# Energy transfer from $Ce^{3+}$ to $Tb^{3+}$ in low quartz and amorphous $SiO_2$ hosts

**KG Tshabalala[1,2], HC Swart[2] and OM Ntwaeaborwa[2,3]**
[1]Department of Physics, University of the Free State (Qwaqwa Campus), Private Bag X 13,Phutaditjhaba 9866, South Africa
[2]Department of Physics, University of the Free State, IB51, Box 339, Bloemfontein 9300, South Africa
E-mail: ntwaeab@ufs.ac.za

**Abstract**. Low quartz and amorphous $Ce^{3+}$-$Tb^{3+}$ co-activated $SiO_2$ phosphors were synthesized by a solution combustion method using urea as a fuel and sol-gel respectively. The objective of this study was to compare the efficiency of energy transfer form $Ce^{3+}$ to $Tb^{3+}$ in low quartz and amorphous $SiO_2$ hosts. The phosphors were annealed in a reducing atmosphere of 4%$H_2$/96% Ar mixture at an elevated temperature of 1000°C for 2 hours. This was meant to reduce incidental presence of $Ce^{4+}$ (non-luminescent) to a fully homogeneous distribution of $Ce^{3+}$ ions in the silica matrix. As confirmed by X-ray diffraction (XRD) data, $SiO_2$ was produced as either low quartz or in the amorphous phase. The photoluminescence (PL) data showed that green emission of $Tb^{3+}$ at 543 nm was sensitized by $Ce^{3+}$, i.e. there was energy transfer from $Ce^{3+}$ to $Tb^{3+}$ resulting in an improvement of the green line emission due to the $^5D_4 \rightarrow {}^7F_5$ transitions of $Tb^{3+}$ ions. A possible mechanism of UV down-converted green emission due to energy transfer from $Ce^{3+}$ to $Tb^{3+}$ is discussed.

## 1. Introduction

Silica is widely used in so many fields such as medium layer and silicon-based photoelectron material for its excellent chemical stability, thermal stability as well as interfacial combination with silicon semiconductor. However, taking into consideration that $SiO_2$ can either be generated in the crystalline or amorphous form, it has then stimulated a long history of experimental and theoretical investigations. On that note, $SiO_2$ doped with metal ions can also be studied as a luminescence material. The rare earth or transition metal ions [1-4] are often used as activator ions to enhance the luminescent properties of silica for their unique electronic structures. For example, $Tb^{3+}$ ions due to their extensive use as materials for fabricating various optical re-radiators and cathodoluminescent screens when incorporated into glasses have developed great interest for many researchers [5,6]. However, the problem of enhancing the light output of $Tb^{3+}$ - containing glasses upon UV excitation still remains unresolved. The reason is that the light output of these materials is limited by the occurrence of intense absorption bands in the high-frequency range due to $4f^8 \rightarrow 4f^7(^8S_{7/2})5d^1(T_2)$ and $4f^7(^8S_{7/2})5d^1(E)$ inter configurational transitions [7] and a relatively low efficiency of excitation transfer from the luminescence sensitizers. In this work we synthesized low quartz and amorphous $SiO_2$ hosts doped with $Ce^{3+}$ and $Tb^{3+}$ ions to attempt to solve the problem through the comparative study on their structures and spectroscopic properties. In particular, we focus the attention in the performance of the energy transfer from $Ce^{3+}$ to $Tb^{3+}$ in low quartz and the amorphous phases..

## 2. Experimental procedure

Nano sized pure $SiO_2$, singly doped $SiO_2$ with Ce and Tb, and $SiO_2$ co-doped samples with ($Ce3^+$/ $Tb^{3+}$) were prepared by a solution combustion method as described in reference [8]. Silicic acid ($SiO_2 \cdot nH_2O$) and ammonium nitrate ($NH_4NO_3$) were used as the starting materials, urea ($CH_4N_2O$) was used as fuel and both cerium and terbium nitrates were used as dopant precursors. On the other hand, the same set of samples were prepared by using a sol-gel method where the starting materials were as follow: tetraethylorthosilicate ($Si(OC_2H_5)_4$, TEOS), ethanol (ETOH), distilled water and nitric acid

---

[3] Corresponding Author: ntwaeab@ufs.ac.za

(0.15 M $HNO_3$, as a catalyst). All the samples prepared were annealed in a reducing atmosphere of a 4%$H_2$/96%Ar mixture at an elevated temperature of 1000°C for 2 hours. The phase purity and crystallinity of the powder samples was characterized by X-ray powder diffraction (XRD). XRD measurements were carried out with a Bruker D8 Advanced powder diffractometer with Cu-Kα radiation ($\lambda$ = 1.5418 Å) in the 2θ range from 10° to 80°. The morphology of the prepared nanoparticles was analyzed by scanning electron microscopy (SEM) using a Shimadzu model ZU SSX−550 Superscan. The photoluminescence (PL) properties of the powder phosphors were characterized using a Cary Eclipse fluorescence spectrophotometer.

## 3. Results and discussion

### *3.1. X-ray diffraction*

The XRD patterns of the pure $SiO_2$ and singly doped $SiO_2$:$x$mol% $Tb^{3+}$ ($x$ = 1, 4), $SiO_2$:2mol%$Ce^{3+}$ and co-doped $SiO_2$:2mol%$Ce^{3+}$, $x$mol%$Tb^{3+}$ (x =1, 4) powders prepared with the combustion method are shown in figure 1. The undoped $SiO_2$ and singly doped $SiO_2$: xmol%$Tb^{3+}$ (x =1, 4) patterns show only a broad peak around 2θ = 23.6°. On the other hand, a singly doped $SiO_2$:2mol%$Ce^{3+}$ co-doped samples show a broad peak and some small signatures emanating from low quartz silica. The observed peaks were assigned by comparing the JCPDS database file no 86-1565, which is the characteristics diffraction pattern of the low quartz's phase of a $SiO_2$ glassy matrix. Figure 2 shows the XRD patterns of the sol-gel derived pure $SiO_2$ and singly doped $SiO_2$:$x$mol% $Tb^{3+}$ ($x$ = 1, 4), $SiO_2$:2mol%$Ce^{3+}$ and co-doped $SiO_2$:2mol%$Ce^{3+}$, $x$mol%$Tb^{3+}$ (x =1, 4) powder phosphors. The observed broad peak from a pure $SiO_2$ and a singly doped $SiO_2$:$x$mol% $Tb^{3+}$ ($x$ = 1, 4) at 2θ = 23.6° is similar to the XRD pattern shown in Figure 1. The only exception here is that pure $SiO_2$ derived from sol-gel is completely amorphous when compared with pure $SiO_2$ derived from the combustion of which has a peak shift towards lower angle suggesting that there is a uniform strain present since the preparation temperature for combustion is higher that of sol-gel route. Singly doped $SiO_2$:$x$mol% $Tb^{3+}$ ($x$ = 1, 4) have a broad peak respectively, and there is a shift towards a lower angle. For $SiO_2$:2mol%$Ce^{3+}$ and co-doped $SiO_2$:2mol%$Ce^{3+}$, $x$mol%$Tb^{3+}$ (x =1,4) the XRD data confirmed that all the powder samples crystallize and match well with the JCPDS standard (Fig. 1) in a low quartz after heat treatment.

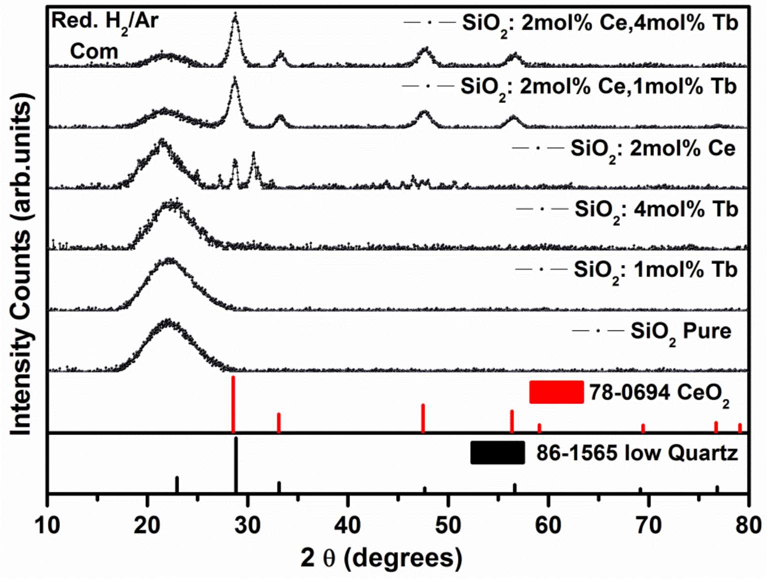

**Figure 1.** Room temperature XRD patterns of (as cast) pure $SiO_2$ and a singly doped $SiO_2$:$x$ mol%$Tb^{3+}$ ($x$ = 1, 4), $SiO_2$:2mol%$Ce^{3+}$ and co-doped $SiO_2$:2mol%$Ce^{3+}$, $x$mol%$Tb^{3+}$ ($x$= 1,4) from combustion derived route.

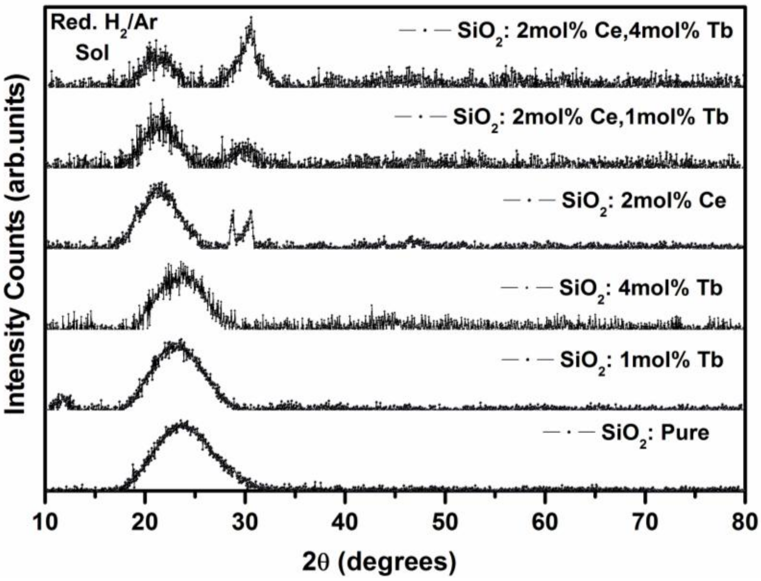

**Figure 2.** Room temperature XRD patterns of (as cast) pure $SiO_2$ and a singly doped $SiO_2$:$x$ mol%$Tb^{3+}$ ($x$ = 1, 4), $SiO_2$:2mol%$Ce^{3+}$ and co-doped $SiO_2$:2mol%$Ce^{3+}$, $x$mol%$Tb^{3+}$ ($x$= 1,4) from Sol-gel derived route.

### 3.2. *Scanning electron microscopy (SEM)*

The SEM images in figure 3 show the general morphology of the (a) $SiO_2$:2mol% Ce and $SiO_2$:2mol% Ce, 1mol% Tb samples, respectively. The SEM image in figure 3 (a) shows the agglomerated $SiO_2$:Ce with small particles appearing circular confirming spherical shapes. However, in figure 3 (b) the particles are relatively smaller than shown in (a), which suggest that the Tb incorporation interferes with the crystal growth [9].

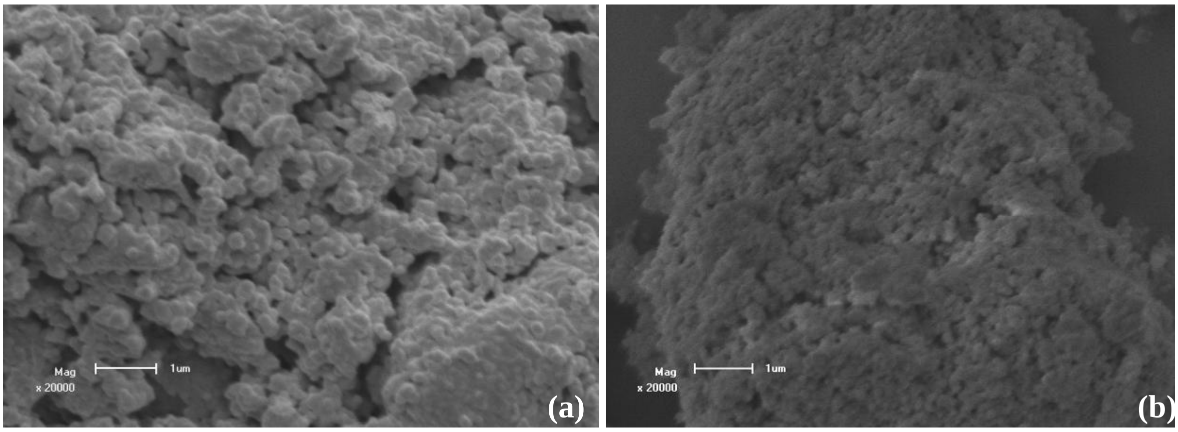

**Figure 3.** SEM images of the (a) $SiO_2$:2mol%Ce and (b) $SiO_2$:2mol%Ce,1mol%Tb samples

### 3.3. *Photoluminescence studies*

Figure 4 exhibit the PL emission spectra of the reduced singly doped $SiO_2$:2mol% $Ce^{3+}$ and $SiO_2$:1mol% $Tb^{3+}$ respectively. The emission from singly doped $SiO_2$:2mol% $Ce^{3+}$ at 402 nm is consistent with the 400 nm emission ascribed to $Ce^{3+}$ ions as reported by Kroon et al [10]. On the other hand, PL emission corresponding to $Tb^{3+}$ characteristics show sharp emission peaks from upper-laying levels, i.e., $^5D_4 \rightarrow {}^7F_{6,5,4,3}$ at 488, 543, 585 and 620 nm, respectively. These peaks match well with emissions from $Tb^{3+}$ ions into nanocrystalline silica, confirming their incorporation into the system, according to the previous results obtained by the authors using sol–gel derived $SiO_2$ doped with $Tb^{3+}$ [11].

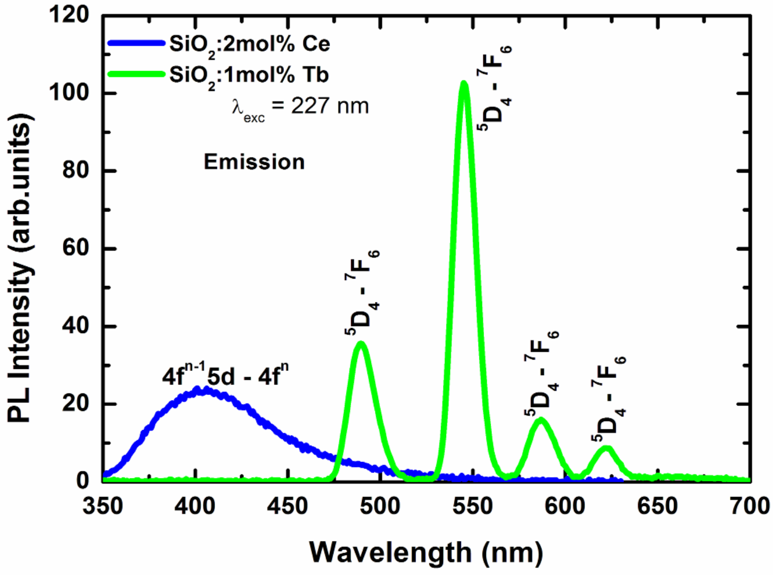

**Figure 4.** PL emission spectra $SiO_2$:2 mol% Ce and $SiO_2$:1mol% Tb ($\lambda_{exc}$ = 227 nm).

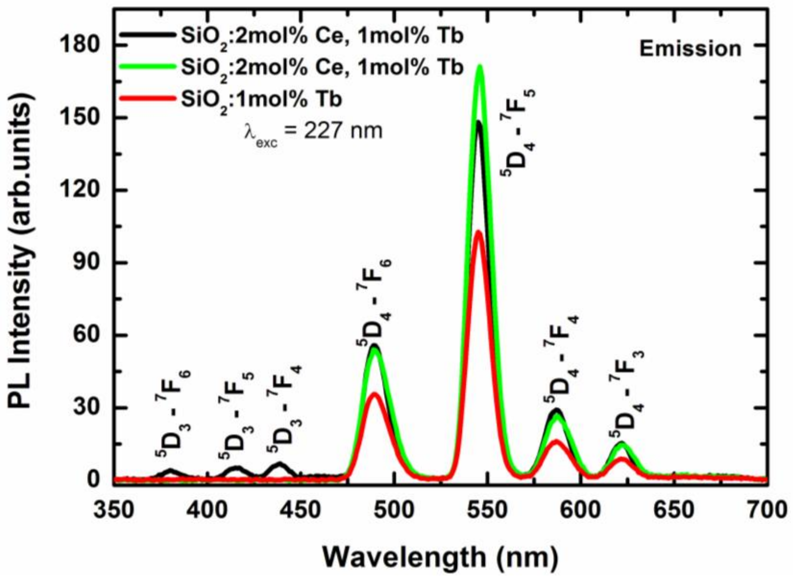

**Figure 5.** PL emission spectra of $SiO_2$ singly doped with 1 mol%$Tb^{3+}$ and co-doped with $2Ce^{3+}$ and $1Tb^{3+}$ in mol% under excitation at 227 nm. Corresponding transitions are indicated (Green: sol-gel, Black: combustion).

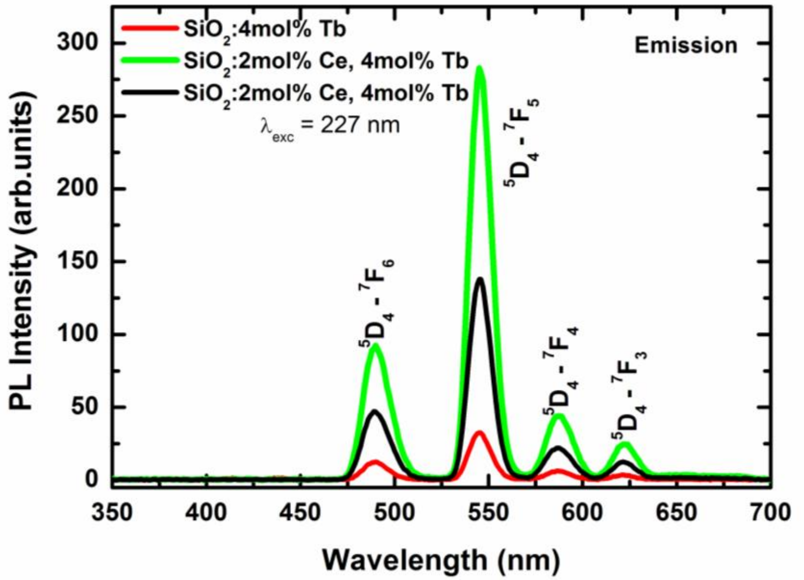

**Figure 6.** PL emission spectra of $SiO_2$ singly doped 4 mol%$Tb^{3+}$ and co-doped with $2Ce^{3+}$ and $4Tb^{3+}$ in mol% under excitation at 227 nm. Corresponding transitions are indicated (Green: sol-gel, Black: combustion).

Figure 5 & 6 respectively, mainly focuses on the samples obtained as low quartz after some heat treatment in a reduced atmosphere with 2 mol% of $Ce^{3+}$ ions while varying the concentration of $Tb^{3+}$ ions. In particular, samples exhibiting low quartz were derived from the combustion route while that derived from the sol-gel route became crystalline after heat treatment was applied. Therefore, the rest of the paper is design to compare the performance of $Ce^{3+}$ and $Tb^{3+}$ into low quartz and amorphous $SiO_2$ hosts through energy transfer (ET) efficiency studies. In figure 5 the PL emission ($\lambda_{exc}$ = 227 nm) spectra of the co-doped $SiO_2$:$Ce^{3+}$, $Tb^{3+}$ and singly doped $SiO_2$:$Tb^{3+}$are compared. It can be noted that all characteristic emission peaks of $Tb^{3+}$ ions from $^5D_3 \rightarrow {}^7F_J$ $_{(J\,=\,6,5,4)}$ to $^5D_4 \rightarrow {}^7F_J$ $_{(J=6,5,4,3)}$ are well pronounced from the low quartz matrix, confirming their incorporation into nanocrystals as shown in section 3.2. However, the intensity of the emission at 543 nm in $SiO_2$:$Ce^{3+}$,$Tb^{3+}$ derived from nanocrystals silica due to some heat treatment was much bigger than that of a singly doped $SiO_2$:$Tb^{3+}$. This excitation wavelength 227 nm is attributed to the absorption spectrum of the Ce(IV) valence states as a series of excitonic excitations from orbitals of atoms that surround tetravalent Ce into a silica matrix [12]. Therefore, taking a look at a broad Ce emission (350 – 500 nm) in Figure 4 in comparison to the co-doped systems represented in Figure 5 & 6 respectively, we can conclude that the energy transfer from $Ce^{3+}$ to $Tb^{3+}$ took place. Furthermore, the intensity of the $Ce^{3+}$ as seen from Figure 4 decreases completely in a co-doped $SiO_2$: Ce,Tb meanwhile increases the $Tb^{3+}$ emission when the $Tb^{3+}$ content is enlarged i.e (from 1 to 4 mol% $Tb^{3+}$). As a result, the energy transfer rate from $Ce^{3+}$ to $Tb^{3+}$ is the best in nanocrystalline $SiO_2$ host instead of amorphous.

## 4. Conclusions

$SiO_2$, $SiO_2$: Ce, $SiO_2$: Tb and $SiO_2$: Ce,Tb powders were successfully synthesized through combustion and sol-gel routes and later reduced in a mixture of 4%$H_2$/96%Ar at 1000°C for 2 hr. The structural and spectroscopic study in $Ce^{3+}$ and $Tb^{3+}$ single and co-doped $SiO_2$ has been carried out. The XRD data confirmed that the samples crystallized after heat treatment in a reduced atmosphere. The SEM images showed the agglomerated platelet-like particles of $SiO_2$: Ce with encrusted small spheroidal particles. Due to the incorporation of $Ce^{3+}$ and $Tb^{3+}$ ions in the silica hosts, energy transfer from $Ce^{3+}$ to $Tb^{3+}$ ions was observed. The transfer rate was more efficient in the low quartz than the amorphous host. Thus, the maximum energy transfer was observed from the sample co-doped with 2 mol%$Ce^{3+}$ and 4 mol%$Tb^{3+}$.

## Acknowledgements

This work is supported by the South African National Research Foundation (NRF), and Nanomaterials Cluster fund of the University of the Free State. The authors would like to extend their thanks to Prof. FB Dejene for the use of his laboratory and chemicals during the sample preparations.

## References

[1] Chryssou CE, Kenyon AJ and Pitt CW 2001 *Mater. Sci. Eng.* **B 81** 16

[2] Ferrari M and Armellini C 2000 *J. Sol-Gel Sci. Technol* **19** 569

[3] Morita M, Kajiyama S , Kai T, Rau D and Sakurai 2001 *J. Lumin.* **94** 91

[4] Garcia MA, Borsella E, Paje SE, Llopis J, Villegas MA and Polloni R 2001 *J. Lumin.* **93** 253

[5] Maciel GS, Biswas A and Prasad PN 2000 *Opt. Commun.* **178** 65

[6] Martin GS, Yanes AC, Mendez-Ramos J, Torres ME and Rodriguez VD 2001 *J. Appl. Phys.* **89** (5) 2520

[7] Arbuzov VI, Ya. Grabovaskins V, Kovaleva NS, Rogulis UT and Tolstoĭ 1988 *Opt. Spectrosc.* **65** 555

[8] Nagpure IM, Pitale S Shreyas, Kumar Vinay, Ntwaeaborwa OM, Terblans JJ and Swart HC 2011 *Materials Research Bulletin* **46** 23604

[9] Lu Xi-Hong, Li Gao-Ren, Yu Xian-Lan and Tong Ye-Xiang 2008 *Electrochemical and Solid-State letters* **11** (9) K86

[10] Kroon RE, Seed Ahmed HAA, Ntwaeaborwa OM, Koao LF, Nagpure IM, Gusowski MA, Botha JR and Swart HC 2011 *Physica* ***B*** 407 1596

[11] Seed Ahmed HAA, Ntwaeaborwa OM, Gusowski MA, Botha JR and Kroon RE 2012 *Physica* ***B*** 407 1654

[12] Efimov AM, Ignat'ev AI, Nikonorov NV and Postnikov ES 2011 *Optics and Spectroscopy* **111** 432

---