New localized/delocalized emitting state of Eu\(^{2+}\) in orange-emitting hexagonal EuAl\(_2\)O\(_4\)

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Eu\(^{2+}\)-activated phosphors are being widely used in illuminations and displays. Some of these phosphors feature an extremely broad and red-shifted Eu\(^{2+}\) emission band; however, convincing explanation of this phenomenon is lacking. Here we report a new localized/delocalized emitting state of Eu\(^{2+}\) ions in a new hexagonal EuAl\(_2\)O\(_4\) phosphor whose Eu\(^{2+}\) luminescence exhibits a very large bandwidth and an extremely large Stokes shift. At 77 K, two luminescent sites responsible for 550 nm and 645 nm broadband emissions are recognized, while at room temperature only the 645 nm emission band emits. The 645 nm emission exhibits a typical radiative lifetime of 1.27 \(\mu\)s and an unusually large Stokes shift of 0.92 eV. We identify the 645 nm emission as originating from a new type of emitting state whose composition is predominantly that of localized 4\(f^5\)d character but which also contains a complementary component with delocalized conduction-band-like character. This investigation provides new insights into a unique type of Eu\(^{2+}\) luminescence in solids whose emission exhibits both a very large bandwidth and an extremely large Stokes shift.

Eu\(^{2+}\)-activated phosphors usually exhibit broadband luminescence under external excitations\(^1\)\(^{-3}\). Most of these emissions are attributed to the dipole-allowed 4\(f^5\)d\(\rightarrow\)4\(f^7\) transitions associated with relatively large transition probabilities and short radiative lifetimes (0.4 \(- 1.8 \mu s)\(^1\). In these phosphors, the emissions from the localized 4\(f^5\)d\(_m\) states exhibit typical Stokes shifts in the range of 0.1 \(- 0.5 \) eV.\(^1\)

Besides the normal Eu\(^{2+}\) 4\(f^5\)d\(\rightarrow\)4\(f^7\) transitions, some Eu\(^{2+}\)-activated phosphors exhibit extraordinarily broad emission bands associated with abnormally long radiative lifetimes (typically \(>2 \mu\)s) and extremely large Stokes shift (typically \(>0.6\) eV). This type of emission was described as anomalous luminescence by McClure and Pedrini\(^1\). In their model, the lowest 4\(f^5\)d states of Eu\(^{2+}\) generally lie inside the host conduction band, and the excitation of a Eu\(^{2+}\) ion results in its autoionization, followed by trapping of a conduction electron close to the ionized Eu\(^{2+}\) ion. As a result, a Eu-trapped exciton becomes the emitting state. The transition between the exciton-like state and the 4\(f^7\) ground state of Eu\(^{2+}\) is forbidden by the dipole selection rule in the anomalous luminescent phosphors\(^1\); therefore the transition probabilities for both anomalous luminescence and its corresponding excitation are generally small, resulting in a long radiative lifetime and an weak (often undetectable) exciton excitation band. Moreover, in anomalous luminescent phosphors, the delocalization of the lowest excited state (i.e., the exciton-like state) induces the ligand ions around the Eu\(^{2+}\) to undergo a considerably larger relaxation than for the normal case of Eu\(^{2+}\), which is reflected in the emission spectrum by an extremely large Stokes shift\(^1\).

There is also a special class of Eu\(^{2+}\)-activated phosphors that exhibit the characteristics of both normal 4\(f^5\)d\(\rightarrow\)4\(f^7\) transitions (e.g., large transition probabilities for emission and excitation) and anomalous luminescence (e.g., very large bandwidth and Stokes shift of emission)\(^1\)\(^{-15}\). Based on the relationship between the luminescence and host crystalline structure in this special class of Eu\(^{2+}\)-activated phosphors, Poort et al. attributed this type of emission to 4\(f^5\)d\(\rightarrow\)4\(f^7\) transitions and suggested that the linear chain structure of large cations in the lattice (depending on the values of lattice parameters) contributed to this special luminescence\(^6\). However, with the emergence of more and more novel Eu\(^{2+}\)-activated phosphors, in which the chain structure of the large cations is usually absent in the hosts\(^1\)\(^{-15}\), Poort’s explanation is no longer adequate for this special type of broadband emissions.

In this study, we identify and investigate a Eu\(^{2+}\) broadband emission associated with both a large transition probability and an extremely large Stokes shift (0.92 eV) in a new concentrated europium aluminate phosphor,
hexagonal $\text{EuAl}_2\text{O}_4$ ($h$-EAO). We attribute this unusual emission to the delocalized nature of the excited electrons in the $4f^55d$ emitting level. That is, a ground-state $4f$ electron is excited to the lowest $4f^55d$ state, from where the excited electron may delocalize to the host continuum state according to a small probability, followed by radiative emission from the $4f^55d$ state. This investigation provides new insights into a unique type of $\text{Eu}^{2+}$ luminescence in solids whose emission exhibits both a very large bandwidth and an extremely large Stokes shift.

**Results**

**Photoluminescence (PL) at room temperature and low temperature.** The $h$-EAO phosphor was fabricated by carbothermal reaction and evaporation of a mixture of $\text{Eu}_2\text{O}_3$ and graphite powders at 1450°C in a flowing argon environment in a tube furnace system. The detailed fabrication process was described in ref. 16. The carbothermal reaction produced a weakly reducing environment which facilitated the formation of effective $\text{Eu}^{2+}$ luminescence centers in the concentrated $h$-EAO phosphor$^{16,17}$. The $h$-EAO phosphor is nanoribbon-like with typical widths of 200–1000 nm, thicknesses of 50–300 nm, and lengths of 50–500 μm$^{16}$. The $h$-EAO nanoribbons exhibit a hexagonal space lattice with a new set of lattice parameters of $a = b = 6.15$ Å and $c = 10.57$ Å, as determined by synchrotron X-ray Laue microdiffraction$^{16}$ and further confirmed by synchrotron X-ray microcrystallographic measurements (see Supplementary Information, including Supplementary Table 1 and Supplementary Fig. 1, for the determination of the unit cell structure of $h$-EAO). The X-ray microdiffraction results showed that each nanoribbon in the phosphor is a single crystal with composition $\text{EuAl}_2\text{O}_4$, and no evidence was found to suggest the presence of second phases or inclusions embedded in the single crystals. X-ray absorption near edge structure measurement on $\text{Eu}^{2+}$ edge showed that the Eu ions in $h$-EAO are predominantly in the divalent state, i.e., $\text{Eu}^{2+}$ (ref. 16).

Under blue light or ultraviolet excitation, the $h$-EAO phosphor exhibits intense orange emission. Figure 1a shows the normalized PL emission and excitation spectra of $h$-EAO at room temperature, as well as the low-energy side of the diffuse reflectance absorption spectrum. At room temperature, the shapes of the emission and excitation spectra are independent of the corresponding excitation and monitoring wavelengths, respectively (Supplementary Fig. 2a). The emission spectrum contains a Gaussian-shaped emission band peaking at 645 nm ($\sim 1.93$ eV) with a full width at half maximum (FWHM) of 0.45 eV. The PL excitation spectrum in Fig. 1a contains two excitation bands: a high-energy band peaking at 365 nm ($\sim 3.40$ eV) and a low-energy band peaking at 435 nm ($\sim 2.85$ eV). The low-energy 435 nm excitation band starts at $\sim 540$ nm ($\sim 2.3$ eV), which coincides with the onset of the diffuse reflectance absorption spectrum and conforms to the “mirror image” of the 645 nm emission band (dashed curve in Fig. 1a), indicating that the 435 nm excitation band corresponds to the lowest excited state in the phosphor. Thus, the Stokes shift of the emission can be determined to be 0.92 eV, which is equal to the energy difference between the intensity maxima in the lowest excitation band and the emission band.

In contrast to the room-temperature luminescence, at 77 K the shapes of the emission and excitation spectra become dependent on their respective excitation and monitoring wavelengths (Fig. 1b). A Gaussian-shaped emission band peaking at 645 nm is obtained under 460 nm excitation; the spectral profile of this emission band is similar to that obtained at room temperature except for reduced FWHM of the emission (0.38 eV). Under the excitation of 355 nm light, however, a shoulder appears on the high-energy side of the 645 nm emission band (for comparison, the 645 nm emission spectra acquired at 77 K and 300 K under 355 nm excitation are re-displayed in Supplementary Fig. 2b). The difference between the normalized emission spectra excited under 355 nm and 460 nm is represented by an additional emission band peaked at 550 nm.

**Figure 1 | PL emission and excitation spectra of $h$-EAO phosphor.** (a), Emission (red), excitation (blue), and diffuse reflectance absorption spectra of $h$-EAO phosphor acquired at room temperature. The dashed line curve represents the “mirror image” reflection of the emission spectrum about the zero-phonon line energy $E_0$. (b), Normalized emission and excitation spectra of $h$-EAO acquired at 77 K. The difference between the emission spectra excited by 355 nm and 460 nm is represented by an additional emission band peaked at 550 nm.

**Spectral identification of two $\text{Eu}^{2+}$ luminescent sites.** To confirm the presence of two $\text{Eu}^{2+}$ sites in $h$-EAO, we measured wavelength dependent luminescence decays under the excitation of a 355 nm pulsed laser at 77 K. A set of luminescence decay curves were recorded at 77 K by monitoring emission wavelengths between 550–690 nm in 10 nm steps (Supplementary Fig. 3). Under the assumption that there exist two $\text{Eu}^{2+}$ sites, we fitted the decay curves using a double exponential formula $I(t,\lambda) = A_1(\lambda) \times \exp(-t/\tau_1) + A_2(\lambda) \times \exp(-t/\tau_2)$, where $I(t,\lambda)$ represents the total
emission intensity at time $t$ after the excitation pulse and at the monitoring wavelength $\lambda$: $A_1(\lambda)$ and $A_2(\lambda)$ are the fractional PL emission intensities contributed by Eu$_1$ site and Eu$_2$ site, respectively, at the monitoring wavelength $\lambda$; $\tau_1$ and $\tau_2$ are the luminescence lifetimes of Eu$_1$ site and Eu$_2$ site, respectively. It is expected that once the lifetimes $\tau_1$ and $\tau_2$ are determined, the existence of Eu$_1$ site and Eu$_2$ site can then be confirmed. At the same time, the PL spectral contributions from the two sites can be determined using the $A_2(\lambda)/A_1(\lambda)$ ratios. Our fitting results showed that the luminescence decay curves monitored between 630–690 nm can be well reproduced by a series of monoexponential functions (i.e., $A_1(630–690) = 0$) with the fitted lifetime $\tau_1 = 1.27 \mu$s (Supplementary Fig. 3). As an example, the decay curve monitored at 650 nm and its fitted profile are given in Fig. 2a. In contrast to the monoexponential decay curves obtained between 630–690 nm, the decay curves monitored between 550–620 nm can be well reproduced by a series of double-exponential functions with the fitted lifetime $\tau_2 = 0.57 \mu$s and a fixed $\tau_1$ (1.27 $\mu$s) (Supplementary Fig. 3). The $A_1(550–620)$ and $A_2(550–620)$ values were obtained in the same fitting. As an example, the decay curve monitored at 550 nm and its fitted profile are also shown in Fig. 2a. The $A_2(\lambda)/A_1(\lambda)$ ratios are then plotted as a function of emission wavelengths (550–690 nm) in Fig. 2b (solid ball curve), along with the emission spectra from the two sites at 77 K. The monoexponential decay behavior ($A_2/A_1 = 0$) between 630–690 nm is consistent with the absence of the emission from the Eu$_2$ site in this long-wavelength emission region (Fig. 2b). In the range of 550–620 nm, the $A_2/A_1$ value increases as the wavelength decreases, which corresponds to the increase of the 550 nm emission contribution and the decrease of the 645 nm emission contribution; this verifies the existence of the additional 550 nm emission band from Eu$_2$ site at 77 K.

We attribute the 550 nm emission band and its corresponding excitation spectrum at 77 K (Fig. 1b) to the $4f^{5}5d^{1} \rightarrow 4f^{7}$ transitions of the Eu$^{2+}$ luminescent center (Eu$_2$ site) due to the spectral similarity between the current spectra and the reported spectra of Eu$^{2+}$-activated green aluminate phosphors. However, the lifetime of the 550 nm emission ($\tau_2 = 0.57 \mu$s) is much shorter than the typical radiative lifetimes of the green emissions from the Eu$^{2+}$-activated green aluminate phosphors ($\sim 1.2 \mu$s). This can occur because the 550 nm emission from Eu$_2$ site might be partially quenched by the energy transfer between Eu$_2$ site and Eu$_1$ site even at 77 K. That is, the lifetime of 0.57 $\mu$s at 77 K may not represent the radiative lifetime of Eu$_2$ site. Indeed, the small spectral overlap between the 550 nm emission band (Eu$_2$ site) and the 435 nm excitation band (Eu$_1$ site) at 77 K (Fig. 1) makes it possible for the energy transfer to occur from the Eu$_2$ site to the Eu$_1$ site. Moreover, the decay curve monitored at 650 nm (Eu$_1$ site only) exhibits a build-up at the initial decay stage (0.34–0.46 $\mu$s, the shaded area in the inset of Fig. 2a), while during that same time period the decay curve monitored at 550 nm (dominated by Eu$_2$ site) exhibits a faster decay. The different initial decays at the 650 nm and 550 nm emissions provide unambiguous evidence for energy transfer from the Eu$_2$ site to the Eu$_1$ site. At higher temperature, e.g., room temperature, more efficient energy transfer from the high-energy Eu$_2$ site to the low-energy Eu$_1$ site is expected due to the stronger spectral overlap. Thus, the energy transfer can cause the complete quenching of the 550 nm emission band at room temperature (Fig. 1a).

**Localized/delocalized characters of the 645 nm emitting state.** The above results reveal that the 645 nm emission band from the Eu$_1$ site is the dominant emission band at 77 K and the only emission band at room temperature. The nature of the emitting state corresponding to the 645 nm emission band can be initially revealed by its radiative lifetime whose value (1.27 $\mu$s) is close to the typical value ($\sim 1.1 \mu$s) of the normal Eu$^{2+}$ $4f^{5}5d^{1} \rightarrow 4f^{7}$ emission in solids. This indicates that the wave function of the emitting state (i.e., the lowest excited state) should contain dominant $4f^{7}$ electronic compositions. Meanwhile, the presence of a distinct PL excitation band at 435 nm indicates that there is a large transition moment between the $4f^{7}$ ground state and the lowest excited state, which further confirms the dominant $4f^{7}$ character of the emitting state. Thus, the 645 nm emission may originate from the lowest $4f^{7}$ level of Eu$^{2+}$ luminescent center (Eu$_1$ site) whose eigenfunction is a localized $4f^{7}$ electronic composition. However, both the FWHM (0.38 eV at 77 K and 0.45 eV at room temperature) and the Stokes shift (0.92 eV) of the 645 nm emission are significantly larger than those reported previously in Eu$^{2+}$-activated aluminate phosphors. These extraordinarily large values suggest that the 645 nm broadband emission is uncharacteristic of the normal Eu$^{2+}$ $4f^{5}5d^{1} \rightarrow 4f^{7}$ transition. Based on the above discussion, we deduce that the emitting state corresponding to the

![Figure 2](https://example.com/figure2.png)

**Figure 2** | Spectral identification of Eu$^{2+}$ luminescent sites in h-EAO. (a), Normalized luminescence decay curves of h-EAO monitored at 650 nm and 550 nm emissions at 77 K. The excitation source is a 355 nm Nd:YAG pulsed laser. The red solid lines are the fitted profiles. The black dashed lines are the decomposed decay compositions. Inset is a zoomed-in view of the initial stage of the decays for the two emission wavelengths. (b), Plot of PL spectral distribution ($A_2/A_1$) over two Eu$^{2+}$ sites (Eu$_1$ and Eu$_2$) as a function of emission wavelengths at 77 K (solid balls). The line curves are the PL emission spectra from Eu$_1$ and Eu$_2$ sites at 77 K, which are the same as the emission curves in Fig. 1b.
The autoionization-associated 4\textit{f}5\textit{d} emitting state proposed here is different from either the localized 4\textit{f}5\textit{d} state of the normal 4\textit{f}5\textit{d}−4\textit{f}7 transition or the delocalized exciton-like state of anomalous luminescence. As a result of electron delocalization in the emitting state, the ligand ions around the luminescent center (i.e., Eu\textsubscript{1} site) will undergo a considerable relaxation, which is reflected in the emission spectrum by an extraordinarily large FWHM and an extremely large Stokes shift in h-EAO. Besides the energy threshold at \(\sim 500\) nm, the TL creation spectrum in Fig. 3b also contains a higher energy threshold at \(\sim 420\) nm. The strong electron delocalization in the high-energy region (i.e., 320–420 nm) can be attributed to the autoionizing intermediate states, i.e., the autoionization of 4\textit{f}5\textit{d} states lying in the host conduction band\textsuperscript{20,22}.

We have carried out a detailed study on a new hexagonal EuAl\textsubscript{2}O\textsubscript{4} phosphor whose Eu\textsuperscript{3+} luminescence exhibits a very large bandwidth and an extremely large Stokes shift. At 77 K, two luminescent sites responsible for 645 nm and 550 nm broadband emissions were identified, while at room temperature, the 550 nm emission band was quenched due to energy transfer. The 645 nm emission exhibits both characteristic and uncharacteristic properties of a normal Eu\textsuperscript{3+} 4\textit{f}5\textit{d}−4\textit{f}7 transition, evidenced by a typical Eu\textsuperscript{3+} lifetime of 1.27 \(\mu\)s and an extremely large Stokes shift of 0.92 eV, respectively. Photoionization experiments showed that the emitting state of the 645 nm emission is a mixed state consisting of dominant localized 4\textit{f}5\textit{d} states and complementary delocalized conduction-band-like states.

**Methods**

The optical properties of the h-EAO phosphor were studied using an array of spectral methods. The PL spectra were recorded using a Fluorolog-3 spectrophotometer equipped with a 450-W xenon arc lamp as the excitation source. The diffuse reflectance absorption was measured using a Shimadzu UV-2450 UV-Vis spectrometer. The luminescence lifetime was recorded using a photomultiplier tube and a digital oscilloscope under excitation with the third harmonic (355 nm) of a Nd:YAG pulsed laser. The TL curves were recorded using the Fluorolog-3 spectrophotometer and a homemade TL setup. Appropriate optical filters were used to avoid stray light in all optical measurements.

1. Blasse, G., Wannemaker, W. L., ter Vrugt, J. W. & Bril, A. Fluorescence of Eu\textsuperscript{2+}−activated silicates. *Philips Res. Rep.*, 23, 189–200 (1968).
2. Poort, S. H. M. & Blasse, G. The influence of the host lattice on the luminescence of divalent europium. *J. Lumin.* 72–74, 247–249 (1997).
3. Dorenbos, P. Energy of the first 4\textit{f}2−4\textit{f}7 transition of Eu\textsuperscript{3+} in inorganic compounds. *J. Lumin.* 104, 239–260 (2003).
4. McClure, D. S. & Pédrini, C. Excitons trapped at impurity centers in highly ionic crystals. *Phys. Rev. B* 32, 8465–8468 (1985).
5. Moine, B., Pédrini, C. & Courtois, B. Photoionization and luminescences in BaF₂:Eu²⁺. J. Lumin. 50, 31–38 (1991).
6. Dorenbos, P. Anomalous luminescence of Eu²⁺ and Yb⁺ in inorganic compounds. J. Phys.: Condens. Mater. 15, 2645–2665 (2003).
7. Swiatek, K., Godlewski, M. & Hommel, D. Deep europium-bound exciton in a ZnS lattice. Phys. Rev. B 42, 3628–3633 (1990).
8. Gatch, D. B. et al. Pressure dependence of the impurity-trapped exciton emission in BaF₂:Eu and BaS₁₋ₓFₓ:Eu. Phys. Rev. B 74, 195117 (2006).
9. Smet, P. F. et al. Anomalous photoluminescence in BaS:Eu. Phys. Rev. B 74, 035207 (2006).
10. Poort, S. H. M., Blokpoel, W. P. & Blasse, G. Luminescence of Eu²⁺ in barium and strontium aluminate and gallate. Chem. Mater. 7, 1547–1551 (1995).
11. Tang, Y. S. et al. Near-ultraviolet excitable orange-yellow Sr₅(AlO₄)Cl₂:Eu²⁺ phosphor for potential application in light-emitting diodes. Appl. Phys. Lett. 93, 131114 (2008).
12. Srivastava, A. M. et al. Unusual luminescence of octahedrally coordinated divalent europium ion in Ca₂M₄PO₈ (M²⁺ = Ca, Sr). J. Lumin. 129, 919–926 (2009).
13. Krings, M., Montana, G., Dronskowski, R. & Wölkler, R. α-MnCN:Eu⁺⁺ – a novel efficient orange-emitting phosphor. Chem. Mater. 23, 1694–1699 (2011).
14. Daicho, H. et al. A novel phosphor for glareless white light-emitting diodes. Nat. Commun. 3, 1132 (2012).
15. Li, X. F. et al. New yellow Ba₃₀Eu₄₀₋ₓAl₂O₄ phosphor for warm-white light-emitting diodes through single-emitting-center conversion. Light: Sci. Appl. 2, e50 (2013).
16. Liu, F. et al. New ternary europium aluminate luminescent nanoribbons for advanced photonics. Adv. Funct. Mater. 23, 1998–2006 (2013).
17. Poort, S. H. M., Meijerink, A. & Blasse, G. Lifetime measurements in Eu⁺⁺-doped host lattices. J. Phys. Chem. Solids 58, 1451–1456 (1997).
18. Pédrini, C., Joubert, M. F. & McClure, D. S. Photoionization processes of rare-earth dopant ions in ionic crystals. J. Lumin. 125, 230–237 (2007).
19. Schierning, G., Batentschuk, M., Osvet, A., Stiegelschmitt, A. & Winnacker, A. The influence of lattice defects on fluorescence and phosphorescence in the europium aluminate EuAl₂O₄. Phys. Stat. Sol. (C) 2, 109–112 (2005).
20. Flensiken, J., Wang, J., Grimm, J., Weber, M. J. & Happel, U. Thermally stimulated luminescence excitation spectroscopy (TSLES): a versatile technique to study electron transfer processes in solids. J. Lumin. 94–95, 465–469 (2001).
21. van der Kolk, E., de Haas, J. T. M., Bos, A. J. J., van Eijk, C. W. E. & Dorenbos, P. Luminescence quenching by photoionization and electron transport in a LaAlO₃:Ce⁺⁺ crystal. J. Appl. Phys. 101, 083703 (2007).
22. You, F. T., Bos, A. J. J., Shi, Q. F., Huang, S. H. & Dorenbos, P. Thermoluminescence investigation of donor (Ce⁺⁺, Pr⁺⁺, Tb⁺⁺) acceptor (Eu⁺⁺, Yb⁺⁺) pairs in Y₃Al₅O₁₂. Phys. Rev. B 85, 115101 (2012).

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Author contributions
Z.W.P. and F.L. conceived the study and wrote the paper. F.L. synthesized the material. F.L. and X.F.L. carried out spectral measurements. F.L., R.S.M. and Z.W.P. investigated the luminescence mechanism. J.D.B. and Y.S.C. carried out crystallographic measurements and analysis. All authors discussed the results and commented on the manuscript.

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