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Photoluminescence properties of $Ca_{0.99}Eu_{0.01}(Mo_{1-x}Si_x)O_4$ nanocrystals red-phosphors obtained by the hydrothermal method

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ABSTRACT

In this paper, we report the obtention of a novel red-emitting $Ca_{0.99}Eu_{0.01}(Mo_{1-x}Si_x)O_4$ nanocrystals phosphor synthesized by the hydrothermal method for the first time, and its photoluminescence (PL) properties were investigated for application to white-light-emitting diodes (W-LEDs). The as-synthesized phosphors were characterized by means of X-ray powder diffraction (XRD), transmission electron microscope (TEM), high-resolution transmission electron microcopy (HR-TEM), photoluminescence excitation (PLE) and PL emission spectra. XRD patterns, TEM images and PL emission indicated that the introduction of Si^{4+} ions promotes the distortion and slight shrinking of the unit cell, narrow size distribution and the blue-shift of the charge transfer bands of $Ca_{0.99}Eu_{0.01}MoO_4$ red-phosphors. PL properties revealed that the optical brightness as well as the intensity ratio of $^5D_0 \rightarrow {}^7F_2$ to $^5D_0 \rightarrow {}^7F_1$ was highly dependent on the Si^{4+} ions concentration. The morphological evolution was explained via a crystal growth mechanism. Introduction of 5 mol% Si^{4+} ions into the crystal structure enhanced the PL emission brightness, and the nanocrystals $Ca_{0.99}Eu_{0.01}(Mo_{0.95}Si_{0.05})O_4$ red-phosphors showed the relatively most promising PL performance with the most intense emission. The CIE chromaticity coordinates for nanocrystals $Ca_{0.99}Eu_{0.01}(Mo_{1-x}Si_x)O_4$ red-phosphors were simulated and located in the red region. All the results imply that the studied $Ca_{0.99}Eu_{0.01}(Mo_{1-x}Si_x)O_4$ nanophosphors could be potentially used as W-LEDs.

1. Introduction

Solid-state lighting based on InGaN semiconductors has attracted great attention due to the long lifetimes, high energy efficiency, compact structure, and environmental friendliness of white LEDs (W-LEDs) [1,2]. Recently, most commercially available W-LEDs are based on the phosphor-converted emission process [3,4]. The most common and convenient method to generate a W-LEDs is to combine a blue LED with a yellow-emitting phosphors, which has low color rendering index (CRI) because of lack of red component in their spectra [5,6]. So another way of obtaining W-LEDs is sought out, utilizing a near-UV LED chip combined with phosphors including red, green and blue emitting phosphors designed to convert the UV light to visible light [7,8]. Similarly, the red-emitting phosphors for W-LEDs are also essential. Therefore, the search for a stable red-emitting phosphor with a high absorption in the near-ultraviolet or blue spectral region is consequently an attractive and challenging research assignment [9–12].

In recent years, $CaMoO_4:Eu^{3+}$, as a red emitting phosphor, has been investigated extensively because of its attractive luminescence property with the promising applications in NUV GaN chip based w-LEDs [13–22]. The red emission is originated from $^5D_0 \rightarrow {}^7F_2$ transition of Eu^{3+} and the NUV excitation performs at around 395 nm through $^7F_0 \rightarrow {}^5L_6$ absorption of Eu^{3+}. To further improve its luminescent properties, a few significant investigations have been done of this phosphor by codoping other ions, such as Na^+ [18,19], Bi^{3+} [20], Sm^{3+} [21], and Si^{4+} [22]. For example, Ci et al. [22] synthesized the series $Ca_{1-x}Eu_{0.01}Mo_{1-y}Si_yO_4$ phosphors and investigated the properties of luminescence in detail. However, most of them were synthesized by a conventional solid-state reaction route, which usually requires high temperature, time-consuming heat treatment process, subsequent product grinding. The grinding damages the phosphor surfaces, resulting in an emission intensity loss. Meanwhile, the phosphors are relatively large in sizes and have inhomogeneous composition and morphology fabricated by conventional reactions at high temperature [23]. In view of the disadvantages of the high-temperature strategy, hydrothermal synthesis method has been well developed as one of facile methods for the preparation of phosphors [15].

Therefore, to the best of our knowledge, no investigations have been performed on studying the luminescence properties of of $Ca_{0.99}Eu_{0.01}(Mo_{1-x}Si_x)O_4$ nanophosphors via hydrothermal method. In the present work, we report the luminescence properties of

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$Ca_{0.99}Eu_{0.01}(Mo_{1-x}Si_x)O_4$ nanophosphors, and discuss the influence of the Si^{4+} ion on the crystal structure, morphology, PL properties and CIE of these phosphors in detail.

2. Experimental

The nanostructure $CaMoO_4$ phosphors were synthesized via a facile hydrothermal method. The required device is a 50 mL Teflon-lined stainless steel autoclave. All the raw chemical materials were used without further purification. The detail of reaction procedure is as follows: $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (Shanghai Chemical Reagent, A.R. grade) was used to offer MoO_4^{2-}, and it was prepared by adding 2 mmol of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ into 20 mL of deionized water. Meanwhile, 2 mmol of CaO (Shanghai Chemical Reagent, A.R. grade) was solved in 20 mL of thin nitrate to be $Ca(NO_3)_2$ solution. Then, the dopant ions were added into $Ca(NO_3)_2$ solution by dropping appreciated $Eu(NO_3)_3$(0.1 M) (Shanghai Yuelong New Materials Co. Ltd., 99.99%) solution, which was prepared in advance. The $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ and tetraethyl orthosilicate (TEOS, $(C_2H_5O)_4Si$, Shanghai Chemical Reagent, A.R. grade) solution were dropped into $Ca(NO_3)_2{:}Eu^{3+}$ solution slowly under vigorous stirring. A white precipitate was observed in the glass beaker. The pH value was adjusted to an appropriate constant with diluted ammonia or diluted nitric acid, which is a key factor to the morphology of the crystals. The vigorous stirring was continued for 30 min. Finally, the precursor solution was transferred into a 50 mL Teflon-lined stainless steel autoclave, which was subsequently sealed and maintained at 160 °C for 10 h. After that, the autoclave was cooled to room temperature naturally. The product was collected by filtering and washing several times with deionized water and absolute ethanol. Then, the powder was obtained after being dried in air at 100 °C for 2 h.

The synthesis reaction could be described as follows:

$$(C_2H_5O)_4Si + 2H_2O \rightarrow 4C_2H_5OH + SiO_2 \tag{1}$$

$$\begin{aligned}&(1-x)Ca(NO_3)_2\cdot 4H_2O + 1/7(NH_4)_6Mo_7O_{24}\cdot 4H_2O\\&\quad + x/2Eu_2O_3 \xrightarrow{160\,^{\circ}\mathrm{C}10\mathrm{h}} Ca_{1-x}MoO_4 : xEu^{3+}\end{aligned} \tag{2}$$

The structural order of the as-synthesized crystals red-phosphors was investigated by X-ray diffraction (XRD) patterns with a X-ray Diffractometer (Brucker D8) with Cu Kα radiation at 40 kV and 40 mA. The XRD patterns were collected in the range of $10^{\circ} \leqslant 2\theta \leqslant 90^{\circ}$. The morphology of the samples was inspected using transmission electron microscope, model H-7650, operated at 100 kV. The PL and PLE spectra were recorded on a Hitachi F-7000 fluorescence spectrometer with a 150 W-xenon lamp. All the measurements were carried out at room temperature.

3. Results and discussion

3.1. Crystal structure

$CaMoO_4$ nanocrystals crystallizes in a Scheelite-type tetragonal structure with a space group ($I41/a$) symmetry group point (C_{4h}^6) and lattice parameters ($a = b = 5.243$ Å, $c = 11.381$ Å, $V = 312.89$ Å^3) [24]. The detailed crystal structure of $CaMoO_4$ is shown in Fig. 1. This unit cell was modeled through the Visualization for Electronic and Structural Analysis (VESTA) program, version 3.0.9, for Windows [25]. In this structure, the molybdenum atoms are coordinated to four oxygen's, forming $[MoO_4]$ clusters with tetrahedral configuration and tetrahedral polyhedra, while the calcium atoms are bonded to eight oxygen's, resulting in $[CaO_8]$ clusters with deltahedral configuration and snub disphenoid polyhedra [26]. It is also suggested that Ca and Mo sites present S_4 point symmetry [27,28]. According to the rule that an acceptable percentage difference in the ion radii between doped and substituted ions must not exceed 30% [29], Ca^{2+} (1.12 Å, CN = 8) and Mo^{6+} (0.41 Å, CN = 4) can be replaced by Eu^{3+} (1.07 Å, CN = 8) and Si^{4+} (0.26 Å, CN = 4) in the $CaMoO_4$ structure, respectively [30].

3.2. XRD and transmission electron microscopy analysis

XRD patterns of $Ca_{0.99}Eu_{0.01}(Mo_{1-x}Si_x)O_4$ ($0 \leqslant x \leqslant 0.07$) together with the Joint Committee on Powder Diffraction Standards (JCPD#PDF) card No. 29-0351 are shown in Fig. 2a [31]. From a comparison between them, the position and intensity of the peaks are the same. No impurity lines were observed, and the entire pattern could be well indexed to a $CaMoO_4$ single phase.

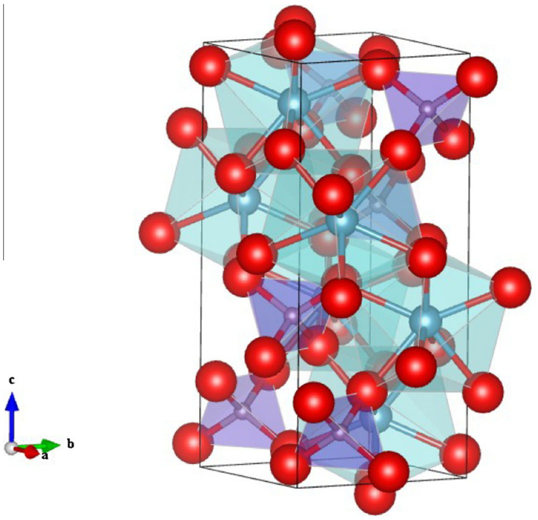

Fig. 1. Crystal structure of $CaMoO_4$ (The pink, blue and red spheres represent Ca^{2+}, Mo^{6+} and O^{2-}, respectively). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

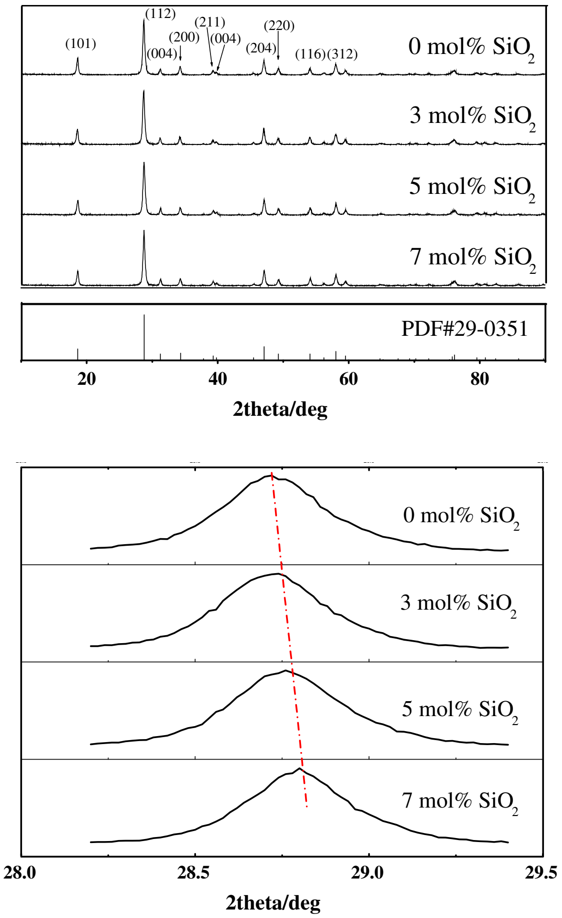

Fig. 2. XRD patterns of $Ca_{0.99}Eu_{0.01}(Mo_{1-x}Si_x)O_4$ nanocrystals ($0 \leqslant x \leqslant 0.07$) and vertical lined are correspondent to JCPD#PDF card no. 27-0212 (a). The inset shows the local amplification of (a), which were indexed as (1 1 2) crystallographic plane.

Fig. 2b shows the shifts of the main XRD peak to the lower-angle side in the Si^{4+} ions -added samples compared to the Si^{4+} ions-free sample, which can be attributed to the lattice shrinking because the ionic radii of Si^{4+} ions is smaller than that of Mo^{6+} ions.