



High efficiency energy transfer in Ce,Tb co-doped silica prepared by sol-gel method

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ABSTRACT

Amorphous Ce,Tb co-doped silica (SiO₂) was prepared using the sol-gel method with the aim of studying the energy transfer from Ce to Tb ions. It was initially found that adding Ce reduced the Tb emission intensity, implying that energy transfer did not occur. In fact, the Ce single doped sample exhibited very poor emission. Ultraviolet-visible diffuse reflectance measurements displayed the signature of non-luminescent Ce⁴⁺ rather than Ce³⁺ ions. We therefore annealed the samples in a reducing atmosphere of 4% hydrogen in argon gas at 1000 °C. The reduced Ce single doped samples exhibited bright luminescence and the diffuse reflectance measurements now showed the characteristic of Ce³⁺ ions. The reduced Ce,Tb co-doped samples excited at the Ce absorption wavelength gave characteristic Tb emission (with negligible Ce emission), indicating that very efficient energy transfer from Ce to Tb was achieved. For samples containing 1 mol% Tb, the maximum luminescence was found when co-doping with 0.5 mol% Ce. Using such co-doped silica samples exhibiting energy transfer, it is possible to obtain effective luminescence from the Tb³⁺ ions via excitation of Ce³⁺ ions at 325 nm, instead of exciting the Tb³⁺ ions directly which requires a shorter wavelength of about 227 nm.

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1. Introduction

Phosphors are widely applied in lighting, displays, lasers, scintillators, etc. Generally host materials should exhibit good optical, mechanical and thermal properties [1]. Microporous silica prepared by the sol-gel technique is considered to be an optically inert medium and its chemical and thermal stability increase its attractiveness as a host for luminescent ions [2]. Further advantages of the sol-gel process are that it can produce very pure glass at temperatures well below the melting point, and it allows incorporation of much higher concentration of dopants than the melt process [3,4]. Lanthanide group ions may be used as luminescent centres [5]. These ions have partially filled f-level electron shells, giving rise to various electron transitions in the UV, visible and IR regions of spectrum.

Energy transfer can play an important role in phosphor materials as it can be used to enhance the luminescence efficiency [6]. Ce³⁺ ions are an efficient sensitizer to Tb³⁺ ions and co-doping has been studied in a variety of hosts [7–13]. Tb ions are used as the activator because their bright green emission is suitable for many applications. Although Tb ions can be excited efficiently through their allowed 4f–5d transition, it can be

advantageous to use Ce ions as a sensitizer because their allowed 4f–5d transition occurs at a longer (generally more accessible and convenient) wavelength. Tb and Ce can also be used to sensitize other lanthanides e.g. Tb may sensitize Sm in oxyfluoride aluminosilicate glasses to produce white light [14] and Ce may sensitize Yb in lithium–yttrium silicate glasses to produce near infrared light [15]. Ce ions can occur in a trivalent or a tetravalent state. Only the trivalent Ce³⁺ state with a single 4f electron is optically active, while the tetravalent Ce⁴⁺ ion is non-luminescent. Annealing in a reducing atmosphere can convert tetravalent Ce ions to the trivalent form, thus improving the Ce luminescence [16]. Ntwaeaborwa et al. [10] have reported some initial results on energy transfer from Ce to Tb in sol-gel silica. In this paper we report a much greater enhancement of the Tb luminescence excited via Ce at 325 nm in co-doped samples by annealing the samples in a reducing atmosphere, instead of air, in order to convert Ce from non-luminescent tetravalent ions to optically active trivalent ions.

2. Experimental details

Ce and Tb single doped, as well as Ce,Tb co-doped silica was produced using the sol-gel method by allowing tetraethylorthosilicate (TEOS) to react with water. Ethanol was used as a solvent, nitric acid was added to catalyze the reaction and Ce and/or Tb

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nitrate was added to produce doped and co-doped samples. After stirring for several hours, mixtures were stored in closed containers at 50 °C until a gel was formed. This was dried, ground to a fine powder and annealed in air at 600 °C or 1000 °C for 2 h. The reduced samples were annealed in flowing 4% hydrogen in argon gas for the same temperatures and time. Some samples were reduced in charcoal environment. Details of the preparation procedure have been published elsewhere [17]. X-ray diffraction (XRD) measurements were performed with a Bruker D8 diffractometer. A Bruker Tensor 27 was used to perform the Fourier Transform Infrared (FTIR) absorption measurements from 4000 to 400 cm^{-1} . Diffuse reflectance spectra were recorded using a Lambda 950 UV-vis spectrophotometer with an integrating sphere and using spectralon as a reflectance standard. Photoluminescence (PL) measurements were made at room temperature using a Cary Eclipse fluorescence spectrophotometer equipped with a xenon lamp.

3. Results and discussion

Fig. 1 shows the XRD results of $\text{SiO}_2\text{:Ce}$ 0.5 mol% annealed at 600 °C and 1000 °C. The sample annealed at 600 °C exhibited the well known characteristics broad peaks of amorphous silica [18,19], which narrowed slightly after annealing at 1000 °C, indicating a less disordered yet still amorphous sample. This is in contrast to the results of Nagpure et al. [20] who reported a low-quartz crystalline phase in silica prepared by the combustion method and annealed at 1000 °C, indicating the advantage of the sol-gel process for producing a single amorphous phase. There are no significant changes in the XRD spectra for the samples due to the dopants, nor for those heated in a reducing atmosphere instead of air.

Fig. 2 shows the excitation and emission spectra of $\text{SiO}_2\text{:Tb}$ 1 mol% annealed at 600 °C and 1000 °C. The optimum excitation wavelength of 227 nm is associated with the 4f–5d transition of Tb^{3+} ions [21]. The emission spectra showed the characteristic emission bands attributed to the $^5\text{D}_4\text{--}^7\text{F}_j$ transitions ($J=6,5,4,3$), with the dominant green band of the $^5\text{D}_4\text{--}^7\text{F}_5$ transition at 544 nm. Blue luminescence from $^5\text{D}_4\text{--}^7\text{F}_5$ transitions of Tb is not observed. The relatively high Tb concentration (1 mol%) allows cross relaxation which quenches emission from the $^5\text{D}_3$ level, whereas for a lower Tb concentration of 0.1 mol% in silica the $^5\text{D}_4\text{--}^7\text{F}_5$ transitions are observed [22]. The Tb doped sample annealed at 1000 °C exhibited higher luminescence intensity compared to the sample annealed at 600 °C. In FTIR spectra (Fig. 3) the absorption near 3447 cm^{-1} is attributed to the stretching vibration of hydroxyl ions

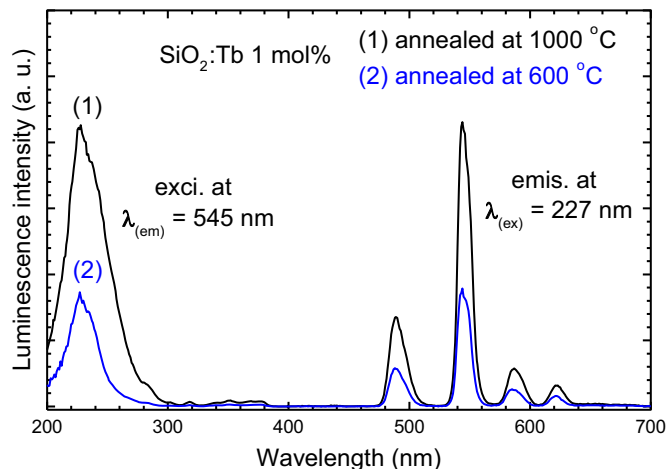


Fig. 2. Excitation and emission spectra of $\text{SiO}_2\text{:Tb}$ 1 mol% annealed at 600 °C and 1000 °C in air.

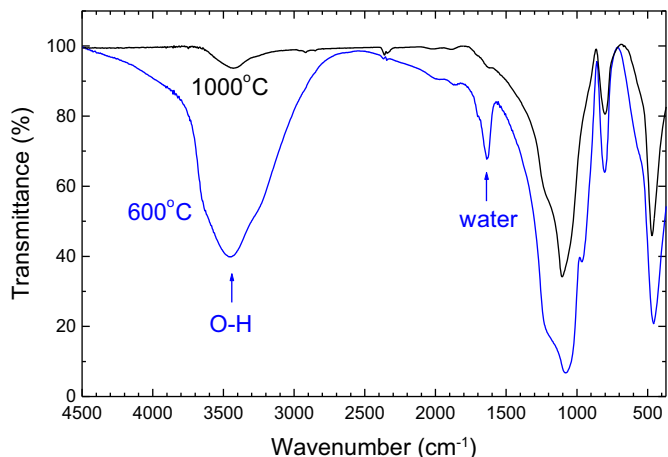


Fig. 3. FTIR spectra of $\text{SiO}_2\text{:Ce}$ 0.5 mol% annealed at 600 °C and 1000 °C in air. The unlabelled bands below 1200 cm^{-1} are characteristic of silica.

(O–H), while the absorption near 1636 cm^{-1} is attributed to water molecules. The three bands near 460, 798 and 1094 cm^{-1} are attributed to the silica host Si–O–Si, O–Si–O and Si–O asymmetric stretching respectively [23]. Although the FTIR spectra of Fig. 3 are for Ce doped samples, the absorption bands are associated either with the host silica or the water and hydroxyl ions rather than the dopants which are present in low concentration and it is expected that similar results would be obtained for Tb doped samples. The FTIR results indicate that annealing at 600 °C could not effectively remove water and hydroxyl ions present in samples produced with the sol-gel process. The very high vibration frequency of the hydroxyl groups (3447 cm^{-1}) makes them very effective at quenching the Tb luminescence by allowing excited ions to decay non-radiatively through multiphonon relaxation. Annealing at 1000 °C reduces the concentration of hydroxyl ions and multiphonon relaxation is then limited by the vibration frequency of O–Si bonds (up to 1094 cm^{-1}). The reduced quenching results in stronger luminescence, consistent with the PL results, and therefore all subsequent annealing was performed at the higher temperature of 1000 °C. Although the phonon frequency of the silica is low compared to hydroxyl groups, it is still large compared to some others hosts (e.g. fluorides) and can limit the emission from lanthanide ions. The higher temperature annealing might also allow further rearrangement of Si–O bonds that produce denser

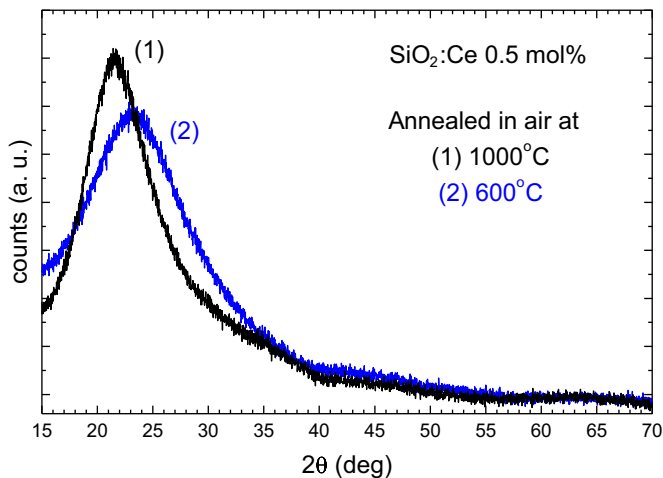


Fig. 1. XRD spectra of sol-gel $\text{SiO}_2\text{:Ce}$ 0.5 mol% (measured at room temperature after annealing at 600 °C and 1000 °C).

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