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$^5D_3 \rightarrow ^7F_J$ emission of Tb doped sol-gel silica

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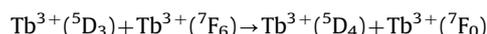
ABSTRACT

Amorphous silica samples doped with 0.1 and 1 mol% of terbium (Tb) were synthesized by the sol-gel method. In addition to the green light associated with $^5D_4 \rightarrow ^7F_J$ transitions of Tb^{3+} , the sample containing 0.1 mol% also emitted blue light as a result of $^5D_3 \rightarrow ^7F_J$ transitions during photoluminescence (PL) measurements. As a result of concentration quenching this blue emission was not observed for the samples doped with the higher concentration (1 mol%). However the blue $^5D_3 \rightarrow ^7F_J$ emission was observed in the 1 mol% doped samples during cathodoluminescence (CL) measurements. Since a rough calculation indicated that the excitation rate in the CL system where the blue emission is observed may be similar to a laser PL system under conditions where the blue emission is not observed, the difference is attributed to the nature of the excitation sources. It is suggested that during the CL excitation incident electrons can reduce non-luminescent Tb^{4+} ions in the silica, substituting for Si^{4+} ions, to the excited $(Tb^{3+})^*$ state and that these are responsible for the blue emission, which does not occur during PL excitation.

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1. Introduction

Sol-gel silica (SiO_2) has been widely used as a host material for rare earth ions because it has good physical properties and chemical stability [1]. The sol-gel method is an attractive technique for SiO_2 preparation since it can produce very pure glass at temperatures well below the melting point and allows incorporation of much higher concentration of dopants than the melt process. Trivalent terbium is a rare earth ion widely used as a dopant in a variety of host matrices [2]. The ion exhibits narrow line emissions located between 400 and 650 nm. The blue light below 480 nm can be attributed to the $^5D_3 \rightarrow ^7F_J$ transitions, while the green emission above 480 nm results from the $^5D_4 \rightarrow ^7F_J$ transitions [3]. Fig. 1(a) shows a partial energy level diagram of trivalent terbium with labeled transitions that correspond to the observed emission lines. The intensity of blue fluorescence from the 5D_3 level is highly dependent on the terbium concentration [3–5]. Since the energy difference between 5D_3 and 5D_4 levels is approximately equal to the energy difference between 7F_0 and 7F_6 levels, the excited electrons in the 5D_3 level populate the 5D_4 level through cross-relaxation, which involves a transfer of energy from an ion in the 5D_3 state to a nearby ion in the ground state (see Fig. 1(b)) and can be represented as [6]



Thus, in samples of low Tb^{3+} concentration where cross-relaxation is improbable both blue $^5D_3 \rightarrow ^7F_J$ and green $^5D_4 \rightarrow ^7F_J$ emissions are observed, while the blue $^5D_3 \rightarrow ^7F_J$ emission is generally not observed in samples containing higher Tb^{3+} concentrations. This concentration quenching effect is well known and blue emission can be expected only if the cross-relaxation is inhibited, e.g. by decreasing the Tb concentration or increasing the average distance between terbium ions by co-doping with Al, as reported by Silversmith et al. [4]. In this paper we present different emission spectra obtained for highly doped (1 mol%) silica samples during photoluminescence and cathodoluminescence characterization. What is surprising is that the blue emission, which does not occur during photoluminescence measurements, is observed during cathodoluminescence measurements. Possible reasons for this are evaluated.

2. Experimental

Samples of 0.1 and 1 mol% Tb-doped SiO_2 glass were prepared by the sol-gel method using tetraethylorthosilicate (TEOS), water, ethanol (C_2H_5OH) and $Tb(NO_3)_3$ as starting materials and nitric acid (HNO_3) as a catalyst. The molar ratio of $TEOS:H_2O:C_2H_5OH$ was 1:5:10, and the HNO_3 concentration was 0.015 M in water. TEOS was mixed with ethanol and stirred for 30 min after which the acidified water was added and stirring continued for another 30 min. After that $Tb(NO_3)_3$ was dissolved in a little ethanol and added to the mixture, which was stirred for a further 4 h. Then the

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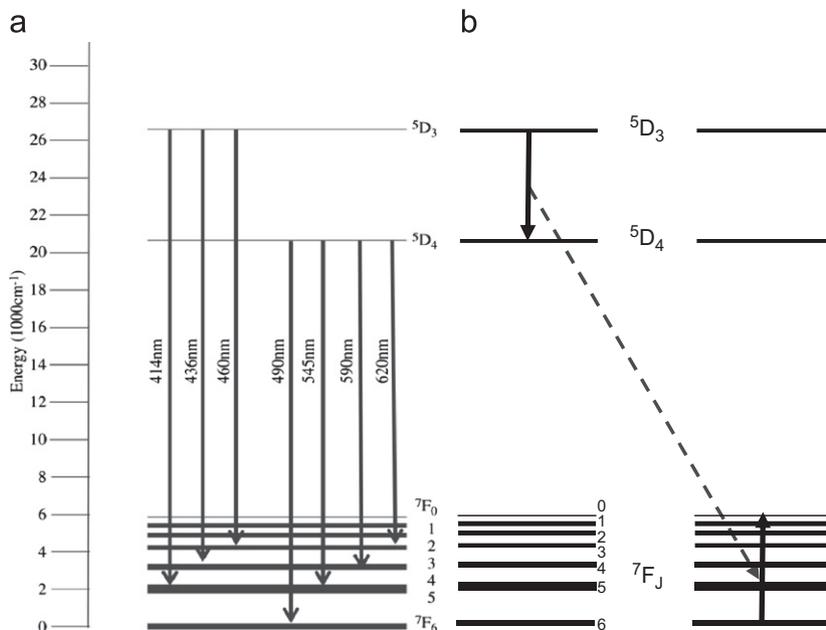


Fig. 1. (a) Energy level diagram of Tb^{3+} [4] and (b) cross-relaxation between adjacent Tb^{3+} ions.

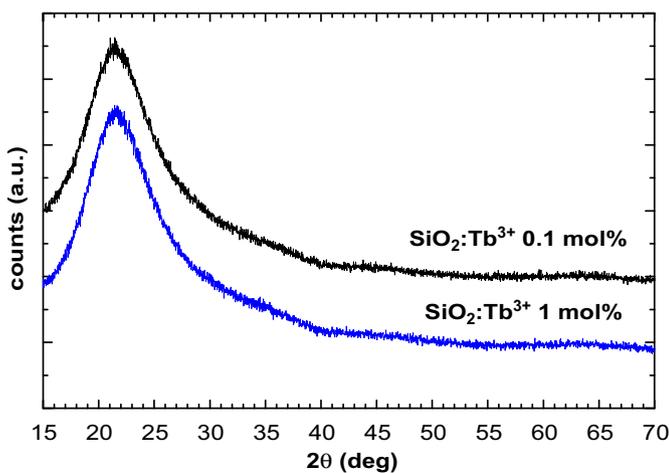


Fig. 2. XRD of Tb^{3+} 1% and 0.1% doped silica annealed in air at 1000 °C.

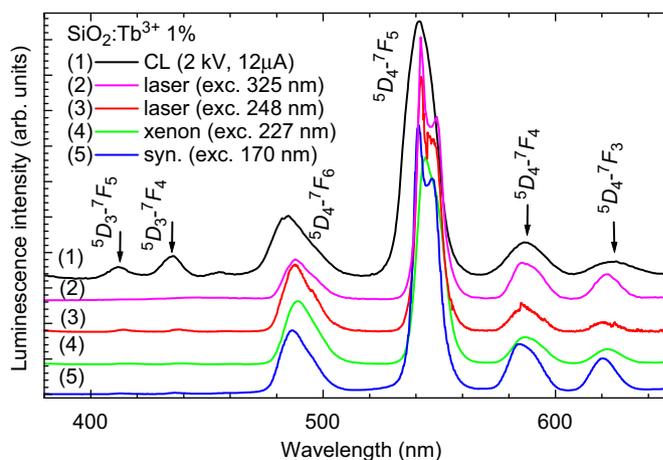


Fig. 3. CL and PL spectra of $SiO_2:Tb^{3+}$ 1%.

mixture was stored in a closed container and transferred to a water bath at 50 °C until a gel was formed. The gel was dried and annealed in air at 1000 °C for 2 h. X-ray diffraction (XRD) measurements were performed with a Bruker D8 diffractometer while photoluminescence was measured at room temperature with a variety of excitation sources including a xenon lamp, Cary Eclipse Fluorescence Spectrophotometer, a 248.6 nm Ne–Cu laser mini-PL system, a 325 nm He–Cd laser PL system as well as synchrotron radiation using the SUPERLUMI beam-line at HASYLAB. Cathodoluminescence was measured in a PHI Model 549 Auger system with S2000 spectrometer at a pressure of $\sim 2 \times 10^{-8}$ Torr, an accelerating voltage of 2 kV and a beam current of $\sim 12 \mu A$.

3. Results and discussion

The XRD spectra (Fig. 2) exhibited the well known characteristics broad peaks of amorphous silica (SiO_2) at $2\theta \approx 23^\circ$ and no differences between samples with low and high Tb concentrations were found. The PL spectra of $SiO_2:Tb^{3+}$ (1 mol%) recorded using

the xenon lamp, lasers and synchrotron radiation showed the characteristic green emission bands attributed to the $^5D_4 \rightarrow ^7F_J$ transitions ($J=6, 5, 4, 3$) with the dominant green band at 545 nm (Fig. 3), but no blue emission band from $^5D_3 \rightarrow ^7F_J$ transitions were observed, except for very small peaks in the spectrum excited with the 248 nm laser. However, in the same sample the CL spectrum showed blue emission from $^5D_3 \rightarrow ^7F_J$ transitions ($J=5, 4$) in addition to the $^5D_4 \rightarrow ^7F_J$ green emission bands. Fig. 4 shows that for the lower concentration Tb^{3+} (0.1 mol%) the blue $^5D_3 \rightarrow ^7F_J$ emissions were observed from the PL spectra. The absence of $^5D_3 \rightarrow ^7F_J$ blue emission in the PL results at high Tb^{3+} concentration (1 mol%) (Fig. 3) can be attributed to the cross-relaxation process (concentration quenching). It is, however, interesting to find out why the blue $^5D_3 \rightarrow ^7F_J$ emission is present in the CL spectra of the sample with a high concentration (1 mol%) of Tb^{3+} .

Similar observations of blue emission in CL spectra have been reported in 1% Tb^{3+} doped Lu_2O_3 [7] and 1.5% Tb^{3+} doped $Al_2O_3-ZrO_2$ [8]. Zych et al. [7] could not explain their observation, while Zawadzki et al. [8] considered that the terbium ions may be found both in Tb^{4+} and Tb^{3+} oxidation states, suggesting that some Tb^{4+} ions substituting Zr^{4+} ions may be converted into excited

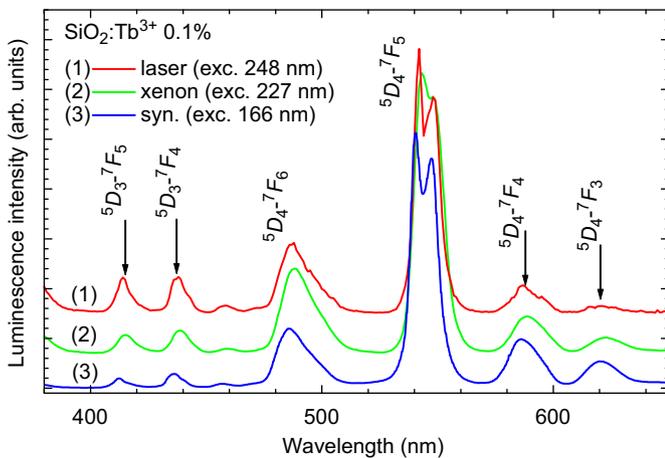
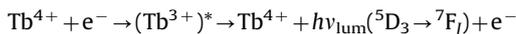


Fig. 4. PL spectra of $\text{SiO}_2:\text{Tb}^{3+}$ 0.1%.

$(\text{Tb}^{3+})^*$ ions as a result of the electron beam excitation. They propose that the normally non-luminescent Tb^{4+} ions, which became the transient $(\text{Tb}^{3+})^*$ ions under electron beam excitation, are responsible for the blue emission according to



A different environment of Tb^{4+} ions compared to Tb^{3+} ions, with a lower concentration, may account for the lack of concentration quenching. This mechanism is associated with the electron beam excitation and therefore explains why the blue emission is found in the CL spectrum but not in the PL spectra (Fig. 3). In our case a similar mechanism may account for the blue terbium luminescence observed in 1% doped samples using CL, where Tb^{4+} ions substitute Si^{4+} ions in the silica.

As an alternative explanation we considered that the quantum efficiency of CL is given as approximately 10^3 times the quantum efficiency of PL [9]. This suggested the possibility that for CL the rate of excitation is higher and both the $^5\text{D}_3$ and $^5\text{D}_4$ Tb^{3+} levels could be appreciably populated. Then the high population of electrons in the lower $^5\text{D}_4$ levels may actually prevent the cross-relaxation process in some ions (due to the exclusion principle) and therefore relaxation directly from the $^5\text{D}_3$ level would occur, i.e. blue $^5\text{D}_3 \rightarrow ^7\text{F}_j$ emission would be observed. For 2 keV electrons, if the bandgap of the SiO_2 host is taken as 9 eV [10] each electron is capable of creating ~ 220 electron hole pairs. This is lower than the estimate of 10^3 for the CL to PL relative quantum efficiency given earlier, because in this case the electron energy is fairly low and the bandgap is quite large. A current of 12 μA corresponds to 7.5×10^{13} electrons per second, giving an excitation rate of 1.7×10^{16} electron-hole pairs per second. The power of all the light sources used to obtain the PL results in Fig. 3 has not been well characterized, except the 325 nm He-Cd laser for which the power onto the sample was measured to be 5 mW. For this wavelength the photon energy is 3.8 eV or 6.1×10^{-19} J and so the photon flux is 8.2×10^{15} photons per second. If each photon has the same probability of producing a luminescent photon as an electron-hole pair (which is unlikely to be the case, and introduces some uncertainty in the rough calculation), then the ratio of excited states produced by CL compared to PL is only

about 2:1. This suggests that the $^5\text{D}_3 \rightarrow ^7\text{F}_j$ blue emission presented in the CL spectra of the sample with 1% Tb^{3+} concentration cannot be attributed to the high quantum efficiency of CL compared to PL, as the excitation rates are similar in the two processes. The calculation rather supports the view that it is the difference in the nature of the excitation source between CL and PL that is mainly responsible for the difference in emission from the same sample, and that the mechanism proposed by Zawadzki et al. [8] can be used to explain this phenomenon.

4. Conclusion

Tb^{3+} ions were successfully incorporated into silica produced by the sol-gel process. Concentration quenching became significant, removing the blue emission below 480 nm in the PL results, when the Tb^{3+} concentration was increased from 0.1 to 1 mol%. Yet the blue emission was observed in the CL results even at the higher concentration of Tb^{3+} . We conclude that it is not as a result of the difference in excitation rates between CL and PL (or the high quantum efficiency of CL compared to PL), but rather due to the difference in the nature of excitation. During CL excitation it is possible for electrons to reduce non-luminescent Tb^{4+} ions into an excited $(\text{Tb}^{3+})^*$ state, and it appears that this source of luminescence is not concentration quenched, possibly because it has a lower concentration on a different site of the Tb^{4+} ions compared to the Tb^{3+} ions. It is clear that whether the blue $^5\text{D}_3 \rightarrow ^7\text{F}_j$ emission of terbium doped silica occurs or not depends not only on the terbium concentration, but also on the nature of the excitation source.

Acknowledgments

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