



Luminescent enhancement of cyan $\text{BaSi}_2\text{O}_2\text{N}_2\text{:Eu}^{2+}$ phosphor by addition of Ho^{3+}

Shuai He^{1,3} , Liangliang Zhang^{1,*}, Xueqing Liu^{1,2}, Dashuai Sun^{1,2}, Hao Wu¹, Huajun Wu¹, Guohui Pan¹, Zhendong Hao¹, and Jiahua Zhang^{1,2,*}

¹ State Key Laboratory of Luminescence and Applications, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, 3888 Eastern South Lake Road, Changchun 130033, China

² Center of Materials Science and Optoelectronics Engineering, University of Chinese Academy of Sciences, Beijing 100049, China

³ School of Science, Inner Mongolia University of Science and Technology, Baotou 014010, China

Received: 30 December 2021

Accepted: 11 May 2022

Published online:

6 June 2022

© The Author(s), under exclusive licence to Springer Science+Business Media, LLC, part of Springer Nature 2022

ABSTRACT

Efficient cyan phosphors are needed for filling the cyan cavity in the spectra of phosphor converted white light-emitting diodes (pc-WLEDs). In this paper, we reported a strategy to enhance the emission of cyan $\text{BaSi}_2\text{O}_2\text{N}_2\text{:Eu}^{2+}$ phosphor by adding Ho^{3+} to promote conversion from Eu^{3+} to Eu^{2+} . External quantum efficiency reached up to 68.9%, excited by 405 nm, based on the observation of emission intensity decrease of Eu^{3+} and absorption enhancement of Eu^{2+} with addition of Ho^{3+} . Using the luminescence-enhanced cyan phosphor, commercial yellow, and red phosphors, full-color WLEDs with high color rendering at various color temperatures were packaged on blue LED chips. A WLED with ultra-high color rendering index (CRI = 98) and high luminous efficiency (95 lm/W) at correlated color temperature of 5112 K was achieved.

1 Introduction

Good lighting should not only provide the needed level of visual performance but also protect people's physical and mental health [1]. Bright light can be used in the treatment, sleep conditioning, emotion improving, and the circadian clock regulation. Hence, the concepts of full-spectrum lighting [2] and human centric lighting [3] have been proposed one after another in lighting field. Therefore, spectral distribution design of white-light-emitting diodes (WLEDs) for visual comfortable is extremely

important [1]. The WLEDs are mostly realized by coating phosphors, mainly including cyan $\text{BaSi}_2\text{O}_2\text{N}_2\text{:Eu}^{2+}$ (BSON:Eu²⁺), yellow YAG:Ce³⁺, and red $\text{CaAlSiN}_3\text{:Eu}^{2+}$ phosphors, on blue LED chips [4–7]. The latest research reported a new kind of receptor of human, which can control biological rhythms via the effect of melatonin secretion [1]. The most sensitive wavelength of the receptor was located in cyan region. Therefore, cyan BSON:Eu²⁺ phosphor has attracted much attention [8]. Different from some other cyan light-emitting materials like $\text{LiBaBO}_3\text{:Eu}^{2+}$ [9], $\text{BaZrSi}_3\text{O}_9\text{:Eu}^{2+}$ [10], and $(\text{Sr}, \text{Ba})_{4.7}\text{Eu}_{0.3}(\text{-PO}_4)_3\text{Cl:Eu}^{2+}$ [7], BSON:Eu²⁺ can be effectively

Address correspondence to E-mail: zhangliangliang@ciomp.ac.cn; zhangjh@ciomp.ac.cn

excited by blue light. However, the conversion efficiency of cyan BSON:Eu²⁺ phosphor needs to be improved.

Luminescent properties of BSON:Eu²⁺ were first reported by Li et al. [11]. After that, plenty of work have been done in the synthesis method and the PL properties of it [12–20]. It is well known that it is difficult to obtain the pure phase of BSON. Yun et al. [13] and Pan et al. [14] proved the validity of the two-step method (using Ba₂SiO₄:Eu²⁺ as a precursor), compared with the conventional solid-state reaction. To enhance the emission intensity of BSON phosphor, Song et al. [18] obtained a rod-like single-phase BSON:Eu²⁺ phosphor, using Eu₂O₃@B₂O₃ core-shell structure as an activator; Wang et al. [19] improved the optical performance of BSON:Eu²⁺ by incorporating La³⁺ and Y³⁺; Wang et al. [20] improved the optical performance of BSON:Eu²⁺ by partial Ge⁴⁺ substitution for Si⁴⁺.

In this paper, we report the realization of emission enhancement of cyan BSON:Eu²⁺ phosphor, by adding Ho³⁺ to promote the conversion of Eu³⁺ to Eu²⁺. The mechanism of the enhancement is studied. Using the improved cyan phosphor as well as commercial yellow and red phosphors, full-color WLEDs with high color rendering at various color temperatures are packaged on blue LED chips.

2 Experiment

2.1 Synthetic process

The phosphors BSON:xEu²⁺, xHo³⁺ are synthesized via a high-temperature solid-state reaction of two-step method. At the first step, appropriate amounts of BaCO₃ (99.99%), SiO₂ (AR), and Eu₂O₃ (99.99%) are fired at 1200 °C for 6 h in a reducing gas flow of 95%N₂/5%H₂ to make a precursor, Ba₂SiO₄:xEu²⁺. Secondly, the precursor is ground and mixed with Si₃N₄ (99.99%), Li₂CO₃ (99.99%), and Ho₂O₃ (99.99%) in a stoichiometric ratio and then fired again at 1100 °C for 1 h and 1450 °C for 6 h, in the same reducing gas flow. Finally, the samples are cooled down to room temperature under the same atmosphere. The synthesis process has been presented in detail with a flow chart for easy understanding (Figure S1). To satisfy the requirement of charge balance, the substitution of Ho³⁺ for Ba²⁺ is conducted by adding equivalent concentrations of Li⁺.

And the concentration of Li⁺ is changed with the Ho³⁺ concentration, as a 1:1 weight ratio.

2.2 Characterization

The crystal structure of phase formation is detected by X-ray diffraction (XRD) (Bruker D8 Focus diffractometer, in the 2θ range from 10° to 70° with Cu Kα radiation (λ = 1.54056 Å) operating at 40 kV, 30 mA). The Photoluminescence excitation (PLE) and photoluminescence emission (PL) spectra are measured by FLS900 spectrometer (Edinburgh Instruments, U.K.). The measurements of diffuse reflection spectra are performed by Hitachi F-7000 spectrometer, equipped with a 150 W xenon lamp. A process controller (OMEGA CN76000), equipped with a thermocouple, is used to measure the temperature and control the heating rate. In fluorescence decay measurements, an optical parametric oscillator (OPO) is used as an excitation source, and the signal is detected by Tektronix digital oscilloscope (TDS 3052). The quantum efficiency is measured by Hitachi F-7000 spectrometer, equipped with an integral ball. Prototype LEDs are fabricated by applying an intimate mixture in weight of the phosphor powder and transparent silicone resin on blue InGaN LED chips (ex = 450 and 460 nm). The chromaticity coordinates, Ra, CRI, and CCTs of white LEDs are measured by Ocean Optics USB4000 spectrometer.

3 Results and discussion

3.1 Observation of Eu³⁺ in BSON

Figure 1a shows the XRD pattern of BSON:Eu²⁺, xHo³⁺ with different x. The main diffraction peaks agree well with that of BSON reported in previous work [11, 12]. BSON:Eu²⁺ has been proposed to have an orthorhombic crystal structure with a space group Pbcn. Ba²⁺ is surrounded by O²⁻ in the inter-layer of SiON₃ tetrahedron (Figure S1). Eu²⁺ and Ho³⁺ occupy the position of Ba²⁺ by virtue of having an atomic radius similar to Ba²⁺. And due to the smaller atomic radius of Eu²⁺ and Ho³⁺, the XRD peaks shows a left shift as the increase of x. Figure S2 shows a same left shift at the higher doping of Eu²⁺.

Figure 1b shows the scanning electron microscopy (SEM) mapping of BSON:Eu²⁺. Some rod-like type morphologies are observed. Lee et al. considered that these rods are BSON:Eu³⁺ rather than BSON:Eu²⁺.

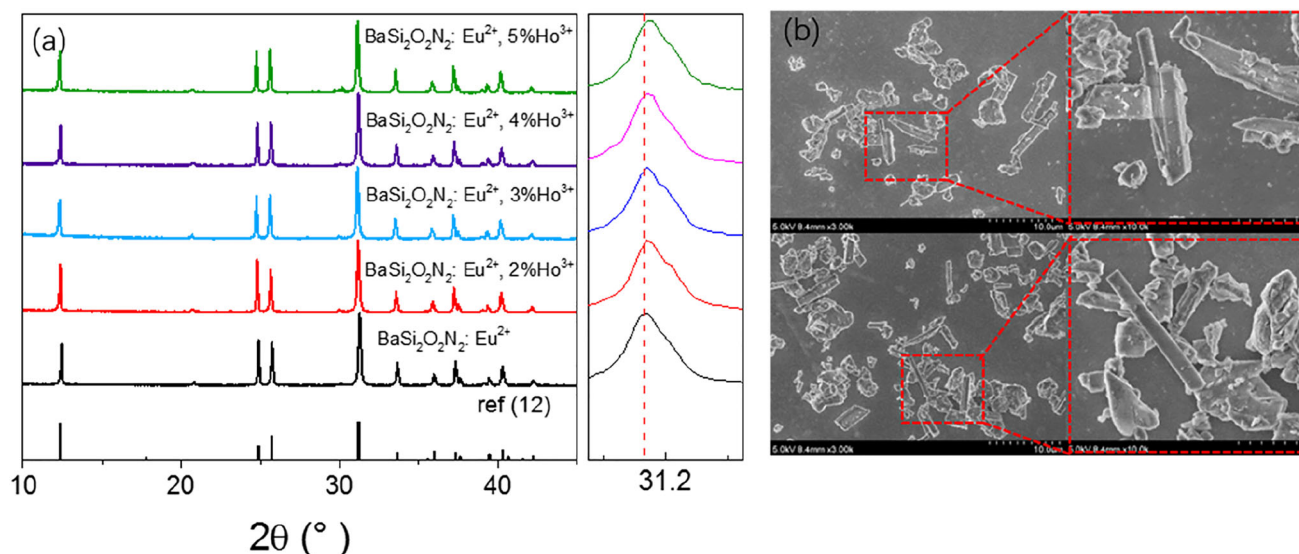


Fig. 1 **a** The X-ray diffraction (XRD) pattern of BSON:0.04Eu²⁺, xHo³⁺ (x = 0, 0.02, 0.03, 0.04, 0.05) and **b** Scanning electron microscopy (SEM) mapping of BSON:Eu²⁺

The rod-like type morphology is a preference orientation, which is common in BSON. [21]. An intensity change about the XRD peak can be seen at 24.9° and 25.7°, which is because the crystal plane diffraction intensity is caused by preferred orientation. To precisely determine the degree of reduction of Eu³⁺ to Eu²⁺, the X-ray photoelectron spectroscopy is measured. However, as shown in Figure S3, the peak with Eu²⁺ and Eu³⁺ in the XPS is not founded [22, 23].

The PL and PLE spectra of BSON:Eu²⁺ are shown in Fig. 2a. The PLE spectrum shows two broad excitation bands, covering 260–485 nm, which is originated from 4f⁶–4f⁵5d transition of Eu²⁺ [15]. The PL spectrum of BSON:Eu²⁺, excited at 405 nm, shows a narrow cyan band at 495 nm, originated from the transition from the lowest lying 4f⁵5d state to the ground state of Eu²⁺. In addition, emission lines with the main peak at 612 nm is also detected, under 532 nm excitation, which is assigned to ⁵D₀–⁷F_J (J = 0,1,2,3,4) transitions of Eu³⁺, compared with the emission spectrum of BSON:Eu³⁺ as shown in Fig. 2c. The PLE spectrum of the 612 nm emission (Fig. 2b) shows a O²⁻→Eu³⁺ charge transfer band at 302 nm and a series PLE lines for the transitions of ⁷F₀→⁵D_J (J = 1,2,3) [24]. The observation of Eu³⁺ emission indicates that Eu³⁺ is not reduced completely to Eu²⁺ in the preparation of the BSON:Eu²⁺. The vacancy and non-equilibrium potential are formed in the synthetic process, due to the similar

radius between O²⁻ and N³⁻. And N³⁻ with a smaller radius is easy to occupy the O²⁻ case for the formation of excess negative charge. This will lead to a result that Eu³⁺ is not reduced completely to Eu²⁺ in the preparation. Therefore, the luminescence intensity of BSON:Eu²⁺ will be improved by converting the residual Eu³⁺ to Eu²⁺.

3.2 Emission enhancement of BSON:Eu²⁺ by adding Ho³⁺

It can be found that the cyan emission of BSON:Eu²⁺ can be enhanced by adding Ho³⁺ in the phosphor. As can be seen from Fig. 3, the cyan emission (Fig. 3a) and UV blue absorption (Fig. 3b) of Eu²⁺ are both enhanced as the increasing of Ho³⁺, while the Eu³⁺ emission, at 612 nm, is weakened (Fig. 3c). The cyan luminescent enhancement is attributed to the increase of Eu²⁺, which is resulted from the promotion of Eu³⁺ to Eu²⁺ conversion by the increase of Ho³⁺. There is a limit solubility of trivalent cations to replace Ba²⁺ sites in BSON host, due to charge mismatch between Ba²⁺ and trivalent cation. Ho³⁺ will occupy the limit sites, allowed to be occupied by trivalent cations, as it introduced in BSON. Therefore, there is a competition between Eu³⁺ and Ho³⁺ for occupying these limit sites. The luminescence characteristics of BaSi₂O₂N₂:Eu²⁺, Ho³⁺ without Li⁺ doping was presented in Figure S4.

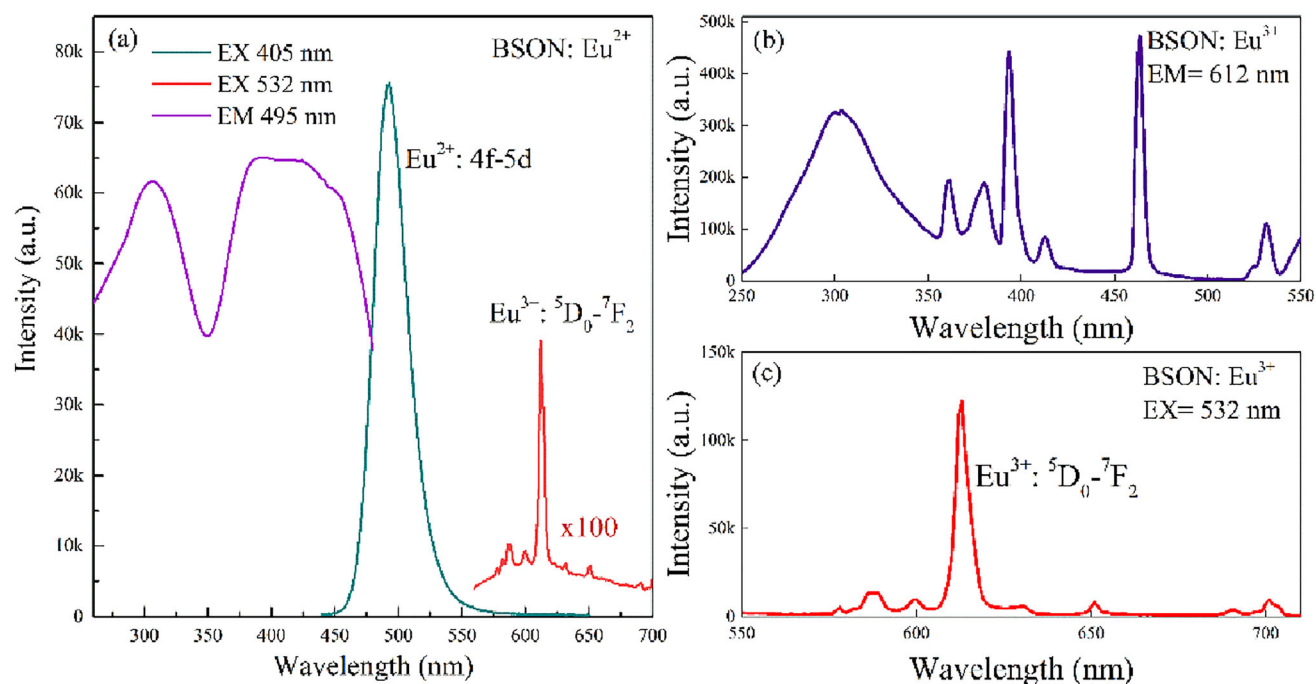


Fig. 2 PL and PLE spectra of BSON:Eu²⁺ (a), PLE spectrum (b), and PL spectrum (c) of BSON:Eu³⁺

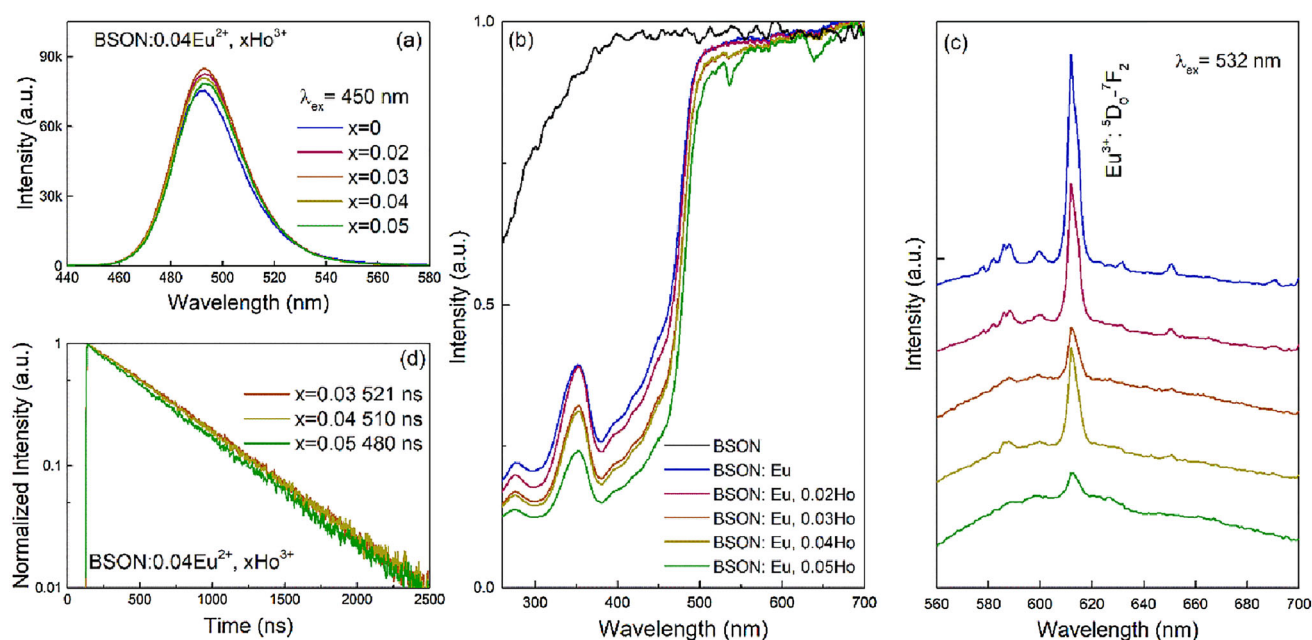


Fig. 3 PL spectra of Eu²⁺ (a), powder diffuse reflection spectra (b), and PL spectra of Eu³⁺ (c) of BSON:Eu²⁺, xHo³⁺ ($x = 0, 0.02, 0.03, 0.04, 0.05$). Excited state decay curve of the BSON:Eu²⁺, xHo³⁺ ($x = 0.03, 0.04, 0.05$) monitoring at 495 nm excited by 450 nm

It can be seen a same enhancement by Ho³⁺ doping. Different from the previous report [25, 26], the effect of the trace Li⁺ is small in this paper. With the increase of x , Eu³⁺ fails to compete with Ho³⁺, and they have to convert Eu²⁺ to occupy Ba²⁺ site. In addition, the cyan emission intensity reaches the

maximum at $x = 0.03$ (Fig. 3a and d) and it starts to decrease, as $x > 0.03$. The decrease of cyan emission intensity is attributed to the reduction of quantum efficiency of the cyan emission, based on the experimental observation that the cyan fluorescence lifetime becomes slightly shortening as the increasing of

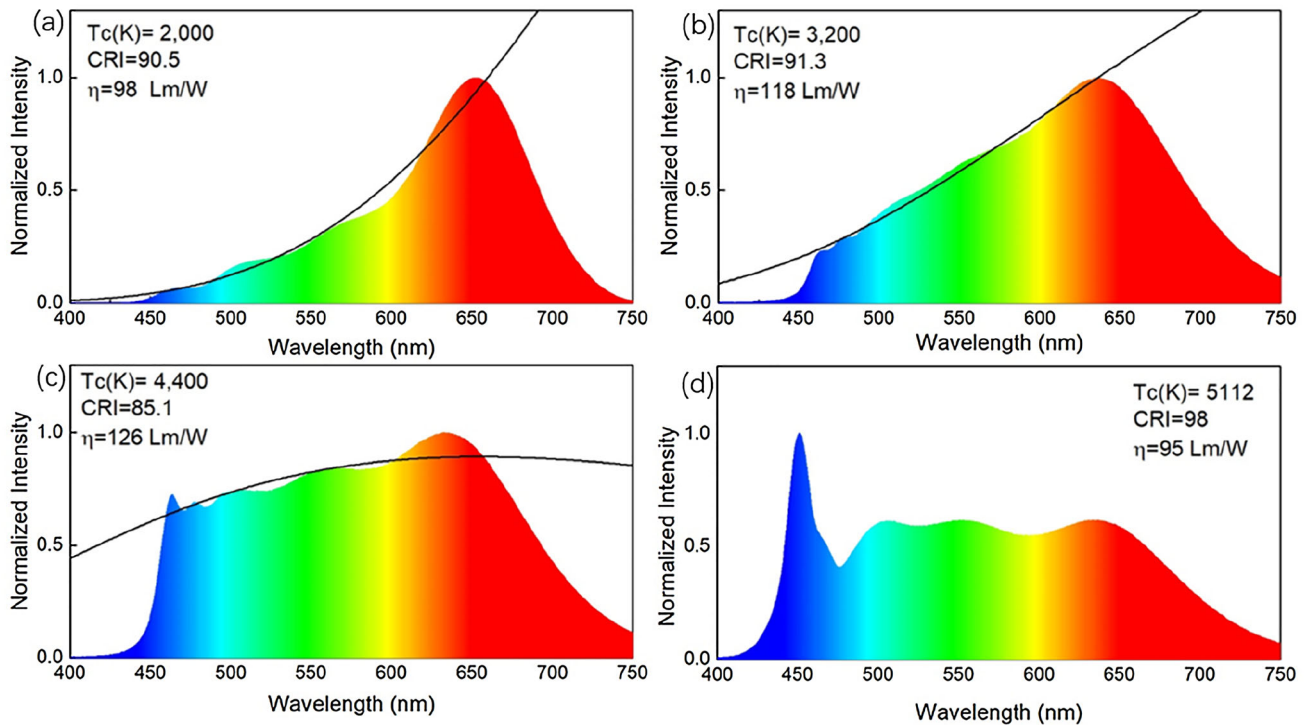


Fig. 4 Emission spectra of LEDs packaged by BSON and Commercial phosphors yellow LuAG:Ce^{3+} and red $\text{CaAlSiN}_3\text{:Eu}^{2+}$ phosphors on blue LED chip and the

corresponding black body radiation curve with the same CCT **a** 2000 K, **b** 3200 K, **c** 4400 K, and **d** 5112 K (Colour figure online)

x (Fig. 3d). The lifetime shortening may be due to energy transfer to some unknown centers induced by Ho^{3+} co-doping. Moreover, it can be observed that all of the BSON:xEu^{2+} phosphors ($x = 0, 2\%, 3\%, 4\%, 5\%$, and 6%) show notable emission enhancement as 0.03Ho^{3+} is added, as shown in Figure S5. Finally, the EQE of Optimal sample is 68.9% and the IQE is 88.6%, upon 405 nm excitation. And its thermal stability is shown in Figure S6.

3.3 Full-color WLEDs

Series WLEDs, that have emission spectra resembling black body radiation curves for various correlated color temperatures (CCTs), from 2000 to 4400 K, are fabricated, using cyan BSON:Eu^{2+} , Ho^{3+} phosphors, and commercial phosphors (yellow LuAG:Ce^{3+} and red $\text{CaAlSiN}_3\text{:Eu}^{2+}$), which is based on 460 nm blue LED chips, as shown in Fig. 4a and c. And the emission spectra of LEDs, packaged by three phosphors on blue LED chip, respectively, are shown in Figure S7. It can be found that the CRIs are less

than 93 in Fig. 4a and c. This is because the spectra components with the wavelength shorter than 450 nm are insufficient. Figure 4d shows a WLED with an ultra-high CRI close to 98, at 5112 CCT, based on 450 nm blue LED chips, with high luminous efficiency of 95 lm/W. The spectrum of the high CRI WLED shows a high blue emission intensity for compensating the deficient shorter wavelength blue components.

4 Conclusion

Efficient cyan emission BSON:Eu^{2+} , Ho^{3+} phosphors, suitable for blue LED excitation, are developed. Eu^{2+} emission of BSON phosphor is enhanced by co-doping Ho^{3+} . As the competition between Eu^{3+} and Ho^{3+} for occupying limited trivalent cations sites, Ho^{3+} -doped samples show the best performance with EQE reach up to 68.9%. The WLEDs with different CCTs are encapsulated with excellent performance. High-efficiency WLEDs with high CRI are obtained by packaging the BSON:Eu^{2+} , Ho^{3+} . The

CRI reaches up to 98, with the high luminous efficiency of 95 lm/W. It initiates a new way to enhance luminescent intensity of phosphors.

Acknowledgements

This work was partially supported by the National Natural Science Foundation of China (Grant No. 52072361, 12074373, 12074374, 51772286, 11974346, 11874055, and 11904361), the Youth Innovation Promotion Association CAS No. 2020222, the Key Research and Development Program of Jilin province (20200401050GX), the Cooperation project between Jilin Province and Chinese Academy of Sciences (2020SYHZ0013), and the Opening Project Key Laboratory of Transparent Opto-functional Inorganic Material, Chinese Academy of Sciences.

Author contributions

SH contributed to conceptualization, methodology, investigation, data curation, visualization, and writing—original draft. LZ contributed to conceptualization, methodology, resources, formal analysis, and project administration. XL contributed to investigation and resources. DS contributed to methodology and resources. HW contributed to methodology and validation. HW contributed to methodology and validation. GP contributed to methodology and validation. ZH contributed to methodology and validation. JZ contributed to conceptualization, methodology, funding acquisition, supervision, visualization, validation, and writing—review & editing.

Data availability

The datasets generated during and/or analyzed during the current study are available from the corresponding author on reasonable request.

Declarations

Conflict of interest There are no conflicts to declare.

Supplementary information: The online version contains supplementary material available at <http://doi.org/10.1007/s10854-022-08414-3>.

References

1. L. Bellia, F. Bisegna, G. Spada, *Build. Environ.* **46**(10), 1984–1992 (2011)
2. M.H. Fang, C.C. Ni, X.J. Zhang, Y.T. Tsai, S. Mahlik, A. Lazarowska, M. Grinberg, H.S. Sheu, J.F. Lee, B.M. Cheng, R.S. Liu, *ACS Appl. Mater. Inter.* **8**(45), 30677–30682 (2016)
3. Y.R. Xia, O.Y. Wan, K.W. Cheah, *Opt. Mater. Express* **6**(6), 1905–1913 (2016)
4. Oh J.H., Yang S.J., Do Y.R., *Light Sci. Appl.*, 2014, 3
5. D. Wu, Z.D. Hao, X. Zhang, G.H. Pan, Y.S. Luo, L.G. Zhang, H.F. Zhao, J.H. Zhang, *J. Lumin.* **186**, 170–174 (2017)
6. C.H. Huang, Y.C. Chiu, Y.T. Yeh, T.S. Chan, T.M. Chen, *ACS Appl. Mater. Inter.* **4**(12), 6661–6667 (2012)
7. G. Deressa, K.W. Park, H.S. Jeong, S.G. Lim, H.J. Kim, Y.S. Jeong, J.S. Kim, *J. Lumin.* **161**, 347–351 (2015)
8. R.J. Xie, N. Hirosaki, *Sci. Technol. Adv. Mat.* **8**(7–8), 588–600 (2007)
9. Z.H. Huang, H.P. Ji, M.H. Fang, M.S. Molokeev, S.Y. Liu, Y.G. Liu, X.W. Wu, *Chem. Phys. Lett.* **628**, 21–24 (2015)
10. D.Y. Wang, C.H. Huang, Y.C. Wu, T.M. Chen, *J. Mater. Chem.* **21**(29), 10818–10822 (2011)
11. Y.Q. Li, A.C.A. Delsing, G. de With, H.T. Hintzen, *Chem. Mater.* **17**(12), 3242–3248 (2005)
12. J.A. Kechele, O. Oeckler, F. Stadler, W. Schnick, *Solid State Sci.* **11**(2), 537–543 (2009)
13. B.G. Yun, T. Horikawa, H. Hanzawa, K.I. Machida, *J. Electrochem. Soc.* **157**(10), J364–J370 (2010)
14. H. Pan, L. Dong, W. Le, Y. Li, *Intel. Conference on Manu. Sci. Eng.* 2015
15. Y.X. Gu, Q.H. Zhang, Y.G. Li, H.Z. Wang, *J. Mater. Chem.* **20**, 6050–6056 (2010)
16. G.G. Li, C.C. Lin, W.T. Chen, M.S. Molokeev, V.V. Atuchin, C.Y. Chiang, W.Z. Zhou, C.W. Wang, W.H. Li, H.S. Sheu, T.S. Chan, C.G. Ma, R.S. Liu, *Chem. Mater.* **26**(9), 2991–3001 (2014)
17. V. Bachmann, C. Ronda, O. Oeckler, W. Schnick, A. Meijerink, *Chem. Mater.* **21**(2), 316–325 (2009)
18. Y.H. Song, M.J. Lee, Y.L. Song, G.S. Han, K. Senthil, M.K. Jung, H.S. Jung, D.H. Yoon, *Mater. Lett.* **129**, 178–181 (2014)
19. L.L. Wang, H.Y. Ni, Q.H. Zhang, F.M. Xiao, *J. Nanosci. Nanotechnol.* **16**(4), 4008–4011 (2016)
20. B.C. Wang, J. Chen, Y.F. Xia, Y.G. Liu, *J. Nanosci. Nanotechnol.* **16**(4), 3608–3612 (2016)
21. S. Lee, T. Kang, H. Kang, Y. Jeong, J. Kim, H. Heo, *Korean J. Mater. Res.* **29**(7), 437–442 (2019)
22. P.J. Dereń, D. Stefańska, M. Ptak, P. Wiśniewski, *J. Phys. Chem. C* **125**, 24505–24514 (2021)

23. H. Wu, G.T. Fei, X.L. Ma, Z.M. Hu, L.D. Zhang, *Nanoscale Res. Lett.* **14**(1), 298 (2019)
24. X.M. Liu, W.J. Xie, Y. Lu, J.C. Feng, X.H. Tang, J. Lin, Y.H. Dai, Y. Xie, L.S. Yan, *Inorg. Chem.* **56**(22), 13829–13841 (2017)
25. S.K. Gupta, K. Sudarshan, A.K. Yadav, R. Gupta, D. Bhat-tacharyya, S.N. Jha, R.M. Kadam, *Inorg. Chem.* **57**(2), 821–832 (2018)
26. X. Gao, W.T. Zhang, X.M. Wang, X. Huang, Z. Zhao, J. *Alloys Compd.* **10**(893), 162265 (2022)

Publisher's note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.