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$Cs_6RE_2(PO_4)_4$ (RE = Y and Gd): Two New Members of Alkali Rare-earth Double Phosphates

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Two new alkali rare-earth double phosphates, $Cs_6Y_2(PO_4)_4$ (CYP) and $Cs_6Gd_2(PO_4)_4$ (CGP), have been successfully synthesized by using the conventional solid-state reaction method. The two compounds crystallize in the same space group $P2_1$ (No. 4) and feature a three-dimensional network composed of CsO_n (n = 8, 10 and 11) distorted polyhedra and isolated YO_6 and PO_4 groups. IR spectroscopy, UV−vis−NIR diffuse reflectance spectroscopy, and electronic band structures of the two compounds were reported. In addition, the Ce^{3+} -doped CYP and CGP phosphors were synthesized and their photoluminescence properties were investigated. The results indicate that CYP:Ce^{3+} and CGP:Ce^{3+} phosphors can be efficiently excited by ultraviolet (UV) light to realize a blue luminescence corresponding to the electric-dipole allowed 4*f*–5*d* transition of the Ce^{3+} ions.

Introduction

In recent years, rare-earth phosphates have been systematically investigated due to their interesting optical properties.[1] In particular, alkali rare-earth double *ortho*-phosphates with a general formula $M_3RE(PO_4)_2$ (M = alkali metal cation, RE = trivalent rare-earth cation) have been exclusively studied.[2] They exhibit structural diversity and good chemical stability, and are suitable phosphate hosts for optically active rare earth ions. Therefore, this type of compounds and those doped with optically active ions have potential applications as laser, scintillator and luminescent materials. For example, $K_3Nd(PO_4)_2$ has been reported as a new laser material with high Nd concentrations and long radiative lifetime;[3] Eu^{3+}-doped $K_3Y(PO_4)_2$ phosphor exhibits intense reddish orange emission under near UV light excitation, which has a potential application on near UV InGaN chip-based white light-emitting diodes;[4] $Na_3Gd(PO_4)_2$:Dy^{3+} can emits bright white light providing the possibility for applications in deep UV phosphors such as plasma display phosphors or mercury-free lamps;[5] Single crystals of $K_3Lu(PO_4)_2$, $Rb_3Lu(PO_4)_2$ and $Cs_3Lu(PO_4)_2$ activated with ~0.1 mol % Ce exhibit promising scintillation properties with high light yields and relatively fast decay time.[6]

In general, the crystal structure of $M_3RE(PO_4)_2$ type compounds all consist of isolated PO_4^{3-} tetrahedra separated by different cations, which can be regarded as the derivatives of the mineral *Glaserite*, $K_3Na(SO_4)_2$.[7] Ideally, this type of structure crystalizes in a hexagonal system and contains the smaller cations (Na^+ or rare-earth metal ions) in octahedral coordination environment while the larger cations (alkali metal ions) are coordinated by 8~12 oxygen atoms. However, $M_3RE(PO_4)_2$ shows great variety of structures, and their detailed symmetry and structure depend on the relative sizes of the alkali and rare-earth metal cations. In addition, polymorphism as a function of temperature is frequently observed. An overall description of these phases and relationships among various structural types have been analyzed and discussed by Wickleder[1a] and Vlasse et al.[8] Although $M_3RE(PO_4)_2$ family with M = Na, K and Rb has been described in the literature, to our best knowledge, nothing is known about the Cs derivatives.

In this work, we report on the synthesis and characterization of two new members of alkali rare-earth double phosphates in the $M_3RE(PO_4)_2$ family: $Cs_6Y_2(PO_4)_4$ (CYP) and $Cs_6Gd_2(PO_4)_4$ (CGP). After structural analysis, IR spectroscopy, UV−vis−NIR diffuse reflectance spectroscopy, and electronic band structure calculations of the title compounds were described. It is noted that the double phosphates have been widely used as host materials for luminescent lanthanide ions.[2e, 4-5] The Ce^{3+} ion is one of the most commonly used activate ions for phosphors due to the intense and broad excitation as well as emission bands derived from their dipole allowed 4*f*–5*d* electronic transitions. Therefore, we also synthesized Ce^{3+} -doped CYP and CGP, and present preliminary investigation on the photoluminescence properties.

Experimental

Synthesis

Cs_2CO_3 (99%), Y_2O_3 (99.95%), Gd_2O_3 (99.95%), CeO_2 (99.95%), H_3BO_3 (99.9%) and $NH_4H_2PO_4$ (99.9%) were used as received.

Single crystals of CYP and CGP were grown from a high temperature solution with the Cs_2CO_3-H_3BO_3 flux system in air. The solution was prepared in a platinum crucible by melting a mixture of Cs_2CO_3/M_2O_3 (M = Y and Gd)/$H_3BO_3/NH_4H_2PO_4$ in the molar ratio of 7.5:0.5:10:3. The crucible was placed in the center of a vertical programmable temperature furnace. It was held at 850 ℃ for 12 h and then slowly cooled down to 750 ℃ at a rate of 3 ℃/h, and finally cooled down to room temperature at a rate of 50 ℃/h. Colorless block crystals were separated from the crucible for structural characterization.

Polycrystalline samples of CYP and CGP were synthesized *via* conventional solid-state reactions. A separate stoichiometric mixture of Cs_2CO_3, Y_2O_3/Gd_2O_3, and $NH_4H_2PO_4$ was initially ground well. The samples were placed in alumina crucibles and heated to 750 ℃, held for 2 days, and then cooled to room temperature. CYP: $0.01Ce^{3+}$ and CGP: $0.01Ce^{3+}$ phosphors were synthesized by similar solid-state route. Raw materials of Cs_2CO_3, Y_2O_3/Gd_2O_3, CeO_2 and $NH_4H_2PO_4$ were mixed stoichiometrically and ground well. The mixture was pre-heated in an alumina crucible at 600 °C for 8 h in air. The pre-heated powder was then placed in an alumina crucible inside a tube furnace and heated to 750 °C for 40 h in CO reducing atmosphere, followed by an additional grinding. After that, the samples were furnace-cooled to room temperature.

X-ray crystallography

Single crystal data were collected at room temperature on a Bruker SMART APEX II CCD diffractometer with graphite-monochromatic Mo Kα radiation (λ = 0.71073 Å) at 293(2) K. The reductions of data were carried out with the Bruker Suite software package. The numerical absorption corrections were performed with the SADABS program and integrated with the SAINT program.[9] All calculations were performed with programs from the SHELXTL crystallographic software package.[10] The structures were solved by direct methods with space group $P2_1$ (No. 4), and all of the atoms were refined using full-matrix least-squares techniques with anisotropic thermal parameters and final converged for $F_o^2 \geq 2\sigma(F_o^2)$. The crystal powdered samples were prepared and irradiated by a Q-switched Nd:YAG solid-state laser (1064 nm, 10 kHz, 10 ns), respectively. Weak green light (frequency-doubled output) emitted from the samples, which further prove that both compounds are noncentrosymmetric. The structures were examined using the *Adsym* subroutine of PLATON.[11] For CGP, the Flack parameter was refined and converged to 0.470(14), which indicates that the crystal is racemically (inversion) twinned at an approximately 50% ratio. Crystallographic data and structural refinements for the two compounds are summarized in Table 1 and important bond lengths are listed in Table 2. The atomic coordinates and isotropic displacement coefficients are listed in Table S1 in the ESI†.

The purity of the polycrystalline samples was investigated by powder X-ray (XRD) studies. Data were obtained on a Bruker D2 PHASER diffractometer with Cu Kα radiation (λ = 1.5418 Å) at room temperature. The 2θ range was 10–70 ° with a step size of 0.02 ° and a fixed counting time of 1 s per step.

Spectral measurements

The IR spectroscopy was measured on a Shimadzu IR Affinity-1 spectrometer in the 500−4000 cm^{-1} range with a resolution of 4 cm^{-1}. The sample was mixed thoroughly with dried KBr (5 mg of the sample and 500 mg of KBr). The UV−vis-NIR diffuse-reflectance data were collected with a SolidSpec-3700DUV spectrophotometer using polytetrafluoroethylene as a standard in the wavelength range from 190 to 2600 nm. Photoluminescence (PL) and photoluminescence excitation (PLE) spectra of the powder phosphors were measured using a Scinco FS-2 fluorescence spectrophotometer equipped with a 150W continuous Xenon light source and a R928 PMT detector for emission.

Table 1 Crystal data and structural refinements for the two compounds.

Compound	$Cs_6Y_2(PO_4)_4$	$Cs_6Gd_2(PO_4)_4$
Formula weight ($g\cdot mol^{-1}$)	1355.16	1491.84
Crystal system	Monoclinic	
Space group	$P2_1$ (No. 4)	
a (Å)	10.1897(5)	10.2819(4)
b (Å)	10.3703(5)	10.4257(4)
c (Å)	10.5504(5)	10.5785(4)
β (deg)	107.526(3)	107.649(2)
Volume ($Å^3$)	1063.11(9)	1080.60(7)
Z	2	
D_{calcd} ($g\ cm^{-3}$)	4.233	4.585
Absorption coefficient (mm^{-1})	15.923	16.406
Crystal size (mm)	0.12 × 0.10 × 0.07	0.23 × 0.12 × 0.06
GOF on F^2	0.966	1.067
R_1, wR_2 $[F_o^2>2\sigma(F_o^2)]^a$	0.0277, 0.0450	0.0245, 0.0531
R_1, wR_2 (all data) ^{a}	0.0327, 0.0468	0.0264, 0.0542
Largest diff. peak and hole ($e\cdot Å^{-3}$)	0.810 and – 0.965	0.755 and – 1.466
Absolute structure parameter	– 0.018(8)	0.470(14)

^{a} $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/ \Sigma w F_o^4]^{1/2}$ for $F_o^2 > 2\sigma(F_o^2)$.

Computational details

The crystallographic data of CYP and CGP determined by single-crystal X-ray diffraction were used to calculate the electronic band structures. The calculations were performed using density functional theory (DFT) based *ab* initio calculations implemented in the CASTEP package.[12] The exchange-correlation effects were treated with the Perdew–Burke−Ernzerhof (PBE) functional within the generalized gradient approximation (GGA) scheme.[13] The interactions between the ionic cores and the electrons were described by the ultrasoft pseudopotentials.[14] The plane-wave cutoff energy was set to 570.0 eV, and the Monkhorst-Pack scheme was set at 3 × 3 × 5 in the primitive cell of the Brillouin zone (BZ), which proved to be an optimal level of the total energy convergence. The following orbital electrons were treated as valence electrons, Cs, $5s^25p^66s^1$; Y, $4d^15s^2$; Gd, $4f^75s^25p^65d^16s^1$; P, $3s^23p^3$; O, $2s^22p^4$. In addition, considering the effect of localized f orbitals in Gd element, the LDA+U method with the on-site orbital dependent Hubbard U energy term was employed.[15] We set different values (3.0, 4.0, 5.0, 6.0, 7.0 and 8.0 eV) of U for the calculation of electronic structure. The results indicated that the electronic structure is non-sensitive to the selected value of U, and the U potential = 7.0 eV was adopted to further investigate the electronic structure and densities of states of CGY (Table S2 in the ESI†). The other parameters and convergent criterions were set by the default values of CASTEP code.

Results and discussion

Structure characterization

X-ray analysis reveals that CYP and CGP are isotypic and crystallize in the same space group $P2_1$ (No. 4); consequently, only the structure of CYP will be discussed in detail as a representation. In the asymmetric unit of CYP, there are six unique cesium atoms, two unique yttrium atoms, four unique phosphorus atoms, and sixteen unique oxygen atoms (Table S1 in the ESI†). Therefore, the formula of CYP are better to be written as $Cs_6Y_2(PO_4)_4$ instead of $Cs_3Y(PO_4)_2$. In general, the crystal structure of CYP features a two-dimensional infinite $[Y_2P_4O_{16}]_n^{6n-}$ layer composed of corner/edge- sharing distorted YO_6 octahedra and PO_4 tetrahedra, and Cs^+ cations are inserted into the void space forming the three-dimensional framework (Fig. 1). In the structure, each P atom is tetrahedrally coordinated by four O atoms, forming a PO_4 tetrahedron with P-O bond lengths ranging from 1.505(7) to 1.564(6) Å. There are two symmetry-independent Y atoms coordinated by six O atoms forming distorted YO_6 octahedra with Y−O distances ranging from 2.183(6) to 2.373(6) Å. It is noted that each YO_6 octahedron is connected with five corner-sharing PO_4 tetrahedra and one edge-sharing PO_4 tetrahedron (Fig. 1a), and then all YO_6 octahedra and PO_4 tetrahedra are further linked to generate a two dimensional $[Y_2P_4O_{16}]_n^{6n-}$ layer (Fig. 1b). The IR spectrum of CYP reveals several absorption bands in the range of 1240–540 cm^{-1} on account of stretching and bending vibrations of the P−O bonds (Fig. S1 in the ESI†), which are similar to those of other phosphates.[2c] The absence of the P−O−P modes indicates that no bridging oxygen atoms (e.g. the diphosphate groups) are present. There are six different Cs atoms surrounded by O atoms forming distorted CsO_n (n = 8, 10 and 11) polyhedra (Fig. S2 in the ESI†), with Cs−O bond distances ranging from 2.928(6) to 3.677(6) Å (an average bond distance of 3.282 Å, with the upper limit of 3.7 Å). In connectivity terms, the structure of CYP may also be written as $\{2[YO_{6/2}]^{3-}4[PO_{3/2}O_{1/1}]^0\}^{6-}$ with the charge balanced by the Cs^+ cations (Fig. 1c). In addition, based on bond valence calculations,[16] the bond valence sums (BVS) for Cs, Y and P atoms are in the range of 0.97–1.0, 3.1–3.2 and 4.7–5.0, in accordance with their normal valences + 1, + 3 and + 5, respectively.

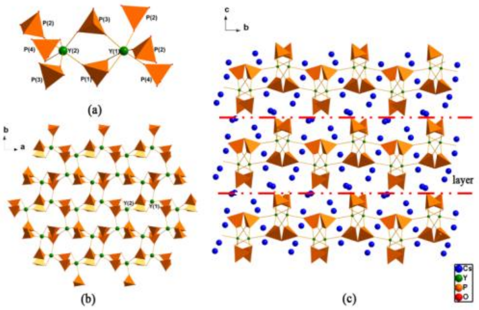


Fig. 1 View of crystal structure of CYP (PO_4 tetrahedra, yellow).

Table 2 Selected bond distances (Å) and bond valence sums (V_i) for the two compounds.

	CYP		
Y(1)-O(1)	2.186(6)	P(2)-O(4)	1.516(6)
Y(1)-O(3)	2.225(6)	P(2)-O(2)	1.518(7)
Y(1)-O(11)	2.225(6)	P(2)-O(3)	1.535(6)
Y(1)-O(8)	2.240(6)	P(2)-O(1)	1.543(6)
Y(1)-O(15)	2.338(6)	$V_{P(2)}$	4.91
Y(1)-O(14)	2.373(6)	P(3)-O(7)	1.506(7)
$V_{Y(1)}$	3.10	P(3)-O(8)	1.540(6)
Y(2)-O(5)	2.183(6)	P(3)-O(5)	1.540(6)
Y(2)-O(4)	2.202(6)	P(3)-O(6)	1.550(7)
Y(2)-O(6)	2.203(6)	$V_{P(3)}$	4.84
Y(2)-O(13)	2.226(6)	P(4)-O(10)	1.505(7)
Y(2)-O(12)	2.319(6)	P(4)-O(11)	1.542(6)
Y(2)-O(9)	2.365(6)	P(4)-O(9)	1.546(6)
$V_{Y(2)}$	3.22	P(4)-O(12)	1.564(6)
P(1)-O(16)	1.517(6)	$V_{P(4)}$	4.77
P(1)-O(13)	1.547(6)		
P(1)-O(14)	1.550(6)		
P(1)-O(15)	1.563(6)		
$V_{P(1)}$	4.71		
	CGP		
Gd(1)-O(14)	2.236(8)	P(2)-O(11)	1.510(7)
Gd(1)-O(11)	2.248(6)	P(2)-O(8)	1.524(8)
Gd(1)-O(12)	2.257(7)	P(2)-O(10)	1.536(7)
Gd(1)-O(1)	2.278(6)	P(2)-O(9)	1.553(7)
Gd(1)-O(4)	2.352(7)	$V_{P(2)}$	4.88
Gd(1)-O(6)	2.406(7)	P(3)-O(5)	1.514(7)
$V_{Gd(1)}$	3.25	P(3)-O(7)	1.545(7)
Gd(2)-O(10)	2.228(7)	P(3)-O(6)	1.550(7)
Gd(2)-O(9)	2.235(7)	P(3)-O(4)	1.573(7)
Gd(2)-O(7)	2.253(6)	$V_{P(3)}$	4.69
Gd(2)-O(13)	2.274(6)	P(4)-O(15)	1.511(8)
Gd(2)-O(2)	2.370(7)	P(4)-O(14)	1.522(8)
Gd(2)-O(16)	2.403(7)	P(4)-O(12)	1.525(8)
$V_{Gd(2)}$	3.28	P(4)-O(13)	1.541(6)
P(1)-O(3)	1.517(7)	$V_{P(4)}$	4.95
P(1)-O(1)	1.538(6)		
P(1)-O(16)	1.551(7)		
P(1)-O(2)	1.574(7)		
$V_{P(1)}$	4.70		

The crystal structure of $M_3RE(PO_4)_2$ type compounds depends on both the M and RE cations. On the one hand, compounds with small RE cations may be possible to retain the *Glaserite* structure, such as $K_3Lu(PO_4)_2$[17] and $K_3Sc(PO_4)_2$ (space group $P\overline{3}$);[18] while large RE cations can cause severely distorted REO_6 octahedron leading to lower symmetry structures, such as $K_3Ce(PO_4)_2$[19] and $K_3Sm(PO_4)_2$ (space group $P2_1/m$).[20] On the other hand, variety of structures also arise from the size and different coordination requirements of the M (Na, K, Rb, and Cs) cations when the RE cation is kept fixed. The compounds with large M cations often show reduced symmetry (from trigonal to orthorhombic and monoclinic) along with the rotation of PO_4 tetrahedra.[1a] Compared with other $M_3RE(PO_4)_2$ compounds, CYP and CGP reported in this work crystalize in the space group $P2_1$ with the lowest symmetry among this type of compounds on account of the largest alkali metal cation Cs^+. In addition, CYP and CGP also have double crystallographic unique sites in the asymmetric unit with $Z= 2$. In particular, these two independent RE^{3+} sites in CYP or CGP could be both used as the photoluminescence emission centers.

Spectroscopic studies

UV-vis-NIR diffuse reflectance spectra of CYP and CGP in the region 190–2600 nm are shown in Fig. 2. The reflectance spectra were converted to absorbance using the Kubelka-Munk function.[21] It is clear that both compounds have wide transmission ranges with UV absorption edges around 275 and 280 nm. In addition, the experimental energy gaps of CYP and CGP are 4.51 and 4.43 eV, respectively.

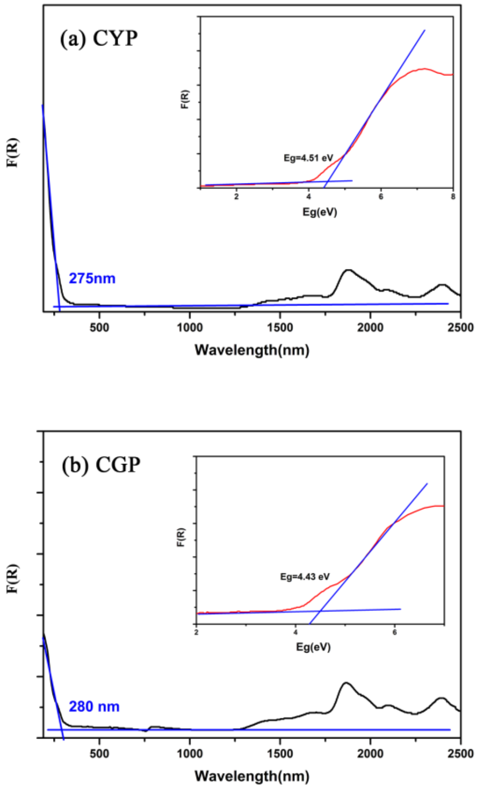
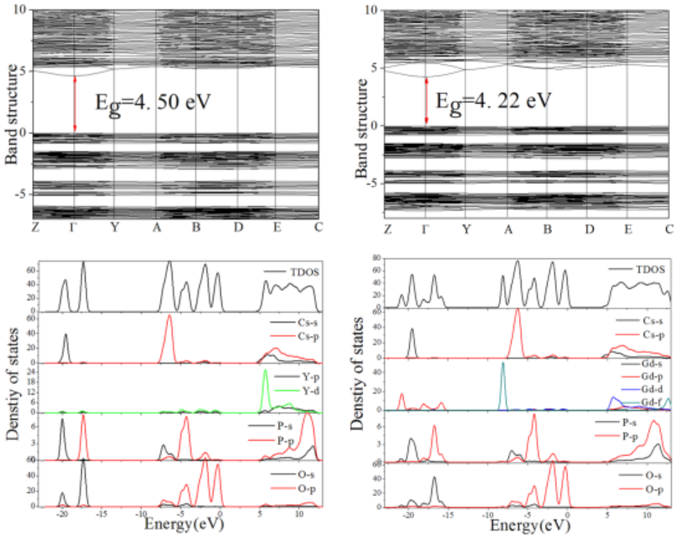


Fig. 2 The UV-vis-NIR diffuse reflectance spectra of (a) CYP, (b) CGP.

Electronic band structures

In order to investigate the structure-property relationship, the electronic structure calculations of CYP and CGP were performed. The calculated energy band structures of CYP and CGP along the high symmetry directions in the BZ are plotted in Fig. 3. For both compounds, their conduction band minimum and the valence band maximum are located at the same point Γ, resulting in direct band gaps with the values of 4.50 and 4.22 eV for CYP and CGP, respectively. The calculated band gaps of these compounds are very close to the experimental band gaps (Fig. 2).

As seen from the total and partial densities of states (TDOS, PDOS) analyses, both compounds have similar electronic structures except for small differences in the Y/Gd contributions. For CYP, the top of the valence band is mostly from contributions of O 2*p* states with small amount of P 3*p* orbitals while the conduction band is mainly made up by Cs 5*s* 5*p* and Y 4*d* states (Fig. 3a). For CGP, the top of the valence band is almost the same with CYP, however, its conduction band is mainly composed of Cs 5*s* 5*p* and Gd 5*d* unoccupied states (Fig. 3b). From the PDOS calculations, we can state that the band gaps of the two compounds are dominated by the hybridizations of O 2*p*, Cs 5*s* 5*p* and Y 4*d* or Gd 5*d* orbitals. The similarity in electronic structures of the two compounds may be ascribed to almost the same coordination environments of Cs^+, Y^{3+}/Gd^{3+}, and P^{5+} cations.



(a) CYP (b) CGP

Fig. 3 Band structures, TDOS and PDOS of (a) CYP, (b) CGP.

Photoluminescence properties

The powder XRD patterns for the prepared polycrystalline samples and phosphors are shown in Fig. 4. The XRD patterns of CYP:0.01Ce^{3+} and CGP:0.01Ce^{3+} are in good agreement with the calculated ones derived from the single-crystal data. No impurities were observed. It is noted that the effective ionic radii for the six-coordinated Ce^{3+} is 1.01 Å, which is very close to those of the six-coordinated Y^{3+} (0.89 Å) and Gd^{3+} (0.94 Å).[22] Therefore, based on the comparison of effective ionic radii of cations and electric charge balances, it would be easy to deduce that the Ce^{3+} doping ions should occupy the Y^{3+} and Gd^{3+} ion sites.

Fig. 5 displays the room temperature PL and PLE spectra of the CYP:0.01Ce^{3+} and CGP:0.01Ce^{3+} phosphors. Both CYP:0.01Ce^{3+} and CGP:0.01Ce^{3+} have broad PLE spectra, covering the spectral range from 240 to 365 nm for the former, and 240 to 380 nm for the later. It can be seen that each excitation spectrum consists of two distinct bands, specifically, a weak one at about 270 nm and a stronger one at 320 nm for CYP:0.01Ce^{3+}, and similarly 276 and 330 nm for CGP:0.01Ce^{3+}. The former weak excitation peaks are attributed to the host absorptions, which consist with the result of UV−vis-NIR diffuse-reflectance spectra (275 and 280 nm for CYP and CGP, respectively). And the later stronger asymmetric peak is due to the transitions of the crystal field splitting of Ce^{3+} 5*d* orbitals and the ground state.[23] The optimal excitation wavelength is 320 nm for CYP:0.01Ce^{3+} and 331 nm for CGP:0.01Ce^{3+}, respectively. Under the optimal excitation, as prepared two phosphors exhibit violet-blue emissions extending from about 340 to 550 nm.

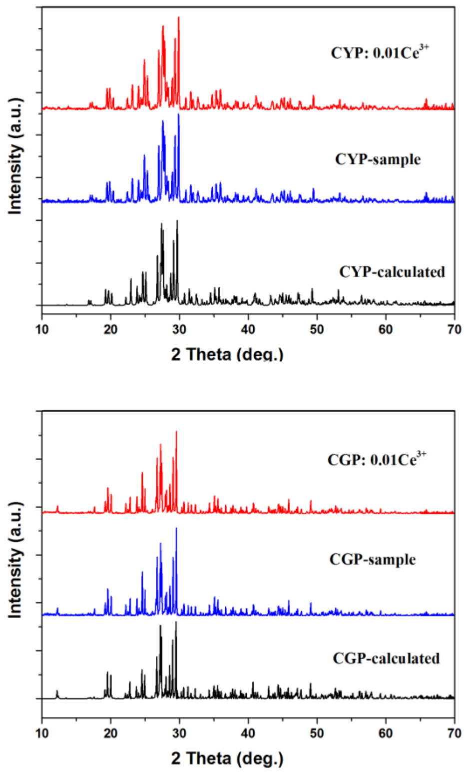


Fig. 4 XRD patterns of (a) CYP and (b) CGP.

Generally, for each site that occupied by Ce^{3+}, the emission spectra should be split into a double band because of the electron transition from the lowest 5*d* excited state to ground 4*f* ($^2F_{7/2}$ and $^2F_{5/2}$) states. As given in Fig. 4, Gaussian-type profiles are used for multi-peak fitting to deconstruct and analyze the asymmetric PL emission bands. For CYP:0.01Ce^{3+}, the PL emission band can be decomposed into four bands centered at 28985 cm^{-1} (345 nm), 26954 cm^{-1} (371 nm), 25575 cm^{-1} (391 nm), and 23923 cm^{-1} (418 nm). The energy difference between the bands A and B is 2031 cm^{-1}, and that for C and D is 1652 cm^{-1}, both of which are close to the theoretical value 2000 cm^{-1} (energy difference between $^2F_{7/2}$ and $^2F_{5/2}$ multiplets).[24]

Similarly, four Gaussian-type bands for PL emission spectrum of CGP:0.01Ce^{3+} are peaked at 25445 cm^{-1} (393 nm), 23640 cm^{-1} (423 nm), 23364 cm^{-1} (428 nm), and 21367 cm^{-1} (468 nm). Further the energy gap from E to F, and G to H is 1805 cm^{-1} and 1997 cm^{-1}, respectively, both of which either show a small difference compared with the theoretical value 2000 cm^{-1}. Therefore, it can be deduced that there are two types of Ce^{3+} luminescent centers in both CYP:0.01Ce^{3+} and CGP:0.01Ce^{3+} systems, originating from two types of six-coordinated Y(1)$^{3+}$ and Y(2)$^{3+}$ for the former, and Gd(1)$^{3+}$ and Gd(2)$^{3+}$ for the later.

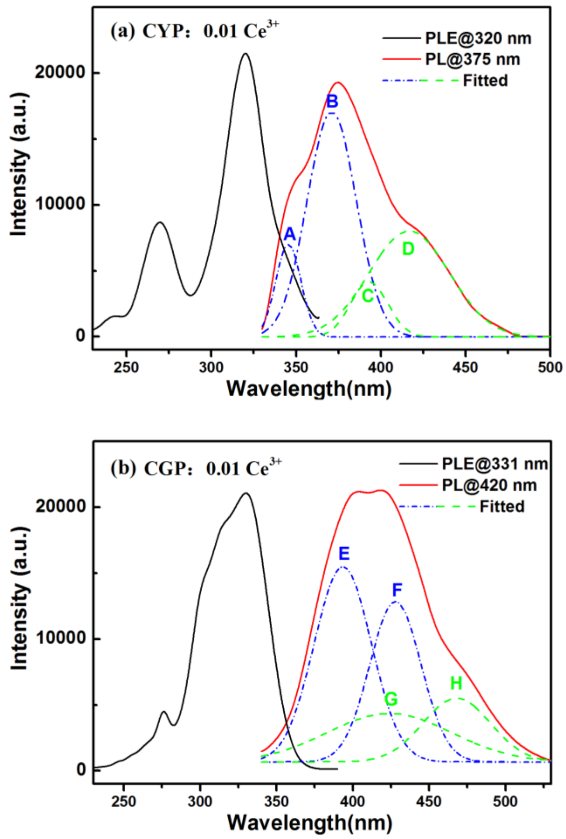


Fig. 5 PL and PLE spectra of (a) CYP:0.01Ce^{3+} and (b) CGP:0.01Ce^{3+}.

Conclusions

In conclusion, two new alkali-rare earth metal phosphates $Cs_6M_2(PO_4)_4$ (RE = Y and Gd), have been successfully synthesized and characterized. These two compounds are isotypic and exhibit two dimensional infinite $[RE_2P_4O_{16}]_n^{6n-}$ layer structures with the Cs$^+$ cations located in the space and aided in charge balance. Their band structures, total and partial densities of states were calculated. Theoretical calculations suggest that these two compounds have direct energy gaps with the value of 4.50 and 4.22 eV for $Cs_6Y_2(PO_4)_4$ and $Cs_6Gd_2(PO_4)_4$, respectively. After structure analysis, Ce^{3+} -doped $Cs_6Y_2(PO_4)_4$ and $Cs_6Gd_2(PO_4)_4$ phosphors were successfully synthesized and their photoluminescence properties have been analyzed. The results indicate that these phosphors have broad excitation bands in the UV area with the maximum intense band at 375 and 420 nm, respectively. In addition, two phosphors also exhibit intense broad violet-blue emissions extending from about 340 to 550 nm. Thus, Ce^{3+} -doped $Cs_6Y_2(PO_4)_4$ and $Cs_6Gd_2(PO_4)_4$ phosphors can be used as candidates for UV-based luminescence materials.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Single crystal XRD data in CIF format (CCDC 1007298 and 1007299), atomic coordinates and equivalent isotropic displacement parameters, calculated band gaps for selected values of U, IR spectra and the coordinate environments of Cs^+ cations. See DOI: 10.1039/b000000x/

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