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ARTICLE TYPE

$Ca_6BaP_4O_{17}:Eu^{2+},Gd^{3+}$: a yellow emitting long lasting phosphor with high brightness and long afterglow duration

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A yellow emitting long-lasting phosphor based on $Ca_6BaP_4O_{17}$ matrix was successfully synthesized by means of solid state method in reducing atmosphere. The persistent phosphor was characterized in detail by X-ray powder diffraction (XRD), photoluminescence (PL), persistent luminescence and decay curves as well as thermoluminescence (TL) spectra. When irradiated by ultraviolet light in advance, 10 $Ca_6BaP_4O_{17}:0.02Eu^{2+},0.015Gd^{3+}$ phosphor shows a yellow persistent luminescence dominated at ~553 nm at room temperature due to the 5d-4f transitions of Eu^{2+} ions and the chromaticity coordinate was calculated to be (0.431, 0.545), which is in the yellow region. Moreover, investigation of TL curves reveals that the incorporation of Gd^{3+} ion creates more appropriate energy traps and increases the density of intrinsic traps leading to the enhancement of afterglow. Consequently, the initial long lasting 15 phosphoresce (LLP) intensity of $Ca_6BaP_4O_{17}:0.02Eu^{2+},0.015Gd^{3+}$ (0.21 cd/m^2) is significantly enhanced by a factor of 2 compared with $Ca_6BaP_4O_{17}:0.02Eu^{2+},0.015Ho^{3+}$ and the sustained phosphorescence also can last approximately 19 h above the recognizable intensity level (0.32 mcd/m^2). In order to study the trapping process and explain the mechanism of long afterglow, a schematic model is also proposed and discussed in detail.

20 1. Introduction

Long-lasting phosphorescence (LLP) phosphors are well-known as a kind of important optical functional materials which can absorb, store energy and then release visible or near-infrared light for several minutes or tens of hours after the removal of the 25 activated light source.[1,2,3] This phenomenon is due to thermally stimulated recombination of charge carriers (electrons and/or holes) which are released slowly from electron and hole traps at room temperature.[4,5,6,7] LLP can be widely applied in various important fields including high-energy irradiation dosimeters, 30 optical storage media, decoration, traffic signage, medical diagnostics, solar energy utilization, and bio-imaging attributed to their outstanding properties such as energy saving, recycling and environmental protection.[8,9,10,11]

In the middle of the 1990s, the first commercial applications of 35 persistent luminescence came with ZnS:Cu,Co for marking watch dials.[12] Nevertheless, the drawback of sensitivity to moisture hampered the utility of this phosphor. In 1996, Matsuzawa *et al.*[13] discovered the green persistent phosphors of $SrAl_2O_4:Eu^{2+},Dy^{3+}$. Since then, research on different afterglow materials has been 40 extensively conducted and has brought efficient and stable afterglow phosphors emitting mainly in the blue-green spectral range. Until now, these phosphors still play a dominant role in visible light scope owing to extremely long-persistent times and strong emitting intensities. Unfortunately, the efficient long-45 wavelength LLP emission from yellow to red is lacking, e.g. $Ca_6BaP_4O_{17}:Eu,Ho$ (yellow, >47 h),[14] $Li_2SrSiO_4:Eu,Dy$ (orange-yellow, >15 h),[15] $Sr_3SiO_5:Eu,Dy$ (yellow, >6 h),[16] and $Ca_2Si_5N_8:Eu,Tm$ (red, >1 h),[17] Thus, we need explore new LLP phosphors to extend the family of this kind of light-storing 50 materials. In recent years, many novel LLP phosphors based on different hosts have been reported and their possible mechanisms were discussed.[18-23] But the step of developing new LLP materials with excellent performance is still slow because of lacking a detail LLP mechanism. In fact, one of the researching focuses of 55 the LLP material is how to fabricate the appropriate traps in the corresponding material and only the suitable host doped with the right activator could yield considerable phosphorescence.[24]

Phosphate compounds have excellent thermal stabilities and ionic charge stabilizaties in the lattice.[25] Besides, the luminescence of 60 Eu^{2+} activated phosphors usually results from the allowed electric dipole transition ($4f^7$ to $4f^65d^1$) and thus the efficient Eu^{2+} emission can be expected in a large number of hosts.[26] On the other hand, the incorporation of Gd^{3+} could improve the luminescence of rare earth ions. Accordingly, Gd^{3+} acts as the 65 sensitizer of Eu^{2+}, Sm^{3+}, Tb^{3+} and Dy^{3+} in many compounds.[27,28,29,30] Recently, Naoyuki Komuro *et al.* discovered the phase of $Ca_6BaP_4O_{17}$ with a monoclinic structure in space group C2/m and a large band gap (5.79 eV).[31] In a previous work, we found that the incorporation of Ho^{3+} ion into the 70 $Ca_6BaP_4O_{17}:Eu^{2+}$ system as an auxiliary activator can enhance its afterglow intensity and duration.[14] In our present paper, it was found that codoping Gd^{3+} ion can significantly enhance initial LLP intensity (0.21 cd/m^2) by a factor of 2 compared with $Ca_6BaP_4O_{17}:0.02Eu^{2+},0.015Ho^{3+}$ and the LLP also can last

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approximately 19 h. The luminescence and phosphorescence properties of $Ca_6BaP_4O_{17}$:Eu^{2+},Gd^{3+} were systematically investigated by photoluminescence (PL) spectra, LLP emission spectra and decay curves and thermoluminescence (TL) glow
5 curves. Also, the possible LLP mechanism of this phosphor was discussed in this paper.

2. Experimental

A series of persistent phosphors of $Ca_6BaP_4O_{17}$:$0.02Eu^{2+}$,xGd^{3+} (x=0, 0.005, 0.01, 0.015, 0.02 and 0.025 which are denoted as
10 samples S1-S6, respectively) were synthesized by the solid-state reaction technique with $CaCO_3$ (A.R.), $BaCO_3$ (99.99%), $NH_4H_2PO_4$ (A.R.), Gd_2O_3 (99.99%) and Eu_2O_3 (99.99%) as starting materials. The required amounts of starting materials were homogeneously mixed and thoroughly ground in an agate
15 mortar by adding an appropriate amount of ethanol, followed by further grinding for 30 min. Subsequently, the mixture were transferred into an alumina crucibles and sintered at 1280 °C for 10 h in weak reductive atmosphere (5%H_2-95%N_2 mixed flowing gas) in a tubular oven. After annealing, the samples were cooled
20 to room temperature naturally and ground again to obtain final sample products in the form of fine powders.

The phase and purity identification of the synthesized phosphor samples were investigated by a Rigaku D/Max-2400 X-ray diffractometer (XRD) using a Rigaku diffractometer with
25 Nifiltered Cu Ka 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 equipped with Xe 900 (450W xenon arc lamp) as the excitation source and the scanning step was 1 nm. The decay curves were
30 recorded using a PR305 long afterglow instrument after the samples were irradiated with ultraviolet light for 15 min. The TL curves were detected using 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. Prior to the TL
35 measurements, about 0.0001 g samples pressed in pellets were exposed to radiation for 2 min by UV lights. All measurements except for the TL curves were carried out at room temperature.

3. Results and discussion

3.1. Phase identification and Crystal structure analysis

40 A novel persistent phosphor material of $Ca_6BaP_4O_{17}$:Eu^{2+},Gd^{3+} was synthesized by a conventional solid-state method. The $Ca_6BaP_4O_{17}$ sample was refined using the Maud refinement program by the Rietveld method.[32,33] The value of the profile R factor (R_{wp}) = 10.68%, and the profile R factor (R_p) = 8.91%,
45 indicating that the structural date are reliable. The crystal structure of $Ca_6BaP_4O_{17}$ and the cationic sites made with Balls-Sticks are showed in Fig. 1. The Ca1 site is surrounded by eight oxygen atoms with an average bond length of 2.51 Å, and the Ca2 site by seven oxygen atoms with an average bond length of
50 2.42 Å, the Ba site is coordinated by twelve oxygen atoms with an average bond length of 3.04 Å. The ionic radii of Ba^{2+} is 1.61 Å for twelve coordinated ions, and the ionic radii of Ca^{2+} for seven and eight coordinated ions is 1.06 Å and 1.12 Å, respectively. Therefore, for the consideration of ionic radii
55 matching, the doping Eu^{2+} (r =1.20 Å, CN =7; r =1.25 Å, CN =8)

and Gd^{3+} (r =1.20 Å, CN =7; r =1.25 Å, CN =8) ions trend to substitute for the the two different Ca^{2+} sites rather than Ba^{2+} sites in the $Ca_6BaP_4O_{17}$ matrix.
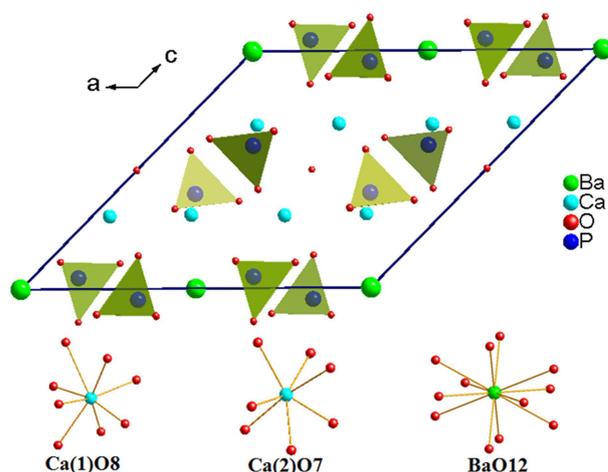
50 Fig. 1 Crystal structure of $Ca_6BaP_4O_{17}$:$0.02Eu^{2+}$ and the cationic sites made with Balls-Sticks.

Fig. 2 shows the XRD of $Ca_6BaP_4O_{17}$:Eu^{2+},Gd^{3+} phosphors. The typical XRD patterns of samples (S1-S6) are in good agreement with refine results indicating that all samples are of a single phase.
55 It can be clearly seen that no impurity peak was detected in the compositions, and results clearly suggest that the Eu^{2+} and Gd^{3+} ions are successfully incorporated in the host lattice without inducing significant changes of the crystal structure. Besides, all the peaks of $Ca_6BaP_4O_{17}$:Eu^{2+},Gd^{3+} (S2-S6) slightly move to a
70 higher 2θ value referring to the position of $Ca_6BaP_4O_{17}$ and $Ca_6BaP_4O_{17}$:Eu^{2+} (S1). This finding can be explained by the fact that Gd^{3+} ion with smaller ionic radii substitutes for Ca^{2+} leading to a decrease in the lattice constants of $Ca_6BaP_4O_{17}$:Eu^{2+},Gd^{3+}.
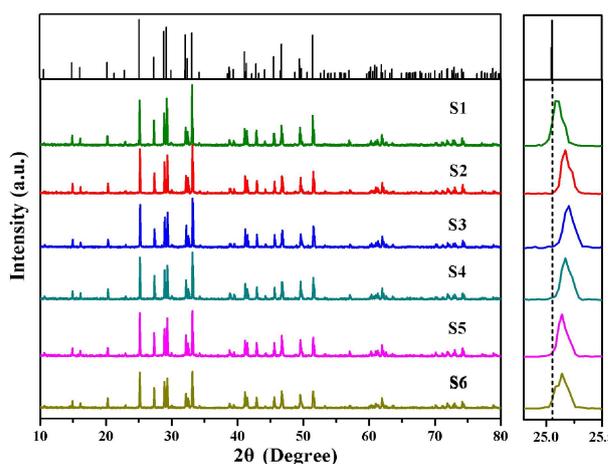
75 Fig. 2 XRD patterns of $Ca_6BaP_4O_{17}$:$0.02Eu^{2+}$,xGd^{3+} (0≤x≤0.025).

3.2. Photoluminescence and phosphorescence properties of $Ca_6BaP_4O_{17}$:$0.02Eu^{2+}$,xGd^{3+} (0≤x≤0.025).

Fig. 3 displays both the excitation and emission spectra of $Ca_6BaP_4O_{17}$:Eu^{2+},Gd^{3+} samples. The monitored emission
80 wavelength for the excitation spectra is 553 nm and the excitation spectra of the corresponding emission wavelength is 370 nm. Monitored at 370 nm, the emission spectra show an unresolved

broad band predominating at 553 nm from 480 to 730 nm, which can be ascribed to the electric-dipole-allowed $4f^65d^1 \rightarrow 4f^7$ transition of the Eu^{2+} ions. The $Ca_6BaP_4O_{17}:Eu^{2+},Gd^{3+}$ phosphors exhibit intense yellow luminescence. In addition, the typical

5 emission of Gd^{3+} is not observed, indicating that Gd^{3+} ions are not serving as luminescence center in $Ca_6BaP_4O_{17}:Eu^{2+},Gd^{3+}$ but may play as a role of trapping center. When the content of Gd^{3+} ions raised to 0.01 mol, its codoping markedly enhanced the PL intensity of the phosphor. It is noted that the PL intensity is

10 reduced when the concentration of Gd^{3+} ions is 0.015 mol and then the PL intensity gradually increases until the concentration of Gd^{3+} ions reaches to 0.025 mol. The unusual quenching concentrations may be related to the occupancy sequence of two Ca^{2+} sites for Eu^{2+} ions, the defects and lattice distortion by

15 codoping different concentrations of Gd^{3+} ions.
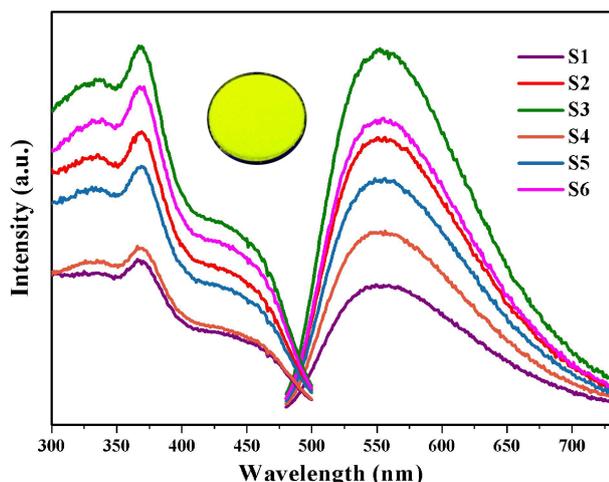
Fig. 3 Emission (λex = 370 nm) and excitation (λem = 553 nm) spectra of $Ca_6BaP_4O_{17}:0.02Eu^{2+},xGd^{3+}$ (0≤x≤0.015); (inset) photograph of $Ca_6BaP_4O_{17}:0.02Eu^{2+},0.015Gd^{3+}$ under UV irradiation.

20 An interesting result of the present work is that we have observed yellow-emitting afterglow phosphorescence in $Ca_6BaP_4O_{17}:0.02Eu^{2+},xGd^{3+}$ (0≤x≤0.025) phosphors after switching off the excitation source. Fig. 4 shows the phosphorescence spectra of $Ca_6BaP_4O_{17}:0.02Eu^{2+},0.015Gd^{3+}$

25 sample after the excitation source is stopped at different times (t = 90, 180, 300, 600, 1200 s). The phosphorescence spectra still reveal one broad band located at 553 nm, which is similar to its emission spectrum. In addition, the typical emission of Gd^{3+} is not observed. Therefore, it is fair to say that its phosphorescence

30 also can be derived from Eu^{2+} in the above-mentioned two crystallographic Ca sites. Calculated from phosphorescence spectrum using chromaticity coordinate calculation method based on the CIE1931 (Commission International de I'Eclairage France) system, the phosphorescence chromaticity coordinates of

35 $Ca_6BaP_4O_{17}:0.02Eu^{2+},0.015Gd^{3+}$ are (0.431, 0.545) and the LLP color is yellow.
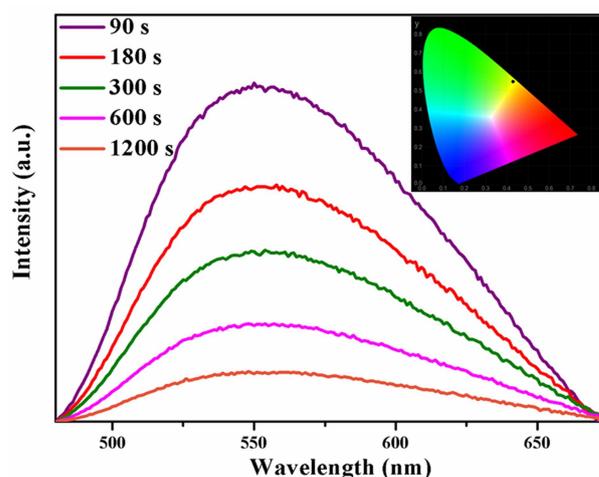
Fig. 4 Phosphorescence spectra of $Ca_6BaP_4O_{17}:0.02Eu^{2+},0.015Gd^{3+}$ measured at different times after the removal of the UV irradiation source;
40 (inset) CIE 1931 Chromaticity Diagram of $Ca_6BaP_4O_{17}:0.02Eu^{2+},0.015Gd^{3+}$ phosphor.

3.3. Afterglow decay curves of $Ca_6BaP_4O_{17}:0.02Eu^{2+},xGd^{3+}$ (0≤x≤0.025).
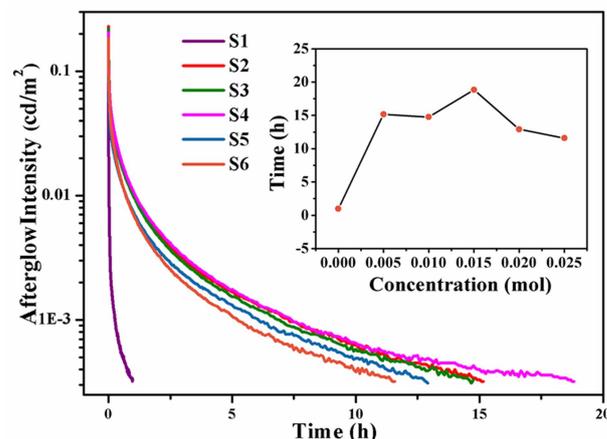
45 Fig. 5 Afterglow decay curves of $Ca_6BaP_4O_{17}:0.02Eu^{2+},xGd^{3+}$ (0≤x≤0.025); (inset) the delay time as a function of the Gd^{3+} contents.

Fig. 5 depicts the LLP decay curves of the $Ca_6BaP_4O_{17}:Eu^{2+},Gd^{3+}$ phosphors recorded immediately after removing the UV irradiation source. It can be seen that all the LLP decay curves of

50 codoped phosphors consist of a rapid decay process in the beginning dominating an intense LLP intensity and later a slow decay process responsible for longer afterglow duration. Whereas, the LLP decay curve of $Ca_6BaP_4O_{17}:0.02Eu^{2+}$ resembles a vertical line and the phosphorescence can only be visible for 1 h by naked

55 eyes. Compared with other samples, the $Ca_6BaP_4O_{17}:0.02Eu^{2+},0.015Gd^{3+}$ phosphor obviously exhibits the best phosphorescence property. Interestingly, the PL intensity of $Ca_6BaP_4O_{17}:0.02Eu^{2+},0.015Gd^{3+}$ phosphor is not the strongest compared with that of other reference samples. After the

60 excitation source was switched off, the yellow phosphorescence of $Ca_6BaP_4O_{17}:0.02Eu^{2+},0.015Gd^{3+}$ was observed for 19 h by naked eyes and the initial intensity can reach about 0.21 cd/m². Since the eye sensitivity is about 100 times better than 0.32 mcd/m², we can observe a much longer LLP in complete darkness

65 in fact.[34]

3.4. Thermoluminescence characteristics.

It is well known that trapping centers play an crucial role in photo-energy storage in persistent, photostimulated and thermo-stimulated phosphors.[35,36] Generally speaking, the corresponding information about the trapping level can be obtained by TL measurements, the shallower the trap depth, the lower the temperature of the TL peak.[37] Fig. 6 presents the TL glow curves of $Ca_6BaP_4O_{17}:0.02Eu^{2+},xGd^{3+}$ ($0\leq x\leq0.025$). It can be seen that the TL glow curve of $Ca_6BaP_4O_{17}:0.02Eu^{2+}$ consists of three very weak peaks located at about 307 K, 343 K and 397 K. This result reveals that there are at least three types of traps with different depths in $Ca_6BaP_4O_{17}:0.02Eu^{2+}$ material. According to Clabau *et al.*[37], Eu^{2+} can exist in oxidized state Eu^{3+} so that the electron excited to a 5d orbital can potentially be trapped by anion vacancies. Therefore, the traps involved in LLP of $Ca_6BaP_4O_{17}:0.02Eu^{2+}$ material could be due to oxygen vacancies or clusters which are created during the synthesis process at high temperature and in reducing atmosphere.[38,39] Furthermore, the weak TL signal suggests that the concentration of carriers captured at the intrinsic traps is very low. However, we can see that there emerge a new peak around at 330 K and the TL intensity of P2 (343 K) and P3 (397 K) are greatly enhanced for the co-doped sample, which means the doping of Gd^{3+} ions largely improves the trap levels and creates new traps in the samples of $Ca_6BaP_4O_{17}:Eu^{2+},Gd^{3+}$. Due to the nonequivalent substitution, an excess of positive charge in the host must be compensated. The only possible way to fulfill the charge compensation is that two Gd^{3+} ions replace three Ca^{2+} ions to balance the charge of the phosphor, which will form two $Gd_{Ca}^{\bullet}$ positive defects and one V_{Ca}'' negative defect. The positive defects could form electron-traps while negative defects act as hole-traps. Thus, the new traps can be caused by $Gd_{Ca}^{\bullet}$ and V_{Ca}'' defects. The TL intensity of P1 (330 K) and P3 (397 K) peaks as a function of the Gd^{3+} contents are showed in the inset of Fig. 6. It is found that the TL intensity of two peaks increases simultaneously and then decreases when the Gd^{3+} content is more than 0.015 mol due to the concentration quenching effect.[40] Thus, taking the analyses of decay and TL properties into account together, it can be concluded that $Ca_6BaP_4O_{17}:0.02Eu^{2+},0.015Gd^{3+}$ sample shows the best persistent luminescence performance.
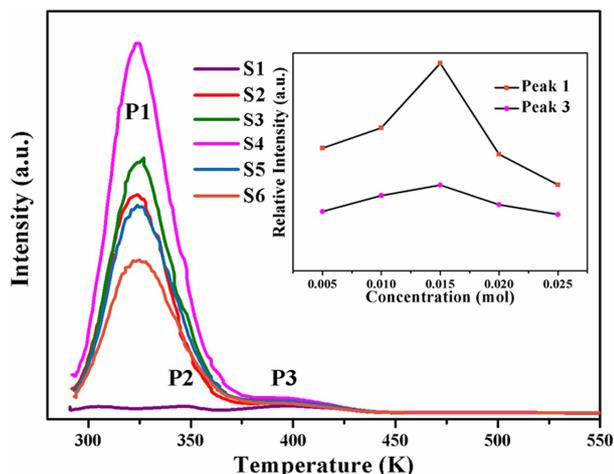
Fig. 6. The TL glow curves of $Ca_6BaP_4O_{17}:0.02Eu^{2+},xGd^{3+}$ ($0\leq x\leq0.025$); (inset) the TL intensity of P1 (340 K) and P3 (382 K) peaks as a function of the Gd^{3+} contents.

The fading of TL is due partly to the bleaching of the trapped carriers by thermal energy. The TL glow curves with different delay time after ceasing the UV irradiation may also provide important information on the trap distribution in materials.[39] The effective TL peak is situated slightly above room temperature (320-400 K), which is a temperature leading to better LLP properties.[41,42] So, in our present work, the TL peaks at 330 K (P1), 343 K (P2) and 397 K (P3) account for the LLP in room temperature. As shown in Fig. 7, the TL intensity of P1 (330K) due to the shallow traps decreases very quickly and approximately has disappeared after 30 minutes because that the charge carriers escape from shallower traps much faster than that in deep ones. At the same time, it is found that the deep traps at 343 K (P2) and 397 K (P3) plays a major role and their TL intensities relatively slow decrease with time as showed in the inset of Fig. 7. This result indicates that the shallow traps corresponding to the P1 (340K) peak should be mainly responsible for an intense LLP intensity and a rapid decay process in the beginning, while the deep traps at 343 K (P2) and 397 K (P3) leading to darker initial phosphorescence and longer afterglow duration of $Ca_6BaP_4O_{17}:0.02Eu^{2+},0.015Gd^{3+}$ material.
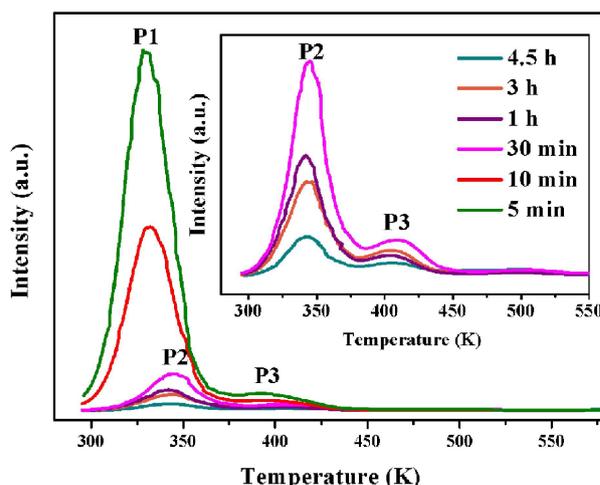
Fig. 7 The TL glow curves of $Ca_6BaP_4O_{17}:0.02Eu^{2+},0.015Gd^{3+}$ sample after UV irradiation for 2 min and then delaying for different time.

3.5. Afterglow mechanism.

Based on the above results, a simple model of $Ca_6BaP_4O_{17}:Eu^{2+},Gd^{3+}$ LLP mechanism is proposed and illustrated in Fig. 8. Under ultraviolet-light excitation, the ground-state electrons of Eu^{2+} ions are promoted to the 5d electron state (process 1), which is partly overlapped with the conduction band. The excited electrons are subsequently captured by both shallow electron traps $Gd_{Ca}^{\bullet}$ (P1) and deep electron traps oxygen vacancies or clusters (P2 and P3) through the conduction band (process 2) and thus the excitation energy is efficiently stored. After a sufficient illumination time, all of the appropriate traps are filled. Subsequently, the electrons are released from traps in temperature order under the action of thermal activation at an appropriate temperature and then transferred to the emission centers (process 3), followed by the recombination and finally

resulting in the LLP.
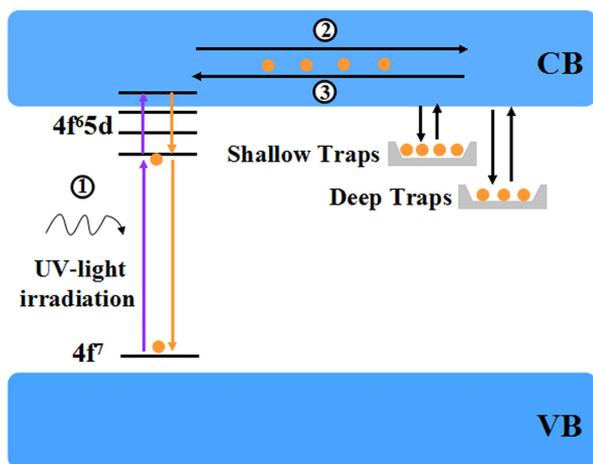
Fig.8. Schematic diagram of the afterglow process.

4. Conclusions

By introducing Gd^{3+} ions into Eu^{2+} doped calcium barium phosphate $Ca_6BaP_4O_{17}$, we first obtain a novel LLP phosphor $Ca_6BaP_4O_{17}$: Eu^{2+},Gd^{3+} by conventional solid state method. When the content of Gd^{3+} ions raised to 0.015 mol, its codoping markedly enhanced the PL and phosphorescence intensity. After the UV light excitation source was switched off, the bright yellow LLP was observed in $Ca_6BaP_4O_{17}$: Eu^{2+},Gd^{3+} phosphor and the LLP can last near 19 h at recognizable intensity level. The analysis of TL glow curves reveals that the shallow traps (330 K) are mainly responsible for an intense LLP intensity and a rapid decay process, while the deep traps (343 K and 397 K) leading to darker initial phosphorescence and longer afterglow duration of $Ca_6BaP_4O_{17}$:0.02Eu^{2+},0.015Gd^{3+} material.

Acknowledgments

Notes and references

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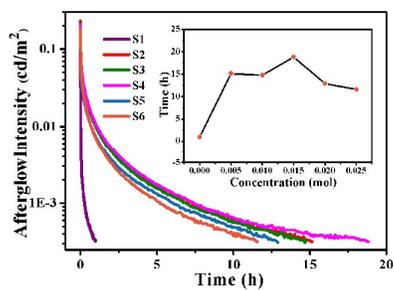
The brand new LLP material $Ca_6BaP_4O_{17}:Eu^{2+},Gd^{3+}$ exhibits about 0.21 cd/m^2 initial LLP intensity and a 19 h afterglow.