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COMMUNICATION

Breakdown of the geometry restriction of crystallographic site on the valence state of Eu in CaGdAlO₄: realization of white emission from Eu singly-doped phosphors

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We demonstrate a strategy to manipulate the valence state of Eu in CaGdAlO₄ based on breakdown of the geometry restriction on the activators, which would shed light on the exploration of novel phosphors for white light emission diodes (WLEDs).

Considering the global issues of energy demand and climate deterioration, solid-state lighting (SSL) technique has become a promising alternative to conventional incandescent and fluorescent lamps on the illumination.1-3 As the mainstream in SSL, phosphors-converted white light-emitting diodes (pcWLEDs) have aroused fast growing interests because of their merits of high efficiency, long lifetime, environmental friendliness and energy saving.4-7 Thus, phosphors applying to WLEDs are expected to have good performances including suitable excitation range, high quantum yield, chemical stability and low thermal quenching. So, the development of novel phosphors is critical for advanced technological applications.8-10

Eu, as the most widely used activator, has been playing an indispensable role in modern lighting and display fields due to the fact that both Eu³⁺ and Eu²⁺ can function as an emission center in the host lattice.11-14 Eu³⁺ ions mainly show characteristic parity-forbidden 4f-4f transitions of ¹D₂→²F₇ (J = 0,..,4), resulting a red emission. While the line emission and color characteristics of Eu³⁺ ions are promising for WLEDs, the low oscillator strength (about 10⁻⁶) would restrict their applications due to the low absorption efficiency.4 Eu³⁺ activated phosphors usually have broad excitation band and tunable emission colors ranging from blue to deep red because the 4f-5d transitions of Eu²⁺ ion are parity-allowed, which is more suitable for WLEDs application.15,16 Obviously, calcination of the raw materials at high temperature under a reducing atmosphere is the easiest way to reduce Eu³⁺ to Eu²⁺. However, the optical properties of activators are sensitive to their local environment including the crystal structure and crystallographic site size, which would hinder the valence transform feasibility to some extent.17-21 Thus, how to break down the geometry restriction on the valence state of Eu is crucial to optimizing its optical properties for future applications. In addition, majority of research has been dedicated to using the principle of energy transfer (ET) from sensitizer (Eu³⁺ or Ce³⁺) to activator (Tb³⁺ or Mn²⁺) for generating white light. It is unavoidable that energy is consumed during the ET process, which would decrease the WLEDs efficiency.22-25 Thus, it is a promising strategy of combine intrinsic transitions of the Eu ion from different valence states in a single host lattice directly to produce white light, based on the characteristic emissions of Eu²⁺ from blue to green and that of Eu³⁺ from orange to red.

Herein, we design and control the valence state of Eu in CaGdAlO₄ via release the geometry restriction on activators through the replacement of Al³⁺-Gd⁴⁺ by Si⁴⁺-Ca²⁺. Rietveld refinements and detailed PL measurements have been performed on the synthesized samples, and lead to the following conclusions:26 (1) Direct reduction of Eu³⁺ to Eu²⁺ under a reducing atmosphere is not realized in CaGdAlO₄ owing to the compression of Ca³⁺ sites; (2) Incorporation of Si⁴⁺-Ca²⁺ into the CaGdAlO₄ host to replace Al³⁺-Gd⁴⁺ has been attempted to expand the activator site, then fulfill the reduction of Eu³⁺ to Eu²⁺, because Si⁴⁺ has a smaller radius than Al³⁺ and Ca²⁺ replacing Gd⁴⁺ can achieve charge compensation in the whole structure; (3) Following this mechanism, Ca₀.₉₀ₓ,Gd₀.₁₀ₓAl₀.₈₀ₓSi₀.₂₀ₓO₄: Eu (x = 0-0.25) phosphors present tunable emission colors from coexistence luminescence of Eu²⁺ and Eu³⁺, which holds great promise for application in WLEDs.

Fig. 1 (a) The Rietveld refinement to XRD pattern for CaGdAlO₄: 0.01Eu³⁺ sample (b) Typical crystal structure of CaGdAlO₄ and the Al³⁺ and Ca²⁺/Gd⁴⁺ sites are depicted with six- and nine-coordination with oxygen atoms, respectively.
The samples of Ca$_{0.99-x}$Gd$_x$Al$_2$Si$_2$O$_{12}$: Eu$_{0.01}$ (x = 0.0-0.25) were prepared by conventional high temperature solid state reaction process under a reducing atmosphere of N$_2$ (90%) and H$_2$ (10%). Fig. 1a describes the results of Rietveld refinement for CaGdAlO$_2$: 0.01Eu$^{3+}$ sample. The final refinement converged with weighted profiles of $R_p = 2.34\%$ and $R_wp = 3.29\%$, indicating a good quality of fit. As the crystallographic data shown in Table S1, CaGdAlO$_2$ belongs to tetragonal crystal system with space group I$4/mmm$ (No. 139). The coordination numbers (CNs) for Ca$^{2+}$/Gd$^{3+}$ and Al$^{3+}$ are 9 and 6, respectively, which means there is only one site for Ca$^{2+}$/Gd$^{3+}$ to occupy with the composition ratio of 1:1. It is obvious that the (Ca/Gd)O$_6$ polyhedron is compactly surrounded by AlO$_6$ octahedrons to form an cage structure due to the rigid framework of CaGdAlO$_2$ as displayed in Fig. 1b.

Fig. 2 presents the photoluminescence excitation (PLE) and emission (PL) spectra of CaGdAlO$_2$: 0.01Eu$^{3+}$. Monitored at 624 nm, the PLE spectrum reveals a broad band in the range of 200-350 nm related to the charge transfer band (CTB) of O$_2$-Eu$^{3+}$ with some weak peaks in the range of 350 to 450 nm due to the 4f-4f transitions of Eu$^{3+}$. The characteristic line emissions under 278 nm excitation can be assigned to forced electric dipole transitions ($D_2^0$-$F_0$) of Eu$^{3+}$, producing a red emission as the ionic potential ($\phi$), which can be calculated from the attractive force of the central cations towards the anions can be roughly evaluated by the photoelectric effect ($\varphi = Zr$, where Z is the electric charge number of ion, and r is the ion radius (pm)). Generally, the attractive force of the central cations towards the anions can be roughly evaluated by the ionic potential ($\phi$), which can be calculated from the attractive force of the central cations towards the anions can be roughly evaluated by the ionic potential ($\phi = Zr$, where Z is the electric charge number of ion, and r is the ion radius (pm)).

With the aim to breakdown the limitation, Si$^{4+}$-Ca$^{2+}$ has been incorporated into the CaGdAlO$_2$ host to replace Al$^{3+}$-Gd$^{3+}$, attempting to shrink the AlO$_6$ polyhedron, accompanied by the expansion of Ca$^{2+}$ site, and then realize the reduction of Eu$^{3+}$. Firstly, Rietveld refinement has been performed to reveal the formation of a single phase in Ca$_{0.99-x}$Gd$_x$Al$_2$Si$_2$O$_{12}$: Eu$_{0.01}$ (CGASO: Eu, x = 0.05-0.25) as summarized in Fig. S1 and Table S2. The lattice parameters of intermediate compounds varied linearly with changing x (Fig. S2) obeying the Vegard’s rule.

In addition, the comparison of the Raman spectra of the CGASO: Eu (x = 0, 0.10 and 0.25) samples also indicates that the crystal structure and phonon modes basically would not change with incorporation of Si$^{4+}$-Ca$^{2+}$ (Fig. S3). Furthermore, the (Al/Si)-O bond length decreases with increasing x in CGASO as presented in Fig. 3. Accordingly, the (Ca/Gd)-O bond length is further elongated due to contraction of the (Al/Si)O$_6$ octahedron.
4f5d-4f transition of Eu²⁺ ions under the excitation of 335 nm. As displayed in Fig. S4, a conspicuous overlap of PLE spectrum between Eu³⁺ and Eu²⁺ is found at about 300 nm. Thus, breakdown the geometry restriction on the valence s tate of Eu at selected times have been summarized in Table S3. Taking CGASO: Eu²⁺ efficient PL of Eu²⁺ and Eu³⁺ can be expected to occur simultaneously in CGASO host under the 300 nm excitation, which is confirmed by the PL spectrum (the blue line) shown in Fig. S4. In addition, the decay curves of Eu²⁺ and Eu³⁺ in CGASO: Eu₀.01 (x = 0-0.25) have been performed and the lifetimes have been summarized in Table S3. Taking CGASO: Eu₀.01 (x = 0.15) sample for simplicity, the corresponding decay curves could be well fitted to single exponential functions as I = I₀ exp(-t/τ) as presented in Fig. S5, from which the lifetimes of Eu²⁺ and Eu³⁺ were calculated to be 0.863 µs and 1.11 ms, respectively, confirming the coexistence of Eu²⁺ and Eu³⁺ activators. Furthermore, the Eu²⁺ luminescence can be distinctly separated from Eu³⁺ from kinetic perspective through time-resolved spectra. The emission spectra under short delay time (t = 12 µs) show a dominate band from Eu²⁺ (4f⁵5d-4f transition) as shown in Fig. 5. The stronger Eu²⁺ (F′D₂7/2,F₀5/2 transition) emission can be observed by monitoring at a longer delay time (t = 100 µs) after laser excitation along with the disappearance of Eu³⁺ emission, demonstrating that two valence states, +2 and +3, are available for Eu ions. Thus, we can conclude that partial of Eu³⁺ was successfully reduced to Eu²⁺ in CGASO: Eu₀.01 (x = 0.05-0.25) system.

Under the excitation with 300 nm, the PL spectra of CGASO: Eu₀.01 (x = 0-0.25) present both green emission of Eu³⁺ (4f⁵5d-4f, broadband around 500 nm) and red emission of Eu²⁺ (F′D₂7/2,F₀5/2, 594 and 624 nm) simultaneously, as shown in Fig. 6a. This result can be therefore attributed to that Eu³⁺ is partially reduced to Eu²⁺ in CGASO system with increasing x. Besides, the PL intensity of Eu²⁺ increases with increasing x in CGASO system, suggesting that the reduction process becomes easily with the gradual introduction of Si⁺⁺-Ca⁺⁺. Due to the simultaneous presence of emission of Eu³⁺ and Eu²⁺, the CIE coordinates of CGASO: Eu₀.01 (x = 0-0.25) upon 300 nm excitation are regularly shifted from (0.424, 0.308) to (0.282, 0.430) with changing x as depicted in Fig. 6b, and the inset shows the corresponding luminescent photographs. Especially the CIE coordinates (x = 0.372, y = 0.363) of CGASO: Eu₀.01 (x = 0.05) sample locate in white light zone, indicating the potential application for WLEDs. Under excitation with 335 nm, the PL spectra of CGASO: Eu₀.01 (x = 0-0.25) only present the broad band emission of Eu²⁺, producing a bright green emission with the CIE (0.184, 0.474) as the photograph shown inset of Fig. 6c. Similarly, the PL intensity gradually increases with increasing x due to the increasing level of Eu²⁺ as shown in Fig. 6d. In addition, the QY have been listed in Table S3. Furthermore, the influence of doping concentration of Eu ions on the emission intensity of the obtained CaₓGd₁₋ₓAl₁₋ₓSiO₄: Euₓ (x = 0.25, y = 0.005-0.07) phosphor is displayed in Fig. S6. It is apparent that the optimum doping concentration of Eu ions is y = 0.03 and the corresponding QY is 36.5% (λex = 335 nm). Thus, this approach is promising because only a single activator, Eu, generates the multiband even a white light by optical combination of different valences of europium (Eu²⁺ and Eu³⁺ emission).
Because the average bond lengths of Al2O and Ca2O are systematically shortened and elongated simultaneously, which plays a critical role in the reduction of Eu3+ to Eu2+. This research reveals the correlations between structure and property of host lattice, which would facilitate the discovery of novel phosphors. Furthermore, the relative intensity of Eu2+ and Eu3+ could be easily tuned through changing x in Ca0.99-xGd1-xAlxSi1-xO4:Eu3+ (x = 0-0.25), producing tunable emission colors in a wide range including white light, indicative of the potential application in WLEDs.

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**Notes and references**

The geometry restriction of crystallographic site on the valence state of Eu in CaGdAlO$_4$ has been overcome by the replacement of Al$^{3+}$-Gd$^{3+}$ by Si$^{4+}$-Ca$^{2+}$. Tunable colors originated from the coexistence of Eu$^{2+}$ and Eu$^{3+}$ have been obtained in Ca$_{0.99+x}$Gd$_{1-x}$Al$_{1-x}$Si$_x$O$_4$: Eu$_{0.01}$ ($x = 0$-0.25) system.