Synthesis and luminescence properties of composite CaAl$_2$O$_4$·2CaAl$_4$O$_7$ : Re$^{3+}$ (Re$^{3+}$ = Tb$^{3+}$, Sm$^{3+}$) phosphors for application white LEDs

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Composite CaAl$_2$O$_4$·2CaAl$_4$O$_7$ : Re$^{3+}$ (Re$^{3+}$ = Tb$^{3+}$, Sm$^{3+}$) phosphors were prepared by the SPCS technique, which were studied via XRD, SEM, FT-IR spectra and luminescent spectra. The results show that the crystal lattice structure of them needs slight distortion to improve luminescence properties. They exhibit wider near-UV excitation band around 380 nm. Upon exciting with 380 nm, CaAl$_2$O$_4$·2CaAl$_4$O$_7$ : Tb$^{3+}$ shows a strong green-light at 548 nm corresponding to a $^5D_{4} \rightarrow ^7F_2$ transition of Tb$^{3+}$ ions, and CaAl$_2$O$_4$·2CaAl$_4$O$_7$ : Sm$^{3+}$ presents strong red-light at 604 nm corresponding to a $^5D_{4} \rightarrow ^7H_{15/2}$ transition of Sm$^{3+}$ ions. The product fired at 900°C exhibit high quality crystallinity and with a size of that is approximately 1-3 µm. All the above characteristics of the products are beneficial for phosphors for white LEDs.

Key words: SPCS, CaAl$_2$O$_4$·2CaAl$_4$O$_7$ : Re$^{3+}$ (Re$^{3+}$ = Tb$^{3+}$, Sm$^{3+}$), luminescence properties, white LEDs.

Introduction

Electric lamps, color TVs and medical imaging etc have been widely used from the mid-20th century. Since high power output blue indium gallium nitride (GaN) light-emitting diodes (LEDs) were reported by Nakamura and co-workers [1-2], white LEDs have been developed rapidly. After nitride and phosphate LEDs gave line three primary colors of light, the study of high brightness, high reliability, low electric consumption, long lifetime and environmentally friendly characteristics [3-6]. For these reasons, a focus of investigation has become exploring the preparation of superior phosphors meeting the requirements for wide application of white LEDs. The appropriate phosphors for near-UV white LEDs must show a stronger and broader absorption band around 400 nm. It is well known that Tb$^{3+}$ and Sm$^{3+}$ ions present stronger absorption around 380 nm. When the host compound is doped by rare earth ions, the sublattice structure around luminescent center ions will be somewhat distorted. Consequently, the spectral lines of rare earth ions are expected to be broadened. Recently, most attention mainly concentrates on red Y$_2$O$_3$:Eu$^{3+}$ and green ZnS : Cu$^{2+}$/Al$^{3+}$ phosphors etc. However, the efficiency and lifetime of the traditionally applied Y$_2$O$_3$:Eu$^{3+}$ phosphor is much lower compared to that of the green and blue phosphors. In addition, sulfide phosphors are unstable and are accompanied with the released of harmful sulfide gas [7-8].

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Experimental

Al(NO$_3$)$_3$·9H$_2$O (15.0054g, A.R.), Ca(NO$_3$)$_2$·4H$_2$O(2.7771g, A.R.), Tb$_2$O$_3$(0.0299g, 99.9%) and Sm$_2$O$_3$(0.0279g, 99.9%) were exactly weighted. Tb$_2$O$_3$ or Sm$_2$O$_3$ was put in 250 ml beaker and dissolved using a little concentrated HNO$_3$(A.R.), then adding Al(NO$_3$)$_3$·9H$_2$O, Ca(NO$_3$)$_2$·4H$_2$O, CO(NH$_2$)$_2$ (A.R.) were added and the appropriate amount of distilled water. The solution was stirred and heated until the solution was evaporated to become viscous. Subsequently, the beaker was put in a muffle furnace at 500°C. After a few
minutes, the solution boiled and underwent dehydration, decomposition, with swelling and frothing, following combustion. This combustion process resulted in ruptured foams with a flame and glowed to incandescence. A foamy, voluminous and amorphous precursor was obtained after five minutes. The precursor was later transferred into a corundum crucible and calcined in a muffle furnace at 900 for 6h. A white product was obtained.

The X-ray powder diffraction (XRD) patterns of the products were carried out with a Rigaku Dmax-2200 powder diffractometer (Cu Kα1 = 1.54056 × 10−10 m, scanning speed 6°/minute, scanning 20 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 range of 4000-400 cm−1. The scanning electron microscopy (SEM) was performed on a Hitachi S-3000N. Excitation and emission spectra were measured by a Hitachi F4500 fluorospectrophotometer (EX slit 2.5 nm/EM slit 2.5 nm, scanning speed 12000 nm/minute). All the measurements were performed at room temperature.

**Results and Discussion**

Fig. 1 shows the XRD pattern of the CaAlO4−2CaAlO7· Tb3+ phosphor, which presents that two types X-ray diffraction peaks of aluminate crystal phases that are CaAlO4 and CaAlO7, the diffraction intensities of CaAlO4 peaks (the peaks are marked using the symbol ▼) are stronger than from CaAlO7 (the peaks marked using the symbol ▲), which indicates that raw material produced were CaAlO4 with a quantity of CaAlO7. However, the relative intensity of the main diffraction peaks from them show on evident change, which indicates that crystal lattice becomes distorted when Ca2+ ions are non-equivalently replaced by Tb3+ doped into CaAlO4−2CaAlO7. This will affect the crystal field at the Ca2+ sites, consequently, cause a change of luminescent properties. FT-IR spectra of CaAlO4−2CaAlO7· Tb3+ and CaAlO4−2CaAlO7· Sm3+ phosphors are displayed in Fig. 2. We believe that the structure of CaAlO4−2CaAlO7· Tb3+ is similar to CaAlO4−2CaAlO7· Tb3+ due to the similar FT-IR spectra of them, although a XRD of CaAlO4−2CaAlO7· Sm3+ is not measured. The absorption bands around 1550 cm−1 and 3450 cm−1 belong to vibration absorption from CO2− and OH− groups, respectively, because of the CO2 and H2O existing in the air.

Fig. 3 shows the excitation and emission spectra of the CaAlO4−2CaAlO7· Tb3+ phosphor. The excitation spectrum was obtained by monitoring the 5D4 → 7F2 transition of Tb3+ ions (scanning wavelength 548 nm), whose excitation peaks that are located in the 200-300 nm result from the well-known 4f6−4f5 5d1 transition absorption of Tb3+ ions. This is easily excited by a lower energy because 4f6 possesses a stable half-filled electronic configuration. According to the Reisfeld and Jørgensen investigation, the 5D energy level of 4f6 → 5d configuration displays more obvious coulomb exchange interaction than the 5D of that. Thereby, the transition absorption of 5F4(4f6) → 5D(4f5 5d1) is relatively located in the higher energy region by contrast with 5F4(4f6) → 5D(4f5 5d1) [13]. The excitation peak at 250 nm maybe comes from 5F6 → 5D, correspondingly, that at
288 nm maybe comes from \( ^7F_6 \rightarrow ^9D \). This phenomenon is similar to the excitation characteristics of Tb\(^{3+}\) ions in the zeolite. Another three excitation peaks in the 300-400 nm near-UV excitation region relate to the 4f-4f transition absorption of Tb\(^{3+}\) ions, which respectively are attributed to \( ^7F_6 \rightarrow ^9D_3 \), \( ^7F_6 \rightarrow ^9D_5 \), and \( ^7F_6 \rightarrow ^9D_7 \) at 320 nm, 358 nm and 376 nm. The emission spectrum of CaAl\(_2\)O\(_4\)-2CaAlO\(_3\); Tb\(^{3+}\) is excited by 380 nm wavelength irradiation. In general, the common linear characteristic spectra of the Tb\(^{3+}\) doped phosphors are only displayed [14-15], while the emission spectrum of Tb\(^{3+}\) ions is broadened in Fig. 3. The emission peaks are attributed to 4f-4f transition of Tb\(^{3+}\) ions, which respectively correspond to \( ^5D_1 \rightarrow ^7F_4 \), \( ^5D_2 \rightarrow ^7F_4 \), \( ^5D_3 \rightarrow ^7F_4 \), \( ^5D_4 \rightarrow ^7F_3 \), \( ^5D_4 \rightarrow ^7F_4 \) and \( ^5D_4 \rightarrow ^7F_5 \) at 445 nm, 466 nm, (496 nm, 511 nm), 548 nm, (586, 594 nm) and (618, 624 nm). It is well known that the luminescent spectra of trivalent lanthanide ions in crystals mainly come from two types of electronic transitions that are the 4f-4f and 5d-4f transitions. The former generally shows sharp emission lines, while the latter have a broad band character. In order to eliminate forbidden parity, electronic configurations that are mixed with the opposite parity energy levels are not a charge transfer state (CTS) but the lower self-energy 4f\(^6\) \( \rightarrow \) 5d\(^1\) levels, so the 4f-4f transition are broadened. In addition, the \( ^5D_3 \rightarrow ^7F_4 \) electric dipole transition of Tb\(^{3+}\) ions is less sensitively affected by ligand environments than the \( ^5D_0 \rightarrow ^7F_2 \) of Eu\(^{3+}\) [16]. Therefore, a magnetic dipole transition \( ^5D_3 \rightarrow ^7F_2 \) of Tb\(^{3+}\) is strongest at 548 nm. The CaAl\(_2\)O\(_4\)-2CaAlO\(_3\); Tb\(^{3+}\) phosphor emits green-light under 380 nm near-UV irradiation. The \( ^5D_1 \rightarrow ^7F_1 \) and \( ^5D_4 \rightarrow ^7F_1 \) transition emissions originating from higher excited states are observed, which indicate that the usual cross relaxation effect (\( ^5D_3 + ^7F_4 \rightarrow ^5D_4 + ^7F_3 \)) is not complete.

As can be seen from the emission spectrum of the CaAl\(_2\)O\(_4\)-2CaAlO\(_3\); Sm\(^{3+}\) phosphor that is excited by 380 nm irradiation in Fig. 4, there is a broad band emission at 493 nm, besides the four emission peaks arising from the 4f-4f transition of Sm\(^{3+}\) ions that respectively are attributed to \( ^4G_{5/2} \rightarrow ^4H_{5/2}, ^4G_{5/2} \rightarrow ^4H_{7/2}, ^4G_{5/2} \rightarrow ^4H_{5/2} \) and \( ^4G_{5/2} \rightarrow ^4H_{11/2} \) at 568 nm, 604 nm, 654 nm and 713 nm. The emission intensity of the \( ^4G_{5/2} \rightarrow ^4H_{5/2} \) transition is strongest, so the CaAl\(_2\)O\(_4\)-2CaAlO\(_3\); Sm\(^{3+}\) phosphor emits red-light under near-UV irradiation. In general, the symmetry of luminescent centers in a crystal lattice is determined by the relative strength of the electric dipole transition and magnetic dipole transition. May and co-workers believe that the \( ^4G_{5/2} \rightarrow ^4H_{5/2} \) transition is due to its predominant magnetic dipole character. On the other hand, the \( ^4G_{5/2} \rightarrow ^4H_{7/2} \) transition principally presents an electric dipole character, although a magnetic dipole transition is allowed. However, the hypersensitive \( ^4G_{5/2} \rightarrow ^4H_{5/2} \) transition is forbidden by the magnetic dipole, in contrast, allowed by a forced electric dipole [17]. The \( ^4G_{5/2} \rightarrow ^4H_{5/2} \) transition occurring in the emission peaks indicates that the symmetry of the CaAl\(_2\)O\(_4\)-2CaAlO\(_3\); Sm\(^{3+}\) structure is lower. Namely, a portion of the Sm\(^{3+}\) ions are located at a non-symmetric centered lattice. Tamura reports that Sm\(^{3+}\) ions, if mainly occupy a non-symmetric centered lattice, produce a typical emission around 650 nm, by contrast, if they mainly occupy a symmetric centered lattice, produce a typical emission around 602 nm [18]. The \( ^4G_{5/2} \rightarrow ^4H_{5/2} \) transition is stronger than the \( ^4G_{5/2} \rightarrow ^4H_{5/2} \) transition, which indicates that Sm\(^{3+}\) ions mainly occupy a symmetric centered lattice in CaAl\(_2\)O\(_4\)-2CaAlO\(_3\); Sm\(^{3+}\). The excitation spectra of CaAl\(_2\)O\(_4\)-2CaAlO\(_3\); Sm\(^{3+}\) which is measured by monitoring the \( ^4G_{5/2} \rightarrow ^4H_{5/2} \) transition of Tb\(^{3+}\) ions (wavelength of irradiation 604 nm), whose strongest excitation peak at 380 nm originates from the 4f-4f (\( ^4H_{5/2} \rightarrow ^4D_{15/2} \) or \( ^4H_{5/2} \rightarrow ^4P_{1/2} \)) transition absorption of Sm\(^{3+}\) ions. The relatively weaker excitation peak at 285 nm maybe results from the charge transfer state (CTS) of Sm\(^{3+}\)-O\(^2-\).

In the application of phosphors for white LEDs, the size distribution and shape of the particles are very important. Fig. 5 presents the size and morphology of the green CaAl\(_2\)O\(_4\)-2CaAlO\(_3\); Tb\(^{3+}\) and the red CaAl\(_2\)O\(_4\)-2CaAlO\(_3\); Sm\(^{3+}\)
Synthesis and luminescence properties of composite \( \text{CaAl}_2\text{O}_4\cdot2\text{CaAl}_4\text{O}_7: \text{Re}^{3+} \) (\( \text{Re}^{3+} = \text{Tb}^{3+}, \text{Sm}^{3+} \)) phosphors for application...

Both \( \text{CaAl}_2\text{O}_4\cdot2\text{CaAl}_4\text{O}_7: \text{Tb}^{3+} \) Fig. 5(a) and \( \text{CaAl}_2\text{O}_4\cdot2\text{CaAl}_4\text{O}_7: \text{Sm}^{3+} \) Fig. 5(b) show that the products present have an irregular bulky shape distribution and are slightly agglomerated, which are due to calcination of the precursors at 900 °C. Correspondingly, both \( \text{CaAl}_2\text{O}_4\cdot2\text{CaAl}_4\text{O}_7: \text{Tb}^{3+} \) Fig. 5(c) and \( \text{CaAl}_2\text{O}_4\cdot2\text{CaAl}_4\text{O}_7: \text{Sm}^{3+} \) Fig. 5(d) show the product surfaces are smooth, dense, with high crystallinity and present a honeycomb shape. The particles adhere to each other to give approximate ellipsoidal particles. A lot of gases are released in the SPCS process due to the burning of urea, which holds back formation of the massive products. So crystal nuclei grow along the directions for the formation of the smooth spherical shape containing low surface energies [19]. This investigation indicates that spherical surfaces contribute to enhancing the luminescent intensity. The products fired at 900 °C exhibit high quality crystallinity and a size approximately is 1-3 µm, which are suitable for the requirements of phosphors for white LEDs.

Conclusions

Composite \( \text{CaAl}_2\text{O}_4\cdot2\text{CaAl}_4\text{O}_7: \text{Re}^{3+} \) (\( \text{Re}^{3+} = \text{Tb}^{3+}, \text{Sm}^{3+} \)) phosphors were prepared for the first time by the SPCS technique. The synthesis temperature was decreased significantly compared to the conventional solid-state reactive method (starting oxides \( \text{CaO} \) and \( \text{Al}_2\text{O}_3 \)). A small quantity of dopant \( \text{Tb}^{3+} \) or \( \text{Sm}^{3+} \) ions give a slight distortion to the crystal lattice structure of \( \text{CaAl}_2\text{O}_4\cdot2\text{CaAl}_4\text{O}_7 \). The products show the particle sizes of approximately 1-3 µm dimension and high quality crystallinity. The composite \( \text{CaAl}_2\text{O}_4\cdot2\text{CaAl}_4\text{O}_7 \) is a good type of candidate as a host material. The luminescence properties of them indicate that they possess a wilder near-UV excitation band around 380 nm and emit green-light and red-light under near-UV irradiation. All the above mentioned results are beneficial to the requirements of the phosphors for white LEDs.

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References