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A novel yellow emitting long lasting phosphate phosphor Ca$_6$BaP$_4$O$_{17}$:Eu$^{2+}$,Ho$^{3+}$ is developed. The incorporation of Ho$^{3+}$ ions, which act as trap centers, largely extends the thermoluminescence characteristics and evidently enhances the persistent luminescence behavior of the phosphor. Both fluorescence and phosphorescence spectra of Ca$_6$BaP$_4$O$_{17}$:0.02Eu$^{2+}$,0.015Ho$^{3+}$ reveal only one asymmetric broad emission band located at 553 nm, ascribed to the 5d-4f transitions of Eu$^{2+}$ ions in two different Ca$^{2+}$ sites. After 15 min excitation, the initial long lasting phosphorescence (LLP) intensity of Ca$_6$BaP$_4$O$_{17}$:0.02Eu$^{2+}$,0.015Ho$^{3+}$ can reach about 0.13 cd/m$^2$ and its LLP can last more than 47 h above the recognizable intensity level (0.32 mcd/m$^2$), a phenomenon that is infrequent and excellent. Furthermore, the direct bandgap of about 4.081 eV for Ca$_6$BaP$_4$O$_{17}$ provides suitable bandgap for Eu$^{2+}$ and Ho$^{3+}$ ions. The results indicate that the phosphor has potential to become a novel commercial LLP phosphor used in the field of emergency lighting and display. Detailed processes and possible mechanism are studied and discussed.

1. Introduction

Long-lasting phosphorescence (LLP) phosphors are a special kind of energy-storing materials, which could store the energy and then release it in the form of persistent visible light usually in room temperature. In recent years, persistent luminescence materials have attracted much attention worldwide due to their commercial applications in the field of emergent lighting and display and their potential applications in such fields as high-energy irradiation dosimeters, rewritable and erasable optical memory materials, persistent photocatalytic, medical diagnostics and vivo bio-imaging, etc. Since Matsuzawa et al. discovered SrAl$_2$O$_4$:Eu$^{2+}$,Dy$^{3+}$ in the middle of the 1990s, extensive research on different afterglow materials has been conducted aimed at tuning their emission color, prolonging their persistent luminescence and providing fundamental understanding of the afterglow mechanism. Different synthesis methods, various co-dopants, and fluxes were investigated. Those studies have brought new interesting afterglow phosphors emitting mostly in the blue-green spectral range. Until now, the most efficient afterglow phosphors are blue-green emitting Eu$^{2+}$ ions doped aluminates and silicates, e.g. Sr$_2$Mg$_5$Si$_6$O$_{19}$Eu$^{2+}$,Dy$^{3+}$ (blue, >10 h), Sr$_5$Al$_4$O$_{12}$Eu$^{2+}$,Dy$^{3+}$ (blue, >15 h), SrAl$_2$O$_4$:Eu$^{2+}$,Dy$^{3+}$ (green, >24 h). Yellow and red emitting afterglow phosphors are in great scarcity, e.g. Sr$_5$Si$_2$O$_7$:Eu$^{2+}$,Dy$^{3+}$ (yellow, >6 h), Y$_2$O$_2$S:Eu$^{3+}$,Ti$^{4+}$,Mg$^{2+}$ (orange-red, >5 h), Ca$_5$Si$_3$N$_2$:Eu$^{2+}$,Tm$^{3+}$ (red, >1 h) and Mg$_2$SiO$_4$:Dy$^{3+}$,Mn$^{2+}$ (red, >17 min), Ca$_5$Si$_3$N$_2$:Eu$^{2+}$,Tm$^{3+}$ (red, >17 min), Mg$_2$SiO$_4$:Dy$^{3+}$,Mn$^{2+}$ (red, >17 min), but most of them have poor chemical stability, low luminous intensity, short duration time and the preparation condition of nitrides is rigorous compared with other commercial persistent phosphors. Besides, yellow-emitting match the maximum sensitivity of human vision. Thus, the development of efficient yellow emitting afterglow phosphors is still an ongoing challenge.

In order to achieve a yellow emitting long-persistent phosphor, we tentatively aimed at a calcium barium phosphate, Ca$_6$BaP$_4$O$_{17}$. Although there is no reports on the LLP phenomenon of Ca$_6$BaP$_4$O$_{17}$ to the best of our knowledge, phosphate compounds have excellent thermal stability and stabilization of ionic charge in the lattice, compared to other oxide phosphors. Moreover, rare earth activated phosphate phosphors have been proven to be efficient phosphors. Recently, Naoyuki Komuro et al. discovered the phase of Ca$_5$BaP$_4$O$_{17}$ with a monoclinic structure in space group C2/m and reported Ca$_5$BaP$_4$O$_{17}$:Eu$^{2+}$ phosphor with strong yellow emission and a new blue-green phosphor Ca$_5$BaP$_4$O$_{17}$:Ce$^{3+}$ for light emitting diodes. In this article, Ho$^{3+}$ ions were considered and introduced as trap centers into Ca$_6$BaP$_4$O$_{17}$:Eu$^{2+}$ host due to Ho$^{3+}$ ions can provide appropriate traps under Dorenbos’ theory. On the basis of these, we successfully synthesized a novel yellow emitting long lasting phosphor Ca$_6$BaP$_4$O$_{17}$:Eu$^{2+}$,Ho$^{3+}$ with excellent afterglow properties via a traditional solid-state reaction method. We also investigated the defect properties of Ca$_5$BaP$_4$O$_{17}$:Eu$^{2+}$,Ho$^{3+}$ by means of decay curves and thermoluminescence (TL) spectra, which revealed that the Ho$^{3+}$ ions incorporated into the phosphor dramatically increased the afterglow performance via promoting defect levels in the phosphor.
2. Experimental

In this work, the investigated samples Ca$_6$BaP$_4$O$_{17}$:0.02Eu$^{2+}$:0.02Ho$^{3+}$ (y=0, 0.005, 0.01, 0.015, 0.02 and 0.03, which are denoted as S1-S6, respectively) were synthesized through the conventional high-temperature solid-state method with CaCO$_3$ (A.R.), BaCO$_3$ (99.99%), NH$_4$H$_2$PO$_4$ (A.R.), Ho$_2$O$_3$ (99.99%) and Eu$_2$O$_3$ (99.99%) as raw materials. The stoichiometric amounts of the corresponding starting materials were homogeneously mixed and thoroughly ground in an agate mortar by adding an appropriate amount of ethanol, and ground for 30 min, and subsequently the mixture was placed into an alumina crucibles and sintered at 1280 °C for 10 h under reducing atmosphere (N$_2$:H$_2$ = 95:5) in an electric tube furnace. After calcining, the samples were cooled to room temperature in the furnace and ground again for subsequent use.

All the phase structures of samples were characterized by powder X-ray diffraction (XRD) using a Rigaku diffractometer with Ni-filtered Cu Kα radiation at scanning steps of 0.02° in the 2θ range from 10° to 80°. The excitation and emission spectra were measured by a FLS-920T fluorescence spectrophotometer with Xe 900 (450 W xenon arc lamp) as the excitation source. The scanning step was 1 nm. Afterglow decay curve measurements were measured with a PR305 long afterglow instrument after the samples were irradiated with ultraviolet light for 15 min. The TL curves were measured with a FJ-427A TL meter (Beijing Nuclear Instrument Factory) with a heating rate of 1 K s$^{-1}$ in the temperature range from 20 to 400 °C. Before measurement, 0.0001 g samples pressed in pellets were exposed to radiation for 2 min by UV lights. All measurements were carried out at room temperature except for the TL curves.

The calculations of the electronic structure for Ca$_6$BaP$_4$O$_{17}$ were carried out with density functional theory and performed with CASTEP code. The local-density approximations based on density functional theory were chosen for the theoretical basis of the density function.

3. Results and discussion

3.1. XRD patterns and Rietveld refinement

The experimental values, calculated values, peak positions and difference of Rietveld refinement XRD patterns of Ca$_6$BaP$_4$O$_{17}$ host are shown in Fig. 1a. The Ca$_6$BaP$_4$O$_{17}$ sample was refined using the Maud refinement program by the Rietveld method. The residual factors are $Rwp = 10.68\%$, and $Rp = 8.91\%$, indicating that there found results were reliable. Besides, the unit cell parameters are $a = 12.3052$ (2) Å, $b = 7.1040$ (1) Å, $c = 11.7167$ (2) Å, $\alpha = 134.4407$ (6)$^\circ$. It can be seen that all the observed peaks satisfy well with the simulated XRD patterns. The final refinement results indicate that the powder sample is crystallized in Ca$_6$BaP$_4$O$_{17}$ structure with space group C2/m and provides two different sites for Ca$^{2+}$ ions as shown in the inset of Fig. 1a and a single Ba site. Based on the consideration of effective ionic radii with different coordination numbers (CN), the doping rare-earth ions, Eu$^{2+} (r = 1.20$ Å, CN = 7; $r = 1.25$ Å, CN = 8) and Ho$^{3+} (r = 1.015$ Å, CN = 8) are proposed to occupy two Ca$^{2+} (r = 1.06$ Å, CN = 7; $r = 1.12$ Å, CN = 8) sites rather than Ba$^{2+} (r = 1.61$ Å, CN = 12) sites in the Ca$_6$BaP$_4$O$_{17}$ host lattice. Fig. 1b shows the typical XRD patterns of samples (S1-S6). As can be seen, no extra phase is observed, indicating that the samples obtained have a single phase and that doping with a small amount of Eu$^{2+}$ ions and Ho$^{3+}$ ions will not induce any impurity phase.

3.2. Band structure

The density functional theory calculations of Ca$_6$BaP$_4$O$_{17}$ based on crystal structure refinement are shown in Fig. 2. The local density approximation (LDA) was chosen for the theoretical basis of the density function. This compound possesses a direct bandgap of about 4.081 eV with the valence band (VB) maximum and the conduction band (CB) minimum at the G point of the Brillouin zone. It is expected that the value of the calculated bandgap of about 4.081 eV is smaller than the experimental one as the LDA underestimates the size of the bandgap. The electronic structure of the VB originates predominantly from O 2p states, whereas the CB is composed mostly of Ca 3d states and a small amount of Ba 5d states. Eu$^{2+}$ and Ho$^{3+}$ ions, which occupy Ca$^{2+}$ sites, exchange electrons more easily, resulting in a CB composed of Ca 3d states. With such a large band gap, it is expected that the energy levels of the 5d-4f transitions of the Eu$^{2+}$ ions in the host lattice of Ca$_6$BaP$_4$O$_{17}$ should have small interferences with the valence and conduction bands. Thus, Ca$_6$BaP$_4$O$_{17}$ host provides a suitable band gap for Eu$^{2+}$ to act as emission center and for Ho$^{3+}$ to act as trap center.
3.3. Photoluminescence and phosphorescence properties of Eu\(^{2+}\) and Ho\(^{3+}\) ions co-doped Ca\(_6\)BaP\(_4\)O\(_{13}\)

As a usual sample, Fig. 3 exhibits normalized excitation and emission spectra for Ca\(_6\)BaP\(_4\)O\(_{13}:0.02\text{Eu}^{2+},0.015\text{Ho}^{3+}\) phosphor excited at 370 nm.

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(Commission International de l’Eclairage France) system, the CIE chromaticity coordinate of Ca$_6$BaP$_4$O$_{17}$:0.02Eu$^{2+}$,0.015Ho$^{3+}$ is (0.43, 0.54) and the color is yellow showed in the inset of Fig. 3.

As shown in Fig. 4, with the concentration of Ho$^{3+}$ ions increasing, no characteristic emissions of Ho$^{3+}$ ions are observed. Clearly, the Ho$^{3+}$ ions are not luminescent centers in this phosphor, but its codoping have great influence on the PL intensity of the phosphor. When the content of Ho$^{3+}$ ions raised to 0.015 mol, its codoping markedly enhanced the PL intensity of the phosphor which could be involved with Eu$^{2+}$ ions redistribution, the defects and lattice distortion of the crystal caused by Ho$^{3+}$ codoping. Besides, the dash curves of Fig. 4 show the phosphorescence spectra of Ca$_6$BaP$_4$O$_{17}$:0.02Eu$^{2+}$,0.015Ho$^{3+}$ at different times after the removal of the excitation source. The profiles of the phosphorescence spectra do not change with decay time compared with the emission spectra of Ca$_6$BaP$_4$O$_{17}$:0.02Eu$^{2+}$,0.015Ho$^{3+}$ (0≤y≤0.03) indicating that the phosphorescence should be derived from the 5d-4f transition of Eu$^{2+}$ ions in the above-mentioned two crystallographic Ca sites rather than Ho$^{3+}$ ions during the afterglow process. In a word, Eu$^{2+}$ ions act as an emission center and Ho$^{3+}$ ions act as a trap center in the co-doped samples.

3.4. Afterglow decay curves of Ca$_6$BaP$_4$O$_{17}$:0.02Eu$^{2+}$,yHo$^{3+}$ (0≤y≤0.03) and phosphorescence spectra of Ca$_6$BaP$_4$O$_{17}$:0.02Eu$^{2+}$,0.015Ho$^{3+}$

To study the decay performance of Ca$_6$BaP$_4$O$_{17}$:0.02Eu$^{2+}$,yHo$^{3+}$ (0≤y≤0.03) emission in more particulars, the afterglow decay curves for all as synthesized samples (S1-S6) were measured, as shown in Fig. 5. Generally, the afterglow decay process consists of a rapid decay process in the beginning dominating the initial intensity and later a slow decay process responsible for the long-term behavior. Here the decay curves of samples (S1-S6) have been analyzed by curve fitting technique and found that they can be well fitted with a double-exponential equation Eq. (1) as follows:

$$ I = A_1 \exp \left( -\frac{t}{\tau_1} \right) + A_2 \exp \left( -\frac{t}{\tau_2} \right) + A_0 \quad (1) $$

where $I$ and $A_0$ represents the phosphorescence intensity; $A_1$ and $A_2$ are constants; $t$ is the time, and $\tau_1$ and $\tau_2$ are decay time for exponential components, respectively. Since the performance of LLP is chiefly determined by $\tau_2$, the $\tau_2$ of all samples are listed in Table 1. It can be seen that the value of $\tau_2$ increase in the beginning and then decrease later along with the content increase of Ho$^{3+}$ ions. They reach the maximum when the content of Ho$^{3+}$ ions raised to 0.015 mol. Hence, it is suggested that the concentration of Ho$^{3+}$ ions in Ca$_6$BaP$_4$O$_{17}$:0.02Eu$^{2+}$,0.015Ho$^{3+}$ phosphors has great effect on the LLP properties and Ca$_6$BaP$_4$O$_{17}$:0.02Eu$^{2+}$,0.015Ho$^{3+}$ sample presents the best LLP characteristic for possessing the longest decay time $\tau_2$. As shown in the left inset of Fig. 5, the initial LLP intensity of Ca$_6$BaP$_4$O$_{17}$:0.02Eu$^{2+}$,0.015Ho$^{3+}$ can reach about 0.13 cd/m$^2$ and its LLP can last more than 47 h above the recognizable intensity level (0.32 mcd/m$^2$). Whereas, the phosphorescence of Ca$_6$BaP$_4$O$_{17}$:0.02Eu$^{2+}$ can only be visible for 1 h by naked eyes, leading to the afterglow decay curve resembling a vertical line. That phenomenon indicates the phosphorescence of Ca$_6$BaP$_4$O$_{17}$:0.02Eu$^{2+}$ is improved largely by the introduction of Ho$^{3+}$ ions and detailed reasons will be discussed later. The afterglow decay curve of Ca$_6$BaP$_4$O$_{17}$:0.02Eu$^{2+}$,0.015Ho$^{3+}$ was also plotted as a function of reciprocal persistent luminescence intensity ($I^{-1}$) versus time ($t$), as shown in the right inset of Fig. 5. The $I^{-1} \sim t$ curve was divided into two parts. The two linear
The luminescence in the Ca$_6$BaP$_4$O$_{17}$:0.02Eu$^{2+}$,0.015Ho$^{3+}$ phosphor is due to the capture of charge carriers by effective trap centers, which will be discussed in the mechanism.

### Table 1: Decay times for two exponential components of Ca$_6$BaP$_4$O$_{17}$:0.02Eu$^{2+}$,0.015Ho$^{3+}$ (0.05≤0.03)

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>$A_0$</th>
<th>$A_1$</th>
<th>$\tau_1$ / s</th>
<th>$A_2$</th>
<th>$\tau_2$ / s</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>0.0016</td>
<td>0.1991</td>
<td>5.5336</td>
<td>0.0432</td>
<td>54.9999</td>
</tr>
<tr>
<td>S2</td>
<td>0.0017</td>
<td>0.0784</td>
<td>78.9404</td>
<td>0.0467</td>
<td>2573.0443</td>
</tr>
<tr>
<td>S3</td>
<td>0.0017</td>
<td>0.0630</td>
<td>99.3610</td>
<td>0.0463</td>
<td>2834.2989</td>
</tr>
<tr>
<td>S4</td>
<td>0.0015</td>
<td>0.0546</td>
<td>87.4473</td>
<td>0.0358</td>
<td>3923.0419</td>
</tr>
<tr>
<td>S5</td>
<td>0.0017</td>
<td>0.0737</td>
<td>63.0186</td>
<td>0.0387</td>
<td>2558.8203</td>
</tr>
<tr>
<td>S6</td>
<td>0.0016</td>
<td>0.0640</td>
<td>72.5315</td>
<td>0.0398</td>
<td>2426.7347</td>
</tr>
</tbody>
</table>

3.5. TL curves of Ca$_6$BaP$_4$O$_{17}$:0.02Eu$^{2+}$,0.015Ho$^{3+}$ (0.05≤0.03)

![TL Curves of Ca$_6$BaP$_4$O$_{17}$:0.02Eu$^{2+}$,0.015Ho$^{3+}$](image)

The TL curves of Ca$_6$BaP$_4$O$_{17}$:0.02Eu$^{2+}$ and Ca$_6$BaP$_4$O$_{17}$:0.02Eu$^{2+}$,0.015Ho$^{3+}$ are shown in Fig. 6. After excitation for 2 min, the TL curves of Ca$_6$BaP$_4$O$_{17}$:0.02Eu$^{2+}$,0.015Ho$^{3+}$ exhibit three weak peaks, while the TL curves of Ca$_6$BaP$_4$O$_{17}$:0.02Eu$^{2+}$ show a single main peak.

![TL Curves of Ca$_6$BaP$_4$O$_{17}$:0.02Eu$^{2+}$,0.015Ho$^{3+}$](image)

The TL curves of Ca$_6$BaP$_4$O$_{17}$:0.02Eu$^{2+}$ and Ca$_6$BaP$_4$O$_{17}$:0.02Eu$^{2+}$,0.015Ho$^{3+}$ can be fitted into two Gaussian components located at 333 K and 347 K, respectively. The main peak of Ca$_6$BaP$_4$O$_{17}$:0.02Eu$^{2+}$,0.015Ho$^{3+}$ is located at 347 K, which is slightly higher than the main peak of Ca$_6$BaP$_4$O$_{17}$:0.02Eu$^{2+}$ at 333 K. The TL curve of Ca$_6$BaP$_4$O$_{17}$:0.02Eu$^{2+}$,0.015Ho$^{3+}$ is characterized by two Gaussian components located at 333 K and 347 K, respectively. The TL curve of Ca$_6$BaP$_4$O$_{17}$:0.02Eu$^{2+}$,0.015Ho$^{3+}$ can be fitted into two Gaussian components located at 333 K and 347 K, respectively.

![TL Curves of Ca$_6$BaP$_4$O$_{17}$:0.02Eu$^{2+}$,0.015Ho$^{3+}$](image)

The parameters of the TL curves of Ca$_6$BaP$_4$O$_{17}$:0.02Eu$^{2+}$,0.015Ho$^{3+}$ are shown in Table 2. The formation of persistent luminescence in the Ca$_6$BaP$_4$O$_{17}$:0.02Eu$^{2+}$,0.015Ho$^{3+}$ phosphor is characterized by the presence of effective trap centers.

### Table 2: The parameters of the TL curves of Ca$_6$BaP$_4$O$_{17}$:0.02Eu$^{2+}$,0.015Ho$^{3+}$

<table>
<thead>
<tr>
<th>Trap</th>
<th>$T_m$</th>
<th>$\delta$</th>
<th>$\omega$</th>
<th>$\mu_\delta$</th>
<th>$\omega_\delta$</th>
<th>$n_\delta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>333</td>
<td>20</td>
<td>14</td>
<td>34</td>
<td>0.412</td>
<td>0.627</td>
</tr>
<tr>
<td>2</td>
<td>347</td>
<td>17</td>
<td>10</td>
<td>27</td>
<td>0.370</td>
<td>0.714</td>
</tr>
</tbody>
</table>

Trapping centers play a crucial role in the photo-energy storage of persistent and thermo-stimulated phosphors. After the source of excitation is removed, the captured charge carriers can escape under thermal disturbance and transfer to luminescent centers, resulting in phosphorescence. Generally, it is not beneficial for those traps with shallow depths to stabilize the charge carriers, which results in an extremely short period of persistent luminescence duration. Reversely, the charge carriers that are captured by traps with deep depths are very difficult to be released at room temperature leading to poor persistent luminescence performance. So the formation of appropriate trap depth is crucial for achieving LLP performance. Meanwhile, the trap density is also an important influencing factor for LLP. In order to characterize the traps in our samples, TL measurements were performed on Ca$_6$BaP$_4$O$_{17}$:0.02Eu$^{2+}$ and Ca$_6$BaP$_4$O$_{17}$:0.02Eu$^{2+}$,0.015Ho$^{3+}$ and their TL curves are illustrated in Fig. 6. For Ca$_6$BaP$_4$O$_{17}$:0.02Eu$^{2+}$, we just observe three very weak peaks. The TL band is possibly due to intrinsic defects of the host because Eu$^{2+}$ ions equivalently substitute for Ca$^{2+}$ ions in Ca$_6$BaP$_4$O$_{17}$:0.02Eu$^{2+}$. Furthermore, the weak TL signal suggests that the concentration of carriers captured at the intrinsic defects is very low. When Ho$^{3+}$ ions are doped, the intensity of one peak is greatly enhanced, and the main peak position moves to 335 K, which means the doping of Ho$^{3+}$ ions largely improves the defect levels. The main peak of Ca$_6$BaP$_4$O$_{17}$:0.02Eu$^{2+}$,0.015Ho$^{3+}$ TL curve can be fitted into two Gaussian components located at 333 K and 347 K, respectively. With the careful comparison between Ca$_6$BaP$_4$O$_{17}$:0.02Eu$^{2+}$ and Ca$_6$BaP$_4$O$_{17}$:0.02Eu$^{2+}$,0.015Ho$^{3+}$ glow curves in Fig. 6, we suppose that there exist new defects in the sample of Ca$_6$BaP$_4$O$_{17}$:0.02Eu$^{2+}$,0.015Ho$^{3+}$. The effective TL peak is situated slightly above room temperature (320–400 K), which is a temperature leading to better LLP properties.

The parameters of the TL curves of Ca$_6$BaP$_4$O$_{17}$:0.02Eu$^{2+}$,0.015Ho$^{3+}$ can be calculated based on the following two Eqs. (2) and (3).

$$E_t = \frac{2.52 + 10.2 \times (\mu_\delta - 0.42)}{2k_B T_m}$$

$$n_\delta = \frac{1}{\beta} \times \frac{2.52 + 10.2 \times (\mu_\delta - 0.42)}{\omega - 2k_B T_m}$$

Where $T_m$ is the temperature of the TL peak, $k_B$ is the Boltzmann constant ($1.38 \times 10^{-23}$ J K$^{-1}$), $\omega$ is known as the shape parameter and defined as $\omega = r^+ \delta$, $r$ is the low-temperature half-width, $\delta$ is the high-temperature half-width, the asymmetry parameter $\mu_\delta = \delta/(r^+ \delta)$, $\beta$ is the heating rate, and $I_m$ is the intensity of the TL peak. The calculated results $E_t$ and $n_\delta$ corresponding to band 1 and 2 are presented in Table 2. The former peak (333 K) which has a higher trap density ($3.56 \times 10^7$) and a low trap depth (0.627 eV) will result in an intense LLP intensity and a relatively rapid decay, while the latter with a lower trap density ($1.69 \times 10^7$) and a deeper trap depth (0.714 eV) will lead to a long slow one, which corresponds to the second order decay process of LLP shown in Fig. 5.
In order to investigate the number of trapping centers concerned and the kinetic order of the TL, the TL glow curves of sample Ca$_6$BaP$_4$O$_{17}$:0.02Eu$^{2+}$,0.015Ho$^{3+}$ with different delay time were recorded in the inset of Fig. 6. The results suggest that the TL intensity of the glow peak reduces and the peak position of the glow curve gradually shifts to higher temperature. According to the research of Wu et al., two possibilities could be responsible for the shifting TL peak maximum. One possibility is that many traps of closer depth comprise a trapping center, leading to a broad TL spectrum, in which case, the lower temperature ingredients will decay relatively faster than the higher temperature ones so justifying the TL peak to shift. The full width at half maximum (ɷ) of TL curve will diminish as the delay time increases. From the results listed in Table 3, we can see the full width at half maximum to become gradually diminished with increased delay time, suggesting the model containing closely spaced traps with varying depths is applicable. We also recorded the TL spectra of samples S2-S6 in Fig.7. All samples were measured after exposure to UV-irradiation 2 min. The TL spectra of samples show intensity increases until the Ho$^{3+}$ ions concentration reaches 0.015 mol before decreasing as concentration quenching occurs. Due to the non-equivalent substitution, an excess of positive charge in the host must be compensated. The only possible way to fulfill the charge compensation is that two Ho$^{3+}$ ions replace three Ca$^{2+}$ ions to balance the charge of the phosphor, which will create two Ho$^{3+}$ positive defects and one V Ca" negative defect. Therefore, the doped Ho$^{3+}$ ions concentrations greatly affect trap density. The trap centers increase with the increasing content of Ho$^{3+}$ ions up to 0.015 mol, then decrease beyond the content. A higher trap concentration means more free excited electrons are captured by electron-traps rather than immediately to emission centers leading to darker initial phosphorescence and longer afterglow duration. For this reason, Sample S4 shows the best afterglow performance for the greatest value of trap density, which is consistent with the result of the decay curve analysis.

<table>
<thead>
<tr>
<th>Delay time</th>
<th>$Tm/K$</th>
<th>$ɷ/K$</th>
<th>$κ_p$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 h</td>
<td>340</td>
<td>40</td>
<td>0.525</td>
</tr>
<tr>
<td>5 h</td>
<td>354</td>
<td>34</td>
<td>0.5</td>
</tr>
<tr>
<td>10 h</td>
<td>358</td>
<td>33</td>
<td>0.515</td>
</tr>
<tr>
<td>30 h</td>
<td>361</td>
<td>32</td>
<td>0.5</td>
</tr>
</tbody>
</table>

3.6 Afterglow mechanism of Eu$^{2+}$ and Ho$^{3+}$ ions co-doped Ca$_6$BaP$_4$O$_{17}$

The above results clearly show that Ca$_6$BaP$_4$O$_{17}$:0.02Eu$^{2+}$,0.015Ho$^{3+}$ (0≤y≤0.03) has excellent persistent luminescence. Eu$^{2+}$ ions which occupy Ca1 and Ca2 sites acts as an emission center and Ho$^{3+}$ ions which occupy Ca1 site acts as a trap center in the co-doped samples. So the introduction of Ho$^{3+}$ ions into Ca$_6$BaP$_4$O$_{17}$ matrix can be accomplished via the following pathway:

$$2Ho^{3+} + 3Ca^{2+} \rightarrow 2Ho^{3+}_{Ca^{2+}} + V_{Ca^{2+}}^{n-}$$

which creates two positive defects Ho$_{Ca^{2+}}^{n-}$ and one negative defect V$_{Ca^{2+}}^{n-}$ to get the charge compensation. All of the experiments indicate that there exist highly efficient trapping levels in this material. A possible afterglow mechanism for the formation of such an efficient yellow emission long-persistent phosphor of Eu$^{2+}$ and Ho$^{3+}$ ions co-doped Ca$_6$BaP$_4$O$_{17}$ is exhibited in Fig. 8. Eu$^{2+}$ ions have been recognized as an excellent activator for long-persistent phosphors because its 5d electron state is usually close to the CB of the host, which makes trapping of electrons possible. After UV-light excitation, electrons in the valence band (VB) are excited directly through the host into the conduction band (CB) (process 1). Some of excited electrons can shift freely in the CB and transfer to 4f$^5$5d$^1$ level of Eu$^{2+}$ ions, whereas the holes left behind move randomly in the VB. Then electron transitions occur from the 4f$^5$5d$^1$ level to lower levels 4f$^6$ followed by the characteristic emissions of Eu$^{2+}$ ions as luminescence (process 2). After switching off the ultraviolet light source, the residual electrons moving in the CB can be trapped by Ho$_{Ca^{2+}}^{n-}$ whereas holes shifting in VB can be trapped by V$_{Ca^{2+}}^{n-}$ instead of returning to the ground state (process 3). Under thermal agitation, the carriers (electrons and holes) will be released from the trapping centers and transfer via the host to the Eu$^{2+}$ ions after a series of non-radiation transitions (process 4), followed by recombination and causing the characteristic emissions of Eu$^{2+}$ ions as persistent phosphorescence (process 5). The whole process is consistent with the generally accepted mechanism that persistent luminescence occurs through the direct recombination of the conduction electrons released from traps with the emission centers.

![Fig.8. The schematic diagram of phosphorescence mechanism for (Ca$_6$BaP$_4$O$_{17}$:0.02Eu$^{2+}$,0.015Ho$^{3+}$)](Image)

4. Conclusions

In summary, a novel yellow emitting long-persistent phosphor Ca$_6$BaP$_4$O$_{17}$:0.02Eu$^{2+}$,0.015Ho$^{3+}$ with excellent afterglow properties was successfully identified via a high temperature solid state method. Eu$^{2+}$ ions show a broad asymmetric emission band located at 553 nm, because of the two different Ca$^{2+}$ sites in Ca$_6$BaP$_4$O$_{17}$. The influence of Ho$^{3+}$ ions concentrations on PL, afterglow decay curves and TL properties were studied revealing the double exponential decay mode in Ca$_6$BaP$_4$O$_{17}$:Eu$^{2+}$Ho$^{3+}$ phosphor. At least two types of independent traps corresponding to peaks at about 333 K and 347 K exist in
Ca$_2$BaP$_2$O$_7$:0.02Eu$^{2+}$:0.015Ho$^{3+}$ material and all of them responsible for the visible long lasting phosphorescence. According to analysis of TL glow curves, the defects V$_{Ca}^{+}$ were regarded as hole traps, while the defects Ho$_{Ca}^{2+}$ were regarded as electron traps. The result indicated that suitable trap depth and high trap concentration are critical to the energy storage and excellent performance of LLP and new traps caused by Ho$^{3+}$ ions have an indelible effect on its afterglow. A possible afterglow mechanism is proposed and the processes of LLP are explained.

This brand new LLP material exhibiting a 47 h afterglow will have great potential to be applied commercially in many different fields.

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Notes and references

The brand new LLP material Ca₆BaP₄O₁₇:Eu²⁺,Ho³⁺ exhibits about 0.13 cd/m² initial LLP intensity and a 47 h afterglow.