Design, synthesis and characterization of a novel bluish-green long-lasting phosphorescence phosphor BaLu₂Si₃O₁₀:Eu²⁺, Nd³⁺

Jie Liu, Gen Li, Haijie Guo, Dongwei Liu, Peng Feng and Yuhua Wang

Through drawing upon a solid-state reaction, a newly proposed long-lasting phosphor BaLu₂Si₃O₁₀:Eu²⁺, Nd³⁺ is presented and prepared in this work. The thermoluminescence properties of the phosphor are substantially extended, and the long-lasting phosphorescence behavior is markedly intensified by virtue of the consolidation of Nd³⁺ ions which serve as trap centers. In line with density functional theory calculations, the conduction band is mostly composed of Lu 5d states while the Ba 5d states only have a tiny contribution. We analyzed the relationship between the phosphor’s electronic structure and its optical properties. The photoluminescence emission spectrum shows a blue emitting band with a wide asymmetric property and an extremum of 426 nm, arising from the 5d–4f transitions of the Eu²⁺ ions which occupy the Ba and Lu sites. It is asserted that the long-lasting phosphorescence of the Eu²⁺ ions which take up both Ba and Lu sites stems from the special form of conduction band and the occupying environment of the emission center. Yet, they have different contributions and induce an interesting phenomenon in which the blue emitting phosphor shows a bluish-green phosphorescence. The long-lasting phosphorescence can last in excess of 6 h at the recognized intensity level (0.32 mcd m⁻²) after excitation for 10 min. This work provides a new way of thinking for the development of multicolored LLP materials. This work analyzes and sheds light on the specific courses and provides a likely mechanism for the process.

1. Introduction

Long-lasting phosphorescence (LLP) is an optical phenomenon of great significance. Luminescence can be observed after ceasing the excitation after a couple of minutes and probably persists over a longer period of time of several hours. Under excitation, energy can be stored and absorbed by LLP materials (inclusive of artificial light and sunlight). Subsequently, the stored and absorbed energy can be released as persistent visible light under thermal stimulation, commonly at room temperature. LLP materials have aroused considerable attention and have been applied in extensive important fields by virtue of its prominent characteristics which include being recyclable, energy saving, and eco-friendly. Initially, LLP materials were adopted for night-time displays, traffic signs, in or on buildings, in public places, for emergency signs, and security signs. Additionally, the foregoing materials have been adopted in structural damage sensors, radiation detectors, and optical storage media. Thus far, LLP materials have been adopted in a growing number of fields to address relevant challenges, such as in in vivo bio-imaging, medical diagnostics and solar energy utilization, etc.

Moreover, large numbers of LLP materials have been developed and reported. LLP materials colored red, green and blue are primarily highlighted and discussed with a predominant amount of the research reported adopting these materials for a particular purpose. Theoretically, any color material can be attained through blending these three predominant colors and changing their proportions. Yet, implementing the mentioned approach is difficult. Although two of the tricolor LLP materials, blue (CaAl₂O₄:Eu²⁺, Nd³⁺, >24 h) and green (SrAl₂O₄:Eu²⁺, Dy³⁺, >24 h), are very bright and can be adopted for use in the market, red LLP materials are overall inadequate when adopted for a particular purpose. Making the various components consistent with each other during the phosphorescent decay can be hard and ensuring that the color of the phosphorescence is uniform can be difficult. Furthermore, a single source of excitation can be inefficient in exciting the majority of LLP materials.

In this regard, newly proposed LLP materials consisting of multiple colors will be critically and urgently explored and developed. Currently, there is a growing interest in silicate-based luminescent materials due to their excellent chemical stability, thermal stability, weather resistance, and low
temperature synthesis. In 2010, M. Wierzbicka-Wieczorek et al. initially developed and reported the trisilicates BaRe$_2$Si$_3$O$_{10}$ (Re = Sc, Yb, Er, and Gd). The topological structure of the BaRe$_2$Si$_3$O$_{10}$ trisilicates consists of trisilicate Si$_3$O$_{10}$ groups in the shape of a horseshoe and ReO$_6$ octahedra distorted by zigzag chains of edge-sharing. Subsequently, the foregoing trisilicate compounds, e.g. BaSc$_2$Si$_3$O$_{10}$ and BaY$_2$Si$_3$O$_{10}$ are adopted to synthesize numerous versatile lanthanon doped phosphors. Additionally, the application of these phosphors in white LEDs has been investigated, as well as their photoluminescent properties. In 2014, the bivalent Eu$^{2+}$ doped BaM$_2$Si$_3$O$_{10}$Eu$^{2+}$ (M = Sc, Lu) phosphor was prepared and proposed by Jakoah Brgoch et al. In 2016, Kai Li et al. reported the preparation and photoluminescent properties of the tervalent Ce$^{3+}$ and Tb$^{3+}$ co-doped BaLu$_2$Si$_3$O$_{10}$ phosphor. The BaLu$_2$Si$_3$O$_{10}$ phosphor has prominent luminescence properties, which has aroused massive research interest. Until now, as indicated by a literature review, no papers have studied the LLP properties of this phosphor. Traps are significant for photo-energy storage of persistent and thermo-stimulated phosphors. Suitable trap depths and trap densities are beneficial for improving LLP properties. Co-doping Re$^{3+}$ ions counts as one of the most frequently adopted approaches to generate new traps or update the internal properties of traps arising from nonequivalent substitution. As Dorenbos' theory indicates that Nd$^{3+}$ ions count as adequate traps, Nd$^{3+}$ ions are deemed trap centers and can be incorporated into BaLu$_2$Si$_3$O$_{10}$Eu$^{2+}$ hosts. Based on the above reasons, we have synthesized a LLP BaLu$_2$Si$_3$O$_{10}$Eu$^{2+}$, Nd$^{3+}$ phosphor. In this work, the electronic structure, photoluminescence, and phosphorescence properties of this phosphor are investigated systematically and shed light on.

2. Experimental

2.1 Synthesis

Following a frequently adopted method using high-temperatures in the solid state, this work fabricated the desired samples Ba$_{1-x}$Lu$_x$Si$_3$O$_{10}$Eu$^{2+}$, xNd$^{3+}$ (x = 0, 0.004, 0.006, 0.008, 0.01 0.02 and 0.03, respectively presented as S1 to S6) whereby the raw materials were Eu$_2$O$_3$ (99.99%), Nd$_2$O$_3$ (99.99%), SiO$_2$ (99.99%), and BaCO$_3$ (99.99%). The relative raw materials were mixed in stoichiometric amounts and intensively ground uniformly in an agate mortar for 40 min, while incorporating an adequate amount of ethanol. The mixture was placed in alumina crucibles and sintered for 5 h at 1400 °C [N$_2$ : H$_2$ = 95 : 5] in a reducing atmosphere in a tube furnace powered by electricity. After calcining, the temperature of the samples was reduced within the furnace to room temperature and ground a second time for further application.

2.2 Characterization

These samples were characterized by powder X-ray diffraction (XRD) using a Rigaku diffractometer featuring Ni-filtered Cu Kα radiation at scanning steps of 0.02° with the 2θ value ranging from 10° to 80°. This enabled the overall phase structures of the samples to be examined. Through employing a F30 S-TWIN electron microscope (Tecnai™G2, FEI Company) high-resolution transmission electron microscopy (HRTEM) images, transmission electron microscopy (TEM) images, and an energy dispersive X-ray spectroscopy (EDX) spectrum were attained. Using a UV-Vis spectrophotometer (PE Lambda 950) and a sample of BaSO$_4$ an ultraviolet-visible (UV-vis) diffuse reflectance spectra (DRS) was attained and used as a reference. A Xe-900 xenon arc lamp (450 W), with a FLS-920T fluorescence spectrophotometer as the source of excitation, was used to measure the luminescence decay curves, the LLP spectra, the photoluminescence excitation (PLE), and the photoluminescence emission (PL). 1 nm was established as the scanning step. 10 min after irradiating the samples with ultraviolet light a PR305 long afterglow instrument was used to measure the decay curve of the LLP. TL curves were provided using a FJ-427A TL meter (Beijing Nuclear Instrument Factory) with a heating rate of 1 K s$^{-1}$ and a temperature range of 20 to 400 °C. In this work, UV light was used to irradiate 0.0020 g samples which had been pressed into pellets for 5 min prior to measuring. The photographs of BaLu$_2$Si$_3$O$_{10}$Eu$^{2+}$ and BaLu$_2$Si$_3$O$_{10}$Eu$^{2+}$, Nd$^{3+}$ under/after UV irradiation were taken in a dark room by a common digital camera with certain parameter settings (exposure time, ISO value, and aperture value). With the exception of the TL curves, these measurements were conducted at room temperature. Through using the CASTEP code and abiding by density functional theory, this work calculated the electronic structure adopted by BaLu$_2$Si$_3$O$_{10}$. Among the theories of density function, this work selected the local-density approximations (LDA).

3. Results and discussion

3.1 XRD patterns and Rietveld refinement

XRD was used to ascertain the phase purity adopted by the prepared samples. Given that the structure of BaLu$_2$Si$_3$O$_{10}$ has never previously been proposed in literature, this work references the crystallographic data and initial model structure with the purpose of refining them for BaYb$_2$Si$_3$O$_{10}$ (ICSD 17781). The representative XRD patterns for the relative samples are presented in Fig. 1a [S1–S6]. All of the diffraction peaks are used as a standard reference for the BaYb$_2$Si$_3$O$_{10}$ (ICSD 17781) compound. No impure phases were detected in the attained samples, which indicates that a single phase is taken up by all of the attained samples, and the Eu$^{2+}$ and Nd$^{3+}$ ions are successfully incorporated into the BaLu$_2$Si$_3$O$_{10}$ host. The XRD pattern of the BaLu$_2$Si$_3$O$_{10}$ host is presented in Fig. 1b on the basis of the Rietveld structural refinement which was attained using the Materials Studio program. The background, the experimental pattern and the calculated pattern are denoted by a yellow solid line, black crosses, and a red solid line, respectively. The Bragg reflection positions taken up by the acquired pattern are indicated by short vertical pink lines. At the bottom, the blue line shows how the calculated and experimental results are different from each other. Rietveld refinement effectively examines how atoms are positioned in a primitive cell. The residual factors are $R_{wp} = 13.78\%$, $R_p = 9.75\%$ and $\chi^2 = 3.127$, which demonstrate that the refined results are reliable. The refinement results...
confirm that the compound is in the monoclinic space group P2_1/m (no. 11) with cell parameters a = 5.3541(1) Å, b = 12.1224(3) Å, and c = 6.7829(2) Å. The final refinement results indicate that this phosphor has two diverse cations, namely 8-coordinated Ba^{2+} (r = 1.42 Å) and 6-coordinated Lu^{3+} (r = 0.861 Å), presented in Fig. 1b. Distorted SiO_4 tetrahedra which form corner-sharing zig-zag trimers are contained in the crystal structure. Two Si^{4+} cations are given which are crystallographically independent. Through adopting two highly distorted edge-sharing LuO_6 octahedra, this work connects the foregoing SiO_4 trimers. Generally, the radii difference between the two cations primarily determines whether the doped ions can substitute for the host cation. The percentage difference in ionic radii between the substituted and the doped ions should be less than 30%. The equation below can calculate the difference between the possible substituted ions (Ba^{2+}, Lu^{3+}) and the doped rare ions (Eu^{2+}, Nd^{3+}) in radius percentage.

\[ \text{Dr} = 100 \times \frac{\text{Rm}(\text{CN}) - \text{Rd}(\text{CN})}{\text{Rm}(\text{CN})} \] (1)

where Dr is the radius percentage difference; CN is the coordination number; Rm(CN) is the radius of the host cation; and Rd(CN) is the radius of the doped ion. The radii and calculated values of Dr between Eu^{2+}/Nd^{3+} and Ba^{2+}/Lu^{3+} are shown in Table 1. In light of calculated results from empirical equations, it can be deduced that Nd^{3+} ions could enter into both Ba and Lu sites while Eu^{2+} ions only seem to enter into the Ba sites.

### Table 1: The radius and Dr values between Eu^{2+}/Nd^{3+} and Ba^{2+}/Lu^{3+}

| Cation   | Radius (Å) | Dr (%) |
|----------|------------|-------|
| Eu^{2+}  | 1.250 Å    | 12%   |
| Nd^{3+}  | 1.109 Å    | 22%   |
| Ba^{2+}  | 1.420 Å    | 14%   |
| Lu^{3+}  | 0.861 Å    | 35%   |

3.2 Scanning electron microscopy and transmission electron microscopy analyses

The morphology of the two selected BaLu_2Si_3O_10 host and BaLu_2Si_3O_10:Eu^{2+}, Nd^{3+} samples was detected using SEM technology. As shown in Fig. 2a and c, the morphologies of these two samples are similar to each other. As shown, the blocky particles are irregularly shaped and approximately 2-10 μm in size, making their form and structure suitable for the fabrication of phosphors. The elemental composition of the BaLu_2Si_3O_10 host was investigated by EDX spectroscopy and the spectrum is shown in Fig. 2b. It confirms the presence of Ba, Lu, Si, and O in the BaLu_2Si_3O_10 sample. The elements of C and Cu come from the carbon membrane. The distance between the crystal planes reaches 0.325 nm, which is consistent with the (002) planes of...
BaLu$_2$Si$_3$O$_{10}$ in Fig. 2b (inset). In addition, the elemental composition of BaLu$_2$Si$_3$O$_{10}$:Eu$^{2+}$, Nd$^{3+}$ was also investigated by EDX spectroscopy with the spectrum shown in Fig. 2d. As shown in Fig. 2d (inset), the elements of Eu and Nd are also detected.

### 3.3 Band structure

Fig. 3a–d show the computations of BaLu$_2$Si$_3$O$_{10}$ abiding by the density functional theory and on the basis of the crystal structure refinement. This paper selects the LDA as the theoretical basis of the density function. The relevant compound takes on an indirect bandgap which reaches approximately 4.843 eV, with the conduction band (CB) peaking at the G point and the valence band (VB) peaking at the D point of the Brillouin zone, which suggests that this is an appropriately wide bandgap for Eu$^{2+}$ to serve as a center to emit light and for Nd$^{3+}$ to serve as a trap center. The electronic structure taken on by the valence band primarily stems from O 2p states, whereas the conduction band is mostly encompassed by Lu 5d states. It is worth mentioning that Ba 5d states also have a tiny contribution to the conduction band. This special band structure characteristic has great effects on the phenomena of photoluminescence and phosphorescence.

### 3.4 UV-visible diffuse reflectance spectrum

Fig. 4 shows the DRS of the undoped BaLu$_2$Si$_3$O$_{10}$ host and concentration gradient samples of BaLu$_2$Si$_3$O$_{10}$:Eu$^{2+}$. For the host, the absorption in the ultraviolet region ranging from 200 to 400 nm arises from the valence-to-conduction band. For the samples of BaLu$_2$Si$_3$O$_{10}$:Eu$^{2+}$, the feature absorbance peaks of 290 nm and 325 nm are consistent with the excitation peaks as shown in Fig. 5a, which are attributed to the Eu$^{2+}$ ions. The observed white color of the sample is a consequence of the spectral range being in the visible region. Kubelka–Munk-transformed DRS of the BaLu$_2$Si$_3$O$_{10}$ host, in line with the formula of $F(R) = A(n/V)E_g$, is presented in the inset of Fig. 4 where $F(R)$ is the Kubelka–Munk function with $F(R) = (1 - R)^{1/2}$; $R$ is the observed reflectance in the DRS; $n$ equals 1/2 for an indirect allowed transition, or 2 for a direct allowed transition, in this case $n$ equals 1/2 according to the above calculated results of the band structure for BaLu$_2$Si$_3$O$_{10}$; $A$ is the proportional constant; $v$ is the photon energy; and $E_g$ is the value of the host bandgap.

By adopting the methods proposed by Cao et al. the optical bandgap energy of BaLu$_2$Si$_3$O$_{10}$ is determined to be 5.5420 eV by extrapolation to $F(R) = 0$. It is expected that...
3.5 Photoluminescence and phosphorescence properties

The emission and excitation spectra for the BaLu₂Si₃O₁₀:Eu²⁺ phosphor at room temperature is presented in Fig. 5a. The excitation spectrum that was monitored at 426 nm shows a broad excitation band ranging from 250 nm to 400 nm which arises from the 4f⁷⁻⁴f⁶5d¹ transition of Eu²⁺ ions. Two primary peaks at 290 nm and 325 nm which are contained in the broad band show that Eu²⁺ ions are present and that their role is as an emission center. In the case of a 325 nm optimal excitation, the material merely shows one wide asymmetric band with a long shoulder peaking at 426 nm. Such an emission peak arises from the Eu²⁺ ions undergoing equally allowed electronic 4f⁶5d¹-4f⁷ transitions, which is considerably affected by the lattice of the host. In light of calculated results from the empirical equation, it can be deduced that Eu²⁺ ions only seem to access the Ba sites. However, on the basis of the analysis performed on the emission and excitation spectra, the incorporated Eu²⁺ ions could take up both Lu and Ba sites in the BaLu₂Si₃O₁₀ host. Accordingly, the emission centers fall into two types. In this regard, this work adopts Gaussian deconvolution which takes into account the emission spectrum of the BaLu₂Si₃O₁₀:Eu²⁺ phosphor being widely asymmetric, and the spectrum is compatible with two peaks at 507 nm and 430 nm. As the higher emission intensity shown by Eu₁ in contrast to Eu₂ elucidates, the Eu²⁺ ions preferably take up Ba sites instead of Lu sites. Fig. 5a presents (0.2018, 0.1595) as the CIE chromaticity coordinate for BaLu₂Si₃O₁₀:Eu²⁺ and blue as the color, which is acquired from the spectrum for emitting light whereby the calculation of the chromaticity coordinate follows the CIE1931 (Commission International de l’Eclairage France) system. As shown in Fig. 5b as the concentration of Nd³⁺ ions increases the emission spectra of BaLu₂Si₃O₁₀:Eu²⁺,Nd³⁺ merely show one band being asymmetrically wide, which is similar to that of the single doped sample. As shown in Fig. 5b (inset), all doped samples have a broad asymmetric emission peak at 426 nm with a long shoulder. It also means Eu²⁺ ions fill both Ba and Lu sites. As the doping concentration increases the brightness increases and then decreases and shows BaLu₂Si₃O₁₀:0.008Eu²⁺,Nd³⁺ to be the best doped sample. Additionally, this work fails to observe the representative emissions of the Nd³⁺ ions. As the foregoing results indicate, trivalent lanthanide ions Nd³⁺ are not deemed emission centers in BaLu₂Si₃O₁₀:Eu²⁺,Nd³⁺ but are centers for trapping in numerous LLP phosphors.

Fig. 6a shows the phosphorescence spectra of BaLu₂Si₃O₁₀:0.008Eu²⁺, 0.008Nd³⁺ at different times after removing the excitation source. Interestingly, the profiles do not change with the phosphorescence decay time, but are greatly different from the emission profiles. This interesting phenomenon indicates that the LLP originates from both emissions [Eu₄₄u and Eu₄₄u] but they have very different contributions during the LLP process. In Fig. 6b, the phosphorescence spectrum of BaLu₂Si₃O₁₀:0.008Eu²⁺,
which was measured 30 min after the source of excitation was switched off is processed by Gaussian deconvolution and is consistent with two peaks at 430 nm and 507 nm, which is similar to the PL spectrum. The phosphorescence CIE chromaticity coordinate is (0.2062, 0.2614) and the color is bluish-green, as shown in the inset of Fig. 6b. The PL color is blue but the phosphorescence color is bluish-green, indicating that the phosphorescence is derived from the 5d–4f transition of Eu2+ ions in the Ba and Lu sites. EuLu has a greater contribution during the LLP process, so the color of phosphorescence tends to be green, rather than blue.

3.6 Luminescence decay curves

To demonstrate that the phosphorescence stems from the EuLu emission in the current BaLu2Si3O10 host, luminescence decay curves were measured at an excitation of 325 nm and monitored at 426 and 507 nm. The results are shown in Fig. 7. The luminescence decay curves were able to be adjusted by a double-exponential mode and the average luminescence decay time \( \tau \) could be ascertained from the formula below:

$$
\tau = \frac{(A_1 \tau_1^2 + A_2 \tau_2^2)}{(A_1 + A_2)}
$$

where \( A_1 \) and \( A_2 \) are constant and \( \tau_1 \) and \( \tau_2 \) are the two exponential components of the fitting luminescence decay curve. Table 2 lists the fitting parameters specifically. In line with the equation above and the fitting parameters, the average luminescence decay times monitored at 426 and 507 nm were calculated to be 671 and 2114 ns for the BaLu2Si3O10:Eu2+ phosphor, and 638 and 1239 ns for the BaLu2Si3O10:Eu2+, Nd3+ phosphor, respectively. We found that both the luminescence decay times monitored at 426 and 507 nm are characteristic of the 5d–4f allowed transition of Eu2+, indicating that the green phosphorescence at 507 nm indeed originates from the Eu2+ emission, rather than from some defect levels.54 The Eu2+ luminescence decay time decreases with the introduction of Nd3+ ions. The reason is that with the introduction of Nd3+ ions there is an inequivalence of substitution which leads to lattice distortion and causes lots of defects. Those defects could play a role as energy traps, where the energy from Eu2+ ions can transfer. This new approach for energy transfer causes a decrease in the luminescence decay time. Furthermore, the dual-exponential curve fitting arising from the spectral overlap of the two emission bands and can support the statement that Eu2+ occupies both the Ba and Lu sites in BaLu2Si3O10.30

| Sample | \( \lambda_{em} \) (nm) | \( \tau_1 \) (ns) | \( \tau_2 \) (ns) | \( A_1 \) | \( A_2 \) |
|--------|----------------|-------------|-------------|------|------|
| Eu2+   | 426            | 722.81      | 235.58      | 1438.98 | 524.39 |
|        | 507            | 2618.30     | 470.54      | 545.66 | 930.57 |
| Eu2+*, Nd3+ | 426         | 671.06      | 160.98      | 1584.67 | 448.23 |
|        | 507            | 1606.05     | 288.46      | 313.56 | 673.59 |

Table 2 The fitting parameters of the luminescence decay curves of BaLu2Si3O10:Eu2+ and BaLu2Si3O10:Eu2+, Nd3+ excited at 325 nm and monitored at 426 nm and 507 nm.
3.7 LLP decay curves

As presented in Fig. 8a, this work measured the LLP decay curves for all of the as-synthesized samples (S1–S6) in order to delve into the decay performance of the BaLu2Si3O10:Eu2+,Nd3+ emission. The decay process of the LLP is encompassed by a slow decay process and a fast decay process. Those fast decay processes occur initially and dominate the intensity at the very beginning, and the slow decay processes occur later which lead to the long term behavior.\textsuperscript{35–38} This work, through adopting curve-fitting technology, analyzes the decay curves of the samples (S1–S6), and these curves are found to adequately match the following double-exponential equation.

\[ I = A_1 \exp(-t/t_1) + A_2 \exp(-t/t_2) + A_0 \]  \hspace{1cm} (3)

where \( I \) is the phosphorescence intensity, \( A_0, A_1 \) and \( A_2 \) are constants, \( t \) is time, and \( t_1 \) and \( t_2 \) are the decay times of the exponential components. Since the performance of LLP is chiefly determined by \( t_2 \), the \( t_2 \) values for all of the samples are listed in Table 3. The value of \( t_2 \) increases in the beginning and then decreases later with the increase in Eu\(^{2+}\) and Nd\(^{3+}\) ion content. They reach a maximum when the amount of the Eu\(^{2+}\) and Nd\(^{3+}\) ions reaches 0.008 mol. LLP decay curves of BaLu\(_2\)Si\(_3\)O\(_{10}\):Eu\(^{2+}\) are shown in the inset of Fig. 8a. The values peak when there is 0.008 mol of Eu\(^{2+}\) ions. The initial LLP intensity of BaLu\(_2\)Si\(_3\)O\(_{10}\):0.008Eu\(^{2+}\), 0.008Nd\(^{3+}\) is in the vicinity of 0.03 cd m\(^{-2}\) and its LLP can continue in excess of 6 h over an intensity level which is able to be recognized (0.32 mcd m\(^{-2}\)). The phosphorescence of BaLu\(_2\)Si\(_3\)O\(_{10}\):0.008Eu\(^{2+}\) is only visible for 199 s by the naked eye, which indicates that the introduction of Nd\(^{3+}\) ions greatly optimizes the phosphorescence of BaLu\(_2\)Si\(_3\)O\(_{10}\):Eu\(^{2+}\). The LLP decay curve of BaLu\(_2\)Si\(_3\)O\(_{10}\):0.008Eu\(^{2+}\), 0.008Nd\(^{3+}\) is also plotted as a function of reciprocal persistent luminescence intensity (\( I^{-1} \) \textit{versus} \( t \)) as presented in Fig. 8b. The detailed reasons are discussed later in the section on TL curves.

3.8 Thermoluminescence curves

Trapping centers play a momentous role in the photo-energy storage of persistent and thermo-stimulated phosphors.\textsuperscript{49} After removal of the excitation source, the captured charge carriers are able to escape due to thermal disturbance and are transferred to centers for luminescence, which triggers the phosphorescence. Accordingly, shallow depth traps are negatively and adversely affected by stabilizing the charge carriers, which considerably shortens the duration period of persistent luminescence. In contrast, the charge carriers that are captured by deep depth traps are extremely hard to release at room temperature, which leads to the defective performance of the LLP.\textsuperscript{40–42} For this reason, as the appropriate trap depth is formed, a solid foundation is laid for attaining a perfect LLP performance. Meanwhile, the trap density is also a significant factor for LLP. To characterize the traps in our samples TL measurements were conducted on BaLu\(_2\)Si\(_3\)O\(_{10}\):0.008Eu\(^{2+}\) and BaLu\(_2\)Si\(_3\)O\(_{10}\):0.008Eu\(^{2+}\), 0.008Nd\(^{3+}\); their TL curves are shown in Fig. 9, we only observe three very weak peaks in BaLu\(_2\)Si\(_3\)O\(_{10}\):Eu\(^{2+}\) and it is possible that the TL bands arise from intrinsic defects in the host as the Eu\(^{2+}\) ions are equally replaced by Ba\(^{2+}\) ions in BaLu\(_2\)Si\(_3\)O\(_{10}\). Additionally, as the weak TL signal indicates, the concentration of carriers that is captured by the intrinsic defects is extremely low. When Nd\(^{3+}\) ions are co-doped, the intensity of the peaks are evidently enhanced, and the primary peak position moves to 330 K, meaning that the doping of the Nd\(^{3+}\) ions considerably elevates the defect levels. To further evaluate the trap states, the trap depths \( (E_t) \) and the trap densities \( (n_t) \) can be acquired from eqn (4) and (5),\textsuperscript{43}

**Table 3** Decay times for two exponential components of Ba\(_{1-x}\)Lu\(_{2-x}\)Si\(_3\)O\(_{10}\):Eu\(^{2+}\), xNd\(^{3+}\) (x = 0, 0.004, 0.008, 0.01, 0.02 and 0.03)

| Sample | \( A_0 \) | \( A_1 \) | \( \tau_1 \) (s) | \( A_2 \) | \( \tau_2 \) (s) |
|--------|--------|--------|--------|--------|--------|
| S1     | 7.2266x10\(^{-4}\) | 0.0110 | 55.5423 | 0.0054 | 1224.0458 |
| S2     | 6.7820x10\(^{-4}\) | 0.0086 | 62.6299 | 0.0046 | 1242.8820 |
| S3     | 8.3097x10\(^{-4}\) | 0.0170 | 60.0109 | 0.0065 | 1326.3692 |
| S4     | 6.6350x10\(^{-4}\) | 0.0093 | 50.3919 | 0.0037 | 1323.1464 |
| S5     | 8.0447x10\(^{-4}\) | 0.0150 | 55.4197 | 0.0061 | 1191.9548 |
| S6     | 3.9931x10\(^{-4}\) | 0.0022 | 26.1850 | 0.0012 | 236.5758 |

Fig. 8 (a) LLP decay curves of BaLu\(_2\)Si\(_3\)O\(_{10}\):Eu\(^{2+}\), Nd\(^{3+}\). Inset: LLP decay curves of BaLu\(_2\)Si\(_3\)O\(_{10}\):Eu\(^{2+}\) (b) function of reciprocal LLP intensity (\( I^{-1} \)) \textit{versus} time (t) of BaLu\(_2\)Si\(_3\)O\(_{10}\):0.008Eu\(^{2+}\), 0.008Nd\(^{3+}\) excited for 10 min.
$$E_t = [2.52 + 10.2 \times (\mu_g - 0.42)] \times (K_B T_m^2/\omega) - 2K_B T_m$$ (4)

$$n_0 = \omega I_m/\beta \times [2.52 + 10.2 \times (\mu_g - 0.42)]$$ (5)

Where $I_m$ is the intensity of the TL peak, $\delta$ is the high-temperature half-width, $\tau$ is the low-temperature half-width, the asymmetry parameter $\mu_g = \delta/(\tau + \delta)$, $\beta$ is the heating rate, $K_B$ is the Boltzmann constant ($1.38 \times 10^{-23}$ J K$^{-1}$), $T_m$ is the temperature of the TL peak, and $\omega$ is known as the shape parameter and is defined as $\omega = \tau + \delta$. As shown in Table 4, for the BaLu$_2$Si$_3$O$_{10}$:0.008Eu$^{2+}$ sample, although the trap depth is appropriate for releasing the trapped carriers, the low trap density directly results in a brief LLP of 199 s. For BaLu$_2$Si$_3$O$_{10}$:0.008Eu$^{2+}$, 0.008Nd$^{3+}$, by co-doping with Nd$^{3+}$ ions, more traps are generated with a suitable energy depth which greatly improves the duration of the LLP and the LLP brightness in the very beginning. This result suggests that co-doping indeed has a great effect upon the LLP performance of the phosphor.

### 3.9 LLP mechanism

Under normal conditions, for the majority of LLP materials, the color of the phosphorescence is identical to the color of the PL arising from the identical emission centers. Yet the blue emitting phosphors show a phosphorescence which is characterized as bluish-green in this paper. In line with the previous analysis, Eu$^{2+}$ ions which occupy Ba and Lu sites serve as emission centers and Nd$^{3+}$ ions which take up Ba sites serve as trapping centers in the co-doped samples. As these experiments overall indicate, this material provides highly-efficient trapping conditions. A probable LLP mechanism for forming the efficient bluish-green LLP in Eu$^{2+}$ and Nd$^{3+}$ co-doped BaLu$_2$Si$_3$O$_{10}$ is shown in Fig. 10. Under UV excitation, the 4f$^7$ ground-state electrons of the Eu$^{2+}$ ions are promoted to the 4f$^6$5d$^1$ excited state (excitation process 1). Partial electrons which are promptly excited are reincorporated with the Eu$^{2+}$ ions excited on the Ba and Lu sites to produce luminescence (PL process 2). As most Eu$^{2+}$ ions occupy the Ba sites and tiny Eu$^{2+}$ ions occupy the Lu sites, the phosphor emits blue light. Simultaneously other excited electrons are able to move via the conduction band and are captured later by the traps (electron trapping process 3). When the electrons captured by shallow traps are thermally released at room temperature, they move back to the conduction band directly and a few of the captured electrons in deep traps escape through a quantum tunneling process. In view of the conduction band primarily being formed by Lu 5d states rather than Ba states, the released electrons prefer to transfer to the excited Eu$^{3+}$ ions on the Lu sites which are in the same form of resonance and recombine with them, which gives rise to the green phosphorescence (LLP process 4). In short, it is the special form of the conduction band and the occupation situation of the emission centers that result in the interesting optical phenomenon.

### 4. Conclusions

In a nutshell, a newly proposed bluish-green emitting long-lasting phosphor with prominent LLP properties is successfully achieved via a high temperature solid state method. Eu$^{2+}$ ions show a broad asymmetric emission band with a peak at 426 nm as it occupies both the Ba and Lu sites in BaLu$_2$Si$_3$O$_{10}$. The blue emitting phosphors show a kind of green phosphorescence phenomenon, which is induced mostly by the emission of Eu$^{2+}$ ions occupying the Lu sites. Co-doping with Nd$^{3+}$
ions can effectively improve the LLP performance. The LLP can last more than 6 h above the recognizable intensity level (0.32 med m⁻²). This work also provides direct experimental evidence that the conduction band is of critical significance for the course of LLP. And the analysis regarding this experimental work backs up the LLP mechanism. This new LLP material exhibits a 6 h LLP and has considerable potential for extensive applications.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

1 Z. Pan, Y. Y. Lu and F. Liu, Nat. Mater., 2012, 11, 58–63.
10 H. J. Guo, W. B. Chen, W. Zeng and Y. H. Wang, Phys. Chem. Phys., 2015, 17, 27292–27299.
11 Z. Hong, P. Zhang, X. Fan and M. Wang, J. Mater. Chem. C, 2015, 3, 7139–7147.
12 V. K. Van den Eeckhout, P. F. Smet and D. Poelman, Acta Crystallogr., 2001, 57, 701–705.
13 T. Matsuzawa, Y. Aoki, N. Takeuchi and Y. Murayama, J. Electrochem. Soc., 1996, 143, 2670–2673.
14 H. Yamamoto and T. Matsuzawa, J. Lumin., 1997, 72–74, 287–289.
15 P. J. Wang, X. H. Xu, D. C. Zhou, X. Yu and J. B. Qiu, Inorg. Chem., 2015, 54, 1690–1697.
16 P. J. Wang, X. H. Xu, D. C. Zhou, X. Yu and J. B. Qiu, Inorg. Chem., 2015, 54, 1690–1697.
17 T. L. Barry, J. Electrochem. Soc., 1968, 115, 1181–1183.
18 Y. Lin, Z. Zhang, Z. Tang, X. Wang and Z. Zheng, J. Eur. Ceram. Soc., 2001, 21, 683–685.
19 M. Wierzbicka-Wieczorek, U. Kolitsch and E. Tillmanns, Eur. J. Mineral., 2010, 22, 245.
20 Q. Wang, G. Zhu, S. Y. Xin, X. Ding, J. Xu, Y. S. Wang and Y. H. Wang, Phys. Chem. Chem. Phys., 2015, 17, 27292–27299.
21 J. Q. Wang, W. R. Zhao, J. M. Zhong and L. C. Lan, J. Mater. Sci.: Mater. Electron., 2014, 25, 2162–2168.
22 J. Zhou and Z. G. Xia, J. Mater. Chem. C, 2015, 3, 7552–7560.
23 W. R. Liu, C. C. Lin, Y. C. Chiu, Y. T. Yeh, S. M. Jang, R. S. Liu and B. M. Cheng, Opt. Express, 2009, 17, 18103–18109.
24 J. Zhou and Z. G. Xia, Opt. Mater., 2016, 52, 116–122.
25 J. Brzych, K. Hasz, K. A. Denault, C. K. Borg, A. A. Mikhailovsky and R. Seshadri, Faraday Discuss., 2014, 176, 333–347.
26 K. Li, S. S. Liang, H. Z. Lian, M. M. Shang, B. G. Xing and J. Lin, J. Mater. Chem. C, 2016, 4, 3443–3453.
27 P. Dorenbos, J. Phys.: Condens. Matter, 2003, 15, 8417.
28 M. Y. Peng, Z. W. Pei, G. Y. Hong and Q. Su, J. Mater. Chem., 2003, 13, 1202–1205.
29 R. D. Shannon, Acta Crystallogr., 1976, 32, 751–767.
30 G. Li, Y. H. Wang, H. J. Guo, J. Liu, D. W. Liu and P. Feng, J. Lumin., 2017, 192, 98–104.
31 G. Cao, L. K. Rabenberg, C. M. Nunn and T. E. Mallouk, Chem. Mater., 1991, 3, 149–156.
32 Y. Q. Li, Y. H. Wang, X. H. Xu, G. Yu and F. Zhang, J. Electrochem. Soc., 2010, 157, 39–43.
33 N. Ruelle, M. P. Thi and C. Fouassier, Jpn. J. Appl. Phys., 1992, 31, 2786–2790.
34 C. Y. Liu, Z. G. Xia, Z. P. Lian, J. Zhou and Q. F. Yan, J. Mater. Chem. C, 2013, 1, 7139–7147.
35 J. Zhang, X. Ma, Q. Qin, L. Shi, J. Sun, M. Zhou, B. Liu and Y. Wang, Mater. Chem. Phys., 2012, 136, 320–324.
36 J. Wang, S. Wang and Q. Su, J. Mater. Chem., 2004, 14, 2569–2574.
37 R. Pang, C. Li, L. Shi and Q. Su, J. Phys. Chem. Solids, 2009, 70, 303–306.
38 B. Lei, H. Zhang, W. Mai, S. Yue, Y. Liu and S. Man, Solid State Sci., 2011, 13, 525–528.
39 T. Wang, Y. H. Hu, L. Chen, X. J. Wang and G. F. Ju, Radiat. Meas., 2015, 73, 7–13.
40 J. Glodo and A. Wojtowicz, J. Alloys Compd., 2000, 300, 289–294.
41 T. Aitasalo, P. Deren, H. Hölsä, H. Junger, J. C. Krupa, M. Lastusaari, J. Legendziewicz, N. Niiltykoski and W. Strek, J. Solid State Chem., 2003, 171, 114–122.
42 T. Kinoshita, M. Yamazaki, H. Kawazoe and H. Hosono, J. Appl. Phys., 1999, 86, 3729–3733.
43 R. Chen, J. Appl. Phys., 1969, 40, 570–585.