Preparation and luminescence properties of CaSnO$_3$:Sm^{3+} phosphor emitting in the reddish orange region

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Abstract

A novel reddish orange light emitting phosphor, CaSnO$_3$:Sm^{3+}, is prepared via a two-step approach including the room temperature synthesis of CaSn(OH)$_6$ precursor and then convert it into CaSnO$_3$ by calcination and its optical properties are systematically investigated. X-ray diffraction, photoluminescence, long persistent phosphorescence and thermoluminescence spectra are used to characterize the synthesized phosphor. This phosphor is found to be well-crystallized by calcination at 750 °C for 3 h. Photoluminescence measurement indicates that Sm^{3+}-doped CaSnO$_3$ shows an overall reddish orange emission with a CIE values of $x = 0.57$, $y = 0.37$. After irradiation under the 254-nm UV light, the $^4G_{5/2}$ to ^6H_J ($J = 5/2, 7/2, 9/2, 11/2$) afterglow emissions of Sm^{3+} are obviously observed. Furthermore, the thermoluminescence and the possible mechanism for the long persistent phosphorescence (LPP) of the CaSnO$_3$:Sm^{3+} phosphor is also discussed in this paper.
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1. Introduction

As a kind of perovskite dielectric materials, alkaline-earth tin oxides (MSnO$_3$, M = Ca, Sr, Ba) have received a considerable amount of attention over the past few years resulting from their potential applications in various fields, such as display phosphor matrix, ceramic materials, thermally stable capacitors in electronic industries, and gas sensor host [1,2]. SnO$_4^{4-}$ anions are reported to be optically-inert and could be a candidate as a host material [3]. However, little attention has been paid to the luminescence properties of alkaline-earth stannate phosphors. Recent progress in optical equipments, such as lasers and optical amplifiers, based on electronic transitions of rare-earth ions, has inspired a lot of work in different materials doped with these ions [4]. Of the many rare-earth ions, Sm^{3+} ion is well-known as an important activator for many different inorganic lattices producing reddish orange light emitting due to its $^4G_{5/2} \rightarrow {}^6H_J$ ($J = 5/2, 7/2, 9/2, 11/2$) transitions [5]. From the viewpoint of practical applications, the light which emitting wavelength located at the longer side (red or orange) is the most suitable source for illuminating light and is appropriate for various displays. This motivated us to design and fabricate Sm^{3+}-doped CaSnO$_3$ phosphor. In present work, we report some preliminary results on the CaSnO$_3$:Sm^{3+} reddish orange light emitting phosphor.

2. Experimental

A two-step method was employed for the sample preparation including the room temperature synthesis of

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precursor $CaSn(OH)_6$ and then convert it into $CaSnO_3$ by calcination, which was similar to the method previous reported [6].

In a typical synthesis of $CaSn(OH)_6$ precursor, 7.02 g $SnCl_4 \cdot 5H_2O$ was dissolved in 30 ml of 80 °C distilled water while appropriate amount of 2 M NaOH solution was added to completely precipitate the Sn^{4+} to $Sn(OH)_4$ slurry. Similarly, the $Ca(OH)_2$ slurry was obtained through precipitating the $CaCl_2$ solution. The two slurries were then mixed thoroughly by vigorous stirring and the pH value of the mixture was adjusted at about 10 by 1 M NaOH solution. To this mixture was then added 35 ml surfactant (CTAB, cetyltrimethylammonium bromide) solution in distilled water (30 wt.%) and the pH value was controlled at about 12. The resulting mixture was stirred at 80 °C for 24 h. The white precipitation was collected and washed 10 times with alcohol and distilled water, respectively, and then allowed to dry in air at ambient temperature. The as-prepared precursor was successively heat-treated at several conditions of temperature and duration time using alumina crucibles with alumina lids in air, followed by subsequent cooling in air at ambient temperature to obtain the final product. The Sm^{3+}-doped $CaSnO_3$ phosphor was prepared by replacing 2 mol% amount of $CaCl_2$ with $SmCl_3 \cdot 6H_2O$.

The structures of all synthesized samples were checked by using a Rigaku Model D/max-II B X-ray diffractometer. The photoluminescence (PL) spectra and the afterglow intensity decay curve were obtained with a Hitachi F-4500 fluorescence spectrophotometer. Thermoluminescence (TL) glow curve was measured using a Thermal Luminescence Meter System equipped with a temperature-controlled oven (2 K/s heating rate). The sample was irradiated for 5 min at 254 nm from a 15 W mercury lamp before TL measurement.

3. Results and discussion

The structures of the as-synthesized precursor and the final samples were checked by the XRD measurement. The XRD results revealed that all the reflections of the as-synthesized precursor can be readily indexed to a pure cubic phase of $CaSn(OH)_6$ (JCPDS 090030). Upon calcination at 750 °C for 3 h, the $CaSn(OH)_6$ precursor thermally decomposed to yield monophase orthorhombic $CaSnO_3$ with perovskite structure (JCPDS 310312). According to the XRD analysis, the sample was found in single $CaSnO_3$ phase. In our work, phase-pure polycrystalline $CaSnO_3$ can be produced at 750 °C, a much lower temperature than normal solid-state reaction as high as about 1400 °C [2]. This may be due to the $CaSn(OH)_6$ precursor was produced at molecular level, showing high activity when the precursor are broken under calcination.

The excitation and emission spectra of $CaSnO_3$:Sm^{3+} are shown in Fig. 1. The excitation spectrum for the 601 nm emission consists of a series of sharp peaks in the 300–530 nm range with the strongest one at 408 nm and some peaks at 319, 348, 365, 378, 421, 443 and 478 nm,
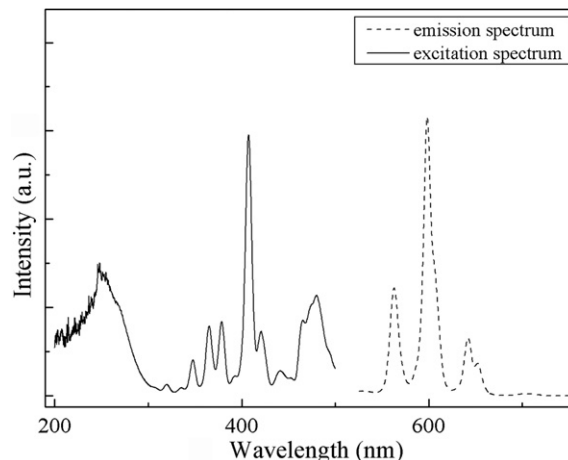

Fig. 1. Emission (dashed line, $\lambda_{ex} = 408$ nm) and excitation (solid line, $\lambda_{em} = 601$ nm) spectra of the $CaSnO_3$:2%Sm^{3+} phosphor sintered at 1000 °C for 3 h.

which are ascribed to the transitions from the ground state to the excited states of Sm^{3+}. Under the excitation at 254 or 408 nm, at least four strong sharp peaks located at 566, 601, 649 and 716 nm can be observed and they can be assigned to the $^4G_{5/2} \rightarrow {}^6H_J$ ($J = 5/2, 7/2, 9/2, 11/2$) transitions of Sm^{3+} [5].

To study the decay behavior of $CaSnO_3$:Sm^{3+} emission in more details, the afterglow intensity decay curve for the 2% Sm^{3+}-doped $CaSnO_3$ sample was measured monitoring at 601 nm, as shown in Fig. 2. The estimated uncertainties on the afterglow emission intensities are 1–4% based on the precision of the individual afterglow measurement and the instrument drift. Because the phosphorescence decay could be due to a sum of several first-order decays related to the emptying of several different traps, Fig. 2 need to be shown as semi-logarithmic format in order to find how many processes there are involved in the afterglow decay process. The decay curve has been analyzed by curve fitting and found that it can be fitted perfectly using the bi-exponential decay function [4,7]

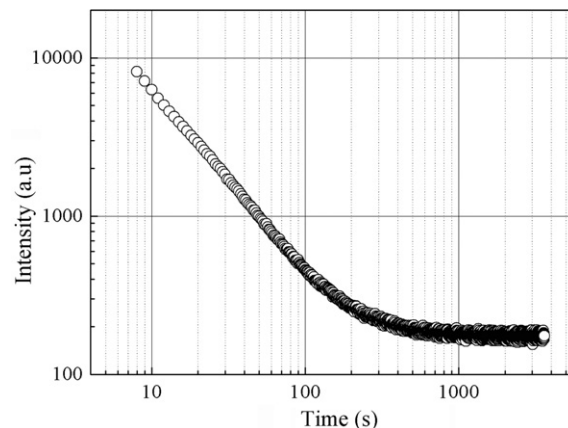$$I = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) \qquad (1)$$

Fig. 2. Afterglow intensity decay curve of the $CaSnO_3$:2%Sm^{3+} phosphor.

where I is the phosphorescence intensity at time t; A_1 and A_2 are constants; τ_1 and τ_2 are the decay times for the exponential components, respectively. It is not surprising given the well-known ability of bi-exponentials to give excellent fits to complex decay curves, which are made up of distribution function of exponential decays, especially at the count levels used on most single-photo-counting instruments. The fitting parameters obtained are: $\tau_1 = 7.04 \pm 0.05$ and $\tau_2 = 46.79 \pm 0.32$ s. This result indicated that the long persistent phosphorescence of Sm^{3+} in $CaSnO_3$ behaviors in terms of a bi-exponential decay model. Firstly, the LPP acts on the first exponential, when the decay time is longer, the decay will act on the second exponential. The decay ratio speed-down when the decay time increases. The hyperbolic characteristic of the afterglow decay curve suggests that the afterglow process in $CaSnO_3:Sm^{3+}$ phosphor is a second-order mechanism [4,8,9]. The second-order decay model of this $CaSnO_3:Sm^{3+}$ phosphor is fully in line with the behavior of a wide variety of rare-earth ions doped long persistent phosphors [4,7,9–13].

Theoretically, long persistent phosphorescence (LPP) is a phenomenon due to the thermalstimulated recombination of trapped holes or electrons which leave electrons or holes in a metastable state at room temperature. It is well known that trapping centers play an essential role for photoenergy storage in persistent, photostimulatable, and thermostimulable phosphors [14]. It is also reported that the dominant trapping centers are situated above room temperature or trap depths at 0.4–0.6 eV if materials show excellent long persistent phosphorescence performance [7–10,13–15]. However, a detailed description of the LPP mechanism has not been known until now due to the lack of general methods and techniques to directly detect the trap's nature and monitor the trapping process. The TL technique is a useful tool for revealing the nature of trapping centers produced in insulator or semiconductor excitation by using X-rays, laser, or ultraviolet light [11,16]. Under heating, the trapped electrons can be released from the traps and this process results in the thermoluminescence signal. When only one kind of trap is emptied under heating, the TL spectrum will present as one single TL peak. In contrast, the TL spectrum will be composite when several traps are emptied under heating due to the sum of single TL peaks [8–10]. Therefore, it is necessary to take the TL spectrum of the phosphor into consideration.

Fig. 3 shows the TL spectrum of the $CaSnO_3:2\%Sm^{3+}$ phosphor. As shown in Fig. 3, the shape of the TL spectrum is broad and not appears as a single peak, indicating the presence of various traps. According to the method reported in the literatures [8,9], this TL curve can be fitted to good approximation by at least two Gaussian curves. The two TL peaks locating at around 330 and 350 K in Fig. 3 demonstrate that the introduction of Sm^{3+} into the $CaSnO_3$ matrix has produced two trap centers within the $CaSnO_3$ host. Utilizing the peak-shape method and the usual general order kinetics expressions, depth values
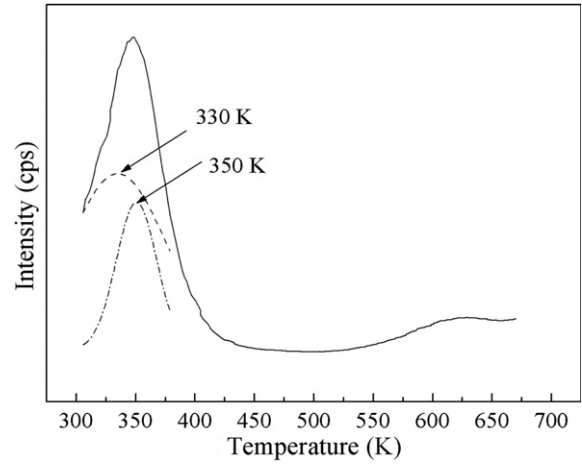

Fig. 3. TL glow curve of the $CaSnO_3:2\%Sm^{3+}$ phosphor sintered at 1000 °C for 3 h.

of these traps in the $CaSnO_3:2\%Sm^{3+}$ can be calculated from the TL spectrum by the following function [17–19]:

$$I(T) = sn_0 \exp\left(-\frac{E_t}{k_B T}\right)\left[\frac{(l-1)s}{\beta}\right.$$
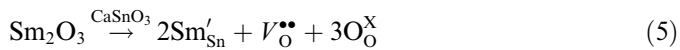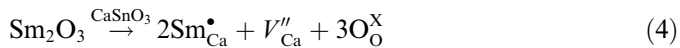$$\left. \times \int_{T_0}^{T} \exp\left(-\frac{E_t}{k_B T'}\right)dT' + 1\right]^{-l/(l-1)} \quad (2)$$

where n_0 is the concentration of trapped charges at $t = 0$, k_B is Boltzmann's constant, and β is the heating rate (2 K/s for our experiment). The kinetics order l has a value 2 for the second-order process [8], and the frequency factor s is obtained by taking the derivative of Eq. (1) with respect to T and setting it to zero at the peak temperature (T_m). For a second-order mechanism, the depth of a trap (E_t) can be obtained by using an equation given by Chen et al. [16–20]

$$E = 3.5(k_B T_m^2/\omega) - 2k_B T_m \quad (3)$$

where ω is the full width at half maximum (FWHM), k_B is Boltzmann's constant, T_m is the thermal peak temperature. Using the above-mentioned method and putting the measured values of T_m, ω, and k_B into Eq. (3), the depths of the traps (E_t) corresponding to the 330 and 350 K TL peaks are calculated as 0.44 and 0.73 eV, respectively.

As Sm^{3+} ions are introduced into the $CaSnO_3$ host, Ca^{2+} sites are replaced by Sm^{3+} because of the small size difference between Ca^{2+} (0.099 nm) and Sm^{3+} (0.096 nm). But it is also possible for Sm^{3+} ions to substitute Sn^{4+} ions. Charge-defect related traps that the electrons or holes can be trapped by them via the Coulomb attraction should be created due to the non-equivalent substitution of Sm^{3+} for Ca^{2+} or Sn^{4+} in this $CaSnO_3:Sm^{3+}$ system. This kind of traps created due to the charge-defects have been found in many other reported LPP materials [8,12,13]. The formation of defects and vacancies due to different valence

states of Ca^{2+}, Sn^{4+} and Sm^{3+} in $CaSnO_3$ host lattice can be expressed as follows:

$$Sm_2O_3 \xrightarrow{CaSnO_3} 2Sm_{Ca}^{\bullet} + V_{Ca}'' + 3O_O^X \qquad (4)$$

$$Sm_2O_3 \xrightarrow{CaSnO_3} 2Sm_{Sn}' + V_O^{\bullet\bullet} + 3O_O^X \qquad (5)$$

Due to the non-equivalent substitution of Sm^{3+} for Ca^{2+}, an excess of positive charge in the lattice must be compensated to maintain the electroneutrality of the CaSnO_3:Sm^{3+} phosphor. There are two possible patterns to fulfill the charge compensation. One possible way is that two Sm^{3+} ions replace three Ca^{2+} ions to balance the charge of the phosphor, which create two $Sm_{Ca}^{\bullet}$ positive defects and one V_{Ca}'' negative defect ($2Sm^{3+} \rightarrow 3Ca^{2+}$ or $2Sm^{3+} + 2Ca^{2+} \rightarrow 5Ca^{2+}$). The other possibility of the charge compensation is the Sn^{4+} vacancies created during the high-temperature synthesis process, which should be also feasible because of the deoxidization of tin oxide component. The 330 K TL peak originates from the defects created by the replacement of Ca^{2+} by Sm^{3+} ions and the latter ~350 K TL peak can be assigned to be related to the cation vacancies. To confirm this assignation, CaSnO_3:Sm^{3+} codoped with CaF_2 and CaSnO_3:Sm^{3+} sintered under H_2 reducing atmosphere condition have also been synthesized and their TL spectra have also been investigated. The TL result revealed that the addition of 1% CaF_2 can greatly reduce the 330 K TL peak and the long persistent phosphorescence, indicating that the addition of F^- ions has significantly reduced the positive $Sm_{Ca}^{\bullet}$ defects density. Furthermore, the CaSnO_3:Sm^{3+} phosphor sintered under H_2 reducing atmosphere has pale body color and not shows any long persistent phosphorescence. The TL peak of the CaSnO_3:Sm^{3+} phosphor synthesized under reducing atmosphere shows high-temperature shift, which confirms that the 350 K according to the cation vacancies because the reducing atmosphere condition favors the cation vacancies.

On the basis of the above-mentioned result, it is reasonable to postulate that when Sm^{3+}-doped into CaSnO_3, the Sm^{3+} ions act as a role of creating the electron traps ($Sm_{Ca}^{\bullet}$) due to the chemically non-equivalent substitution. The hole-trap centers are the cation vacancies created during the high-temperature synthesis process. Under the incident light irradiation, free electrons and holes are formed in the CaSnO_3 matrix. The holes or electrons were trapped by different defect centers. After the excitation source is turned off, the trapped electrons or holes are thermal released at room temperature and they recombined with electrons or holes trapped by other defect centers. The released energy due to the recombination of holes and electrons is transferred to the activator ions and finally leads to the characteristic activator ions afterglow emissions

because the energy transferred from the trap has a slow released ratio.

4. Conclusion

In summary, a novel phosphor, CaSnO_3:Sm^{3+}, which emits in the reddish orange region, is synthesized by a two-step method. The PL and TL properties of it have been systematically investigated. Furthermore, reddish orange LPP emission upon UV light excitation is obvious observed in CaSnO_3:Sm^{3+}. The TL results revealed that there are at least two different traps in this phosphor. The TL glow curve shows that the ca. 330 K TL peak is responsible for the origin of the afterglow. The possible mechanism of this phosphor has also been discussed in detail.

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