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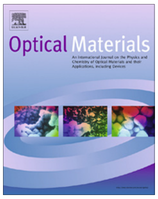

Long afterglow properties of $Zn_2GeO_4:Mn^{2+}$, Cr^{3+} phosphor

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ABSTRACT

$Zn_2GeO_4:Mn^{2+}$, Cr^{3+} phosphors were prepared by conventional solid state reaction and the photoluminescence properties were investigated. The Mn^{2+} activated Zn_2GeO_4 phosphors exhibited green emission at 533 nm due to the ${}^4T_1({}^4G) \rightarrow {}^6A_1({}^6S)$ transition of Mn^{2+} ions. With Cr^{3+} co-doping in Zn_2GeO_4 host, long afterglow characteristics were found from the same transition of Mn^{2+}. The TL results revealed the presence of same traps in the phosphor, and the doping of Cr^{3+} ions deepened the V_{Ge} traps. The native defect V_{Ge} as a hole traps is responsible for the long afterglow emission in $Zn_2GeO_4:Mn^{2+}$, Cr^{3+} phosphor. The possible mechanism of this phosphor has also been discussed.

1. Introduction

The long afterglow is a phenomenon whereby luminescence can last for hours after the stoppage of excitation. Phosphors with long persistent luminescence have been rapidly developed in the past decades and have been widely applied in many areas such as traffic signs, emergency signage, display, optical memory, image storage and high energy ray detection [1–3]. Since the novel long persistent phosphorescence phenomena of $SrAl_2O_4:Eu^{2+}$, Dy^{3+} were first reported in 1996 [2], the alkali earth aluminates long-afterglow materials have attracted much attention and have been rapidly developed. To date, the most efficient long-afterglow materials are still based on alkali earth aluminates. Thus, many efforts have been made to discover new persistent luminescence host materials and activators with high performance. Zinc germanate doped with manganese (Zn_2GeO_4:Mn) is a native defect material which has attracted much attention and has been widely investigated as a new green phosphor for field emission displays (FEDs) [4,5]. As a FEDs using phosphor, the green emission from $Zn_2GeO_4:Mn^{2+}$ has a short lifetime, which is a typical value for luminescence caused by defects [6].

The density of traps generally plays a key role in the persistent emission of phosphor materials [7]. To improve the phosphorescence intensity and persistent time, it is necessary to introduce defects by adding auxiliary activators. Suitable emitters capable of emitting light and traps storing excitation energy are therefore required in persistent phosphors design. In this paper, the green long afterglow emission enhancement of $Zn_2GeO_4:Mn^{2+}$ by co-doping Cr^{3+} into the phosphor is reported. Mn^{2+} ions acting as emitters showed narrow emission band with a peak at about 533 nm due to the ${}^4T_1$–${}^6A_1$ transition. While the native defects produced during the synthesis process serve as the trapping centers. In the dark, the long afterglow emission of $Zn_2GeO_4:Mn^{2+}$, Cr^{3+} could be observed by naked eyes after the UV irradiation have been removed for about 1 h. The mechanism of afterglow decay is analyzed according to the photoluminescence (PL) and thermoluminescence (TL) spectra results.

2. Experimental

2.1. Materials synthesis

Samples of $Zn_2GeO_4:Mn^{2+}$, Cr^{3+} were synthesized by conventional high temperature solid state reaction using ZnO, GeO_2, Cr_2O_3, $Mn(CH_3COO)_2·4H_2O$ as starting materials. The powders were finely mixed in an agate mortar with ethanol to ensure homogeneous, and then adequately triturated for a well mixing. The dried powders were then fired in the air at 900 °C for 2 h. After cooling, the samples were grounded again and then sintered at 1350 °C for 6 h. The as-prepared products were in the form of white powders.

2.2. Characterization methods

The structural characterization was carried out by X-ray diffraction (XRD; Rigaku D/max-IIB) spectra with the Cu Kα line of 0.15405 Å. The emission and the excitation spectra were measured using a Hitachi F-4600 fluorescence spectrophotometer equipped with a Xenon lamp as the excitation source. The afterglow decay

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curves were measured using the same facilities, while after irradiation by 254 nm UV light for 5 min. Thermoluminescence (TL) glow curves of the samples were measured after irradiation with the same UV lamp for 5 min using a FJ-427A1 TL dosimeter (Beijing Nuclear Instrument Factory) with a fixed heating rate of 2 °C/s within the range 25–300 °C. Mean while, the same TL curves were measured without UV irradiation for comparison.

3. Results and discussion

3.1. Phase structure

Fig. 1(a) shows the XRD patterns of Zn_2GeO_4 host, 0.5 mol% Cr^{3+} and 1 mol% Mn^{2+} doped Zn_2GeO_4 samples, respectively. All the diffraction peaks of the samples can be assigned to a pure rhombohedral Zn_2GeO_4 phase (JCPDS No. 11-0687). There is no extra peak observed in the XRD patterns from the Cr^{3+} and Mn^{2+}-doped samples, suggesting that the Cr^{3+} and Mn^{2+} ions are completely substituted in the Zn_2GeO_4 lattice. A close check of the XRD peaks from 30°(1 1 3) to 35°(4 1 0) in Fig. 1(b) shows that the diffraction peaks of Cr^{3+} doped sample locate at lower angle compared with the Zn_2GeO_4 host sample which is attributed to the lattice expansion, while the Mn^{2+} doped sample locate at higher angle which is attributed to the lattice contraction. It is indicated that Cr^{3+} and Mn^{2+} ions dissolved in Zn_2GeO_4 by replacing different ions, and the lattice constant slightly changes with Mn^{2+} and Cr^{3+} doping. The ionic radii of Cr^{3+}, Mn^{2+}, Zn^{2+}, and Ge^{4+} are 0.61 Å, 0.80 Å, 0.74 Å, and 0.53 Å, respectively. Mn^{2+} ions substituted for Zn^{2+} ions in Zn_2GeO_4, and Cr^{3+} ions are expected to occupy the Ge^{4+} sites.

3.2. Photoluminescence properties

The photoluminescence (PL) and PL excitation (PLE) spectra of Zn_2GeO_4 host and Zn_2GeO_4 doped with 1 mol% Mn^{2+} samples are shown in Fig. 2. Zn_2GeO_4 is a native defect phosphor with blue emission. A blue emission band with a full width at half maximum (FWHM) of 100 nm centered at 410 nm and a weaker green band centered at 525 nm is attributed to the donor ($V_O^{\cdot\cdot}$ and $Zn_i^{\cdot}$)-acceptor (V_{Ge} and V''_{Zn}) recombination in Zn_2GeO_4 host [8,9]. The excitation spectrum monitoring the 410 nm emission consists of a broadband centered at 270 nm which is related to the host lattice or band-to-band excitation in the Zn_2GeO_4 matrix [4].

The tetrahedral coordinated Mn^{2+} ion gives a green emission, while the octahedral coordinated Mn^{2+} ion exhibits an orange-to-red emission [10]. In the Zn_2GeO_4 matrix, there are only tetrahedral Zn^{2+} sites available for Mn^{2+} ions. Therefore, the emission spectrum of Mn^{2+} doping Zn_2GeO_4 phosphor exhibits a bright green emission band centered at 533 nm under UV excitation, originating from the spin-forbidden d-d transition $^4T_1(^4G) \rightarrow {}^6A_1(^6S)$ of Mn^{2+}. Monitored at 533 nm, the excitation spectrum of the Zn_2GeO_4: 1 mol% Mn^{2+} sample consists of a broad excitation band with a maximum at 330 nm, which corresponds to the charge-transfer transition of Mn^{2+} ions [4,5]. The excitation at 330 nm for Mn^{2+} doped sample overlaps with the host emission band, suggesting a possible energy transfer from the host to Mn^{2+} ions.

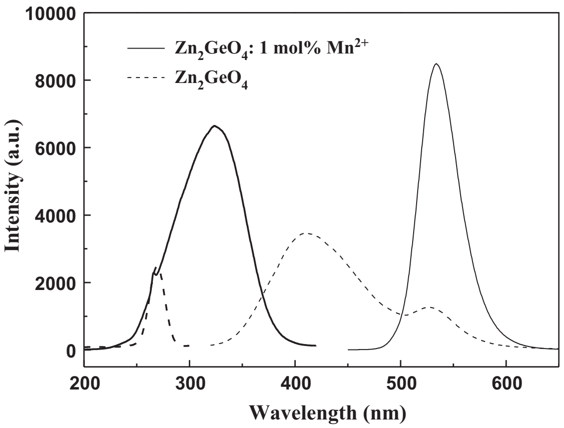

Fig. 2. Excitation and emission spectra of Zn_2GeO_4 (dot) and Zn_2GeO_4:1 mol% Mn^{2+} (solid).

3.3. Long afterglow properties

The green luminescence from Zn_2GeO_4:Mn^{2+} with good chromaticity coordinates and appropriate intensity was widely reported as FEDs using phosphor. The Zn_2GeO_4:Mn^{2+} phosphor has a short lifetime at display fields. The Zn_2GeO_4:Mn^{2+} yields strong green long afterglow emission by addition of Cr^{3+} ions. Fig. 3 displays the PL spectra and afterglow emission spectrum, respectively. It is found that the center (533 nm) and the profile of green afterglow emission remain unchanged and are consistent with the PL emission. It is indicated that both PL and long afterglow characteristics are from the same $^4T_1(^4G) \rightarrow {}^6A_1(^6S)$ transition of Mn^{2+}.

Fig. 4 illustrates the time decay curves of phosphorescence in the Zn_2GeO_4:Mn^{2+} with different co-doping Cr^{3+} concentrations after irradiation with 330 nm UV light for 5 min. The Cr^{3+} free sam-

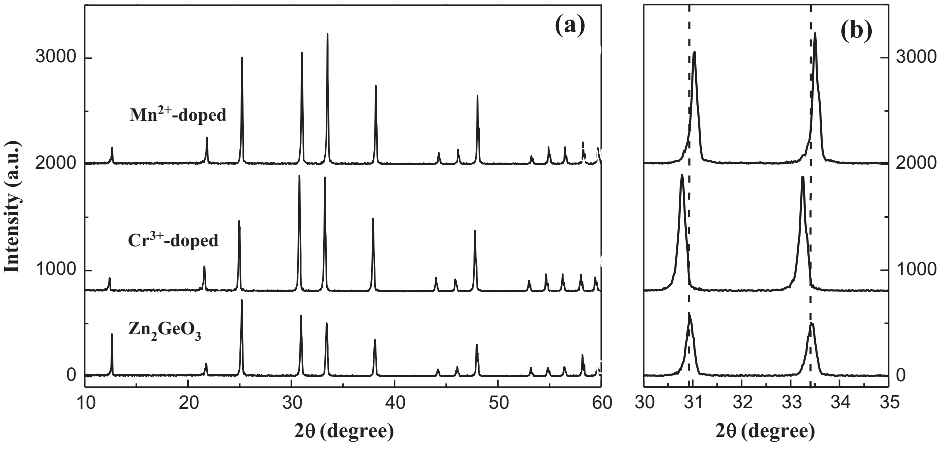

Fig. 1. (a) XRD patterns of Zn_2GeO_4, 0.5 mol% Cr^{3+} and 1 mol% Mn^{2+} doped Zn_2GeO_4; (b) partial enlarge detail of (1 1 3) and (4 1 0) peaks.