



Study on the photoluminescence properties of a color-tunable $\text{Ca}_9\text{ZnK}(\text{PO}_4)_7: \text{Eu}^{3+}$ phosphor



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ARTICLE INFO

Article history:

Received 30 November 2015

Accepted 14 January 2016

Keywords:

Phosphor

Phosphate

Energy transfer

Color-tunable

ABSTRACT

A series of Eu^{3+} -doped phosphors $\text{Ca}_{9(1-x)}\text{ZnK}(\text{PO}_4)_7: 9x\text{Eu}^{3+}$ ($x = 0 - 0.08$) have been synthesized by the high temperature solid state method. The X-ray diffraction (XRD) and photoluminescence (PL) were utilized to characterize the phosphors. The phosphors can be effectively excited by near-ultraviolet (NUV) light. The $\text{Ca}_9\text{ZnK}(\text{PO}_4)_7$ host exhibits broad blue emission band centered at 440 nm, while $\text{Ca}_9\text{ZnK}(\text{PO}_4)_7: \text{Eu}^{3+}$ shows both the blue emission band and the characteristic red emission in the region of 570 – 700 nm. With increasing Eu^{3+} content, the relative emission intensity of the host at 440 nm decreased remarkably, indicating that energy transfer occurred from the $\text{Ca}_9\text{ZnK}(\text{PO}_4)_7$ host to Eu^{3+} ions. The phosphors show tunable color from blue to orange based on energy transfer from the host to Eu^{3+} ions.

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1. Introduction

White-light-emitting diodes (WLEDs) are considered to be the next generation light source due to their advantages, such as high efficiency, long operational time and environmental friendliness [1]. There are several approaches to generate white light in WLEDs. One approach is to combine blue chips with yellow phosphor (YAG: Ce^{3+}). However, the obtained white light has low color rendering index (CRI) and high color temperature because of the lack of red emission from YAG: Ce^{3+} [2,3]. To avoid these deficiencies, another method to generate light is the combination of near-ultraviolet (NUV) LED chips and red/green/blue tricolor phosphors. WLEDs combined by this strategy can provide a broadband spectrum with high CRI and low color temperature because the white light is generated only by phosphors. Unfortunately, the conventional red phosphor $\text{Y}_2\text{O}_2\text{S: Eu}^{3+}$ shows some drawbacks: instability and environmental friendliness due to a release of sulfide gas [4], and a low efficiency because of weak excitation in the range of 370 – 410 nm [5]. Though Eu^{2+} doped nitrides phosphors such as CaAlSiN_3 have high stability and high quantum efficiency, they suffer from a relatively difficult preparation process [6]. Therefore, it is important to develop new red phosphors that are prepared by mild synthesis routes and suitable for NUV LED chip.

Eu^{3+} ion is expected to provide efficient and high-purity red emission when doped in suitable host [7–10]. The fluorescence spectra of Eu^{3+} can give information about the occupied sites of Eu^{3+} in the lattices since each Eu^{3+} center with different crystal field symmetry has a unique optical transition in the $^7F_0 \rightarrow ^5D_0$ excitation spectrum. The energy level of Eu^{3+} center is very sensitive to the local environment of the corresponding cation [11,12]. On the other hand, the compounds formed by combination of tetrahedral anions such as MoO_4 , WO_4 , PO_4 and VO_4 , etc., are good hosts for phosphors thanks to their easy synthesis, low cost and chemical/thermal stability over a wide range of temperatures [13].

In the present study, Eu^{3+} -doped $\text{Ca}_9\text{ZnK}(\text{PO}_4)_7$ phosphors were synthesized by the high temperature solid state method. The photoluminescence excitation and emission spectra were investigated. The energy transfer behavior from the host to Eu^{3+} was observed in the phosphor and the energy transfer mechanism was also studied.

2. Experimental

$\text{Ca}_{9(1-x)}\text{ZnK}(\text{PO}_4)_7: 9x\text{Eu}^{3+}$ ($x = 0 - 0.08$) were synthesized using a solid-state reaction. The starting material was a stoichiometric mixture of CaCO_3 (AR), K_2CO_3 (AR), ZnO (AR), $\text{NH}_4\text{H}_2\text{PO}_4$ (AR) and Eu_2O_3 (99.99%). The mixture was heated up to 950 °C and kept at this temperature for 3 h. Then, the sample was slowly cooled down to room temperature.

XRD patterns of the samples were collected with a D-MAX2500/PC X-ray diffractometer (RIGAKU Corporation of Japan) operating at 40 kV, 20 mA and $\text{Cu K}\alpha$ radiation (1.5406 Å).

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The photoluminescence excitation (PLE) and emission (PL) spectra were measured by a fluorescence spectrometer (F-2700, HITACHI High-Technologies Corporation) with a 450 W xenon lamp as excitation source.

3. Results and discussion

Fig. 1 shows the X-ray diffraction (XRD) patterns of $\text{Ca}_{9(1-x)}\text{ZnK}(\text{PO}_4)_7: 9x\text{Eu}^{3+}$ ($x=0$ and 0.03) phosphors. All the observed peaks can be indexed to the standard data of $\text{Ca}_9\text{ZnK}(\text{PO}_4)_7$ with the Joint Committee on Powder Diffraction Standards (JCPDS) card No. 50-0344. Clearly, all the diffraction peaks of $\text{Ca}_{8.73}\text{ZnK}(\text{PO}_4)_7: 0.27\text{Eu}^{3+}$ are in good agreement with those of pure $\text{Ca}_9\text{ZnK}(\text{PO}_4)_7$, indicating that the Eu^{3+} ions were completely incorporated into the host lattice and has no significant influence on the crystal structure. $\text{Ca}_{9(1-x)}\text{ZnK}(\text{PO}_4)_7: 9x\text{Eu}^{3+}$ ($x=0$ and 0.03) crystallize into a rhombohedral structure with the space group $R\bar{3}c(161)$. The lattice parameters were determined to be $a=b=10.414\text{ \AA}$, $c=37.125\text{ \AA}$, $V=3486.74\text{ \AA}^3$ and $Z=6$.

Fig. 2 presents the emission and excitation spectra of $\text{Ca}_9\text{ZnK}(\text{PO}_4)_7$. The excitation spectrum exhibits a broad excitation band ranging from 220 to 310 nm with the maximum absorption at 260 nm, which is attributed to the charge transfer (CT) transition from oxygen ligands to the central phosphorus ions (P^{5+}) in the PO_4 tetrahedron [14]. When excited by 260 nm light, $\text{Ca}_9\text{ZnK}(\text{PO}_4)_7$ exhibits a broad band emission with a maximum intensity at 440 nm without adding any other activators. In the $\text{Ca}_9\text{ZnK}(\text{PO}_4)_7$ phosphor, the host lattice complex (tetrahedral PO_4) operates as the luminescence center. The CT transition from the 2p orbital of O^{2-} to the 3p orbital of P^{5+} in the PO_4 tetrahedron is the main reason for their luminescence properties.

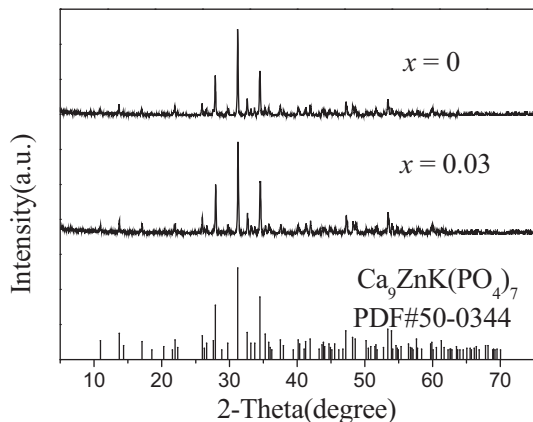


Fig. 1. XRD patterns of $\text{Ca}_{9(1-x)}\text{ZnK}(\text{PO}_4)_7: 9x\text{Eu}^{3+}$ prepared at 950°C .

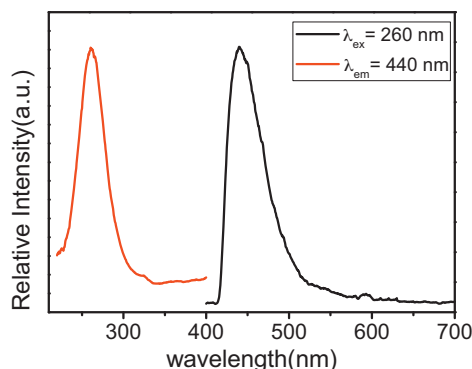


Fig. 2. The emission and excitation spectra of $\text{Ca}_9\text{ZnK}(\text{PO}_4)_7$ phosphor.

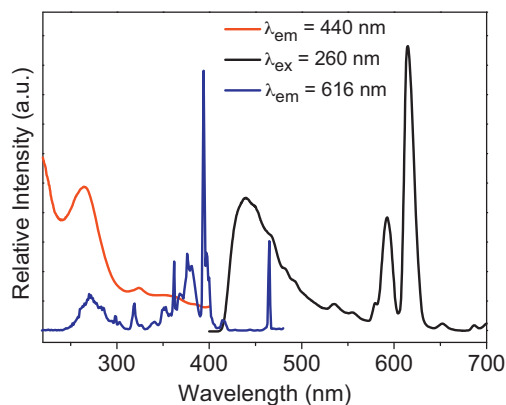


Fig. 3. The PLE ($\lambda_{\text{em}}=440$ and 616 nm) and PL ($\lambda_{\text{ex}}=260\text{ nm}$) spectra of $\text{Ca}_{8.91}\text{ZnK}(\text{PO}_4)_7: 0.09\text{Eu}^{3+}$ phosphor.

The PL spectrum of $\text{Ca}_{8.91}\text{ZnK}(\text{PO}_4)_7: 0.09\text{Eu}^{3+}$ under 260 nm excitation are shown in Fig. 3. It can be seen that the emission spectra consist of the line emissions in the region of 570 – 700 nm besides the blue emission band at 440 nm ascribed to the emission of the host $\text{Ca}_9\text{ZnK}(\text{PO}_4)_7$. The line emissions at 580, 592, 616, 653 and 686 nm result from the $^5D_0 \rightarrow ^7F_J$ ($J=0, 1, 2, 3$ and 4) transitions of Eu^{3+} ions, respectively. In general, for Eu^{3+} ions, the magnetic dipole transition ($^5D_0 \rightarrow ^7F_1$) will appear when Eu^{3+} ions locate in an symmetric environment, and the electric dipole transition ($^5D_0 \rightarrow ^7F_2$) can be observed when Eu^{3+} ions occupy the asymmetric site [15]. As shown in Fig. 3, both the magnetic dipole transition ($^5D_0 \rightarrow ^7F_1$) and the electric dipole transition ($^5D_0 \rightarrow ^7F_2$) are observed, which suggests that there should be two different Eu^{3+} lattice sites in the phosphor $\text{Ca}_{9(1-x)}\text{ZnK}(\text{PO}_4)_7: 9x\text{Eu}^{3+}$. That is to say, there may be at least two different Ca sites in $\text{Ca}_9\text{ZnK}(\text{PO}_4)_7$ lattice.

Fig. 3 also shows the PLE spectra of $\text{Ca}_{8.91}\text{ZnK}(\text{PO}_4)_7: 0.09\text{Eu}^{3+}$ phosphor ($\lambda_{\text{em}}=440$ and 616 nm) at room temperature. When monitored at 440 nm, which is assigned to the luminescence of the $\text{Ca}_9\text{ZnK}(\text{PO}_4)_7$ host, the excitation spectrum exhibits a broad excitation band with the maximum absorption at 260 nm. When monitored at 616 nm, the broad absorption band centered at 270 nm is approximately consistent with the PLE band monitored by 440 nm light (the $\text{Ca}_9\text{ZnK}(\text{PO}_4)_7$ host emission), which means that Eu^{3+} are essentially excited through the host, demonstrating an efficient energy transfer from the $\text{Ca}_9\text{ZnK}(\text{PO}_4)_7$ host to Eu^{3+} [16]. Several sharp lines in the range of 300 – 500 nm corresponding to the 4f – 4f transitions of Eu^{3+} ions were observed in the excitation spectrum, indicating that the phosphors can be effectively excited by NUV LED chip (360 – 400 nm). It is worth noting that there is a significant overlap between the $\text{Ca}_9\text{ZnK}(\text{PO}_4)_7$ host PL (410 – 520 nm) and Eu^{3+} PLE spectra (the sharp line at 465 nm), indicating that the energy transfer behavior may occur from the $\text{Ca}_9\text{ZnK}(\text{PO}_4)_7$ host to the Eu^{3+} by radiation re-adsorption mechanism.

In order to understand the energy transfer process, a series of samples $\text{Ca}_{9(1-x)}\text{ZnK}(\text{PO}_4)_7: 9x\text{Eu}^{3+}$ ($x=0.01 - 0.08$) were prepared. As shown in Fig. 4, with increasing Eu^{3+} content x , it was found that the relative emission intensity of the host at 440 nm decreased remarkably from $x=0.01$ to 0.08 assigned to the enhancement of energy transfer from the $\text{Ca}_9\text{ZnK}(\text{PO}_4)_7$ host to Eu^{3+} ions. Meanwhile, the emission intensity of Eu^{3+} was found to increase initially with increasing Eu^{3+} content x and reached a maximum at $x=0.06$, beyond which it decreased ascribed to the Eu^{3+} – Eu^{3+} internal concentration quenching.

The concentration quenching occurs due to the energy transfer from one activator to another [17]. In this process of energy

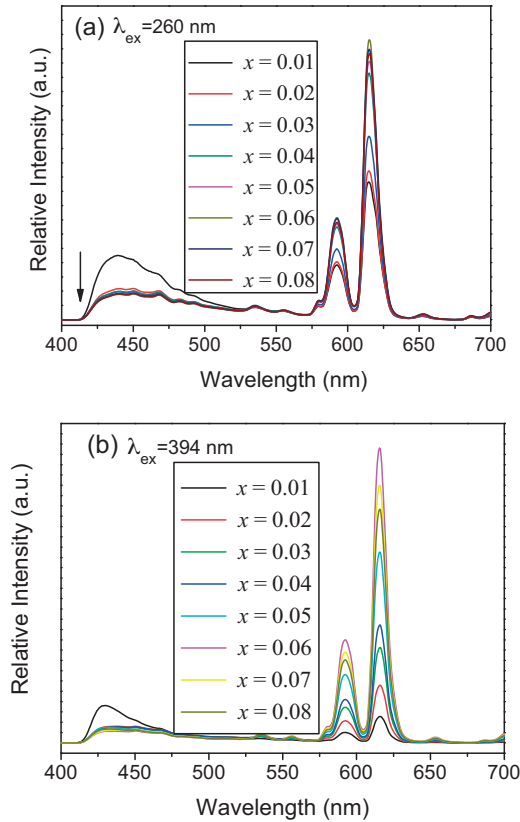


Fig. 4. The photoluminescence spectrum of $\text{Ca}_9(1-x)\text{ZnK}(\text{PO}_4)_7: 9x\text{Eu}^{3+}$ ($x = 0.01 - 0.08$) phosphor. (a) $\lambda_{\text{ex}} = 260$ nm and (b) $\lambda_{\text{ex}} = 394$ nm.

transfer, the non-radiative transition is produced, which leads to the concentration quenching phenomenon. While discussing the mechanism of energy transfer in phosphors, the critical transfer distance (R_c) can be estimated according to the following formula suggested by Blasse [18]:

$$R_c \approx 2 \left[\frac{3V}{4\pi x_c Z} \right]^{1/3} \quad (1)$$

where, V is the volume of the unit cell, Z is the number of total Eu^{3+} sites per unit cell, x_c is the critical concentration. For the $\text{Ca}_9\text{ZnK}(\text{PO}_4)_7: \text{Eu}^{3+}$ system, $Z = 6$, $V = 3486.74 \text{ \AA}^3$, and $x_c = 0.06$. The critical transfer distance of Eu^{3+} in $\text{Ca}_9\text{ZnK}(\text{PO}_4)_7: \text{Eu}^{3+}$ is determined to be $26.46 \text{ \AA}$.

Non-radiative energy transfer between different activator ions may take place through exchange interaction, radiation re-absorption, or multipole – multipole interaction. In general, when the overlapping of the wave functions of the sensitizer and activator is enough to exchange electronics or the activator and sensitizer occupy adjacent lattice sites, the mechanism of exchange interaction plays the role in the energy transfer process. Eu^{3+} is an isolated emission center in $\text{Ca}_9\text{ZnK}(\text{PO}_4)_7: \text{Eu}^{3+}$ phosphor and the critical transfer distance R_c is $26.46 \text{ \AA}$, which is far more than the typical critical distance ($\sim 5 \text{ \AA}$) [19]. Therefore, energy transfer between different Eu^{3+} ions in $\text{Ca}_9\text{ZnK}(\text{PO}_4)_7: \text{Eu}^{3+}$ phosphor does not belong to exchange interactions. The radiation re-absorption mechanism occurs only when there is a broad overlap of the fluorescent spectra of the sensitizer and activator. In this case, there is no overlap between the PLE ($\lambda_{\text{em}} = 616$ nm) and PL ($\lambda_{\text{ex}} = 394$ nm) spectra of Eu^{3+} in $\text{Ca}_9\text{ZnK}(\text{PO}_4)_7: \text{Eu}^{3+}$ phosphor as shown in Fig. 5. Therefore, the concentration quenching mechanism is impossible to be radiation re-absorption mechanism.

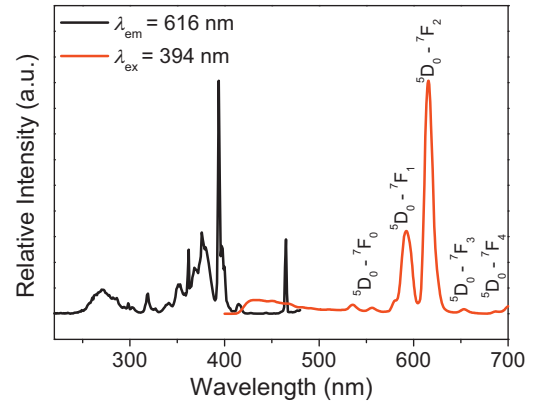


Fig. 5. The PLE ($\lambda_{\text{em}} = 616$ nm) and PL ($\lambda_{\text{ex}} = 394$ nm) spectra of $\text{Ca}_{8.28}\text{ZnK}(\text{PO}_4)_7: 0.72\text{Eu}^{3+}$ phosphor.

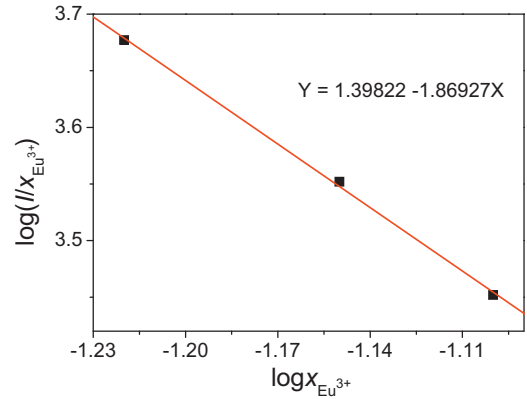


Fig. 6. The curve of $\log(I/x_{\text{Eu}^{3+}})$ vs. $\log(x_{\text{Eu}^{3+}})$ in $\text{Ca}_9(1-x)\text{ZnK}(\text{PO}_4)_7: 9x\text{Eu}^{3+}$ phosphor ($\lambda_{\text{ex}} = 394$ nm).

With the in-depth study, more and more evidence shows that the concentration quenching behavior may be caused by electric multipolar interactions. The electric multipolar interaction mechanism between sensitizer and activator can be estimated by the following equation [20,21]:

$$I/x = k[1 + \beta(x)^{\theta/3}]^{-1} \quad (2)$$

where, x is the activator concentration, I/x is the emission intensity (I) per activator concentration (x), k and β are constants for the same excitation condition for a given host crystal. The value of θ is 6, 8 and 10, corresponding to dipole – dipole ($d - d$), dipole – quadrupole ($d - q$) and quadrupole – quadrupole ($q - q$) interactions, respectively. In order to further confirm the energy transfer process between Eu^{3+} ions in the $\text{Ca}_9\text{ZnK}(\text{PO}_4)_7: \text{Eu}^{3+}$ phosphor, the curve of $\log(I/x_{\text{Eu}^{3+}})$ versus $\log(x_{\text{Eu}^{3+}})$ is drawn in Fig. 6. It can be seen that the dependence of $\log(I/x_{\text{Eu}^{3+}})$ on $\log(x_{\text{Eu}^{3+}})$ is linear and the slope is -1.87 . The value of Q can be calculated as 5.61, which is approximately equal to 6, by using Eq. (2). The result suggests that the $d - d$ interaction is the major mechanism for concentration quenching of the Eu^{3+} ions emission in $\text{Ca}_9\text{ZnK}(\text{PO}_4)_7: \text{Eu}^{3+}$.

The x and y values of CIE chromaticity coordinates for the $\text{Ca}_9\text{ZnK}(\text{PO}_4)_7: \text{Eu}^{3+}$ phosphors with different dopant contents were measured and showed in Fig. 7 and Table 1, respectively. It is clearly observed that with increasing the doping content of Eu^{3+} , the corresponding color tone of the phosphors shifts gradually from blue to orange along the edge of white light region in color coordinate diagram. It is attributed to the increase of red/blue light ratio according to the emission spectra.

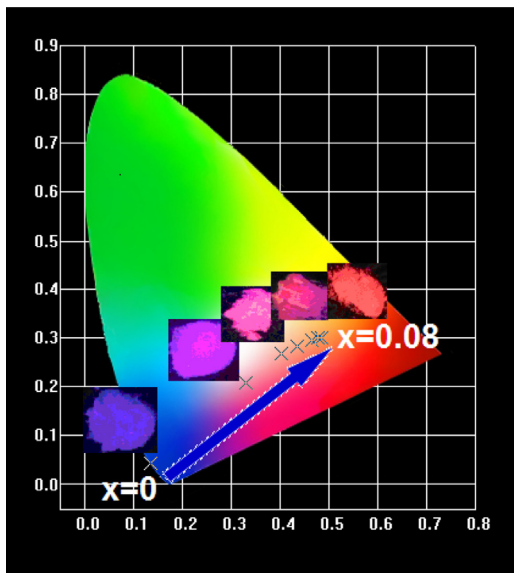


Fig. 7. CIE chromaticity diagram for $\text{Ca}_9(1-x)\text{ZnK}(\text{PO}_4)_7: 9x\text{Eu}^{3+}$ ($x = 0.01 - 0.08$) phosphor ($\lambda_{\text{ex}} = 260 \text{ nm}$).

Table 1

CIE chromaticity coordinates of $\text{Ca}_9(1-x)\text{ZnK}(\text{PO}_4)_7: 9x\text{Eu}^{3+}$ phosphors.

Phosphor $\text{Ca}_9(1-x)\text{ZnK}(\text{PO}_4)_7: 9x\text{Eu}^{3+}$	CIE (x, y)
$x = 0$	(0.134, 0.043)
$x = 0.01$	(0.330, 0.207)
$x = 0.02$	(0.403, 0.267)
$x = 0.03$	(0.436, 0.282)
$x = 0.04$	(0.464, 0.294)
$x = 0.05$	(0.479, 0.299)
$x = 0.06$	(0.484, 0.301)
$x = 0.07$	(0.480, 0.300)
$x = 0.08$	(0.478, 0.299)

4. Conclusions

In summary, $\text{Ca}_9\text{ZnK}(\text{PO}_4)_7: \text{Eu}^{3+}$ phosphors have been synthesized by solid state reaction and their photoluminescence properties were investigated. The $\text{Ca}_9\text{ZnK}(\text{PO}_4)_7$ host exhibits a broad blue emission band peaked at 440 nm. The emission spectrum of $\text{Ca}_9\text{ZnK}(\text{PO}_4)_7: \text{Eu}^{3+}$ consists of characteristic red light emission of Eu^{3+} in the region of 570 – 700 nm besides the blue emission band ascribed to the emission of the host $\text{Ca}_9\text{ZnK}(\text{PO}_4)_7$. Energy transfer from the host to Eu^{3+} ions was confirmed by the photoluminescence properties of $\text{Ca}_9\text{ZnK}(\text{PO}_4)_7: \text{Eu}^{3+}$. The dipole – dipole interactions should be mainly responsible for the concentration quenching behavior of Eu^{3+} ions in $\text{Ca}_9\text{ZnK}(\text{PO}_4)_7: \text{Eu}^{3+}$ phosphors. The varied emitted color from blue to orange can be achieved by tuning the Eu^{3+} content in the phosphors. The phosphor exhibits efficient emission when excited by 394 nm light, suggesting that it has favorable properties as an NUV LED conversion phosphor.

Acknowledgments

This work was financially supported by the National Natural Science Foundation of the People's Republic of China (No. 51472132), the Natural Science Foundation of Shandong Province (ZR2012BQ017), Qingdao Project of Science and Technology (13-1-4-114-jch) and the Opening Foundations of State Key Laboratory of Geological Processes and Mineral Resources (GPMR201510).

References

- [1] S. Nakamura, M. Senoh, T. Mukai, High-power InGaN/GaN double-heterostructure violet light-emitting-diodes, *Appl. Phys. Lett.* 62 (1993) 2390–2392.
- [2] T.W. Kuo, W.R. Liu, T.M. Chen, Emission color variation of $(\text{Ba}, \text{Sr})_3\text{BP}_2\text{O}_{12}: \text{Eu}^{2+}$ phosphors for white light LEDs, *Optik Express* 18 (2010) 1888–1897.
- [3] M.M. Shang, C.X. Li, J. Lin, How to produce white light in a single-phase host, *Chem. Soc. Rev.* 43 (2014) 1372–1386.
- [4] S. Neeraj, N. Kijima, A.K. Cheetham, Novel red phosphors for solid-state lighting: the system $\text{NaM}(\text{WO}_4)_{2-x}(\text{MoO}_4)_x: \text{Eu}^{3+}$ (M Gd, Y, Bi), *Chem. Phys. Lett.* 387 (2004) 2–6.
- [5] X. Dong, J. Zhang, X. Zhang, Z. Hao, Y. Luo, New orange-red phosphor $\text{Sr}_9\text{Sc}(\text{PO}_4)_7: \text{Eu}^{3+}$ for NUV-LEDs application, *J. Alloys Compd.* 587 (2014) 493–496.
- [6] K. Uheda, N. Hirotsaki, Y. Yamamoto, A. Naito, T. Nakajima, H. Yamamoto, Luminescence properties of a red phosphor, $\text{CaAlSiN}_3: \text{Eu}^{2+}$, for white light-emitting diodes, *Electrochem. Solid-State Lett.* 9 (2006) H22–H25.
- [7] F. Chen, X. Liu, Structure and photoluminescence properties of $\text{La}_2\text{Mo}(\text{W})\text{O}_6: \text{Eu}^{3+}$ as red phosphors for white LED applications, *Optik Mater.* 35 (2013) 2716–2720.
- [8] G.M. Cai, H.X. Liu, J. Zhang, Y. Tao, Z.P. Jin, Luminescent properties and performance tune of novel red-emitting phosphor $\text{CaInBO}_4: \text{Eu}^{3+}$, *J. Alloys Compd.* 650 (2015) 494–501.
- [9] F. Baur, F. Glocker, T. Jüstel, Photoluminescence and energy transfer rates and efficiencies in Eu^{3+} activated $\text{Tb}_2\text{Mo}_3\text{O}_{12}$, *J. Mater. Chem. C* 3 (2015) 2054–2064.
- [10] Z.W. Zhang, D.Q. Ma, Y. Yue, M.Z. Ma, R.P. Liu, Wide-band excited $\text{LaBMoO}_6: \text{Eu}^{3+}$ red phosphor for white-light-emitting diode, *J. Alloys Compd.* 636 (2015) 113–116.
- [11] C. Gorller-Walrand, K. Binnemans, Chapter 155 Rationalization of crystal-field parametrization, in: K.A. Gschneidner Jr., L. Eyring (Eds.), *Handbook on the Physics and Chemistry of Rare Earths*, 23, North-Holland, Amsterdam, 1996.
- [12] F.B. Cao, L.H. Wei, W.M. Liu, Preparation of red-emitting phosphors $[\text{K}_{0.8}\text{Y}_{0.65}\text{Eu}^{3+}_{0.08}][\text{Mo}_{0.2}\text{W}_{0.8}\text{O}_4]$ and calculation of $\text{Eu}^{3+} {}^5\text{D}_0$ quantum efficiency, *Optik* 126 (2015) 1625–1628.
- [13] X.G. Zhang, M.Y. Chen, J.L. Zhang, X.Z. Qin, M.L. Gong, Photoluminescence studies of high-efficient red-emitting $\text{K}_2\text{Y}(\text{WO}_4)(\text{PO}_4): \text{Eu}^{3+}$ phosphor for NUV LED, *Mater. Res. Bull.* 73 (2016) 219–225.
- [14] S.P. Kuang, Y. Meng, J. Liu, Z.C. Wu, L.S. Zhao, A new self-activated yellow-emitting phosphor $\text{Zn}_2\text{V}_2\text{O}_7$ for white LED, *Optik* 124 (2013) 5517–5519.
- [15] V. Sivakumar, U.V. Varadaraju, A promising orange–red phosphor under near UV excitation, *Electrochem. Solid State Lett.* 9 (2006) H35–H38.
- [16] N. Guo, H.P. You, Y.H. Song, M. Yang, K. Liu, Y.H. Zheng, Y.J. Huang, H.J. Zhang, White-light emission from a single-emitting-component $\text{Ca}_9\text{Gd}(\text{PO}_4)_7: \text{Eu}^{2+}, \text{Mn}^{2+}$ phosphor with tunable luminescent properties for near-UV light-emitting diodes, *J. Mater. Chem.* 20 (2010) 9061–9067.
- [17] S.H. Park, K.H. Lee, S. Unithrattil, H.S. Yoon, H.G. Jang, W.B. Im, Melilite-structure $\text{CaYAl}_3\text{O}_7: \text{Eu}^{3+}$ phosphor: structural and optical characteristics for near-UV LED-based white light, *J. Phys. Chem. C* 116 (2012) 26850–26856.
- [18] G. Blasse, Energy transfer between inequivalent Eu^{2+} ions, *J. Solid State Chem.* 62 (1986) 207–211.
- [19] W.B. Im, N.N. Fellows, S.P. DenBaars, R. Seshadri, Y.I. Kim, $\text{LaSr}_2\text{AlO}_5$, a versatile host compound for Ce^{3+} based yellow phosphors: structural tuning of optical properties and use in solid-state white lighting, *Chem. Mater.* 21 (2009) 2957–2966.
- [20] L.G. Van Uniter, Characterization of energy transfer interactions between rare earth ions, *J. Electrochem. Soc.* 114 (1967) 1048–1053.
- [21] L. Ozawa, P.M. Jaffe, The mechanism of the emission color shift with activator concentration In^{3+} activated phosphors, *J. Electrochem. Soc.* 118 (1971) 1678–1679.