Room Temperature Luminescence of Silicate Sol−Gel Materials Containing Trisodium Tris(dipicolinato)neodymate(III)

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The sol−gel process is a convenient and versatile method of preparing transparent optical materials at low temperature.[1] Many useful optical properties are induced by encapsulating molecules that possess the desired attribute (e.g. luminescence, laser action, photochromism).[2−7] The dopant molecule is dissolved in the liquid phase at the beginning of the preparation, and the hydrolysis and condensation of tetraalkoxysilanes form the solid silicate around the dopant. Glass prepared by melting silica is not a feasible host matrix for most molecules because of the extreme temperatures required.

Lanthanide compounds have been encapsulated into a variety of sol−gel matrices and their luminescence properties studied.[8−21] A common problem that is encountered with sol−gel materials is quenching of the luminescence by hydroxyl groups and water, both of which are present in relatively high abundance after room temperature synthesis. Concentration quenching of the luminescence may also pose a problem. Quenching of the luminescence of neodymium is particularly severe, and room temperature luminescence from this ion in sol−gel materials is very rare. Two obvious strategies to alleviate the quenching are to dry the sol−gel materials at high temperatures[18−21] and to isolate the metal ion from the deactivating groups.[15−17] The former method negates the advantage of the low temperature processing and destroys other molecules whose presence may be desired for purposes such as energy transfer to the lanthanide. The most successful demonstration of the latter method involved hydrolysis and condensation of $Nd(OR)_3$ with $Zr(OR)_3$ to produce nanoparticles in an organically modified silicate,[16] but only as multilayer films. The dominant deactivation mechanism was concentration quenching.

In this note we report the room temperature luminescence of neodymium in sol−gel monoliths processed at room temperature. The neodymium ions are partially isolated from hydroxyl deactivation by a chelating ligand, 2-6-pyridinedicarboxyate. The spectra, emission lifetimes, and studies of concentration quenching and water quenching are reported.

Experimental Section

Sample Preparation. The compound $Na_3[Nd(C_7H_3NO_4)_3]{\cdot}15H_2O$, NDP, used for this study was a neodymium chelate containing the tridentate ligand 2,6-pyridine-dicarboxylic acid.[22] The structure has been determined by X-ray diffraction.[22] Three different materials were prepared: pure NDP crystals, NLDP crystals containing 1% NDP doped in the corresponding lanthanum compound $Na_3[Nd_{0.01}La_{0.99}(C_7H_3NO_4)_3]{\cdot}15H_2O$, and sol-gel materials containing encapsulated $Na_3[Nd(C_7H_3NO_4)_3]{\cdot}15H_2O$.

NDP was prepared by mixing an aqueous neodymium nitrate solution and a boiling aqueous solution of the ligand, 2,6-pyridinedicarboxylate (dipicolinate acid), in a 1:3 molar ratio followed by the dropwise addition of 1.0 M sodium hydroxide until a pH of about 8 was obtained. Slow evaporation (over a period of several days) under ambient conditions resulted in prismatic crystals. The crystals were stored in the mother liquor water to prevent efflorescence.

For the synthesis of NLDP crystals, the above method was modified in the following manner. During the synthesis of NDP, a solution of La_2O_3 in dilute nitric acid was added to the aqueous solution of $Nd(NO_3)_3$ in a 99:1 lanthanum to neodymium mole ratio. The resulting crystals were also stored in the mother liquor.

The sol−gel samples were prepared by mixing 3.38 g of H_2O and 15.24 g of TMOS (tetramethyl orthosilicate) and immediately sonicating the mixture in an ultrasonic bath. After 10 min of ultrasound exposure, 0.22 g of 0.04 M HCl was added as a catalyst and the sol was futher sonicated at 10 °C. After about 20 min, the two phase mixture became a single-phase solution. The resultant silanol solution was then diluted by the addition of a sodium phosphate buffer solution in a 1:1 ratio. Meanwhile, an aqueous 0.07 M NDP solution was dissolved directly into the sol at room temperature. Polycondensation of the doped sols was carried out at room temperature in polystyrene cuvettes covered with paraffin films. Gelation of the samples occurred within 20 min at room temperature. The samples were then aged at room temperature for 11 weeks in sealed cuvettes. The NDP concentration in the gels was 2.3×10^{-2} M. Afterward, the cuvettes were uncovered and left in the open to dry for 5 days more. Some gels were also dried in an oven at about 60 °C.

Spectroscopic Measurements. Absorption spectra of doped gels and solutions of NDP and NLDP were measured with a Shimadzu model UV260 UV−visible double-beam spectrophotometer. The absorption spectrum of the monolith of aged-gel was taken before shrinkage in cuvettes with a volume of about 1.5 mL. Emission spectra were taken with 568.2 nm excitation from a Kr ion laser. The crystal or dry glass sample was mounted in a Displex closed-cycle refrigerator equipped with a thermocouple. The emitted light was passed through

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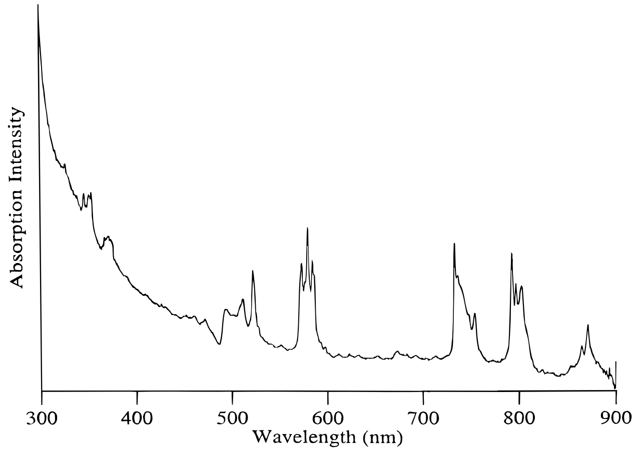

Figure 1. Absorption spectrum of a xerogel monolith containing 2.3 × 10^{-2} M $Na_3[Nd(C_7H_3NO_4)_3]\cdot 15H_2O$ at room temperature.

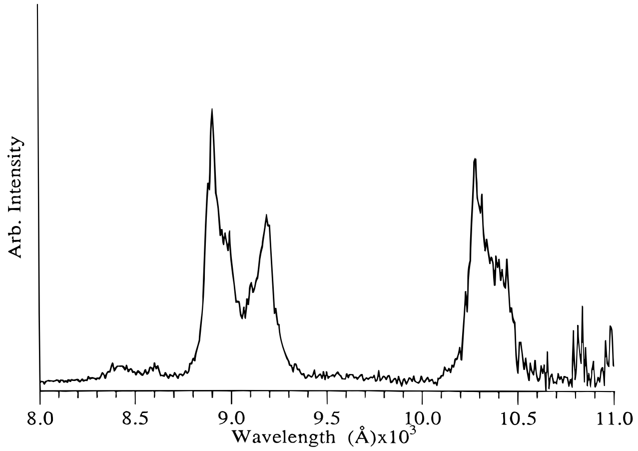

Figure 2. Emission spectrum of a xerogel monolith containing 2.3 × 10^{-2} M $Na_3[Nd(C_7H_3NO_4)_3]\cdot 15H_2O$ at room temperature.

a Spex 1702 0.75 m single monochromator. A Hamamatsu R316-02 photomultiplier tube and a S-1 photomultiplier tube were used to detect the signal in the visible and the infrared region respectively. The signal was then fed into a Stanford Research System SR-400 two-channel gated photon counter. The data were downloaded to an IBM computer for further analysis.

Lifetime Measurements. Measurements of luminescence lifetimes were carried out using a synchronously pumped Molectron DL II Model UV14 pulsed nitrogen dye laser excitation source at 570 nm. The luminescence was detected by an RCA 7102 S-1 photomultiplier tube operating at 1.1 kV. The portion of the excitation pulse that reflects from the sample was focused onto a Thorlabs 201-574-7227 photodiode. The electric pulse generated by the photodiode and photomultiplier tube were input to a Tektronix 2230 100 MHz digital storage oscilloscope, which was connected to a computer. The response time of the instrument was 0.1 μs.

Results

Absorption Spectroscopy. The absorption spectrum of a gel containing encapsulated 2.3 × 10^{-2} M NDP is shown in Figure 1. Resolved peaks or shoulders are observed at 352, 506, 530, 670, 726, 793, 853, and 866 nm. The spectra of NDP and NLDP aqueous solutions were also taken. The positions of the bands in the solution and gel spectra are similar. The absorption spectra of all samples indicate the presence of neodymium.

Emission Spectroscopy. The luminescence spectrum of a 2.3 × 10^{-2} M NDP-doped aged-gel at room temperature is shown in Figure 2. Transitions at 889, 897, 918, 1027, and 1040 nm were detected. Emission spectra of NDP-doped xerogels and oven-dried gels were also taken at room temperature. Although the signal to noise ratio of the xerogel spectrum is not as high as that in the oven-dried gel spectrum, the emission transitions of both xerogel and dried gel are the same as the aged gel.

The emission spectrum of a NDP-doped aged gel was also taken at 15 K. Again, there are no changes in the band energies compared to those in the room temperature luminescence spectrum.

The emission of NDP crystals was measured at room temperature and at 15 K. Transitions were detected at 871, 909, and 1053 nm, similar to those observed in the spectrum of the NDP-doped aged gel. The NDP crystal emission exhibits inhomogeneous broadening, characteristic of Nd^{3+} ions in a disordered matrix. The room temperature spectrum contains broader peaks.

Lifetime Measurements. The decay lifetime of the metastable state $^4F_{3/2}$ of various samples were measured at 300 K and 77 K. The time decay constants are characterized by the 1/e intensity decrements as the decay profiles of all solid samples are multiexponential. The shortest lifetime is on the order of tenths of microseconds while the longest exponential decay is around 3 μs. On addition of water and deuterium oxide to the solid crystals, the luminescence decays become single exponential. The lifetime of aqueous solutions of NDP is about 0.2 μs and that of NDP in deuterium oxide is about 1.0 μs. All of the fluorescence lifetimes are considerably smaller than the radiative lifetime of Nd^{3+} ions.

Discussion

1. Room Temperature Emission in Sol−Gel Monoliths. Sol−gel materials provide excellent optical hosts for a variety of applications. The materials are made on the bench top at room temperature from solutions. They are transparent from the near UV to the near-IR regions of the spectrum. The microporosity enables small molecules to penetrate to the interior of solid monoliths while large molecules are physically trapped in the matrix. These materials are under active investigation for a very wide range of applications ranging from tunable solid state lasers to biosensors.[2−6,24,25] The mild processing temperatures are an important advantage of the sol−gel method of making silicate optical materials, especially where they need to be integrated with other components that cannot withstand elevated temperatures.

It is unusual for neodymium to luminesce at room temperature in sol−gel materials because of the presence of water. The water content of air-dried gels at room temperature is on the order of 30% by weight. The water molecules are probably strongly interacting with the pore walls. A recent study showed that proton mobility in air-dried gel monoliths is only a factor of two slower than in fluid solution.[23] These attributes are advantageous for some applications such as chemical sensors[6,24,25] but are detrimental for applications involving rare earth luminescence.

Binding the neodymium ion with bulky chelating ligands provides one strategy for minimizing the quenching effects of water on the ion's luminescence. Complexes formed with the dipicolinate ligand have been shown to be particularly stable.[28,29] Three tridentate ligands form a mononuclear complex with the

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trivalent neodymium ion. The nine neodymium coordination sites form a geometric polyhedron which is similar to a tricapped trigonal prism with the three nitrogens occupying the three equatorial positions. There are approximately 15 water molecules in the unit cell of NDP, 10 of which have been crystallographically located,[22] but the water molecules do not directly bind to the metal.

The observation of room temperature luminescence from sol−gel monoliths containing encapsulated NDP shows that this strategy is at least partially successful. However, the excited state lifetimes are too short to allow the material to be useful for laser applications. The effects of two of the major quenching mechanisms, concentration quenching and water quenching on the luminescence lifetime of NDP are discussed below.

2. Quenching. Concentration quenching of the luminescence of Nd^{3+} has been the subject of many investigations. For a given f−f transition, the energies of absorption and emission are very similar and Nd-Nd energy transfer is probable. In many different media, neodymium decay lifetimes have been shown to decrease with increasing neodymium concentration. One major explanation is that the excitation energy of one ion can be transferred between ions until it reaches a lattice imperfection which traps and dissipates the energy.[26] A very low concentration of impurities can easily lead to rapid quenching. This mechanism can be present in any host. A second mechanism, cross relaxation, is the transfer of the excitation energy from one ion to an unexcited Nd ion, each of which dissipates its share of the energy. One of the final states in this process must decay faster compared to the initial level. Cross relaxation therefore relies critically on the relative positions of Stark levels which depend on the host. Finally, Auger recombination describes the excitation of two ions being combined to form a ground state atom and a doubly excited state atom.

Because decreasing the Nd ion concentration lengthens the fluorescence lifetime, the lifetimes in NDP and in NLDP crystals were measured. The neodymium concentration in the latter crystals is 1% that of the former. The crystals were studied because the concentrations are at least three orders of magnitude larger than those in the sol−gel monoliths. Neodymium and lanthanum, having similar ionic radii, can be substituted for each other in the crystal and can be assumed to have a random distribution. Absorption and emission spectra of the NLDP crystals are similar to those of NDP crystals. No experimentally meaningful difference in the decay time was observed between the two crystals. This result shows that in our system concentration quenching is not significant. The Nd−Nd interaction is shielded by the presence of the bulky ligands.

Neodymium fluorescence can also be severely quenched in the presence of hydroxyl ions and water.[27] The vibrational frequencies of O−H groups usually are between 2800 and 3600 cm^{-1}. For the deactivation of the Nd^{3+} ion from the $^4F_{3/2}$ state, several vibrations must be excited simultaneously since the energy gap between the upper state and the next nearest energy state is usually several times greater than the maximum energy vibrational quantum. The probability of deactivation is inversely proportional to the number of the vibrational quanta that must be excited; therefore, the highest frequency vibrations, usually the O−H stretches, play an important role in the energy transfer process.

Table 1. Emission Lifetimes[a]

		lifetime ($\mu\Delta$)	
sample	temp (K)	shortest component	longest component
xerogel	300	0.3	3.2
xerogel	77	0.5	2.3
oven-dried xerogel	300	0.6	2.0
NDP crystal	300	0.22	1.7
NDP crystal	77	0.38	2.1
oven dried NDP cryst	300	0.4	4.3
NDP soln (H_2O)	300	0.2	
NDP soln (D_2O)	300	1.0	
NLDP cryst	300	0.4	3.4
oven dried NLDP cryst	300	0.5	1.9

[a] For multiexponential decays, the decay constants are characterized by the 1/e intensity decrements. The sample to sample variation is less than ±10%.

It is generally believed that only O−H oscillators in the first coordination sphere of the metal significantly affect the luminescence decay mechanism.[17] There are no water molecules directly coordinated to the central neodymium ion in the crystal, although some of the waters of hydration present in the unit cell of the crystal are hydrogen bonded to the oxygen atoms of the coordinated carboxylate groups.

In order to examine the effect of the high O−H frequency mode, decay lifetime measurements of both H_2O and D_2O solutions were examined. As shown in Table 1, the O−D frequency modes are much less efficient in effecting the deexcitation process. The presence of the O−H groups does indeed lead to a quenching of the luminescence of the Nd^{3+} ion. Therefore, the ligand does not provide full protection of the Nd^{3+} ion even though all solid samples emit.

Summary

The organic ligand (2,6-pyridine dicarboxylic acid) partially protects Nd^{3+} ion from the immediate local surroundings in the sol−gel matrix and reduces radiationless deactivation of the excited state. By comparing NDP and NLDP crystals, we conclude that concentration quenching is not very important in this system. Water quenching, however, is more significant as shown by the differences between the lifetime of the neodymium in H_2O and D_2O solutions. The ligand does not fully protect the neodymium ion from OH deactivation even though room temperature emission is observed from the gel.

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