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Optical properties of Pr^{3+}-doped lithium tetraborate glasses

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Abstract

The visible luminescence of Pr^{3+}-doped lithium tetraborate glass has been investigated for different Pr^{3+}-concentrations and temperatures by using steady-state and time-resolved laser spectroscopy. At low Pr^{3+} concentration the luminescence is dominated by emission from the $^1D_2$ state which is populated by fast multiphonon relaxation from the $^3P_0$ level. As concentration increases the emission from the $^1D_2$ state shows a strong concentration quenching which indicates the existence of energy transfer processes. The time evolution of the decays from the $^1D_2$ level together with the concentration dependence of the energy migration rates suggest that migration of the excitation energy is competitive with cross relaxation in the concentration range studied. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Amorphous materials; Optical properties; Luminescence; Time-resolved spectroscopies; Electron–electron interactions

1. Introduction

Lithium tetraborate, $Li_2B_4O_7$ (LTB), has attracted much attention as a newly developed material which has potential applications to surface acoustic wave devices [1], ultraviolet frequency conversion, including fourth and fifth harmonic generation of Nd:YAG laser [2], and to nonlinear devices [3]. LTB is superior in UV applications to other commonly used nonlinear optical (NLO) materials such as potassium dihydrogen phosphate (KDP) or $LiNbO_3$ because of high UV transmittance at wavelengths down to 180 nm combined with a high damage threshold (around 40 GW/cm^2). These characteristics evidently show that LTB is a promising material for electro-optical devices as well as an attractive host to incorporate trivalent lanthanide ions.

Among rare-earth ions, trivalent praseodymium is an attractive optical activator which offers the possibility of simultaneous blue, green, and red emission for laser action, as well as infrared emission for optical amplification at 1.3 μm [4]. As far as we know, there does not exist any optical characterization of Pr^{3+} ions in LTB glass. In this work, together with a characterization of the optical properties of the visible luminescence from Pr^{3+} doped lithium tetraborate glass, we report a dynamical study of the energy transfer mechanism for different Pr^{3+} concentrations. This study includes absorption, emission, lifetime results, and fluorescence quenching of the $^1D_2$ emission.

2. Experimental techniques

LTB is a solid which can be produced in either crystalline or glassy state depending on the cooling rate from the melt. The Pr^{3+}-doped lithium tetraborate glasses used in this work were prepared by melting the appropriate molar amounts of $Li_2B_4O_7$ (ALFA 99.998%) with the molar ratio B/Li of 2.00 and Pr_6O_{11} (ALFA 99.996%). Doped and undoped glasses were prepared in high purity Argon atmosphere, using cylindrical graphite crucibles and a Bridgman type furnace. The dry mixtures were melted at 980°C for 1 h to exclude bubbles. Glasses were doped with 0.01, 0.05, 0.1, 0.2, 0.3, 0.5, 1, and 2 mol% of Pr^{3+}. Finally the samples were cut and polished for optical measurements.

The samples temperature was varied between 77 K and 300 K with a continuous flow cryostat. Conventional absorption spectra were performed with a Cary 5 spectrophotometer. The steady-state emission measurements

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were made with an argon laser as exciting light. The fluorescence was analyzed with a 0.25 m monochromator, and the signal was detected by a Hamamatsu R928 photomultiplier and finally amplified by a standard lock-in technique.

Lifetime measurements were performed by exciting the samples with a pulsed frequency doubled Nd:YAG pumped tunable dye laser of 9 ns pulse width and 0.08 cm^{-1} linewidth. The fluorescence was analyzed with a 1 m Spex monochromator, and the signal was detected by a Hamamatsu R928 photomultiplier. Data were processed by a boxcar integrator.

3. Results

3.1. Absorption and emission properties

The room temperature absorption spectra were obtained for all concentrations in the 400–2500 nm range by making use of a Cary 5 spectrophotometer. As an example Fig. 1 shows the absorption coefficient as a function of wavelength at room temperature for the sample doped with 2 mol% of Pr^{3+}. It consists of several bands corresponding to transitions between the $^3H_4$ ground state and the excited multiplets belonging to the $4f^2$ configuration of Pr^{3+} ions. The broad lines are due to large site-to-site variations of the crystal field strengths. The positions of the bands and the corresponding bandwidths do not change with concentration, indicating that the dopants are homogeneously distributed. In order to estimate the content of praseodymium in the different samples, we have calculated the integrated absorption coefficient for different absorption bands. As Fig. 2 shows, a linear dependence on concentration was found, which indicates that the relative concentrations of Pr^{3+} are in agreement with the nominal values.

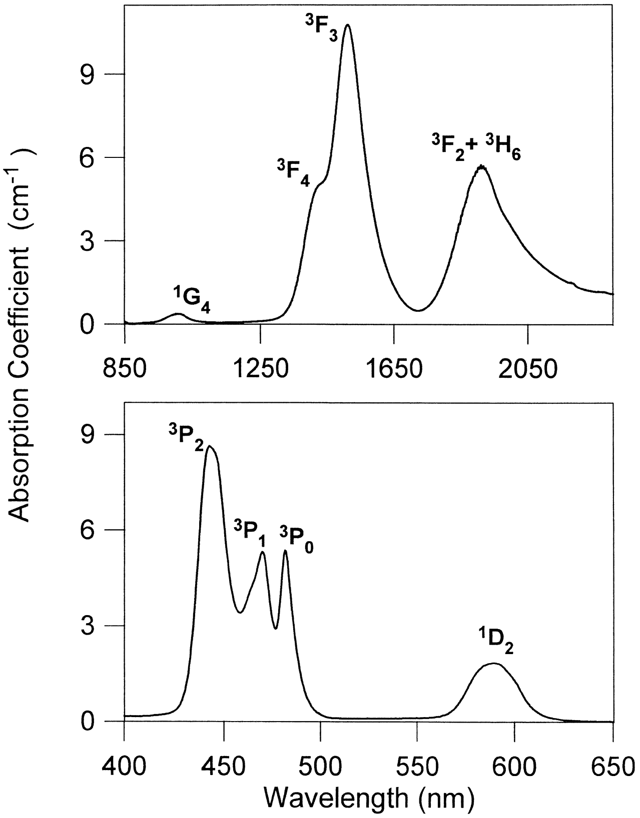

Fig. 1. Room temperature absorption spectrum of the sample doped with 2 mol% of Pr^{3+}.

The room temperature steady-state emission spectra were obtained in the 460–800 nm spectral range by exciting with an argon laser. In order to compare the emission of samples with different Pr^{3+} concentrations, emission measurements were performed in such a way that an absolute comparison could be made among them. The samples were thin slabs cut and polished to have exactly the same thickness. The pumping radiation was focused into the sample using a microscope stage with a 0.25 m monochromator and a photomultiplier at the tube end. A low magnifying objective was used for a close approximation to the upper surface of the sample. To avoid the direct entrance of pumping light on the monochromator, appropriate filters were used. Moreover, the Bertrand lens of the polarizing microscope was also used to slightly misalign the path of the remaining pumping light reaching the entrance of the slit of the monochromator. The sample was placed so that the spectrometer collected all the luminescence coming from the sample volume contained within the solid angle subtended by the microscope objetive. Fig. 3 shows, as an example, the emission spectra for the samples doped with 0.1, 0.5, 1, and 2 mol% of Pr^{3+}. As can be seen, after excitation in the $^3P_2$ level (454 nm) there is emission from levels $^3P_0$ and $^1D_2$. Simultaneous emissions from the transitions $^1D_2 \rightarrow {}^3H_4$ and $^3P_0 \rightarrow {}^3H_6$ are observed in the region between 600 and 630 nm. At low concentration the most intense emission

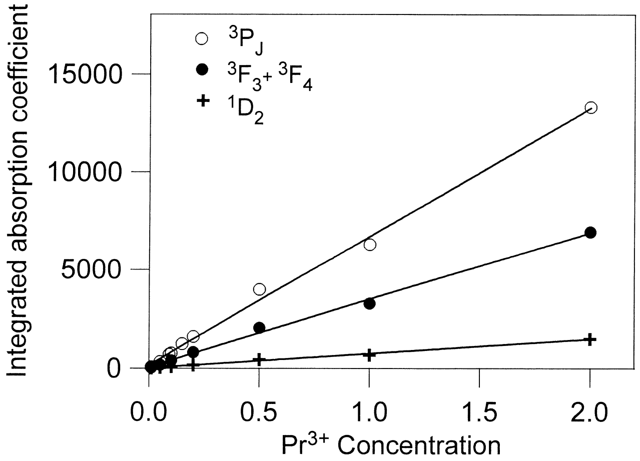

Fig. 2. Integrated absorption coefficient as a function of Pr^{3+} concentration.

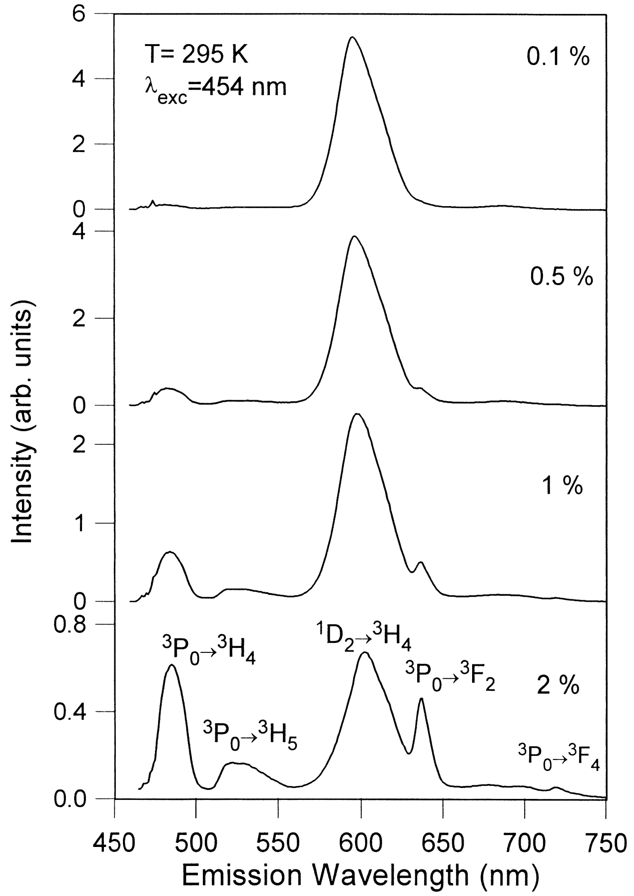

Fig. 3. Steady-state emission spectra of the samples doped with 0.1, 0.5, 1, and 2 mol% of Pr^{3+}obtained at room temperature by exciting the samples at 454 nm.

corresponds to the $^1D_2 \rightarrow {}^3H_4$ transition, but as concentration rises this emission shows a strong quenching and at high concentration its intensity is similar to the emission from the $^3P_0$ level. This concentration quenching of the $^1D_2$ emission is often observed in the emission spectra of Pr^{3+} and has been attributed to cross-relaxation between Pr^{3+} ions [5–8].

3.2. Lifetime results

In order to obtain additional information about the luminescence properties of Pr^{3+}ions in this glass, the fluorescence dynamics of the $^1D_2$ level was investigated for different Pr^{3+} concentrations at different temperatures. Decay curves for all samples were obtained under laser pulsed excitation at 598 nm ($^1D_2$). Fig. 4 shows the lifetime values of the $^1D_2$ level as a function of concentration at 77 K. As can be observed the lifetimes become shorter with increasing concentration even at low temperature which indicates the presence of energy transfer processes at concentrations higher than 0.01 mol%. The lifetime values correspond to the average lifetime defined by

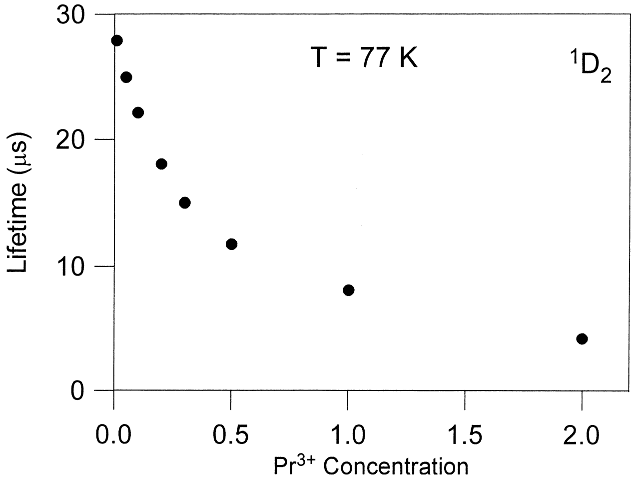

Fig. 4. Lifetime values of the $^1D_2$ level as a function of concentration at 77 K.

$$\tau_{\mathrm{avg}} = \frac{\int tI(t)\,\mathrm{d}t}{\int I(t)\,\mathrm{d}t}.$$

The decays of the $^1D_2$ level can be described by an exponential function for Pr^{3+} concentrations up to 0.2 mol%. As concentration increases up to 1 mol% they slightly deviate from a single exponential and a rapid decrease of the lifetimes occurs. However, for the sample doped with 2 mol%, the decay approaches again a single exponential function. The lifetimes are almost independent on temperature between 77 K and 300 K.

The lifetime of the $^3P_0$ excited state is too short to be measured with the temporal resolution of our equipment (laser pulse width 9 ns). Data in the available literature give a value around 1 μs in the case of a zinc borate glass. The relaxation mechanism from this level in the zinc borate glass is predominantly nonradiative [9]. The spectra in Fig. 3 show emission from $^1D_2$ level after excitation in the $^3P_2$ level. The $^1D_2$ level can be populated by multiphonon emission from level $^3P_0$ or cross relaxation via the $[^3P_0, {}^3H_4] \rightarrow [^3H_6, {}^1D_2]$ process. The latter depends on the concentration of Pr^{3+} ions in the sample. As shown in Fig. 3, concentration quenching of the $^3P_0$ emission is not observed from the emission spectra, which indicates that cross-relaxation process can be disregarded and multiphonon relaxation seems to be responsible for the population of level $^1D_2$ after excitation in the ^3P_J levels. The multiphonon transition rate between the $^3P_0$ and $^1D_2$ levels can be estimated from the modified energy gap law [10]. The energy gap between the $^3P_0$ and $^1D_2$ levels is ≈3780 cm^{-1} and the maximum energy of the phonons is 1400 cm^{-1}. With these values we estimate the multiphonon relaxation rate to be $\approx 10^6$ s^{-1}.

4. Discussion

The characteristic decay time of the $^1D_2$state of Pr^{3+} ions should be governed by a sum of probabilities for several competing processes: radiative decay, nonradiative decay by multiphonon emission, and by energy transfer to other Pr^{3+} ions. Nonradiative decay by multiphonon emission from the $^1D_2$ level is expected to be small because of the large energy gap to the next $^1G_4$lower level ($\approx$7000 cm^{-1}) as compared with the highest energies of the phonons involved ($\approx$1400 cm^{-1}) [10]. In addition, the decay curves are similar at room temperature and at 77 K, which indicates that the host phonons do not contribute to the relaxation rates from the $^1D_2$ level. Hence, at low temperature and low concentration (0.01 mol%) the measured lifetime should approach the radiative lifetime of the $^1D_2$ level. As the concentration rises, the lifetime decreases even at low temperature which indicates that Pr–Pr relaxation processes play an important role. One or both of the following two mechanisms can be operative: (i) cross-relaxation between pairs of Pr^{3+} ions; (ii) migration of the excitation energy due to resonant energy transfer among Pr^{3+} ions until a quenching center is reached (any other ion or defect to which the energy can migrate). Energy migration has been described either as a diffusion process or as a random walk (hopping model) and it was shown that these two models lead to similar results [11]. In the diffusion model, in the case of dipole–dipole interaction, at long times after the pulse excitation the fluorescence of the donors decay exponentially with an effective decay time, τ, given by [11]:

$$\frac{1}{\tau}=\frac{1}{\tau_0}+VC_A C_D \qquad (1)$$

where τ_0 is the intrinsic decay time, V is a constant involving donor–donor and donor–acceptor transfer constants, and C_A and C_D are the acceptor and donor concentrations respectively. The donor decay regime described by relation (1) is known as diffusion-limited decay [11]. An increase in the donors concentration produces a faster migration of energy and it was shown that in the case of very fast diffusion, the donor fluorescence decay is purely exponential and the effective decay is given by:

$$\frac{1}{\tau}=\frac{1}{\tau_0}+UC_A \qquad (2)$$

where U is a constant depending of the type of interaction.

In our case the donors and acceptors are the Pr^{3+} ions, hence a logarithmic plot of the effective decay versus concentration should show a slope equal to two if the $^1D_2$ decay is diffusion limited, or else a linear dependence on concentration in the case of fast diffusion.

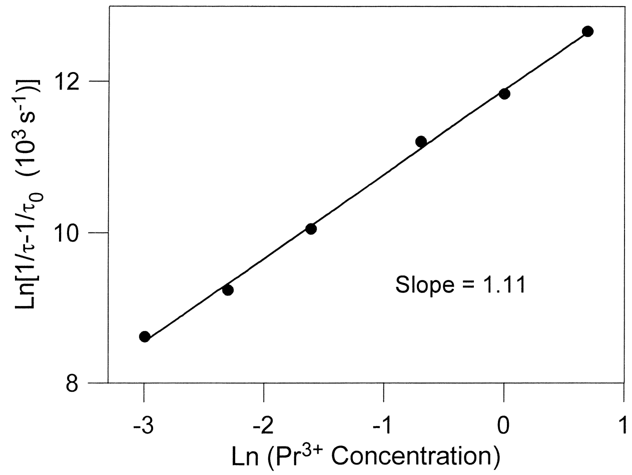

Fig. 5. Logarithmic plot of the energy migration rate of the $^1D_2$ emission as a function of concentration at 77 K.

Fig. 5 shows a logarithmic plot of the energy migration rate ($1/\tau$-$1/\tau_0$) as a function of the Pr^{3+} concentration. The intrinsic decay time τ_0 is obtained from the low temperature decay of the least concentrated sample which is purely exponential, and τ corresponds to the effective lifetime obtained from the decays at long times after the laser pulse. As can be observed, the slope is 1.11. In spite of the observed deviation from a single exponential of the $^1D_2$ decays for Pr^{3+} concentrations between 0.2 and 1 mol%, the absence of a quadratic dependence on concentration of the effective decay rates, indicates that there is a considerable migration of excitation energy before cross-relaxation occurs.

5. Conclusions

The study of the visible luminescence of Pr^{3+} ions in LTB glass shows that at low concentration the luminescence mainly corresponds to the $^1D_2$ level, which is populated by fast multiphonon nonradiative relaxation (10^6 s^{-1}) from the higher lying ^3P_J states. Fluorescence quenching from the $^1D_2$ state has been demonstrated to occur for Pr^{3+} concentrations higher than 0.01 mol% even at 77 K. This behavior is attributed to nonradiative relaxations which reduce the quantum efficiency and consequently the emission of the $^1D_2 \rightarrow {}^3H_4$ transition. The time evolution of the decays from the $^1D_2$ state together with the nearly linear dependence on concentration of the diffusion rates suggest that there is a considerable contribution of migration of excitation energy before cross-relaxation occurs.

Acknowledgements

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