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# Luminescence properties and site occupancy of Ce<sup>3+</sup> in Ba<sub>2</sub>SiO<sub>4</sub>: a combined experimental and *ab initio* study†

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Photoluminescence properties of Ba<sub>2-2x</sub>Ce<sub>x</sub>Na<sub>x</sub>SiO<sub>4</sub> ( $x = 0.0005$ ) prepared by a solid-state reaction method are first studied with excitation energies in the vacuum-ultraviolet (VUV) to ultraviolet (UV) range at low temperature. Five bands are observed in the excitation spectrum of Ce<sup>3+</sup> 5d → 4f emission at 26.5 K. The highest energy band is attributed to the host excitonic absorption, from which the band gap energy of the host is estimated to be around 7.36 eV. The four lower energy bands are assigned to the 4f → 5d transitions of Ce<sup>3+</sup> located at one of the two types of Ba sites in Ba<sub>2</sub>SiO<sub>4</sub>, based on a comparison of excitation spectra at different monitoring wavelengths. Under UV excitation, the material exhibits bright luminescence at 350–450 nm, with a fast decay time (~26 ns at 4 K) and a high thermal quenching temperature (>500 K). In view of this, X-ray excited luminescence measurements are then conducted, and the results suggest a potential application of Ba<sub>2</sub>SiO<sub>4</sub>:Ce<sup>3+</sup> as scintillation phosphors. Hybrid density functional theory (DFT) calculations within the supercell model are carried out to optimize the local structures of Ce<sup>3+</sup> at the two Ba sites in Ba<sub>2</sub>SiO<sub>4</sub>, on which wave function-based *ab initio* embedded cluster calculations are performed to derive the 4f<sup>1</sup> and 5d<sup>1</sup> energy levels of Ce<sup>3+</sup>. On the basis of the calculated DFT total energies and the comparison between experimental and calculated 4f → 5d transition energies, we find that the luminescence originates predominantly from Ce<sup>3+</sup> occupying nine-coordinated Ba2 sites. Furthermore, electronic properties of Ce<sup>3+</sup> in Ba<sub>2</sub>SiO<sub>4</sub> are evaluated to provide an understanding of the high thermal stability of the 5d luminescence at the level of electronic structures.

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## 1. Introduction

Silicate compounds have been considered as suitable hosts of lanthanide ions for applications as luminescent materials due to their good chemical stability, low manufacturing cost, and environment-friendly characteristics.<sup>1</sup> Recently, alkaline earth orthosilicate phosphors, M<sub>2</sub>SiO<sub>4</sub>:Ce<sup>3+</sup>, Eu<sup>2+</sup> (M = Ca, Sr, Ba) have received renewed interest due to their potential use as phosphors in white light-emitting diodes (LEDs),<sup>2–5</sup> although they were first reported more than four decades ago.<sup>6,7</sup> A significant feature of this class of phosphors is the ease of

tuning the emission wavelength by changing the composition of M cations or by manipulating the crystalline polymorphism. For instance, the emission color of Sr<sub>x</sub>Ba<sub>2-x</sub>SiO<sub>4</sub>:Eu<sup>2+</sup> can be varied from green for Ba<sub>2</sub>SiO<sub>4</sub>:Eu<sup>2+</sup> to yellow for Sr<sub>2</sub>SiO<sub>4</sub>:Eu<sup>2+</sup>,<sup>8</sup> and Ca<sub>2</sub>SiO<sub>4</sub>:Ce<sup>3+</sup> exhibited yellow emission in the γ-phase and light-blue emission in the β-phase.<sup>9</sup> The light emission originates from spin- and parity-allowed 5d → 4f transition of Eu<sup>2+</sup> or Ce<sup>3+</sup>, and the transition energy depends strongly on the geometric structure of the local environment due to the large crystal-field interaction of the 5d electron with its surroundings.<sup>10</sup>

Among the alkaline earth orthosilicates, Ba<sub>2</sub>SiO<sub>4</sub> stabilizes only in an orthorhombic structure with the space group *Pmcn* (no. 62), having two crystallographically distinct Ba sites (Ba1 and Ba2 sites) of C<sub>s</sub> symmetry (Fig. 1a).<sup>11</sup> Within a distance of 3.3 angstrom, the Ba1 and Ba2 sites are coordinated by ten and nine oxygen atoms, respectively. Activated by Ce<sup>3+</sup>, the material displays intense emission at around 384 nm under UV excitations,<sup>7</sup> but the location of Ce<sup>3+</sup> on the Ba1 or Ba2 site is not yet clear. When Ca<sub>2</sub>SiO<sub>4</sub> was added to Ba<sub>2</sub>SiO<sub>4</sub> *via* solid solution, the emission band shifted to longer wavelengths, at around 400 nm for Ba<sub>1.2</sub>Ca<sub>0.8</sub>SiO<sub>4</sub>:Ce<sup>3+</sup> with a high thermal quenching

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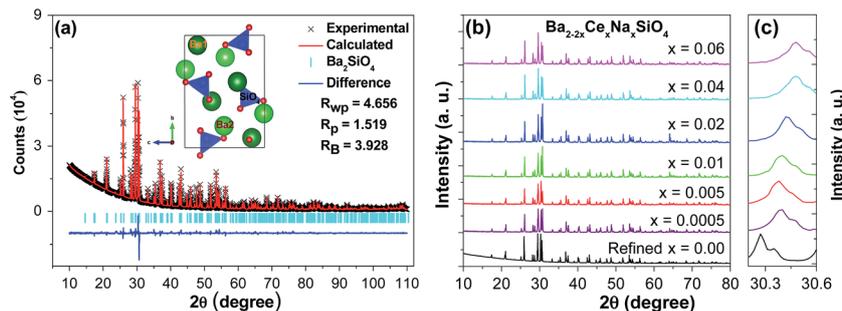


Fig. 1 (a) Rietveld refinement for the powder XRD pattern of the  $\text{Ba}_2\text{SiO}_4$  host and a depiction of the unit cell structure in the inset. (b) The XRD patterns and (c) diffraction peaks corresponding to (130) crystallographic planes of samples  $\text{Ba}_{2-2x}\text{Ce}_x\text{Na}_x\text{SiO}_4$  ( $x = 0.0005\text{--}0.06$ ). The refined XRD pattern for  $\text{Ba}_2\text{SiO}_4$  ( $x = 0.00$ ) is also shown as a reference.

temperature of 225 °C.<sup>12</sup> It is noted that, although photoluminescence properties of  $\text{Ca}_2\text{SiO}_4\text{:Ce}^{3+}$  have been investigated in relation with the local structure of  $\text{Ce}^{3+}$ ,<sup>13</sup> similar studies on the end member  $\text{Ba}_2\text{SiO}_4\text{:Ce}^{3+}$  are still lack. Such basic information is important in tailoring  $\text{Ba}_2\text{SiO}_4\text{:Ce}^{3+}$ -containing phosphors with desired properties.

In the present work, we extend previous measurements of emission and excitation spectra of Ce-doped  $\text{Ba}_2\text{SiO}_4$  by using VUV-UV excitations with synchrotron radiation at low temperatures, and then investigate luminescence properties of the compound under X-ray excitation. Hybrid DFT calculations within the supercell model are performed to optimize the local structures of  $\text{Ce}^{3+}$  located on the Ba1 and Ba2 sites, based on which wave function-based *ab initio* calculations within the embedded cluster model are carried out to derive the  $4f^1$  and  $5d^1$  energy levels of  $\text{Ce}^{3+}$ . By comparing the DFT total energies for the  $\text{Ce}_{\text{Ba1}}$ - and  $\text{Ce}_{\text{Ba2}}$ -doped supercells and the calculated and experimental  $4f \rightarrow 5d$  transition energies, the site occupancy of  $\text{Ce}^{3+}$  in  $\text{Ba}_2\text{SiO}_4$  is discussed in association with the local coordination structure. Moreover, electronic properties of  $\text{Ce}^{3+}$  in  $\text{Ba}_2\text{SiO}_4$  are also evaluated to understand the thermal stability of the 5d luminescence. The paper is organized as follows. The experimental and computational methods are described in Section 2. The results of luminescence measurements and *ab initio* calculations are presented and discussed in Section 3, with the final conclusions collected in Section 4.

## 2. Methodology

### 2.1. Experimental details

Powder samples of  $\text{Ba}_{2-2x}\text{Ce}_x\text{Na}_x\text{SiO}_4$  ( $x = 0.0005\text{--}0.06$ ) were synthesized by the solid-state reaction at high temperature. The starting materials included analytical grade  $\text{BaCO}_3$ ,  $\text{Na}_2\text{CO}_3$ , and 99.99% purity  $\text{SiO}_2$  and  $\text{CeO}_2$ , where  $\text{Na}_2\text{CO}_3$  was used to introduce  $\text{Na}_{\text{Ba}}$  point defects to compensate for the excess charge of  $\text{Ce}^{3+}$  on the  $\text{Ba}^{2+}$  site. After being thoroughly mixed in an agate mortar using alcohol as the mixing medium, stoichiometric amounts of the materials were calcined in 10%  $\text{H}_2/90\%$   $\text{N}_2$  reducing atmosphere at 1350 °C for 5 h. The phase purity and crystal structures of the samples were examined by powder X-ray diffraction patterns on

a Rigaku D-MAX 2200 VPC X-ray diffractometer with a wavelength of 1.54056 Å Cu K $\alpha$  radiation at 40 kV and 26 mA. High quality diffraction data of the  $\text{Ba}_2\text{SiO}_4$  host for the Rietveld refinement were collected over a  $2\theta$  range from 10° to 110° at Bruker D8 advanced X-ray diffractometer also with Cu K $\alpha$  radiation (40 kV and 40 mA), and the refinement was performed using TOPAS-Academic program. The UV-vis excitation and emission spectra as well as the luminescence decay curves were recorded at an Edinburgh FLS-920 combined with a steady-state and fluorescence lifetime spectrometer. The excitation and emission spectra in the VUV-UV range were measured on the beam line 4B8 of the Beijing Synchrotron Radiation Facility (BSRF) under normal operating conditions by using the spectrum of sodium salicylate (*o*- $\text{C}_6\text{H}_4\text{OHCOONa}$ ) as a reference.<sup>14</sup> The spectra of X-ray excited luminescence were recorded *via* Ocean Optics QE65000 spectrometer combined with an X-ray tube with tungsten anode as excitation source operating at 90 kV and 5 mA.

### 2.2. Computational details

The Ce-doped  $\text{Ba}_2\text{SiO}_4$  crystal was modeled by a  $2 \times 1 \times 2$  supercell containing 112 atoms, in which one of the 32  $\text{Ba}^{2+}$  ions was replaced by a  $\text{Ce}^{3+}$  and another by  $\text{Na}^+$  for charge compensation, corresponding to the chemical formula  $\text{Ba}_{2-2x}\text{Ce}_x\text{Na}_x\text{SiO}_4$  ( $x \approx 0.0625$ ). Four different  $\text{Ce}_{\text{Ba}}\text{--Na}_{\text{Ba}}$  double substitutions were considered, with  $\text{Ce}^{3+}$  located at a Ba1 or Ba2 site and  $\text{Na}^+$  at a nearest-neighbor or distant Ba site within the supercell. The nearest distance between  $\text{Ce}^{3+}$  ions in the supercell systems is around 10.2 Å, which is large enough to avoid their mutual influence in the computational study of localized electronic states of an individual  $\text{Ce}^{3+}$ . The lattice parameters and atomic coordinates of the supercells were first optimized by periodic DFT with a hybrid functional in the PBE0 scheme,<sup>15</sup> as implemented in the VASP package.<sup>16,17</sup> The  $\text{Ba}(5s^25p^66s^2)$ ,  $\text{Si}(3s^23p^2)$ ,  $\text{O}(2s^22p^4)$ , and  $\text{Ce}(5s^25p^64f^15d^16s^2)$  were treated as valence electrons, and their interactions with the cores were described by the projected augmented wave method.<sup>18</sup> The convergence criteria for total energies and atomic forces were set to  $10^{-4}$  eV and 0.02 eV Å<sup>-1</sup>, respectively, with a cutoff energy of 530 eV for the plane wave basis. One  $k$ -point  $\Gamma$  was used to sample the Brillouin zone.



The  $4f \rightarrow 5d$  transition energies of  $Ce^{3+}$  were calculated with a wave function-based embedded cluster approach. The Ce-centered cluster was first constructed on the basis of the DFT-optimized crystal structure, each comprising the central  $Ce^{3+}$  and the oxygen ions in the first coordination shell. Its immediate surrounding within a sphere of radius 10.0 Å was represented by several hundreds of *ab initio* model potentials (AIMPs),<sup>19</sup> and the remainder of the surroundings were simulated by tens of thousands of point charges at lattice sites, which were generated with Lepetit's method.<sup>20</sup> Wave function-based CASSCF/CASPT2 calculations with the spin-orbit effect were then carried out to obtain the  $4f^1$  and  $5d^1$  energy levels of  $Ce^{3+}$  by using the program MOLCAS.<sup>21</sup> In the CASSCF calculations, a  $[4f, 5d, 6s]$  complete active space was adopted, and in the CASPT2 calculations, the dynamic correlation effects of the  $Ce^{3+}(5s, 5p, 4f, 5d)$  electrons and the  $O^{2-}(2s, 2p)$  electrons were taken into account. Further details of the calculations can be found in ref. 22 and 23.

## 3. Results and discussion

### 3.1. Structural characterization

Rietveld refinement of the XRD pattern of  $Ba_2SiO_4$  was performed, for which the orthorhombic structure (ICSD no. 6246)<sup>11</sup> was employed as the initial model. A comparison of the experimental and calculated results (Fig. 1a) shows that the sample is of single phase without detectable impurities or a second phase. The sample crystallizes in an orthorhombic structure with the space group *Pmcn*, and the lattice parameters were determined to be  $a = 5.807$  Å,  $b = 10.213$  Å,  $c = 7.504$  Å,  $V = 445.057$  Å<sup>3</sup>. The atomic positions and occupancy factors are listed in Table 1. The average Ba–O bond lengths of the  $Ba1O_{10}$  and  $Ba2O_9$  coordination polyhedra are 2.985 and 2.826 Å, respectively. The present results for the structure of  $Ba_2SiO_4$  are in good agreement with those reported in ref. 11. For Ce-doped samples,  $Ba_{2-2x}Ce_xNa_xSiO_4$  ( $x = 0.0005$ – $0.06$ ), the XRD patterns are shown in Fig. 1b. No significant impurities peaks can be observed, indicating the  $Ce^{3+}$  and  $Na^+$  are completely dissolved into the host. The diffraction peak of (130) crystallographic plane shifts to larger angles as the doping concentration increases (Fig. 1c), which is due to a decrease in the size of the unit cell with increasing dopant content, in light of the smaller ionic sizes of  $Ce^{3+}$  and  $Na^+$  than that of  $Ba^{2+}$ .<sup>24</sup>

Table 1 The atomic coordinates and occupancy factors for  $Ba_2SiO_4$ <sup>a</sup>

Atom	Site	x	y	z	Occupancy
Ba1	4c	0.2500	0.0870	0.1608	1
Ba2	4c	0.2500	0.6955	−0.0084	1
Si	4c	0.2500	0.4200	0.2282	1
O1	4c	0.2500	0.5705	0.3097	1
O2	8d	0.0195	0.3479	0.3051	1
O3	4c	0.0250	0.4159	0.0130	1

<sup>a</sup>  $a = 5.80737(3)$  Å,  $b = 10.21296(5)$  Å,  $c = 7.50385(4)$  Å,  $V = 445.057(4)$  Å<sup>3</sup>; space group, *Pmcn*;  $Z = 4$ ;  $d = 5.47$  g cm<sup>−3</sup>.

### 3.2. Photoluminescence properties

Fig. 2 shows the emission and excitation spectra of  $Ba_{1.999}Ce_{0.0005}Na_{0.0005}SiO_4$  recorded at low temperatures. In Fig. 2a, the emission spectra were measured at 4 K under excitation at different wavelengths from 315 to 350 nm. All the spectra exhibit two-band profiles with the peak wavelengths almost overlapped with each other. The separations of the two bands are around 1940 cm<sup>−1</sup>, which is typical of 5d emission from a given kind of  $Ce^{3+}$  centers, and can be attributed to the transitions from the lowest excited 5d level to the spin-orbit split  $^2F_{5/2}$  and  $^2F_{7/2}$  multiplet terms of  $4f^1$  configuration. The relative intensities of the emission spectra are in line with those at the excitation wavelengths within the lowest-energy excitation band profile (Fig. 2b). Since the doping concentration is low in the sample under investigation, the energy transfer between  $Ce^{3+}$  activators is expected to be inefficient. Thus, the above observations imply that the emissions come predominantly from one kind of  $Ce^{3+}$  centers with similar coordination environments. Considering the smaller ionic size of  $Ce^{3+}$  than  $Ba^{2+}$ , we suppose that the emissions originate from  $Ce^{3+}$  centers located at nine-coordinated Ba2 sites rather than ten-coordinated Ba1 sites, as will be confirmed by *ab initio* calculations (see Section 3.3).

Fig. 2b shows four representative VUV-UV excitation spectra of  $Ba_{1.999}Ce_{0.0005}Na_{0.0005}SiO_4$  measured at 26.5 K, by monitoring the emission at different wavelengths. The relative intensities of the excitation spectra are consistent with those at the monitoring wavelengths within the emission spectral profile. Each of the spectra consists of four distinct bands at around 327 (band A), 248 (band B), 229 (band C) and 182 nm (band D), and a clear shoulder (A') on the shorter-wavelength side of the band A. In light of the similarity of the spectral shapes, we assign the band A, B, C and the shoulder A' to transitions from the ground 4f level to excited 5d levels of a given type of  $Ce^{3+}$  centers, presumably located at Ba2 sites. From the maximum energies of the lowest-energy excitation band (A) and the higher-energy emission band, the Stokes shift of the 5d  $\rightarrow$  4f emission is estimated to be 3843 cm<sup>−1</sup> (0.48 eV), within the range of those for Ce-doped silicate compounds.<sup>25</sup> The excitation band D at 182 nm (6.81 eV) is attributed to the host excitonic absorption, corresponding to the excitation of an electron from the top of the host valence band to the energetically lowest bound excitonic state. By taking into account the electron-hole binding energy of the exciton,<sup>26</sup> the band gap of the host is estimated to be  $\sim 1.08 \times 6.81 = 7.36$  eV.

Fig. 3 shows the decay curves of  $Ce^{3+}$  5d  $\rightarrow$  4f emission at different wavelengths within the emission profile (Fig. 2a) upon 325 nm excitation of  $Ba_{1.999}Ce_{0.0005}Na_{0.0005}SiO_4$  at 4 K. All the curves are overlapped with each other, and can be well fitted by the monoexponential function with lifetimes of about 26 ns, as indicated in the figure. These luminescence decay behaviors at different wavelengths are consistent with the presence of a single type of  $Ce^{3+}$  centers in the studied sample.

In addition, we have also measured low-temperature emission and excitation spectra and luminescence decay curves of  $Ba_{1.9995}Ce_{0.0005}SiO_4$  without the presence of  $Na^+$  as charge compensators (see Fig. S1 and S2 in ESI†). Comparison of the



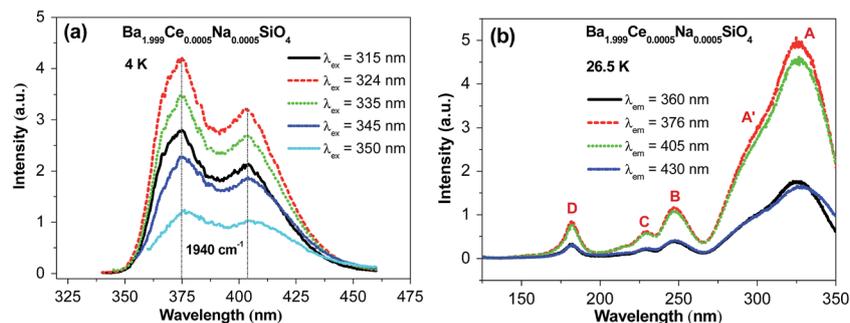


Fig. 2 (a) The UV-vis emission ( $\lambda_{\text{ex}} = 315, 324, 335, 345,$  and  $350$  nm) spectra of  $\text{Ba}_{1.999}\text{Ce}_{0.0005}\text{Na}_{0.0005}\text{SiO}_4$  at  $4$  K, and (b) the synchrotron radiation VUV-UV excitation ( $\lambda_{\text{em}} = 360, 376, 405,$  and  $430$  nm) spectra of the sample at  $26.5$  K.

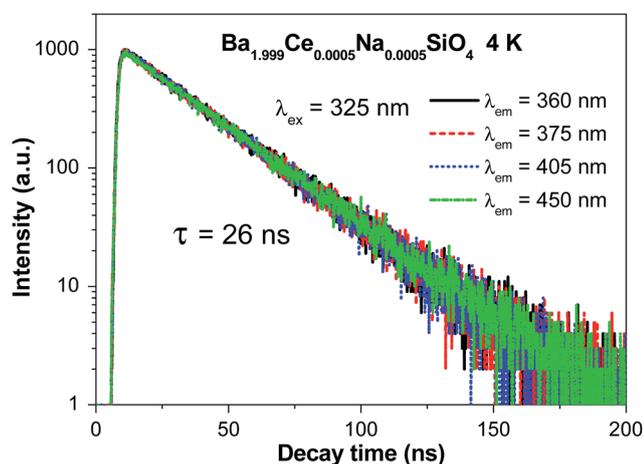


Fig. 3 Luminescence decay curves ( $\lambda_{\text{ex}} = 325$  nm;  $\lambda_{\text{em}} = 360, 375, 405,$  and  $450$  nm) of  $\text{Ba}_{1.999}\text{Ce}_{0.0005}\text{Na}_{0.0005}\text{SiO}_4$  at  $4$  K.

results with those for  $\text{Ba}_{1.999}\text{Ce}_{0.0005}\text{Na}_{0.0005}\text{SiO}_4$  indicates that the presence of  $\text{Na}^+$  has no obvious influence on spectral properties of  $\text{Ce}^{3+}$ , and thus does not affect the occupation of  $\text{Ce}^{3+}$  at a given type of  $\text{Ba}^{2+}$  sites. Nevertheless, the addition of  $\text{Na}^+$  for charge compensation can lead to a lower concentration of point defects when compared to samples without  $\text{Na}^+$ . These defects could act as electron-hole recombination centers and hence deteriorate the emission properties of the material.

Fig. 4a displays the emission spectra of  $\text{Ba}_{1.999}\text{Ce}_{0.0005}\text{Na}_{0.0005}\text{SiO}_4$  upon  $325$  nm excitation at temperatures from  $77$  to  $500$  K. The emission profile becomes more featureless with increasing temperature, which can be ascribed to thermally induced band broadening. The inset shows the CIE chromaticity coordinate of  $\text{Ba}_{1.999}\text{Ce}_{0.0005}\text{Na}_{0.0005}\text{SiO}_4$ , the emission colors at various temperatures all showing the same purple-blue ( $0.164, 0.013 \pm 0.001$ ). In addition, the temperature dependence of the integrated emission intensity is displayed in the right inset of the figure. It shows that from  $77$  to  $500$  K only  $\sim 4\%$  of the initial intensity is lost, indicating an excellent thermal stability of the phosphor. Fig. 4b gives the decay curves of  $376$  nm emission under excitation at  $325$  nm at different temperatures. All the curves exhibit similar monoexponential behaviors, and the derived lifetimes are plotted in the inset of the figure, which shows no luminescence quenching at up to  $500$  K. Instead, a slight increase in lifetime can be observed, probably due to an enhanced reabsorption at raised temperatures.<sup>27</sup>

### 3.3. X-ray excited luminescence properties

Considering the fast decay time ( $\sim 26$  ns under UV excitation at  $4$  K) and excellent thermal stability ( $T_{0.5} > 500$  K) of luminescence in  $\text{Ba}_{1.999}\text{Ce}_{0.0005}\text{Na}_{0.0005}\text{SiO}_4$ , as well as the large density ( $5.47$  g  $\text{cm}^{-3}$ ) and effective atomic number ( $49.9$ ) of  $\text{Ba}_2\text{SiO}_4$ , we have further evaluated the potential application of  $\text{Ba}_2\text{SiO}_4:\text{Ce}^{3+}$  as a scintillation phosphor. Fig. 5 shows a comparison of X-ray

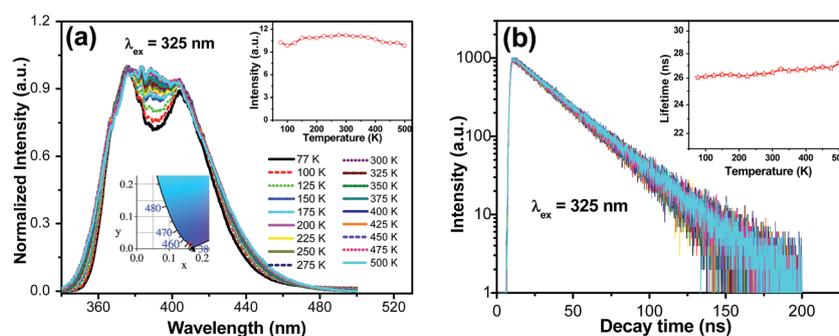


Fig. 4 Temperature-dependence of emission spectra (a),  $\lambda_{\text{ex}} = 325$  nm) and decay curves (b),  $\lambda_{\text{ex}} = 325$  nm,  $\lambda_{\text{em}} = 376$  nm) of  $\text{Ba}_{1.999}\text{Ce}_{0.0005}\text{Na}_{0.0005}\text{SiO}_4$ . The CIE chromaticity coordinate of the sample is also shown in the inset.



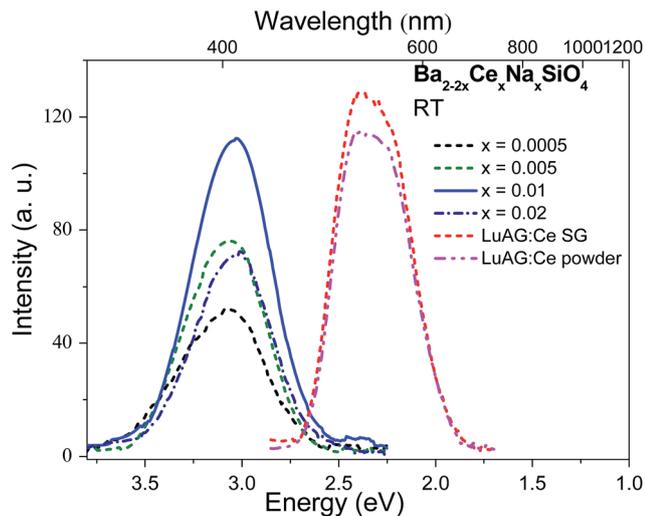


Fig. 5 X-ray excited emission spectra of  $\text{Ba}_{2-2x}\text{Ce}_x\text{Na}_x\text{SiO}_4$  ( $x = 0.0005, 0.005, 0.01, \text{ and } 0.02$ ) and the commercial  $\text{Lu}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$  (LuAG:Ce) single crystal (SG) and powder measured at room temperature (RT).

excited luminescence spectra of  $\text{Ba}_2\text{SiO}_4:\text{Ce}^{3+}$  and the commercial scintillators  $\text{Lu}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$  in single-crystal and powder forms measured at the same experimental conditions. Under X-ray excitation,  $\text{Ba}_2\text{SiO}_4:\text{Ce}^{3+}$  samples give broad and featureless emission bands at  $\sim 408$  nm due to  $5d \rightarrow 4f$  transitions of  $\text{Ce}^{3+}$ . This is in line with the room temperature emission spectrum in Fig. 4, with slight difference in emission peaks as a result of detector and instrument responses. By using that of the commercial  $\text{Lu}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$  powder (18 000 photon per MeV)<sup>28</sup> as a reference, the absolute light yields for the  $x = 0.0005, 0.005, 0.01, \text{ and } 0.02$  samples were estimated to be 10 300, 13 500, 19 600 and 12 600 photon per MeV respectively. The large light yield of the  $x = 0.01$  sample implies that  $\text{Ba}_2\text{SiO}_4:\text{Ce}^{3+}$  could be a promising scintillation material worth further optimization.

### 3.4. *Ab initio* calculations

**3.4.1. Structural properties.** The orthorhombic structure of pure  $\text{Ba}_2\text{SiO}_4$  was first optimized by using periodic DFT with standard PBE0 hybrid functional that contains 25% Hartree-Fock (HF) exchange. As shown in Table 2, the calculated lattice parameters agree well with experimental data, with the deviations less than 0.79%. The results obtained with the pure PBE

Table 2 Calculated and experimental (expt) values for the lattice parameters and the band gap energy of the  $\text{Ba}_2\text{SiO}_4$  crystal

	$a$ (Å)	$b$ (Å)	$c$ (Å)	$E_g$ (eV)
PBE	5.890	10.407	7.593	4.62
PBE0 (25% HF)	5.833	10.294	7.533	7.09
PBE0 (28% HF)	5.829	10.284	7.524	7.38
Expt	5.807	10.213	7.504	7.36

functional are also listed in the table for comparison. On the basis of the optimized structure, the band gap energy ( $E_g$ ) with standard PBE0 is predicted to be 7.09 eV, smaller than the experimentally estimated value of 7.36 eV. By increasing the fraction of HF exchange up to 28% in the PBE0 functional, this experimental  $E_g$  value can be reached (calc. 7.38 eV), with the optimized lattice parameters being still in good agreements with experiments (the deviations less than 0.70%). In view of these results, we have employed the above modified PBE0 functional in the following calculations of structural and electronic properties of Ce-doped  $\text{Ba}_2\text{SiO}_4$  supercells.

For Ce,Na-codoped  $\text{Ba}_2\text{SiO}_4$  supercells, four different  $\text{Ce}_{\text{Ba}}\text{-Na}_{\text{Ba}}$  double substitutions have been considered, which are distinguished by the shortest (3.793 Å) and longest (7.185 Å) Ba-Ba distances in the undoped supercell. Compared with the undoped supercell, the structural relaxation suggests that the incorporation of  $\text{Ce}_{\text{Ba}}\text{-Na}_{\text{Ba}}$  causes small decreases (by 0.716–0.944%) in the supercell volume, and slightly distorts the orthorhombic structure of the undoped supercell into monoclinic structures, with the deviations of angles to within  $\pm 0.185^\circ$ . Thus, the calculations predict a negligible deformation of the crystallographic phase when a small amount of Ce and Na are substituted into the Ba sites, in consistence with XRD measurements (Fig. 1b).

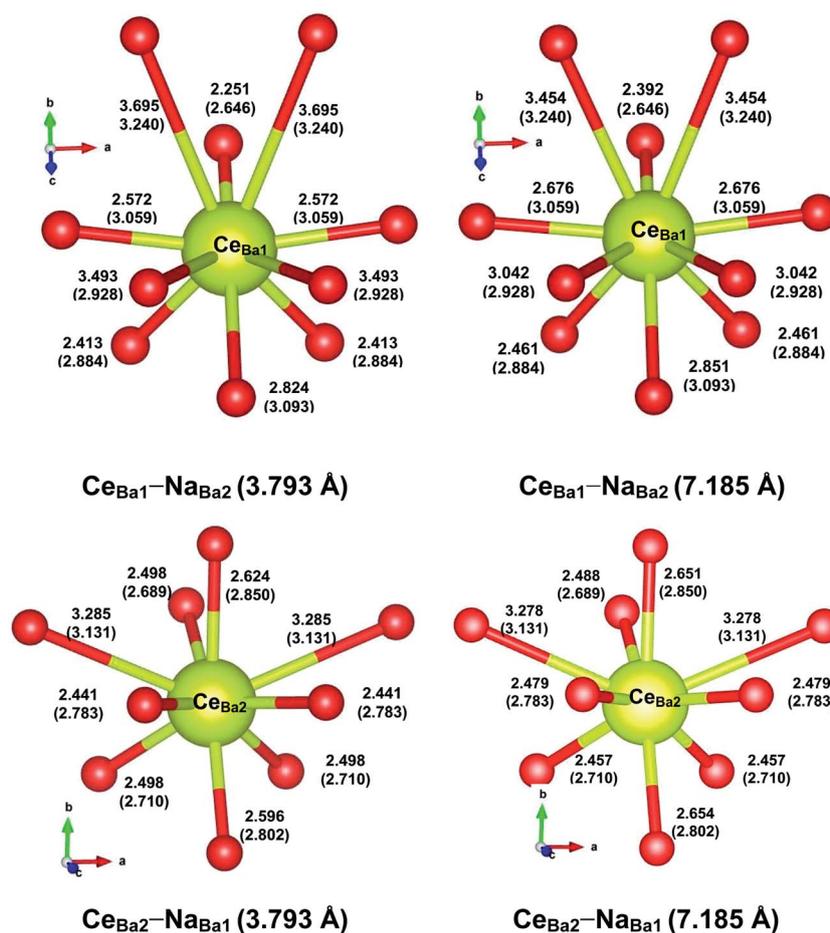
Table 3 presents the calculated DFT total energies for the four Ce,Na-codoped supercells. It shows that the two  $\text{Ce}_{\text{Ba}2}\text{-Na}_{\text{Ba}1}$  substitutions are much more stable than the two  $\text{Ce}_{\text{Ba}1}\text{-Na}_{\text{Ba}2}$  (by at least 670 meV), irrespective of the Ce-Na distance. For a given  $\text{Ce}_{\text{Ba}}\text{-Na}_{\text{Ba}}$  combination, the two single substitutions prefer to be close to each other, as is expected from their opposite effective charges. The relative stabilities may be qualitatively understood by the valences of  $\text{Ce}^{3+}$  and  $\text{Na}^+$  calculated from their optimized local structures using the bond valence sum (BVS) method.<sup>29</sup> The results are listed in the last two columns of Table 3. It shows that the BVS values of  $\text{Ce}^{3+}$  at the Ba2 site are much closer to the formal value (+3) than those of  $\text{Ce}^{3+}$  at the Ba1 site; the same is true for  $\text{Na}^+$ . This suggests that the greater stability of  $\text{Ce}_{\text{Ba}2}\text{-Na}_{\text{Ba}1}$  than  $\text{Ce}_{\text{Ba}1}\text{-Na}_{\text{Ba}2}$  is due to the preference of  $\text{Ce}^{3+}$  at the Ba2 site over the Ba1 site. This point is further supported by the calculated DFT total energies for the optimized supercells with a single  $\text{Ce}^{3+}$  ( $\text{Na}^+$ ) substituted at the Ba1 or Ba2 site, with the net defect charge compensated by a uniform charge density. The results show that the  $\text{Ce}_{\text{Ba}2}$  ( $\text{Na}_{\text{Ba}2}$ ) substitution is energetically more favorable by 979 meV (118 meV) than the  $\text{Ce}_{\text{Ba}1}$  ( $\text{Na}_{\text{Ba}1}$ ) substitution, consistent with the above BVS analysis.

The local structures of  $\text{Ce}^{3+}$  in the optimized supercells are depicted in Fig. 6, with the values of selected relaxed (unrelaxed) bond lengths indicated. All the  $\text{Ce}_{\text{Ba}}$  substitutions cause decreases in the average bond length by 0.054–0.158 Å, consistent with the smaller ionic size of  $\text{Ce}^{3+}$  than  $\text{Ba}^{2+}$ . The local structural distortion around  $\text{Ce}_{\text{Ba}1}$  is more severe than that around  $\text{Ce}_{\text{Ba}2}$ . Specifically, the bond distances from  $\text{Ce}_{\text{Ba}1}$  ( $\text{Ce}_{\text{Ba}2}$ ) to the six (seven) nearest O atoms are decreased by 0.242–0.487 Å (0.148–0.342 Å), whereas to the four (two) farthest O atoms, the distances are increased by 0.114–0.565 Å (0.147–0.154 Å), presumably due to steric repulsion. It also shows that



**Table 3** Calculated total energies for Ce,Na-codoped Ba<sub>2</sub>SiO<sub>4</sub> supercells. The Ce–Na distances (*d* in Å) in the unrelaxed and optimized supercells are also included

	<i>d</i> (Å)		Total energy (eV)	Relative total energy (meV)	Valence by BVS	
	Unrelaxed	Optimized			Ce	Na
Ce <sub>Ba2</sub> –Na <sub>Ba1</sub>	3.793	3.333	–1029.4551	0	2.759	0.698
Ce <sub>Ba2</sub> –Na <sub>Ba1</sub>	7.185	6.972	–1029.3598	95	2.711	0.605
Ce <sub>Ba1</sub> –Na <sub>Ba2</sub>	3.793	3.642	–1028.6900	765	2.636	0.916
Ce <sub>Ba1</sub> –Na <sub>Ba2</sub>	7.185	6.977	–1028.1342	1321	2.259	0.882



**Fig. 6** DFT-optimized local coordination structures of Ce at the Ba1 and Ba2 sites. The relaxed (unrelaxed) Ce–O distances (Å) are indicated.

the nearby Na<sup>+</sup> has a more pronounced effect on the local structures of Ce<sub>Ba1</sub> than that of Ce<sub>Ba2</sub>, when compared with their respective local structures with a distant Na<sup>+</sup> present. This indicates that the local structure of Ce<sub>Ba2</sub> is more rigid than that of Ce<sub>Ba1</sub>, which could be correlated with greater stability of the former substitution than the later.

**3.4.2. 4f → 5d transitions of Ce<sup>3+</sup>.** On the basis of the DFT-optimized structures for Ce,Na-doped Ba<sub>2</sub>SiO<sub>4</sub> supercells, Ce-centered embedded clusters, (Ce<sub>Ba1</sub>O<sub>10</sub>)<sup>17-</sup> and (Ce<sub>Ba2</sub>O<sub>9</sub>)<sup>15-</sup>, were constructed, with their surroundings simulated by AIMPs and point charges at lattice sites. Wave function-based CASSCF/CASPT2 calculations at the spin-orbit level were performed to

obtain the 4f<sup>1</sup> and 5d<sup>1</sup> energy levels of Ce<sup>3+</sup>, and the results are given in Table 4. We note that, for Ce<sup>3+</sup> at the Ba1 (Ba2) site, the two sets of 5d<sup>1</sup> energy levels obtained in the presence of a nearby or a distant Na<sup>+</sup> are quite different from (close to) each other, with absolute average deviations of 2712 cm<sup>-1</sup> (464 cm<sup>-1</sup>). This is consistent with the above analysis of the effect of Na<sup>+</sup> position on the local structures of Ce<sup>3+</sup> (see Section 3.4.1), considering the strong crystal field interaction of the Ce<sup>3+</sup> 5d electron with the local environment.

To facilitate comparison with experimental excitation spectra, the calculated 4f<sub>1</sub> → 5d<sub>i</sub> (*i* = 1–5) transitions are schematically presented in Fig. 7, where the relative transition



**Table 4** Calculated  $4f^1$  and  $5d^1$  energy levels for Ce-centered embedded clusters in  $\text{Ba}_2\text{SiO}_4$  using the CASSCF/CASPT2 method at the spin-orbit level. The values in parentheses of the second row indicate the unrelaxed Ce–Na distances

	$\text{Ce}_{\text{Ba1}}-\text{Na}_{\text{Ba2}}$ (3.793 Å)	$\text{Ce}_{\text{Ba1}}-\text{Na}_{\text{Ba2}}$ (7.185 Å)	$\text{Ce}_{\text{Ba2}}-\text{Na}_{\text{Ba1}}$ (3.793 Å)	$\text{Ce}_{\text{Ba2}}-\text{Na}_{\text{Ba1}}$ (7.185 Å)
$4f_1$	0	0	0	0
$4f_2$	679	398	472	411
$4f_3$	1066	496	863	671
$4f_4$	2259	2230	2325	2343
$4f_5$	2948	2585	2647	2572
$4f_6$	3034	2710	3172	2892
$4f_7$	3599	2941	3340	3223
$5d_1$	32 391	35 856	30 445	30 886
$5d_2$	33 740	36 968	31 870	32 069
$5d_3$	37 599	40 571	42 534	41 937
$5d_4$	46 380	46 260	46 304	45 774
$5d_5$	54 605	50 830	51 951	52 504

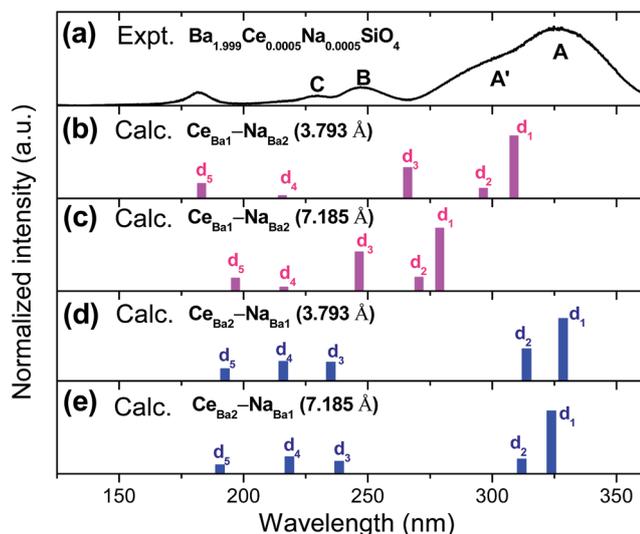
intensities within each cluster were calculated using the wave functions and energies at the spin-orbit level. It is apparent from the figure that the experimental excitation spectrum can be assigned to the  $4f_1 \rightarrow 5d_i$  transitions of  $\text{Ce}^{3+}$  located at Ba2 sites. The lowest excitation band (band A, Fig. 7a) can be clearly ascribed to  $4f_1 \rightarrow 5d_1$  transitions of  $\text{Ce}_{\text{Ba2}}^{3+}$ , and the shoulder (A') on the shorter wavelength side to  $4f_1 \rightarrow 5d_2$  transitions. The two higher excitation bands, *i.e.*, bands B and C, can be attributed to  $4f_1 \rightarrow 5d_{3,4}$  transitions, respectively, but with an average underestimation of about  $2140 \text{ cm}^{-1}$ . Thus, the above comparison provides direct evidence for the predominant preference of the dopant  $\text{Ce}^{3+}$  for the nine-coordinated Ba2 site over the ten-coordinated Ba1 site, which is also in consistence with the results of DFT total energy calculations.

**3.4.3. Electronic properties.** Fig. 8 depicts calculated total and orbital projected density of states (DOSs) of the supercell

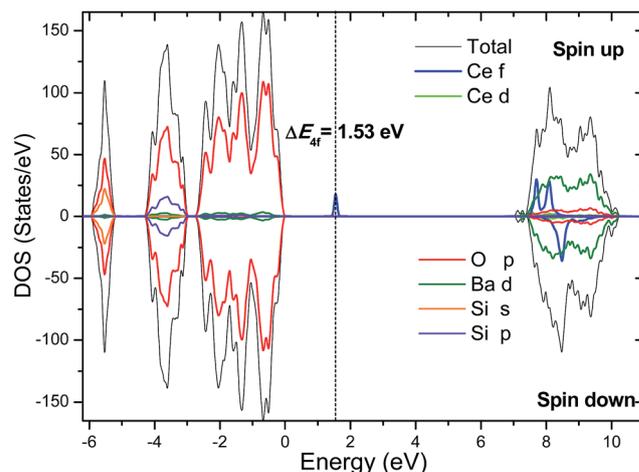
containing the stable  $\text{Ce}_{\text{Ba2}}-\text{Na}_{\text{Ba1}}$  (3.793 Å) substitution. It shows that the top of the host valence band is dominated by O 2p states with a dispersion of  $\sim 6.0 \text{ eV}$ , while the bottom of host conduction band is mainly composed of Ba 5d states. The double substitution leads to the formation of an occupied 4f state deep inside the host band gap (indicated by the dashed line in the figure), in correspondence to a lone  $\text{Ce}^{3+}$  4f electron. This occupied 4f state resides at  $\Delta E_{4f} = 1.53 \text{ eV}$  above the valence band maximum (VBM) of the host.

It is worth stressing that  $\Delta E_{4f}$  was derived in the single particle approximation of DFT (Kohn–Sham eigenvalues), and a more rigorous determination of the energy position of the occupied  $\text{Ce}^{3+}$  4f state requires to calculate the charge transition level.<sup>30</sup> The Ce-induced charge transition level  $\varepsilon(\text{Ce}^{3+/4+})$  with reference to the host VBM is defined as the Fermi level at which the defect formation energies of  $\text{Ce}^{3+}$  and  $\text{Ce}^{4+}$  are equal to each other, and can be computed using

$$\varepsilon(\text{Ce}^{3+/4+}) = E_{\text{tot}}(\text{Ce}^{3+}) - E_{\text{tot}}(\text{Ce}^{4+}) - \varepsilon_{\text{VBM}}$$



**Fig. 7** Schematic representation of the calculated energies and relative intensities of the  $4f_1 \rightarrow 5d_i$  ( $i = 1-5$ ) transitions of  $\text{Ce}^{3+}$  on the  $\text{Ba}^{2+}$  sites of  $\text{Ba}_2\text{SiO}_4$ . The VUV-UV excitation spectrum of  $\text{Ba}_{1.999}\text{Ce}_{0.0005}\text{Na}_{0.0005}\text{SiO}_4$  ( $\lambda_{\text{em}} = 376 \text{ nm}$ ) at 26.5 K (see also Fig. 2b) is also shown for comparison.



**Fig. 8** Calculated total and orbital projected DOSs for the  $\text{Ba}_2\text{SiO}_4$  supercell with the  $\text{Ce}_{\text{Ba2}}-\text{Na}_{\text{Ba1}}$  (3.793 Å) substitution. The occupied  $\text{Ce}^{3+}$  4f state is indicated by the dashed line, and its energy position with respect to the host VBM is indicated.



where  $E_{\text{tot}}$  is the total energies of the relaxed structure of the supercell containing  $\text{Ce}^{3+}$  or  $\text{Ce}^{4+}$ , and  $\varepsilon_{\text{VBM}}$  is the energy of the host VBM. The predicted value for  $\varepsilon(\text{Ce}^{3+/4+})$  is 2.44 eV, which also means that the thermal ionization energy of  $\text{Ce}^{3+}$  into  $\text{Ce}^{4+}$  is  $E_{\text{gap}} - \varepsilon(\text{Ce}^{3+/4+}) = 4.92$  eV, as could be determined, for example, from photoconductivity measurements.<sup>31</sup>

Given the value of  $\varepsilon(\text{Ce}^{3+/4+})$ , the energy difference ( $\Delta E_{5d_1}$ ) between the lowest  $\text{Ce}^{3+} 5d_1$  level and the conduction band minimum (CBM) of the host can also be estimated by

$$\Delta E_{5d_1} = E_{\text{gap}} - [\varepsilon(\text{Ce}^{3+/4+}) + \Delta E(4f_1 \rightarrow 5d_1) - (1/2)\Delta E_{\text{SS}}]$$

where  $\Delta E(4f_1 \rightarrow 5d_1)$  is the lowest  $4f_1 \rightarrow 5d_1$  transition energy of  $\text{Ce}^{3+}$  and  $\Delta E_{\text{SS}}$  is the Stokes shift. From the values of  $E_{\text{gap}}$  (7.36 eV),  $\Delta E(4f_1 \rightarrow 5d_1)$  (3.79 eV), and  $\Delta E_{\text{SS}}$  (0.48 eV), the value of  $\Delta E_{5d_1}$  is estimated to be 1.37 eV, corresponding to a thermal quenching temperature ( $T_{0.5}$ ) of 932 K on the basis of a crude relationship between  $\Delta E_{5d_1}$  and  $T_{0.5}$ , i.e.,  $T_{0.5} = 680 \times \Delta E_{5d_1}$ .<sup>32</sup> This is in qualitative agreement with the experimental result (see Section 3.2) that luminescence quenching was not yet observed when the temperature was raised up to 500 K.

## 4. Conclusions

We have investigated photoluminescence properties of Ce-doped  $\text{Ba}_2\text{SiO}_4$  from a combination of experimental and theoretical methods. Under UV excitation, the compound  $\text{Ba}_{1.999}\text{Ce}_{0.0005}\text{Na}_{0.0005}\text{SiO}_4$  exhibits bright luminescence at 350–450 nm, with a fast decay time ( $\sim 26$  ns) and a high thermal quenching temperature ( $> 500$  K). The X-ray excited luminescence measurements were then conducted, and a comparison of the results with those of the commercial  $\text{LuAG}:\text{Ce}^{3+}$  suggests a potential application of  $\text{Ba}_2\text{SiO}_4:\text{Ce}^{3+}$  as scintillation phosphors. The VUV-UV excitation spectra obtained for  $\text{Ba}_{1.999}\text{Ce}_{0.0005}\text{Na}_{0.0005}\text{SiO}_4$  by monitoring emission at different wavelengths at low temperature revealed that the emission originates predominantly from  $\text{Ce}^{3+}$  located at one type of Ba sites. This was found to be the nine-coordinated Ba2 site, on the basis of computations using hybrid DFT and wave function-based *ab initio* methods. In addition, the energy location of  $\text{Ce}^{3+} 4f$  and  $5d_1$  states within the host band gap was derived theoretically, and the large energy separation ( $\sim 1.37$  eV) between the  $5d_1$  state and the host CBM is consistent with the high thermal stability of the 5d luminescence as observed experimentally. The present work also demonstrate that low-temperature excitation spectral measurements in combination with elaborate *ab initio* calculations are able to offer microscopic insight into the structure–property relationship of  $\text{Ce}^{3+}$  in a local environment of low symmetry, which is common in Ce-activated phosphors for practical applications.

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