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Synthesis and photoluminescence properties of $CaGd_2(MoO_4)_4:Eu^{3+}$ red phosphors

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Abstract

The novel red-emitting Eu^{3+} ions activated $CaGd_2(MoO_4)_4$ phosphors were prepared by a citrate sol–gel method. The X-ray diffraction patterns confirmed their tetragonal structure when the samples were annealed above 600 °C. The photoluminescence excitation spectra of $CaGd_2(MoO_4)_4:Eu^{3+}$ phosphors exhibited the charge transfer band (CTB) and intense f–f transitions of Eu^{3+} ion. The optimized annealing temperature and Eu^{3+} ion concentration were analyzed for $CaGd_2(MoO_4)_4:Eu^{3+}$ phosphors based on the dominant red ($^5D_0 \rightarrow {}^7F_2$) emission intensity under NUV (394 nm) excitation. All decay curves were well fitted by the single exponential function. These luminescent powders are expected to find potential applications such as WLEDs and optical display systems.

Keywords: A. Sol–gel processes; C. Lifetime; C. Optical properties

1. Introduction

Recently, GaN chip based solid-state lighting applications has been paid much attention towords the development of white light-emistting diodes (WLEDs) due to their lower energy consumption, high reliability, environmentally-friendly nature, small in size, long working lifetime and high efficiency, which starts to approach the theoretical limits [1–4]. Nowadays, most of the commercial WLEDs are producing by the combination of blue LED chip and yellow emitting $Y_3Al_5O_{12}:Ce^{3+}$ phosphors [5–7]. Unfortunately, $Y_3Al_5O_{12}:Ce^{3+}$ phosphors based WLEDs possesses high thermal quenching and low color rendering index (CRI) owing to the lack of a red component. To solve this problem, the recent research focused on the RGB phosphors based triband WLED, which are excited by near-UV LED in order to get excellent color rendering index.

In order to improve color rendering index, it is still necessary to develop new red phosphors with good color purity and high absorption in near UV or blue wavelength region. Nowadays, Eu^{3+} ion doped molybdate compounds as a red emitting phosphor for near-UV LED were gained much attention due to their brighter red emission and excellent thermal stability compared with the well-known Eu^{3+} doped Y_2O_2S [8–10]. Double molybdate with formula $AR(MoO_4)_2$ (A=Li, Na, K, R=Y, La, Gd) and $AR(MoO_4)_4$ (A=Ca, Sr, Ba, R=Y, La, Gd) which exhibits the scheelite-type ($CaMoO_4$) structure and possess excellent physical and chemical stability [11,12]. These double molybdates are also considered as effective luminescent host materials due to their high efficiency, excellent thermal and mechanical stability and also easy to dope a large number of rare earth ions [13].

Generally, most common approach to prepare phosphors is the traditional solid-state reaction method [14]. This approach typically requires high temperature, time-consuming heating and subsequent grinding processes. The grinding process damages the phosphor surfaces, resulting in the loss of

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emission intensity. Therefore, sol–gel process has gained much attention due to their advantages in obtaining novel chemical compositions with unique properties, excellent purity and relatively low reaction temperature, resulting in more homogeneous product and also possible to synthesize the phosphors with reduced crystallite size [15].

Herein, we report a synthesis of Eu^{3+} ions doped $CaGd_2(MoO_4)_4$ phosphors with a scheelite structure by sol–gel process because it can be excited under the near-UV region and also exhibited more stable chemical and physical properties than that of $Y_2O_2S:Eu^{3+}$ red phosphor [8–10]. The structural properties were investigated by the X-ray diffraction (XRD) patterns. The optical properties of these phosphors were examined in detailed by the measurements of photoluminescence excitation, emission and decay curves.

2. Experimental

$CaGd_2(MoO_4)_4$ phosphors were prepared by a sol–gel method using the stoichiometric amounts of calcium nitrate tetrahydrate $[Ca(NO_3)_2 \cdot 4H_2O]$ (Sigma-Aldrich, $\geq 99.0\%$), Gadolinium nitrate hexahydrate $[Gd(NO_3)_3 \cdot 6H_2O]$ (Sigma-Aldrich, $\geq 99.99\%$), ammonium molybdate tetrahydrate $[(NH_4)_6MoO_7O_{24} \cdot 4H_2O]$ (Sigma-Aldrich, 99.98%) and citric acid $[HOC(COOH)(CH_2COOH)_2]$ (Sigma-Aldrich, $\geq 99.5\%$). The concentration ratio of citric acid and metal ions used in this experiment was 1:2. Initially, the parent host lattice $CaGd_2(MoO_4)_4$ was synthesized by dissolving 1 mmol of calcium nitrate, 2 mmol of gadolinium nitrate, 4 mmol of ammonium molybdate, and 14 mmol citric acid in 200 ml of de-ionized water under magnetic stirring for 1 h. Then, the beaker was closed with a polyethylene cover and the solution was heated to 80 °C on a hot plate with continuous magnetic stirring and this temperature was maintained for 5 h. After 5 h, the cap was removed, and thus the solution was evaporated within 1 h and yellowish wet gel was produced. The gel dried at 100 °C in an oven for a day in ambient atmosphere. The dried powder was annealed at different temperatures from 600 to 1000 °C for 5 h in ambient atmosphere.

The structure of $CaGd_2(MoO_4)_4$ phosphors was analyzed with powder X-ray diffraction recording on X'PERT PRO X-ray diffractometer with a CuKα = 1.5406 Å and beam voltage of 40 KV and 30 mA beam current. The reflectance spectra were measured by using the JASCO V-670 UV–visible spectrophotometer. The luminescence properties were measured at room temperature using the luminescence spectrophotometer (Photon Technology International (PTI)) with a 60 W xenon arc lamp and the decay curve was measured with a phosphorimeter attachment to the main system with a xenon flash lamp (25 W power).

3. Results and discussion

Fig. 1 illustrates the TG/DTA curves of the powder precursor of Eu^{3+} doped $CaGd_2(MoO_4)_4$ obtained by a sol–gel method. The TG curve shows three distinct weight loss steps upto 700 °C and no further weight loss was registered between 700 and 1200 °C. The weight loss is related to the decomposition of the organic matrix. The DTA curve consist of four exothermic peaks at 269, 550, 699 and 742 °C. The first peak indicate that the thermal events can be associated with the exhaustion of organic species of surface absorbed water and citric acid, and the second exothermic peak at 550 °C is due to the crystallization of $CaGd_2(MoO_4)_4$ powder from the amorphous component. The crystallization temperature is well in agreement with the XRD analysis.

Fig. 2 shows the XRD powder patterns of the 3 mol% Eu^{3+} ions doped $CaGd_2(MoO_4)_4$ phosphors at different annealing temperatures from 600 to 1000 °C. All diffraction peaks of $CaGd_2(MoO_4)_4$ annealed at the temperature from 600 to 1000 °C could be indexed to tetragonal phase of $CaMoO_4$ powllite without secondary phase which is very close to that of standard JCPDS card [PDF(77–2238)]. No secondary phase was detected at the current doping level indicating that the Eu^{3+} ions are effectively doped in the host lattice. Due to the small ionic radii difference between Eu^{3+} ($r = 1.066$ Å, CN = 8) and Gd^{3+} ($r = 1.053$ Å, CN = 8) ions, Eu^{3+} ions effectively substitute in the site of Gd^{3+} ions [16]. Typically, the crystallite size can be estimated by using the Scherrer's

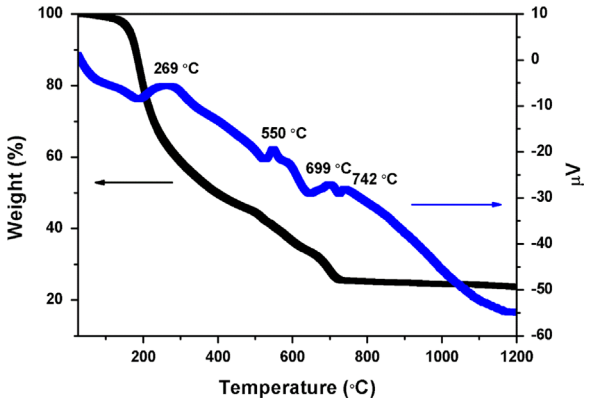

Fig. 1. TG/DTA curves of $CaGd_2(MoO_4)_4:Eu^{3+}$ powder precursor.

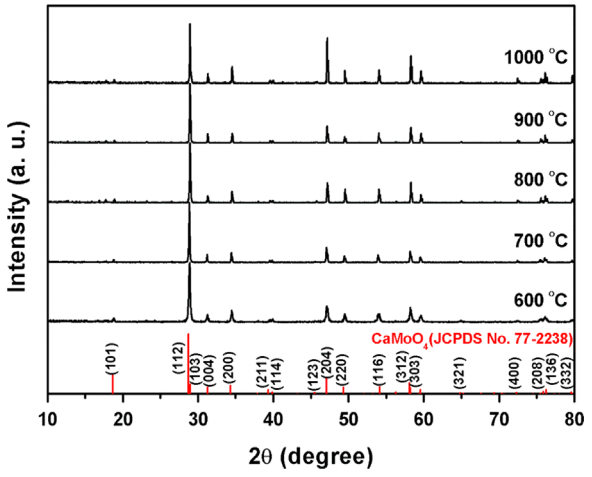

Fig. 2. X-ray diffraction patterns of $CaGd_2(MoO_4)_4:3Eu^{3+}$ phosphors as a function of annealing temperature.