Incorporating Ce\textsuperscript{3+} into a high efficiency phosphor Ca\textsubscript{2}PO\textsubscript{4}Cl:Eu\textsuperscript{2+} and its luminescent properties

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Abstract: A series of Ce\textsuperscript{3+}, Eu\textsuperscript{2+} and Ce\textsuperscript{3+}/Eu\textsuperscript{2+} doped Ca\textsubscript{2}PO\textsubscript{4}Cl phosphors are synthesized by a high temperature solid-state method. Not only the emission intensity of Ca\textsubscript{2}PO\textsubscript{4}Cl:Eu\textsuperscript{2+} is obviously enhanced by codoping Ce\textsuperscript{3+}, but also the spectral profile of excitation band is almost not influenced. The energy transfer from Ce\textsuperscript{3+} to Eu\textsuperscript{2+} in Ca\textsubscript{2}PO\textsubscript{4}Cl has been validated and proved to be a resonant type via a dipole-dipole interaction. Under the 400 nm radiation excitation, the luminescent intensity of Ca\textsubscript{2}PO\textsubscript{4}Cl:Ce\textsuperscript{3+}, Eu\textsuperscript{2+} is found to be about 200\% as high as that of Ca\textsubscript{2}PO\textsubscript{4}Cl:Eu\textsuperscript{2+}, and 300\% as high as that of BaMgAl\textsubscript{10}O\textsubscript{17}:Eu\textsuperscript{2+}. The thermal quenching property reveals that Ca\textsubscript{2}PO\textsubscript{4}Cl:Ce\textsuperscript{3+}, Eu\textsuperscript{2+} has the excellent characteristics. Therefore, Ca\textsubscript{2}PO\textsubscript{4}Cl:Ce\textsuperscript{3+}, Eu\textsuperscript{2+} may have potential application as a blue-emitting phosphor for white LEDs.

Keywords: Luminescence; Phosphors; Energy transfer; White LEDs; Ca\textsubscript{2}PO\textsubscript{4}Cl:Ce\textsuperscript{3+}, Eu\textsuperscript{2+}

1 Introduction

In recent years, there has been growing importance focused on research in light emitting diodes (LEDs) because of their long operation lifetime, energy-saving feature and high material stability \cite{1}. Therefore, white LEDs are promising candidate to replace conventional incandescent and fluorescent lamps. At present, the most wide used method to obtain white emission is the combination of a blue LED chip and a yellow phosphor YAG:Ce. However, the white LEDs exhibit a high correlated color temperature (CCT≈7750 K) and a poor color rendering index (CRI≈70-80), because they are lack of

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red component \cite{2}. During the past few years, white LEDs fabricated using a near ultraviolet (n-UV) LED (380-420 nm) coupled with red, green and blue phosphors have attracted much attention \cite{3}. The most frequently used blue phosphor for n-UV LED is BaMgAl$_{10}$O$_{17}$:Eu$^{2+}$ (BAM) \cite{4}. However, the absorption of BAM for wavelength above 400 nm is quite poor. Accordingly, it is urgent to develop new blue phosphors that could be effectively excited in the n-UV range especially for wavelength of 400 nm \cite{5-7}. For example, Song et al. investigated the luminescent property of RbBaPO$_4$:Eu$^{2+}$ \cite{8}; Liu et al. synthesized a high efficiency and high color purity blue-emitting phosphor NaSrBO$_3$:Ce$^{3+}$ \cite{9}. Moreover, in order to effectively improve the luminescence of phosphor, the interest in this field arises because the energy transfer from a donor to an acceptor. Actually, the energy transfer from the donor (sensitizer) Ce$^{3+}$ to the acceptor (activator) Eu$^{2+}$ has been already reported. For example, the energy transfer from Ce$^{3+}$ to Eu$^{2+}$ in LiSr$_4$(BO$_3$)$_3$ is studied, and the emission color of phosphor can be tuned by appropriate adjustment of the relative proportion of Ce$^{3+}$/Eu$^{2+}$, and the energy transfer mechanism of Ce$^{3+}$→Eu$^{2+}$ in LiSr$_4$(BO$_3$)$_3$ is the dipole-dipole interaction \cite{10}. Actually, for many compounds, such as SrSi$_2$O$_2$N$_2$, CaSi$_2$O$_2$N$_2$, Ba$_{1.3}$Ca$_{0.7}$SiO$_4$, Sr$_5$Gd(PO$_4$)$_3$, Ca$_9$Y(PO$_4$)$_7$, NaMg$_6$(PO$_4$)$_3$, NaMgPO$_4$, Ca$_6$Gd$_2$(PO$_4$)$_9$O$_2$ and BaMg$_3$(PO$_4$)$_2$, the similar types of Ce$^{3+}$→Eu$^{2+}$ energy transfer are also observed \cite{11-19}. Obviously, the Eu$^{2+}$ emission can be efficiently enhanced by Ce$^{3+}$→Eu$^{2+}$ energy transfer. Hence, the exploration of material can effectively support our demand and guarantee the continuation of progress. Ca$_3$PO$_4$Cl:Eu$^{2+}$ which has the excellent internal and external quantum efficiencies, the intense emission, the high quantum efficiency and excellent thermal stability \cite{20}, and may serve as a potential candidate for n-UV LED. Therefore, in the present work, we tentatively introduced Ce$^{3+}$ into Ca$_3$PO$_4$Cl:Eu$^{2+}$ to enhance its emission intensity. The energy transfer from Ce$^{3+}$ to Eu$^{2+}$ is systematically studied using the
photoluminescence excitation and emission spectra, and lifetimes, and the thermal quenching
property of Ca$_2$PO$_4$Cl:Ce$^{3+}$, Eu$^{2+}$ is also investigated.

2 Experimental

2.1 Sample preparation

A series of Ca$_{2-x-y}$PO$_4$Cl:$x$Ce$^{3+}$,$y$Eu$^{2+}$ (x, y molar concentration) samples are synthesized by a high temperature solid-state method. The initial materials, including CaCO$_3$ (A.R.), CaCl$_2$·6H$_2$O (A.R.), NH$_4$H$_2$PO$_4$ (A.R.), CeO$_2$ (99.99%) and Eu$_2$O$_3$ (99.99%), are weighed in stoichiometric proportion, thoroughly mixed and ground by an agate mortar and pestle for more than 30 min till they are uniformly distributed. The obtained mixtures are heated at 1000°C for 2 h in crucibles along with a reducing atmosphere (5%H$_2$/95%N$_2$), and then are naturally cooled to room temperature. In order to measure the characteristics of the phosphor, the samples are ground into powder.

2.2 Materials characterization

The phase formation is determined by X-ray diffraction (XRD) in a Bruker AXS D8 advanced automatic diffractometer (Bruker Co., German) with Ni-filtered Cu Kα1 radiation ($\lambda$=0.15405 nm), and a scan rate of 0.02°/s is applied to record the patterns in the 2θ range from 10° to 70°. The steady time resolved photoluminescence spectra are detected by a FLS920 fluorescence spectrometer, and the exciting source is a 450 W Xe lamp. The curve fittings are performed on the luminescence decay curves to confirm the decay time. The Commission International de l’Eclairage (CIE) chromaticity coordinates of sample are measured by a PMS-80 spectra analysis system. All measurements are carried out at room temperature.

3 Results and discussion

3.1 Phase formation
The XRD patterns of Ca$_2$PO$_4$Cl:Ce$^{3+}$, Ca$_2$PO$_4$Cl:Eu$^{2+}$ and Ca$_2$PO$_4$Cl:Ce$^{3+}$, Eu$^{2+}$ are measured and a similar diffraction patterns are observed for each sample. As a representative, Fig.1 shows the XRD patterns of Ca$_2$PO$_4$Cl:0.03Ce$^{3+}$, Ca$_2$PO$_4$Cl:0.07Eu$^{2+}$, Ca$_2$PO$_4$Cl:0.03Ce$^{3+}$, 0.07Eu$^{2+}$. Compared the diffraction data with the standard JCPDS card (No.19-0247), and there has no difference between the doped impurity Ca$_2$PO$_4$Cl and the pure Ca$_2$PO$_4$Cl. The uniform diffraction patterns indicate that the phase formation of Ca$_2$PO$_4$Cl is not influenced by a little amounts of Ce$^{3+}$, Eu$^{2+}$, or Ce$^{3+}$/Eu$^{2+}$. Ca$_2$PO$_4$Cl which crystallizes in the orthorhombic system with space group of pbcn(57) and with four formula units per unit cell (N=4), and the dimensions of unit cell are a=0.6185 nm, b=0.6983 nm and c=1.082 nm.$^{[20-25]}$

![XRD Patterns](image)

Fig.1. XRD patterns of Ca$_2$PO$_4$Cl:0.03Ce$^{3+}$, Ca$_2$PO$_4$Cl:0.07Eu$^{2+}$ and Ca$_2$PO$_4$Cl:0.03Ce$^{3+}$, 0.07Eu$^{2+}$. The standard data of Ca$_2$PO$_4$Cl (JCPDS No. 19-0247) is shown as reference.
3.2 Luminescent properties of Ce\(^{3+}\), Eu\(^{2+}\) and Ce\(^{3+}/Eu^{2+}\) in Ca\(_2\)PO\(_4\)Cl

Fig.2a presents Ca\(_2\)PO\(_4\)Cl:0.07Eu\(^{2+}\) has a broad emission band under the 370 nm radiation excitation, and the peak locates at 450 nm which is typically attributed to the \(4f^65d^1\rightarrow4f^7\) electronic dipole allowed transition of Eu\(^{2+}\) ion. Because two different crystallographic sites are available for the divalent Ca\(^{2+}\) ions, one with site symmetry C\(_2\) and the other with site symmetry C\(_S\). Therefore, Eu\(^{2+}\) ions may occupy two different Ca\(^{2+}\) sites\(^{[20]}\). The excitation band is observed to mainly consist of unresolved band due to the \(4f^7\rightarrow4f^65d^1\) transition of Eu\(^{2+}\) ion. When the Eu\(^{2+}\) ions occupy the lattice sites with C\(_2\) or C\(_S\) symmetry in Ca\(_2\)PO\(_4\)Cl, the fivefold degeneracy of the 5d levels is expected in the excitation spectrum. Nevertheless, the dominating bands in the excitation spectrum is difficult to resolve because of serious overlap between 5d levels. The broad excitation band is ascribed to the high covalency of Ca\(_{\text{Eu}^{2+}}\)-Cl bonding and large crystal-field splitting. The inset of Fig.2a shows the emission intensity of Ca\(_2\)PO\(_4\)Cl:Eu\(^{2+}\) as function of Eu\(^{2+}\) doping content, and the optimal doping content is 0.07 mol.

Fig.2b depicts Ca\(_2\)PO\(_4\)Cl:0.03Ce\(^{3+}\) exhibits a strong broad emission band between 320-500 nm under the 334 nm radiation excitation, and the emission peak locates at 367 nm due to the \(4f^55d^1\rightarrow4f^6\) transition of Ce\(^{3+}\) ion. The excitation spectrum shows broad band from 200 to 350 nm, and the peaks locate at 268 nm and 334 nm, respectively, which correspond to the \(4f^1\rightarrow4f^55d^1\) transition of Ce\(^{3+}\) ion\(^{[20-22]}\). The inset of Fig.2b presents the emission spectra of Ca\(_2\)PO\(_4\)Cl:Ce\(^{3+}\) with the different Ce\(^{3+}\) doping content. The emission spectra have no obvious change in the wavelength and band shape with increasing the Ce\(^{3+}\) doping content, which indicated that the crystal-field strength experienced by the activator does not change. In other words, doping into the lattice site does not cause the expansion or shrinkage of the unit cell, as revealed by the XRD data. However,
the emission intensity of Ca$_2$PO$_4$Cl:Ce$^{3+}$ is influenced by the Ce$^{3+}$ doping content, and the optimal doping content is 0.03 mol Ce$^{3+}$, and the concentration quenching effect is also observed. Generally, the trivalent rare earths ions, such as Ce$^{3+}$, substitute for the bivalent alkaline earth, such as Ca$^{2+}$, in the compound, there has the charge unbalance which may result in the formation of defects in the phosphor. Hence the incorporation of alkali metal ions might offset the charge unbalance generated by Ce$^{3+}$ ion substitution for Ca$^{2+}$ ion, reduced the lattice distort, and affected the luminescent properties. Among the radii of Li$^+$, Na$^+$ and K$^+$, there has the slightest difference between Na$^+$ and Ca$^{2+}$ ions, Therefore, Na$^+$ ion may lead to the slightest negative influence on the luminescence of Ce$^{3+}$ in Ca$_2$PO$_4$Cl. Under the 334 nm radiation excitation, the emission spectra of Ca$_2$PO$_4$Cl:0.03Ce$^{3+}$, and Ca$_2$PO$_4$Cl:0.03Ce$^{3+}$, 0.03Na$^+$ are shown in Fig.S1 (Supporting Information). The results present that the two phosphors have the same spectral profile, however, the emission

![Emission and excitation spectra of (a) Ca$_2$PO$_4$Cl:0.07Eu$^{2+}$ and (b) Ca$_2$PO$_4$Cl:0.03Ce$^{3+}$.](image)

The inset: (a) the emission intensity of Ca$_2$PO$_4$Cl:0.07Eu$^{2+}$ as function of Eu$^{2+}$ doping content ($\lambda_{em}$=370 nm); (b) the emission spectrum of Ca$_2$PO$_4$Cl:Ce$^{3+}$ ($\lambda_{ex}$=334 nm).
intensity of Ca$_2$PO$_4$Cl:0.03Ce$^{3+}$, 0.03Na$^+$ is appreciably stronger than that of Ca$_2$PO$_4$Cl:0.03Ce$^{3+}$.

The results indicate that incorporating Na$^+$ into Ca$_2$PO$_4$Cl:Ce$^{3+}$ has no negative influence on the luminescence of Ca$_2$PO$_4$Cl Ce$^{3+}$, to some extent, can enhance its emission intensity. In the present work, the research focuses on the luminescence and energy transfer of Ce$^{3+}$→Eu$^{2+}$ in Ca$_2$PO$_4$Cl. Therefore, the problem of charge compensation is no longer discussed.

![Emission spectra of Ca$_2$PO$_4$Cl:0.03Ce$^{3+}$, yEu$^{2+}$ (λ$_{ex}$=334 nm).](image)

Fig.3. Emission spectra of Ca$_2$PO$_4$Cl:0.03Ce$^{3+}$, yEu$^{2+}$ (λ$_{ex}$=334 nm).

The inset: variation of $\eta_T$ for Ca$_2$PO$_4$Cl:0.03Ce$^{3+}$, yEu$^{2+}$ (y=0-0.1) with the Eu$^{2+}$ doping content.

As shown in Fig. 2, there has an obvious spectral-overlap between the emission spectrum of Ce$^{3+}$ and the excitation spectrum of Eu$^{2+}$, indicating the possibility of energy transfer from Ce$^{3+}$ to Eu$^{2+}$ in Ca$_2$PO$_4$Cl. Under the Ce$^{3+}$ 334 nm excitation peak, the spectra of Ca$_2$PO$_4$Cl:0.03Ce$^{3+}$, yEu$^{2+}$ (y=0-0.1) are measured and shown in Fig.3. With the lower Eu$^{2+}$ doping content, there has both Ce$^{3+}$ and Eu$^{2+}$ emission bands, and the emission intensities of Ce$^{3+}$ decrease with increase the Eu$^{2+}$ doping content. With the higher Eu$^{2+}$ doping content, such as 0.05 mol Eu$^{2+}$, the Ce$^{3+}$ emission disappears, only the Eu$^{2+}$ emission exist in the spectra of Ca$_2$PO$_4$Cl:0.03Ce$^{3+}$, yEu$^{2+}$. The results mean that the energy transfer from Ce$^{3+}$ to Eu$^{2+}$ in Ca$_2$PO$_4$Cl is validated. Fig.S2 (Supporting Information) depicts
the emission spectra of Ca$_2$PO$_4$Cl:0.07Eu$^{2+}$, Ca$_2$PO$_4$Cl:0.03Ce$^{3+}$, 0.07Eu$^{2+}$ and BaMgAl$_{10}$O$_{17}$:Eu$^{2+}$ under the 400 nm radiation excitation. The results obviously present that the luminescent intensity of Ca$_2$PO$_4$Cl:Ce$^{3+}$, Eu$^{2+}$ is found to be about 200% as high as that of Ca$_2$PO$_4$Cl:Eu$^{2+}$, and 300% as high as that of BaMgAl$_{10}$O$_{17}$:Eu$^{2+}$.

Generally, the energy transfer efficiency ($\eta_T$) from a sensitizer to an activator can be expressed according to Paulose et al.\textsuperscript{[29]}

$$\eta_T=1-(I_S/I_{S0}) \quad (1)$$

where $I_{S0}$ and $I_S$ are the luminescent intensities of the sensitizer in the absence and presence of the activator. In fact, for Ce$^{3+}$/Mn$^{2+}$, Eu$^{2+}$/Mn$^{2+}$, Ce$^{3+}$/Eu$^{2+}$ and Ce$^{3+}$/Tb$^{3+}$ codoped phosphors, the energy transfer efficiency can be easily achieved using Eq.(1)\textsuperscript{[30-33]}, generally, the energy transfer efficiency ($\eta_T$) from the sensitizer to the activator gradually increases with increase the activator doping content.

In the present work, In order to well understand the energy transfer process, using Eq.(1), the energy transfer efficiencies ($\eta_T$) Ce$^{3+}\rightarrow$Eu$^{2+}$ of Ca$_2$PO$_4$Cl:Ce$^{3+}$, $y$Eu$^{2+}$ ($y=0-0.1$) are calculated, and shown in the inset of Fig.3. As a result, the $\eta_T$ is found to gradually increase with enhancing the Eu$^{2+}$ doping content. The results mean that the efficient energy transfer Ce$^{3+}\rightarrow$Eu$^{2+}$ exist in Ca$_2$PO$_4$Cl.

For the 450 nm emission of Ca$_2$PO$_4$Cl:0.03Ce$^{3+}$, $y$Eu$^{2+}$, the corresponding excitation spectra are shown in Fig.4. It can be seen from Fig.2, Ca$_2$PO$_4$Cl:Eu$^{2+}$ has an obvious absorption in the range of 300-355 nm, and Ca$_2$PO$_4$Cl:Ce$^{3+}$ presents a strong excitation band from 300 to 340 nm. However, Ca$_2$PO$_4$Cl:Ce$^{3+}$ has weaker absorption in the range of 345-355 nm. Therefore, though the intensity of excitation band (from 330 to 355 nm) increases with enhancing the amount of Eu$^{2+}$ doping content.

In fact, the corresponding excitation band which is common to the $4f^7\rightarrow 4f^55d^1$ transition of Eu$^{2+}$ ion and the $4f^1\rightarrow 4f^55d^1$ transition of Ce$^{3+}$ ion. Hence the increase of intensity (330-355 nm) comes from
the emission of Eu$^{2+}$, not Ce$^{3+}$. In other words, the results mean that the excitation characteristics of Ce$^{3+}$ decreases, and that of Eu$^{2+}$ increases. Especially, there has only the excitation characteristics of Eu$^{2+}$ with further increase the Eu$^{2+}$ doping content, viz., the efficient energy transfer from Ce$^{3+}$ to Eu$^{2+}$ ought to exist in Ca$_2$PO$_4$Cl.

![Excitation spectra](image1)

**Fig. 4.** Excitation spectra of Ca$_2$PO$_4$Cl:0.03Ce$^{3+}$, yEu$^{2+}$ ($\lambda_{em}$=450 nm).

![Decay curves](image2)

**Fig. 5.** Decay curves of Ce$^{3+}$ emission monitored at 367 nm for Ca$_2$PO$_4$Cl:0.03Ce$^{3+}$, yEu$^{2+}$ ($\lambda_{ex}$=334 nm).

To further validate the process of energy transfer, the fluorescence lifetimes, $\tau$, for Ce$^{3+}$ with the
different Eu$^{2+}$ doping content are measured, as a representative, the results of Ca$_2$PO$_4$Cl:0.03Ce$^{3+}$, Ca$_2$PO$_4$Cl:0.03Ce$^{3+}$, 0.01Eu$^{2+}$, Ca$_2$PO$_4$Cl:0.03Ce$^{3+}$, 0.05Eu$^{2+}$ and Ca$_2$PO$_4$Cl:Ce$^{3+}$, 0.1Eu$^{2+}$ are shown in Fig.5 ($\lambda_{em}$=334 nm, $\lambda_{em}$=367 nm). The decay curves are well fitted with a second-order exponential decay mode by Eq.2 $^{[34-36]}$

$$I=I_0A_1e^{-t/\tau_1}+A_2e^{-t/\tau_2}$$  \hspace{1cm} (2)

where $I$ is the luminescence intensity; $A_1$ and $A_2$ are constants; $t$ is the time, and $\tau_1$ and $\tau_2$ are the lifetimes for the rapid and slow decays, respectively. The average lifetimes ($\tau^*$) can be calculated by the formula as follow $^{[34-36]}$

$$\tau^*=\frac{(A_1\tau_1^2+A_2\tau_2^2)}{(A_1\tau_1+A_2\tau_2)}$$  \hspace{1cm} (3)

![Graph](image_url)

**Fig.6.** Variation of $\eta_T$ for Ca$_2$PO$_4$Cl:0.03Ce$^{3+}$, yEu$^{2+}$ ($y=0-0.1$) with the Eu$^{2+}$ doping content.

For Ca$_2$PO$_4$Cl:0.03Ce$^{3+}$, yEu$^{2+}$ ($y=0-0.1$), the calculated average lifetimes ($\tau^*$) are 52.96, 43.69, 35.51, 29.68, 23.89, 17.98, 14.91, 10.02 and 6.87 ns, respectively. The energy transfer efficiency ($\eta_T$) can be calculated using the following equation by Paulose et al. $^{[37-39]}$

$$\eta_T=1-(I_s/I_s0)\approx 1-(\tau_s/\tau_S)$$  \hspace{1cm} (4)

where $\tau_S$ and $\tau_s$ are the decay lifetimes of the sensitizer Ce$^{3+}$ in the absence and presence of the
activator Eu$^{2+}$. With increase the Eu$^{2+}$ doping content, the $\eta_T$ value is calculated and shown in Fig.6. And the energy transfer efficiency from Ce$^{3+}$ to Eu$^{2+}$ gradually increases with enhancing the Eu$^{2+}$ doping content. At 0.1 mol Eu$^{2+}$, the energy transfer efficiency is 87.03%.

On the basis of Dexter’s energy transfer formula for exchange and multipolar interactions, the following relation can be obtained \[^{[40-44]}\]

$$\ln(\eta_0/\eta) \propto C \quad (5)$$

$$\left(\frac{\eta_0}{\eta}\right)^{\alpha/3} \propto C \quad (6)$$

where $\eta_0$ and $\eta$ are the luminescence quantum efficiency of Ce$^{3+}$ in the absence and presence of Eu$^{2+}$, respectively; $C$ is the total doping content of the Ce$^{3+}$ and Eu$^{2+}$. Eq.5 corresponds to the exchange interaction, and Eq.6 with $\alpha=6$, 8, 10 corresponds to the dipole-dipole, dipole-quadrupole, and quadrupole-quadrupole interactions, respectively. Actually, for many codoped phosphors, the energy transfer mechanisms for exchange and multipolar interactions have already been discussed using Eq.5 and 6. For example, Guo et al. investigated the energy transfer mechanism of Eu$^{2+}$/Mn$^{3+}$ codoped Ca$_9$Lu(PO$_4$)$_7$ \[^{[41]}\], Shang et al reported the luminescence and energy transfer of Ce$^{3+}$/Eu$^{2+}$ in Ca$_6$La$_2$(PO$_4$)$_6$O$_2$ \[^{[32]}\]. Therefore, in the present work, the energy transfer mechanism of Ce$^{3+}$/Eu$^{2+}$ in Ca$_2$PO$_4$Cl can also be explored by Eq.5 and 6. Because the value of $\eta_0/\eta$ can be approximately estimated from the correlated lifetime ratio ($\tau_{S0}/\tau_S$), hence Eq.5 and 6 can be changed as follows

$$\ln(\tau_{S0}/\tau_S) \propto C \quad (7)$$

$$\left(\frac{\tau_{S0}}{\tau_S}\right)^{\alpha/3} \propto C \quad (8)$$

The relationships of $\ln(\tau_{S0}/\tau_S) \propto C$ and $\left(\tau_{S0}/\tau_S\right)^{\alpha/3} \propto C$ are illustrated in Fig.7. By consulting the fitting factor $R$, the relation $\left(\tau_{S0}/\tau_S\right)^{6/3} \propto C^{6/3}$ has the best fitting, implying that the dipole-dipole interaction is applied for the energy transfer from Ce$^{3+}$ to Eu$^{2+}$. 
In general, the critical distance ($R_c$) can be calculated by the concentration quenching method. The critical distance $R_{Ce-Eu}$ between Ce$^{3+}$ and Eu$^{2+}$ can be estimated by:

$$R_{Ce-Eu} = 2\left[\frac{3V}{4\pi x N}\right]^{1/3} \quad (9)$$

where $x$ is the sum concentration of Ce$^{3+}$ and Eu$^{2+}$, $N$ is the number of Z ions in the unit cell (for Ca$_2$PO$_4$Cl, $N=4$), and $V$ is the volume of the unit cell (for Ca$_2$PO$_4$Cl, $V=0.46731$ nm$^3$).

The estimated distance ($R_{Ce-Eu}$) for Ca$_2$PO$_4$Cl:0.03Ce$^{3+}$, yEu$^{2+}$ phosphors ($x_c=0.03$, 0.035, 0.04, 0.05, 0.06, 0.07, 0.08, 0.1 and 0.13) are 1.95, 1.85, 1.77, 1.65, 1.55, 1.47, 1.41, 1.31 and 1.20 nm, respectively. The distances between Ce$^{3+}$ and Eu$^{2+}$ become shorter with increasing the Eu$^{2+}$ doping content. $x_c$ is the critical concentration at which the emission intensity of the donor (Ce$^{3+}$) in the presence of the acceptor (Eu$^{2+}$) is half that in the absence of the acceptor (Eu$^{2+}$). Therefore, the critical distance ($R_c$) of energy transfer is calculated to be about 1.77 nm for Ca$_2$PO$_4$Cl:0.03Ce$^{3+}$, yEu$^{2+}$. $R_{Ce-Eu}$ for various Eu$^{2+}$ content levels is much larger than the typical critical distance for the exchange interaction (0.5 nm) [46]. The results indicate that the exchange interaction plays no role in
the energy transfer process for Ca$_2$PO$_4$Cl:0.03Ce$^{3+}$, yEu$^{2+}$. Therefore, the energy transfer between Ce$^{3+}$ and Eu$^{2+}$ exists in Ca$_2$PO$_4$Cl, and the emission intensities of Eu$^{2+}$ are obviously enhanced by the efficient energy transfer from Ce$^{3+}$ to Eu$^{2+}$, which belongs to the multipolar interaction.

3.3 Thermal stability and CIE coordinates Ca$_2$PO$_4$Cl:Ce$^{3+}$, Eu$^{2+}$

![Graph showing temperature-dependent emission spectra of Ca$_2$PO$_4$Cl:0.03Ce$^{3+}$, 0.07Eu$^{2+}$ under 370 nm radiation excitation.](image)

Fig. 8. Temperature-dependent emission spectra of Ca$_2$PO$_4$Cl:0.03Ce$^{3+}$, 0.07Eu$^{2+}$ ($\lambda_{ex}=370$ nm).

Inset: Normalized intensity of Ca$_2$PO$_4$Cl:0.03Ce$^{3+}$, 0.07Eu$^{2+}$ and BAM as function of temperature ($\lambda_{ex}=370$ nm).

For the application of high power LEDs, the thermal stability of phosphor is one of important issues to be considered. For Ca$_2$PO$_4$Cl:0.03Ce$^{3+}$, 0.07Eu$^{2+}$, the temperature dependence of emission spectra under the 370 nm radiation excitation is shown in Fig. 8. The activation energy ($E_a$) can be expressed by [20, 47]

$$\ln(I_0/I) = \ln A - E_a/kT$$  \hspace{1cm} (10)

where $I_0$ and $I$ are the luminescence intensity of Ca$_2$PO$_4$Cl:Ce$^{3+}$, Eu$^{2+}$ at room temperature and the testing temperature, respectively. $A$ is a constant; $k$ is the Boltzmann constant (8.617×10$^{-5}$ eV K$^{-1}$). $E_a$ is achieved to be 0.0114 eV K$^{-1}$. The inset depicts and compares the thermal quenching properties of Ca$_2$PO$_4$Cl:Ce$^{3+}$, Eu$^{2+}$ and BAM. We observed only 6% decay at 100 °C for Ca$_2$PO$_4$Cl:Ce$^{3+}$, Eu$^{2+}$,
as shown in Fig.8, Ca$_2$PO$_4$Cl:Ce$^{3+}$, Eu$^{2+}$ has thermal quenching as good as that of BAM.

Color coordinates are one of the important factors for evaluating phosphors’ performance, and the chromatic standard issued by the Commission Internationale de l’Eclairage in 1931 (CIE 1931). For Ca$_2$PO$_4$Cl:0.03Ce$^{3+}$, 0.07Eu$^{2+}$, the CIE color coordinates are (0.1454, 0.0448). It can be seen that the color coordinates of Ca$_2$PO$_4$Cl:0.03Ce$^{3+}$, 0.07Eu$^{2+}$ are about the blue region. The all results also indicate that Ca$_2$PO$_4$Cl:Ce$^{3+}$, Eu$^{2+}$ may be a potential blue phosphor for the high-LED application.

4 Conclusions

In summary, Ca$_2$PO$_4$Cl:Ce$^{3+}$, Eu$^{2+}$ phosphors are synthesized by the conventional solid state method. Ca$_2$PO$_4$Cl:Ce$^{3+}$, Eu$^{2+}$ can produce two emission bands, which correspond to the 4$^f$5$^d$$\rightarrow$4$^f$ transition of Ce$^{3+}$ ion and the 4$^f$5$^d$$\rightarrow$4$^f$ transition of Eu$^{2+}$ ion, respectively. The energy transfer Ce$^{3+}$$\rightarrow$Eu$^{2+}$ in Ca$_2$PO$_4$Cl has been validated and proved to be a resonant type via the dipole-dipole interaction. The thermal quenching property reveals that Ca$_2$PO$_4$Cl:Ce$^{3+}$, Eu$^{2+}$ has an excellent characteristics. Based on the results, we are currently evaluating the potential application of Ca$_2$PO$_4$Cl:Ce$^{3+}$, Eu$^{2+}$ as a blue-emitting n-UV convertible phosphor.

Supporting Information

Fig.S1, emission spectra of Ca$_2$PO$_4$Cl:0.03Ce$^{3+}$ and Ca$_2$PO$_4$Cl:0.03Ce$^{3+}$, 0.03Na$^+$. Fig.S2, emission spectra of Ca$_2$PO$_4$Cl:0.07Eu$^{2+}$, Ca$_2$PO$_4$Cl:0.03Ce$^{3+}$, 0.07Eu$^{2+}$ and BaMgAl$_{10}$O$_{17}$:Eu$^{2+}$.

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