Available online at www.sciencedirect.com

ScienceDirect

Ceramics International 40 (2014) 10407–10413

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Photoluminescence properties and energy transfer of a novel bluish-green tunable $KSrY(PO_4)_2:Ce^{3+}$, Tb^{3+} phosphor

Mengfei Zhang[a,b], Yujun Liang[a,b,*], Miaohui Tong[b], Qiang Wang[b],
Dongyan Yu[b], Jianwen Zhao[b], Jiamin Wu[b]

[a] *Engineering Research Center of Nano-Geomaterials of Ministry of Education, China University of Geosciences, Wuhan 430074, People's Republic of China*
[b] *Faculty of Materials Science and Chemistry, China University of Geosciences, Wuhan 430074, People's Republic of China*

Received 24 February 2014; received in revised form 27 February 2014; accepted 2 March 2014
Available online 12 March 2014

Abstract

A series of single-phased emission Ce^{3+}/Tb^{3+}-coactivated $KSrY(PO_4)_2$ (KSYP) phosphors were synthesized by solid-state reaction. The crystal structures, photoluminescence properties, fluorescence lifetimes and energy transfer of KSYP:Ce^{3+}, Tb^{3+} were systematically investigated in detail. Wavelength-tunable bluish-green light could be realized by coupling the emission bands centered at 401 and 543 nm ascribed to the contribution from Ce^{3+} and Tb^{3+}, respectively. Intense green emission was realized in the $KSrY_{0.59}(PO_4)_2$:0.01 mol Ce^{3+}, 0.40 mol Tb^{3+} phosphors on the basis of the high efficiency energy transfer from Ce^{3+} to Tb^{3+} with an efficiency of over 68%. The energy transfer mechanism from Ce^{3+} to Tb^{3+} in the KSYP host was ascribed to the exchange interaction. These results indicated that the KSYP:Ce^{3+}, Tb^{3+} phosphors have potential applications in the field of lighting and display due to their effective excitation in the ultraviolet range.

Keywords: B. Spectroscopy; C. Optical properties; Phosphor

1. Introduction

Inorganic luminescent materials/phosphors have found extensive applications in cathode ray tubes (CRTs), plasma display panels (PDPs), field emission displays (FEDs), X-ray imaging scintillators and white-light emitting diodes (WLEDs) [1–6]. The majority of these materials are generally obtained by doping luminescent rare-earth ions in hosts. As a result, the chemical nature of the hosts has a great impact on the properties and moreover applications of inorganic luminescent materials. To date, many efforts have been made to search novel hosts for developing luminescent materials with high performance.

As important phosphor hosts, phosphates have been widely used due to their low sintering temperature, chemical stability and environment friendly characteristics [7,8]. Rare earth doped phosphate phosphors have been considered in solid-state lighting and display applications [9]. In order to overcome the disadvantage of strong reabsorption and poor color rendering index, the single-phased multi-color phosphate phosphors are produced by co-doping sensitizers and activators. The energy transfer mechanism from a sensitizer to an activator has been investigated in many phosphate hosts, such as, $Ca_9Y(PO_4)_7:Tm^{3+}$, Dy^{3+} [10], $Sr_3In(PO_4)_3:Ce^{3+}/Tb^{3+}/Mn^{2+}$ [11], $Ca_2Ba_3(PO_4)_3Cl$: Ce^{3+}, Tb^{3+} [12], $KCaGd(PO_4)_2:Eu^{2+}$, Tb^{3+} [13], (K,Na) $SrPO_4:Eu^{2+}$, yTb^{3+} [14], and $LiSrPO_4:Eu^{2+}$, Tb^{3+} [15]. In the above single-phased phosphors, Tb^{3+} ion has been used frequently as the green emission center due to its predominant

---

[*] Corresponding author at: China University of Geosciences, Faculty of Materials Science and Chemistry, No. 388 Lumo Road, Wuhan 430074, China. Tel.: +86 27 67884814; fax: +86 27 67883733.

E-mail address: yujunliang@sohu.com (Y. Liang).

http://dx.doi.org/10.1016/j.ceramint.2014.03.011
0272-8842/

$^5D_4-^7F_5$ transition peak at around 543 nm [16,17]. However, the weak and narrow absorption of Tb^{3+} ions in the near-UV region limits the extensive applications of the corresponding Tb^{3+} doped phosphors for the near-UV convertible phosphors [17]. As a promising sensitizer for Tb^{3+} ions, Ce^{3+} has been widely used [18,19]. Therefore, the luminescence originating from Ce^{3+}/Tb^{3+} couples could facilitate green near-UV convertible phosphors since the 4f–5d transition of the Ce^{3+} ion shows superior absorption in the spectral region of 250–450 nm and efficient energy transfer between Ce^{3+} and Tb^{3+} [18,20]. The energy transfer phenomenon of Ce^{3+}/Tb^{3+} has been investigated in many hosts, especially phosphates, including $Ca_9Y(PO_4)_7$:Ce^{3+}, Tb^{3+} [21], $Ba_3Y(PO_4)_3$:Ce^{3+}, Tb^{3+} [22], $KNaCa_2(PO_4)_2$:Ce^{3+}, Tb^{3+} [23], $Ba_{1.6}Ca_{0.4}P_2O_7$:Ce^{3+}, Tb^{3+} [24] and so on.

Recently, Zhang et al. successfully synthesized the $KMLn(PO_4)_2$ (M^{2+}=Ca, Sr; Ln^{3+}=Y, La, Lu) structures and investigated the vacuum-UV spectroscopic properties of a series of rare earth doped $KMLn(PO_4)_2$ phosphors [25]. Furthermore, Geng et al. reported Ce^{3+}-, Tb^{3+}- and Mn^{2+}-activated $KSrGd(PO_4)_2$ phosphors with high absolute quantum by a Pechini-type sol–gel method [26]. Liu et al. illustrated that the energy transfer from Eu^{2+} to Mn^{2+} in $KCaY(PO_4)_2$ was an electric dipole–quadrupole interaction [27]. Liu et al. reported that $KCaGd(PO_4)_2$:Eu^{2+}, Mn^{2+}, Tb^{3+} phosphor could be a promising single-composition phosphor for WLED under NUV excitation with the mechanism of energy transfer between Eu^{2+}, Mn^{2+} and Tb^{3+} ions [13]. Geng et al. synthesized and reported that a variety of colors could be obtained in $KCaGd(PO_4)_2$:Ln^{3+}/Mn^{2+} (Ln=Tb, Dy, Eu, Tm, and Ce) samples under low-voltage electron beam excitation and the phosphors, especially $KCaGd(PO_4)_2$:Ce^{3+}, Tb^{3+} samples, had potential applications in WLEDs and FEDs [28]. However, to the best of our knowledge, there is no report focused on the luminescent properties of co-doped Ce^{3+} and Tb^{3+} ions in the host of $KSrY(PO_4)_2$ (KSYP). In this study, KSYP was used as the host and Ce^{3+}/Tb^{3+} as co-activators to prepare single-phased multicolor phosphors for their possible applications in solid-state lighting and display. The photoluminescence (PL) spectra, concentration quenching, fluorescence lifetimes, CIE chromaticity and energy transfer between Ce^{3+} and Tb^{3+} were investigated in detail.

2. Experimental

A series of polycrystalline $KSrY_{1-x\%-y\%}(PO_4)_2$:x mol% Ce^{3+}, y mol% Tb^{3+} powder samples were prepared by the conventional high temperature solid state reaction process. On the basis of similar effective ionic radius and valence of the cations [11,29], we suggested that Ce^{3+}/Tb^{3+} ions prefer to occupy Y^{3+} sites. The formula of $KSrY_{1-x\%-y\%}(PO_4)_2$:x mol% Ce^{3+}, y mol% Tb^{3+} in the following sections is abbreviated as KSYP:$x$$Ce^{3+}$, $y$$Tb^{3+}$. For example, $KSrY_{0.91}(PO_4)_2$:0.01 mol Ce^{3+}, 0.08 mol Tb^{3+} is denoted as KSYP:1Ce^{3+}, 8Tb^{3+}. The doping concentrations of Ce^{3+} and Tb^{3+} were chosen as 0–0.01 mol and 0–0.40 mol of Y^{3+} in KSYP, respectively. Typically, stoichiometric amounts of K_2CO_3 (A.R. 99.99%), $SrCO_3$ (A.R. 99.99%), Y_2O_3 (A.R. 99.99%), $(NH_4)_2HPO_4$ (A.R. 99.99%), CeO_2 (A.R. 99.99%) and Tb_4O_7 (A.R. 99.99%) were thoroughly mixed in an agate mortar. In each sample, 5 wt% H_3BO_3 (A.R. 99.99%) was added as a flux. The homogeneous mixture was transferred to an alumina crucible and calcined in a furnace at 1273 K for 8 h under a reducing atmosphere of 15% H_2/85% N_2, and slowly cooled to room temperature.

The crystal structures of the phosphors were characterized by an X-ray powder diffractometer (XRD) (Bruker D8 Focus, Bruker, Kalsruhe, Germany) with Ni-filtered Cu-Kα (λ=1.540598 Å) radiation at 40 kV tube voltage and 40 mA tube current. The XRD data were collected in a 2θ range from 10° to 60°, with the continuous scan mode at the speed of 0.05 s per step with step size of 0.01°. Excitation and emission spectra were measured by a fluorescence spectrometer (Fluoromax-4P, Horiba Jobin Yvon, New Jersey, U.S.A.) equipped with a 150 W xenon lamp as the excitation source and both excitation and emission spectra were set up at 1.0 nm with the width of the monochromator slits adjusted as 0.50 nm. Photochromic properties of the resulting phosphors were tested by UV–vis diffuse reflectance spectroscopy (Shimadzu UV 2550) with $BaSO_4$ as the baseline correction. The fluorescence lifetimes were recorded on a spectro-fluorometer (HORIBA, JOBIN YVON FL3-21), and the 330 nm pulse laser radiation (nano-LED) was used as the excitation source. The other measurement conditions (PMT detector sensitivity, scan peed) were kept consistent from sample to sample in measurements. All the measurements were carried out at room temperature.

3. Results and discussion

All XRD patterns of the $KCaY(PO_4)_2$ JCPDS 51-1632, KSYP, KSYP:8Tb^{3+} and KSYP:1Ce^{3+}, $y$$Tb^{3+}$ (y=0, 2, 4, 8, 12, 20, 24, 32 and 40) phosphors are showed in Fig. 1. In $KCaY(PO_4)_2$ and $KSrY(PO_4)_2$ crystal lattices, Ca^{2+} and Sr^{2+} belong to a group of alkaline earth cations with extremely similar properties. To some degree, the ionic radius of Ca^{2+} (0.99 Å) is very close to that of Sr^{2+} (1.18 Å) when both of them are coordinated by four O atoms [25]. Therefore, it is reasonable to assume that a complete solid solution is very likely to form in the series of $KMY(PO_4)_2$ (M^{2+}=Ca, Sr) compounds. Furthermore, this phenomenon had been observed by Zhang [25] and Saito [30] As can be observed in Fig. 1, as the Ca^{2+} ions are substituted completely by Sr^{2+} ions, the XRD patterns are almost the same from $KCaY(PO_4)_2$ and $KSrY(PO_4)_2$ except for a discernible shift of diffraction peak. It can be explained by the difference between the ionic radii of these metals and a similar phenomenon is found in Ci's research [31]. Fig. 1(b) clearly presents the two strongest diffraction peaks ((200) and (102)) and the peaks vary to a low degree. Furthermore, from Fig. 1, we can see that the XRD patterns of doped and undoped KSYP are almost the same. These results indicate that all samples with codopant of Ce^{3+}/Tb^{3+} in KSYP retain a single phase and the co-doped Ce^{3+} and Tb^{3+} ions do not cause any significant change in the host structure.