Optical Materials 75 (2018) 258–266

Contents lists available at ScienceDirect

Optical Materials

journal homepage: www.elsevier.com/locate/optmat

Luminescence enhancement of $Ca_3Sr_3(VO_4)_4$:Eu^{3+}, Sm^{3+} red-emitting phosphor by charge compensation

Qinxue Tang [a], Kehui Qiu [a, *], Wentao Zhang [a], Yuqiao Shen [b], Junlan Wang [b]

[a] College of Materials and Chemistry & Chemical Engineering, Chengdu University of Technology, Chengdu, 610059, China
[b] Institute of Materials Science and Technology, Chengdu University of Technology, Chengdu, 610059, China

ARTICLE INFO

Article history:
Received 6 September 2017
Received in revised form
29 September 2017
Accepted 23 October 2017

Keywords:
Vanadate
Red phosphor
Charge compensation
Combustion method
Photoluminescence

ABSTRACT

A series of red-emitting phosphors $Ca_3Sr_3(VO_4)_4$:$0.05Eu^{3+}$; $Ca_3Sr_3(VO_4)_4$:$0.05Eu^{3+}$, xSm^{3+}; and $Ca_3Sr_3(VO_4)_4$:$0.05Eu^{3+}$, $0.05Sm^{3+}$, yM^+ (M = Li, Na, and K) were fabricated with the combustion method. The microstructure and photoluminescence properties of the phosphors were investigated via X-ray powder diffraction, scanning electron microscopy, and photoluminescence spectroscopy. The obtained results revealed that all samples perfectly matched the rhombohedral structure with *R*3*c* space group. The results showed that the luminescence properties of Eu^{3+} ions could evidently be improved by co-doping with Sm^{3+} ions. When the doping mole fraction of Sm^{3+} ions was 5%, the relative luminous intensity at 619 nm was maximal under an excitation of 464 nm. Moreover, incorporation of charge compensators (i.e., Li^+, Na^+, and K^+) could improve both the luminescence intensity and thermal stability of phosphors under an excitation of 464 nm and this paper discusses and interprets the underlying reason. The optimal concentration of the charge compensator M^+ (M = Li, Na, and K) was 5%. In particular, the Li^+-doped sample exhibited significantly enhanced emission intensity and thermal stability under an excitation wavelength of 464 nm and its emission intensity was approximately 1.9-fold of that of $Ca_3Sr_3(VO_4)_4$:$0.05Eu^{3+}$, $0.05Sm^{3+}$. Furthermore, the CIE chromaticity coordinate of $Ca_3Sr_3(VO_4)_4$:$0.05Eu^{3+}$, $0.05Sm^{3+}$, $0.05Li^+$ phosphor was found to be closer to the standard red-emitting point ($x = 0.67$, $y = 0.33$) compared to $Ca_3Sr_3(VO_4)_4$:$0.05Eu^{3+}$, $0.05Sm^{3+}$. The luminescence performance of $Ca_3Sr_3(VO_4)_4$:Eu^{3+}, Sm^{3+}, Li^+ upon excitation with blue light radiation makes this a potential red-emitting phosphor for application in blue-based white light emitting diodes.

1. Introduction

White light emitting diodes (WLEDs) are a new generation of green lighting source due to their long lifetime, low-energy consumption, small volume, eco-friendliness, and rapid reaction rate [1–4]. Currently, the conventional method for fabricating white light involves the use of a yellow phosphor (typically YAG: Ce^{3+}) in combination with a blue-emitting InGaN LED chip. However, this approach leads to high color temperature and represents an imperfect match in terms of color rendering in the red region. Moreover, this approach does not satisfy the requirements for low-color-temperature illumination [5]. To solve these problems, the following two solutions are available: The first solution involves the use of green-emitting and red-emitting phosphors to completely replace yellow-emitting phosphor. Green- and red-emitting phosphors utilize their green and red lights in combination with the light of blue LEDs to produce white light. A further approach combines semiconductor chips of tri-color phosphors to fabricate white LEDs excited by an ultraviolet (UV) or near-ultraviolet (NUV) chip [6,7]. The color of this type of white LED is determined by phosphors and has excellent color reducibility, high luminous efficiency, and high color rendering index (Ra>90). This approach is considered to dominate white LEDs [8–10]. Currently, the most commonly and commercially available red-emitting phosphors in tri-color LEDs use Y_2O_2S:Eu^{3+} and Y_2O_3:Eu^{3+} and are inefficient under the NUV light excitation and chemically unstable. Therefore, development of a new inorganic red-emitting phosphor is highly desirable to combine appropriately a blue light LED for signaling or illumination applications. Moreover, the majority of currently available commercial red-emitting phosphors use rare-earth elements as the positive ions in the host lattices (e.g., Lu^{3+}, La^{3+}, and Gd^{3+}), which leads to considerably higher cost of red-emitting

* Corresponding author.
E-mail address: qkh2188@163.com (K. Qiu).

https://doi.org/10.1016/j.optmat.2017.10.040
0925-3467/

phosphors compared to yellow-emitting and blue-emitting phosphors.

Currently, red-emitting phosphor that uses sulfide as the matrix is a relatively mature technology that is extensively used [11,12]. However, solid-state phosphors based on vanadates doped with rare-earth ions have attracted increasing attention since they can be easily excited by a broad range of wavelengths and they have stable chemical characteristics [13,14]. In the vanadate (VO_4^{3-}) group, four oxygen ions are coordinated to a V^{5+} ion in a structure with tetrahedral symmetry, which has been considered as an effective luminescent center [15]. Due to the occurrence of energy transfer, the photoluminescence intensity of vanadate-based phosphors can be improved by doping trivalent rare-earth ions into vanadate hosts. Moreover, it has also been reported that the energy between the $^4G_{5/2}$ energy level of Sm^{3+} and the $^5D_0$ energy level of Eu^{3+} is almost similar [16]. Thus, it seemed plausible that Sm^{3+} could transfer absorbed energy to Eu^{3+} in $Ca_3Sr_3(VO_4)_4$ phosphor, while also improving the emission intensity. In particular, Eu^{3+}-doped vanadate-based phosphors have been investigated since they can be extensively applied in the solid-state luminescence industry [17]. Choi et al. [18] reported the use of such a solid state reaction to synthesize $Ca_3Sr_3(VO_4)_4$:Eu^{3+} and $Ca_3Sr_3(VO_4)_4$:Eu^{3+}, M^+ (M = Li, Na, and K) red-emitting phosphors and the authors discussed the effects of Eu^{3+} concentration, of the type of charge compensator, and of their concentration on emission intensity. Sun et al. [19] reported the use of a solid state reaction to synthesize $Ca_3Sr_3(VO_4)_4$:Sm^{3+}, Na^+ red-emitting phosphors. Compared to conventional solid-state reactions, the combustion method can be initiated at relatively low temperatures [20]. Furthermore, it offers many advantages such as short reaction time, high efficiency of energy conservation, and homogeneous grain size. To the best of our knowledge, no reports exist about $Ca_3Sr_3(VO_4)_4$:Eu^{3+}, Sm^{3+} red-emitting phosphors using charge compensator co-doping for the fabrication of white LEDs.

In this study, the citric acid assisted sol combustion method was utilized to synthesize $Ca_3Sr_3(VO_4)_4$:Eu^{3+}; $Ca_3Sr_3(VO_4)_4$:Eu^{3+}, Sm^{3+}; and $Ca_3Sr_3(VO_4)_4$:Eu^{3+}, Sm^{3+}, M^+ (M = Li, Na, and K) phosphors for the first time. The photoluminescent properties of $Ca_3Sr_3(VO_4)_4$:Eu^{3+}, Sm^{3+} and $Ca_3Sr_3(VO_4)_4$:Eu^{3+}, Sm^{3+}, M^+ (M = Li, Na, and K) samples were investigated. Moreover, both the thermal stability and the luminescence lifetime of samples were investigated and the relevant mechanism was analyzed.

2. Experimental

2.1. Sample preparation

The compounds $Ca_3Sr_3(VO_4)_4$:0.05Eu^{3+}; $Ca_3Sr_3(VO_4)_4$:0.05Eu^{3+}, xSm^{3+}; and $Ca_3Sr_3(VO_4)_4$:0.05Eu^{3+}, 0.05Sm^{3+}, yM^+ (M = Li, Na, and K) phosphors were fabricated with the combustion method. The starting materials were high-purity europium oxide (Eu_2O_3), high-purity samarium oxide (Sm_2O_3), analytical reagent (AR) grade calcium carbonate ($CaCO_3$), AR grade strontium carbonate ($SrCO_3$), AR grade ammonium metavanadate (NH_4VO_3), nitric acid (HNO_3), and citric acid ($C_6H_8O_7\cdot H_2O$). Stoichiometric amounts of Eu_2O_3 and Sm_2O_3 were dissolved in 1 mL HNO_3 with 15 mL distilled water to obtain a homogeneous solution. Then, $CaCO_3$, $SrCO_3$, $C_6H_8O_7\cdot H_2O$, and NH_4VO_3 were added to the solution under heating and stirring at a temperature of 70–80 °C. After stirring this solution for approximately 30 min, the blue sol precursor was obtained, which was placed in a furnace at a definite temperature of 900 °C for 1 h under air atmosphere. In some cases, the appropriate stoichiometric ratio of AR grade Li_2CO_3, AR grade Na_2CO_3, and AR grade K_2CO_3 was applied as charge compensator. The final products were allowed to cool to room temperature in the furnace.

2.2. Characterization

The crystal structure of samples was determined via X-ray diffraction (XRD, Philips X'Pert Pro MPD, 40 KV, 40 mA, λ = 1.5418 Å) with CuKα radiation. The sample morphologies and particle sizes were obtained via scanning electron microscopy (SEM) using a JEX-100CX scanning electron microscope at a running voltage of 10 kV. Excitation and emission spectra of all synthesized samples were measured with a Hitachi F-7000 fluorescence spectrophotometer. The thermal quenching characteristics of phosphors were measured via a heating stage (LINKAMHFS600, England) in the range of 25–250 °C at a heating rate of 50 °C min^{-1}. The luminescence lifetime of the synthesized samples was obtained via fluorescence spectrophotometer (Fluorolog-3-Tau, JobinYvon Inc. USA). All samples were measured at room temperature.

3. Results and discussion

3.1. Crystal structure and characterization

Powder XRD patterns of $Ca_3Sr_3(VO_4)_4$:Eu^{3+}, Sm^{3+} and $Ca_3Sr_3(VO_4)_4$:Eu^{3+}, Sm^{3+}, M^+ (M = Li, Na, and K) phosphors are shown in Fig. 1. All samples consisted of the same concentration of Eu^{3+}, Sm^{3+}, and the charge compensator and were fired under the same conditions. Fig. 1 shows that the diffraction peaks of all samples perfectly matched the standard diffraction peaks of $Ca_3Sr_3(VO_4)_4$ (PDF card: JCPDS 52-0468), which had a rhombohedral structure. These results confirmed that all samples synthesized in this study (after firing at 900 °C for 1 h) were of high purity and belonged to the *R*3*c* space group, without the occurrence of other apparent mixed phases. Furthermore, Eu^{3+}, Sm^{3+}, and the charge compensator M^+ (M = Li, Na, and K) entered into the crystal lattice of $Ca_3Sr_3(VO_4)_4$ without affecting the structure of the host [21]. Considering the ionic sizes and coordinated number (CN) of Sr^{2+} (0.118 nm for CN = 8), Ca^{2+} (0.099 nm for CN = 8), Eu^{3+} (0.094 nm for CN = 8), and Sm^{3+} (0.096 nm for CN = 8) and their valence states, Eu^{3+} and Sm^{3+} ions can easily substitute Ca^{2+} ions in $Ca_3Sr_3(VO_4)_4$ phosphor, which is reflected by diffraction patterns.

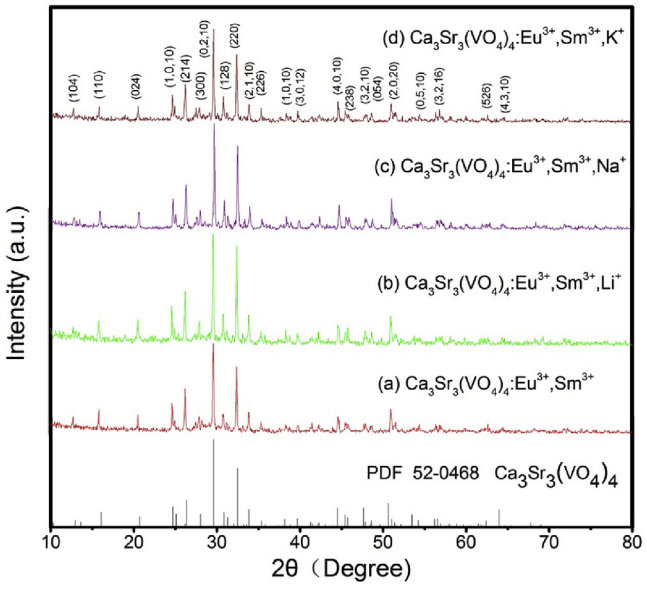

Fig. 1. XRD patterns of $Ca_3Sr_3(VO_4)_4$:Eu^{3+}, Sm^{3+} and $Ca_3Sr_3(VO_4)_4$:Eu^{3+}, Sm^{3+}, M^+ (M = Li, Na, and K) phosphors obtained at 900 °C.