



Crystallographic-site induced multi-color emission with high efficiency in $\text{Ca}_3(\text{SiO}_3)_3:\text{Ce}^{3+}$ phosphor

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ABSTRACT

Ce^{3+} single-doped $\text{Ca}_3(\text{SiO}_3)_3$ phosphors were synthesized by a traditional solid-state reaction at elevated temperature. The phase impurities of phosphors prepared at different conditions were characterized and analyzed and an optimal one was obtained. The synthesis and luminescent properties of the phosphors were studied in detail. As a result, two different emission bands can be observed under excitations at 330 and 360 nm, which peak at 380 and ~400 nm, respectively. Further analyses of emission spectra reveal that there should exist four different emission bands originating from four Ce^{3+} luminescence centers on different Ca^{2+} sites. The phosphor with optimal Ce^{3+} content [$\text{Ca}_{2.82}(\text{SiO}_3)_3:0.18\text{Ce}^{3+}$] exhibits high absolute quantum efficiencies up to 90.1% and 79.5% for emission bands at 380 and 400 nm, respectively. Moreover, the emission intensity of $\text{Ca}_{2.82}(\text{SiO}_3)_3:0.18\text{Ce}^{3+}$ at 150 °C remains ~65% of that at room temperature. The phosphor deserves further investigation for the purpose of application in pc-WLEDs.

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1. Introduction

White light-emitting diodes (WLEDs) have now been used as solid state lighting all over the world. The most common strategy for WLEDs by using phosphors (pc-WLEDs) is the combination of a blue LED chip and a $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$ phosphor that emits yellow light [1,2], which is now modified by introducing a red-emitting Mn^{4+} -doped phosphor to improve its color rendering index (CRI) [3–11]. Before that, several strategies were applied to solve this drawback, such as the combination of a blue chip and two phosphors that emit green and red light [12,13], a near-UV chip combined with the red, green, and blue phosphor blend [14–18], the combination of a near-UV chip and a white-emitting phosphor [19–23] or glass [24,25].

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No matter what kind of combination is used, high quantum efficiency and thermal stability are very important for phosphors as candidates in pc-WLEDs. Generally, the host with a rigid structure is the best choice for phosphors [26], which is in favor of high quantum efficiency and thermal stability [1,27]. On the other hand, Ce^{3+} ions have parity- and spin-allowed transition between 4f and 5d energy levels, and usually possess better efficiency and stability than Eu^{2+} ions when they occupy the same crystallographic site of a host, due to higher excitation/emission energy and smaller Stokes shift [28].

As a classical family of host materials, silicates are the brilliant one due to high chemical-physical stability and varied crystal structure. Among numerous silicate hosts, alkaline earth orthosilicate is the most common used one, such as M_2SiO_4 ($\text{M} = \text{Ca}, \text{Sr}, \text{Ba}$) for Eu^{2+} activator [29–33], however, low connectivity of the structure due to isolated SiO_4 tetrahedra will result in poor thermal stability [26]. Liu et al. found that the existence of $\text{SiO}_4\text{-LuO}_6\text{-SiO}_4$ units limited the vibrational degrees of freedom and resulted in a thermally stable $\text{Ba}_9\text{Lu}_2\text{Si}_6\text{O}_{24}:\text{Ce}^{3+}$ phosphor [34]. In $\text{Ca}_3(\text{SiO}_3)_3$, pseudowollastonite, SiO_4 tetrahedra are in the form of $[\text{Si}_3\text{O}_9]^{6-}$

rings, showing a higher connectivity [35]. Therefore, higher thermal stability and quantum efficiency are expected for Ce^{3+} -doped $\text{Ca}_3(\text{SiO}_3)_3$. To the best of our knowledge, there has no papers on the luminescence properties of $\text{Ca}_3(\text{SiO}_3)_3:\text{Ce}^{3+}$.

In this work, synthetic conditions and luminescence properties of $\text{Ca}_3(\text{SiO}_3)_3:\text{Ce}^{3+}$ were studied. Results indicate that $\text{Ca}_{2.82}(\text{SiO}_3)_3:0.18\text{Ce}^{3+}$ phosphor has a high quantum efficiency and thermal stability. Therefore, the phosphor deserves further investigation for the purpose of application in pc-WLEDs.

2. Experimental

2.1. Materials and synthesis

$\text{Ca}_{3(1-2x)}(\text{SiO}_3)_3:3x\text{Ce}^{3+}, 3x\text{Na}^+$ ($\text{CSO}:3x\text{Ce}^{3+}$, $x = 0.01\text{--}0.08$) phosphors with different synthesis conditions were prepared by a solid-state reaction at elevated temperature. CaCO_3 (AR), SiO_2 (AR), Na_2CO_3 (AR), and CeO_2 (99.99%) were used as raw materials. In a typical synthesis, stoichiometric raw materials were mixed and ground for 30 min with the addition of alcohol in an agate mortar. Sodium ion (Na^+) was used as a charge compensator to solve the charge imbalance after replacing Ca^{2+} by Ce^{3+} , and H_3BO_3 (5% of the total weight of the mixtures) was also added as flux. The mixed powders were transferred into alumina crucibles and calcined at 1250°C for 5 h in a tube furnace with the gas flow of a mixture of 5% H_2 and 95% N_2 . After cooled to room temperature naturally, the obtained samples were ground to powders for subsequent analyses.

2.2. Measurements and characterization

X-ray powder diffraction (XRD) patterns of all samples were collected by a PANalytical X'Pert Pro diffractometer with Cu K α radiation operated at 40 kV and 40 mA. The measurement of photoluminescence (PL), photoluminescence excitation (PLE) spectra, and temperature-dependent PL spectra for $\text{CSO}:3x\text{Ce}^{3+}$ phosphors is achieved on a Hitachi F4500 spectrophotometer equipped with a TAP-02 high temperature controller (Orient KOJI, China). The absolute quantum efficiencies (QE) and decay curves were measured at room temperature on an Edinburgh FLS980 fluorescence spectrometer combined fluorescence lifetime and steady state spectrometer with a 450 W xenon lamp and a nanosecond flash lamp.

3. Results and discussion

3.1. Phase characterization and crystal structure

The phase formation of the $\text{CSO}:3x\text{Ce}^{3+}$ phosphors was detected with X-ray powder diffraction. The XRD patterns of $\text{CSO}:0.06\text{Ce}^{3+}$ ($x = 0.02$) obtained under different conditions are shown in Fig. 1a. Most diffraction peaks of the representative samples match well with the standard card of $\text{Ca}_3(\text{SiO}_3)_3$ phase (JCPDS no. 89-6485) crystallizing in monoclinic phase (space group $C2/c$, No.15) with $Z = 8$. However, for the samples obtained without H_3BO_3 that acts as flux, there exist some other peaks belonging to the impurity phases, silicon oxide SiO_2 (JCPDS no. 71-0785) and Ca_2SiO_4 (larnite, monoclinic, JCPDS no. 77-0409). Impurity phases can be reduced, however, unable to be removed by increasing the synthesis temperature. Pure $\text{Ca}_3(\text{SiO}_3)_3$ phase can be synthesized after the addition of H_3BO_3 as indicated in Fig. 1a. Fig. 1b exhibits the XRD patterns of $\text{CSO}:3x\text{Ce}^{3+}$ with different Ce^{3+} content obtained under 1250°C for 5 h with H_3BO_3 . Pure $\text{Ca}_3(\text{SiO}_3)_3$ phase can be obtained at low Ce^{3+} content. While a small amount of SiO_2 (JCPDS no. 73-1748) appears at higher Ce^{3+} content, and a $\text{Ca}_2\text{Pr}_8(\text{SiO}_4)_6\text{O}_2$ phase forms when $x \geq 0.07$. Properly speaking, it should be

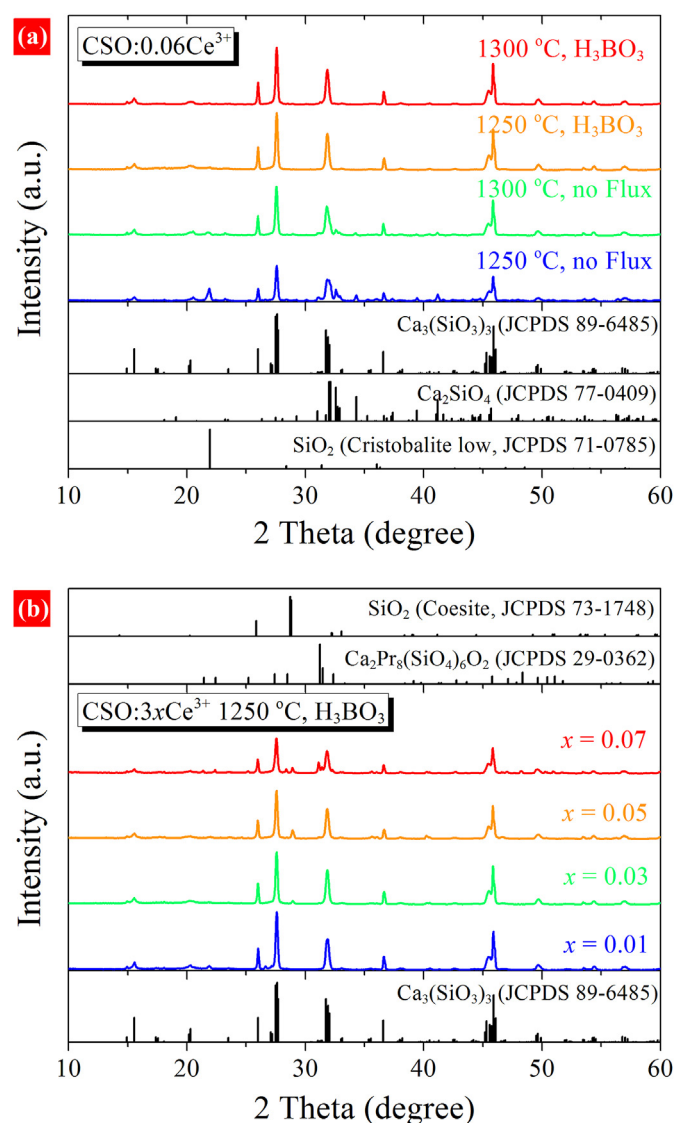


Fig. 1. XRD patterns of $\text{CSO}:3x\text{Ce}^{3+}$ phosphors, (a) $x = 0.02$ obtained at different synthesis conditions, (b) obtained under 1250°C for 5 h with H_3BO_3 .

$\text{Ca}_2\text{Ce}_8(\text{SiO}_4)_6\text{O}_2$ due to the similar radii between Pr^{3+} and Ce^{3+} with equal valence.

A unit cell of $\text{Ca}_3(\text{SiO}_3)_3$ is illustrated in Fig. 2a according to the crystal structure data reported by Yang [35]. The unit cell can be described as Ca atoms layers separated by Si atoms layers viewing along a axis. Si atoms arrange in the form of $[\text{Si}_3\text{O}_9]^{6-}$ rings, one of which is shown clearly in Fig. 2b. There are five Ca crystallographic sites in the unit cell of $\text{Ca}_3(\text{SiO}_3)_3$ as shown in Fig. 2c, which are all coordinated with eight oxygen atoms and denoted as Ca(1), Ca(2), Ca(3), Ca(4), and Ca(5), respectively. The number of Ca(5) site is 8, while those of other Ca sites are all 4 in the unit cell. Typically, activators are expected to occupy the cation sites with similar effective ionic radius (IR). Therefore, in view of ionic radius, Ce^{3+} ions (IR = 1.14 Å when CN = 8) will preferably occupy the Ca sites (IR = 1.12 Å when CN = 8) because 4-coordinated Si^{4+} sites (IR = 0.26 Å) are too small for Ce^{3+} ions.

3.2. Photoluminescence properties

The emission and excitation spectra of $\text{CSO}:0.18\text{Ce}^{3+}$ ($x = 0.06$)

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