TRANSITION-METAL IONS IN Nd-DOPED GLASSES: DE86 006676
SPECTRA AND EFFECTS ON Nd FLUORESCENCE

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ABSTRACT

We have measured transition-metal ion (Ti, V, Cr, Mn, Fe, Co, Ni, Cu) spectra and their effects on Nd fluorescence quenching in Nd-doped phosphate and silicate glasses. Our purpose was to determine the maximum allowable impurity content given particular limits on the absorption loss at 1053 nm and the Nd fluorescence quenching rate. To keep the absorption loss $< 0.1 \text{ m}^{-1}$ the transition-metal impurity content should be kept below 0.5 ppmw. To keep the increase in the Nd fluorescence decay rate below 1%, the impurity content should be $< 3 \text{ ppmw}$. We have also found that the Nd quenching rates do not scale as predicted by the Forster-Dexter dipole-dipole energy transfer theory if we assume that the dominant variation with transition metal is the overlap integral of the Nd fluorescence spectrum and the transition-metal absorption. We suggest that phonon-assisted energy transfer to transition metals is effective in quenching Nd. We find that quenching rates increase 1.5 to 4 times as the Nd concentration increases from 0.5 to $10 \times 10^{20} \text{ cm}^{-3}$.

INTRODUCTION

Neodymium-doped glasses have an important role in laser systems, particularly those associated with inertial confinement fusion research [1]. These systems use Nd:glass of high optical quality in sizes up to 66 cm. Nd:glass amplifiers have demonstrated storage efficiencies greater than 4% at a stored energy density of 0.2 J cm^{-3} [2]. Depending on the maximum energy fluence that can be propagated through the glass without damaging it, a sizable fraction of this stored energy can be extracted. At the Lawrence Livermore National Lab (LLNL) we have a program that is developing higher efficiency, more cost-effective amplifiers for potential use in a multi-megajoule laser driver for inertial fusion. Part of this effort is directed toward improving the quality of the Nd-doped laser glass. In the study reported here, we have concerned ourselves with the detrimental effects of transition-metal (TM) ion impurities in these glasses. Knowing the magnitude of these effects, we can determine the maximum allowable TM impurity content in laser glasses.

The effects of TM impurities are detrimental in two ways. First their absorption bands may overlap the laser transitions in the 1050-1060 nm range. This absorptive loss will lower the maximum possible energy that can be extracted from that stored in the glass. As energy is extracted from a pumped laser glass the gain coefficient drops in value until it becomes equal to the loss coefficient. At this point no further energy extraction is possible. The maximum possible extraction efficiency (η) is proportional to the initial gain (G_0) and the loss (L) through the expression [3]

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$$n = \{ (1-L)^{1/2} n [(G_0-1) (1/L-1)^{-1}] - (1-L)^{-1/2} n [(1-1/G_0) L^{-1}] \} (2nG_0)^{-1} \quad (1)$$

To obtain 75% extraction efficiency at $G_0=7.4$ requires a gain-to-loss ratio of 20/1. Because typical laser glasses in amplifiers have gain coefficients of 2.5 to 5 m⁻¹, this implies that the loss coefficient should be less than 0.1 m⁻¹.

Transition-metal impurities also quench the Nd fluorescence; that is, they induce non-radiative transitions from the ⁴F_{3/2} excited state of Nd [4]. Shorter lifetimes lower amplifier efficiency in flashlamp-pumped systems because the lamp pump pulse width is about the same as the Nd fluorescence lifetime. As the lifetime decreases, the pump efficiency decreases as τ^x where x is in the range of 0.5 to 0.7. Trying to compensate for the shorter Nd lifetime by decreasing the flashlamp pump pulse does not work because the radiative efficiency of the lamp decreases and its emission shifts toward the ultraviolet, which increases its spectral mismatch with Nd. As a goal we want less than a 1% decrease in the Nd fluorescence lifetime due to impurities.

Our approach was to measure the spectra and quenching effects of TM in a silicate and two phosphate glasses, which have possible applications in future fusion research lasers. To generalize our results, we have attempted to explain our experimental data in terms of the dipole-dipole energy transfer theory of Forster-Dexter.

THEORETICAL BACKGROUND OF ND FLUORESCENCE QUENCHING

The ⁴F_{3/2} state of Nd³⁺ is metastable with about a 400 micro-second fluorescence lifetime. The radiative quantum efficiency of this state is near unity in most glasses.[5,6] The fluorescence can be quenched, however, by non-radiative energy transfer to vibronic or electronic energy states of the host material or of ionic or molecular impurities. Forster [7] and Dexter [8] analyzed the dipole-dipole process of energy transfer between localized energy states, which is now known as the Forster-Dexter theory. In brief, the probability of energy transfer from a donor(D) to an acceptor (A) is given by the expression,

$$W_{DA} = \frac{9\chi^2}{128\pi^5 N_A n^4 \tau_{0D}^6 R_{DA}} \int g_D(\nu) K_A(\nu) \nu^{-4} d\nu \quad (2)$$

where N_A is the acceptor concentration, n is the refractive index, R_{DA} is the donor-acceptor distance, τ_{0D} is the donor radiative lifetime, χ^2 is a factor that takes into account the orientational averaging of the dipoles, $g_D(\nu)$ is the shape factor of the fluorescence band, $K_A(\nu)$ is the attenuation coefficient of the acceptor, and ν is the frequency on the wavenumber scale. From this expression we can see that there are four important physical parameters determining energy transfer: the distance between the donor and acceptor, the strengths of the donor fluorescence and acceptor absorption, and their spectral overlap. There have been a large number of papers which have applied, extended, and modified this theory for rare-earth energy transfer in crystals and glasses; reviews can be found in references [9] and [10].

Following previous work, there are three regimes of quenching depending on the relative concentrations of the acceptors and donors. First, in the dilute case we have what is called "static" quenching in which there is only energy transfer from the donor to the acceptor, where non-radiative energy decay is assumed to occur rapidly. The donor decay kinetics are then described by the expression,

$$N_D(t) = I(t) \exp [- \gamma \sqrt{t}]$$

and

(3)

$$\gamma = \frac{4\pi^{3/2}}{3} N_A \sqrt{C_{DA}}$$

where $N_D(t)$ is the donor population, $C_{DA}=W_{DA}(R_{DA})^6$ and $I(t)$ is the donor decay in the absence of acceptors.

The second case occurs when there is some energy diffusion within the donor subsystem, but the diffusion rate is slow compared with the donor-acceptor quenching rate. This case is sometimes called "migration-controlled" quenching because the rate governing step is the migration within the donor subsystem. In this case the decay function can be written as,

$$N_D(t) = I(t) \exp [- \gamma \sqrt{t} - Wt]$$
(4)

where $W = AN_A N_D (C_{DA})^{(1-x)} (C_{DD})^x$, C_{DD} is the microparameter for donor-donor energy transfer, and x ranges from 0.5 to 0.8, depending on the model.

The third case occurs when the donor subsystem energy diffusion is very rapid compared with the acceptor quenching rate, which is known as the kinetic stage of quenching. Then W is independent of N_D and is equal to:

$$W = \frac{2}{3} \pi^2 N_A C_{DA} (R_{min})^{-3}$$
(5)

where R_{min} is the minimum donor-acceptor distance.

For transition metal ions in glass the nonradiative quenching process has a high rate ($>10^5 \text{ sec}^{-1}$); therefore, the kinetic stage of quenching is not expected for Nd concentrations up to 10^{21} cm^{-3} . Our data appears to confirm this.

EXPERIMENTAL

We chose three glasses to investigate: two phosphates and one silicate. The phosphate glasses are designated UP-91 and UP-16 with the following compositions:

UP-91 - 68.2 P₂O₅, 11.8 Al₂O₃, 14.0 K₂O, 6.0 (La+Nd)₂O₃

UP-16 - 70 P₂O₅, 20 K₂O, 10 (La+Nd)₂O₃

UP-91 is a possible laser glass candidate for future fusion research lasers. It has good spectroscopic properties [1] and is an easy glass to melt in production. It was developed primarily for its relatively low Nd self-quenching and good thermo-mechanical properties. UP-16 has even lower Nd self-quenching than UP-91, but it is not a practical glass because of its poor thermo-mechanical properties and poor environmental stability. The silicate glass is LG-660, a commercial alkali-zinc silicate laser glass. Its Nd transition strengths and fluorescence lifetimes are near the medians for silicate laser glasses. This glass has been tested in large amplifiers and shows good storage efficiency. [2]

We chose Nd doping concentrations for which we could observe quenching effects with and without energy diffusion in the Nd system. We melted glasses with $0.5 \times 10^{20} \text{ ions cm}^{-3}$ where there is no diffusion

and little Nd self-quenching. To see the effects of diffusion at two different Nd concentrations we melted glasses with 5 and 10×10^{20} Nd ions cm^{-3} . In these cases Nd self-quenching is present.

Transition-metal impurities are generally in laser glasses at levels <10 ppmw. Therefore, we kept the same condition in which the acceptor concentration is considerably less than that of Nd, and added TM concentrations of only 30, 100, 300, or 1000 ppmw of the metal, depending on the magnitude of the absorption or quenching effect.

We inductively melted the silicate glass in a Pt crucible and the phosphates in quartz with an atmosphere of dry nitrogen and homogenized them with a Pt stirrer. The melted glass was cast into a steel mold coated with graphite and annealed at 30°C/hr . The Pt crucible and stirrers were cleaned in HCl solution between each TM series. Samples of the resultant glass were cut and polished into $20 \times 20 \times 10 \text{ mm}^3$ for absorption measurements and $20 \times 20 \times 1 \text{ mm}^3$ for fluorescence decay measurements. We took care to keep the glasses as free as water as possible because OH^- is a well-known quencher of Nd fluorescence. [12] In the case of phosphates, dry nitrogen was bubbled through the melt. Most of the glasses had water absorption coefficients $<1 \text{ cm}^{-1}$ at the infrared band peak ($\sim 2900 \text{ cm}^{-1}$). At a level of 1 cm^{-1} the quenching rate is about 60, 160, and 300 sec^{-1} for Nd concentrations of 0.5, 5, and $10 \times 10^{20} \text{ cm}^{-3}$, respectively. When necessary we corrected the fluorescence decay rates for variations in the water content.

The absorption spectra were taken on a Cary 17 or Perkin-Elmer Lambda 9 spectrophotometer. Because all the glass samples contained Nd, we obtained the TM spectra by subtracting the Nd spectrum from the spectrum of the codoped samples. Some small errors due to this subtraction can be seen in the Figures.

The fluorescence decays were obtained by exciting the sample with a 10- μs pulse from a flashlamp. The resultant fluorescence was detected by a S-1 PMT and digitized by an HP-R7912 transient digitizer. Because many of our decays were exponential or nearly so, we used the inverse of the first e-folding time as the decay rate. To a first approximation this procedure is accurate enough for our analyses. In addition, in a laser amplifier the efficiency is more dependent on the decay rate within the first e-folding time than on the later e-folding times. More detailed analyses look at the time dependence of the decay function, which procedure is valid for crystals, but has problems in glasses where there are variations in the Nd environments due to the random nature of the glass structure. For silicates the decay function, even in the absence of quenching acceptors, is nonexponential. Phosphate glasses, on the other hand, have nearly exponential decays.

RESULTS

Absorption Spectra:

We first consider the spectra of the TM in the glasses. Figures 1 through 4 show the V, Mn, Co, and Ni spectra in various glasses. The titania doped glasses only have an increased ultraviolet absorption. The chromium-doped glasses have the usual Cr^{3+} spectra [13] and in the silicate glass Cr^{6+} is evident [14]. The Fe and Cu spectra are similar to previous measurements [13]. After analysis of the spectra and comparing them with previous measurements and analysis, we assign the charge states and coordinations for each TM and list them in Table I.

Figure 1. Vanadium spectra in UP-91 and LG-660 laser glasses. Sample thickness: 1 cm. Nominal concentration: 300 ppmw.

Figure 2. Manganese spectra in UP-91 and LG-660 laser glasses. Sample thickness: 1 cm. Nominal concentration: 300 ppmw.

Figure 3. Cobalt spectra in UP-91 and LG-660 laser glasses. Sample thickness: 1 cm. Nominal concentration: 300 ppmw.

Figure 4. Nickel spectra in UP-91 and LG-660 laser glasses. Sample thickness: 1 cm. Nominal concentration: 300 ppmw.

Table I.
Observed ionic states and coordinations of transition metals in two laser glass types.

Phosphate (UP-91)	Silicate (LG-660)
Cu^{2+} , octahedral	Cu^{2+} , octahedral Cu^+ (implied)
Fe^{2+} , octahedral (tetrahedral)	$\text{Fe}^{3+}, \text{Fe}^{2+}$ octahedral (tetrahedral)
Co^{2+} , tetrahedral (octahedral?)	Co^{2+} , tetrahedral
Ni^{2+} , octahedral	Ni^{2+} , octahedral (tetrahedral)
Cr^{3+} , octahedral	$\text{Cr}^{3+}, \text{Cr}^{4+}$, octahedral
Mn^{2+} (?)	Mn^{3+} , octahedral
V^{3+} , octahedral	V^{4+} (?)

In general the crystal field, or Dq , for the ions that are in octahedral coordination is higher for the silicate glass, LG-660, than for the phosphate glasses, UP-91 and UP-16. This higher Dq for LG-660 is probably a result of the truly three-dimensional cross-linked nature of the silicate; whereas, the phosphate glasses are primarily chain structures with some chain cross-linking for these ultraphosphates. Thus, the silicate structure is tighter with smaller "holes" for the TM.

We also find that under our melting conditions higher oxidation states are found in the silicate than in the phosphates. The one exception could be Cu-doped LG-660, in which the Cu^{2+} band intensity is considerably smaller than expected. This result suggests that some of the Cu may be in the monovalent state.

We determined the TM absorption coefficients at 1053 nm per ppmw of metal added, using the nominal added concentrations. The results are listed in Table II. In phosphate glasses Cu^{2+} is the strongest absorber whereas in silicate Fe^{2+} is. To keep the absorption coefficient below 0.1 m^{-1} in laser glasses the concentrations of these ions must be kept below 0.5 to 1 ppmw.

Table II.
Absorption coefficients of transition metals at the Nd laser wavelength (m^{-1} per ppmw metal added)

Ion	Phosphate glasses ($\lambda=1053 \text{ nm}$)		Silicate glasses ($\lambda=1057 \text{ nm}$)
	UP-91	UP-16	LG-660
Cu	0.23	0.21	0.038
Fe	0.07	0.06	0.110
Co	0.035		0.084
Ni	0.028		0.064
V	0.017		0.013
Mn	(0.002)		0.009

Fluorescence Quenching:

The quenching rates (i.e., the difference in decay rates with and without the TM impurity) of Nd fluorescence for 300 ppmw added TM impurity is shown in Figure 5 for the case of $5 \times 10^{19} \text{ Nd ions cm}^{-3}$. In phosphate glass Cu is the most effective quencher whereas in LG-660 silicate Co is. Previous work of Arbutov et al [4] on quenching by TM in GLS-22 barium-phosphate glass found following order for quenching effectiveness: $\text{Cu} > \text{V} > \text{Ni}$, $\text{Co} > \text{Fe}$. What is surprising to us is the large effect of Co in both the phosphate and silicate glasses. Can we explain the quenching effectiveness of the various TM by the variation in the spectral overlap of the Nd fluorescence and the TM absorption (i.e., the integral in Eqn. 2)?

Figure 5. Quenching rate of Nd fluorescence for 300 ppmw added transition-metal impurity.

We found the quenching rate in these glasses to be approximately linearly proportional to the impurity content as determined from the measured absorption band intensities. For a true Forster-Dexter static decay function (eqn. 3), the inverse of the first e-folding time does not depend linearly on the acceptor concentration. In fact, for high quenching rates the dependence is quadratic. In addition, the Forster-Dexter function does not correctly describe the initial decay, which is an exponential whose rate is determined by the smallest Nd-acceptor distance. We side-step this issue by accepting the measured linearity and asking how the slope value is related to the elementary dipole-dipole quenching process as described by the overlap integral (eqn. 2). They should be proportional as we change the TM impurity for a given glass assuming the Nd-TM distance distribution is the same.

We have listed in Table III the quenching rate divided by $100 \int g(\nu) K_A(\nu) \nu^{-4} d\nu$ for the various TM in UP-91, UP-16, and LG-660. We calculated the overlap integral from the branching ratios

Table III.

Normalized* quenching rates of Nd by transition-metal ions for 5×10^{19} Nd ions cm^{-3}

Ion	UP-91	UP-16	LG-660
V ³⁺	92		
Cr ³⁺	53		
Fe ²⁺	66	98	34
Co ²⁺	107		47
Ni ²⁺	111		60
Cu ²⁺	38	47	51
$\tau_{0D}(\mu\text{s})$	390		540

*Quenching rate (sec^{-1}) divided by $100 \int g(\nu) \alpha(\nu) (\nu/\nu_0)^4 d\nu$ (cm^{-1}), $\nu_0 = 1053$ nm

of the $4F_{3/2}$ transitions determined by using the Judd-Ofelt theory (which has been confirmed experimentally [15]) and the measured TM spectra. We have also included the fluorescence transition from the $4F_{5/2}$ state, which has a small population at room temperature.

According to a straight-forward application of the dipole-dipole quenching theory, we expected that for a given glass all the listed values should have been nearly the same. The observed variation could be due to deviations from a random distribution of acceptors; however, we suggest that the presence of phonon-assisted energy transfer, which is not included in the overlap integral description, probably explains the differences between the TM ion quenching. For instance, both cobalt and nickel have low energy states to which Nd can transfer with the emission of phonons. Because the theory of phonon-assisted energy transfer is not well developed, we are unable to be more quantitative in our analysis.

Comparing the values in Table III for UP-91 and LG-660, we see that those for LG-660 are a factor of two smaller. Part of this is due to the smaller Nd radiative rate of LG-660, which is 0.72 of that for UP-91.

Note that energy transfer from Nd to Cr is observed in UP-91. The Cr^{3+} absorption band overlaps only the Nd fluorescence bands at 874 and 802 nm, but the observed effect is consistent with the other TM. Several previous attempts have been made to use Cr^{3+} as a sensitizer for Nd in glass [16-18] without success. The measured low quantum efficiency of Cr^{3+} in glass [19], coupled with the Nd to Cr back transfer appears to explain this failure.

At higher Nd concentrations the quenching rates increase as diffusion within the Nd system takes place. Figure 6 shows the ratio of the quenching rate for 5 and 10×10^{20} Nd ions cm^{-3} to that rate at $0.5 \times 10^{20} cm^{-3}$. We have not yet attempted to explain these results in terms of the quenching theories.

Figure 6. Quenching rate increase with Nd concentration, expressed as ratio to quenching rate at 5×10^{19} Nd ions cm^{-3} .

CONCLUSIONS

1. Transition metal absorption measured in laser glasses. To keep absorption loss below 0.2 m^{-1} TM content must be $<0.5 \text{ ppw}$.
2. Quenching rates of Nd by TM measured; maximum TM impurity content for $<1\%$ change in decay rate must be $<3 \text{ ppw}$.
3. Quenching rates increase 1.5 to 4 times when Nd concentration increased from 0.5 to $10 \times 10^{20} \text{ cm}^{-3}$.
4. Phonon-assisted energy transfer is likely a strong contributor to Nd quenching by TM.

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