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## 1. Introduction

Solid-state lighting devices based on white-light-emitting diodes (WLEDs) have been shown to have the advantages of robustness, energy-saving capability, environmental friendliness, long lifetime and high luminous efficiency, and have already replaced conventional incandescent, fluorescent and high-intensitydischarge lamps in both working and domestic situations.<sup>1–3</sup> WLEDs are most commonly fabricated by combining a blue LED chip with yellow, yellow/red or green/red phosphors.<sup>4–8</sup> WLEDs where a blue LED chip is combined with only a yellow phosphor often manifest high efficiency but suffer from poor color rendering properties; the addition of a second red phosphor or indeed use of green and red phosphors improves the color rendering but usually with a sacrifice in efficiency. In addition other drawbacks have been encountered with such approaches to generating white light

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## An excellent cyan-emitting orthosilicate phosphor for NUV-pumped white LED application<sup>†</sup>

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In this paper, a cyan-emitting phosphor BLS:Ce<sup>3+</sup> is reported that has a broad emission band covering both the blue and green regions of the visible spectrum, which can be used instead of two separate blue and green phosphors. The excitation peak of BLS:Ce<sup>3+</sup> is located at 400 nm, which matches well with the emission light of efficient near-ultraviolet (NUV) chips. The BLS:Ce<sup>3+</sup> phosphor has an internal quantum efficiency (IQE) higher than 90% at room temperature (RT) and an excellent thermal stability (a small reduction of 3% at 150 °C relative to the IQE at RT) and is environmentally robust (a small degradation of 6% occurs after aging for 1600 h at 85 °C/85% RH relative to the room-temperature IQE value). Using the BLS:Ce<sup>3+</sup> phosphor, coupled only with a CaAlSiN<sub>3</sub>:Eu<sup>2+</sup> red phosphor and a 395 nm NUV chip, a NUV-based WLED with a high color rendering index of 90.6 has been achieved. Moreover, the luminous efficiency reaches as high as 32.2 lm W<sup>-1</sup>, which is much better than that of the NUV-WLEDs employing three phosphors (blue, green and red).

including chromaticity drifting and problems with the exciting blue light source. The emission spectra of WLEDs usually have a strong blue spike present from the unconverted blue light.<sup>9,10</sup> This blue light can have two serious effects, the first is that if the WLED is a bright light source or the viewer is looking at it directly or even indirectly for some time it can cause retinal injury, and the second is that the blue light affects the human body clock. This latter problem needs to be addressed as such lighting is often used throughout the day as well as at night. In 2001 research studies in the USA discovered a fifth human "photoreceptor" in the human eye; this has turned out to be important in the regulation of the biological (non-visual) effects of light on the human body.<sup>11,12</sup> They further identified a photopigment in the eye that reacts with the incoming blue light and controls the production of melatonin. The production of melatonin plays an important role in the body's circadian rhythms. In natural light, blue light dominates as the sun rises hence the daily setting or regulating of bodily rhythms. Thus if WLEDs and also the blue laser diodes that could replace them are used in white lighting where the color rendering does not change over the course of a day then the blue light levels could have long term health problems. In addition in WLEDs the blue light is often directional and so some lit areas can be richer in blue light (the so called "cone angle" problem).

One approach to avoid the problems associated with using blue LEDs is to use near-ultraviolet (NUV)-driven WLEDs that employ NUV-LED chips and blue/green/red-emitting phosphors. In this type of approach blue emission is given out by the phosphors as a broad band rather than a spike. The broader

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blue emission makes such an approach desirable as it enhances the achievable color rendering properties and the light uniformity, and of course it reduces the blue light toxicity to eyes of the bluepumped WLEDs<sup>13–18</sup> and also does not interfere with the body's rhythms.

For the NUV-pumped WLEDs, blue- and green-emitting phosphors are necessary to provide the blue and green components of white light. Currently, many blue- or green-emitting phosphors have been developed,<sup>17,19–31</sup> but only some nitride(oxy) phosphors show an acceptable quantum efficiency (QE) and thermal stability. However, the synthetic methodology needed for nitride(oxy) phosphors is complex requiring expensive raw materials, high reaction temperature (even near 2000 °C) and high pressure (nitrogen or ammonia gas of about 100 MPa), which leads to high costs and high prices, and in addition the positions of most of their main excitation wavelengths are shorter than 380 nm. Such wavelengths are far from the emission light of efficient NUV chips that emit typically in the range of 380-420 nm. A further problem is that the full widths at half maximum (FWHM) of the emission peaks of these phosphors are narrow in the range of 20-60 nm. So what is needed is a complete mixture of blue- and green-emitting phosphors to achieve a high color rendering property and uniform light. In addition using a three phosphor mixture will always increase the complexity of manufacture and obviously reabsorption between different phosphors leading to a reduction in efficiency. If a cyan-emitting phosphor that has a wide emission spectrum band covering both blue and green components is developed, then part of the problem produced by the mixture process can be avoided.

Ideally a cyan-emitting phosphor that can be practically used for NUV-pumped WLEDs should meet all of the following requirements: (1) it should have excitation bands that match the wavelength of the emission light from the NUV-LED chips; (2) the phosphor emission spectrum should be a wide band with a larger FWHM value in the blue region than that of 470 nm LEDs; (3) the luminescence intensity or QE should be high upon NUV light excitation; (4) the thermal or environmental stability of the phosphor should be good enough as the NUV light is stronger in energy than the blue light. It should also be easy to synthesize at a low cost so that it can be produced at a low price. However, cyan-emitting phosphors are quite rare and most of them cannot meet these requirements.<sup>32-34</sup> In fact, the cyanemitting phosphor BaLa2Si2S8:Ce3+ has a low internal QE (IQE, 36%) and a strong degradation at high temperatures.<sup>32</sup>  $Ca_6BaP_4O_{17}$ :  $Ce^{3+}$ ,  $Si^{4+}$  has a relatively high IQE (~70%) but with a relatively strong degradation (  $\sim\!20\%$  at 150  $^\circ\!\mathrm{C}$  relative to the room-temperature IQE value), and its emission peak is at 477 nm with a relatively narrow FWHM of 98 nm, which is not broad enough and its use still requires it to be combined with both green and red phosphors to generate white light.<sup>34</sup>

Previously, we reported a novel phosphor,  $Ba_9Lu_2Si_6O_{24}:Ce^{3+}$ (BLS:Ce<sup>3+</sup>), which emits cyan luminescence peaking at 490 nm upon 400 nm NUV-light excitation, with a large FWHM  $\approx$ 120 nm and a IQE higher than 80%.<sup>35</sup> The BLS:Ce<sup>3+</sup> cyan phosphor can be easily synthesized by a high-temperature solid-state reaction at a relatively low temperature (1400 °C). In particular, BLS:Ce<sup>3+</sup> manifests an excellent thermal stability. In this article, the IQE value of BLS:Ce<sup>3+</sup> is enhanced by more than 90% and the improved phosphor is environmentally robust (a small degradation of 6% occurs after aging for 1600 h at 85 °C/85% RH relative to the room-temperature IQE value). Moreover, these properties have facilitated the fabrication of a NUV-pumped WLED composed of a NUV chip only with BLS:Ce<sup>3+</sup>, instead of blue- and green-emitting phosphors, and a red phosphor CaAlSiN<sub>3</sub>:Eu<sup>2+,36</sup> NUV-pumped WLEDs employing blue/green/red phosphors can have excellent color rendering properties,  $R_a$  higher than 90, but with a luminous efficiency (7–23  $\text{Im W}^{-1}$ ) always smaller than 30  $\text{Im W}^{-1}$ .<sup>25,27,29</sup> Based on our phosphor, we achieved a NUV-pumped WLED with a luminous efficiency of 32.2 lm  $W^{-1}$ , as well as a high  $R_a$ of 90.6. These results demonstrate the promising application of our cyan-emitting phosphor for NUV-based WLEDs.

## 2. Experimental

#### 2.1 Sample synthesis

Commercial BaCO<sub>3</sub> (99.8%), Lu<sub>2</sub>O<sub>3</sub> (99.99%), SiO<sub>2</sub> (99.9%), and CeO<sub>2</sub> (99.99%) powders were used as the starting materials. The starting powders were weighted according to the nominal composition of Ba<sub>9</sub>Lu<sub>2</sub>Si<sub>6</sub>O<sub>24</sub> and Ba<sub>9</sub>(Lu<sub>2-x</sub>Ce<sub>x</sub>)Si<sub>6</sub>O<sub>24</sub> (x = 0-0.15) and mixed by using ball milling for 12 h in alcohol at a rotation speed of 300 rpm. The mixtures were dried and sintered in a tube furnace under a reducing atmosphere of 95% N<sub>2</sub> + 5% H<sub>2</sub> at 1400 °C for 4 h. The products were all colorless powders. Each mixture was subsequently ground to a fine powder with an agate mortar and pestle for further analysis.

#### 2.2 Characterization

X-ray powder diffraction (XRD) data were collected for all samples on a Bruker D8 Advance diffractometer with Cu K $\alpha$  radiation ( $\lambda = 1.54056$  Å). To study the crystalline structure and the phase purity of the samples, XRD profiles were recorded in the range of 10–80° with a step size of 0.02° (2 $\theta$ ). All the operations were carried out at 40 kV and 40 mA. The diffraction data were fit by Rietveld refinements using the general structure analysis system (GSAS).<sup>37,38</sup> The elementary composition was tested by using field emission scanning electron microscopy (FE-SEM, Hitachi S-4800 and Oxford-IE250) equipped with an energy dispersive spectrometer (EDS). TEM images were taken on a JEM-2100F instrument with an acceleration voltage of 200 kV.

Photoluminescence (PL), photoluminescence excitation (PLE) and diffuse reflectance (DR) spectra at room temperature for the Ce<sup>3+</sup>-doped samples were obtained on a Hitachi F-4600 spectrometer from Japan equipped with a 150 W Xenon lamp under a working voltage of 400 V. Both the excitation and emission slits were set at 5.0 nm. The DR spectra for the BLS host were measured by using a Lambda 950 spectrometer from Perkin Elmer Co., USA. A BaSO<sub>4</sub> white plate was used as the standard reference for the reflection measurement. The PL and PLE spectra and the fluorescence decay curves of Ce<sup>3+</sup> at 77 K by

dipping the sample in liquid nitrogen were measured on a Horiba Fluorolog FL3-111 spectrometer with a scintillating nano-LED lamp. The temperature-dependent luminescence properties of IQE, external QE (EQE), and absorbance (A) were measured by using a QE-2100 spectrophotometer from Otsuka Photal Electronics, Japan. The temperature was heated from RT to 300 °C in 50 °C intervals and held at each temperature for 10 min with a heating rate of 50 °C min<sup>-1</sup>.

Prototype NUV-pumped WLEDs were fabricated by applying an intimate mixture by weight of the BLS:Ce<sup>3+</sup> and CaAlSiN<sub>3</sub>:Eu<sup>2+</sup> phosphors and transparent silicone resin on NUV-LED chips (emission max at about 395 nm). The  $R_a$ , correlated color temperature (CCT), luminous efficiency, and Commission Internationale de L'Eclairage (CIE) color coordinates of the fabricated WLEDs were measured using an Ocean Optics USB4000 spectrometer.

#### 2.3 Computational methodology

The calculations of the electronic band structure were based on the density function theory (DFT) method in the generalized gradient approximation (GGA) using the Perdew–Burke–Ernzerhof (PBE) functional,<sup>39</sup> as implemented in the Vienna *Ab initio* Simulation Package (VASP), which employs a plane-wave basis.<sup>40,41</sup> The plane-wave energy cutoff is set to be 560.00 eV, and the electronic energy convergence is  $10^{-5}$  eV. A  $\Gamma$ -centered  $7 \times 7 \times 7$  Monkhorst–Pack *k*-point mesh is used to sample the irreducible Brillouin zone.

#### 3. Results and discussion

#### 3.1 Crystal structure

In the last few years silicate phosphors have been the subject of several studies because of their chemical stability and remarkable optical properties.<sup>42–46</sup> BLS:Ce<sup>3+</sup> is a novel phosphor derived from the orthosilicate family of Ba<sub>9</sub>Sc<sub>2</sub>Si<sub>6</sub>O<sub>24</sub> (BSS)<sup>47</sup> and Ba<sub>9</sub>Y<sub>2</sub>Si<sub>6</sub>O<sub>24</sub> (BYS).<sup>48</sup> In 1994, Wang et al.<sup>47</sup> first reported that BSS crystals have a rhombohedral structure made up of characteristic layers separated by a layer of Ba<sup>2+</sup> cations, as shown in Fig. 1. The luminescent ions commonly used in LED phosphors Ce<sup>3+</sup> or  $Eu^{2+}$  can only sit at the  $Ba^{2+}$  site where they experience a relative weak crystal-field splitting energy (in BSS). In these sites these cations emit narrow bands in the UV-blue or green parts of the spectrum: such bands cannot meet the demand of a cyanemitting phosphor.<sup>49-52</sup> In 2013, Jakoah Brgoch et al. substituted  $\mathrm{Sc}^{3+}$  ions totally by larger  $\mathrm{Y}^{3+}$  cations, and thus facilitated the introduction of Ce<sup>3+</sup> into the Y<sup>3+</sup> site (where it experiences a strong crystal-field splitting energy) and thereby obtained the cyan-emitting phosphor of BYS:Ce<sup>3+</sup>.<sup>48</sup> BYS:Ce<sup>3+</sup> has the same rhombohedral structure and exhibits a cyan emission peaking at 480 nm with a broad band FWHM  $\approx$  110 nm under 394 nm excitation. The emitted light is cyan; however, the IQE is not higher than 60%, limiting this phosphor's practical application. Usually, atoms that possess both heavy mass and small radius stabilize crystal structures and enhance the luminescence intensity of the activator ions. If the atom is too small, however, the



**Fig. 1** Crystal structure of  $Ba_9R_2Si_6O_{24}$  (R = Sc, Y and Lu) viewed perpendicular to the *b* axis showing the layer structure (a) and the *c* axis (b) and the coordinated environment of Ba(1) (blue balls), Ba(2) (pink balls), Ba(3) (gold balls) and R (green balls) with oxygen atoms (c).

cyan emission of  $Ce^{3+}$  will also disappear due to the extrication of  $Ce^{3+}$  from a strong crystal-field.<sup>48</sup> Therefore in this work the aim was to identify a suitable small and heavy atom which not only can form the rhombohedral structure but also can facilitate the  $Ce^{3+}$  ions settling in crystal sites where they experience a strong crystal field to retain and improve their cyan emission.

Cation substitutions have been shown to be an effective method to tune luminescence.53,54 Based on the results that both BSS and BYS crystallize into the same rhombohedral structure, we made the assumption that a solid solution should be formed in BRS ( $Ba_9R_2Si_6O_{24}$ , R = Sc and Y) as R changes from Sc to Y. If the assumption is correct then a linear dependence of the lattice constants and cell volumes on the Sc/Y contents should exist as anticipated from Vegard's law. Thus the ionic radius (r) values for the Sc/Y contents were fitted linearly using the lattice parameters in BSS47 and BYS.48 The corresponding equations of the lattice parameters as a function of r are presented in Fig. 2. It should be noted that the heaviest lanthanide ion  $Lu^{3+}$  is smaller than  $Y^{3+}$  but larger than  $Sc^{3+}$ . If Lu<sup>3+</sup> is incorporated into the solid solution successfully, it should experience a strong crystal field splitting due to its contact with the other atoms in the crystal structure. If a rhombohedral crystal structure also can be formed when R = Lu, the unit cell parameters can be calculated to be a = 9.989339 Å, c = 22.10995 Å and V = 1910.90579 Å<sup>3</sup> (dashed lines) according to the fitting function. Fortunately, we were able to synthesise a rhombohedral BLS with lattice parameters of a = 9.9905(06) Å, c = 22.1088(31) Å and V = 1911.04(7) Å<sup>3</sup> (magenta circles in Fig. 1), as reported previously.35 Clearly, the experimental results agree very well with the predicted values. As expected, the BLS:Ce<sup>3+</sup> also exhibits an enhanced cyan emission with an IQE up to 82%.<sup>35</sup>

In this work for the BLS: $xCe^{3+}$  (x = 0.01-0.15) phosphors, the Ce<sup>3+</sup>-doping does not change the rhombohedral structure; all the samples exhibit the single BSS phase (PDF No. 82-1119),<sup>47</sup> as shown in the XRD patterns in Fig. S1 (ESI†). To get more structural information, XRD Rietveld refinements for all the BLS: $xCe^{3+}$  samples were carried out by adopting the



**Fig. 2** Dependence of the lattice parameters (*a*, *c* and *V*) on the ionic radius (*r*) of *r* in the compounds  $Ba_9R_2Si_6O_{24}$  (R = Sc, Y and Lu). based on the linear relationship, fitting by the lattice parameters for R = Sc and Y (green and blue balls) in ref. 47 and 48, *a*, *c* and *V* for R = Lu are calculated to be 9.989339 Å, 22.10995 Å and 1910.90579 Å<sup>3</sup> (dash lines), respectively. these values are almost the same as those of the experimental results: *a* = 9.9905(06) Å, *c* = 22.1088(31) Å and *V* = 1911.04(7) Å<sup>3</sup> (magenta circles).

crystallographic data of BSS as the initial structural model. The refinement results and crystallographic data are summarized and listed in Table S1 (ESI<sup>†</sup>). In Fig. S2 (ESI<sup>†</sup>) an example for BLS:5%Ce<sup>3+</sup> is presented and the detailed lattice parameters are listed in Table S2 and S3 (ESI<sup>+</sup>). Rietveld refinements confirm that all the samples are in single phase and isostructural to the known crystal structure of BSS, and there is no evidence for the by-product Ba<sub>2</sub>SiO<sub>4</sub> which was easily observed in BYS.  $Ba_2SiO_4:Ce^{3+}$  has a low IQE (~50%) under 351 nm excitation, although there is no emission for Ba<sub>2</sub>SiO<sub>4</sub>:Ce<sup>3+</sup> under 400 nm excitation.<sup>48</sup> The thermal stability of Ba<sub>2</sub>SiO<sub>4</sub>:Ce<sup>3+</sup> also is not good.<sup>35,48</sup> Thus, Ba<sub>2</sub>SiO<sub>4</sub>:Ce<sup>3+</sup> will lower the luminescence properties of BYS:Ce<sup>3+</sup> or BLS:Ce<sup>3+</sup>. There is no Ba<sub>2</sub>SiO<sub>4</sub> in BLS:Ce<sup>3+</sup> which indicates the impact of  $Ba_2SiO_4:Ce^{3+}$  on the luminescence of BLS: $Ce^{3+}$  can be ignored. The lattice parameters of a, c and V summarized in Table S1 (ESI $\dagger$ ) increase with increasing x, due to the replacement of  $Lu^{3+}$  ( $r^{VI} = 0.861$  Å) by the larger Ce<sup>3+</sup> ( $r^{VI} = 1.01$  Å).<sup>55</sup> Furthermore, the lattice parameters almost change linearly with the x value,

as presented in Fig. S3 (ESI<sup>†</sup>). This indicates that a solid solution successfully forms in the BLS host lattice when Ce<sup>3+</sup> is incorporated over the concentration range studied (x = 0.01-0.15). In this work, all the samples were synthesized based on the substitution of Ce<sup>3+</sup> for Lu<sup>3+</sup> by charge balance. However, it does not follow that the Ce<sup>3+</sup> only occupies the Lu<sup>3+</sup> site. As illustrated in Fig. 1(c), there are three Ba<sup>2+</sup> sites, Ba(1), Ba(2) and Ba(3) coordinated to 12, 9 and 10 oxygen atoms, respectively, and one Lu<sup>3+</sup> site coordinated to 6 oxygen atoms. The Ba<sup>2+</sup> sites are large and by comparing the Ba<sup>2+</sup> radii ( $r^{IX} = 1.47$  Å,  $r^X = 1.52$  Å,  $r^{XII} = 1.61$  Å) with those of the Ce<sup>3+</sup> ions ( $r^{IX} = 1.196$  Å,  $r^X = 1.25$  Å,  $r^{XII} = 1.34$  Å) they appear to be large enough to easily accommodate the latter; although there is a difference in charge between Ba<sup>2+</sup> and Ce<sup>3+</sup>. Actually, as will be explained herein there is evidence that the Ce<sup>3+</sup> ions occupy both Ba<sup>2+</sup> and Lu<sup>3+</sup> sites simultaneously.

Fig. 3 presents the elemental mapping, TEM, HRTEM and FFT images of BLS:11%Ce<sup>3+</sup>. The mapping images indicate a homogeneous distribution of Ba, Lu, Si and O. The HRTEM image exhibits a clear lattice fringe with lattice interplanar spacings of 2.85 and 3.33 Å, corresponding to the (300) and (024) planes of BLS. The HRTEM and FFT images demonstrate that the as-prepared sample has a rhombohedral crystal structure like that of the illustrated structure of BRS (R = Sc, Y and Lu) in Fig. 1(b).

#### 3.2 Electronic band structures and optical band gap

The host lattice of a phosphor usually has a large bandgap to accommodate the energy levels of the luminescent ion activator. To ensure that the BLS host has a wide enough band gap to accommodate the Ce<sup>3+</sup> f-d transition, the electronic band structures of pure BLS were calculated by the DFT method using VASP. This is illustrated in Fig. 4(a), the top of the valence band (VB) is at the  $\Gamma$  point, and the bottom of the conduction band (CB) is within the *F*-*Z* region. The VB maximum and the CB minimum do not appear at the same *k*-point, indicating that the BLS host has an indirect band gap. The band gap value (*E*<sub>g</sub>) is computed to be 4.62 eV, implying that BLS could also be a good host lattice for accommodating both the ground and excited states of luminescent ions within its wide band gap. Assignments of the electronic band structure are performed on the basis of the calculated total



Fig. 3 Mapping, TEM, HRTEM and FFT images of BLS:11%Ce<sup>3+</sup>.



Fig. 4 Electronic band structure (a and c) and total and partial density of states (b and d) of the BLS and BYS host

and partial DOS (TDOS/PDOS) diagrams as given in Fig. 4(b). The valence band mainly consists of Ba-5p5d, Lu-4f5d, Si-3s3p and O-2s2p states, varying from about -11.2 eV to the Fermi level ( $E_f$ ). Only the isolated Ba-5p state dominates the valence band from -11.2 to -10 eV and has little interaction with the neighboring atoms. However, the Lu-4f, Si-3s3p and O-2p states dominate at the top of the valence band (-6.2 to 0 eV), and they are strongly hybridized indicating that a strong covalent bonding is present in Lu/Si-O interactions. These phenomena are very likely to be related to the layered structure of BLS, in which the [LuO<sub>6</sub>] octahedra are linked tight with the [SiO<sub>4</sub>] tetrahedra forming the rigid Lu-Si-O layers and in turn resulting in the large orbital hybridization of the Lu, Si and O atoms; while the Ba atoms mainly array in the interlayer gap in turn resulting in little covalent interaction with the neighboring atoms. The conduction band spans the energies between 4.6-8.2 eV, in which the Ba-5d, Lu-5d and O-2p states are dominant.

In Fig. 4(c), BYS shows a similar electronic band structure to that of BLS and has an indirect bandgap value of 4.74 eV. For both BLS and BYS, it can be seen from Fig. 4(b) and (d) that their Fermi levels are dominated by the O-2p state, and their conduction bands are mainly determined by Ba, O and Lu or Y atoms. Thus, the energy differences of the bandgap of BLS and

BYS mainly results from the differences between the  $Lu^{3+}$  and  $Y^{3+}$  ions. The Lu-5d state dominates the CB in BLS, and the Y-4d state dominates the CB in BYS. The Lu-5d state energy is lower than that of the Y-4d state energy, leading to the smaller bandgap of BLS (4.62 eV) than that found for BYS (4.74 eV).

The band gap of powder samples can also be determined by extrapolating the linear portion based on their diffuse reflection (DR) spectra. Commonly, three methods have been explored to do this: method one (M-1) is directly based on the measured diffuse reflectance (R) either in energy or wavelength;<sup>35,56</sup> method two (M-2) is acquired by converting the R spectrum into the Kubelka-Munk absorption function of  $F(R) = (1-R)^{2/(2R)}$ ;<sup>32,57</sup> method three (M-3) based on changing the *F*(*R*) function into the expression of  $(h\nu F(R))^n = A(h\nu - E_g)$ , n = 2 and 1/2 for a direct and an indirect band gap, respectively, was proposed by Tauc *et al.*<sup>58–60</sup> The  $E_g$  values for the BLS host using M-1, M-2 and M-3 are shown in Fig. S4 (ESI<sup>†</sup>). These three methods are widely used to estimate the optical band gap, but unfortunately different methods will give rise to different results. For M-3,  $E_g$  = 3.97 and 3.05 eV for the direct and the indirect band gap; for M-2,  $E_{\rm g}$  = 3.52 and 3.43 eV onto the wavelength and energy. These  $E_g$  values are much smaller than the calculated value of 4.62 eV by the DFT method. It is well

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known that the band gap is always underestimated by using the GGA in the DFT calculations.<sup>61,62</sup> Thus, we believe that M-2 and M-3 are not suitable for a phosphor material manifesting a large band gap. In fact, M-3 is commonly used for semiconductor materials. The  $E_{\rm g}$  values of M-1 using wavelength or energy are 7.99 and 5.51 eV, these also greatly differ from each other, although they are larger than the those of the DFT calculation. According to the R and F(R) spectra, the BLS host material has an absorption starting from about 400 nm and reaches a peak around 240 nm. Therefore, we believe that the estimated value from M-2 is only the absorption edge,<sup>32,57</sup> while the 5.51 eV value from M-1 using energy is a reasonable optical band gap. That is, M-1 using energy is more reliable than M-2 and M-3 to estimate the optical band gap for phosphor materials. This also can be seen in estimating the BYS optical band gap (Fig. S5, ESI<sup>†</sup>). As presented in Fig. S5(a) (ESI<sup>†</sup>), the value  $E_{\rm g}$  = 8.86 eV obtained by using M-1 with wavelength seems too large to be reasonable. However using M-1 with energy produces a reasonable optical band gap of  $E_g$  = 5.98 eV that is nearly consistent with the 5.85 eV for BYS reported by Sangmoon Park et al.<sup>63</sup> The optical band gap of BLS is smaller than that of BYS, which is a similar result to that from DFT calculations as well.

#### 3.3 Luminescence properties

The DR spectra in Fig. 5(a) indicate that  $Ce^{3+}$  exhibits intense absorptions around 330 and 400 nm in BLS: $xCe^{3+}$  (x = 0.01-0.15). Correspondingly, the PLE spectra in Fig. 5(b) and (c) manifest main excitation peaks at 400 and 330 nm, respectively. The excitation band from 350 to 450 nm peaking at 400 nm, (which matches well with the emission wavelength of the NUV LED chips), results from the presence of  $Ce^{3+}$  on the Lu<sup>3+</sup> site (previously named the  $Ce^{3+}$ -1 center).<sup>35</sup> The relative integrated  $Ce^{3+}$ -1 emission intensities (under 400 nm excitation) are presented in the inset of Fig. 5(a), in which an optimal Ce<sup>3+</sup> concentration of x = 0.11 is observed. The normalized emission spectra from Ce<sup>3+</sup>-1 manifest a consistent profile for various Ce<sup>3+</sup> concentrations; the PL spectrum ( $\lambda_{ex} = 400$  nm) for the optimum concentration is given in Fig. 5(b). The PL band in Fig. 5(b) exhibits an emission peak at 490 nm with a large FWHM of 118 nm (4519 cm<sup>-1</sup>), this band arises from the transitions of Ce<sup>3+</sup> from the 5d excited state to the <sup>2</sup>F<sub>5/2</sub> and <sup>2</sup>F<sub>7/2</sub> ground states. The band can be deconvoluted into two Gaussian bands (dashed lines) centered at 20 992 cm<sup>-1</sup> (476.37 nm) and 19 017 cm<sup>-1</sup> (525.85 nm) with an energy difference of 1975 cm<sup>-1</sup>, which is close to the energy separation between the <sup>2</sup>F<sub>5/2</sub> and <sup>2</sup>F<sub>7/2</sub> levels.

Compared to the Ce<sup>3+</sup>-1 excitation ( $\lambda_{max}$  = 394 nm) and emission ( $\lambda_{max}$  = 480 nm) in BYS:Ce<sup>3+,48</sup> a red-shifted excitation  $(\lambda_{\text{max}} = 400 \text{ nm})$  and emission  $(\lambda_{\text{ex}} = 490 \text{ nm})$  are present in BLS:Ce<sup>3+</sup>. It is well established that the lowest 5d energy level of Ce<sup>3+</sup> is strongly influenced by crystal-field splitting. The reason for the observed red shift is attributed to an increased crystal-field splitting. The crystal-field splitting,  $D_q$ , is expressed as  $D_q = Ze^2 r^4 / 6R^5$ , where Z is the anionic charge, e is the charge of the electron, r is the radius of the 5d-wavefunction, and R is the bond length.<sup>64</sup> The R values of the Lu–O bonds  $(2.162-2.223 \text{ Å})^{35}$  in BLS are shorter than those of Y–O (2.190– 2.255 Å)<sup>48</sup> in BYS due to the smaller size of the Lu<sup>3+</sup> cations. It is important to realise that r is directly related to the distortion of the [LuO<sub>6</sub>] or [YO<sub>6</sub>] polyhedron. Based on the Lu-O and Y-O bond lengths, the distortion for the  $[LuO_6]$  octahedron (2.82%) is larger than that for the  $[YO_6]$  octahedron (1.60%), thus the r value is increased in BLS. Both the increased r and the decreased R enhance the  $D_q$  value in BLS; this reduces the energy of the lowest 5d energy level giving rise to the red-shifted luminescence observed in BLS:Ce<sup>3+</sup>. Also arising from the



**Fig. 5** DR, PL and PLE spectra of BLS:  $xCe^{3+}$  (x = 0.01-0.15). The DR intensities in (a) are normalized. The PL spectrum ( $\lambda_{ex} = 400$  nm) in (b) is that for the sample for x = 0.11 and the relative PL intensities with different  $Ce^{3+}$  concentrations are illustrated in the inset figure in (a). The PLE spectra ( $\lambda_{em} = 422$  nm) in (c) are normalized and the inset figure exhibits the peak change with x. Results in (a), (b) and (c) were measured at RT. (d) PL and PLE spectra of BLS:11%Ce<sup>3+</sup> at various excitation and emission wavelengths measured at 77 K.

larger distortion of [LuO<sub>6</sub>] than that of [YO<sub>6</sub>], BLS:Ce<sup>3+</sup> manifests a broader emission (FWHM  $\approx$  120 nm) than that of BYS:Ce<sup>3+</sup> (FWHM  $\approx$  110 nm). The red-shifted broader emission could play an important role in enriching the red component and enhancing the color rendering when BLS:Ce<sup>3+</sup> is used in NUV-based WLEDs.

The excitation bands from 200 to 350 nm (with a main peak at 330 nm) presented in Fig. 5(b) and (c) are attributed to the presence of Ce<sup>3+</sup> on the Ba<sup>2+</sup> sites (previously named the Ce<sup>3+</sup>-2 center).<sup>35,65</sup> These bands are located in nearly the same energy range in both BSS:Ce<sup>3+50-52</sup> and BYS:Ce<sup>3+,48</sup> and can be deconvoluted into three peaks at low temperature. Their most likely origin is from the Ce<sup>3+</sup> occupation in the three independent Ba<sup>2+</sup> sites in the structure. In the nominal composition of BLS: $Ce^{3+}$  where  $Ce^{3+}$  substitutes only for  $Lu^{3+}$  (in the formula), the luminescent centers of Ce<sup>3+</sup>-1 and Ce<sup>3+</sup>-2 appear at the same time, indicating that the activator Ce<sup>3+</sup> cations locate at the Ba<sup>2+</sup> and Lu<sup>3+</sup> sites simultaneously. A further observation is apparent in the PLE spectra in Fig. 5(b) (monitored at 490 nm) regarding the Ce<sup>3+</sup>-1 centers, it is notable that the Ce<sup>3+</sup>-2 excitation band that is apparent at very low concentrations of  $Ce^{3+}$  (for x = 0.01 and 0.03) does not grow relative to the  $Ce^{3+}$ -1 excitation band as the Ce3+ content exceeds 0.03; in fact the Ce<sup>3+</sup>-1 excitation band begins to dominate the emission spectra. These phenomena reflect the fact that Ce<sup>3+</sup> cations occupy the Ba<sup>2+</sup> sites firstly (at low concentrations) but the lattice does not facilitate further occupation of these sites at higher concentrations where the site preferred is that of the Lu<sup>3+</sup> cations. This probably means that the local charge imbalance caused by the presence of Ce<sup>3+</sup> cations on the Ba<sup>2+</sup> sites cannot be tolerated by the lattice at higher Ce<sup>3+</sup> concentrations. Based on the evidence from both the XRD data and the luminescence properties, therefore, it can be concluded that Ce<sup>3+</sup> cations can occupy the Ba<sup>2+</sup> and the Lu<sup>3+</sup> sites simultaneously, and the Ba<sup>2+</sup> site will be the preference at a low Ce<sup>3+</sup> content. After reaching saturation tolerance in the Ba<sup>2+</sup> sites, the Lu<sup>3+</sup> site is preferred with increasing Ce<sup>3+</sup> cation concentration.

Monitoring the Ce<sup>3+</sup>-2 emissions, in the normalized PLE spectra ( $\lambda_{em}$  = 422 nm) and the peak positions shown in Fig. 5(c), the PLE peak red-shifts slightly from 328 nm for x = 0.01 to 334 nm for x = 0.15. A similar red-shifting trend was also observed in BSS:Ce<sup>3+</sup> with increasing Ce<sup>3+</sup> content and was ascribed as arising from the reabsorption between the different Ce<sup>3+</sup> cations on the Ba<sup>2+</sup> sites, rather than to the lattice expansion caused by the larger Ce<sup>3+</sup> cations (the latter would lead to a blue-shifted emission).<sup>50</sup> In BLS:Ce<sup>3+</sup>, the reabsorption should also involve the Ce<sup>3+</sup> luminescent centers in both the  $Ba^{2+}$  and  $Lu^{3+}$  sites, arising from the overlap between the  $Ce^{3+}-2$ emission and the Ce<sup>3+</sup>-1 excitation; this is evidenced by the PL  $(\lambda_{ex}$  = 330 nm) in Fig. 5(c) and the PLE  $(\lambda_{em}$  = 490 nm) in Fig. 5(b). This then provides a condition for energy transfers (ETs) from the  $Ce^{3+}-2$  centers to the  $Ce^{3+}-1$  centers. Therefore, under the Ce<sup>3+</sup>-2 excitation, both the Ce<sup>3+</sup>-1 and Ce<sup>3+</sup>-2 emissions are observed, leading to a broad band emission consisting of multiple peaks as the PL spectra ( $\lambda_{ex}$  = 330 nm) show in Fig. 5(c).

To understand the ET processes, the PL and PLE spectra at various wavelengths for BLS:11%Ce<sup>3+</sup> at a low temperature (77 K) were recorded. As shown in Fig. 5(d), three excitation peaks around 280, 330 and 360 nm resulting from the Ce<sup>3+</sup> cations in the three independent Ba<sup>2+</sup> sites are clearly identified at 77 K. When the excitation wavelength increases from 280 to 360 nm (only the  $Ce^{3+}-2$  centers are excited), the  $Ce^{3+}-1$ emissions are apparent. When only the Ce<sup>3+</sup>-1 emission wavelength (610 nm) is monitored, the Ce<sup>3+</sup>-2 center excitation is still obvious. These findings directly demonstrate the ETs from the Ce<sup>3+</sup>-2 center to the Ce<sup>3+</sup>-1 center. It is also noted that the Ce<sup>3+</sup>-1 emission peak is greatly red-shifted by 28 nm, from 490 nm (at RT) to 518 nm (at 77 K), due to the lattice contraction at low temperature (which leads to a stronger crystal-field splitting and the observed red shift). The FWHM of the Ce<sup>3+</sup>-1 emission is also broadened from 118 nm (at RT) to 132 nm (at 77 K). This broad emission can be deconvoluted into two Gaussian bands centered at 19898  $\text{cm}^{-1}$  (502.56 nm) and 17865 cm<sup>-1</sup> (559.76 nm) with an energy difference of 2033  $\text{cm}^{-1}$ . This value is close to the energy separation between the  ${}^{2}F_{5/2}$  and  ${}^{2}F_{7/2}$  levels of Ce<sup>3+</sup>.

The ET processes can also be directly observed from the fluorescence decay curves. Thus in Fig. 6(a)-(f) the Ce<sup>3+</sup> fluorescence decays for BLS:11%Ce<sup>3+</sup> at 77 K are presented. As seen in Fig. 6(a)-(f), when the Ce<sup>3+</sup>-2 center (at 330 nm) is excited, the decays of both Ce<sup>3+</sup>-2 (emission at 360, 380 and 420 nm) and  $Ce^{3+}$ -1 (emission at 610 nm) deviate from a single-exponential model, but can be well fitted by a double-exponential function. The fitting results are given in Fig. 6(a)-(d). For the Ce<sup>3+</sup>-2 decays at 360, 380 and 420 nm, slow components with  $\tau_2 = 24.1 - 37.0$  ns are observed, these are in the lifetime range expected when Ce<sup>3+</sup> gives rise to short wavelength emissions (usually from UV to blue regions). For the  $Ce^{3+}$ -1 decay at 610 nm, a slow component with  $\tau_2 = 60.6$  ns is observed; this is the common lifetime of Ce<sup>3+</sup> at long wavelength emissions (usually from green to red regions). Combining the normalized decay curves in Fig. 6(e) and (f), it is obvious that Ce<sup>3+</sup>-2 manifests a fast decay process while Ce3+-1 shows a slow build-up process that takes place over a time of 100 ns. These results provide direct evidence for the ET from the Ce<sup>3+</sup>-2 center to the Ce<sup>3+</sup>-1 center. The average lifetime ( $\tau_{ave}$ ) is calculated by integrating the normalized decay curves, and the results are shown in Fig. 6(e). It should be noted that the build-up of intensity of Ce<sup>3+</sup>-1 is not from zero time, indicating that the Ce<sup>3+</sup>-1 decay at 610 nm does not totally derive from the ET from  $Ce^{3+}-2$ . Thus it is apparent that the  $Ce^{3+}-1$  center is also partially excited directly when the Ce<sup>3+</sup>-2 center is excited. This, however, cannot be distinguished from the PLE spectra due to the influence of the Ce<sup>3+</sup>-2 center. For the ET process, the critical distance,  $R_c$ , can be estimated using the following equation,

$$R_{\rm c} = 2 \left[ \frac{3V}{4\pi x_{\rm c} N} \right]^{\frac{1}{3}} \tag{1}$$

where *V* is the unit cell volume,  $x_c$  is the critical Ce<sup>3+</sup> concentration, *N* is the number of lattice sites in the unit cell that the





Fig. 6 (a–f) Fluorescence decay curves and residuals of fit to a double-exponential function of BLS:11%Ce<sup>3+</sup> obtained at 77 K using excitation at 330 nm, monitoring at 360, 380, 420 and 610 nm. Residual = experiment – theory.

activator ions can occupy.<sup>66</sup> Based on the results above, the Ce<sup>3+</sup> quenching occurs at x = 0.11. So the critical Ce<sup>3+</sup> concentration in respect to Lu<sup>3+</sup> is about 5.5 mol%. The number of Ce<sup>3+</sup> cations occupying the unit cell has a range between N = 6 and 33 depending on the replacement of Ce<sup>3+</sup> on the Lu<sup>3+</sup> and Ba<sup>2+</sup> sites. V = 1912.797 Å<sup>3</sup> as listed in Table S1. Using these values, the quenching distance can be calculated to be in the range 12.6 to 22.3 Å, which is much larger than that in BLS:Ce<sup>3+</sup> with an  $R_c$  of 7.1 to 12.7 Å.<sup>48</sup>

#### 3.4 Greatly enhanced QEs and thermal stability properties

The IQE ( $\eta_{int}$ ) and external QE (EQE,  $\eta_{ext}$ ) are direct measures to evaluate the effectiveness of a phosphor.<sup>67</sup> Their relationship can be expressed as

$$\eta_{\rm ext} = \frac{N_{\rm em}}{N_{\rm inc}} \quad \eta_{\rm int} = \frac{N_{\rm em}}{N_{\rm abs}} \quad \eta_{\rm ext} = A\eta_{\rm int} \tag{2}$$

where  $N_{inc}$ ,  $N_{abs}$  and  $N_{em}$  are the number of incident, absorbed and emitted photons, respectively. *A* is the absorbance.

Compared with our previous results ( $\eta_{int} = 82\%$ ,  $\eta_{ext} = 49\%$ ),<sup>35</sup> the IQE and EQE of the optimal sample BLS:11%Ce<sup>3+</sup> are enhanced to a value as high as 90.9% ( $\pm 0.5\%$ ) and 59.2%  $(\pm 0.5\%)$ , respectively, under 400 nm excitation, as presented in Fig. S7(b) (ESI<sup>†</sup>) and Fig. 7(b). Usually, the working temperature of LED chips is higher than 100 °C and even reaches 150 °C for high-power LED chips. This working environment will certainly cause the thermal quenching of the phosphor luminescence and may even degrade the phosphors. Thus, for the phosphors to be practically used they must manifest a small thermal quenching and degradation to maintain the long lifetime required for WLED devices. The temperature-dependent and time-dependent luminescence of BLS:11%Ce<sup>3+</sup> were therefore measured. As Fig. 7(a) shows, at 150 °C, there is only 3% and 6% reduction for IQE and EQE, respectively. The thermal quenching behavior can be fitted by the Arrhenius equation  $I_{\rm T} = I_0/[1 + A \exp(-\Delta E/kT)]$ , where  $I_0$  and  $I_{\rm T}$  are the QEs at absolute zero temperature and temperatures in the range 23–300 °C, A is a constant, k is the Boltzmann constant and

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Fig. 7 Temperature-dependent normalized IQEs, EQEs and absorbance. (b) EQEs and normalized EQEs dependent on temperature. (c) CIE chromaticity coordinates *versus* temperatures. (d) Normalized IQEs, EQEs and PL spectra dependent on aging times at 85 °C/85% RH. All of these experiments and measurements were based on the sample of BLS:11%Ce<sup>3+</sup>.

 $\Delta E$  is the activation energy for thermal quenching.<sup>68</sup> The small thermal quenching of BLS:11%Ce<sup>3+</sup> is attributed to the high thermal barrier energy ( $\Delta E = 0.454$  and 0.385 eV for IQE and EQE, respectively, shown in Fig. S6 (ESI<sup>†</sup>)) that arises from the rigid crystal structure of the BLS host.<sup>35</sup>

It is worth comparing the properties of the BLS:11%Ce<sup>3+</sup> phosphor to existing blue, green and cyan phosphors, as listed in Table 1. BAM:Eu<sup>2+</sup> is a typical blue-emitting phosphor with a

high IQE of 92.4%,<sup>19,20</sup> however its maximum excitation wavelength is at 320 nm and it falls of dramatically at 400 nm. A commercial BAM: $Eu^{2+}$  phosphor sample was measured in this work at the same excitation wavelength (400 nm) as BLS:11%Ce<sup>3+</sup>, its IQE remained at 90.4%, but its absorption was only 39.6% giving rise to a low EQE of 35.7%.<sup>21</sup> For another typical blue-emitting phosphor family (Sr, Ca, Ba)<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>Cl: $Eu^{2+}$ , their excitation peaks are around 270 nm, and the IQE values are

Table 1Comparation of luminescence properties of BLS:11%Ce<sup>3+</sup> and some existing blue, green and cyan phosphors.  $I_{150 \circ C}$  denotes the luminescenceintensity or QE at 150 °C relative to the value at RT

Color	Phosphor	Excitation peak (nm)	Emission peak (nm)	IQE (%)	EQE (%)	I <sub>150</sub> °C (%)	Ref.
Blue	BaMgAl <sub>10</sub> O <sub>17</sub> :Eu <sup>2+</sup>	320	460	92.4	_	88.31	19–21 and 26
	0 10 11			90.4 at 400 nm	35.7 at 400 nm		
	$Ca_2Ba_3(PO_4)Cl:Eu^{2+}$	274	490	72 at 274 nm	_	_	23
				61 at 365 nm			
	(Sr <sub>3</sub> ,Ca,Ba)(PO <sub>4</sub> ) <sub>3</sub> Cl:Eu <sup>2+</sup>	270	450	85 at 365 nm	_	_	24
	$Al_{1-x}Si_{x}C_{x}N_{1-x}:Eu^{2+}$	290	465-471	81.4-81.99 at 365 nm	54.3-61 at 365 nm	90	25
					30 at 400 nm		
	$KMg_4(PO_4)_3:Eu^{2+}$	300	450	50.44 at 365 nm	_	90.77	26
	AlOH	379 and 440	388-513	65 at 400 nm	—	80	27
Green	β-SiAlON:Eu <sup>2+</sup>	303 and 405	530	70 at 303 nm	61 at 303 nm	_	28
				54 at 405 nm	41 at 405 nm		
	Ba <sub>2</sub> SiO <sub>4</sub> :Eu <sup>2+</sup>	395	511	89.3 at 400 nm	74.8 at 400 nm	45	15 and 29
	Ca <sub>3</sub> Si <sub>2</sub> O <sub>4</sub> N <sub>2</sub> :Eu <sup>2+</sup>	289-405	510-550	23.8 at 400 nm	17.1 at 400 nm	70	29
Cyan	BaLa <sub>2</sub> Si <sub>2</sub> S <sub>8</sub> :Ce <sup>3+</sup>	365 and 410	470	36.07 at 410 nm	_	20	32
	$Y_4Si_2O_7N_2:Ce^{3+}$	296-395	507	47 at unknown	_	25	33
	$Ca_6BaP_4O_{17}:Ce^{3+},Si^{4+}$	370	477	70 at 400 nm	_	80	34
	BLS:Ce <sup>3+</sup>	400	490	90.9 at 400 nm	59.2 at 400 nm	94-97	This work

around 61-85% under 365 nm excitation.<sup>22-24</sup> In 2015, Wang et al.<sup>25</sup> reported a thermally stable nitride phosphor (  $\sim$  10% degradation at 150 °C), Al<sub>1-x</sub>Si<sub>x</sub>C<sub>x</sub>N<sub>1-x</sub>:Eu<sup>2+</sup>, which exhibits a blue emission peaking around 465-471 nm and a excitation peak at 290 nm, its IQE is 81.4-81.99% and EQE is 54.3-61% under 365 nm excitation, however, its EQE is only around 30% under 400 nm excitation. The typical green phosphor Ba<sub>2</sub>SiO<sub>4</sub>:Eu<sup>2+</sup> has a suitable excitation wavelength for NUV-LED chips, and its IQE and EQE are as high as 89.3% and 74.8% at RT, respectively, under 400 nm excitation.<sup>15,29</sup> Unfortunately, it has a strong thermal quenching ability and not more than 50% of the RT EQE value is maintained at 150 °C. The decrease is  $\sim 30\%$ for the  $Ca_{3}Si_{2}O_{4}N_{2}{:}Eu^{2+}$  green phosphor at 150  $^{\circ}C,$  but its IQE and EQE are only 23.8% and 17.1% at RT, respectively, under 400 nm excitation.<sup>29</sup> For cyan-emitting phosphors, BaLa<sub>2</sub>Si<sub>2</sub>S<sub>8</sub>:Ce<sup>3+</sup> shows an excitation peak at 410 nm but has a low IOE of 36.07% under 410 nm excitation and in addition suffers from extreme thermal quenching of 80% at 150 °C.<sup>32</sup> Y<sub>4</sub>Si<sub>2</sub>O<sub>7</sub>N<sub>2</sub>:Ce<sup>3+</sup> has an excitation peak at 395 nm and an emission peak at 507 nm with a FWHM nearly of 150 nm, but its IQE is only about 47% and it manifests a thermal quenching of 25% at 150 °C.<sup>33</sup> In 2015, Komuro et al.<sup>34</sup> discovered the Ca<sub>6</sub>BaP<sub>4</sub>O<sub>17</sub>:Ce<sup>3+</sup>,Si<sup>4+</sup> cyan-emitting phosphor, which has a relatively small quenching of 20% at 150 °C, and its IQE reaches up to  $\sim$ 70% under 400 nm excitation. On the basis of QE and thermal stability, BLS:11%Ce3+ exhibits much better luminescence properties than most blue, green and cyan phosphors for NUV-WLEDs.<sup>15,17-34</sup>

As noted above for BLS:11%Ce<sup>3+</sup> the EQE exhibits a stronger quenching (6%) than the IQE (3%), and the absorbance also decreases when the temperatures rise. According to eqn (2), the thermal degradation of absorbance is most likely to be responsible for the quenching difference between IQE and EQE. The thermal quenching of luminescence is usually attributed to a thermal activation process in which the excited electron energy is released preferentially through heat dissipation by phonons rather than radiation by photons. Evidence reveals that the thermal degradation of absorbance also makes a contribution to the luminescence quenching.

In Fig. 7(b) the temperature-dependent EQE of BLS:11%Ce<sup>3+</sup> in a thermal cyclic process of heating and cooling from 23 to 300 °C is presented. The EQE decreases from 59.2% to 34.1% as temperature increases from 23 to 300 °C, while the EQE increases from 32.1% to 52.6% as the temperature cools from 300 to 23 °C. As the EOE values are normalized, based on 59.2% and 52.6% as a maximum for the heating and cooling processes, respectively, the curves manifest a similar dependence on temperature. Although it appears that from the normalized EQE values there is full recovery temperature cycling, this is not the case as the real EOE values (from 59.2% to 52.6%) indicate there is degeneration due to the temperature changes. This is also evidenced in the IOE values (from 90.9% to 81.9%) and indeed in the absorbance values (from 65.2% to 64.2%) (Fig. S7, ESI<sup>†</sup>). This means that heating to 300 °C does really degrade the luminescence intensity of BLS:11%Ce<sup>3+</sup> but heating to lower temperatures, *i.e.*, 150 °C, is much less destructive. However, the temperature-dependent CIE coordinates are almost invariant after the heating and cooling process, as shown in Fig. 7(c), demonstrating a stable color property. Furthermore, the stability evaluation of the powder BLS:11%Ce<sup>3+</sup> was carried out in a test chamber under a controlled temperature of 85 °C and a relative humidity of 85% (85 °C/85%RH), and only a minor degradation of about 6% and 10% for IQE and EQE, respectively, was observed after aging for more than 1600 hours (more than two months), as shown in Fig. 7(d). This property is much better than that of some used phosphors (the aluminum hydroxide blue phosphor decreases by 10% after aging for one month at 65 °C/85%,<sup>27</sup>  $(Ba,Sr)_2SiO_4:Eu^{2+}$  decreases more than 60% after aging for 500 h at 85 °C/85%RH<sup>14</sup>), indicating that the BLS:11%Ce<sup>3+</sup> phosphor has environmental stability. The normalized PL spectra at different aging times remain consistent, as per the inset shown in Fig. 7(d), which further demonstrates the stable emission color property.



Fig. 8 Emission spectrum, optical properties and fabricated NUV-pumped WLED using the cyan-emitting BLS:11%Ce<sup>3+</sup> phosphor and a commercial CaAlSiN3:Eu<sup>2+</sup> red phosphor.

Table 2 Optical properties of fabricated NUV-pumped WLED compared with results reported previously

Year	Phosphor	CIE $(x, y)$	CCT (K)	R <sub>a</sub>	Luminous efficiency (lm $W^{-1}$ )	Ref.
2015	Blue/green/red	0.4357, 0.4035	3015	90.1	7.16	25
2011	Blue/green/red	0.322, 0.330	6209	88.3	20.1	29
2016	Blue/green/red	0.337, 0.352	5301	94.3	23.5	27
2017	Cyan/red	0.3496, 0.3730	4913	90.6	32.2	This work

#### 3.5 Performance on NUV-driven WLED

To evaluate the performance of the BLS:11%Ce<sup>3+</sup> phosphor, a WLED consisting of a NUV-LED chip with a emission peak wavelength of about 395 nm and coupled only with the commercial CaAlSiN<sub>3</sub>:Eu<sup>2+</sup> red phosphor was fabricated. The emission spectrum, optical properties and the fabricated WLED are shown in Fig. 8. The WLED manifests white light with a CCT of 4913 K and CIE color coordinates of (x, y) = (0.3496, 0.3730) at an operating current of 20 mA. The color rendering properties from R1 to R14 are also listed, these give rise to a high average  $R_{\rm a}$  of 90.6 with a high R9 of 69.5. This demonstrates that only using the single cyan-emitting phosphor BLS:Ce<sup>3+</sup>, instead of a mixture of blue and green phosphors can lead to excellent color rendering properties arising from its broad band emission. Moreover, the luminous efficiency is up to  $32.2 \text{ lm W}^{-1}$ , which is the highest value for NUV-pumped WLEDs employing blue/green/red phosphors or a single cyan phosphor so far reported,<sup>25,27,29</sup> as listed in Table 2. These results validate the promising applications of the cyan-emitting BLS:Ce<sup>3+</sup> phosphor in future NUV-driven WLEDs.

### 4. Conclusion

In summary, a cyan-emitting phosphor for NUV-LED chips, BLS:Ce<sup>3+</sup> which is based on a novel host crystal that has a layered rhombohedral structure has been developed. BLS:Ce<sup>3+</sup> exhibits a broad emission band covering the blue and green light regions of the visible spectrum, with an excellent IQE of more than 90% and excellent thermal stability. Instead of using both blue and green phosphors, the use of only BLS:Ce<sup>3+</sup> in conjunction with a NUV-LED chip facilitated the fabrication of a WLED suitable for general illumination with adequate color rendering properties ( $R_a = 90.6$ ) and a high luminous efficiency (32.2 lm W<sup>-1</sup>). Based on first-principle calculations and its optical spectrum, a reliable method to estimate the bandgap value of phosphor materials that always have larger band gaps is also presented. This is achieved by extrapolating the linear portion of the diffuse reflection spectra against the energy.

## Conflicts of interest

There are no conflicts to declare.

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