Effects of charge compensation on red emission in CaYAl$_3$O$_7$:Eu^{3+} phosphor

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Monovalent ions Li$^+$, Na$^+$, and K$^+$, as charge compensators, are introduced into CaYAl$_3$O$_7$: M (M = Eu^{3+}, Ce^{3+}) in this letter. Their crystal phases and photoluminescence properties of different alkali metal ions doped in CaYAl$_3$O$_7$ are investigated. In addition, the influence of charge compensation ion Li$^+$ which has a more obvious role in improving luminescence intensity on CaYAl$_3$O$_7$: Eu^{3+} phosphor is intentionally discussed in detail and a possible mechanism of charge compensation is given. The enhancement of red emission centered at 618 nm belonging to Eu^{3+} is achieved by adding alkali metal ion Li$^+$ under 393-nm excitation.

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Because of high reliability, long lifetime, low energy consumption, and environmentally friendly characteristics, white light-emitting diodes (W-LEDs) have emerged as the most promising solid-state lighting sources to replace conventional incandescent and fluorescent lamps. Yet, commercial phosphors which are combined a blue LED with a yellow phosphor cannot succeed in applications where a true bright white light of high intensity and brightness is desired[1,2]. Alternatively, white light can be produced by using an ultraviolet (UV) LED chip coated with three emitting blue, green, and red (RGB) phosphors. As an essential component in the three-converter (RGB) system, red-emitting phosphors have attracted much interest for several years. As one kind of melilite structure ABC$_3$O$_7$ (A = Ca, Sr, Ba; B = La, Gd, Y; C = Al, Ga), CaYAl$_3$O$_7$ host materials have attracted much attentions because of great advantages in terms of their good stability, cheap raw materials, simple synthesis conditions, and good luminescence properties[3]. Thus we studied Ca$_{1-x}$YAl$_3$O$_7$: xEu^{3+} phosphors in this work, which were expected to be a good candidate for red-emitting phosphors matching the requirements for three-converter system.

However, when Eu^{3+} replaces some lattices of the Ca^{2+} ions, it will make defects form and influence the luminescence center which may reduce emission intensity. The phenomenon is common in other Eu^{3+} doped phosphors: CaMoO$_4$: Eu^{3+}[4], Ca$_3$WO$_6$: Eu^{3+}[5], and so on. Moreover, most applications that employ red oxide phosphors suffer from problems such as low color purity. Therefore, the purposes of this work were to modify imbalance of charge and improve the luminescence efficiency of Eu^{3+}-activated CaYAl$_3$O$_7$ phosphors through the introduction of alkali-metal ions Li$^+$, Na$^+$, and K$^+$. Similar studies have been done to confirm the effects of charge compensation on Eu^{3+} co-doping red phosphors. For instance, Shi et al.[6] studied the effects of Li$^+$, Na$^+$, and K$^+$ on the luminescence behavior of the Eu^{3+}-activated CaWO$_4$ phosphor. Ghildiyal *et al.*[7] reported the charge-compensation phosphor by incorporating Na$^+$ in Ca$_3$(PO$_4$)$_2$: Eu^{3+}. It is found that the alkali-metal ions could not only play a significant role in enhancing the red-emitting components, but also improve the color purity of the red phosphor.

In this letter, we reported our investigation results on luminescent properties of Ca$_{1-0.08}$YAl$_3$O$_7$: 0.04M, 0.04R (M = Eu^{3+}, Ce^{3+}; R = Li$^+$, Na$^+$, K$^+$) systems, in which charge compensation approach was applied. Moreover, the influence of charge compensation ion Li$^+$ which had a more obvious role in improving luminescence intensity on CaYAl$_3$O$_7$: Eu^{3+} phosphor was intentionally discussed in detail. And the red emission enhancement of Ca$_{1-2x}$YAl$_3$O$_7$: xEu^{3+}, xLi$^+$ phosphor was realized by co-doping Li$^+$.

Ca$_{1-0.04}$YAl$_3$O$_7$: 0.04M (M = Eu^{3+}, Ce^{3+}) and Ca$_{1-2x}$YAl$_3$O$_7$: xM, xR (M = Eu^{3+}, Ce^{3+}; R = Li$^+$, Na$^+$, K$^+$) samples were prepared by a simple combustion reaction. The starting materials Ca(NO$_3$)$_2$·4H$_2$O (A.R), Al(NO$_3$)$_3$·9H$_2$O (A.R), Y(NO$_3$)$_3$·6H$_2$O (A.R), Ce(NO$_3$)$_3$·6H$_2$O (A.R), Eu$_2$O$_3$ (99.99%), LiNO$_3$ (A.R), NaNO$_3$ (A.R), KNO$_3$ (A.R), and NH$_2$CH$_2$COOH (A.R) were used for preparation of the phosphor. The appropriate additive ratio of NH$_2$CH$_2$COOH was added as a fuel making for complete combustion. Eu$_2$O$_3$ was dissolved in deionized water and dilute nitric acid, and Eu(NO$_3$)$_3$ solutions were obtained. All the raw chemical materials were used without further purification. The reagents were added into 20 mL of deionized water with stirring to form a transparent and homogeneous solution. After stirring for about 30 min, the resultant solution was transferred into an evaporation pan to dry at 95 °C. Subsequently the mixture was rapidly heated to 300 °C and an auto combustion process took place yielding a yellowish fluffy precursor. The as-prepared precursor was calcined at 850 °C in air without reducing atmosphere.

The phases of the obtained samples were identified by X-ray powder diffraction (XRD) with Cu Kα (λ = 0.154060078 nm) radiation at a scanning step of 0.02^o in the 2θ range from 10 °C to 90 °C, operated at 40 kV and 40 mA (Bruker D8-Advance). The photoluminescence

(PL) spectra were measured with a HITACHI F-7000 fluorescence spectrophotometer, using a static 150-W Xe lamp as the excitation source. All the measurements were carried out at room temperature.

Figure 1(a) exhibits the results of the refinement of XRD patterns of $CaYAl_3O_7$ with the as-obtained fit parameter $\chi^2 =1.22$ and $R_{wp} =14.28\%$. The black line and red crosses depict the observed and calculated patterns, respectively. From the Rietveld refinement results, all the diffraction peaks can be indexed to a pure tetragonal structure of $CaYAl_3O_7$ without the presence of any extra phase, in good agreement with JCPDS 49-0605[8]. Furthermore, the XRD patterns of the typical Eu^{3+}-doped $CaYAl_3O_7$ phosphors in the absence and presence of alkali-metal ions are shown in Fig. 1(b). All phosphor powders fundamentally maintain the characteristics of $CaYAl_3O_7$, which is not greatly affected by doping with Eu^{3+} ions and alkali-metal ions.

In order to further understand the crystal structure and substitution of RE ions in $CaYAl_3O_7$ host, Fig. 2 presents the crystal structure of $CaYAl_3O_7$ emphasizing the AlO_4^{5-} tetrahedra and the coordination environment of cations (Ca^{2+} and Y^{3+}). Furthermore, the refined residual factors and unit cell parameters are summarized in Table 1. The compound $CaYAl_3O_7$ crystallizes in the tetragonal system with space group: P -421 m as mentioned above. In the unit cell ($Z = 2$) of $CaYAl_3O_7$, Ca^{2+} and Y^{3+} atoms occupy only the 4e positions, and the crystallographic sites of Ca^{2+} and Y^{3+} with 6-fold coordination are the same. Half of the 4e sites are expected to be filled by Y atoms, the other half by Ca/Eu atoms. It is also found that eighteen AlO_4^{5-} tetrahedral groups sharing edges or corners arrange averagely in (000) and (001) crystal face respectively, which forms alternating layers with Ca^{2+} and Y^{3+} cations, as shown in Fig. 2. These alternating layers of Ca^{2+}/Y^{3+} (or Eu^{3+}) are very
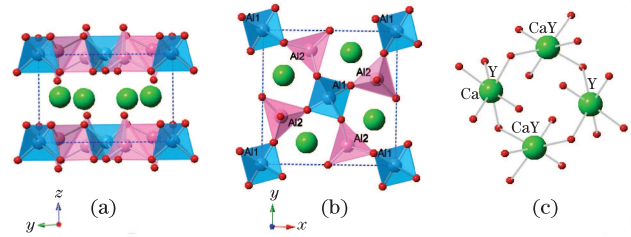
Fig. 2. (Color Online) (a) and (b) Unit cell representation of the crystal structure of $CaYAl_3O_7$. Green, light blue and red spheres represent Ca/Y, Al, and O atoms, respectively. (c) Coordination geometry of $(Ca/Y)O_6$ is depicted.

Table 1. Refined Structural Parameters for $CaYAl_3O_7$

Atom	#	Wyckoff Symbol	x	y	z
Ca	1	4e	0.33968(7)	0.16032(8)	0.5127(2)
Y	1	4e	0.33968(7)	0.16032(8)	0.5127(2)
Al1	1	2a	0	0	0
Al2	2	4e	0.1437(2)	0.3563(2)	0.9574(3)
O1	1	2c	0.5	0	0.190(1)
O2	2	4e	0.1407(6)	0.3593(3)	0.2995(8)
O3	3	8f	0.0916(6)	0.1603(5)	0.7997(6)

important in the development of highly efficient phosphors using the direct excitation band from the excited $^5D_0$ level to the ^7F_J ($J = 0 - 6$) levels of the $4f^6$ configuration in Eu^{3+}[9].

Figure 3 shows the relative emission intensity as a function of dopants Li^+, Na^+, and K^+ in Eu^{3+}-activation $CaYAl_3O_7$ phosphors. The lines corresponding to transitions of Eu^{3+} from the excited $^5D_0$ level to the $^7F_1$ (598 nm), $^7F_2$ (618 nm), $^7F_3$ (656 nm), and $^7F_4$ (703 nm) levels of the $4f^6$ configuration were observed in all emission spectra of $Ca_{1-0.08}YAl_3O_7$: $0.04Eu^{3+}$, $0.04R$ ($R = Li^+$, Na^+, K^+) upon 393 nm excitation. The changes in the relative intensity of the emission spectra with different charge compensation approaches can be observed, especially the main emission lines $^5D_0 \rightarrow {}^7F_2$ transition of Eu^{3+} at 618 nm. By comparing the four curves in Fig. 3, it can be found that the relative emission intensity at 618 nm in alkali-metal ions co-doped materials is higher than that of $Ca_{1-0.04}YAl_3O_7$: $0.04Eu^{3+}$[10].

To further demonstrate the influence of different alkali-metal ions on the rare earth ions emission in $CaYAl_3O_7$ host, the emission spectra of Ce^{3+} ion-doped $Ca_{1-2x}YAl_3O_7$: xCe^{3+}, xR ($R = Li^+$, Na^+, K^+) where $x = 0.04$ are also depicted in the Fig. 4. The PL intensity of the blue emission with Li, Na, and K ions doped is greatly enhanced compared with pure $CaYAl_3O_7$: Ce^{3+} phosphors, of which the effect of Li-doping is the most significant. The different effects of doped Li^+, Na^+, and K^+ ions on luminescence property of $CaYAl_3O_7$: Ce^{3+} phosphors can be ascribed to diversity in ionic radius. Considering that Li^+ has the shortest ionic radius (0.0590) of the three ($r_{Na}^+ = 0.0990$ nm, $r_K^+ =0.1370$ nm),
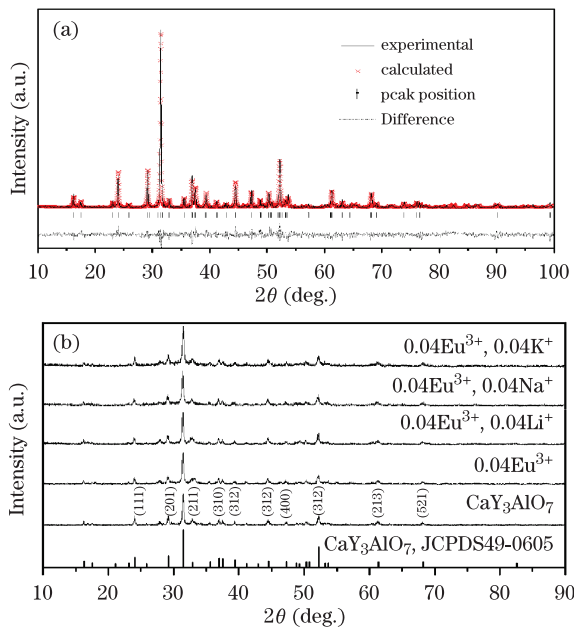

Fig. 1. (a) Rietveld refinement XRD patterns of $CaYAl_3O_7$ at room temperature; (b) XRD patterns of the typical Eu^{3+}-doped $CaYAl_3O_7$ phosphors with and without Li^+, Na^+, and K^+.

it is suggested to get into Ca^{2+} cells ($r_{Ca}^{2+} = 0.1000$ nm) more easily which creates a more effective influence on the emission of Ce^{3+} ions. Thus, the relative emission intensity of $CaYAl_3O_7$: Ce^{3+} doped with different charge compensators is varied. And apparently, the influence of alkali-metal ions on Ce^{3+} is more distinct comparing with that of Eu^{3+}, which can be attributed to 4f-5d transitions of Ce^{3+} is more sensitive to the crystal field than the 4f-4f transitions of Eu^{3+}[11].

Figure 5 presents the emission spectra of $Ca_{1-x}YAl_3O_7$: xEu^{3+} and $Ca_{1-2x}YAl_3O_7$: xEu^{3+}, xLi^+ ($x = 0.01$–0.13) samples by exciting at 393 nm, which quantifies the red emission enhancement resulting from charge compensation. As is shown in Fig. 5, with Li^+ concentration increasing, the red-emitting intensity of Eu^{3+} first increases and then reaches a maximum value when the Li^+ concentration is equal to that of Eu^{3+} (0.10 mol). In order to clarify the influence of Li^+ concentration as a function on luminescence performance, the emission intensity of $Eu^{3+5}D_0-^7F_2$ (618 nm) transition is shown in Fig. 6. As is shown in Fig. 6, the intensity in 618 nm peak at $Li^+ =0.10$ is almost 10 times for the lowest intensity sample ($Li^+ =0.01$) and increased by 25% comparing with that of the phosphor without charge compensation, $Ca_{1-0.04}YAl_3O_7$: $0.04Eu^{3+}$. In addition, the color purity of the red emitting phosphor in our work is up to 0.815539 by introducing 0.10

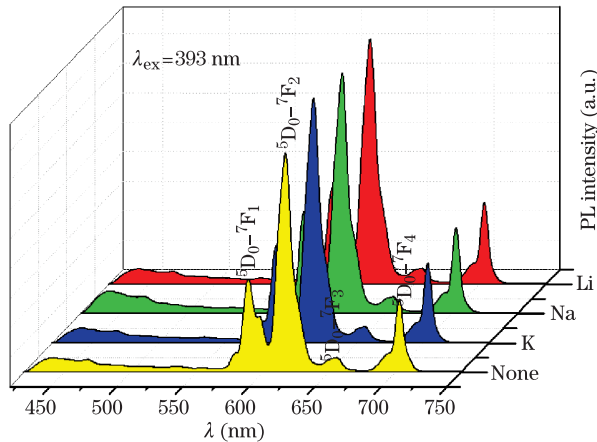Fig. 3. Emission spectra of $Ca_{1-0.04}YAl_3O_7$: $0.04Eu^{3+}$ and $Ca_{1-0.08}YAl_3O_7$: $0.04Eu^{3+}$, $0.04R$ ($R = Li^+$, Na^+, K^+) phosphors excited at 393 nm.
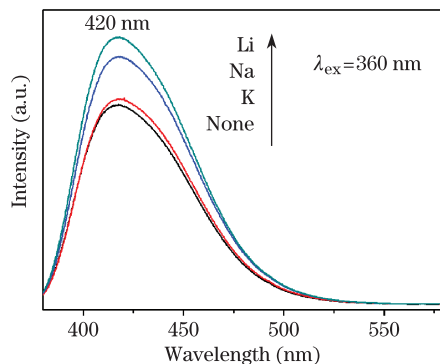
Fig. 4. Emission spectra of $Ca_{1-0.04}YAl_3O_7$: $0.04Ce^{3+}$ and $Ca_{1-0.08}YAl_3O_7$: $0.04Ce^{3+}$, $0.04R$ ($R = Li^+$, Na^+, K^+) phosphors excited at 360 nm.
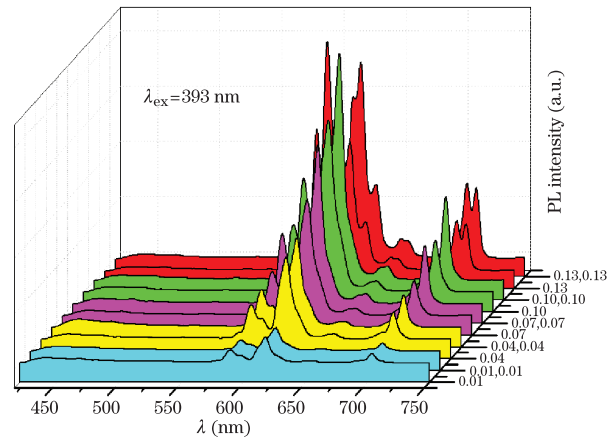
Fig. 5. Emission spectra ($\lambda_{ex} = 393$ nm) of $Ca_{1-x}YAl_3O_7$: xEu^{3+} and $Ca_{1-2x}YAl_3O_7$: xEu^{3+}, xLi^+ phosphor samples ($x = 0.01$, 0.04, 0.07, 0.10, and 0.13).
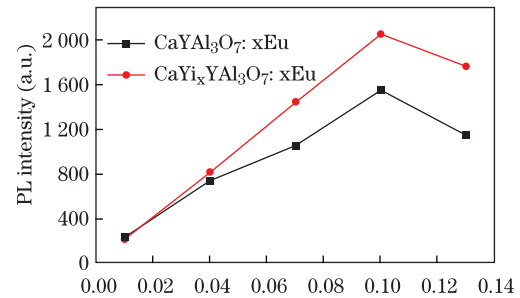

Fig. 6. Dependence of emission intensity corresponding to $^5D_0-^7F_2$ transition on Eu^{3+} and Li^+ concentration, respectively.

mol Li^+ comparing with 0.789341 in 0.10 mol Eu^{3+} singly doped phosphors. The result indicates that Li^+ charge compensation can not only enhance the relative intensity but also be advantageous to the improvement of the phosphor color purity[12]. Based on the above analysis, a possible mechanism of charge compensation was discussed in detail below.

For materials in which the trivalent activator like Eu^{3+} substitutes a divalent host cation, such as Ca^{2+}, might form defects and destroy the lattice that in turn reduce the emission intensity. So charge compensation is needed to change the coordination conditions for Eu^{3+}, balance out the defects, reduce the crystal symmetry and break the parity-selection rules of $^5D_0-^7F_2$ electric dipole transition to achieve the enhancement of Eu^{3+} emission[13].

In general, there are two possible mechanisms in charge compensation system:

(a) two Ca^{2+} ions are replaced by one Eu^{3+} ions and one charge compensator ion[14],

$$2Ca_{Ca}^* \rightarrow Eu_{Ca}^\bullet + R_{Ca}'(R = Li/Na/K), \qquad (1)$$
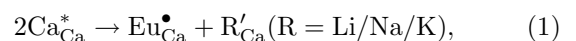
(b) the charge compensation is provided by a calcium vacancy (V_{Ca}''),

$$3Ca_{Ca}^* \rightarrow 2Eu_{Ca}^\bullet + V_{Ca}''. \qquad (2)$$
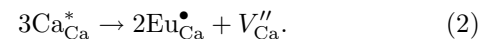
In our work, we synthesis samples and descript optical properties according to the stoichiometric ratio 2:1:1 of

Ca^{2+}, Eu^{3+}, and R^+ ($Ca_{1-2x}YAl_3O_7$: xEu^{3+}, xR^+), which conforms to Eq. (1). Furthermore, long-lasting luminescence properties, which can be observed when it meets Eq. (2), haven't been monitored in this work. Thus, we propose the charge compensation pattern in these phosphors is Eq. (1). When a trivalent metallic ion Eu^{3+}, is incorporated into a host lattice and substitutes for a divalent metallic ion Ca^{2+}, the monovalent-ion Li^+ substitution would lead to charge balance as well as a reduction in Ca^{2+} vacancy concentration[15]. As a result, the sub-lattice structure around the luminescent center is distorted, which adjusts their relative emission intensity and makes red emission enhancement possible.

In conclusion, $CaYAl_3O_7$: M (M = Eu^{3+}, Ce^{3+}) phosphors with and without alkali-metal ions (Li^+, Na^+, and K^+) are successfully prepared through combustion method at 850 °C. Spectral analysis indicated that luminescence intensity in $CaYAl_3O_7$: Eu^{3+} is enhanced with the help of Li^+, Na^+, and K^+ ions. Further study showes that the red emission intensity of $CaYAl_3O_7$: Eu^{3+} phosphors can be significantly improved by 25% with increasing Li^+ concentration up to 0.10, the mechanism for this is suggested to charge compensation. Therefore, $CaYAl_3O_7$: Eu^{3+}, Li^+ phosphors can be a potential candidate for the red-emitting phosphors of W-LEDs.

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