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Structure and luminescence properties of pure $CaAl_4O_7:Eu^{3+}$ by self-propagating combustion synthesis

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Series of $CaAl_4O_7:Eu^{3+}$ were firstly synthesized as high-purity luminescence ceramic powders by using Self-Propagating Combustion Synthesis (SPCS) methods. XRD showed the unit cell of $CaAl_4O_7:Eu^{3+}$ was confirmed monoclinic system and belonged to C2/c space groups. Lattice constant refinement was a=1.2888nm, b=0.8887nm, c=0.5445nm, β=106.9264°, Z=1. Luminescence spectra analysis indicated all peaks were attributed to $^5D_0 \rightarrow {}^7F_J$ (J = 0, 1, 2, 3, 4) transition at 578nm, 590nm, 616nm, 649nm and 701nm, respectively, and energy transfer coming from host to Eu^{3+} enhanced luminescence intensity. FT-IR spectra investigated vibration feature of the samples. SEM revealed the samples had smooth surface, the better crystallization and ~ 1 μm size.

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Keywords: SPCS, $CaAl_4O_7:Eu^{3+}$, Pure samples, Luminescence properties

1. Introduction

In recent years, energy shortage, environment pollution had become the focus of the world concern. In the meantime, green production and saving energy were gradually becoming the research topics. Luminescence material activated by rare-earth held low-cost, pollution-free, nontoxic and other advantages, which has been widely used in aviation, construction, electronics, display device, optical conversion plastic, bio-molecular probe and many other fields [1].

Considerable attention has been paid to a series of aluminates luminescence materials doped by rare-earth ions because they are plenty of excellent advantages which include wide range of luminescence, high quantum efficiency, good stability, high quenching temperature, resistant radiation and so forth [2-14]. For instance, $MgAl_{11}O_{19}:Ce^{3+}$, Tb^{3+} and $BaMgAl_{10}O_{17}:Eu^{2+}$ are two kinds of highly efficient green and blue luminescence powders that have been widely applied. Considering they were usually prepared by traditional high temperature solid phase method craft in industrial production, synthesis temperature came up to 1500℃-1700℃. The products displayed the larger particle sizes and more serious agglomeration phenomena. It took a long time to shatter in order to be satisfactory for the coating requirements. Crystal shape of the phosphors is seriously damaged, in addition, luminescence intensity decreases significantly.

Whereas SPCS method had fast reaction [15-22], low temperature, saving energy etc evident advantages. In particular, the products represented loose powders, small particle size, large specific surface area, effective crystal, easy shattering and so on. There was proved that SPCS is a promising synthesis method of luminescence materials.

In the present paper, we report the structure, morphology, IR and luminescence characterization of $CaAl_4O_7:Eu^{3+}$ synthesized by SPCS method using urea as fuel.

2. Experimental

In accordance with $Ca_{1-x}Al_4O_7$: xEu ($0 \leq x \leq 0.1$) stoichiometric ratio, $Al(NO_3)_3 \cdot 9H_2O$, $Ca(NO_3)_2 \cdot 4H_2O$ and Eu_2O_3 were weighted in corresponding amounts making use of electronic balance. Eu_2O_3 was transferred to 250ml beaker and dissolved using concentrated HNO_3, then adding $Al(NO_3)_3 \bullet 9H_2O$, $Ca(NO_3)_2 \bullet 4H_2O$, $CO(NH_2)_2$ 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 dehydrated, 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 of combustion was a foamy, voluminous and amorphous precursor of the desired. Then the precursor was transferred into corundum crucible and calcined in the muffle furnace at 900 °C for 8 h to obtain the final white products.

The X-ray powder diffraction (XRD) patterns of all products were recorded on a Rigaku Dmax-2200 powder diffractometer with Cu Kα radiation (λ= 0.15418 nm). Infrared absorption spectra were recorded on a FT–IR360 infrared spectrometer using KBr pellets in the region of 4000-400cm^{-1}. The morphology was investigated with S-3000N scanning electron microscopy (SEM). Photoluminescence spectra under UV excitation were measured with a F4500 fluoro-spectrophotometer.

3. Results and discussion

3.1 Structure analysis of $CaAl_4O_7$: Eu^{3+}

Structural refinements were performed on the powder sample calcined at 900 ^{o}C. Fig.1 showed the X-ray powder diffraction pattern of $CaAl_4O_7$:Eu^{3+} synthesized by SPCS method, which accorded with JCPDS PDF#23-1037 and was confirmed monoclinic system structure with a space group of C2/c. The refined crystallographic unit cell parameters were obtained by Powder X software [23]: a=1.2888nm, b=0.8887nm, c=0.5445nm, β=106.93°(Z=1). No diffraction peaks of other phases were observed in Fig.1. The sample was converted completely to $CaAl_4O_7$ crystalline phase, without other types of calcium aluminates generated. The product was pure. Despite Ca^{2+} ions were replaced by a small amount of Eu^{3+}, $CaAl_4O_7$ lattice structure was almost not obviously impacted and caused lattice defects. Consequently, $CaAl_4O_7$ is an excellent host that has simple structure and provided with significance which improves the stability of luminescence materials in applications.

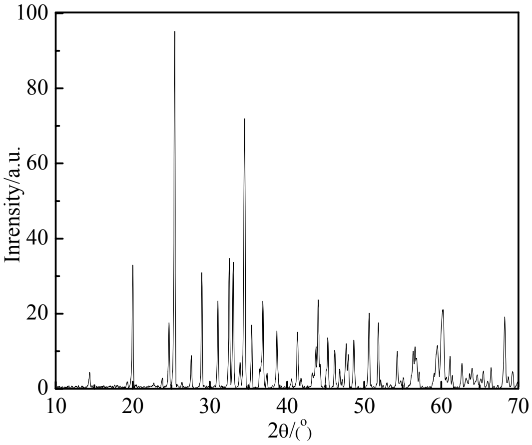

Fig.1. XRD pattern of $CaAl_4O_7$:Eu^{3+}.

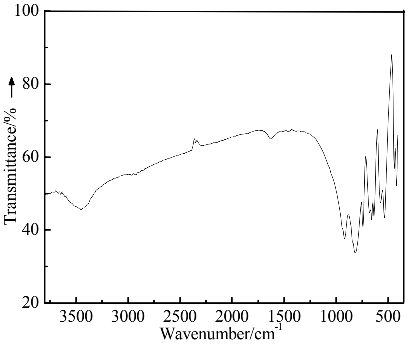

Fig.2. Infrared absorption spectra of $CaAl_4O_7$:Eu^{3+}.

FT-IR absorption spectra of the $CaAl_4O_7$:Eu^{3+} powder was shown in Fig. 2. The typical nitrate (NO_3) characteristic vibrations were not observed over the wavelength range of 1250 cm^{-1}–1650cm^{-1}. It nearly was the same as literature [24]. According to literature [25], absorption bands of the condensed matter AlO_4 are located at the range of 900 cm^{-1}-700 cm^{-1}, however, AlO_6 at 680-500 cm^{-1}. Therefore, we attribute three strong absorptions to AlO_4 libration at 600 cm^{-1}-900 cm^{-1}. Calcium aluminates [24] $Ca_3Al_2O_6$, $CaAl_4O_7$, $Ca_{12}Al_{14}O_{33}$, $CaAl_{12}O_{19}$, and $CaAl_2O_4$ presented two groups of absorption bands at 400 cm^{-1}-600 cm^{-1}. The characteristic absorption is due to 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 from air.

3.2 Luminescence properties of $CaAl_4O_7$:Eu^{3+}

The emission spectra of $CaAl_4O_7$:Eu^{3+} was showed in Fig. 3 (Excitation wavelength =275nm). $CaAl_4O_7$:Eu^{3+} subjected to UV radiation emits characteristic red light with a number of narrow lines at 578nm, 590nm, 616nm, 649nm and 701nm. These emissions are the result of 4f→4f ($^5D_0 \rightarrow {}^7F_J$, J = 0, 1, 2, 3, 4) transitions, respectively. Among them, $^5D_0 \rightarrow {}^7F_2$ was the strongest. The emission spectra of Eu^{3+} ions are hardly influenced by ligands surrounding of the host materials, because the transitions of Eu^{3+} only are involved in a redistribution of electrons within the inner 4f sub-shell. UV was efficiently absorbed by a transition to the charge transfer state (CTS) of Eu^{3+}-O^{2-}. After non-radiative relaxation to the lower 4f levels, luminescence occurred from the ^5D_J (mainly $^5D_0$) states of Eu^{3+}. According to the Judd-Ofelt theory [25-26], magnetic dipole transition $^5D_0 \rightarrow {}^7F_1$ is permitted, but electric dipole transition $^5D_0 \rightarrow {}^7F_2$ is allowed exceptionally in the case that Eu^{3+} ion occupied a non-inversion center site and is sensitive to local symmetry. Consequently, magnetic dipole transition $^5D_0 \rightarrow {}^7F_1$ should be relatively strong when the Eu^{3+} ion occupies inversion center site, while $^5D_0 \rightarrow {}^7F_2$ must be relatively weak. Surprisingly,

$^5D_0\rightarrow{}^7F_0$ transition with very weak intensity, both spin-forbidden and electric dipole forbidden, was observed. Although XRD analysis showed the structure was almost not changed, Ca^{2+} ions were not equivalent valence replaced by Eu^{3+}, which might still slightly result in lattice distortion. In addition, Eu^{3+} was 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 was partly relaxed. In consequence, $^5D_0\rightarrow{}^7F_2$ displayed more intensity than $^5D_0\rightarrow{}^7F_1$[27] , which indicated Eu^{3+} either deviated from inversion center site or local non-inversion center site in $CaAl_4O_7$. The weakest emission peaks attributed to $^5D_1\rightarrow{}^7F_J$ transition at 450 nm-550 nm. The energy level of Eu^{3+} between $^5D_0$ and $^5D_1$ was smaller (1740 cm^{-1}). When Eu^{3+} possessed 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 [28]. The infrared absorption spectra of $CaAl_4O_7$:Eu^{3+} presented the stronger libration frequency at 800 cm^{-1}-1000 cm^{-1} in Fig. 3. Electron of $^5D_1$ could transit into $^5D_0$ in terms of 2-3 phonons, thereby only the weaker $^5D_1\rightarrow{}^7F_J$ transitions were observed.

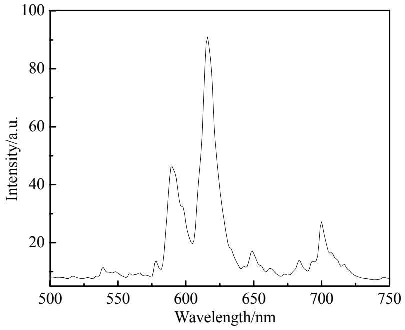

Fig.3. Emission spectra of $CaAl_4O_7$:Eu^{3+}.

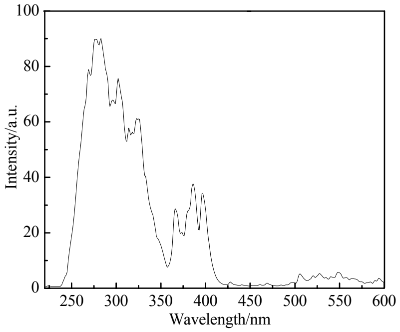

Fig.4. Excitation spectra of $CaAl_4O_7$: Eu^{3+}.

Fig. 4 showed excitation spectra of $CaAl_4O_7$:Eu^{3+} (scanning wavelength = 617 nm). Transition absorptions were belonged to the CTS of Eu^{3+}-O^{2-} at 269 nm, 278 nm and 283 nm. On the basis of energy level picture of literature [29], we deduced that excitation peaks located at 323 nm, 366 nm, 386 nm and 397 nm are attributed to $^7F_0\rightarrow{}^5H_3$, $^7F_0\rightarrow{}^5L_8$, $^7F_0\rightarrow{}^5G_2$ and $^7F_0\rightarrow{}^5L_6$, corresponding, the weaker peaks at 500nm-580nm came from $^7F_0\rightarrow{}^5D_1$ transition absorption. CTS of Eu^{3+}-O^{2-} had more intensity than $^7F_0\rightarrow{}^5D_{0,1}$. while 275nm excitation wavelength is adopted to excite CTS ,The stronger $^5D_0\rightarrow{}^7F_J$ emission is produced. In conclusion, we conjectured energy transfer from host to $^5D_{0,\ 1}$ and electron relaxation process with phonons assistant from $^5H_3$, $^5L_8$, $^5G_2$, $^5L_6$ and $^5D_1$ to $^5D_0$ consisted in $CaAl_4O_7$:Eu^{3+}.

3.3 Morphology of the $CaAl_4O_7$:Eu^{3+}

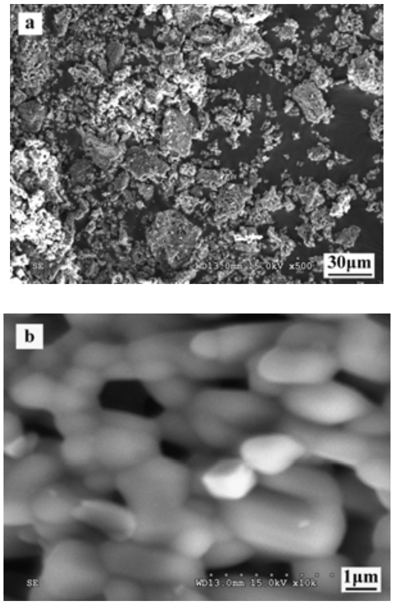

Fig. 5. SEM micrographs of $CaAl_4O_7$:Eu^{3+}: (a) magnified 500 times, (b) magnified 10000 times.

The particle size and morphology of the product powders were investigated by photomicrographs that measured via scanning electron microscopy (SEM) in Fig.5. Image a (magnified 500 times) showed products were layered distribution and each layer was composed of small ellipsoidal crystal particle which adhered to each other. Those phenomena were due to burning the samples at high temperatures. Correspondingly, the image b (magnification 10000 times) shows the product surfaces are porous honeycomb-like, smooth, dense without cracking and better crystallization effect. The average size of particles is about 1 μm. The characteristics of product surface were suitable for coating requirements of luminescence powder materials. Owing to urea burning, a lot of gases are released and have a damaging effect to the formation of massive structures on SPCS synthesis process, so that crystal nuclei growth was along to various directions, for forming a spherical shape characterized by the lower surface energy. Researches have shown that the spherical surface contributes to the enhancement of the luminescence intensity [30].

4. Conclusions

Luminescence materials $CaAl_4O_7$:Eu^{3+} were prepared, for the first time, via the self-propagating combustion synthesis (SPCS) method. Significant decreases in the synthesis temperatures, together with improved compound purities in the final powder bodies, of these compounds have been achieved, as compared to the conventional methods and practices of solid-state reactive firing of the starting oxides (i.e., CaO and Al_2O_3), which require operation temperatures in the range of 1500°–1700°C for prolonged times in kiln-type furnaces. Urea used (as a fuel or oxidizer) in the combustion synthesis noted to yield single-phase, ‘‘pure’’ (as deduced only by XRD and IR analysis). A small quantity of Eu^{3+} ions doped in $CaAl_4O_7$ hardly causes structure to be changed, and the refined crystal unit cell parameters were obtained by XRD analysis. Typical nitrate (NO_3) vibrations were not observed in the FT-IR spectra of $CaAl_4O_7$:Eu^{3+}. SEM micrographs of products showed the presence of micrometer range and regularly shape of particles after calcination at 900 °C. Luminescence properties $CaAl_4O_7$:Eu^{3+} demonstrate the existence of energy transfer and electron relaxation processes. The electric dipole transition $^5D_0 \rightarrow {}^7F_2$ displayed most intensity. $CaAl_4O_7$: Eu^{3+} was a kind of excellent luminescence materials and possessed potential value in applications.

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