Synthesis and photoluminescence properties of CaxSiyOz:Tb3+ nanophosphors prepared using solution-combustion method.

**F. B. Dejene\* and M. A. Kebede**

Department of Physics, University of the Free State(Qwaqwa Campus), Private Bag X13,Phuthaditjhaba, 9866, South Africa

\*Corresponding author: dejenebf@qwa.ufs.ac.za

**Abstract**. Effect of Tb3+ ion composition on the structural and phosphorescence properties from CaxSyyOz:Tb3+ nanocrystals has been evaluated using powders grown by the solution combustion technique. The XRD study indicates the change of phase from CaSiO3 to Ca3Si2O7 as the terbium concentration increase. Broad band emissions peaking between 280 - 360 nm derived from excited states of Tb3+ ions were observed for all powders grown from various Tb compositions. The green emission transition at 545nm due to an electronic transition of 5D4-7F5 was found to be more prominent and intense. Intensity of afterglow phosphorescence was greatly influenced by the composition of the activator ions. The maximum concentration of Tb3+ 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 such as in lower current saturation, high efficiency, and better chromaticity [1]. Oxide phosphor (including silicate phosphor) is more chemically stable than 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]. A calcium silicate phosphor would be ideal from the manufacturing point of view because both calcium and silica are abundant and are relatively inexpensive. The Tb3+ 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. In recent years, the experiment methods, such as sol-gel-microwave process [3], coprecipitation [4, 5], combustion reaction or microwave combustion methods[6], have been investigated to synthesis 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 phases results into amorphous calcium silicate, hence the use of solution combustion to try crystalline materials. Therefore, in the present paper we report the synthesis of CaO–SiO2:Tb3+ green luminescent powders via the solution–combustion process, and investigate their microstructure and luminescence properties as a function of the Ca:Si molar ratios and the Tb3+ doping concentration.

1. Experimental

Tb3+-activated calcium silicate (CaxSyyOz: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 Kα = 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

1. Structure

An XRD pattern of CaxSiyOz nanophosphors, shown in Fig. 1a, reveals that the whole spectrum that can be indexed in peak position to a crystalline hexagonal CaSiO3 phase (JCPDS 84-0655). From the XRD pattern of as-prepared CaxSiyOz: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 is substituted by the Tb ions. The concentration of Tb was changed from 1 to 4 mole %.

Fig. 1: The XRD pattern for CaxSiyOz:Tb3+ 1(a) Tb=0, 1(b) Tb=2%, 1(c) Tb=4%



(c)

(b)

(a)

* 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+. This is presumably resulted from the randomicity of intense combustion process, and the strong influence of *f*→*d* transition of Tb3+ is subjected to two kind of host lattice and incompletely transform from Tb4+ to Tb3+ owing to lack of reductive atmosphere. The group of weak peaks covering 280–360 nm belongs to *f*→*f* transition of Tb3+ in the two host matrix of CaSiO3 and Ca3Si2O7. The phosphorescence emission spectra of the CaxSiyOz:Tb phosphors grown from various Tb3+ ions doping are showed in Fig. 2(b) that were obtained by exciting the samples at the wavelength 257 nm, and exhibit emission transitions of (5D4→7F3,4,5,6). Particularly, the green emission transition at 545nm has been found to be more prominent and intense which is due to an electronic transition of 5D4-7F5 [7-9]. Such green strong emission displaying powder phosphor will find applications in the development of coated screens in certain electronic systems.

Fig. 2(a) Excitation and (b) emission spectra of CaxSiyOz:Tb3+ 1A Tb=0,1B Tb=1%, 1C Tb=4%.

(b)



(a)

2(d)

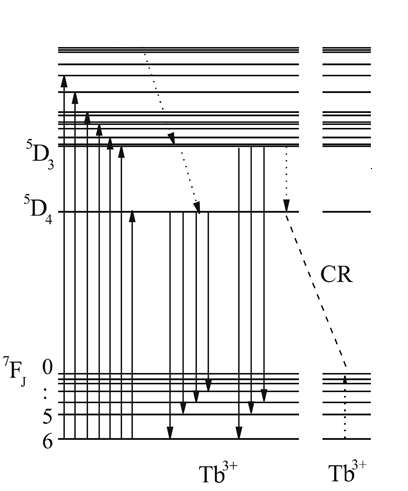


Fig. 2(d) Energy level scheme of Tb3+ ions in a crystal showing cross relaxation process [10]

Fig. 2(c) Graph of Tb3+ ions concentration versus maximum peak intensity

2(c)



The position of the emission peak in the phosphorescence almost shows no change, regardless of the diversity of the Tb3+ ions doping, implying that no obvious change occurs in the crystal field effect on 5d electron states of Tb3+ ions, even though the molar ratio of Tb3+ ions doping varies. The PL spectrum of CaSiO3 nanophosphors 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 CaSiO3:Tb3+ (0.01Tb) which is the highest intensity than the other Terbium concentrations. The effects of Tb3+ ions are clear. An increase in Tb3+ concentrations up to 1% Tb3+ ions increases the luminescence intensity possibly due to an increase in activator centres. Further increase in Tb3+ ions above 1% result in luminescence quenching caused by cross relaxation processes see Fig. 2(d). The graph of maximum PL intensity of CaxSiyOz: *x*% Tb3+ where *x* is the different percentages of Tb3+ (0 ≤ x ≥ 4) as a function of the Tb3+ concentrations is shown in Fig. 2(c). The emission peaks intensity increased when the amount of Tb3+ increased, and a maximum value was found in the *x*=1 sample, thereafter the emission intensity quenches gradually. Persistent luminescence curves of the phosphor powders were shown in Fig. 3. It can be seen from the curves that the powders showed differences in initial intensity and medium persistence when the powders were efficiently activated by fluorescent lamp. The results indicate that the initial luminescence intensity and the decay time of phosphors are enhanced with increase in Tb3+ concentrations. The sample with Tb =1% significantly enhanced the initial luminescence property of the green luminescence.



Fig. 3 Afterglow characteristics of CaxSiyOz:Tb3+ 1A Tb = 0, 1B Tb = 1%, 1C Tb = 4%

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

Table 1 Results for fitted decay curves of thephosphor powders with different Tb3+ moles

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

 (1)

where I represents the phosphorescent intensity; , and  are constants; t is the time; ,  and  are the decay constants, deciding the decay rate for the rapid, medium and slow exponentially decay components, respectively. The fitting results of parameters of ,  and 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 Tb3+ ions doping to CaxSiyOz:Tb phosphors.

1. Conclusion

The CaxSiyOz:Tb3+ phosphor was synthesized by solution combined process. Crystalline structures were obtained without further calcinations after solution combustion although different structures observed with amount of Tb3+ ions doping. The luminescent properties of the phosphors can be greatly modified by the doping of Tb3+ ions. The phosphors doped with an appropriate amount of Tb3+ result in a very intense and bright initial phosphorescent emission. Phosphorescence decay time is found to be influenced greatly by the terbium composition of the phosphor.

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