Journal of Alloys and Compounds 508 (2010) 475–479

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

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

Preparation and luminescent properties of a novel red emitting phosphor of $Ca_{1-2x}M_xIn_2O_4{:}xEu^{3+}$ (M = Li, Na, K) for white LED solid-state lighting

Xiaosong Yan, Wanwan Li*, Kang Sun*

School of Materials Science and Engineering, State Key Lab of Metal Matrix Composites, Shanghai Jiao Tong University, 800 Dongchuan Road, Shanghai 200240, PR China

ARTICLE INFO

Article history:
Received 11 February 2010
Received in revised form 15 August 2010
Accepted 24 August 2010
Available online 19 September 2010

PACS:
42.50.Ex

Keywords:
Phosphor
Luminescence
Solid-state reaction

ABSTRACT

The phosphors of $Ca_{1-2x}M_xIn_2O_4{:}xEu^{3+}$ (M = Li, Na, K) were prepared by solid-state reaction method, which showed the characteristic emissions of Eu^{3+} ($^5D_j \rightarrow {}^7F_{j'}$, $j = 0, 1, 2, 3$ $j' = 0, 1, 2, 3$ transitions). The emission located at 618 nm due to the $^5D_0 \rightarrow {}^7F_2$ transition was dominantly observed in the photoluminescence (PL) spectrum, leading to a red emission of the phosphors. The phosphors can be excited efficiently by both 394 nm and 465 nm light. Li^+, Na^+, K^+ ions were doped as charge compensators to enhance red emission of the phosphors, and different effects of the alkali metal ions on the luminescence of the phosphors were investigated.

1. 1.Introduction

Solid-state white light-emitting diode (w-LED) is an attractive replacement for the current illumination applications because of its longer service lifetime, lower thermal resistance, more compact size and higher efficiency [1]. The devices combining a yellow emitting YAG:Ce phosphor with a blue emitting InGaN LED chip have been widely commercialized since 1997. However, this type of white light has a less satisfactory color rendering (CRI ~ 70) for the deficiency of color in red and green regions [2]. One of the most promising approaches to solve the problem is the utilization of a near-UV-LED chip (360–410 nm) in combination with blue, green and red emitting phosphors, which provides a more balanced white emission spectrum and a higher color rendering. Presently, the main commercial red phosphor for near-UV-LED is $Y_2O_2S{:}Eu^{3+}$ [3–4]. However, the sulfide red phosphor is chemically unstable and the absorption efficiency in the near-UV-region is not desirable compared to that of the blue ($BaMgAl_{10}O_{17}{:}Eu^{2+}$) [5,6] and the green ($ZnS{:}(Cu^+, Al^{3+})$) [7] phosphors. Therefore, more attention has been paid to the investigation of the red emitting materials using near-UV-LED as the excitation source in the past few years [8–11], and it is significant to develop new stable phosphors that emit a more intense component in the red region.

Materials containing Eu^{3+} (f^6) fluoresce via transitions from a $^5D_0$ to $^7F_2$ level at 611 nm when Eu^{3+} presents in a non-centrosymmetric site and form useful red phosphors. This approach has been successfully utilized in molybdate and tungstate scheelites [12–15]. However, the emission is composed of only several red sharp lines in lack of light in orange–yellow regions. Oxide semiconductors have been shown to be promising phosphor materials due to their wide band gap, low absorbance in the visible region and their chemical and thermal stabilities [16–21]. Among the oxides, $M'In_2O_4$ (M′ = Ca, Sr) has been widely used as an excellent host material for rare earth metal ions doped phosphors. Tb^{3+} doped $M'In_2O_4$ (M′ = Ca, Sr) was reported to emit green luminescence [19] and the red emitting material of $SrIn_2O_4{:}Eu^{3+}$ was reported to have not only a broad and intense charge transfer band in UV-region but also the intense excitation of Eu^{3+} at around 395 nm and 465 nm which perfectly matches with the emission spectra of both near-UV and blue-LEDs chips [20,21]. However, the radius of Eu^{3+} is 107 pm, which is highly different from that of In^{3+} (80 pm). Therefore, a part of Eu^{3+} ions will be assumed to substitute Sr^{2+} (126 pm) [22]. The difference between the radii of the two types of ions indicates a distortion in the crystal structure when Eu^{3+} is doped to substitute the position of Sr^{2+}, which may lead to a negative influence on the luminescence of the phosphor. Therefore, we have specifically been interested in Eu^{3+} doped $CaIn_2O_4$ because of the similar radius of Ca^{2+} (112 pm) to that of Eu^{3+}. Recently, the white light emission from Eu^{3+} in the $CaIn_2O_4$ host under the excitation of 397 nm light has been reported by Liu and co-workers [23,24]. The white light consists of emission lines from transitions of $^5D_{0,1,2,3}$ excited states

---

* Corresponding authors.
E-mail addresses: wwli@sjtu.edu.cn (W. Li), ksun@sjtu.edu.cn (K. Sun).

0925-8388/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2010.08.096

Table 1
Calculated lattice parameters of Eu^{3+} doped $CaIn_2O_4$.

	a (Å)	*b* (Å)	*c* (Å)
$CaIn_2O_4$	9.6500	11.3000	3.2100
$CaIn_2O_4$:0.05Eu^{3+}	9.6492	11.3018	3.2106
$CaIn_2O_4$:0.08Eu^{3+}	9.6513	11.3013	3.2122
$CaIn_2O_4$:0.1Eu^{3+}	9.6527	11.2993	3.2141
$CaIn_2O_4$:0.15Eu^{3+}	9.6533	11.2982	3.2154

to the ^7F_j ground states of Eu^{3+}, and is realized at the low doping concentration of Eu^{3+} (∼1%). Red emission from $CaIn_2O_4$ doped with a high concentration of Eu^{3+} (up to 10%) was also reported by Liu and co-workers [23], however, to our knowledge, few report about the charge balance in the host lattice of $CaIn_2O_4$ doped with a high concentration of Eu^{3+} (over 5%) for red phosphor can be found.

In this paper, a novel red phosphor $Ca_{1-2x}M_xIn_2O_4{:}xEu^{3+}$ (M = Li, Na, K) with strong luminescence has been prepared. Eu^{3+} is doped in $CaIn_2O_4$ host lattice to obtain a red emitting phosphor, and alkali metal ions such as Li^+, Na^+, K^+ are co-doped as charge compensators to enhance the luminescence of the Eu^{3+} doped $CaIn_2O_4$. The effects of the charge compensation on the luminescent properties of different alkali metal ions are investigated. The performance of our phosphors is also compared to some popular red phosphors of $Y_2O_2S{:}Eu^{3+}$ and $CaMoO_4{:}Eu^{3+}$.

2. Experimental

A series of Eu^{3+} doped and Eu^{3+}, M^+ (M = Li, Na, K) co-doped $CaIn_2O_4$ phosphors were prepared by traditional solid-state reactions. The starting materials $CaCO_3$(A.R), In_2O_3(A.R) and Eu_2O_3(4N) were weighted with an appropriate stoichiometric ratio. The molar concentration of the activator Eu^{3+} ions varied from 5% to 18%. An appropriate amount of Li_2CO_3(A.R), Na_2CO_3(A.R) and K_2CO_3(A.R) were added as the charge compensators. All the starting powders were blended and grinded by ball milling thoroughly at 300 rpm for 3 h. After dried at 80 °C for 12 h, the homogeneous mixture obtained was put into an alumina crucible and calcined in a muffle furnace at the temperature of 900 °C for 3 h into the intentional sample.

The synthesized samples were identified by X-ray diffraction (XRD), which was recorded on a BRUKER-AXS X-ray diffraction running Cu Kα radiation at 40 kV and 250 mA. The measurements of photoluminescence (PL) and photoluminescence excitation (PLE) spectra were performed by using a SHIMADZU RF-2550 spectrometer equipped with a 150 W xenon lamp under a working voltage of 400 V. The excitation and emission slits were set at 5.0 nm. The CIE chromaticity coordinates were measured by using a SPR 920F scanning spectroradiometer. All the measurements were performed at room temperature.

3. Results and discussion

3.1. Structure of Eu^{3+} doped and Eu^{3+}, M^+ (M = Li, Na, K) co-doped $CaIn_2O_4$

The XRD patterns of Eu^{3+} doped $CaIn_2O_4$ samples are shown in Fig. 1, and the samples are synthesized without any charge compensation. According to JCPDS card 17-0643, $CaIn_2O_4$ has an orthorhombic crystal structure with the P*ca*2$_1$ or P*bcm* space group, and its lattice parameter is *a* = 9.650 Å, *b* = 11.300 Å, *c* = 3.210 Å. $CaIn_2O_4$ has two kinds of InO_6 octahedra. InO_6 octahedra are connected to each other by sharing edges structure, while Ca is located in the tunnel. When the concentration of Eu^{3+} is below 0.18, the XRD patterns of the samples are consistent with the standard data of $CaIn_2O_4$. The calculated lattice parameters of Eu^{3+} doped $CaIn_2O_4$ are listed in Table 1 and little variation is found in all the three lattice parameters with the increasing concentration of Eu^{3+}. The ionic radius of Eu^{3+} is 107 pm, which is similar to that of Ca^{2+} (112 pm), and larger than that of In^{3+} (80 pm). Thus, Eu^{3+} is expected to occupy the Ca^{2+} site in the host lattice [23]. However, the diffraction peaks of In_2O_3 and $EuInO_3$ are found when the concentration of Eu^{3+} is 0.18. With a high Eu^{3+} doping concentration in $CaIn_2O_4$, it may be difficult for the Eu^{3+} ions to be fully introduced into Ca sites in order to keep charge balanced. Thus In_2O_3 and $EuInO_3$ generate as the impurity phase.

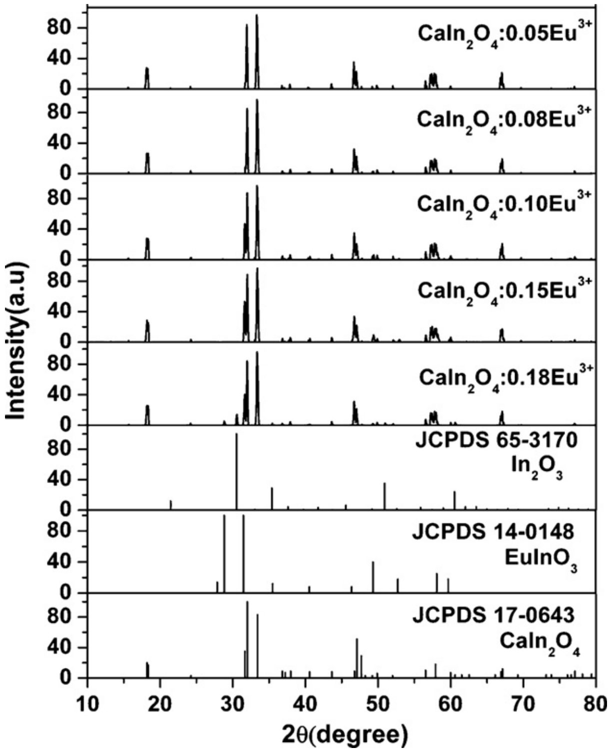

Fig. 1. XRD patterns of Eu^{3+} doped $CaIn_2O_4$, with the standard data of $CaIn_2O_4$ (JCPDS No.17-0643), In_2O_3 (JCPDS No.65-3170), $EuInO_3$ (JCPDS No.14-0148).

The XRD patterns of Eu^{3+}, M^+ (M = Li, Na, K) co-doped $CaIn_2O_4$ samples are shown in Fig. 2. Due to the different valence states with In^{3+}, alkali metal ions are also expected to substitute for the Ca^{2+} sites rather than the In^{3+} sites, and the charge loss of the host lattice compensated by the co-doped alkali metal ions of M^+ can be described by

$$2Ca^{2+} \rightarrow Eu^{3+} + M^+$$

The powder X-ray diffraction results show that all the patterns of the samples are consistent with the standard data of $CaIn_2O_4$, which indicates that the co-doped Eu^{3+} ions and Li^+, Na^+, K^+ ions did

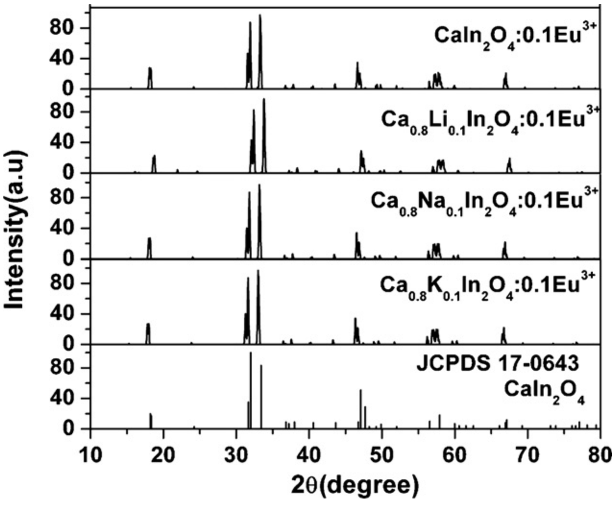

Fig. 2. XRD patterns of Eu^{3+} M^+ (M = Li, Na, K) co-doped $CaIn_2O_4$, with the standard data of $CaIn_2O_4$ (JCPDS No.17-0643).