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CONCENTRATION QUENCHING IN Nd-DOPED GLASSES

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1. INTRODUCTION

Fluorescence from trivalent Nd in solids is unfortunately quenched by interactions between Nd ions. Thus, laser materials with high Nd concentrations have reduced efficiencies because of this self-quenching, also known as concentration quenching. Nd self-quenching in different crystals and glasses varies considerably. We are therefore investigating this effect in a large number of materials in an effort to: 1) find those materials with long Nd fluorescent lifetimes at high Nd concentrations; and 2) elucidate the basic mechanisms of quenching and how the material structure controls its magnitude. We have concentrated on Nd-doped glasses because they provide a rich variety of structures, albeit complicated by Nd site inhomogeneities, and are easily and quickly made.

2. EXPERIMENTAL

The glass compositions that we chose for our initial study include: LG-750, a K-Ba-Al phosphate glass used in large-aperture lasers for inertial confinement fusion research (such as Nova); UP-16, an ultraphosphate ($65\text{P}_2\text{O}_5\text{-}23\text{K}_2\text{O-}12\text{Ln}_2\text{O}_3$); LG-650, an alkali silicate with a low Nd induced emission cross-section; LG-660, a medium cross-section Zn-alkali silicate; and LG-670, a high cross-section Li-Ca-Al silicate. These glass compositions span a wide range of practical laser glasses.

Accurate measurements of Nd self-quenching are affected by: other quenching ions, in particular the transition metals and water (OH), and radiation trapping. We have minimized these effects by: 1) using high purity starting materials (<10 ppm transition metal content), 2) melting in a water-free environment, and 3) fabricating a special sample to avoid fluorescence trapping.

To avoid incorporating water in the glasses, we melted them in 1 kg batches with H_2 gas bubbling through the melt and flowing over the melt surface. Except for LP-16, which contained 10 mole% total lanthanide, we varied the Nd content in the following way. For Nd concentrations above $4 \times 10^{20} \text{ cm}^{-3}$, we added Nd_2O_3 to the base compositions; below $4 \times 10^{20} \text{ cm}^{-3}$, we maintained the total lanthanide concentration at 4 wt.% by substituting La for Nd.

Figure 1 shows a schematic of our sample construction. The sample is an array of 1-mm diameter by 1-mm high cylinders surrounded by an index-matched, absorbing optical cement (Summers Type 59 containing Cr_2O_3). The 1-mm cylinders are small enough so that less than 2% of the Nd fluorescence is absorbed in the cylinder at Nd concentrations of $5 \times 10^{20} \text{ cm}^{-3}$. By using a number of these cylinders we increase the available signal. Typically we find the measured fluorescence lifetime with this sample geometry is about 15% less than that of a 2 cm^3 sample.

FIGURE 1

Sample geometry for fluorescence decay measurements.

3. RESULTS

The measured first e-folding times of the Nd fluorescence in these glasses is shown in Figure 2. (The silicate glasses have non-exponential fluorescence decays; however, the second and third e-folding times have similar dependences on concentration.)

The quenching behavior of the silicate glasses confirm the expected dependence on the Nd transition strengths, which is predicted by the dipole-dipole

interaction theory of Forster¹ and Dexter². We find the Nd concentration at which the Nd fluorescence decay time drops to 50% of its value at low concentrations is 9, 5, and $3.8 \times 10^{20} \text{ cm}^{-3}$, respectively, for LG-650, LG-660, and LG-670. The decay times at low Nd concentration for these same glasses are 710, 460, and 360 μs . Thus, in silicates with higher transition strengths, more severe concentration quenching and shorter low concentration lifetimes combine to decrease decay times strongly at high Nd concentrations.

FIGURE 2

Concentration dependence of Nd fluorescence lifetime (first e-folding time) for selected silicate and phosphate glasses.

In the phosphate glasses, UP-16 shows considerably less concentration quenching than the commercial glass LG-750. (UP-16 is the potassium analogue to the Li-La-Nd phosphate reported by Batygov, et al.³). In contrast to its behavior in the silicates, quenching in the phosphates considered here varies greatly, even though the transition strengths do not. Structural differences probably account for this fact; for example, UP-16 has a network or "cage" structure, whereas LG-750 has a linear chain structure. The power dependence of quenching rates of the investigated glasses on Nd concentration is illustrated in Figure 3. "Static" quenching theories, which assume no excitation migration, predict a quadratic dependence, which is approximated only by glasses LG-670 and LG-750. UP-16 follows close to a linear power dependence. In the equivalent Li-La phosphate, Avanesov et al.⁴ suggested the observed linear dependence is probably due to the quenching being dominated by nearest neighbor Nd pairs, which are a sizable distance ($\sim 0.55 \text{ nm}$) apart. In LG-650 and LG-660, the greater than quadratic dependence of concentration quenching is perhaps explainable by a non-random distribution or clusters of more than 2 Nd ions at high concentrations.

We are investigating additional silicate and phosphate glasses, particularly these phosphates in the region of UP-16. Our preliminary measurements indicate quenching decay rates with concentration dependences between linear and quadratic. We conclude that these observations do not fit into present theories. Perhaps computer-based experiments on energy diffusion and quenching or the new concept of fractals can be helpful in understanding these new measurements.

FIGURE 3

Quenching decay rate ($Q = W - W_0$ where W_0 is the measured Nd fluorescence decay rate at a Nd concentration below $2 \times 10^{19} \text{ cm}^{-3}$) for LG-670 (x), LG-660 (▲), LG-650 (△), UP-16 (●), and LG-750 (o).

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