Journal of Alloys and Compounds 728 (2017) 564–570

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Tunable emitting phosphors $K_3Gd(PO_4)_2$: Tm^{3+}-Dy^{3+} for light-emitting diodes and field emission displays

Lei Zhao*, Dandan Meng, Yanyan Li, Yun Zhang, Haiqing Wang

Institute of Physics and Optoelectronics Technology, Baoji University of Arts and Sciences, Baoji 721016, PR China

ARTICLE INFO

Article history:
Received 15 July 2017
Received in revised form
1 September 2017
Accepted 2 September 2017
Available online 5 September 2017

Keywords:
Phosphors
White LEDs
FEDs

ABSTRACT

Spectroscopic properties of $K_3Gd(PO_4)_2$: Tm^{3+}-Dy^{3+} under ultraviolet (UV) light and low-voltage electron beam excitations were investigated. Upon direct excitation Tm^{3+} from its $^6F_6$ level to $^1D_2$ level, the decrease of emission intensity and lifetime of Tm^{3+} $^1D_2$-$^3F_4$ emission with increasing concentration of Dy^{3+} in $K_3Gd(PO_4)_2$: Dy^{3+}, Tm^{3+} confirmed the occurrence of energy transfer from Tm^{3+} to Dy^{3+}. Besides, $K_3Gd(PO_4)_2$: Dy^{3+}, Tm^{3+} could be efficiently excited by 358 nm UV light and its emission color could be tuned from blue to yellow by codoping Tm^{3+}. When 1% Tm^{3+} and 8% Dy^{3+} were codoped in the $K_3Gd(PO_4)_2$, intensive white emitting light with CIE of (0.338, 0.347) was achieved upon 358 nm excitation. The cathodoluminescence spectra of $K_3Gd(PO_4)$: Tm^{3+}, Dy^{3+} phosphors as a function of accelerating voltage and filament current were also measured. Under low-voltage electron-beam excitation, $K_3Gd(PO_4)_2$: Tm^{3+}, Dy^{3+} phosphors exhibit excellent tunable emitting property. All of the above results reveal that the as-prepared $K_3Gd(PO_4)_2$: Tm^{3+}, Dy^{3+} phosphors have potential applications in white LEDs and FEDs.

1. Introduction

For the past few decades, rare-earth activated luminescent materials have been extensively investigated for application in displays and lighting, such as plasma display panels (PDPs), light emitting diodes (LEDs), field-emission displays (FEDs) and so on [1–5]. White light-emitting diodes (WLEDs), the so-called next generation solid-state lighting, offer benefits in terms of reliability, energy-saving, maintenance and safety, and therefore are gaining much attention [6–8]. Hence, W-LEDs are expected to be a promising candidate to replace conventional incandescent and fluorescent lamps. Technically speaking, the two common ways to obtain white light is by a combination of blue chip with yellow emitting phosphor $Y_3Al_5O_{12}$: Ce^{3+} (YAG) or an ultraviolet (UV) chip with red, green and blue (RGB) emitting phosphors. However, white light obtained by combination of blue chip with YAG is not applicable for certain architectural lighting purposes due to its low color rendering index (CRI) and chromatic aberration after a long working period, and the cool white light with a correlated color temperature (CCT) of 7765 K also restricts their use in many vivid applications, the latter technology to generate white light has disadvantages such as low luminous efficiency owing to the strong reabsorption of the blue light by the red and green phosphors [9–13]. A useful solution is to develop an emission-tunable phosphor through the energy transfer between sensitizer and activator into a crystalline matrix. Moreover, as one of the most promising technologies for flat panel displays, FEDs have gained much attention due to their unique advantages, such as thin panel thickness, selfemission, distortion-free images, wide viewing angle, quick response and low power consumption [14–16]. As well as white LEDs, emission-tunable phosphors are also indispensable components in order to realized full color FEDs. Generally, the availability of high-quality color-tunable phosphors operating under the UV and low-voltage electron beam excitation is of prime importance for excellent performance of such W-LEDs and FEDs.

As is well-known, Dy^{3+} can give strong blue and yellow emission bands with peaks at 480 nm and 575 nm, due to the transition from the Dy^{3+} $^4F_{9/2}$ level to $^6H_{13/2}$ and $^6H_{15/2}$, respectively [17–19]. Although the Ln^{3+} ions show relatively weak absorption cross section and thus low external quantum efficiency due to its intrinsic 4f-4f forbidden transitions, there are some potential way to overcome it, e.g., heavily doping. When Dy^{3+} occur at low symmetry without inversion center, the yellow emission of Dy^{3+} is dominant, resulting in a yellowish white light via single Dy^{3+} doping [20,21]. To overcome this problem, Tm^{3+} is introduced because it gives blue emission

---

* Corresponding author.
E-mail address: zhaoleibjwl@163.com (L. Zhao).

http://dx.doi.org/10.1016/j.jallcom.2017.09.025
0925-8388/© 2017 Published by Elsevier B.V.

owing to the $^1D_2$-$^3F_4$ transition (around 455 nm). High quality white light maybe demonstrated by codoping Tm^{3+} and Dy^{3+} in a crystalline matrix [22–24].

It was reported that $K_3Gd(PO_4)_2$ had a monoclinic crystal structure with the space group $P2_1/m$ [25]. Duo to the efficient absorption in the VUV region and the stable structure in the high temperature, rare-earth doped $K_3Gd(PO_4)_2$ phosphors have much attention in PDPs and Hg-free lamps [26,27]. In addition, the Gd in $K_3Gd(PO_4)_2$ only occupy one crystallographic lattice and form the GdO7 monocapped prisms, this characteristic indicates that the forbidden transitions of the doped ions will be allowed if the doped ions replaces Gd. The Dy replaced Gd into the low symmetry site of $K_3Gd(PO_4)_2$, and the yellowish white light will be obtained. In this work, we investigated the tunable photoluminescence and cathodoluminescence properties via changing concentration of co-doped rare earth ions and energy transfer of $K_3Gd(PO_4)_2$: Tm^{3+}-Dy^{3+} with the aim to develop a single phase phosphor for W-LEDs and FEDs.

2. Experimental

All samples were synthesized by high temperature solid state reaction method. K_2CO_3 [analytical reagent (A. R.)], $NH_4H_2PO_4$ (A. R.), Gd_2O_3 (99.99%), Dy_2O_3 (99.99%), and Tm_2O_3 (99.99%) were used as the starting materials. The starting materials were weighed stoichiometrically and calcined at 950 °C in air for 6 h.

The structure and phase purity of samples were identified by using X-ray powder diffraction (XRD) with Cu Kα radiation on a Rigaku D/max-2000 powder diffract meter operating (1.5405 Å) at 40 kV and 60 mA. The photoluminescence (PL), PL excitation (PLE) spectra and the decay curves of the samples were measured by using an FLS-920T fluorescence spectrophotometer equipped with a 450 W Xenon light source. Thermal quenching was tested using a heating apparatus (TAP-02) in combination with PL equipment. The cathodoluminescence (CL) properties of the samples were obtained using a modified Mp-Micro-S instrument. All measurements were carried out at room temperature.

3. Results and discussion

3.1. Crystallization behavior and structure

The purity of all the prepared samples was systematically checked by XRD. Fig. 1 (a) shows the XRD patterns of $K_3Gd(PO_4)_2$: xTm^{3+}, yDy^{3+} ($x = 0, 0.01; 0 \leq y \leq 0.15$) samples. By comparing with JCPDS Card no. 49-1085, which is also plotted in Fig. 1 (a), all the observed peaks can be indexed to the pure phase of $K_3Gd(PO_4)_2$, no second phase is detected in the XRD patterns, revealing the successful doping of Dy^{3+} and Tm^{3+} in $K_3Gd(PO_4)_2$ host. Fig. 1 (b) presents the experimental values, calculated values, peak positions and difference of Rietveld refinement XRD patterns of $K_3Gd(PO_4)_2$: 0.01 Tm^{3+}, $0.05Dy^{3+}$and the crystallographic data are reported in

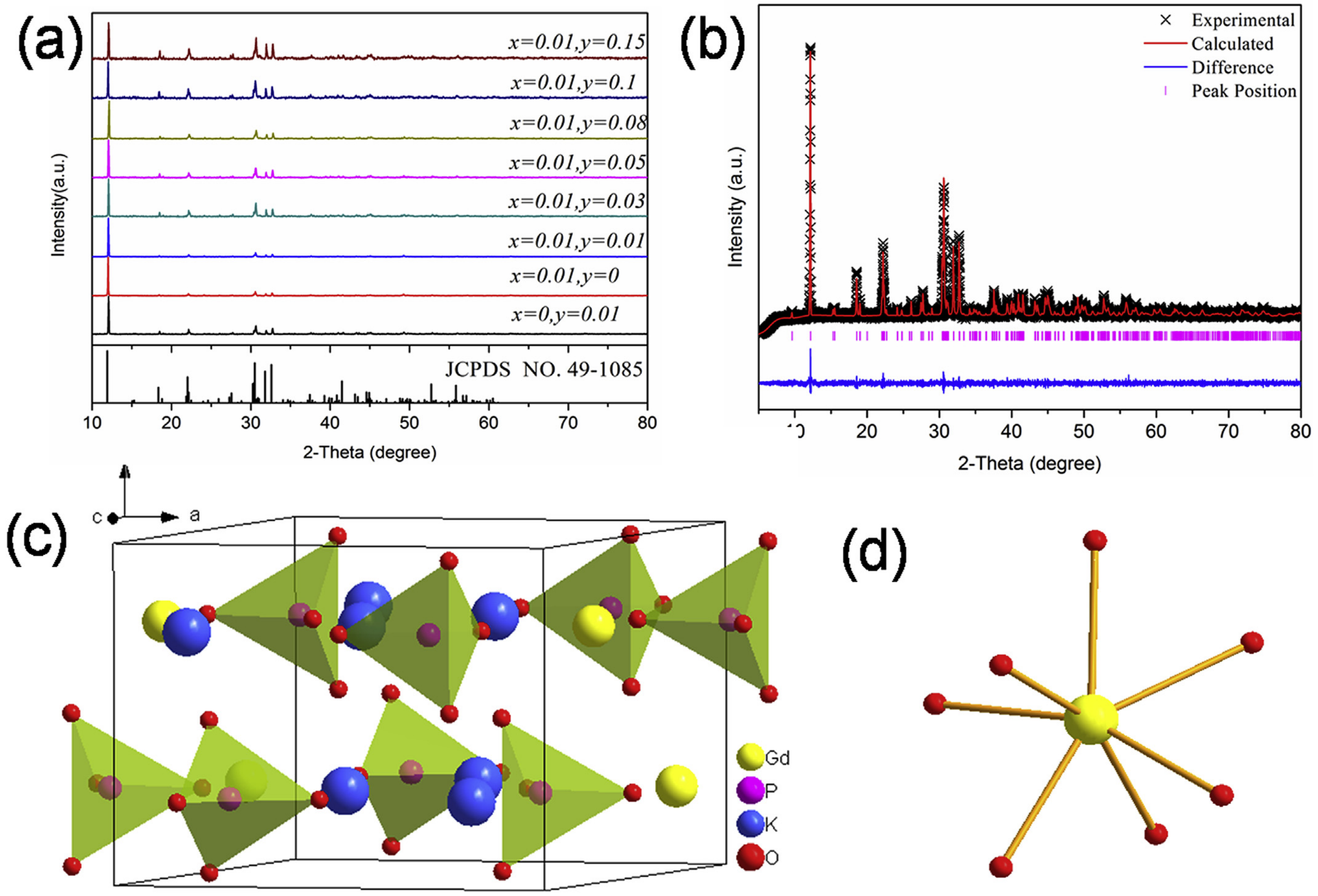

Fig. 1. (a) XRD patterns of $K_3Gd(PO_4)_2$: xTm^{3+}, yDy^{3+} ($x = 0, 0.01; 0 \leq y \leq 0.15$) samples. (b) XRD refinement results of $K_3Gd(PO_4)_2$: 0.01 Tm^{3+}, $0.05Dy^{3+}$ using GSAS program. (c) The crystal structure and (d) Coordination environments for Gd atoms in $K_3Gd(PO_4)_2$: 0.01 Tm^{3+}, $0.05Dy^{3+}$.