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Synthesis and photoluminescence of $Ca_3Si_3O_8F_2$: Ce^{4+}, Eu^{3+}, T^{b3+} phosphor

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Abstract. Ce^{4+}, Eu^{3+}, Tb^{3+} co-doped $Ca_3Si_3O_8F_2$ phosphor was synthesized via solid state reaction method using CaF_2, $CaCO_3$ and SiO_2 as raw materials for the host and Eu_2O_3, CeO_2, and Tb_4O_7 as activators. The luminescent properties of the phosphor was analysed by spectrofluorophotometer at room temperature. The effect of excitation wavelengths on the luminescent properties of the phosphor i.e. under near-ultraviolet (nUV) and visible excitations was investigated. The emission peaks of Ce^{4+}, Eu^{3+}, Tb^{3+} co-doped $Ca_3Si_3O_8F_2$ phosphor lays at 480(blue band), 550(green band) and 611nm (red band) under 380nm excitation wavelength, attributed to the Ce^{4+} ion, Tb^{3+} ion and Eu^{3+} ions respectively. The results reveal that the phosphor emits white light upon nUV (380nm) / visible (465nm) illumination, and a red light upon 395nm / 535nm illumination. RE ions doped $Ca_3Si_3O_8F_2$ is a promising white light phosphor for LEDs. The emission colours can be seen using Commission international de l'eclairage (CIE) co-ordinates. A single host phosphor emitting different colours under different excitations indicates that it is a potential phosphor having applications in many fields.

Keywords: luminescence; phosphor; solid state reaction; raw materials; activators; LED

1. Introduction

For generation of white light emission, three different approaches are developed. These are blue LED with yellow phosphors; an ultraviolet (UV) LED with red, green and blue phosphors; and a device that combines red, green and blue LEDs. The advantage of the blue LED with yellow phosphors is its higher efficacy compared to the other two approaches.

In contrast to silicates of strontium, doped calcium silicates have been poorly investigated from the viewpoint of phosphors for white LEDs. Up to date luminescence properties of doped $Ca_3Si_2O_7$ have not been investigated yet. There are not any data concerning spectroscopic properties of Ce^{3+} in $Ca_3Si_2O_7$ but luminescence properties of Eu^{2+} are actively investigated at present Park *et al*. **(**2008), Nakanishi and Tanabe (2009)**.** Spectroscopic properties of Ca_2SiO_4 doped with Eu^{2+} have

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been investigated in detail and they have been discussed in terms of the crystal field strength and covalence Choi *et al*. (2009), Wang Zhi-Jun *et al*. (2009).

Up to date a lot of investigations concerning synthesis of silicate phosphors with using different fluxes and their influences on phase formation, morphology and photoluminescence properties of the phosphors have been performed but by taking into account topicality of LED phosphors, such studies are still relevant. Effects of various fluxing agents MgF_2, CaF_2 and BaF_2 on the emission spectra of $Sr_3SiO_5:Eu^{2+}$ have been investigated Cheng and Liu (2010). It has been discovered that CaF_2 is the best flux for synthesizing $Ca_3Sc_2Si_3O_{12}:Ce^{3+}$ green phosphors Chen *et al*. (2010) and a NH_4F flux enhances the luminescent performance of $Sr_2SiO_4:Eu^{2+}$ phosphors significantly Guo and Wang (2010). It has been found that the maximum photoluminescence intensity of $Ba_{1.1}Sr_{0.88}SiO_4:Eu_{0.02}$ phosphor powders prepared from spray solution with barium fluoride and barium nitrate is about 600 % of the phosphor powders prepared without barium fluoride Lee *et al*. (2010). Within the framework of the project, it is assumed to synthesize calcium silicates containing fluorine co-doped by Ce^{4+}, Eu^{3+} and Tb^{3+}. Co-doped calcium silicates will be synthesized by a high temperature solid reaction method in particular using calcium fluoride as the source of a Ca component. The Ce^{4+}, Eu^{3+} and Tb^{3+} co-doping concentration on spectroscopic properties of doped calcium silicates will be investigated in detail. $Ca_3Si_3O_8F_2$:5mol% Eu^{3+}, 10mol% Ce^{4+}, 2.5mol% Tb^{3+} phosphors were prepared by the conventional solid state reaction method heated in air atmosphere at 1200^0C for 2 hours. The dependence of Photoluminescence (PL) spectra on doping concentration has been investigated. Photoluminescence studies and CIE co-ordinates of RE ions co-doped $Ca_3Si_3O_8F_2$ phosphor under near ultraviolet (380, 395nm) and (465, 535nm) excitations were discussed.

2. Experimental methods

RE ions doped $Ca_3Si_3O_8F_2$ white light phosphor were synthesized by the conventional solid state reaction method. The Calcium fluoride (CaF_2), calcium carbonate ($CaCO_3$) and silicon dioxide (SiO_2) as raw materials were taken for the host and europium oxide (Eu_2O_3), cerium oxide (CeO_2), and terbium oxide (Tb_4O_7) with purity over 99.9% were taken as activators. The raw materials were weighed according to the compositions in the following reaction $CaF_2 + 2CaCO_3 + 3SiO_2 \rightarrow Ca_3Si_3O_8F_2 + 2CO_2^{\uparrow}$. The composite powders were grounded in an agate mortar and pestle thoroughly about an hour. The grounded phosphor was placed in an alumina crucible with the lid closed. The crucible placed in a muffle furnace and heated at 1200^OC for 2 hr with a heating rate of 5^oC/min and then cooled to room temperature. Before analysis again the phosphor ground into fine powder using an agate mortar and pestle.

The emission and the excitation spectra of the synthesized powders were characterized with a spectroflurophotometer(Shimadzu RF 5301 PC) with xenon lamp as excitation source. All the spectra were recorded at room temperature. Emission and excitation spectra were recorded using a spectral slit width of 1.5nm.The Commission International de l'Eclairage (CIE) co-ordinates were calculated by the spectrophotometric method using the spectral energy distribution. The chromatic coordinates (*x, y*) of prepared materials were calculated with colour calculator version 2, software from Radiant Imaging.

3. Results and discussion

3.1 Photoluminescence of Ce^{4+}: Eu^{3+}: Tb^{3+} co-doped $Ca_3Si_3O_8F_2$ phosphor

The photoluminescent curves of Ce^{4+}, Eu^{3+}, Tb^{3+} activated $Ca_3Si_3O_8F_2$ phosphor obtained at 1200°C are shown in fig.1 and 2(a, b). In details fig.1 shows the excitation spectrum monitored under 611nm wavelength consists of two regions i) the broad band at 260nm is attributed to charge-transfer (CT) transition from ligand (host) to metal (activator) and ii) in the range from 350-550nm the phosphor shows sharp peaks at 380, 395nm, 465 and 535nm located in the nUV/visible regions which are useful for LED applications for white light generation. These sharp bands can be attributed to f-f transitions. $^7F_0 \rightarrow {}^5G_6$ transition at 380nm, $^7F_0 \rightarrow {}^5L_6$ transition at 395nm, $^7F_0 \rightarrow {}^5D_2$ transition at 465nm and $^7F_0 \rightarrow {}^5D_2$ transition at 535nm peak. The lines at 380/395nm and 465nm are the two strongest of these observed lines and match well with the nUV and the blue LED chips well available in the market. This result is not yet reported by others.

Fig. 2a shows the emission spectrum of $Ca_3Si_3O_8F_2$: 5mol% Eu^{3+}, 10mol% Ce^{4+}, 2.5mol% Tb^{3+} phosphor under 380nm excitation wavelength emits various emissions between 450-650nm. In detail the emission peaks centered at 480nm (blue band), 544nm (green band) and 611nm (red band). Among these three bands the green band is the strongest one which is associated with the $^5D_4 \rightarrow {}^7F_5$ transition of Tb^{3+} ion. The blue emission band can be attributed to Ce^{4+} ion, and the red band consists of several lines between 580-625nm which are associated with the $^5D_0 \rightarrow {}^7F_j$ (j=1, 2, 3) transitions of Eu^{3+} ion. The emission peak at 611nm belongs to electric dipole transition. This transition $^5D_0 \rightarrow {}^7F_2$ is much stronger than $^5D_0 \rightarrow {}^7F_{1,3}$ transitions, which suggests that the Eu^{3+} is located in a distorted (or asymmetric) cation environment Chiu *et al.* (2007).

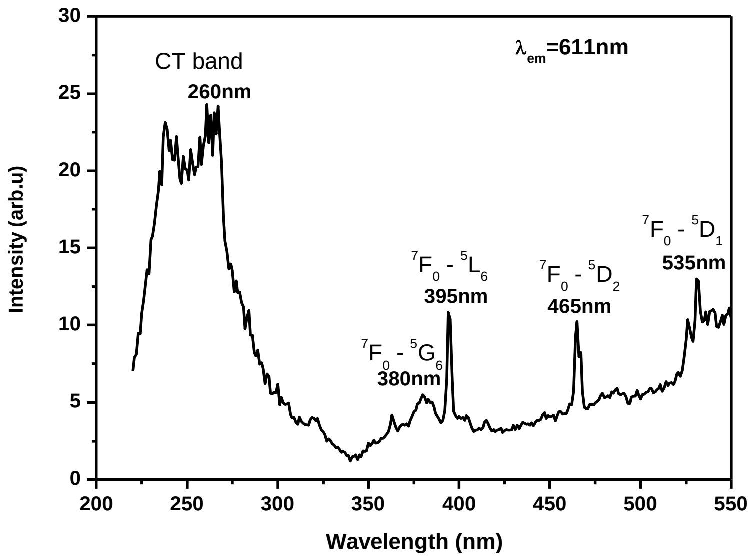

Fig. 1 Excitation spectrum of $Ca_3Si_3O_8F_2$: RE phosphor monitored under 611nm wavelength

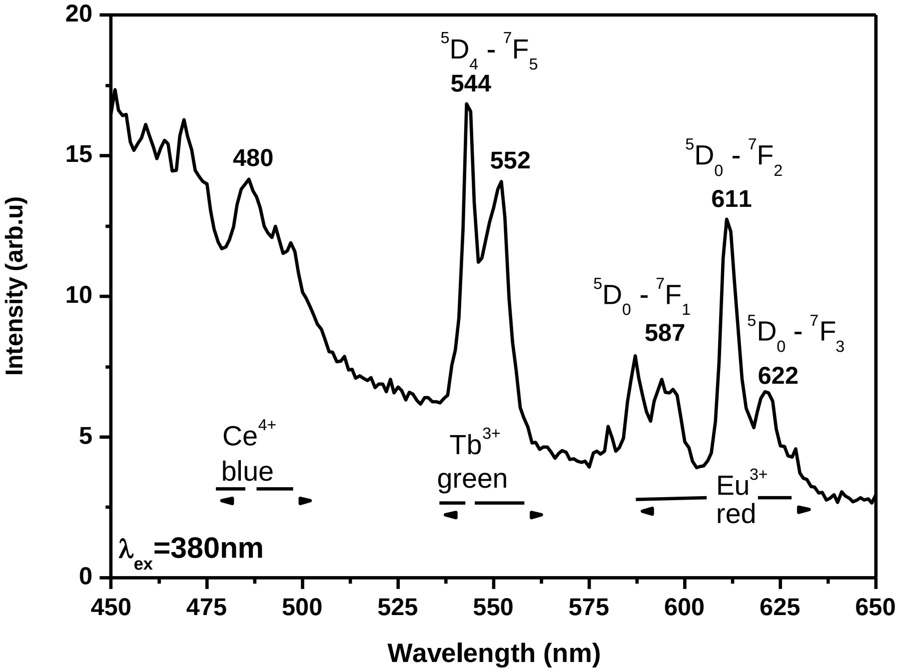

Fig. 2(a) Emission spectrum of $Ca_3Si_3O_8F_2$: RE phosphor under 380nm excitation

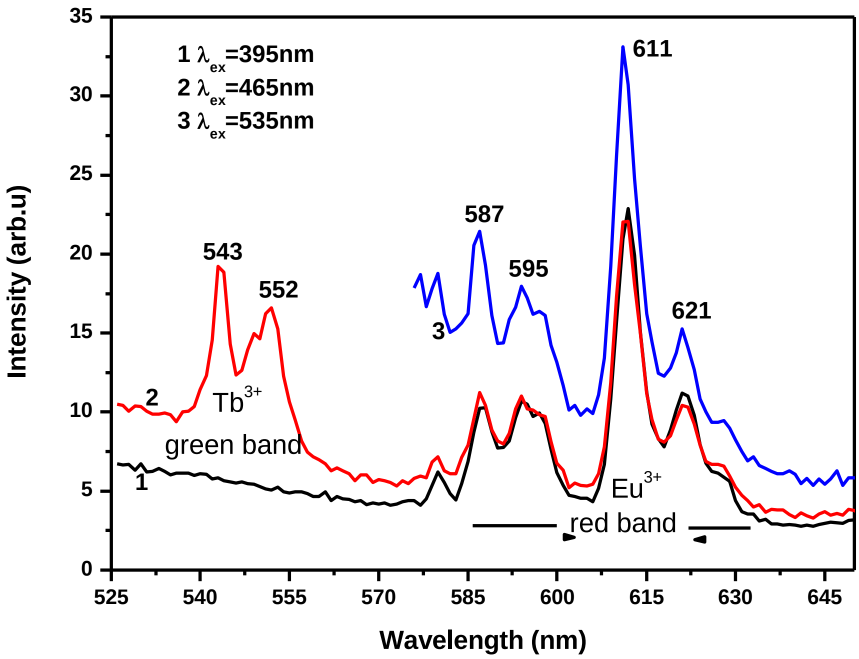

Fig. 2(b) Emission spectrum of $Ca_3Si_3O_8F_2$: RE phosphor under 395nm, 465nm, 535nm excitation

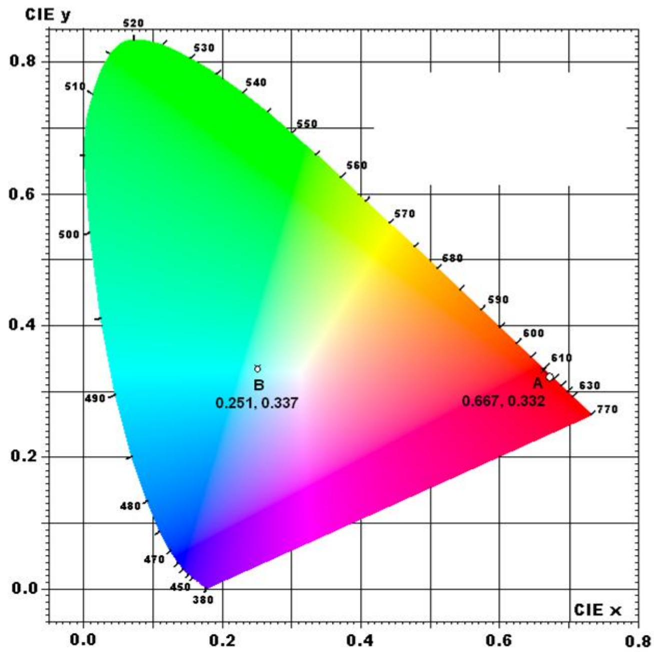

Fig. 3 CIE co-ordinates of $Ca_3Si_3O_8F_2$: RE phosphor

Fig. 2b shows the emission spectrum of $Ca_3Si_3O_8F_2$: 5mol% Eu^{3+}, 10mol% Ce^{4+}, 2.5mol% Tb^{3+} phosphor under 395, 465 and 535nm excitation wavelengths emits various emissions between 525-645nm. In detail curve 1 and 3 shows the emission peaks centered at 611nm (red band only) under 395and 535nm excitation wavelengths. But under 465nm excitation wavelength curve 2 shows the emission peaks centered at 544nm (green band) and 611nm (red band). The results in figs 2a&b clearly showed us that the Ce^{4+}, Eu^{3+}, Tb^{3+} activated $Ca_3Si_3O_8F_2$ phosphor will emit a white light upon nUV (380nm) and visible (465nm) illumination, and a red light upon 395 & 535nm illumination.

3.2 CIE Co-ordinates

The CIE co-ordinates were calculated by the Spectrophotometric method using the spectral energy distribution. Fig.3 shows the color co-ordinates for $Ca_3Si_3O_8F_2$: RE^{3+} phosphor. Point A are x = 0.667 and y = 0.332 indicates red colour under 395 and 535nm excitation wavelengths and CIE co-ordinates at the point B are x = 0.251 and y = 0.337 indicates white colour under 380 and 465nm excitation wavelengths.

4. Conclusions

- $Ca_3Si_3O_8F_2$ phosphor co-doped with Ce, Eu, Tb was successfully synthesized by the high temperature solid state reaction method in the air atmosphere.

- The PL and CIE results clearly showed us that the Ce^{4+}, Eu^{3+}, Tb^{3+} activated $Ca_3Si_3O_8F_2$ phosphor will emit a white light upon nUV (380nm) and visible (465nm) illumination, and a red light upon 395 & 535nm illumination.
- Hence this phosphor can be a promising candidate for the generation of white light in solid state lightning and also in the field of display devices.

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