Mechanism of superior luminescent and high-efficiency photocatalytic properties of Eu-doped calcium aluminate by low-cost self-propagating combustion synthesis technique

Jiancun Rao1,2, Yujin Wang1, Wen Wang1, Hua Ke1, Yechen Li1, Yang Zhao1, Zhiliang Diao1, Dechang Jia1 & Yu Zhou1

Eu-doped calcium aluminate was synthesized via the low-cost self-propagating combustion synthesis (SPCS) technique, whose phase constitutions were identified as Ca9Al6O18 and Ca3Al2O6. The Ca2+ ions in Ca9Al6O18 rather than Ca3Al2O6 phase were replaced by Eu3+ ions. The product exhibits the superior luminescent property and photocatalytic activity, which may find potential applications in the display devices and environment treatments.

In recent years, the energy conversion and environmental issues have attracted more extensive attention. Therefore, exploiting the green functional materials and utilizing non-polluting renewable energy are gradually becoming main topics. The functional materials doped with rare earth ions have been widely used in aviation, construction, electronics, optical conversion device and bio-molecular probe fields because of their advantages of low-cost, pollution-free, and nontoxic1-5, for instance, the rare earth permanent magnetic materials6, the rare earth superconducting materials7, the rare earth hydrogen storage material8 and so on.

Aluminates are a kind of low-cost, stable, anti-radiation and eco-friendly host of the rare earth luminescence materials9-15. However, one hand, the synthesis temperature of aluminates is usually very high and reaches up to 1200–1600 °C when using the traditional high-temperature calcination method by oxides (e.g. CaO and Al2O3) as starting material in the industry. On the other hand, the obtained product is also usually composed of mixed phases of multiple aluminates such as CaAl2O4, CaAl4O7, CaAl12O19, Ca3Al2O6, Ca12Al14O33 and so on, the mixed phase identification of which is hardly been discussed in the past researches. Recently, the SPCS technique was widely applied to synthesize inorganic materials, which can effectively reduce the reaction temperature and shorten the reaction time. For example, Rafiaei et al. prepared Gd and Eu ions doped Y2O3 materials, respectively, which exhibited superior luminescent emission property16, 17.

In this study, a functional material of Eu-doped calcium aluminate was synthesized by the SPCS technique, which realized the obviously fast reaction at low temperature with low energy consumption compared with the traditional high-temperature calcination method. The product presents not only the superior luminescence property but also high-efficiency photocatalytic activity, which casts a potential application in the display devices and environment treatments. The phase constitution is studied by X-ray Diffraction (XRD) pattern, Fourier Translation Infrared (FT-IR) spectrum and transmission electron microscopy (TEM) etc. approaches, as well as the luminescent and photocatalytic mechanisms are also discussed in detail.

1Institute for Advanced Ceramics, School of Materials Science and Engineering, Harbin Institute of Technology, Harbin, 150001, P.R. China. 2Present address: AIM Lab, Maryland NanoCenter, University of Maryland, College Park, MD-20742, USA. Correspondence and requests for materials should be addressed to J.R. (email: jcrao@hit.edu.cn) or D.J. (email: dcjia@hit.edu.cn)
**Results and Discussion**

Figure 1(a) shows the XRD pattern of the as-prepared Eu-doped calcium aluminate, which agrees well with the standard spectrum of both Ca₉Al₆O₁₈ (PDF #70-0839) and Ca₃Al₂O₆ (PDF #38-1429). No other miscellaneous diffraction peaks are observed, indicating that the as-prepared sample is completely converted to Ca₉Al₆O₁₈ or/and Ca₃Al₂O₆ crystalline phases without generating other types of calcium aluminates. In addition, these strong, narrow and sharp diffraction peaks reveal that the sample has a high degree of crystallinity. It is carefully analyzed that the angles of two strong peaks at 2θ = 33.26° and 2θ = 47.72°are slightly increased compared with the standard spectrum, which demonstrates that the doped crystal lattices are slightly contracted owing to the effect of some Eu³⁺ replaced Ca²⁺ ions, considering the ionic diameter of Ca²⁺ and Eu³⁺ are 0.099 and 0.095 nm, respectively. Besides, the metallic element contents in the sample were detected by inductive coupling plasma emission spectrograph (ICP-AES). The results show that the atom ratio of Al, Ca and Eu was 3.9: 6.6: 0.02, which was close to theoretical content in the sample.

The FT-IR spectrum of Eu-doped calcium aluminate sample is also performed. It was reported that the absorption band of AlO₄ and AlO₆ in condensed matter locates in the range of 900–700 cm⁻¹ and 680–500 cm⁻¹, respectively. As we can see from the spectrum, the strong absorption band at 900–600 cm⁻¹ in Fig. 1(b) can be attributed to the AlO₄ vibration, which coincides with the corner-sharing tetrahedron AlO₄ structure in the Ca₃Al₂O₆ or/and Ca₉Al₆O₁₈ crystals. Two groups of absorption at 600–400 cm⁻¹ are derived from characteristic vibration of Al-O bond. It proves that the lattice structures of Ca₃Al₂O₆ or/and Ca₉Al₆O₁₈ crystals have not changed but with slight distortion, and the Ca²⁺ ions rather than Al³⁺ are replaced by Eu³⁺. In addition, the absorption bands at 1300 cm⁻¹ and 3450 cm⁻¹ occurs due to the vibration from CO₃²⁻ and OH⁻ groups, respectively, because of CO₂ and H₂O in the air. The morphology observed in SEM, as shown in Fig. 1(c), indicates significant aggregate and the particle shape is generally irregular due to the high-temperature calcination. Fig. 1(d) confirmed the porous feature. This may be caused by the urea combustion which leading to the gases releasing and then inhibiting the formation of dense bulk samples in the SPCS process.

Figure 2 gives the TEM analysis results of the as-prepared Eu-doped calcium aluminate sample. Fig. 2(a) and (b) are bright field (BF) and high-angle annular dark field (HAADF) images, respectively, from the same aggregation. It is obvious that there are two phases with different contrast, which intersperse with each other. The selected area electron diffraction patterns (EDPs) obtained by careful tilting are shown in Fig. 2(d,e and f). These EDPs can be assigned as either Ca₃Al₂O₆ or Ca₉Al₆O₁₈ phase. It is very difficult to distinguish the isolated Ca₃Al₂O₆ or Ca₉Al₆O₁₈ phase due to their interspersion. The strongest spots in most EDPs can be assigned as both
the two phases, only with the differences of the indices, as shown in the image of Fig. 2(d,e and f). Further TEM study reveals part of the aggregated particles are pure Ca₉Al₆O₁₈ phase. This can be proved by the EDP, as shown in Fig. 2(g), which is from the adjacent area. The intensities of the strongest spots in Fig. 2(g), e.g. (000) and (040), are approximately the same. While in Fig. 2(e) the intensities of those spots, like (000) and (040), is not the same, and the stronger spots, like (020), are also from both the two phases as the strongest spots do. But the weaker spots are only from Ca₉Al₆O₁₈ phase. The HRTEM image in Fig. 2(c), which is corresponding to the EDP in Fig. 2(f), shows the interface between Ca₃Al₂O₆ (right side) and Ca₉Al₆O₁₈ (left side) phases. The [101] planes of both the two phases are labeled by the black solid lines in the image. The increment of the lattice parameters of Ca₉Al₆O₁₈ phase is clearly illustrated by these lines.

The brighter part in the BF image, while darker in HAADF image, is proved as mostly Ca₃Al₂O₆ phase by EDP. Meanwhile, the other contrast is mostly Ca₉Al₆O₁₈ phase. Normally these two phases are formed exactly in the same crystallographic orientation. So the EDPs can be assigned as both as Ca₃Al₂O₆ and Ca₉Al₆O₁₈ phases. However, the fewer cases occur that these two phases are almost, but not completely, in the same crystallographic direction. Figure 3 shows a detailed TEM analysis result for this case. Figure 3(a) is the HAADF image from one corner of the aggregated particles. The EDPs from area marked with numbers “1” and “2”, darker and brighter areas as discussed above, are shown in Fig. 3(b and c), respectively. One enlarged insert in Fig. 3(b) shows clearly two discrete spots from these two phases separately. It is obvious that Ca₃Al₂O₆ and Ca₉Al₆O₁₈ phases are not perfectly in the same crystallographic direction in area “1”. Accordingly, Ca₃Al₂O₆ and Ca₉Al₆O₁₈ phases in area “2” are exactly in the same direction as EDP shown in Fig. 3(c). The elementary maps of Ca, Al, O and Eu are shown in Fig. 3(d–g), respectively. From these elementary maps, it is obvious that the distribution of Ca, Al and O, even the rare Eu, are very homogenous. There seems to be no differences between Ca₃Al₂O₆ and Ca₉Al₆O₁₈ phases. So quantitative EDS analysis should be done carefully and profoundly.

Table 1 gives the chemical constitution (at. %) by the energy dispersive X-ray spectroscopy (EDS) analysis from those three different spots marked by numbers “1”, “2” and “3” in Fig. 3(a). It was confirmed that the relative content of Eu is higher in Ca₉Al₆O₁₈ than in Ca₃Al₂O₆ phase. The content of Eu is slightly higher in spot “2” than in “1” but with a lower Ca percentage. This verifies that the Eu³⁺ replaced Ca²⁺ in the particles. Due to the randomness of Eu³⁺ replacing Ca²⁺, it is necessary to have a large unit cell to contain these Eu³⁺ ions. Then there was formed as the Ca₉Al₆O₁₈ phase, which the lattice parameter is doubled as that of Ca₃Al₂O₆ phase. The replacement of Eu³⁺ for Ca²⁺ results in a different space group of Ca₉Al₆O₁₈ phase, which can be proved by the occurrence of structural-extinction-spots, like (010) spot, in Figs 2(a) and 3(c). Based on this point, the structure of Ca₉Al₆O₁₈ phase is preferred by the authors.

We know that the unit cell of Ca₉Al₆O₁₈ contains 72 Ca, 48 Al and 144 O atoms. The structure is built of six-fold rings centered on three-fold axes and composed of two types of distorted AlO₄ tetrahedra. The holes in between the rings contain the Ca atoms. In the unit cell there are 80 such possible holes; 72 of them are filled up
with Ca atoms leaving 8 vacant on threefold axes at position of (1/8, 1/8, 1/8) together with its symmetry-related positions. The extra atoms could fit into these 8 holes20. Since the sizes of Ca²⁺ and Eu³⁺ are comparable (0.099 nm and 0.095 nm, respectively), it is almost certain that there are two possible ways for Eu³⁺ ions to stay in the unit structure. First, Eu³⁺ ions could replace some of the Ca²⁺ ions and leaving some Ca²⁺ vacancies for balancing charges. Second, Eu³⁺ ions could go into these 8 holes of the structure. If Eu³⁺ ion occupies vacancies site such as (1/8, 1/8, 1/8), there should be some new vacancies of Ca²⁺ as near as possible in order to achieve a localized balancing of charges. The latter would probably not happen for the symmetry of the unit cell structure. So only small amount of Ca²⁺ ions were replaced by Eu³⁺ ions, which is already proved by FT-IR spectrum in Fig. 1(b).

A schematic diagram is given in Fig. 4 showing the unit cell of Ca₉Al₆O₁₈ phase and the replacement of parts of Ca by Eu. Figure 4(a) is the original unit cell of Ca₉Al₆O₁₈ phase and Fig. 4(b) is the final result of the unit cell with parts of Ca replaced by Eu. Figure. 4(c,d) show only Ca atoms at 4a positions (Wyckoff position) for clarity as well as its partial replacement by Eu in the unit cell. This also matches the results of very little Eu doped into Ca₉Al₆O₁₈ phase.

There are six types of Ca atoms in the structure of Ca₉Al₆O₁₈. Two of them form distorted octahedra with O. The distortion in the octahedral arrangement of oxygen atoms and the presence of short Ca-O bonds indicates a certain amount of strain and hence there will be potential energy stored up in the structure. This potential energy might be available to assist the break-up of the structure by the action like water. So the “flash set” phenomenon of Ca₃Al₂O₆ is attributed to its high reactivity with water20. While in our products, the Eu doped calcium aluminate (Ca₃Al₂O₆ and Ca₉Al₆O₁₈) is quite stable. The XRD pattern of the powder leaving in the room for months is almost the same as that from just-produced powder. This is also one advantage of our products. It should be noted that there are fragments on the aggregated particles, e.g. Area “3” in Fig. 3(a). The EDS result from this kind of fragment shows that it may be only calcium oxide (CaO) phase with very little Al solidified inside. There is no Eu detected by EDS in these fragments. This implies that it is not so easy for Eu³⁺ to substitute for Ca²⁺ in calcium oxide due to the strong bond between Ca²⁺ and O²⁻. While it becomes easier in more complicated structure of Ca₉Al₆O₁₈ phase as discussed above.

The luminescent property of the as-prepared Eu-doped calcium aluminate sample is investigated. As the emission spectrum shown in Fig. 5 (λₑₓ = 277 nm), the sample emits characteristic red light. The emissions at (590 nm, 596 nm), (615 nm, 620 nm), (656 nm, 669 nm), and (689 nm, 701 nm) stem from ⁵D₀ → ⁷F₁, ⁵D₀ → ⁷F₂, ⁵D₀ → ⁷F₃
and $^5D_0 \rightarrow ^7F_1$ transitions ($4f \rightarrow 4f$), respectively. Generally, the magnetic dipole transition $^5D_0 \rightarrow ^7F_1$ is permitted. The electric dipole transition $^5D_0 \rightarrow ^7F_2$ is so sensitive to symmetry that it exceptionally allowed if Eu$^{3+}$ ion occupies a non-inversion center site. Therefore, the strongest transition $^5D_0 \rightarrow ^7F_2$ at 620 nm indicates that Eu$^{3+}$ ions locate non-inversion center sites in the calcium aluminate host. Moreover, Eu$^{3+}$ ions are very sensitive to the crystal field. Owing to 4f electronic configuration interfused opposite 5d and crystal field asymmetry, f $\rightarrow$ f forbidden transition can be partly relaxed, which results in more intensive $^5D_0 \rightarrow ^7F_2$ transition than $^5D_0 \rightarrow ^7F_1$.

In addition, Multi-state $^7F_J$ of Eu$^{3+}$ is split into multiple stark energy levels under the crystal field effect, so

**Figure 4.** The schematic diagram of parts of Ca replaced by Eu in the unit cell of Ca$_9$Al$_6$O$_{18}$ phase. (a) Original unit cell structure of Ca$_9$Al$_6$O$_{18}$, (b) parts of Ca replaced by Eu, (c) only Ca at 4a positions for clarity, (d) Ca at 8 corners replaced by Eu.

**Figure 5.** Excitation ($\lambda_{em} = 620$ nm) and emission ($\lambda_{ex} = 277$ nm) spectra of Eu-doped calcium aluminate sample.
considerable splitting results appear in four groups of emission peaks of the $^5D_0 \rightarrow ^7F_J$. The excitation spectrum of the sample by monitoring $^5D_0 \rightarrow ^7F_2$ transition is also carried out (Fig. 5). The peaks at 320–400 nm ascribe to the intra-configurational $4f \rightarrow 4f$ transition of Eu$^{3+}$ ions, in which the strong absorption at 387 nm belongs to $^7F_0 \rightarrow ^5L_6$ transition. Additionally, the strong absorption at 277 nm drives from the calcium aluminate host.

In order to investigate the photocatalytic activity of the as-prepared Eu-doped calcium aluminate sample, the UV-vis DRS of the sample is firstly performed to explore the light absorption property. As shown in Fig. 6(a), the as-prepared sample exhibits two absorption bands, which are in accord with the excitation spectrum in Fig. 5. Therefore, two absorption bands at 200–320 nm and 320–450 nm stem from transition from valence band (VB) to conduction band (CB) of the calcium aluminate host and $4f \rightarrow 4f$ transition of Eu$^{3+}$ ions, respectively.

The methylene blue (MB) dye is used for target molecules to evaluate the degradation ability of the as-prepared sample. Figure 6(b) shows the dynamic curve of MB degradation. After running 15 min, the degradation rate of MB is more than 98%. Moreover, the kinetic curve of MB degradation can be approximated as a pseudo-first-order process.

By plotting the $\ln(c_0/c)$ versus time and making linear fitting for kinetic curves (Fig. 6(c)), the removal rate constant $k$ of MB is estimated to be 0.217 min$^{-1}$. Furthermore, from the absorbance variations of MB solution in the photocatalytic reaction process (Fig. 6(d)), it has no shifting of the maximum absorption wavelength position of MB solution at 663 nm, and the absorption peak at 292 nm in ultraviolet region vanishes besides visible region. It implies that the benzene/heterocyclic rings of MB molecule may be completely decomposed, leading to the thorough mineralization of MB.

In order to assess the reusability of the sample which is crucial for its practical application, the circle runs experiments of MB solution photodegradation over Eu-doped calcium aluminate sample were performed. As shown in Fig. 7, the results indicated the photocatalytic ability of sample had not obviously loss after four recycles, indicating that the sample exhibits superior stability and durability.

The possible transfer behavior of charge carriers as well as luminescent and photocatalytic mechanism are shown in Fig. 8. Under the light excitation, the calcium aluminate host and Eu$^{3+}$ ions are all excited at the same time. Electrons in the CB of calcium aluminate host and the ground state $^7F_0$ of Eu$^{3+}$ ions transfer into the corresponding CB and $^3D_0$, $^3D_1$, $^3D_2$ and $^3L_6$ states of them, respectively. At the luminescent process, electrons in the excitation state $^3D_1$ and $^3D_2$ return to $^7F_1$, $^7F_2$, $^7F_3$, $^7F_4$ states of Eu$^{3+}$ ions to generate luminescence. It should be pointed out that part of the electron in the CB of the calcium aluminate host and $^3L_6$ states can transfer into $^3D_0$, $^3D_1$, $^3D_2$ states by means of multi-phonon assisted relaxation effect to enhance luminescent property. At the MB degradation process, part of the electrons in the CB of the calcium aluminate host migrate to the sample surface and are captured by O$_2$ molecules in water to yield superoxide radicals ($\bullet$O$_2^{-}$). The superoxide radicals may
further transform into hydroxyl radicals (\(\bullet OH\)). Finally, the superoxide radicals, hydroxyl radicals and holes oxidize decompose MB dye.

**Conclusion**

A functional material of Eu-doped calcium aluminate was firstly obtained by the self-propagating combustion synthesis technique with low cost and low energy consumption, which presents a significant decrease in the synthesis temperature compared with the solid-state calcination method using oxides (e.g. CaO and Al\(_2\)O\(_3\)) as starting material. The product is composed of two phases, i.e. Ca\(_3\)Al\(_2\)O\(_6\) and Ca\(_9\)Al\(_6\)O\(_{18}\), as well as exhibits the superior luminescent property and high-efficiency photocatalytic activity, which may have the potential application prospect for serving as phosphor in the display device and photocatalyst in the environment treatment, respectively.

**Methods**

According to the stoichiometric ratio of Ca\(_{2.98}\)Al\(_2\)O\(_6\): 0.02Eu\(^{3+}\), Eu\(_2\)O\(_3\) was transferred to 250 mL beaker and dissolved via concentrated HNO\(_3\) then adding Al(NO\(_3\))\(_3\)\(\bullet\)9H\(_2\)O, Ca(NO\(_3\))\(_2\)\(\bullet\)4H\(_2\)O, CO(NH\(_2\))\(_2\) and appropriate distilled water. We keep on stirring, dissolving and heating until the solution was evaporated to be viscous. Subsequently, the beaker was put into a muffle furnace and kept at 500°C. After a few minutes, the mixture started burning and last for 5–7 min. Finally, the obtained precursor was transferred into the corundum crucible and calcined at 900°C for an additional 6 h to obtain the final white products.

X-ray diffraction (XRD) pattern was recorded by Rigaku D/max-2200 powder diffractometer. FT-IR spectrum was measured on FT-IR360 infrared spectrometer. The morphology was characterized utilizing scanning electron microscope (SEM, FEI Quanta 200FEG) and transmission electron microscope (TEM, FEI Tecnai G\(^2\) F30) with high angle annular dark field (HAADF) detector. Luminescent spectrum was measured via F4500 fluorescence spectrophotometer. The UV-visible diffuse reflectance spectrum (UV-vis DRS) was recorded on UV-vis spectrophotometer (PG, TU-1901).

Figure 7. Cycle photodegradation runs of MB solution over Eu-doped calcium aluminate sample.

Figure 8. The transfer behavior of charge carriers as well as luminescent and photocatalytic mechanism.
The methylene blue (MB) solution (10 mg/L, 100 ml) containing 0.1 g sample was irradiated with a 300 W Xe arc lamp. Before the irradiation, it was stirred for 30 min in the dark environment to achieve the adsorption-desorption equilibrium between MB and sample. The absorbance of MB solution was monitored by UV–vis spectrophotometer (PG, TU-1901) every 5 min.

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Author Contributions
J.C. Rao designed and lead the research work; Y.C. Li, Y. Zhao, Z.L. Diao conducted the experiments; and J.C. Rao wrote the paper. Y.J. Wang, W. Wang, H. Ke, D.C. Jia and Y. Zhou joined the discussion of the experimental results and made some comments on the manuscript.

Additional Information

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