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Reddish orange long afterglow phosphor $Ca_2SnO_4:Sm^{3+}$ prepared by sol–gel method

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ABSTRACT

A reddish orange light emissive long afterglow phosphor, $Ca_2SnO_4:Sm^{3+}$ was prepared by sol–gel method at lower temperature. The synthesized phosphors were characterized by X-ray diffraction, scanning electron micrograph images, photoluminescence spectra, afterglow decay curves and thermoluminescence spectra. Three emission peaks locate at 565 nm, 609 nm and 655 nm corresponding to CIE chromaticity coordinates of $x = 0.53$ and $y = 0.47$, which indicates the reddish orange light emitting. The fluorescent intensity and the afterglow characteristic depends on the concentration of Sm^{3+} and the optimized concentration is 1.5 mol%. The afterglow decay curves are well fitted with triple-exponential decay models. The thermoluminescence glow curves show that the Sm^{3+} induces suitable trap depth and result in the long afterglow phenomenon, and the corresponding increase or decrease in afterglow is associated with trap concentration, nearly no change in trap depth. The 1.5 mol% Sm^{3+}-doped Ca_2SnO_4 sample has the biggest trap concentration and exhibit the best afterglow characteristic, its' afterglow time is about 1 h. The phosphorescence mechanism of this long afterglow phosphor was discussed.

1. Introduction

Long afterglow phosphors (LAPs) is a kind of energy-storing material which can absorb energy and then gradually emit visible light for a long time after the excitation is turned off [1]. These materials are used for lighting, display, detection of high energy rays, multidimensional optical memory and imaging storage [2–6], even to supply light to solar cells in complete darkness [7]. The yellow-green, green-blue, green and blue LAP with high brightness and long persist time have been available in the commercial market [2,8–11]. However, afterglow properties of orange to red LAP is still far away from expected target [12]. The red LAP with better luminescent property is difficult to achieve, and there is still lack of orange to red long afterglow phosphors [13–15]. Although much effort has been devoted to the research of orange to red long afterglow materials, but the progresses is very slow [16]. Hence, there is a great demand to develop orange to red LAP, and it has been a focus in this field.

It is well known that the solid-state reaction process is a conventional method for phosphor synthesis, and it requires high calcinations' temperature. In recent years, numerous methods have been employed to prepare phosphors, including sol–gel process [17–19], chemical precipitation method [20,21], combustion synthesis [22,23], combustion-assisted synthesis method [24,25], sol–gel-combustion process [16], microwave-assisted-sol–gel route [26], reverse microemulsion method [27,28], hydrothermal method [29,30], spray pyrolysis method [31,32], template assisted co-deposition method [33], etc. Among them, sol–gel process is an efficient technique for the preparation of phosphors; it has some advantages, such as good mixing of starting materials, relatively low reaction temperature and more homogeneous products [34,35].

In this study, we report a reddish orange afterglow phosphor $Ca_2SnO_4:Sm^{3+}$ prepared by sol–gel method at lower temperature. Ca_2SnO_4 can be prepared by solid-state reaction at temperature of 1250–1300 °C [36]. In rare-earth ions, Sm^{3+} is 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 [31,37,38]. For example, Lakshminarayana et al. reported photoluminescence properties of Sm^{3+}, Dy^{3+} and Tm^{3+}-doped transparent oxyfluoride silicate glass ceramics containing CaF_2 nanocrystal [39]. These glass ceramics have potential technological applications in optoelectronic materials and displays. White light emission from Sm^{3+}/Tb^{3+} co-doped oxyfluoride aluminosilicate glasses under UV light excitation was also reported by Lakshminarayana et al. [40]. The glasses are promising for white LED. The Sm^{3+} ion was adopted as activator for present material to create long-lasting phosphorescence. The surface morphology,

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photoluminescence (PL) and afterglow characteristics were studied. Since thermoluminescence (TL) technique is a very useful tool to reveal valuable information about the traps and their role in determining the spectroscopic properties of long persistent phosphor [41–45], the thermoluminscent spectra of the phosphors were studied, indicating there appears suitable trap depth which results in long-lasting phosphorescence. In addition, the phosphorescence mechanism of this long afterglow phosphor was discussed.

2. Experimental

2.1. Samples preparation

In solid state reaction, the powder sample Ca_2SnO_4:Sm^{3+} was using $CaCO_3$ (A.R.), SnO_2 (A.R.) and Sm_2O_3 (99.99%) as raw material, NH_4Cl (A.R.) and H_3BO_3 (A.R.) as flux. Appropriate amount of raw material and flux were thoroughly mixed in an agate mortar and then triturated with distilled ethanol for an ideal mixing. Afterwards, the mixtures were put into an alumina crucible and calcined in a muffle furnace at 1250–1300 °C for 4 h in air, followed by subsequent cooling in air to ambient temperature.

In sol–gel preparation, the starting materials were $Ca(NO_3)_2{\cdot}4H_2O$ (AR), $SnCl_4{\cdot}5H_2O$ (AR), Sm_2O_3 (99.99%), HNO_3 (AR) and citric acid ($C_6H_8O_7{\cdot}H_2O$, AR). Sm^{3+} was introduced in the form of $Sm(NO_3)_3$ by dissolving Sm_2O_3 in dilute HNO_3 solution. A typical process is described as follow: 30 mmol citric acid was added to a 100 mL of aqueous solution containing 10 mmol $SnCl_4{\cdot}5H_2O$, 0.10 mmol samarium nitrate and 29.9 mmol $Ca(NO_3)_2{\cdot}4H_2O$ stirred for 3 h. Afterwards, the solutions were keeping at 90 °C under constant stirring and became viscous. The sol was continue dried at 90 °C and obtained dried gels. The dried gels were heated for 2 h on an electric stove, and then were ground. The gels were put into alumina crucibles and calcined in a muffle furnace at 900 °C for 6 h in air, followed by subsequent cooling in air at ambient temperature to obtain the final products. The obtained samples were ground lightly into powders and taken to characterization. The samples with content of Sm^{3+} at 0.5 mol%, 1.0 mol%, 1.5 mol%, 2.0 mol% were labeled as S_1, S_2, S_3 and S_4, respectively.

2.2. Measurements

The thermogravimetry-differential scanning calorimetry (TG-DSC) curves of the dried gels (19.8780 mg) for Ca_2SnO_4:Sm^{3+} precursor was measured at 26–1000 °C by a Mettler Toledo TGA/DSC1 thermogravimetric analyzer in air atmosphere, the gels was heated at a rate of 10 °C min^{-1}. The synthesized products were characterized by X-ray diffraction (XRD) using a RigakuD/MAX-2400 X-ray diffractometer over the range of 10–90°, operating at 40 kV and 60 mA, with a step of 0.02° using CuKαX-rays of wavelength 1.5406 Å. Scanning electron micrograph (SEM) images were taken with a JEOL JSM-6380LV scanning electron microscopy.

The photoluminescence (PL) spectra were measured by a Hitachi F-4500 fluorescence spectrophotometer equipped with a xenon lamp as the excitation source. The excitation spectra were obtained scanning from 320 to 575 nm monitored at 609 nm. The emission spectra were scanned from 580 to 630 nm while excited at 409 nm. Both slit widths of 5 nm at the excitation and emission side. The chromaticity coordinates have been calculated from the spectra using the CIE (Commission International de l'Eclairage, France) system.

The afterglow decay properties measurement were performed on a long afterglow phosphor photometer PR305 (Zhejiang University Sensing Instruments Co., Ltd., China) with 1000Lx xenon lamp as excitation source. Minimum resolution is 10^{-2} mcd/m^2. For the afterglow spectra measurement, phosphors were firstly irradiated with 1000Lx D65 lamp for 10 min, then a FMS-I fluorescent spectroradiometer was employed to record emitting brightness after D65 lamp was turned off for 1 s. The afterglow time measurements also use 1000 Lx xenon lamp as excitation source.

The thermoluminescence (TL) spectra measurements were performed by heating the irradiated sample from 303 to 553 K using the FJ-427A1 TL meter (Beijing Nuclear Instrument Factory, China). The sample (2.0 mg) was first excited for 15 min using 254 nm UV radiation standard lamp with a power of 9 W. Then the radiation source was removed and the sample was heated at a linear rate of 1 K/s.

All measurements were carried out at room temperature except for the TG-DSC curves and TL spectra.

3. Results and discussion

The TG-DTA curves of dried gels for Ca_2SnO_4:Sm^{3+} precursor are shown in Fig. 1. It can be seen that the dried gels through four dominating steps to tranform product. First step, the endothermic peak at 153.7 °C in DSC accounted for 44.78% of the initial weight loss in TG which was assigned to the loss of absorbed or residual water of the gels. Second step, a weight loss stage of about 27.76% in the range of 300–593.5 °C that was accompanied by one manifest exothermic peak at 518 °C, the exothermic peak at 518 °C was due to the burnout of the organic species. Third step, a weak exothermic peak at 722 °C corresponding to a weight loss of about 5.29%, that was associated with the nucleated crystal phase. Last step, there hardly any weight loss when the temperature beyond 816 °C, and a weak exothermic peak at 842 °C may be assigned to the form of Ca_2SnO_4 crystal phase.

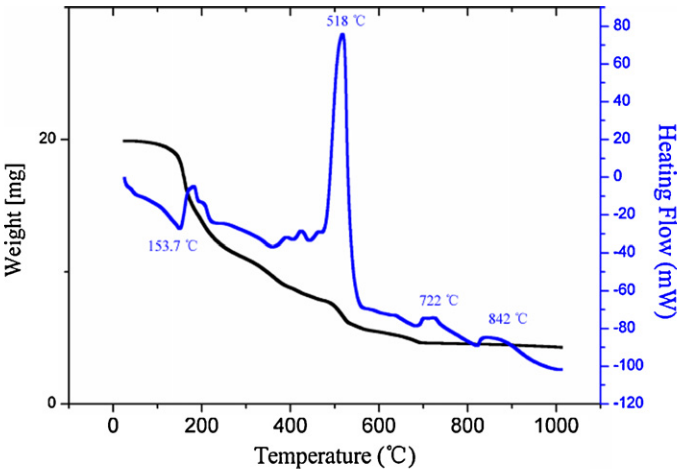

Fig. 1. TG-DTA curves of dried gels for Ca_2SnO_4:Sm^{3+} precursor.

Fig. 2 shows the X-ray diffraction (XRD) patterns of the standard pattern JCPDS No. 74-1493, sample Ca_2SnO_4:Sm^{3+} prepared by solid state reaction and sol–gel method with different mole ratio. When the gel with the molar ratio of Ca:Sn = 2:1, the intermediate phase $CaSnO_3$ appears (Fig. 2b); when the gel with the molar ratio of Ca:Sn = 3:1, the intermediate phase $CaSnO_3$ disappeared, and to form the final product Ca_2SnO_4. The strong peaks of the sample prepared by solid state reaction can be assigned to the phase Ca_2SnO_4. The results suggest that the Ca_2SnO_4 phase can be obtained at lower temperature by sol–gel method.

Ca_2SnO_4 belongs to the Sr_2PbO_4-type structure, with isostructural to that of Sr_2CeO_4 [46,47]. In the structure of Ca_2SnO_4, SnO_6 octahedra are connected in low-dimensional form, SnO_6 octahedra are linked sharing edges with each other and forming

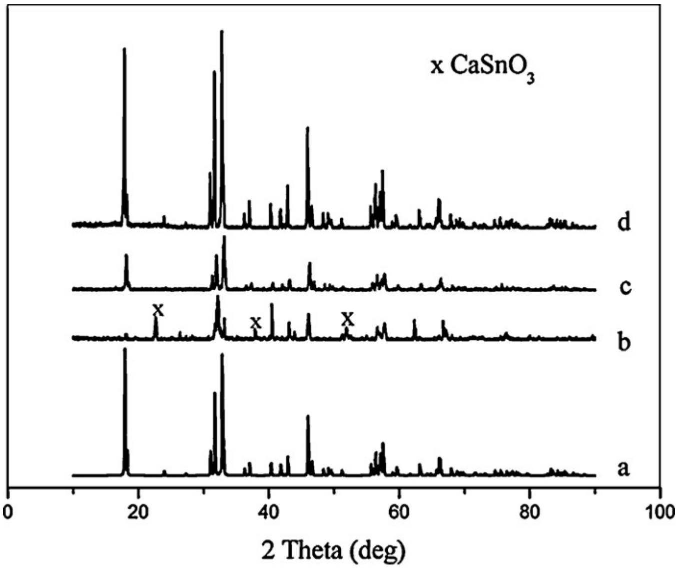

Fig. 2. XRD patterns JCPDS No. 74-1493 database standard for Ca_2SnO_4 (a) and samples Ca_2SnO_4:Sm^{3+} prepared by solid state reaction (d); prepared by sol–gel method with different mole ratio: Ca:Sn = 2:1 (b); Ca:Sn = 3:1 (c).