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Synthesis, structure and luminescence properties of phosphor $CaAl_2O_4$ activated by Tb^{3+}

CHANG-BAO FU, HONG-JUN DONG[a*], CHENG-YOU LIU, YAN-PING WANG
Department of Physics, Tong Hua Normal College, Tong Hua 134002, China
[a]Department of Chemistry, Bai Cheng Normal College, Bai Cheng 137000, China

Series of green $CaAl_2O_4$:Tb^{3+} phosphors were first prepared by the Self-Propagating Combustion Synthesis (SPCS) methods. The unit cell of $CaAl_2O_4$:Tb^{3+} was confirmed monoclinic system with a space group *P21*/n by XRD analysis. Lattice constant refinement was a = 8.6831Å ,b = 8.0728 Å ,c = 15.1890 Å ,β = 90.1647°, *Z* = 12. The completely precise peaks were observed in surprise from excitation and emission spectra. Rare excitation absorption of Tb^{3+} coming from $4f^8 \rightarrow 4f^7 5d^1$ appeared in excitation spectra at 220-320nm. Emission spectra indicated that emission peaks were attributed to $^5D_4 \rightarrow {}^7F_J$ (J = 6, 5, 4, 3, 2, 1, 0) at 500nm-700nm and $^5D_3 \rightarrow {}^7F_J$ at 380nm-500nm. Vibration feature of products were investigated by FT-IR spectra. SEM revealed products had smooth surface, the better crystallization.

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Key words: SPCS, $CaAl_2O_4$:Tb^{3+}, Pure products, Luminescence properties

1. Introduction

Since the mid-20th century, electric lamps, color TV sets, medical imaging and other display devices etc, had made rapid development from basic research to production and application.

Aluminate phosphor as a kind of new materials, with itself peculiarity, such as high quantum efficiency, good stability, high quenching temperature, anti-radiation, low-cost, pollution-free, nontoxic and so forth, had been widely applied[1]. Currently, blue phosphor using strontium aluminates host had been studied [2-5]. Green phosphor played a more major role in the primary colors. In recent years, considerable attention for green phosphor had been mainly paying to sulfide, borate and phosphate [6-11]. Green barium aluminate phosphor doped rare earth ions had also been numerously reported [12-13, 24]. However, series of green calcium aluminate phosphor activated by Tb^{3+} were rarely researched. 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 phosphor was seriously damaged, in addition, luminescence intensity declined significantly. Whereas SPCS method held fast reaction, low temperature, saving energy etc evident advantages [14-20]. In particular, the products represented loose powders, small particle sizes, large specific surface area, effective crystal, easy shattering and so on. Practices had proved that SPCS was a promising synthesis method of phosphor.

In the present works, we reported the structure, morphology, FT–IR and luminescence characteristic of $CaAl_2O_4$:Tb^{3+} synthesized by SPCS method using urea as fuel.

2. Experimental

In the light of $CaAl_2O_4$:xTb^{3+}($0 \leq x \leq 0.1$) stoichiometric ratio, $Al(NO_3)_3 \cdot 9H_2O$(A.R.), $Ca(NO_3)_2 \cdot 4H_2O$(A.R.), Tb_4O_7(≥99.9%) were weighted in appreciate amounts making use of electronic balance, respectively. Tb_4O_7 was transferred to 250ml beaker and dissolved using a little concentrated HNO_3(A.R.), then adding $Al(NO_3)_3 \cdot 9H_2O$, $Ca(NO_3)_2 \cdot 4H_2O$, $CO(NH_2)_2$(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 5-7 min. The product of combustion was a foamy, voluminous and amorphous precursor of the desired. And then the precursor was transferred into corundum crucible and calcined in the muffle furnace at 850□ for 10h to obtained white products.

The X-ray powder diffraction (XRD) patterns of all products were recorded on a Rigaku Dmax-2200 powder diffractometer (scanning speed 6°/min, scanning range 3-80°). 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 fluorospectrophotometer (EX slit 2.5nm/EM slit 2.5nm, scanning speed 12000 nm/min).

3. Results and discussion

3.1 Structure analysis of $CaAl_2O_4:Tb^{3+}$

Structural refinements were performed on the powder product calcined at 850□. Fig.1. showed the X-ray powder diffraction pattern of $CaAl_2O_4:Tb^{3+}$ synthesized by SPCS method, which accorded with JCPDS PDF#53-0191 and was confirmed monoclinic system structure with a space group *P21*/n. The refined crystallographic unit cell parameters were obtained by Powder X software[21], a = 8.6831Å , b = 8.0728 Å , c = 15.1890 Å , β = 90.1647°, Z=12. No other miscellaneous diffraction peaks were observed in Fig.1. The sample was completely converted to $CaAl_2O_4$ crystalline phase, without other types of calcium aluminates generated. The product was pure. Despite Ca^{2+} ions were replaced by a small amount of Tb^{3+}, $CaAl_2O_4$ lattice structure was almost not obviously impacted and caused lattice defects. Consequently, $CaAl_2O_4$ was an excellent host that had simple structure and provided with significance which improving stability of phosphor in application.

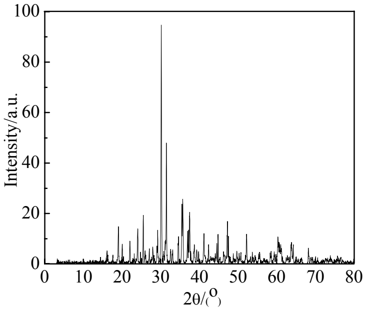

Fig.1. XRD pattern of $CaAl_2O_4:Tb^{3+}$.

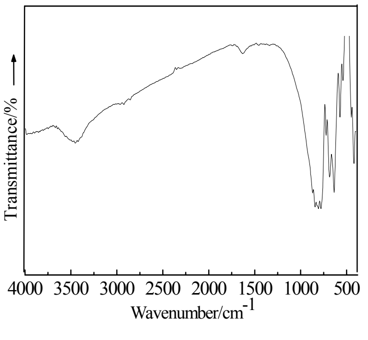

Fig. 2. Infrared absorption spectra of $CaAl_2O_4:Tb^{3+}$.

FT-IR spectra of $CaAl_2O_4:xTb^{3+}$powders were shown in Fig.2.. The typical nitrate (NO_3) characteristic vibrations were not observed over the wavelength range of 1250cm^{-1}-1650cm^{-1}. In accordance with literature [22], absorption bands of the condensed matter AlO_4 located at the range of 900cm^{-1}-700cm^{-1}, however, AlO_6 at 680-500cm^{-1}. Therefore, we guessed two strong absorptions maybe attributed to AlO_4 libration at 600cm^{-1}-900cm^{-1}. It nearly was the same as literature [23], in which all kinds of calcium aluminates presented two groups of absorption at 400cm^{-1}-600cm^{-1}. So, we were convinced of that belonged to characteristic liberation absorption of Al-O bonds in Fig.2. It also proved that $CaAl_2O_4$ lattice structure was almost not obviously changed although Ca^{2+} ions were replaced by a small amount of Tb^{3+}, which was consistent with XRD analysis result. The absorption bands at 1500cm^{-1} and 3450cm^{-1} were due to vibrations from CO_3^{2-} and OH^- groups, respectively, because of CO_2 and H_2O in the air.

3.2 Luminescence properties of $CaAl_2O_4:Tb^{3+}$

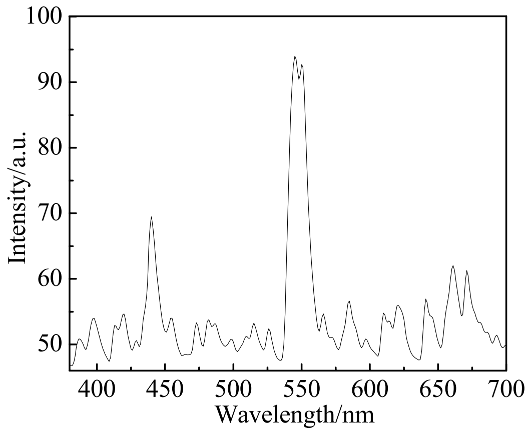

Fig. 3. Emission spectra of $CaAl_2O_4$: Tb^{3+}.

The emission spectra of $CaAl_2O_4:Tb^{3+}$ was showed in Fig. 3. (Excitation wavelength = 275nm). In general, only a few lineal characteristic spectra of common phosphors activated by Tb^{3+} were produced [24-25]. While in Figure 3, energy level transition emissions of Tb^{3+} with refined structure were first observed. Tb^{3+} possessed the larger J value, which resulted in those levels were split into a number of branch energy levels by means of crystal field, so that emission peaks generated splitting phenomena. Emission peaks were attributed to $^5D_4 \rightarrow {}^7F_J$ (J = 6, 5, 4, 3, 2, 1, 0) transition at 500nm-700nm. Rare $4f^8 \rightarrow 4f^7 5d^1$ transition was observed at 220nm-320nm, because $4f^7 5d^1$ energy level of Tb^{3+} was lower, which could be interfused 4f configuration, The result of that lead to parity forbidden was relaxed. However, electric dipole transition $^5D_4 \rightarrow {}^7F_6$ was less sensitive affected by ligands environment than $^5D_0 \rightarrow {}^7F_2$ of Eu^{3+} [26]. Therefore, $^5D_4 \rightarrow {}^7F_5$ characteristic emission of Tb^{3+} was strongest at 545nm and products emitted a green light under the UV ray. The stronger emission coming from the higher excited state $^5D_3 \rightarrow ^7F_J$ were observed at 380nm-500nm, which indicated that cross-relaxation effect usually existing between $^5D_3$ and $^5D_4$ energy levels was not engendered. Otherwise, being due to urea reducing properties, Tb^{4+} might be effortless reduced to Tb^{3+} in Tb_4O_7 on the combustion process, which increased Tb^{3+} concentration so that luminescence intensity was enhanced.

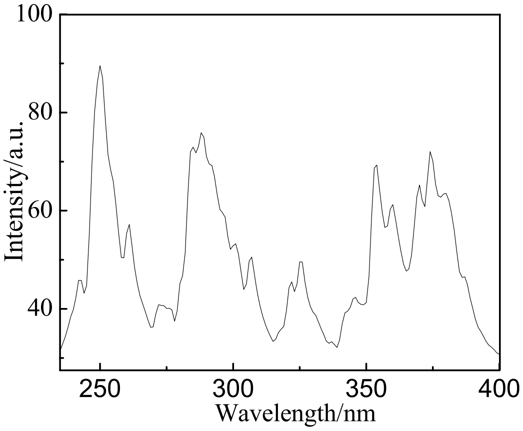

Fig. 4. Excitation spectra of $CaAl_2O_4$:$Tb^{3.+}$

Fig. 4 showed excitation spectra of $CaAl_2O_4$:Tb^{3+} (scanning wavelength = 547nm). Three groups of excitation band were belonged to f→f transition absorptions of Tb^{3+} at 320nm-400nm. On the basis of energy level datum of Tb^{3+} in literature [27], we primitively deduced that excitation peaks were maybe attributed to $^7F_6 \rightarrow (^5D_3, ^5G_6)$, $^5L_{10}$, $^5G_5$, $(^5D_2, ^5G_4, ^5L_9)$, $(^5G_3, ^5L_8, ^5L_7)$, $(^5L_6, ^5G_2)$, $^5D_1$ and $^5D_0$ transition absorption at 380nm, (374, 370nm), 360nm, 354nm, 346nm, 337nm, 325nm and 322nm. Corresponding, the two stronger bands came from $4f^8 \rightarrow 4f^7 5d^1$ transition absorption at 220-320nm, because $4f^7$ possessed stable half-filled electronic configurations, generally considered which could be excited under lower energy. According to research of Reisfeld and Jorgenesen, ^7D of $4f^7 5d^1$ configuration had more obvious coulomb exchange interaction than ^9D. Thereby, transition absorption of $^7F_6 \rightarrow ^7D$ relatively located at higher energy region by contrast with $^7F_6 \rightarrow ^9D$. Emission peaks maybe came from $^7F_6 \rightarrow ^7D$ at 220-270nm, correspondingly, $^7F_6 \rightarrow ^9D$ at 270-310nm. This phenomenon, for the first time, was observed in $CaAl_2O_4$, which was similar with luminescence characteristic of Tb^{3+} in the zeolite.

3.3 Morphology of $CaAl_2O_4$:Tb^{3+}

The particle sizes and morphology of the product powders were investigated by photomicrographs that measured via scanning electron microscopy (SEM) in Fig.5. Image a $CaAl_2O_4$:Tb^{3+} (magnified 500 times) showed that products presented ellipsoidal distribution. Slightly agglomeration phenomena were observed in a $CaAl_2O_4$:Tb^{3+}, which were due to calcining at high temperatures for the products. Correspondingly, image b $CaAl_2O_4$:Tb^{3+} (magnified 4500 times) showed the product surfaces were smooth, dense without cracking and the better crystallization effect. The average size of $CaAl_2O_4$:Tb^{3+} particles were about 1μm-3μm. The characteristics of product surface were suitable for coating requirements of luminescence powder materials. Owing to urea burning, a lot of gases released and damaged to the formation of massive structures on SPCS synthesis process, so that crystal nuclei growth was along to directions for formation sphere shape containing the lower surface energy. Researches shown spherical surface was contributed to enhance luminescence intensity [28].

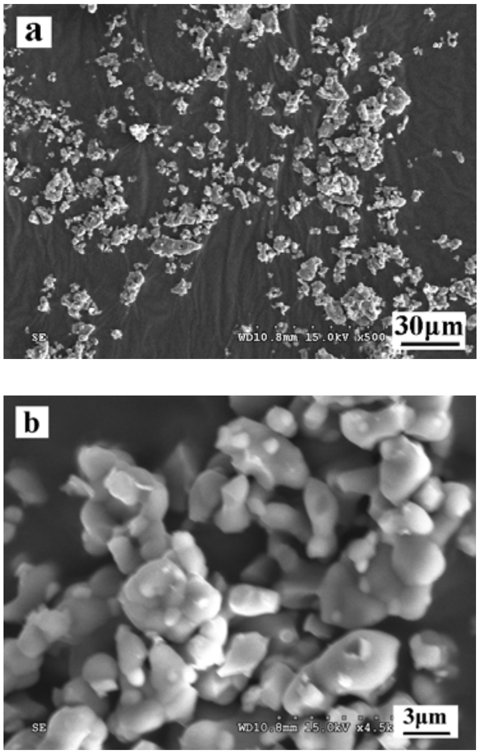

Fig. 5. SEM micrographs of $CaAl_2O_4$:Tb^{3+}*: (a) (magnified 500 times), (b) (magnified 4500 times).*

4. Conclusions

$CaAl_2O_4$:Tb^{3+} phosphors were first successfully prepared via the self-propagating combustion synthesis (SPCS) method. Significant decreases in the synthesis temperatures, together with improved compound purities that were attained in the final powder bodies, of these compounds had 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 required operation temperatures in the range of 1500°–1700°C for prolonged times in kiln-type furnaces.

Urea used (as a fuel) in the combustion synthesis noted to yield single-phase, ''pure'' (as deduced only by XRD and IR analysis). A small quantity of Tb^{3+} ions doped in $CaAl_2O_4$ hadly caused structure to be changed, and the refined crystal unit cell parameters were obtained by XRD analysis. Analysis results of XRD were provided further evidence of $CaAl_2O_4:Tb^{3+}$ structure by FT-IR spectra. SEM micrographs of products showed the presence of micron range and regularly shape particles after calcined at 850°C. luminescence properties study of $CaAl_2O_4:Tb^{3+}$ indicated that they were existence of refined energy level transfer process in emission and excitation spectra, It is noteworthy that, for the first time, the similar luminescence characteristics of Tb^{3+} in $CaAl_2O_4$ with zeolite was observed, which hold potential research value to study energy level of Tb^{3+}. They possessed widely application prospect because of excellent luminescence properties of $CaAl_2O_4:Tb^{3+}$.

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*Corresponding author: donghongjun6698@yahoo.com.cn