

RSC Advances



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. This *Accepted Manuscript* will be replaced by the edited, formatted and paginated article as soon as this is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

A novel blue light pumped yellow-emitting phosphor RbZnPO₄:Dy³⁺ with satisfactory color tune and thermal properties for high-power warm white light emitting diodes

Ge Zhu, Shuangyu Xin*

Received (in XXX, XXX) Xth XXXXXXXXXX 20XX, Accepted Xth XXXXXXXXXX 20XX

DOI: 10.1039/b000000x

In order to explore a suitable yellow emission phosphor for blue light pumped high power warm LEDs, the synthesis and photoluminescence properties of novel yellow phosphors RbZnPO₄: Dy³⁺ were investigated in detail through X-ray diffraction refinement and photoluminescence spectra measurement. The analysis revealed that RbZnPO₄: Dy³⁺ phosphors had strong absorption around 455 nm and could exhibit dominate yellow emission at 577 nm as well as weak red emission at 665 nm due to the ⁴F_{9/2}→⁶H_{13/2} and ⁴F_{9/2}→⁶H_{11/2} transitions of Dy³⁺ ions, respectively, with stable CIE coordinates (0.49, 0.50). The thermal quenching behaviour showed that RbZnPO₄: Dy³⁺ had excellent thermal stability. The results indicated that the novel yellow phosphor RbZnPO₄: Dy³⁺ could be a good candidate for high-power warm white LEDs.

1. Introduction

In the past few decades, with the development of photoelectric technology and materials science, white light-emitting diodes (LEDs) have been regarded as a new generation of lighting source for solid state lighting after incandescent and energy saving lamps because of their unique advantages, such as high efficiency, energy-saving, compactness and being environmentally friendly.¹⁻³ At present, the major white LEDs in the market are phosphor-converted LEDs (pc-LEDs) constituted by a blue InGaN chip and a yellow phosphor (Y,Gd)₃(Al,Ga)₅O₁₂:Ce³⁺ (YAG:Ce³⁺). However, this approach leads to a poor color rendering index (Ra = 70 – 80) and a high correlated color temperature (CCT ≈ 7750 K) because of chromatic aberration after a long working period and the lack of a sufficient red component, which causes a cool white light and restricts their application in indoor lighting.⁴⁻⁷ Moreover, with the increasing market need for high-power operation, the employed phosphors should have strong thermal stability to resist the high temperature in the work process. Although a great deal of efforts have been taken for the development of other methods to generate white light emission, such as ultraviolet (UV) light pumped LED chip combined with two, three, or even four kinds of phosphors, the poor efficiency caused by the UV LED chip and the reabsorption of different phosphors have been commonly encountered, which confines its extensive application.⁸⁻¹² As a result, there is an urgent demand to develop new blue light pumped yellow phosphors with satisfactory and excellent thermal stability to apply in high-power warm LEDs.

Among numerous luminescent centers, Dy³⁺ ion has been widely used in luminescent materials due to the various transitions between its different energy levels that occur in the UV-visible and near infrared (NIR) region, typically its

⁴F_{9/2}→⁶H_{15/2} (~480 nm, blue light), ⁴F_{9/2}→⁶H_{13/2} (~575 nm, yellow light) and ⁴F_{9/2}→⁶H_{13/2} (~665 nm, red light).^{13,14} Till now, a large number of research on Dy³⁺ ions doped phosphors have been investigated, such as Mg₂Al₄Si₅O₁₈: Dy³⁺, Gd₃Al₅O₁₂: Dy³⁺, BaY₂ZnO₅, α-Sr₂P₂O₇: Dy³⁺, LiLaP₄O₁₂: Dy³⁺, YP_xV_{1-x}O₄:Dy³⁺ and LiGd(WO₄)₂:Dy³⁺.¹⁵⁻²¹ However, most of the current works focus on discussing the white light luminescence properties of Dy³⁺ ions in a single host based on their original blue and yellow emission or adjusting their emission ratio through introducing other impurity ions (Li⁺, Na⁺ and Lu³⁺ et al.)^{16,18,22} but losing sight of its origin red emission part at about 665 nm due to their ⁴F_{9/2}→⁶H_{11/2} transitions. In addition, these phosphors are usually excited by UV light due to the strong absorption of Dy³⁺ ions around UV light region in these phosphors,¹⁵⁻²¹ which are mismatched with the current common used blue LED chip. Therefore, in order to develop a single phase yellow emitting phosphor and perform some basic research, in this work, we have synthesized a novel yellow phosphor RbZnPO₄: Dy³⁺ (RZP:Dy³⁺) pumped by blue light and carefully investigated their structure, luminescence properties as well as the thermal stability property.

2. Experimental

2.1 Materials and synthesis

Powder samples of RbZnPO₄: xDy³⁺ (0≤x≤0.05) were prepared by a conventional solid-state reaction method. Stoichiometric amounts of the raw materials Rb₂CO₃ (AR), ZnO (AR), (NH₄)₂HPO₄ (AR), and Eu₂O₃ (AR) were ground thoroughly in an agate mortar for 1-2 h in alcohol. Subsequently, the dried power mixtures were fired in an alumina crucible and heated to 800 °C in air for 12 h. Then the preheated mixture was ground again and fired to 1100 °C for 8 h in box-type furnace. Finally the as-synthesized samples were slowly cooled down with a rate of 5 °C/min to room temperature.

2.2 Measurements and characterization

The crystal structure was identified by using a Rigaku D/Max-2400 X-ray diffractometer (XRD) with Ni-filtered Cu K α radiation. The photoluminescence (PL) and PL excitation (PLE) spectra of the samples at room temperatures were measured by using an FL-1039 (Horiba Jobin Yvon) fluorescence spectrophotometer equipped with a 450 W xenon light source. All of the measurements were performed at room temperature. High-temperature luminescence intensity measurements were carried out by using an aluminum plaque with cartridge heaters; the temperature was measured by thermocouples inside the plaque and controlled by a standard TAP-02 high-temperature fluorescence controller.

3. Results and discussion

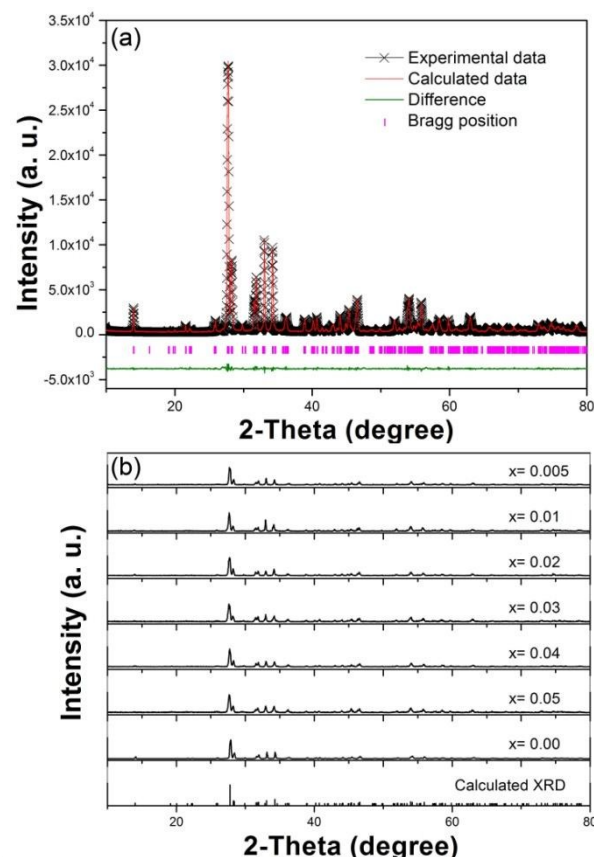


Fig.1 (a) Rietveld structure analysis of RZP host by using Materials Studio program; (b) XRD patterns of RZP: $x\text{Dy}^{3+}$ ($0 \leq x \leq 0.05$)

Figure 1a shows the Rietveld structure analysis of RZP host by using Materials Studio program.²³ All the observed peaks satisfy the reflection condition. The residual factors are $R_{wp} = 9.53\%$, $R_p = 7.66\%$ and the lattice parameters are $a = 8.8495 \text{ \AA}$, $b = 5.4122 \text{ \AA}$, $c = 8.9638 \text{ \AA}$. The results of the final refinement data indicate that the powder sample is well crystallized monoclinic symmetry with space group P121. The effective ionic radius of different cations in RZP host according to Ref. 22 are shown in Table 1. Based on the effective ionic radius information in Table 1 and the ion charge, it is possible that Dy^{3+} ions occupy Zn^{2+} sites in RZP host. In addition, according to our previous report, Zn^{2+} can be replaced by the similar size ion Eu^{3+} to form a solid solution in

RZP host.²⁵ Therefore, it is likely that Dy^{3+} ions can be successfully introduced into RZP host. Fig. 1b clearly illustrated the series XRD patterns of RZP: $x\text{Dy}^{3+}$ ($0 \leq x \leq 0.05$). It can be seen that no detectable impurity phase is observed in the obtained samples even at higher doping concentration. The XRD profiles are well fitted with the calculated XRD patterns, indicating the Dy^{3+} ions have been successfully incorporated in the host lattice without changing the crystal structure.

Table 1 Relative difference in the ionic radii ($\text{dr}(\%) = 100 [R_m(\text{CN}) \times R_d(\text{CN})] / R_m(\text{CN})$) between the matrix cations and the dopant Dy^{3+} ion

Ions	Radius	CN	Dr (100%)
Dy^{3+}	0.91	6	0
	1.02	8	0
Zn^{2+}	0.60	4	<0.33
	0.68	5	<0.34
Rb^+	1.52	6	0.40
	1.61	8	0.37
P^{5+}	0.17	4	0.81

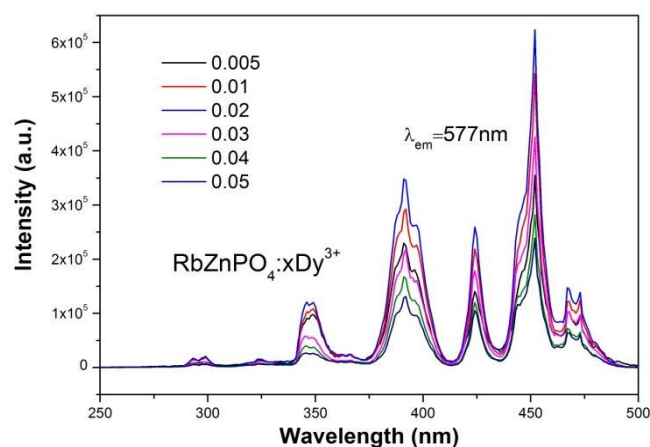


Fig.2 PL excitation spectra of Dy^{3+} ions doped RZP phosphor with different doping concentrations.

Figure 2 illustrated the PL excitation spectra of Dy^{3+} ions doped RZP phosphor with different doping concentrations. When monitored at 577 nm, the spectra consisted of a series of sharp peaks ranging from 280 to 500 nm, which could be attributed to the intra-4f forbidden transitions from the ground level $^6\text{H}_{15/2}$ to higher energy levels of Dy^{3+} ions, as shown in Figure 2.^{13,14} It was interesting that the dominate excitation peak in RZP: Dy^{3+} was located at 452 nm ($^6\text{H}_{15/2} \rightarrow ^4\text{I}_{15/2}$ transitions) in the PL excitation spectra, and it was almost unchanged with increasing Dy^{3+} ions doping concentrations except the excitation intensity. However, in many other Dy^{3+} ions doping phosphors, the dominate excitation of Dy^{3+} ions was usually found to be situated at UV region rather than in blue region in our case due to the strong $^6\text{H}_{15/2} \rightarrow ^6\text{P}_{7/2}$ or $^6\text{H}_{15/2} \rightarrow ^4\text{M}_{21/2}$ transitions.¹⁵⁻²² The reason is complex but we think it should be related to the specific and crowded lattice environment in RZP host as discussed in Ref. 25. An ideal phosphor for blue LEDs should have strong absorption around 450-460 nm (emission wavelengths of blue-LED chips). Obviously, the excitation spectrum exhibits strong absorption at 452 nm, indicating it can be a candidate as a yellow phosphor for blue LEDs.

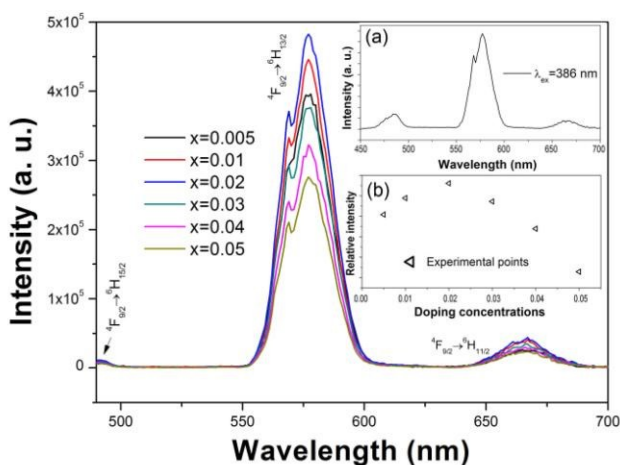


Fig.3 PL emission spectra of RZP: $x\text{Dy}^{3+}$ ($0.005 \leq x \leq 0.05$); the inset shows the emission spectrum of RZP: 0.01Dy^{3+} excited at 386 nm (a) and the relationship between the relative emission intensity and the doping concentrations of Dy^{3+} ions.

Figure 3 presents the PL emission spectra of RZP: $x\text{Dy}^{3+}$ ($0.005 \leq x \leq 0.05$). The emission spectra mainly consist of two characteristic emission peaks located at 577 nm (yellow emission) and 665 nm (red emission), which are attributed to the ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{13/2}$ and ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{11/2}$ transitions of Dy^{3+} ions, respectively.^{13,14} According to the Judd-Ofelt theory, the ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{13/2}$ transition of Dy^{3+} ions belongs to the hypersensitive forced electric dipole transition. When Dy^{3+} ion locates at a low symmetry local site without inversion symmetry, a yellow emission according to the electric dipole transition ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{13/2}$ will be dominant. Conversely, a magnetic dipole transition ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{15/2}$ will predominate in the emission spectra, resulting in a strong blue emission.²⁶ The observed strong yellow emission of RZP: Dy^{3+} phosphor in this work suggests that Dy^{3+} ion is located at Zn^{2+} site with a low symmetry. In order to fully investigate the emission properties, the emission spectrum excited at 386 nm is measured and illustrated in inset (a) of Fig. 3, which is consistent with that excited by 452 nm. With doping different Dy^{3+} ions concentrations, the emission spectra remain unchanged except the relative intensity. As illustrated in the inset (b), the emission intensity of Dy^{3+} ions increases rapidly and reaches a maximum at $x = 0.02$ and then decreases remarkably when Dy^{3+} ion content is further increased due to the concentration quenching effect. Generally, the quenching mechanism of luminescence centers can be understood by Dexter theory and a theoretical description for the relationship between the luminescent intensity and the doping concentration has been developed according to Van Uitert's report as following,²⁷

$$\frac{I}{x} = \frac{k}{1 + (x)^{\theta/3}}$$

where x is the activator concentration. $\theta = 3, 6, 8, 10$ for the energy transfer among the nearest-neighbor ions, dipole - dipole, dipole - quadrupole, quadrupole - quadrupole interactions, respectively. k and $\beta(x)$ are constant for the same excitation conditions for a given host crystal. The abovementioned equation can be rearranged further by assuming $\beta(x) \gg 1$,^{28,29}

$$\ln\left(\frac{I}{x}\right) = k' - \frac{\theta}{3} \ln x$$

where $k' = \lg k - \lg \beta$. Therefore, the θ value can be obtained in terms of the above equation dependent on the relationship between $\lg(I/x)$ and $\lg(x)$, as shown in Fig.4a, which was found to be relatively linear and the slope was determined to be -0.91. Thus, the value of θ could be calculated to be 2.73, which is approximately to be 3, indicating that the concentration quenching for the Dy^{3+} ions is caused by the energy transfer among the nearest-neighbor ions in the RZP: Dy^{3+} phosphor. The ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{11/2}$ transitions of Dy^{3+} ions in the current phosphor is important for improving the color rendering because of its red emission component. Fig. 4b and 4c shows the Commission International edel'Eclairage (CIE) color coordinates of RZP: 0.02Dy^{3+} phosphor. It was found that both of the x and y coordinates were moved to the red region after calculating based on the yellow and red emission transitions. When the doping content was above 0.01, the CIE color coordinates kept unchanged at (0.49, 0.50), which was warmer than that of YAG:Ce^{3+} (CIE (0.41,0.56)). The stable color coordinates independent of the doping contents were beneficial to the enlarging production.

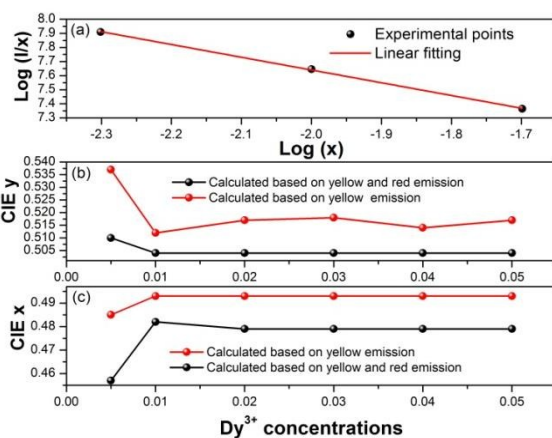


Fig. 4 (a) The linear fitting result of between the luminescent intensity and the doping concentration according to Van Uitert's empirical formula; (b) the relationship between the CIE coordinate y and the doping concentrations of Dy^{3+} ions; (c) the relationship between the CIE coordinate x and the doping concentrations of Dy^{3+} ions.

Figure 5 shows the CIE 1931 chromaticity of RZP: 0.02Dy^{3+} and the commercial yellow phosphor YAG:Ce^{3+} , respectively. The line connecting the blue LED chip chromaticity point with the chromaticity of RZP: 0.02Dy^{3+} yellow phosphor crosses the blackbody locus at the point where the correlated color temperature is 3125 K. This indicates that warm white light (2500 - 3500 K) can be generated by combing the yellow phosphor RZP: 0.02Dy^{3+} with the blue LED radiation.³⁰ It also can be seen that the color temperature of the white light generated by combing the emission of YAG:Ce and the blue LED chip was 8858 K, which was in the cool white region. The stimulant combination results demonstrate that RZP: Dy^{3+} phosphor is a favorable potential phosphor for creating warm white LEDs.

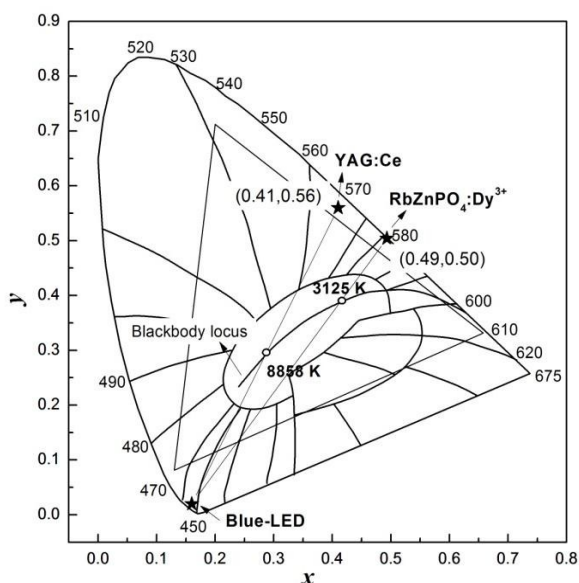


Fig.5 CIE 1931 chromaticity diagram of RZP: 0.02Dy³⁺ and the commercial yellow phosphor YAG:Ce³⁺.

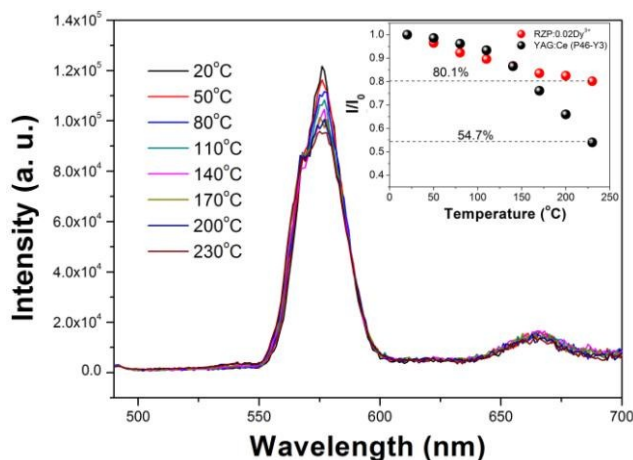


Fig.6 The thermal quenching emission spectra of RZP: Dy³⁺ excited at 452 nm; the inset shows the thermal stability comparison of RZP: Dy³⁺ and the commercial yellow phosphor YAG:Ce³⁺ (P46-Y3).

The thermal quenching property is one of the important technological parameters for phosphors used in solid-state lighting as it has considerable influence on the light output and color rendering index. To evaluate the thermal stability of RZP: Dy³⁺ phosphor, the emission spectra of RZP: 0.02Dy³⁺ were measured at various temperatures under 452 nm excitation, as illustrated in Fig. 6. For comparison, the thermal quenching properties of the commercial YAG: Ce³⁺ has also been measured, as shown in the inset. I_0 means the initial emission intensity of the phosphor and I is the emission intensity at a certain temperature. Through increasing the temperature, both the emission intensity of RZP: 0.02Dy³⁺ and YAG: Ce³⁺ monotonously decreased, which can be attributed to the increased population of higher vibration levels, the density of phonons or the probability of non-radiative transfer (energy migration to defects) as rising the temperature. When the temperature increased to 230 °C, the emission intensity of RZP: 0.02Dy³⁺ still kept 80.1 % of its initial intensity, which was found to be much better than that of the commercial yellow phosphor YAG:Ce³⁺. The excellent thermal

stability indicates that RZP: 0.02Dy³⁺ phosphor is suitable for applying in LEDs, especially the high power warm white LEDs.

30 Conclusion

A series of novel yellow emission phosphors RbZnO₄: Dy³⁺ were successfully synthesized through a solid state reaction. The phase composition and the characteristic photoluminescence properties were investigated in detail. The excitation spectra of RbZnO₄: Dy³⁺ showed strong absorption around 455 nm, which could be well matched with the current common used blue LED chip. Upon 455 nm excitation, RbZnO₄: Dy³⁺ could exhibit dominate yellow emission peaked at 577 nm, accompanied with a small red emission at 665 nm, which were due to the ⁴F_{9/2} → ⁶H_{13/2} and ⁴F_{9/2} → ⁶H_{11/2} transitions of Dy³⁺ ions in RbZnO₄ phosphors. Moreover, RbZnO₄: Dy³⁺ phosphors showed stable color tone with CIE coordinates (0.49, 0.50). The simulated combination of the blue LED chip with RbZnO₄: Dy³⁺ phosphor in CIE 1931 chromaticity showed that warm white light emission with color temperature of 3125 K and CIE of (0.42,0.39) can be obtained. The thermal quenching property investigation showed that RbZnO₄: Dy³⁺ phosphor had excellent thermal stability. When the temperature was increased to 230 °C, the emission intensity of RbZnO₄: Dy³⁺ only dropped to 80.1% of its initial intensity, which was better than the commercial yellow YAG:Ce³⁺ (P46-Y3). The results showed that the novel phosphor RbZnO₄: Dy³⁺ could serve as a potential yellow emission phosphor for applying in blue light pumped high-power warm white LEDs.

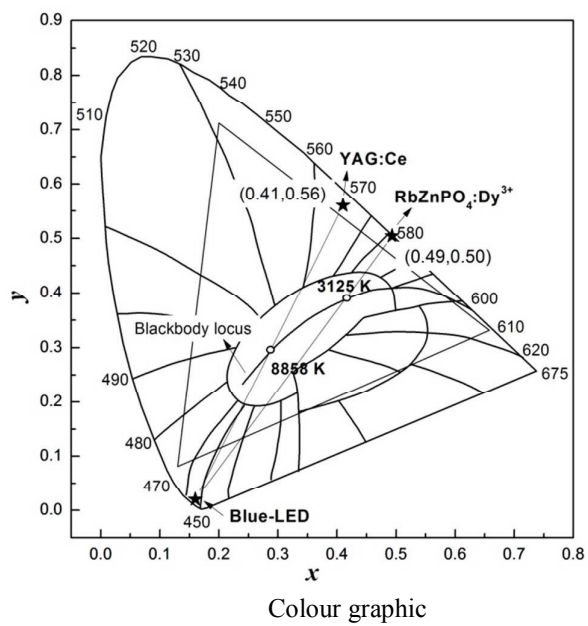
55 Authors' Address

College of New Energy, Bohai University, Jinzhou, Liaoning, 121000, P.R. China.

60 References

1. E. F. Schubert and J. K. Kim, *Science*, 2005, **308**, 1274.
2. S. Pimputkar, JS Speck, SP. DenBaars and S. Nakamura, *Nature Photon*, 2009, **3**, 180.
3. S. Ye, F. Xiao, Y. X. Pan, Y. Y. Ma and Q. Y. Zhang, *Mater. Sci. Eng. Rep.*, 2010, **71**, 1.
4. H. A. Höpfe, *Angew. Chem. Int. Ed.*, 2009, **48**, 3572.
5. AA. Setlur, *Electrochem. Soc. Interface*, 2009, **18**, 32.
6. M. Roushan, X. Zhang and J. Li, *Angew. Chem. Int. Ed.*, 2012, **124**, 451.
7. A. A. Setlur, W. J. Heward, Y. Gao, A. M. Srivastava, R. G. Chandran and M. V. Shankar, *Chem. Mater.*, 2006, **18**, 3314.
8. C. C. Lin, Z. R. Xiao, G. Y. Guo, T. S. Chan and R. S. Liu, *J. Am. Chem. Soc.*, 2010, **132**, 3020.
9. K. Sakuma, N. Hirosaki, N. Kimura, M. Ohashi, Y. Yamamoto, R. J. Xie, T. Suehiro, K. Asano and D. Tanaka, *IEICE Trans. Electron.*, 2005, **88**, 2057.
10. S. E. Brinkley, N. Pfaff, K. A. Denault, Z. Zhang, H. T. Hintzen, R. Seshadri, S. Nakamura and S. P. DenBaars, *Appl. Phys. Lett.*, 2011, **99**, 241106.
11. K. Sakuma, N. Hirosaki and R. J. Xie, *J. Lumin.*, 2007, **126**, 843.
12. X. Q. Piao, T. Horikawa, H. Hanzawa and K. Machida, *Appl. Phys. Lett.*, 2006, **88**, 161908.
13. B. Liu, L. J. Kong and C. S. Shi, *J. Lumin.*, 2007, **122**, 121.
14. L. Lin, M. Yin, C. S. Shi and W. P. Zhang, *J. Alloys Compd.*, 2008, **455**, 327.

15. Z. Ci, Q. Sun, S. Qin, M. Sun, X. Jiang, X. Zhang and Y. Wang, *Phys. Chem. Chem. Phys.*, 2014, **16**, 11597
16. J. Li, J. Li, S. Liu, X. Li, X. Sun and Y. Sakk, *J. Mater. Chem. C*, 2013, **1**, 7614.
- 5 17. C. H. Liang, L. G. Teoh, K. T. Liu and Y. S. Chang, *J. Alloys Compd.*, 2012, **517**, 9.
18. B. Han, P. Li, J. Zhang, J. Zhang, Y. Xue and H. Shi, *Dalton Trans.*, 2015, **44**, 7854.
19. L. Marciniak, D. Hreniak and W. Strek, *J. Mater. Chem. C*, 2014, **2**,
10 5704.
20. Y. Zhang, W. Gong, J. Yu, Y. Lin and G. Ning, *RSC Adv.*, 2015, **5**,
96272.
21. Z. An, X. Xiao, J. Yu, D. Mao and G. Lu, *RSC Adv.*, 2015, **5**, 52533.
22. X. Ding, G. Zhu, Y. Shi and Y. Wang, *Mater. Res. Bull.*, 2013, **48**,
15 3648.
23. H. Miura, T. Ushio, K. Nagai, D. Fujimoto, Z. Lepp, H. Takahashi
and R. Tamura, *Cryst. Growth Des.*, 2003, **3**, 6.
24. R. Shannon, *Acta Cryst.*, 1976, **32**, 751.
25. S. Xin, Y. Wang, G. Zhu, X. Ding, W. Geng and Q. Wang, *Dalton
20 Trans.*, 2015, **44**, 16099.
26. Z. Xiu, S. Liu, M. Ren, J. Liu, J. Pan and X. Cui., *J. Alloys Compd.*,
2006, **425**, 261.
27. L. Van Uitert, *J. Electrochem. Soc.*, 1967, **114**, 1048.
28. D. Dexter and J. H. Schulman, *J. Chem. Phys.*, 1954, **22**, 1063.
- 25 29. H. Du, J. Sun, Z. Xia and J. Sun, *J. Electrochem. Soc.*, 2009, **156**, 12.
30. Z. Jiang, Y. Wang and L. Wang, *J. Electrochem. Soc.*, 2010, **157**,
J155.



Text:

Novel yellow phosphor RbZnPO₄:Dy³⁺ with satisfactory color tune and thermal properties for high-power white LEDs