Synthesis and luminescence properties of composite $CaAl_2O_4$-$2CaAl_4O_7$:Eu^{3+} phosphor applied to white LEDs

H. J. DONG
Department of Chemistry, Bai Cheng Normal College, Bai Cheng 137000, China

Composite $CaAl_2O_4$-$2CaAl_4O_7$:Eu^{3+} phosphor is prepared by the SPCS technique. The study results of XRD and FT-IR spectrum show that crystal lattice structure of that engenders slight distortion to improve luminescence properties. Luminescence spectrum indicates that $CaAl_2O_4$-$2CaAl_4O_7$:Eu^{3+} shows strong red-light at 618 nm corresponding to electric dipole transition $^5D_0$–$^7F_2$ of Eu^{3+} ions, upon exciting with 382 nm. SEM micrographs reveal that the products fired at 900 ℃ exhibit high quality crystallinity and the size of that is approximately 1-3 μm. All above characteristics of the $CaAl_2O_4$-$2CaAl_4O_7$:Eu^{3+} is beneficial to phosphors applying to white LEDs.

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1. Introduction

In recent years, energy shortage and environment pollution have attracted worldwide attention. In the meantime, green production and saving energy are gradually becoming investigation topics of the most researchers. Phosphors doped rare earth hold low-cost, pollution-free and nontoxic advantages, etc, which have been widely used in aviation, construction, electronics, display device, optical conversion plastic, bio-molecular probe and many other fields [1]. Since the high power output blue GaInN light-emitting diodes (LEDs) are reported by Nakamura [2], white LEDs have been developed rapidly. After nitride and phosphide LEDs obtained three primary colors of light, the study of white LEDs has surpassed that of incandescent and fluorescent lamps, due to their high brightness, high reliability, low electric consumption, long lifetime and environmentally friendly characteristics [3-4]. As a result, it becomes a focus of investigation that exploring to prepare the superior phosphor meeting requirements for wide application of white LEDs. The appropriate phosphors for near-UV white LEDs must show stronger and broader absorption band around 400 nm. It is well known that rare earth ions present stronger absorption around near-UV regions, because when the host compounds dope rare earth ions, the sublattice structure around luminescent center ions will engender somewhat distortion so that the spectral lines of rare earth ions are expected to be broadened, e.g. the red Y_2O_2S:Eu^{3+} and green ZnS:Cu^+/Al^{3+} phosphors, etc. However, the efficiency and lifetime of traditional applied Y_2O_2S:Eu^{3+} phosphor is much lower. In addition, sulfide phosphors are unstable with releasing harmful sulfide gas [5-6]. Most attention has been paid to series of aluminate phosphors doped rare earth ions because they possess plenty of excellent advantages that including wide luminescent range, high quantum efficiency, good stability, high quenching temperature, resistant radiation and so forth [7-13]. Considering they are usually prepared by traditional high temperature solid phase method craft, synthesis temperature come up to about 1500℃. The products display larger particle size and more serious agglomeration. It needs taking a long time to shatter in order to adapt to phosphor applying to white LEDs. Crystal shapes of the phosphor are seriously damaged and luminescence intensity declines significantly. Self-Propagating Combustion Synthesis (SPCS) technique possesses fast reaction, low temperature, saving energy advantages, etc [14-18]. In particular, the products represent loose powder, small particle size, large specific surface area, effective crystallization, easy shattering and so on.

In this paper, we first report luminescence properties of Eu^{3+} doped composite $CaAl_2O_4$-$2CaAl_4O_7$ prepared by SPCS technique using urea as fuel.

2. Experimental

A certain amount of $Al(NO_3)_3\cdot 9H_2O$(A.R.), $Ca(NO_3)_2\cdot 4H_2O$(A.R.) and Eu_2O_3(≥99.9%) were exactly weighted using electronic balance, respectively. Eu_2O_3 was transferred to 250 ml beaker and dissolved using a little concentrated HNO_3, then adding $Al(NO_3)_3$•$9H_2O$, $Ca(NO_3)_2$•$4H_2O$, $CO(NH_2)_2$(A.R.) and appropriate distilled water. Kept on stirring, dissolving and heating until the solution was evaporated to be viscous, subsequently, the beaker was put into a muffle furnace at 500℃. After a few minutes, mixture boiled and undergone dehydration, followed by decomposition, with swelling and frothing. This process resulted in foams that ruptured with a flame and glowed to incandescence. The entire combustion process was completed within 5 min. The product was a foamy, voluminous and amorphous precursor. Then the precursor was transferred into corundum crucible and calcined in the muffle furnace at 900 °C for 8h. The white product was obtained.

The X-ray powder diffraction (XRD) pattern of the products were carried out with a Rigaku Dmax-2200 powder diffractometer (Cu $K_{\alpha 1}=1.54056\times10^{-10}$ m, scanning speed 6°/min, scanning 2θ range 3-80° with steps of 0.02°). Fourier transform infrared (FT-IR) absorption spectra were recorded on a Nicolet 360 FT–IR spectrometer using KBr pellets in the ranges of 4000-400 cm^{-1}. The scanning electron microscopy (SEM) micrographs were performed on a Hitachi S-3000N. Emission spectra were measured by a Hitachi F4500 fluorospectrophotometer (EX slit 2.5 nm/EM slit 2.5 nm, scanning speed 12000 nm/min). All the measurements were performed at room temperature.

3. Results and discussion

XRD pattern of $CaAl_2O_4$-$2CaAl_4O_7$:Eu^{3+} phosphor is shown Fig. 1, which presents two kinds of X-ray diffraction peaks of aluminate phase that $CaAl_2O_4$ and $CaAl_4O_7$. Diffraction intensity of $CaAl_4O_7$ (the peaks are marked using symbol ▼) is more strong than that $CaAl_2O_4$ (the peaks marked using symbol ◆), which indicates that samples completely produce $CaAl_4O_7$ with a quantity of $CaAl_2O_4$. But relative intensity of the main diffraction peaks of them exhibit evident change, which indicates that crystal lattice slightly distorts when Ca^{2+} ions are non-equivalently replaced by Eu^{3+}. That will affect crystal field at the Ca^{2+} sites, consequently, cause the improvement of luminescence properties.

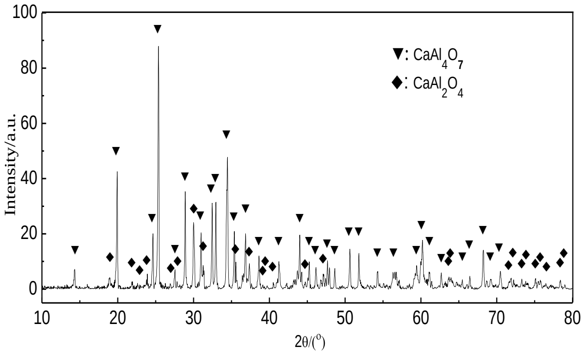

Fig. 1. XRD pattern of $CaAl_2O_4$-$2CaAl_4O_7$:Eu^{3+}.

FT-IR spectrum of the $CaAl_2O_4$-$2CaAl_4O_7$:Eu^{3+} phosphor is shown in Fig. 2. The typical nitrate (NO_3^-) characteristic vibrations are not observed over the wavelength range of 1250–1650 cm^{-1}. The absorption band of AlO_4 in condensed matter locates at the range of 900-700 cm^{-1}, AlO_4 in isolated system locates at the range of 800-650 cm^{-1}; however, AlO_6 in condensed matter locates at the range of 680-500 cm^{-1}, AlO_6 in isolated system locates at the range of 530-400 cm^{-1} [19]. Therefore, we guess strong absorptions maybe attribute to AlO_4 libration in $CaAl_2O_4$-$2CaAl_4O_7$ at 600-900 cm^{-1}. FT-IR spectra of calcium aluminates $Ca_3Al_2O_6$, $CaAl_4O_7$, $Ca_{12}Al_{14}O_{33}$, $CaAl_{12}O_{19}$ and $CaAl_2O_4$ present two groups of absorption at 400-600 cm^{-1} [20]. So, we are convinced of that in Fig. 2 belonged to characteristic liberation absorption coming from Al-O bonds. The absorption bands at 1500 cm^{-1} and 3450 cm^{-1} are due to vibrations from CO_3^{2-} and OH^- groups, respectively, because of CO_2 and H_2O in the air.

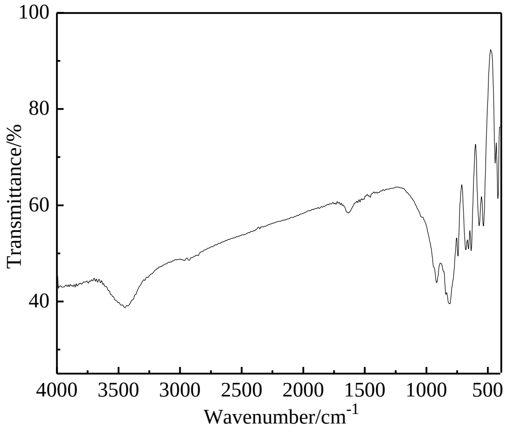

Fig. 2. FT–IR spectrum of $CaAl_2O_4$-$2CaAl_4O_7$:Eu^{3+}.

The emission spectrum of $CaAl_2O_4$-$2CaAl_4O_7$:Eu^{3+} is showed in Fig. 3 (Excitation wavelength = 382 nm). $CaAl_2O_4$-$2CaAl_4O_7$:Eu^{3+} undergoing near-UV radiation emitted characteristic red light. The emission peaks are as the result of 4f→4f ($^5D_0\rightarrow{}^7F_J$, J = 0, 1, 2, 3, 4) transitions at (552 nm, 565 nm) (588 nm, 596 nm), 618 nm, (641nm, 655 nm) and 702 nm, respectively. Among them, $^5D_0\rightarrow{}^7F_2$ is strongest. Near-UV is efficiently absorbed by transition of the lower 4f levels, so luminescence occurs from the ^5D_J (mainly $^5D_0$) states of Eu^{3+}. According to the Judd-Ofelt theory [21-22], magnetic dipole transition $^5D_0\rightarrow{}^7F_1$ is permitted, but electric dipole transition $^5D_0\rightarrow{}^7F_2$ is allowed exceptionally in the event that Eu^{3+} ions occupy non-inversion center sites and are sensitive to symmetry. Consequently, magnetic dipole transition $^5D_0\rightarrow{}^7F_1$ should be relatively strong when the Eu^{3+} ion occupied inversion center site, while $^5D_0\rightarrow{}^7F_2$ must be relatively weak. Surprisingly, $^5D_0\rightarrow{}^7F_0$ transition is observed with very weak intensity that is both spin forbidden and electric dipole forbidden. Ca^{2+} ions are non-equivalent valence replaced by Eu^{3+}, which slightly result in lattice distortion. In addition, Eu^{3+} ions are very sensitive to environmental impacts of crystal field. Due to $4f^6$ electronic configuration interfused opposite 5d and crystal field asymmetry，f→f forbidden transition is partly relaxed. In consequence, $^5D_0 \rightarrow {}^7F_2$ displays more intensity than $^5D_0 \rightarrow {}^7F_1$ [23], which indicates Eu^{3+} ions either deviated from inversion center sites or locate non-inversion center sites in $CaAl_2O_4$-$2CaAl_4O_7$. The weaker emission peaks attribute to $^5D_1 \rightarrow {}^7F_J$ transition at 450-550 nm. The energy level of Eu^{3+} between $^5D_0$ and $^5D_1$ is smaller (1740 cm^{-1}). When it possesses the larger libration frequency in crystals, the energy between $^5D_1$ and $^5D_0$ maybe give birth to non-radiative relaxation process with phonon assistant effect [24]. The FT-IR spectrum of $CaAl_2O_4$-$2CaAl_4O_7$:Eu^{3+} presents the stronger libration frequency at 800-1000 cm^{-1} in Fig. 3. Electron of $^5D_1$ could transit into $^5D_0$ in terms of 2-3 phonons, thereby the weaker $^5D_1 \rightarrow {}^7F_J$ transitions are only observed.

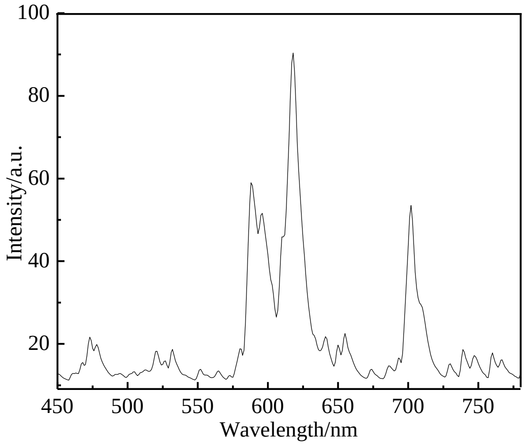

Fig. 3. Emission spectrum of $CaAl_2O_4$-$2CaAl_4O_7$:Eu^{3+}.

The particle size and morphology of the product powders are investigated by photomicrographs that measured via SEM in Fig. 5. Image a (magnified 450 times) shows products are honeycomb bulk shape distribution and each bulk is composed of small ellipsoidal crystal particles that adhere to each other. Those slightly agglomerated phenomena are due to calcination for the precursor at 900℃. Correspondingly, image b (magnified 6000 times) shows the product surfaces exhibit honeycomb, smoothness, densification and high crystallinity. The average size of particles is about 1-3 μm. The characteristics of product surface are suitable for coating requirements of phosphors applying to white LEDs. Owing to urea burning, a lot of gases release and damage the formation of massive structures on SPCS synthesis process, so crystal nucleus grows along with directions for formation of the smooth sphere shape that containing lower surface energies. Researches show that spherical surface is contributed to enhance luminescence intensity [25].

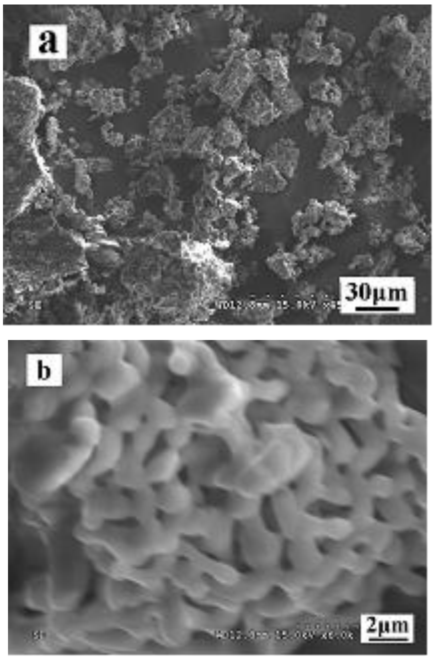

Fig. 4. SEM micrographs of $CaAl_2O_4$-$2CaAl_4O_7$:Eu^{3+}
a: magnified 450 times, b: magnified 6000 times.

4. Conclusions

Composite $CaAl_2O_4$-$2CaAl_4O_7$:Eu^{3+} phosphor is first prepared via the SPCS technique. Synthesis temperature significantly decreases, together with improving compound crystallinity that are attained in the final powder bodies, as compares with the conventional high temperature solid state reaction method (the starting oxides CaO and Al_2O_3), which requires operation temperatures 1500 °C for prolonged times in kiln-type furnaces. A small quantity of Eu^{3+} ions doped $CaAl_2O_4$-$2CaAl_4O_7$ improve luminescence properties. SEM micrographs of product show the presence of approximate 1-3 μm dimension and high quality crystallinity. Composite $CaAl_2O_4$-$2CaAl_4O_7$ is an excellent type of candidates as host materials. Luminescence properties of them indicate that it is excited at around near-UV regions 382 nm to emit red-light. All above mentioned are beneficial to requirements of the phosphors applying to white LEDs.

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*Corresponding author: donghongjun6698@yahoo.com.cn