

# Rare-earth ion distribution in sol–gel glasses co-doped with $\text{Al}^{3+}$

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## Abstract

Terbium spectroscopy is used to probe clustering of rare earth (RE) ions in sol–gel glasses. We use pulsed laser experiments to study energy transfer among  $\text{Tb}^{3+}$  dopants, and analyze the fluorescence decay curves using the Inokuti–Hirayama model. The analysis yields new insights about the role of  $\text{Al}^{3+}$  co-doping. Assuming a multipolar interaction, we derive an effective  $\text{Tb}^{3+}$  concentration for a series of samples with varying amounts of RE. When actual doping concentration is varied over 2 orders of magnitude, the effective  $\text{Tb}^{3+}$  concentration of centers that emit light changes by only a factor of 10. The results indicate that  $\text{Al}^{3+}$  co-doping is only effective at dispersing RE ions when the ratio of Al:RE is 10:1 or greater. At higher RE concentrations, most ions reside in clusters;  $^5\text{D}_3$  fluorescence is observed from a minority of isolated ions. This interpretation contradicts earlier work that used fluorescence line narrowing to demonstrate that  $\text{Al}^{3+}$  co-doping caused RE dispersal at high doping levels.

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## 1. Introduction

The sol–gel technique is a flexible low-temperature preparation method that allows incorporation of impurities such as rare earths (REs) during the liquid phase of the process. A long-term goal of this research is the synthesis of materials with properties comparable to a melt glass: optical clarity and high fluorescence yield. Sol–gels can hold higher dopant concentrations than melt glasses without losing amorphous character, so they have potential applications in many devices. However, it is essential that several fluorescence-quenching mechanisms in these materials be overcome.

$\text{Al}^{3+}$  co-doping improves fluorescence yield remarkably, but the mechanism is not yet understood. One generally accepted explanation has been that  $\text{Al}^{3+}$  prevents RE dopants from clustering in the glass, thus reduces ion–ion energy migration and cross-relaxation. Experimental evidence has been largely based on fluorescence line narrowing (FLN) studies of  $\text{Eu}^{3+}$ , where 2%Al co-doping appeared to preclude energy migration among europium

ions, even at high (1%Eu) doping levels [1]. Two recent molecular dynamics simulations [2,3] question the idea that  $\text{Al}^{3+}$  prevents RE clustering at this concentration. The first suggests that there are regions of relatively high  $\text{Al}^{3+}$  and RE concentration, compared to the rest of the network that is mostly undoped silica. Experiments designed to test whether RE ions are dispersed evenly throughout the glass or are highly concentrated in aluminum rich regions were inconclusive [2]. Lægsgaard [3] suggests that a minimum 10:1 ratio of Al:RE is necessary for RE ion dispersal.

In this paper, we present an experimental study that supports the need to reconsider the role of  $\text{Al}^{3+}$ . We use a well-understood cross-relaxation mechanism in  $\text{Tb}^{3+}$  ( $\{^5\text{D}_3, ^7\text{F}_6\} \rightarrow \{^5\text{D}_4, ^7\text{F}_0\}$ ) to study RE–RE interactions and to probe inter-ion distances in sol–gel glasses. We present convincing evidence that  $\text{Al}^{3+}$  does not cause uniform dopant distribution.

## 2. Experiment

Samples were prepared using the sol–gel method as described elsewhere [4]. Densification and formation of the glass were accomplished by annealing in air at 900 °C.

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Samples were single monoliths with good transparency, but porous compared to melt glasses. Room-temperature fluorescence spectra were generated with a Jobin-Yvon Spex fluorimeter. Excitation at 250 nm ( $4f \rightarrow 5d$ ) populated the  $^5D_3$  and  $^5D_4$  levels. Pulsed excitation of  $^5D_3$  was accomplished with a nitrogen laser. Rehydration upon air exposure alters the spectroscopic behavior of the materials [4]. To minimize this effect, measurements were done within 15 min of annealing.

### 3. Results and discussion

Fig. 1 illustrates the difference in fluorescence yield with and without  $Al^{3+}$  co-doping. Strong  $^5D_4$  emission is observed in all samples due to the  $15,000\text{ cm}^{-1}$  gap below the emitting level, but  $^5D_3$  fluorescence is weak without  $Al^{3+}$  co-doping. If  $Al^{3+}$  disperses  $Tb^{3+}$  clusters, enhanced  $^5D_3$  emission could be due to increased ion–ion distances/decreased cross-relaxation. In dilute  $Tb^{3+}$  crystals (under 0.1%), cross-relaxation has little effect [5]. The porous nature of our materials may encourage clustering even in 0.02% samples. We turn to pulsed methods to probe the cross-relaxation more directly.

Fig. 2 shows 437 nm fluorescence after pulsed excitation for three samples containing 2%Al and varying  $Tb^{3+}$  concentrations. As expected,  $Tb^{3+}$ – $Tb^{3+}$  cross-relaxation leads to faster decay for more concentrated samples. We begin with the Inokuti–Hirayama (IH) model [6], keeping in mind that IH model is based on a random substitutional doping as in a crystal, and does not take into account energy migration, which becomes appreciable at high doping levels. [7] Since our samples have relatively low doping, we believe that cross-relaxation is the dominant effect. Assuming a multipolar process, the density of electrons in  $^5D_3$  is given by

$$\rho(t) = \exp\left[-\frac{t}{\tau} - \left(\frac{C_{\text{eff}}}{C_0}\right)\Gamma\left(1 - \frac{3}{s}\right)\left(\frac{t}{\tau}\right)^{3/s}\right], \quad (1)$$

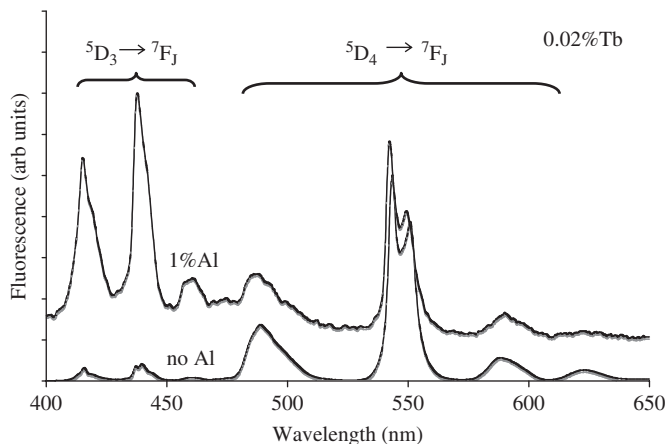


Fig. 1.  $^5D_3$  emission from samples with and without Al illustrates the enhancement of RE emission from co-doping.  $Tb^{3+}$  and  $Al^{3+}$  concentrations are given relative to Si.

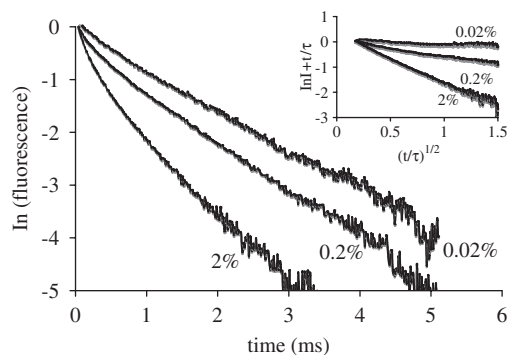


Fig. 2. Fluorescence decays after pulsed excitation for Tb-doped glass containing 2%Al. Inset shows IH plots that allow determination of  $C_{\text{eff}}$ .

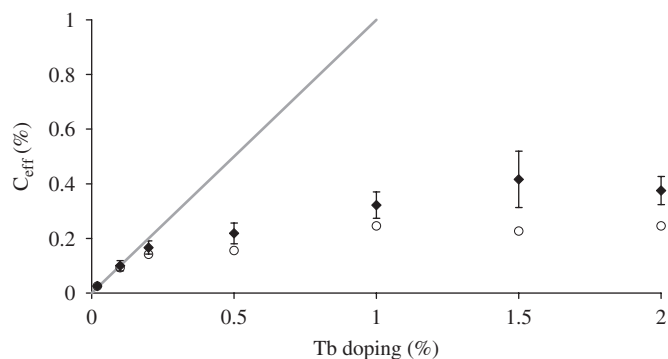


Fig. 3. Effective local Tb concentration ( $C_{\text{eff}}$ ) near emitting Tb ions graphed versus overall Tb concentration in the material.  $\circ$  = 0.5%Al and  $\blacklozenge$  = 2%Al. Line represents  $C_{\text{eff}} = C$ .

where  $\tau$  is the intrinsic lifetime of the emitting ( $^5D_3$ ) level,  $C_{\text{eff}}$  is the effective  $Tb^{3+}$  concentration near emitting centers, and  $C_0$  is a critical concentration.  $C_0 \equiv (\frac{4}{3}\pi R_0^3)^{-1}$ , where  $R_0$  is the distance between ions where the intrinsic decay probability equals the cross-relaxation probability. Finally,  $s = 6, 8$  or  $10$  for dipole–dipole, dipole–quadrupole, and quadrupole–quadrupole processes, respectively. The appropriate choice of  $s$  provides straight line plots of  $[\ln \rho(t) + (t/\tau)]$  vs.  $(t/\tau)^{3/s}$ . In a crystal, concentration is known and the analysis provides a measure of  $R_0$ . In this work, we fix  $R_0$  and determine  $C_{\text{eff}}$ . A literature survey indicates that  $R_0$  varies  $\sim 20\%$  in Tb-doped materials. Assuming a typical value of 1.4 nm, we establish  $C_{\text{eff}}$  from the slope. A dipole–dipole interaction (demonstrated in Tb:YAG [8]) and  $\tau = 1.3$  ms (from a fit to 0.02% Tb 2%Al decay at long times) provided the plots shown in the inset in Fig. 2. Strong short-lived fluorescence that is not associated with Tb prevented use of the first 20  $\mu\text{s}$ .

Values of  $C_{\text{eff}}$  are shown in Fig. 3 for a series of Tb/Al samples ( $\circ$  = 0.5%Al and  $\blacklozenge$  = 2%Al). Error bars correspond to the standard deviation of results from four different sample batches; 0.5%Al data is for a single set of samples. Points near the line (slope = 1) correspond to samples where the effective concentration around emitting  $Tb^{3+}$  ions is equal to the overall Tb concentration in the glass, as expected for fully dispersed dopants. The graph

indicates that Tb ions are dispersed when the ratio of Al:RE is  $\sim 10:1$  or greater, consistent with [3] but not with FLN studies that suggested RE dispersal at much higher doping levels. [1] Analysis done using  $s = 8$  (reported in other Tb-doped systems) yields the same trend as presented in Fig. 3.

$C_{\text{eff}}$  measurements for Tb-doping above 0.2%Tb shed new light on the role of  $\text{Al}^{3+}$ . Although the term *clustering* suggests that  $C_{\text{eff}}$  would be greater than actual doping level, i.e. points would fall above the line in Fig. 3, values of  $C_{\text{eff}}$  are significantly below actual concentration. Fig. 3 implies that for sample concentrations above 0.2%Tb, ions that emit light are in dilute regions of the glass. The remaining RE ions are tightly clustered and  $^5\text{D}_3$  emission is strongly quenched. Low solubility of REs in  $\text{SiO}_2$ , and the need to coordinate with limited numbers of non-bridging oxygens, make RE ions cluster on pore surfaces. Tightly clustered Tb ions do not contribute to the observed  $^5\text{D}_3$  emission because of strong cross-relaxation. We are currently working on experimental methods to separate Tb emission from background at early times in order to probe ions that cross-relax more strongly.

#### 4. Further investigation

The IH plots (Fig. 2 inset) are not perfect straight lines. As expected, the model fails to describe the complex distribution of RE ions in these samples, and the fitting described above should be understood to be an approximation. Current investigations by our group [9] are aimed

at developing realistic modeling for disordered materials. Following work by Even et al. [10], we introduce the possibility of fractal dimensionality of RE's in pores. Preliminary results support our interpretation of Fig. 3, in which emitting ions are in regions of low dopant concentration and are not dispersed uniformly throughout the material. Both approaches indicate that  $\text{Al}^{3+}$  co-doping is only effective at fully dispersing RE ions when the Al:RE ratio is  $\geq 10:1$ . In highly doped glasses, other changes in the RE environment must be responsible for enhanced fluorescence yield in samples containing Al.

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