZnO , respectively [13]. Liu et al. also observed the similar luminescence ZnGe_2O_4 excited at 270 nm, and the emission is assigned to the donor-acceptor recombination, V_{O} and Zn_i were donors, whereas ionized V_{Ge} and V_{Zn} were the acceptors [14]. Therefore, the blue, green, and orange emissions observed from GZA phosphor should be ascribed to the transitions from Ge interstitial (Zn_i), Zn interstitial (Zn_i) and O vacancy (V_{O}) to Zn vacancy (V_{Zn}), respectively [15].

Long persistent luminescence properties

After irradiation by a 254 nm UV lamp for 20 min, long persistent luminescence was also observed from the GZA sample (Fig. 2a). Obviously, the emission intensity of persistent luminescence decreased gradually (Fig. 2a) and the emission peak showed a red shift from 488 to 550 nm (Fig. 2b), indicating that the traps distributes over a wide range of energies. The persistent luminescence was sufficiently bright to be visually confirmed for about 2 h in the dark (Fig. 2c). The decay curve of persistent luminescence follows a hyperbolic function, indicating that emitting centers of persistent luminescence are recombination centers [16].

The decay curves of persistent luminescence after irradiation by the lights from 280 to 360 nm were shown in Fig. 3. Effectiveness for the acquisition of persistent luminescence decreases with the increment of excitation wavelength. It is also observed that persistent luminescence can be effectively achieved under ultraviolet illumination, but less effectively under visible light illumination (The inset of Fig. 3), and the maximum locates at 270 nm, which is similar to the excitation maximum shown in Fig. 1, indicating that shallow traps near the conduction band may be responsible for persistent luminescence [17].

Defects properties

Thermo-luminescence spectra

Thermo-luminescence (TL) spectra are a useful tool for revealing the nature of traps [18–20]. TL curves acquired at 1, 10, 30 min, 1, 3, and 12 h after the stoppage of irradiation were shown in Fig. 4. All curves consist of a broad band, but with different maximum at 77, 105, 119, 139, 173, and 177 $^\circ\text{C}$, respectively. The shift of TL peak to higher temperature confirms the continuous distribution of shallow traps and deep traps. Significantly, the position of TL peak acquired at 3 h and 12 h after the stoppage of irradiation is similar, which means that shallow traps near the conduction band are responsible for persistent luminescence, and electrons in deep traps cannot be released completely, and plenty of electrons are still detained in deep traps at room temperature.

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