

Synthesis and photoluminescence properties of $\text{CaSi}_x\text{O}_y:\text{Tb}^{3+}$ phosphors prepared using solution-combustion method.

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Abstract. Effect of Tb^{3+} ion concentrations on the structural and persistence luminescence properties of $\text{CaSi}_x\text{O}_y:\text{Tb}^{3+}$ crystals were evaluated using powders grown by the solution combustion technique. The XRD study indicates the change of phase from CaSiO_3 to $\text{Ca}_3\text{Si}_2\text{O}_7$ as the terbium concentration increase. Broad band excitations peaking between 280 - 360 nm derived from excited states of Tb^{3+} ions were observed for all powders grown from various Tb compositions. The green emission peak at 545 nm due to an electronic transition of $^5\text{D}_4-^7\text{F}_5$ was found to be more prominent and intense. The persistent luminescent property was greatly influenced by the composition of the activator ions. The maximum concentration of Tb^{3+} ions that is necessary to obtain the optimal PL intensity was 1%.

1. Introduction

Phosphors are widely used in emissive displays. However, all currently used phosphors still need considerable improvement in material properties such as its lower current saturation, high efficiency, and better chromaticity [1]. Oxide phosphors (including silicate phosphor) are more chemically stable than conventional sulfide phosphors under high Coulomb loading. Metal silicates have been widely reported as promising host materials for rare earth and transition metal ions with excellent luminescence properties in the blue, green and red spectral regions [2]. Calcium silicate phosphors are ideal from the manufacturing point of view because both calcium and silica are abundant and are relatively inexpensive. The Tb^{3+} ion shows good luminescence performance in different bulk host materials and through the sol-combustion high quality powders with good crystallinity and homogeneous composition can be obtained at a relatively low temperature. These phosphor materials are usually manufactured using solid state reaction process, which include a mixing process of raw material powders, sintering process under high temperature (1800°C) and high pressure and pulverization of the sintered ceramics compacts to make micron sized phosphor powders. In recent years, the experimental methods, such as sol-gel-microwave process [3], co-precipitation [4,5], combustion reaction or microwave combustion methods [6], have been investigated to synthesize phosphors. Among these methods, solution combustion reaction is attractive because of low synthesis temperature and short reaction time. It has also been reported that other liquid processes results into amorphous calcium silicate, hence the use of solution combustion to prepare crystalline $\text{CaSi}_x\text{O}_y:\text{Tb}^{3+}$ materials. Therefore, in the present paper we report on the synthesis of $\text{CaSi}_x\text{O}_y:\text{Tb}^{3+}$ green luminescent powders via the solution-combustion process, and investigate their morphological, structural and luminescence properties as a function of the Ca:Si molar ratios and the Tb^{3+} doping concentration.

The endothermic processes during the solution-combustion process are determined by decomposition and removal of nitric oxides and significantly vary depending on the precursor composition and ratio of nitrate to urea. These physical-chemical processes results in various crystalline phases from the single host with corresponding effects on the luminescent properties.

2. Experimental

Tb³⁺-activated calcium silicate (CaSi_xO_y:Tb³⁺) nanophosphors have been synthesized by means of simple and low temperatures (500°C) using the solution-combustion of corresponding metal nitrate, TEOS and urea solution mixtures. To determine the optimum amount of silica a series of phosphors was made in which the mole ratio of cation to silica was varied. The amount of activator that could be added to these phosphors was also varied from 0 to about 4%. XRD patterns of as-synthesized samples were recorded on an x-ray diffractometer with Cu K_α = 1.5406 Å, which was operated at 40 kV voltage and 40 mA anode current. Data were collected in 2θ values from 20° to 80°. Photoluminescence (PL) measurements were performed at room temperature on a Cary Eclipse fluorescence spectrophotometer (Model: LS 55) with a built-in 150 W xenon lamp as the excitation source and a grating to select a suitable wavelength for excitation.

Results and Discussion

3. Structure

An XRD pattern of CaSiO₃ phosphors, shown in Fig. 1a, reveals that the whole spectrum can be indexed to a crystalline hexagonal CaSiO₃ phase (JCPDS 84-0655). From the XRD pattern of as-prepared CaSi_xO_y:Tb shown in Fig. 1c, it was found that the structure of the sample becomes Ca₃Si₂O₇ (JCPDS 76-0623). The XRD study indicates that new peaks appear as the terbium concentration increase results in phase changes from CaSiO₃ to Ca₃Si₂O₇. The later phase may be favored as a result of some Si sites substituted by the Tb ions, as the concentration of Tb was changed from 1 to 4 mole %. Due to the differences in size of the two atoms this substitution results in the shrinkage of CaSiO₃ lattice therefore causing phase transitions. On the other hand, the substitution of Tb³⁺ ions were supposed to enhance the hole trapping ability of oxygen vacancies that increases the persistent luminescent property.

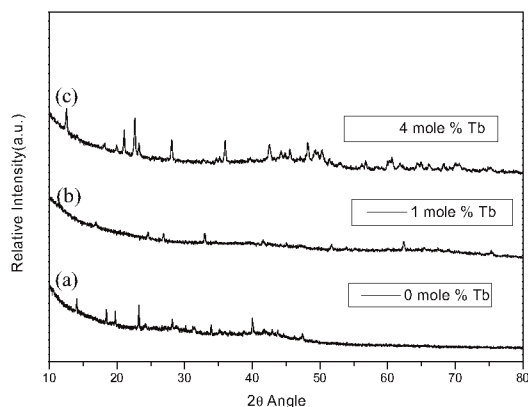


Figure 1: The XRD pattern for CaSi_xO_y:Tb³⁺ 1(a) Tb=0, 1(b) Tb=1%, 1(c) Tb=4%

3.1. Photoluminescence

In Fig. 2(a), the excitation spectra of the samples monitored at 545 nm show two bands at about 240 nm and 280–360 nm. It is well known that there should be a strong absorption peak at 244 nm from spin-allowed transition of ⁷F→⁵D of Tb³⁺. The intensity and slight shift in the 240 nm peak presumably resulted from the randomness of intense combustion process, and the strong influence of

$f \rightarrow d$ transition of Tb^{3+} when subjected to two kind of host lattice and incompletely transform from Tb^{4+} to Tb^{3+} owing to lack of reductive atmosphere. The group of weak peaks covering 280–360 nm belongs to $f \rightarrow f$ transition of Tb^{3+} in the two host matrix of $CaSiO_3$ and $Ca_3Si_2O_7$. The persistent luminescence emission spectra of the $CaSi_xO_y:Tb$ phosphors grown with various Tb^{3+} ions doping are shown in Fig. 2(b) that were obtained by exciting the samples at the wavelength 257 nm, and exhibit emission transitions of ($^5D_4 \rightarrow ^7F_{3,4,5,6}$). Particularly, the green emission peak at 545nm has been found to be more prominent and intense which is due to an electronic transition of $^5D_4 - ^7F_5$ [7-9]. Such strong green emission displays that the phosphor powder can find applications in the development of coated screens in certain electronic systems.

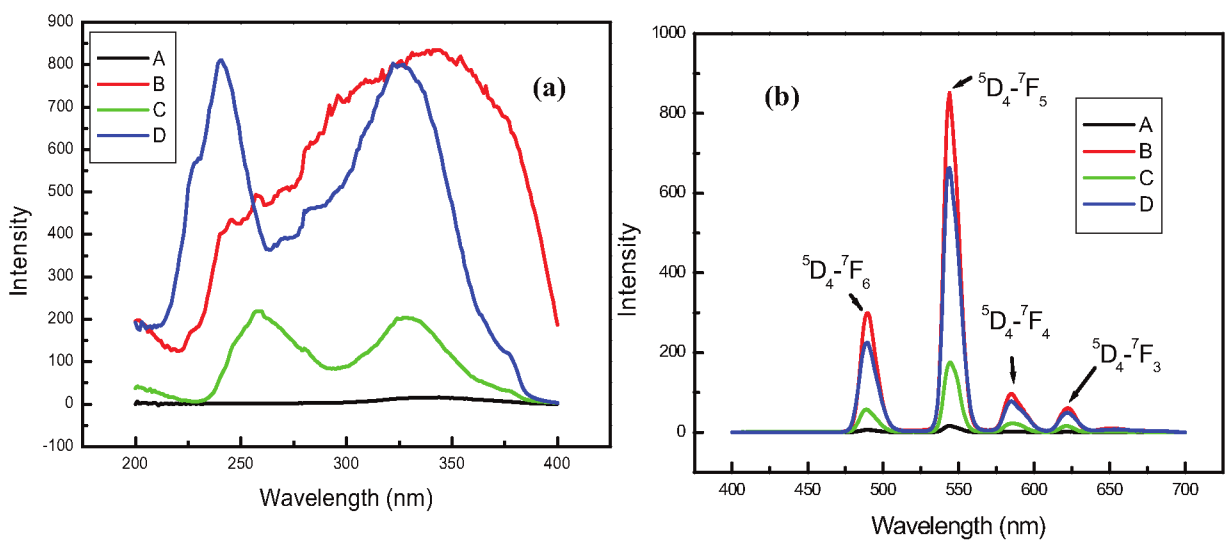


Figure 2(a) Excitation and (b) emission spectra of $CaSi_xO_y:Tb^{3+}$ A Tb=0, B Tb=1%, C Tb=4% and D Tb=2%.

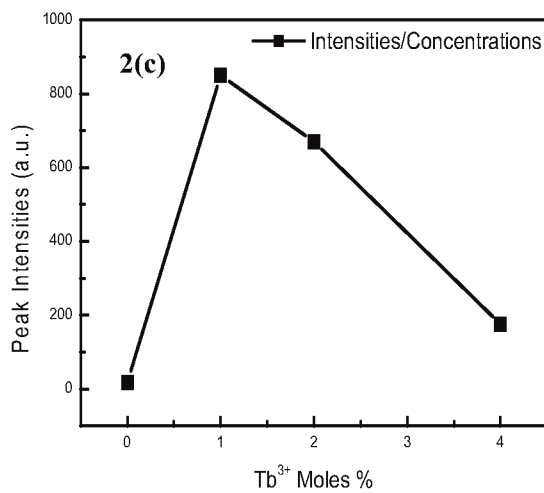


Figure 2(c) Graph of Tb^{3+} ions concentration versus maximum peak intensity

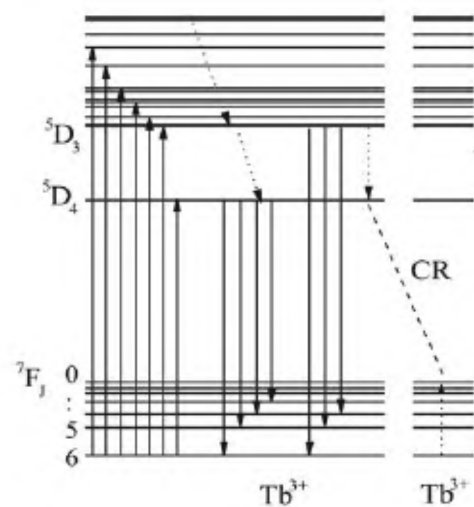


Figure 2(d) Energy level scheme of Tb^{3+} ions in a crystal showing cross relaxation process [10]

The position of the emission peak in the emission spectra almost shows no change, regardless of the concentrations of the Tb^{3+} ions doping, implying that no obvious change occurs in the crystal field effect on 5d electron states of Tb^{3+} ions, even though the molar ratio of Tb^{3+} ions doping varies. The PL spectrum of $CaSiO_3$ phosphors prior to Tb doping is shown in Fig. 2b, which has a band around 540nm in a green region. The Figure depicts the PL spectrum of $CaSiO_3:Tb^{3+}$ (1%Tb) which is the highest intensity than the other Terbium concentrations. The effects of Tb^{3+} ions concentrations on the maximum peak intensities are clear in Figure 2(c). The graph of maximum PL intensity of $CaSi_xO_y$ as a function of the Tb^{3+} concentrations is shown in Fig. 2(c). An increase in Tb^{3+} concentrations up to 1% Tb^{3+} ions increases the luminescence intensity possibly due to an increase in activator centres. Further increase in Tb^{3+} ions above 1% result in luminescence quenching caused by cross relaxation (CR) processes see Fig. 2(d). The CR involves a process in which an electron in an excited state undergoes a nonradiative transition to an intermediate excited state accompanied by an energy-conserving transition of a neighbouring ion from its ground state to some excited state. The CR process depends on ion-ion separations and can occur by multipole –multipole or by exchange interactions. At more dilute concentrations typical of phosphors, the short range exchange-mediated transfer rate will have decreased to the point that the dipole-dipole (or other multipole-multipole) interactions, which fall off more slowly as R^6 , will dominate. This idea has been known for a long time, and serves as one of the main reason for the main mechanisms for concentration quenching. Persistent luminescence curves of the phosphor powders were shown in Fig. 3. It can be seen from the curves that the powders show differences in initial intensity and medium persistence when the powders were efficiently activated by fluorescent lamp. The results indicate that the initial persistent luminescence intensity and the decay time of phosphors are enhanced with increase in Tb^{3+} concentrations. The sample with $Tb = 1\%$ significantly enhanced the initial persistent luminescence property of the green luminescence.

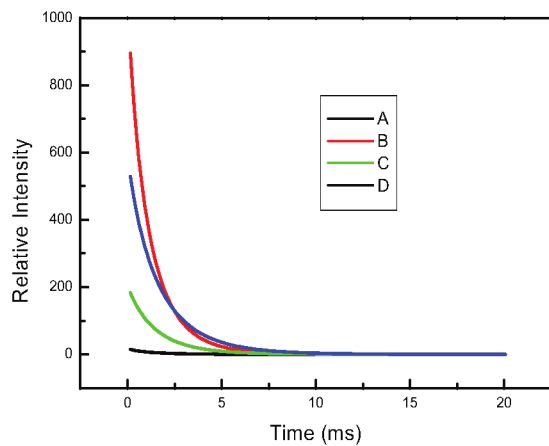


Figure 3 Afterglow characteristics of $CaSi_xO_y:Tb^{3+}$ A $Tb = 0$, B $Tb = 1\%$, C $Tb = 2\%$ and D $Tb = 4\%$

Tb moles %	0	1	2	4
Component	Decay constants (ms)			
Fast (τ_1)	0.89	0.31	0.27	0.99
Medium (τ_2)	2.21	1.03	1.30	0.99
Slow (τ_3)	1.38	1.93	2.36	2.18

Table 1 Results for fitted decay curves of the phosphor powders with different Tb^{3+} moles

The decay behaviour can be analysed by curve fitting [11,12], relying on the following triple exponential equation:

$$I = I_1 \exp\left(-\frac{t}{\tau_1}\right) + I_2 \exp\left(-\frac{t}{\tau_2}\right) + I_3 \exp\left(-\frac{t}{\tau_3}\right) \quad (1)$$

where I represents the phosphorescent intensity; I_1 , I_2 and I_3 are constants; t is the time; τ_1 , τ_2 and τ_3 are the decay constants, deciding the decay rate for the rapid, medium and slow exponentially decay components, respectively. The results of the parameters τ_1 , τ_2 and τ_3 for the fitted decay curves are listed in Table 1. Three components namely slow, medium, and fast component are responsible for the persistent luminescence from the synthesized phosphor. A trend can be observed that the decay constants of the phosphors decrease gradually with the increasing of Tb^{3+} ions doping to $CaSi_xO_y:Tb$ phosphors due to reduced hole trapping ability of oxygen vacancies.

4. Conclusion

The $CaSi_xO_y:Tb^{3+}$ phosphor was synthesized by solution combined process. Different crystalline structures were obtained depending on Ca:Si mole ratios without further calcinations after solution combustion process. The luminescent properties of the phosphors can be greatly modified by the concentration of Tb^{3+} ions although the peak position observed doesn't change with amount of Tb^{3+} ions doping. The phosphors doped with 1% of Tb^{3+} result in a very intense and bright initial phosphorescent emission. The persistent luminescence decay time is found to be influenced greatly by the terbium composition of the phosphor.

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