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Fluorescence enhancement in rare earth doped sol-gel glass by *N,N*-

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Abstract

Studies of terbium fluorescence intensity as a function of annealing temperature reveal the cause of increased fluorescence yields observed in rare earth doped sol-gel silicates prepared using *N,N*-dimethylformamide (DMF) as a drying control chemical additive (DCCA). While gels prepared with DMF actually have lower fluorescence yields than gels prepared without DMF at lower annealing temperatures, DMF gels can be annealed at much higher temperatures while retaining high optical quality. At these higher temperatures, terbium fluorescence yields increase dramatically as the sol-gel network undergoes densification, closing the pores of the network and eliminating the fluorescence quenching silanols on pore surfaces. DMF is therefore found to enhance the fluorescence properties of rare earth sol-gel glasses by reducing micro-fracturing and facilitating network densification. Further investigations are underway to determine the effectiveness of other promising DCCAs, such as glycerol, and to explore the possibility of exploiting the solubility properties of DCCAs to improve rare earth dopant dispersion.

Keywords: sol-gel glass; rare earth; drying control chemical additive

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1. Introduction

The sol-gel process has been regarded as a potential avenue for increasing the dopant concentration of rare earth doped silica glasses beyond the doping levels possible using melt glass techniques. With high enough rare earth concentrations, the fluorescence intensity of these materials can be increased, thus enabling their use in compact applications such as optical amplifiers and laser media. However, rare earth doped glasses prepared using the sol-gel process have suffered from lower fluorescence quantum yields than their melt glass analogues, effectively negating the doping advantages of the sol-gel synthesis.

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Fluorescence quenching in rare earth doped sol-gel glass has been attributed to two non-radiative relaxation mechanisms: dopant-dopant energy transfer, or cross-relaxation, and dopant-hydroxyl energy transfer. The former affects fluorescence from energy levels with relaxation transitions that are well matched with an excitation transition from the ground state of neighboring dopant species, such as terbium's $^5D_3 \rightarrow {}^5D_4$ and $^7F_6 \rightarrow {}^7F_0$ transitions [1]. Cross-relaxation severely decreases fluorescence yields as doping concentration increases. The other quenching mechanism, dopant-hydroxyl energy transfer, affects all rare earth dopants at all dopant concentrations provided there are hydroxyl groups in the first coordination sphere of the rare earth ions [2]. Rare earth doped sol-gel glasses are highly susceptible to relaxation via this mechanism because they are formed in an aqueous environment. Furthermore, even if all aqueous species are removed during processing, the sol-gel pores remain lined with silanol groups, which are not easily dehydrated, and the interconnected pore network allows water from the environment to diffuse back into the sample [3].

Several alterations to the sol-gel synthesis have been made to minimize quenching due to these two non-radiative relaxation mechanisms. Rare earth ions have been introduced as nitrate salts to improve rare earth solubility, perhaps also improving dopant dispersion in the final glass [4]. Aluminum has been introduced as a co-dopant to encase rare earth dopants, preventing hydroxyl species from reaching the dopants and quenching fluorescence [5,6]. Annealing at temperatures up to 900°C drives hydroxyl species from the sample and dehydrates silanols on the surface of the sol-gel pores, reducing the rate of dopant-hydroxyl energy transfer. However, attempts to anneal glasses at higher temperatures have been met with physical and optical degradation.

We recently proposed the incorporation of drying control chemical additives (DCCAs) into the sol-gel preparation as a strategy for annealing rare earth doped sol-gel glasses at temperatures above 1000°C while maintaining their optical clarity [7]. DCCAs decrease the surface tension of the sol, thus decreasing the forces of syneresis during the drying phase of the sol-gel process [8]. The resulting reduction of micro-fracturing and of network deformation causes larger pore sizes and overall lower density. Using *N,N*-dimethylformamide (DMF) as a DCCA, we demonstrated successful annealing of materials up to 1100°C with sample density approaching that of melt glass. Full densification of samples resulted in the contraction of network pores. Preliminary fluorescence studies showed that annealing above 1000°C resulted in a large increase in fluorescence yield.

In this paper, we explore the mechanism through which DMF improves the optical properties of terbium-doped sol-gel silica glasses. We monitor fluorescence quenching mechanisms in samples with and without DMF as a function of annealing temperature. The ratio of $^5D_3 \rightarrow {}^7F_J$ intensity to $^5D_4 \rightarrow {}^7F_J$ intensity is used as probe of the degree of fluorescence quenching since $^5D_4 \rightarrow {}^7F_J$ terbium fluorescence is a well-established internal fluorescence standard and $^5D_3 \rightarrow {}^7F_J$ fluorescence is sensitive to both major fluorescence quenching mechanisms [9]. By exploring how the degree of fluorescence quenching changes with annealing temperature, we develop a better understanding of how DMF actually affects the environment of rare earth dopants and how the sol-gel synthesis can be altered to further improve fluorescence yield.

2. Experimental

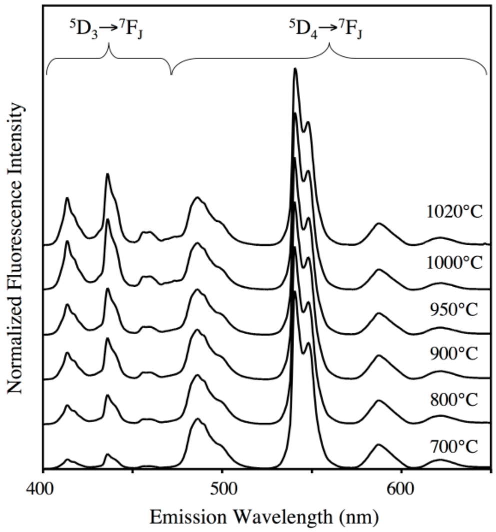
Sol-gel silica glasses were fabricated using three different preparations to vary DMF content. The sols of samples fabricated without DMF were prepared according to the procedure described by Lochhead and Bray [5], while the sols of samples fabricated with DMF were prepared according to the modified procedure described by Silversmith et al. [7]. Gels were doped with terbium nitrate pentahydrate and aluminum nitrate nonahydrate in a 1:10 molar ratio with terbium concentrations of either 0.02% or 0.20% by mole of silica precursor. All samples consisted of 1 mL of sol and were gelled at 60°C for 24 h in dry baths.

After gelling, 1 mL of an anti-wicking agent (AWA) was added to each sample to ensure uniform concentration of dopants throughout the samples. Water was used as an AWA for the gels prepared without DMF and for half of the gels prepared with DMF, while DMF was used as the AWA for the other half of gels prepared with DMF. These three batches are referred to as "noDMF", "halfDMF", and "fullDMF", respectively. Samples were heated in dry baths for 5 days at 75°C, 3 days at 90°C, and 3 days at 110°C.

After gel fabrication, samples were annealed in air at progressively higher temperatures. During each anneal, samples were heated to the indicated temperature at a rate of 1°C/min, allowed to dwell for 5 h, and then cooled at a rate of 3°C/min to 200°C. To anneal samples at 1100°C, previously unannealed gels were heated to 1100°C at a rate of 0.1°C /min, allowed to dwell for 24 h, and then cooled at a rate of 1°C/min to 200°C.

Spectroscopic analysis was conducted immediately after removal from the furnace and samples were immediately returned to the furnace after analysis was complete for the next higher annealing procedure. Continuous wave fluorescence spectra presented in this paper were generated at room temperature with a Jobin-Yvon Spex fluorimeter by exciting the samples at 250 nm (Tb $4f^8 \rightarrow 4f^7 5d^1$) and scanning a range of emission wavelengths.

3. Results



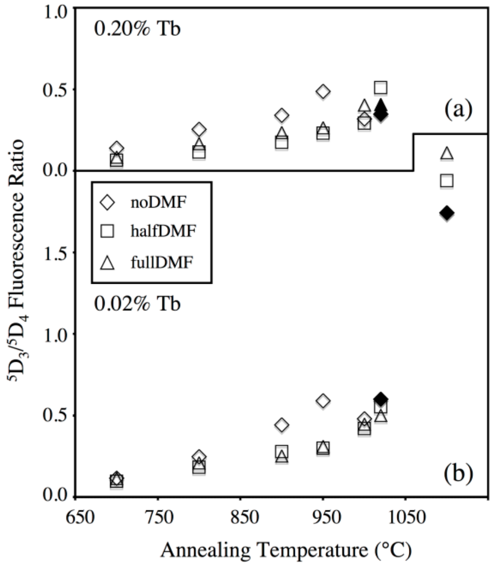


Fig. 1. (left) Fluorescence emission spectra of the 0.20% fullDMF sample after annealing under a range of temperatures. Spectra are normalized by the $^5D_4 \rightarrow {}^7F_J$ emission peak at 541 nm. With increasing annealing temperature, the intensities of $^5D_3 \rightarrow {}^7F_J$ emission peaks increase relative to $^5D_4 \rightarrow {}^7F_J$ emission peaks, which indicate a decrease in fluorescence quenching.

Fig. 2. (right) The $^5D_3/^5D_4$ fluorescence ratio as a function of annealing temperature for samples with 0.20% (a) and 0.02% (b) terbium dopant concentration. Optically clear samples are indicated by a hollow marker and optically deteriorated samples are indicated using a solid marker. Note the drop in $^5D_3/^5D_4$ fluorescence ratio of both noDMF samples between 950°C and 1000°C.

Fluorescence emission spectra were collected after samples were annealed under a range of annealing temperatures for gels made using 0.02% and 0.20% dopant concentrations and noDMF, halfDMF, and fullDMF fabrication procedures. Those corresponding to the 0.20% fullDMF sample are shown in Fig. 1. Emission peaks below 475 nm are due to $^5D_3 \rightarrow {}^7F_J$ terbium fluorescence and emission peaks above 475 nm are due to $^5D_4 \rightarrow {}^7F_J$ terbium fluorescence. For calculation of a $^5D_3/^5D_4$ ratio, representing the degree of fluorescence quenching, the 440 nm emission peak was used as an indicator of $^5D_3$ fluorescence and the 541 nm emission peak was used as an indicator of $^5D_4$ fluorescence.

The behavior of the $^5D_3/^5D_4$ ratio of samples made with each DMF procedure for 0.20% (a) and 0.02% (b) doping concentrations is shown in Fig. 2. Optically clear samples are indicated using a hollow marker, while optically deteriorated samples are indicated using a solid marker. A fluorescence ratio is not reported for 0.20% terbium gels at 1100°C because samples decomposed under this annealing procedure.

4. Discussion

The results of this experiment corroborate previous observations in our group concerning the effects of annealing rare earth doped sol-gel glasses. Increases in annealing temperature are accompanied by steady increases in the yields of sensitive fluorescence transitions for all samples annealed below 1000°C. Furthermore, 0.02%

terbium doped DMF gels annealed at 1100°C were optically clear and had $^5D_3/^5D_4$ fluorescence ratios that were significantly higher than those achievable in sol-gel glass without DMF.

By showing how the fluorescence ratio of each sample evolves with increasing annealing temperature, the data presented in Fig. 2 provide new insight into how the use of DMF causes these improved fluorescence characteristics. At lower annealing temperatures, DMF gels actually have lower $^5D_3/^5D_4$ ratios than noDMF gels, for both studied concentrations. However, between 950°C and 1000°C, the fluorescence ratios of noDMF gels drop to approximately the same level as the DMF gels. This temperature regime is where the fastest rate of densification occurs and where noDMF gels tend to deform and turn opaque [7]. At higher annealing temperatures, the $^5D_3/^5D_4$ fluorescence ratios of DMF and noDMF gels are indistinguishable, although only the gels made with DMF maintain optical clarity.

These observations support the conclusion that DMF's mechanism of fluorescence enhancement is through the effects described by Rao and Rao [8]. DMF acts as a DCCA, reducing the surface tension of the sol and by extension the forces of syneresis and degree of micro-fracturing in the sample. As a result, Rao and Rao observed that gels made with DCCAs had larger average pore sizes. At lower annealing temperatures, the reduction of micro-fracturing in DMF gels causes lower $^5D_3/^5D_4$ fluorescence ratios because dopant ions are more exposed to the larger pores and their silanols-covered walls. However, the improved structural integrity of the network allows the pores to successfully contract during densification. Pore contraction eliminates surface silanols, thus decreasing quenching and improving fluorescence yield from dopant ions.

This study also reveals some of the limitations of DMF as a DCCA in rare earth doped samples. DMF does not effectively facilitate the full densification of terbium doped samples at higher dopant concentrations. Furthermore, the premature optical degradation of the fullDMF 0.20% terbium doped sample indicates that using too much DMF hurts the physical properties of resulting gels. These observations suggest that other DCCAs may be preferable to DMF in fluorescent systems, especially protic DCCAs, which catalyze the formation of the sol-gel network.

Finally, using a DCCA with improved rare earth ion solubility could improve ion dispersion by maintaining the solvation of dopants until the sol-gel network can be more thoroughly established. The slightly improved $^5D_3/^5D_4$ ratios of the 0.20% terbium doped fullDMF sample over the analogous halfDMF sample suggest a slight dispersive effect by DMF. Nevertheless, preliminary studies using terbium-gadolinium energy transfer to probe the average distances between dopants do not support DMF as a dispersing agent. In sol-gel glasses doped 1:10:10 with terbium, gadolinium, and aluminum, the intensity of 541 nm terbium fluorescence was measured after gadolinium excitation. NoDMF gels were found to have higher energy transfer rates than DMF gels at lower annealing temperatures. However, since the transfer rates of all gels increase dramatically during densification, the lower energy transfer rates of DMF gels can be attributed to lower sample bulk density rather than DMF dopant-dispersing effects. This explanation is further supported by the similar energy transfer rates between halfDMF and fullDMF gels. If DMF enhances dopant dispersion by increasing rare earth solubility in the sol, the effectiveness of DMF's dopant dispersion should be heavily dependent on the amount of DMF in the sol.

5. Conclusion and Further Work

This study suggests that DMF primarily improves fluorescence characteristics of rare earth doped sol-gel silicates via the DCCA interactions investigated by Rao and Rao [8]. DMF improves the structural integrity of the sol-gel network, allowing samples annealed at temperatures above 1000°C to approach the density of melt glass. Through this densification process, the pore surface silanols are eliminated and the fluorescence yields of sensitive transitions are enhanced.

There are several potential avenues for improvement using DCCAS that should be explored to further improve the fluorescence properties of rare earth dopants and the physical characteristics of host silica networks. The effectiveness of DMF in facilitating high temperature annealing decreases notably with increasing dopant concentration. Other known DCCAs should be investigated for more effective behavior at higher dopant concentrations, including protic DCCAs, which catalyze network formation. Glycerol is a promising DCCA as it is protic and has been shown to decrease micro-fracturing to a similar degree as DMF [8]. Finally, the use of DCCAs provides an additional avenue for attempts to minimize dopant-dopant energy transfer. Incorporating a DCCA with higher rare earth solubility in the sol-gel synthesis could promote the dispersion of rare earth dopants by keeping the dopants solvated for longer in the fabrication procedure. This has the added benefit of increasing the maximum doping concentration of samples by allowing even higher quantities of dopant ions to be dissolved in the initial sol.

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