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# Sol-gel method and optical properties of $Ca_{12}Al_{14}O_{32}F_2$:$Eu^{3+}$ red phosphors

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**Abstract:** $Ca_{12}Al_{14}O_{32}F_2$:$Eu^{3+}$ red phosphors were prepared by the sol-gel method with $CF_3COOH$ as the fluorine source. X-ray diffraction, transmission electron microscopy, X-ray photoelectron spectra, and photoluminescence spectra, as well as thermogravimetric and differential thermal analysis were utilized to characterize the samples. All the samples were single phase with a cubic structure. The as-obtained $Ca_{12}Al_{14}O_{32}F_2$:$Eu^{3+}$ red phosphors consisted of nanoparticles with sizes of approximately 40–100 nm. Under the excitation of UV light, $Ca_{12}Al_{14}O_{32}F_2$:$Eu^{3+}$ exhibited the characteristic emissions of $Eu^{3+}$, and the effect of annealing temperature, annealing time, and $CF_3COOH$ and $Eu^{3+}$ concentrations on the luminescence intensity were discussed in detail.

**Keywords:** $Ca_{12}Al_{14}O_{32}F_2$; oxyfluoride; sol-gel synthesis; luminescence; $Eu^{3+}$ ions; rare earths

In recent years, increasing attention has been paid to alkaline earth aluminate materials doped with rare earths because of their diverse structures, interesting chemical properties, and encouraging luminescent properties, which make them excellent candidates for applications in white light-emitting diodes[1–6]. Alkaline earth halo-aluminates have structures similar to those of alkaline earth aluminates, and rare earth ion-doped halo-aluminates also exhibit good optical properties. Some related halo-aluminates compounds such as $Sr_3AlO_4F$, $Sr_3Al_2O_5Cl_2$, $Ca_{12}Al_{14}O_{32}F_2$, and $Ca_2Al_3O_6F$ have been reported[7–10]. Compounds of the type $Ca_{12}Al_{14}O_{32}X$, where X=2F, 2Cl, O, and 2OH, are considered to have the same space group, $I43d$[11–15]. Considering that phosphors would be a part of LED packaging materials, it is interesting to develop a wet route for obtaining high-quality nanosystems with tunable phases and chemical compositions and then to improve the functional performance of these systems. The sol-gel process is a well-known method for preparing nanopowders. Unfortunately, alkaline earth metal fluorides are less soluble in water or alcohols, and thus they cannot act as a fluorine source. However, LaOF has been successfully prepared by the sol-gel process[16]. Recently, we developed a sol-gel route for the synthesis of $Mn^{4+}$-activated magnesium fluorogermanate[17]. The present work was devoted to the study of $Ca_{12}Al_{14}O_{32}F_2$:$Eu^{3+}$ nanoparticles prepared by the sol-gel method for the first time. The choice of $Eu^{3+}$ as the luminescent doping species is related to the high efficiency of $Eu^{3+}$ ions as red-light emitters. Moreover, owing to the relatively simple energy level structure and to the presence of nondegenerate ground ($^7F_0$) and emitting ($^5D_0$) states, the emission and excitation transition of $Eu^{3+}$ ions can be suitably exploited to monitor their location within the host lattice. Then, $Ca_{12}Al_{14}O_{32}F_2$:$Eu^{3+}$ were prepared by the sol-gel method with $CF_3COOH$ as fluorine source and annealed in air between 900–1200 ºC. The effects of different synthesis conditions on the composition, phase structure, and optical properties of the obtained samples were investigated.

## 1 Experimental

### 1.1 Chemical and materials

$CF_3COOH$ (fluorine source) was purchased from Aladdin Industrial Corporation (Shanghai, China). Other chemicals, including $C_6H_8O_7{\cdot}H_2O$ (citric acid monohydrate), $Al(NO_3)_3{\cdot}9H_2O$ (aluminum nitrate nonahydrate), $CaCO_3$ (calcium carbonate), and $Eu_2O_3$ (europium oxide), were purchased from National Medicine Group Chemical Reagent Co., Ltd. (Shanghai, China). All chemicals were of analytical grade and were used directly without further purification.

### 1.2 Preparation

Phosphors with a nominal composition of $Ca_{12-x}Al_{14}O_{32}F_2$:$xEu^{3+}$ were synthesized by the sol-gel reaction technique. Typically, $CaCO_3$, $Al(NO_3)_3{\cdot}9H_2O$,

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$CF_3COOH$, and $Eu(NO_3)_3$ were mixed in deionized water with ultrasonic stirring at 35 ºC with a molar ratio of $CaCO_3$:$Al(NO_3)_3 \cdot 9H_2O$:$CF_3COOH$:$Eu(NO_3)_3$ of $(12-x)$:14:$y$:$x$. Citric acid was dissolved in the solution (citric acid/metal ions=2:1 molar ratio) with ultrasonic stirring for 30 min. The solution pH was adjusted to 1–3 using $HNO_3$. The resultant mixtures were heated at 80 °C for 48 h in a thermostatic water bath, and homogeneous gels formed. After drying in an oven at 130 °C for 24 h, the gels were prefired at 500 °C for 4 h in air. Then the mixtures were ground and sintered at high temperature (900, 1000, 1100, and 1200 °C) for a certain time (2, 4, 6, and 8 h) in air. Finally, the as-synthesized samples were cooled slowly to room temperature.

### 1.3 Characterization

The crystalline phases of the samples were identified by powder X-ray diffraction (XRD) measurements using an XD-3 diffractometer (Beijing Persee) with a Cu Kα radiation source ($\lambda$=0.15405 nm). Data were collected over $2\theta$=10º–80º at 8 (º)/min with a scanning step of 0.02º. Transmission electron microscopy (TEM) micrographs were obtained using a Hitachi H-7650 system with tungsten filament electron gun operating at 100 kV, and micrographs were acquired digitally on a charge-coupled device (CCD) camera. X-ray photoelectron spectra (XPS) were obtained using an electron spectrometer with Al Kα radiation (1486.6 eV) as the excitation source (Thermo VG Multilab 2000) at a working pressure lower than $5.0\times10^{-6}$ Pa. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were conducted using a simultaneous thermal analyzer (SDT Q600, TA). Data were collected from room temperature to 1200 °C at 10 °C/min in air. PL excitation and emission spectra were recorded using a spectrophotometer (Shimadzu RF-5301pc, Hitachi F-2500) with a 150 W xenon lamp as the excitation source. Luminescent decay curves were measured on an FLS920 spectrofluorometer (Edinburgh Instruments, UK) equipped with an EPL375 pulse laser diode.

## 2 Results and discussion

TGA and DTA results for the dried gel precursor powders are shown in Fig. 1. The TGA curve shows five mass loss steps at ~40–160 °C (A, mass loss=11%), ~160–350 °C (B, mass loss=35%), ~350–500 °C (C, mass loss=17%), ~500–850 °C (D, mass loss=15%), and ~850–950 °C (E, mass loss=4%). Steps D and E correspond to obvious exothermic peaks in the DTA curve at 560 and 939 °C, respectively. Serious mass loss (~77%) occurs between ~40 and 850 °C. Steps A, B, and C correspond mainly to the decomposition of $NO_3^-$, $CF_3COO^-$, and $C_6H_7O_7^-$, respectively. $CF_3COOH$ used in the precursor solution was responsible for the formation of an F-containing crystalline phase. The $CF_3COOH$ and $CF_3COO^-$ species decompose readily at low temperature. It is likely that highly reactive $F^-$ ions were released during the thermolysis of the dry gel because of the breaking of the C–F bond in $CF_3COO^-$ or $CF_3COOH$. Consequently, fluorination of the Ca–O bond to the Ca–F bond would occur and lead to the formation of $Ca_{12-x}Al_{14}O_{32}F_2$:$x$Eu$^{3+}$ nuclei at higher temperature; this process may appear at step D. The exothermic peak at 939 °C in the DTA curve may come from the growth of $Ca_{12-x}Al_{14}O_{32}F_2$:$x$Eu$^{3+}$ particles, as there is less mass loss (~4%) or phase transition at this stage (E). The TGA and DTA results suggest that the dried gel precursor powders were heat treated in air from ~900–1200 °C to obtain the target samples.

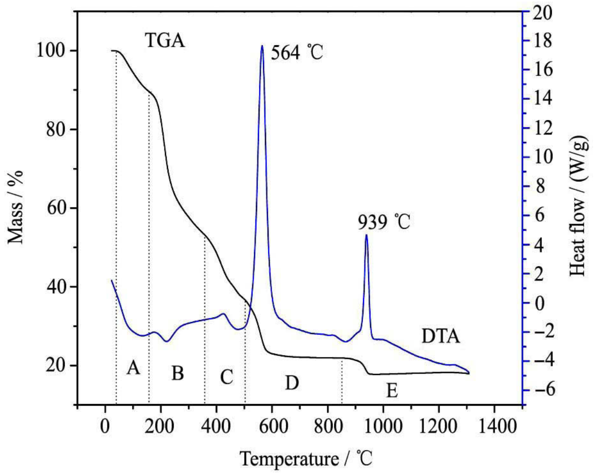

Fig. 1 TGA-DTA spectra of dried gel (temperature rate: 10 ºC/min, instrument: SDTQ 600)

The surface chemical compositions of the synthesized phosphor powders were studied by XPS to examine the formation of the fluorine-containing crystalline phases. Fig. 2(a) shows the XPS survey spectrum for the $Ca_{11.64}Al_{14}O_{32}F_2$:0.36Eu$^{3+}$ phosphor. Ca, Al, O, F, and Eu species were detected in the phosphor powders, in which the Eu $3d_{3/2}$, $3d_{5/2}$ show weak intensities of binding energies owing to the low doping concentration. Fig. 2(b) gives the compositions of fluorine and oxygen, along with the amount of $CF_3COOH$ added in the sol-gel process. XPS analysis showed a fluorine increase from 0.95 at.% for 1 mmol $CF_3COOH$ to 2.76 at.% for 6 mmol $CF_3COOH$, whereas the oxygen content decreased from 54.26 at.% to 53.7 at.%, thereby clearly indicating the formation of fluorine-rich compounds. When the amount of $CF_3COOH$ was more than 6 mmol, the surface atomic percentage of both fluorine and oxygen remained nearly unchanged, implying the saturation of the fluorine. The theoretical contents of oxygen and fluorine were 53.3 at.% and 3.33 at.%, respectively. The experimental results of the fluorine content therefore were somewhat different from the theoretical calculation.

Fig. 3 shows the representative XRD patterns of the