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Structure and luminescence properties of Sm^{3+} doped in $CaAl_2O_4$ phosphor

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Series of high-purity $CaAl_2O_4:Sm^{3+}$ phosphors were first successfully prepared by the Self-Propagating Combustion Synthesis (SPCS) methods. The unit cell of $CaAl_2O_4:Sm^{3+}$ was confirmed monoclinic system with a space group *P21*/n by XRD analysis. Lattice constant refinement was a = 0.8699nm , b = 0.8212 nm, c = 1.5207nm, β = 90.1584°, *Z*=12. Emission peaks attributed to $^4G_{5/2}\rightarrow{}^6H_J$ (J = 5/2, 7/2, 9/2, 11/2) transitions at 568nm, 603nm, 655nm and 715nm, respectively, and Sm^{3+} ions mainly took up symmetry center lattice. Excitation peaks belonged to f→f configuration transition absorption of at 406nm, 379nm, 367nm and 349nm, which maybe attributed to $^6H_{5/2}\rightarrow(^4F_{7/2}, {}^4L_{13/2})$, $(^4D_{1/2}, {}^6P_{7/2})$, $^4F_{9/2}$, $^4K_{15/2}$, respectively. Vibration feature of products was investigated by FT-IR spectra. SEM revealed products had smooth surface, the better crystallization.

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Keywords: SPCS, $CaAl_2O_4:Sm^{3+}$, High-purity products, Luminescence properties

1. Introduction

Evolution and upgrade of telecommunications and electronics required new types of highly effective luminescent materials. Lately special interest was focused on a group of phosphors based on aluminates of alkali-earth metals activated by rare earth ions, with high quantum efficiency, good stability, high quenching temperature, anti-radiation, low-cost, pollution-free, nontoxic and so forth advantages, which were widely applied in projection screens, field emission, plasma displays, scanning systems, medical imaging and other display devices [1]. In recent years, Considerable attention for phosphor activated by Sm^{3+} had been mainly paying to sulfide, borate and germinate [2-14].

However, series of reddish orange calcium aluminate phosphor activated by Sm^{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 [15-23]. In particular, the products represented loose powders, small particle size, large specific surface area, effective crystal, easy shattering and so on. Practices had proved that SPCS was a promising synthesis method of phosphors.

In the present works, we reported the structure, morphology, IR and luminescence characterization of phosphor Sm^{3+} ions doped $CaAl_2O_4$ synthesized via SPCS method using urea as fuel.

2. Experimental

According to $CaAl_2O_4:Sm^{3+}$($0\leq x\leq 0.1$) stoichiometric ratio, $Al(NO_3)_3\cdot 9H_2O$(A.R.), $Ca(NO_3)_2\cdot 4H_2O$(A.R.), Sm_2O_3 (≥99.9%) were weighted in appreciate amounts making use of electronic balance, respectively. Sm_2O_3 was transferred to 250ml beaker and dissolved using a little concentrated HNO_3(A.R.), then adding $Al(NO_3)_3\bullet 9H_2O$, $Ca(NO_3)_2\bullet 4H_2O$, $CO(NH_2)_2$(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 850for 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 spectras were recorded on a FT–IR360 infrared spectrometer using KBr pellets in the region of 4000-400cm^{-1}. The morphologies were investigated with S-3000N scanning electron microscopy (SEM). Photoluminescence spectra under UV excitation were measured with a F4500 fluorospectrophotometer (EX slit 2.5 nm/EM slit 2.5 nm, scanning speed 12000 nm/min).

3. Results and discussion

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

Structural refinements were performed on the product powders calcined at 850. Fig. 1 showed the X-ray powder diffraction pattern of $CaAl_2O_4:Sm^{3+}$ synthesized by SPCS method, which accorded with JCPDS PDF#53-0191 and was confirmed monoclinic system structure with a space group *P21*/n. This was similar with $CaAl_2O_4:Tb^{3+}$ that we had been studied. The refined crystallographic unit cell parameters were obtained by Powder X software[24], a = 0.8699nm ,b = 0.8212 nm, c = 1.5207nm, β = 90.1584°, *Z*=12. No diffraction peaks from other phases were observed in Fig. 1. The sample was converted completely to $CaAl_2O_4$ crystalline phase, without the generation of other types of calcium aluminates. The products were pure. Despite Ca^{2+} ions were replaced by a small amount of Sm^{3+}, $CaAl_2O_4$ lattice structure was almost not obviously impacted and caused lattice defects. Consequently, $CaAl_2O_4$ was an excellent host that has simple structure and provides significance, which improves the stability of phosphor in applications.

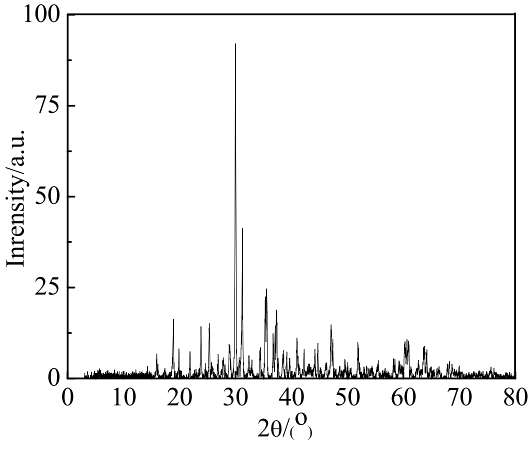

Fig. 1. XRD pattern of $CaAl_2O_4$: Sm^{3+}.

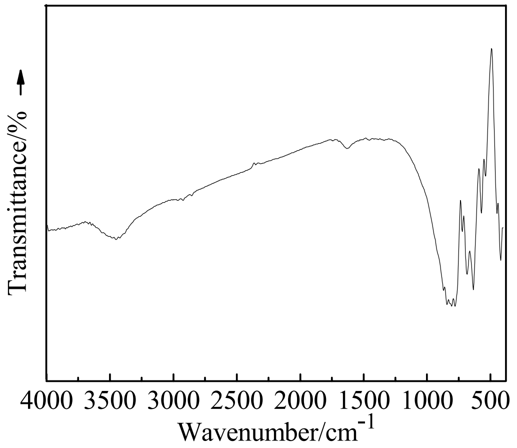

Fig. 2. Infrared absorption spectra of $CaAl_2O_4:Sm^{3+}$.

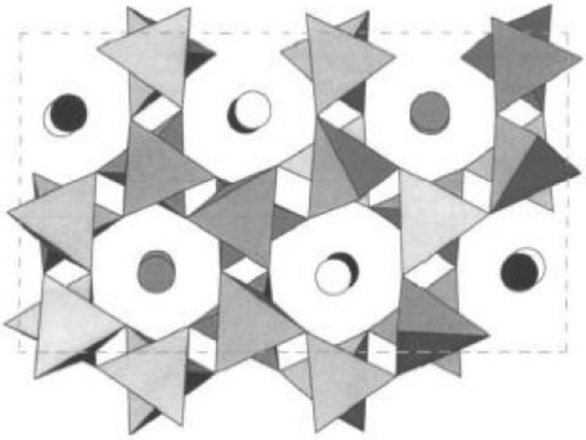

Fig. 3. Monoclinic $CaAl_2O_4$ viewed from [010] direction.

FT-IR spectra of $CaAl_2O_4:Sm^{3+}$ powders were shown in Fig. 2, which was the same as $CaAl_2O_4:Tb^{3+}$ as well. The typical nitrate (NO_3) characteristic vibrations were not observed over the wavelength range of $1250cm^{-1}$-$1650cm^{-1}$. Structure of $CaAl_2O_4$ viewed from [010] direction was showed in Fig. 3, which belonged to stuffed tridymite framework. Three-dimensional network was constituted of AlO_4 tetrahedron shared vertex, in gaps of which Ca^{2+} ions were filled. Therefore, we thought that Ca^{2+} ions were replaced by Sm^{3+}. On the basis of literature [25], absorption bands of the condensed matter AlO_4 located in the range of $900cm^{-1}$-$700cm^{-1}$, isolated AlO_4 located in the range of $800cm^{-1}$-$650cm^{-1}$; however, condensed matter AlO_6 at

680-500 cm^{-1}, isolated AlO_6 at 530-400 cm^{-1}. Hence, we guessed two strong absorptions maybe attributed to AlO_4 libration at 600 cm^{-1}-900 cm^{-1}, which coincided with actual AlO_4 in Fig. 3. It nearly was the same as literature [26], in which all kinds of calcium aluminates such as $Ca_3Al_2O_6$, $Ca_{12}Al_{14}O_{33}$, $CaAl_{12}O_{19}$, $CaAl_4O_7$ and $CaAl_2O_4$ presented two groups of absorption at 400cm^{-1}-600 cm^{-1}. So, we were convinced of that belonged to characteristic liberation absorption coming from Al-O bonds in Fig. 2. It also proved that $CaAl_2O_4$ lattice structure was almost not obviously changed, and this is consistent with XRD analysis result. 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. $CaAl_2O_4$ doped Ce^{3+} was also studied, FT-IR spectra analysis are nearly identical to that from Fig. 2.

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

The emission spectra of $CaAl_2O_4$:Sm^{3+} was showed in Fig. 4. (Excitation wavelength = 275 nm). Emission peaks attributed to transitions of $^4G_{5/2}\rightarrow{}^6H_J$ (J = 5/2, 7/2, 9/2, 11/2) at 568 nm, 603 nm, 655 nm and 715 nm, respectively, in which emission of $^4G_{5/2}\rightarrow{}^6H_{7/2}$ was strongest. We usually determined symmetry of luminescence centers in the crystal lattice via relative strength of electric and magnetic dipole transition. According to literature [27], PS May thought that $^4G_{5/2}\rightarrow{}^6H_{5/2}$ was mainly magnetic dipole transition, some of electric dipole transition; $^4G_{5/2}\rightarrow{}^6H_{7/2}$, although magnetic dipole transition allowed, electric dipole transition was principal; $^4G_{5/2}\rightarrow{}^6H_{9/2}$ electric dipole transition was dominant, however, magnetic dipole transition was formally forbidden. $^4G_{5/2}\rightarrow{}^6H_{9/2}$ emergence in emission peaks of $CaAl_2O_4$:Sm^{3+} indicated decrease of symmetry, namely, parts of the Sm^{3+} ions located at non-symmetry center lattice. Tamura reported Sm^{3+}, if mainly occupied non-symmetry center lattice, produced typical emission in the vicinity of 650nm; on the contrary, if mainly symmetry, produced in the vicinity of 602nm. In Fig.4, $^4G_{5/2}\rightarrow{}^6H_{7/2}$ was stronger than $^4G_{5/2}\rightarrow{}^6H_{9/2}$, Therefore, Sm^{3+} mainly took up symmetry center lattice.

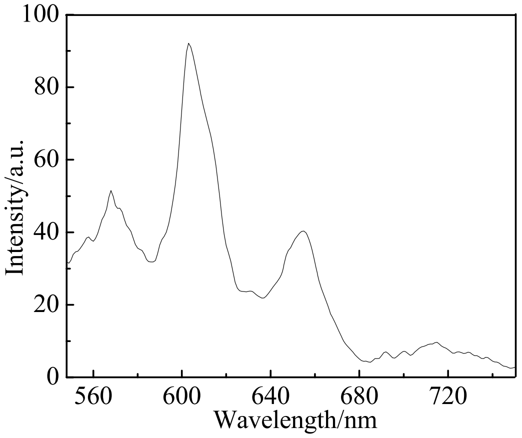

Fig. 4. Emission spectra of $CaAl_2O_4$: Sm^{3+}.

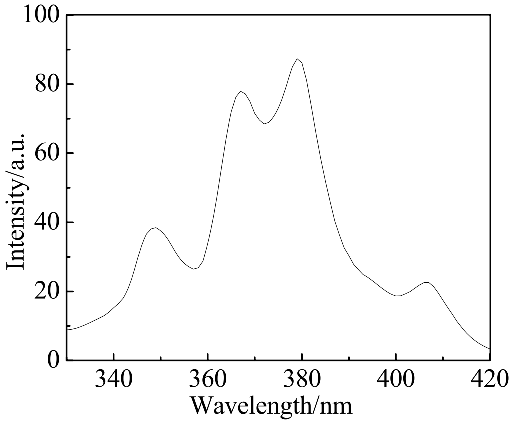

Fig. 5. Excitation spectra of $CaAl_2O_4$: Sm^{3+}.

Fig. 5 showed excitation spectra of $CaAl_2O_4$:Sm^{3+} (scanning wavelength = 604 nm). Excitation peaks belonged to f→f configuration transition absorption of Sm^{3+} at 406 nm, 379 nm, 367 nm and 349 nm. In like manner, according to level datum of Sm^{3+} in literature [28], we primitively deduced that those maybe attributed to $^6H_{5/2}\rightarrow(^4F_{7/2}, {}^4L_{13/2})$, $(^4D_{1/2}, {}^6P_{7/2})$, $^4F_{9/2}$, $^4K_{15/2}$ transition absorption, respectively. The exact ascription about excitation peaks of $CaAl_2O_4$:Sm^{3+} need to be further researched.

3.3 Morphology of the $CaAl_2O_4$:Sm^{3+}

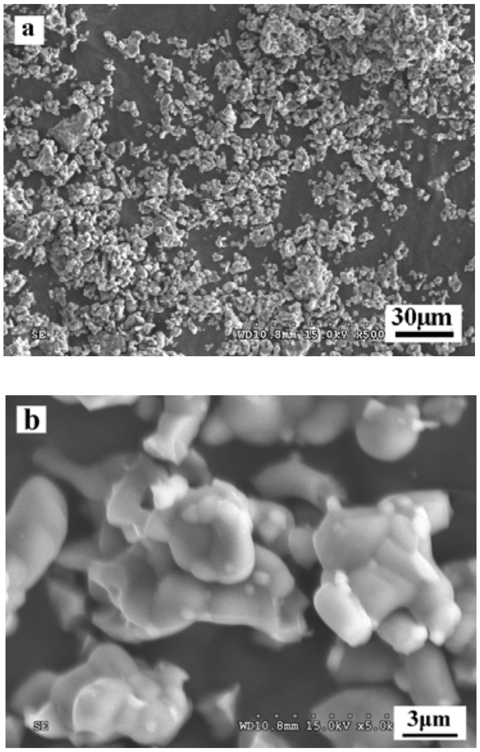

Fig. 6. SEM micrographs of $CaAl_2O_4$:Sm^{3+} (a)(magnified 500 times); (b) (magnified 5000 times).

The particle sizes and morphology of the product powders were investigated by photomicrographs that measured via scanning electron microscopy (SEM) in Fig.6. Image a $CaAl_2O_4$:Sm^{3+} (magnified 500 times) showed that products presented ellipsoidal shape distribution, and dispersion of $CaAl_2O_4$:Sm^{3+} was much better than $CaAl_2O_4$:Tb^{3+} that had been studied. Slightly agglomeration phenomena were observed in $CaAl_2O_4$:Sm^{3+}, which were due to calcining at high temperatures for the samples. Correspondingly, image b $CaAl_2O_4$:Sm^{3+} (magnified 5000 times) showed the product surfaces were smooth, dense without cracking and the better crystallization effect. The average sizes of $CaAl_2O_4$:Sm^{3+} particles were about 3µm-6µm. The characteristics of products 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 showed that spherical surface enhances the luminescence intensity [29].

4. Conclusions

$CaAl_2O_4$:Sm^{3+} phosphors were, for the first time, 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 Sm^{3+} ions doped in $CaAl_2O_4$ hardly caused structure to be changed, and the refined crystal unit cell parameters were obtained by XRD analysis. AlO_4 structure existed in $CaAl_2O_4$:Sm^{3+} was proved by means of the FT-IR spectra, in addition, in which typical nitrate (NO_3) vibrations were not observed. SEM micrographs of products showed the presence of micrometer range and regularly shape particles after calcined at 850°C. Luminescence properties study of reddish orange $CaAl_2O_4$:Sm^{3+} indicated that Sm^{3+} ions mainly located symmetry center lattice. They possessed widely potential research value and application prospect because of excellent luminescence properties of $CaAl_2O_4$:Sm^{3+}

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