A HIGHGAIN ROOMTEMPERATURE LIQUID LASER: TRIVALENT NEODYMIUM IN SELENIUM OXYCHLORIDE

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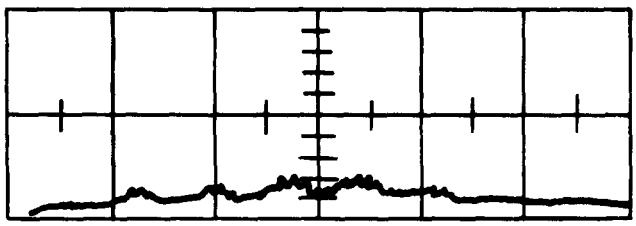

Fig. 3. Power output from the Stokes resonator in the absence of the modulator. The time scale is 10 nsec/div; time increases to the right.

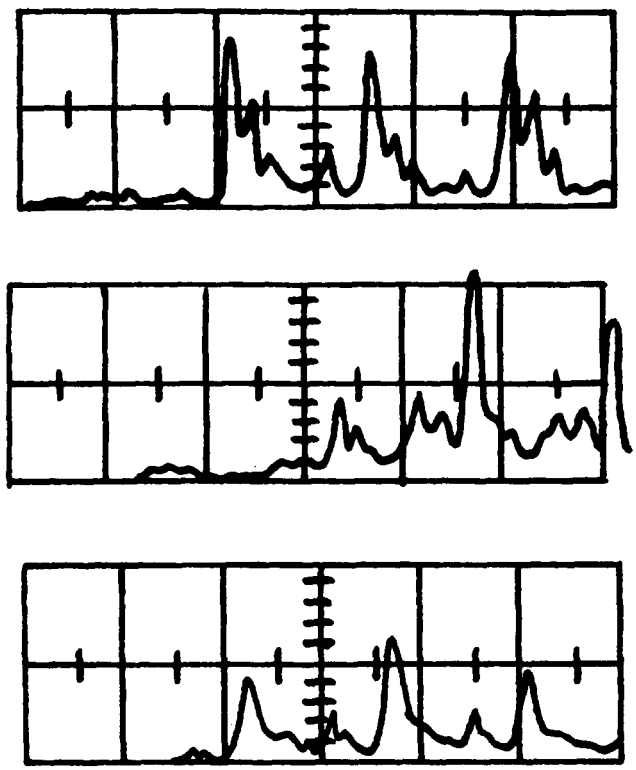

Fig. 4. Power output from the Stokes resonator with the modulator on. The time scale is 5 nsec/div; time increases to the right.

Both from this figure and from interferometric studies, we conclude that most of the power from the ruby laser is provided by a single axial mode.

Figure 3 is a display of the Stokes light output from the resonator with no modulator present. Time increases to the right and the scale is 10 nsec/div. The periodicity of the ripples appearing in Fig. 3 is every 7 nsec, which corresponds to the period of the beat frequency between adjacent axial modes of the Stokes resonator. Thus, although the ruby laser output is in a single axial mode, the Stokes light is distributed among many modes. The beat frequency associated with the ruby resonator is 4.25 nsec, so there is no doubt that the periodicity observed in Fig. 3 results from the Stokes interferometer.

Figure 4 shows several traces of the output from the Stokes resonator with the modulation on and a time scale of 5 nsec/div. The time interval between the peaks of the output power is still 7 nsec as in Fig. 3, but there is a significant narrowing of the light pulses. This narrowing is a consequence of the coupling of axial modes resulting from the loss modulation. From the half-power time duration of the spikes, which is about 1 nsec, it is estimated that there are approximately seven phase-coupled modes.

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A HIGH-GAIN ROOM-TEMPERATURE LIQUID LASER: TRIVALENT NEODYMIUM IN SELENIUM OXYCHLORIDE

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(rm temp; 10560 Å; solution preparation; prevention of radiationless transition; inorganic liquid; E)

Since the first suggestion of optical masers, excellent solid and gaseous laser materials have been developed. However, the only liquids in which laser action has been reported are europium dike-

tonates in organic solutions. The performance of these liquids is limited by the absorbance of the chelating species; their thresholds are relatively high and their energy output comparatively low.[1] Here and in the following Letter[2] we report an inorganic liquid laser that does not have the limitations of the europium chelates and that matches in threshold and output the best known solid-state laser materials, such as neodymium-doped crystals or ruby.

Trivalent neodymium, an ion widely used in crystals[3] and glasses,[4] undergoes rapid radiationless relaxation in most liquid solutions. This relaxation is due to high-energy vibrations of bonds involving light atoms, particularly hydrogen, and is analogous to the vibrational quenching phenomena observed in organic molecules[5,6] and inorganic ions.[7-9] This has been domonstrated by the enhancement of the luminescence of neodymium in an aqueous solution on substituting the hydrogen by deuterium.[10]

Our solution to the problem of radiationless relaxation in excited neodymium ions in liquids is based on the work of Hutchinson and Magnum[5] and Wright, Robinson and Frosch.[6] The applicability of their results to rare-earth ions has been suggested by the work of Kropp and Windsor[7] and Freeman, Lawson and Crosby.[9] Radiationless relaxations were prevented by choosing liquid systems which had no atoms lighter than oxygen and thus no vibrations of sufficient energy to accept, even upon undergoing transitions to reasonably high vibrational states, the energy corresponding to the gap between the excited and the ground multiplets of neodymium.[11,12] The smallest possible gap between the $^4F_{3/2}$ and the $^4I_{15/2}$ levels is of 5500 cm^{-1}, while the highest vibration of the chosen solvent, selenium oxychloride, is of 955 cm^{-1} (ref. 15). Selenium oxychloride has a uniquely high dielectric constant of 46.2 at 20°C (ref. 15) and dissolves ionic compounds.[14] Neodymium oxide dissolves in this solvent to a limited extent yielding a solution with an infrared emission spectrum characteristic of neodymium. The solubility of "anhydrous" neodymium chloride is also limited, presumably because selenium oxychloride undergoes dissociation yielding chloride anion. To dissolve substantial amounts of rare-earth oxides or chlorides the solutions were acidified with aprotic acids. For example, tin tetrachloride and antimony pentachloride react with the solvent to form the powerful acids $(SeOCl^+)_2\ SnCl_6^{2-}$ and $SeOCl^+\ SbCl_6^-$. The reactions which introduce the rare-earth ions into the solutions are

$$NdCl_3 + 3SeOCl^+ \rightarrow Nd^{3+} + 3SeOCl_2$$

$$Nd_2O_3 + 6SeOCl^+ + 3SeOCl_2 \rightarrow 2Nd^{3+} + 3SeOCl_2 + 3SeO_2.$$

The absorption and the emission spectra of the solvated neodymium ion are given in Figs. 1 and 2

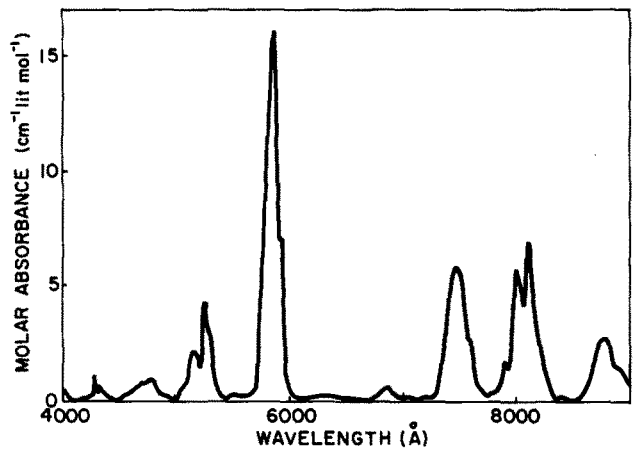

Fig. 1. Absorption spectrum of Nd^{3+} in $SnCl_4$-$SeOCl_2$.

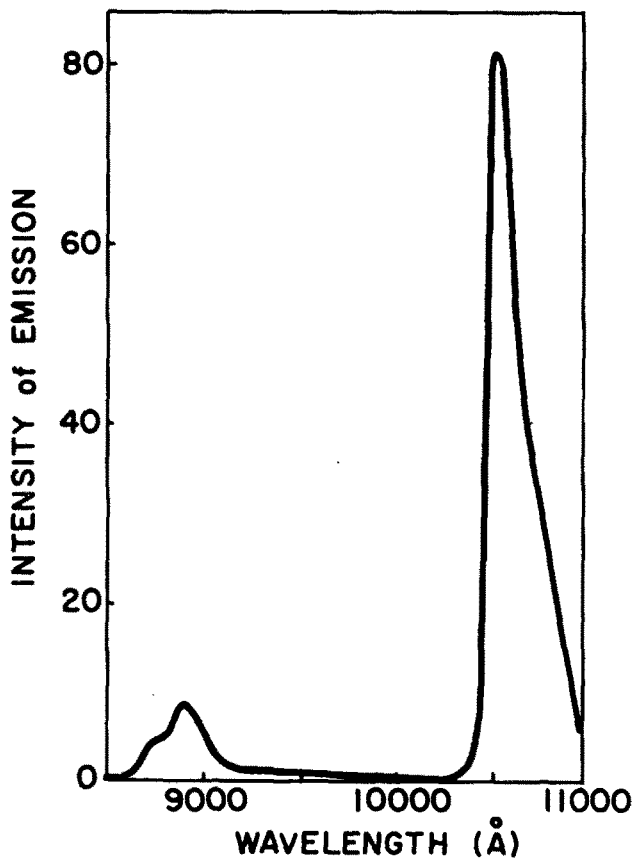

Fig. 2. Emission spectrum of Nd^{3+} in $SnCl_4$-$SeOCl_2$.

respectively. The maxima in the emission spectra occur at 8905 Å and at 10,560 Å,[16] corresponding to the $^4F_{3/2} \rightarrow {}^4I_{9/2}$ and $^4F_{3/2} \rightarrow {}^4I_{11/2}$ transitions. The room-temperature width of the 10,560-Å band, in which the laser action takes place, is 160 Å. While this width is relatively large, it is compensated by a corresponding broadening of the absorption bands. Because of this broadening, the coversion of blackbody radiation to fluorescent emission is more efficient, and the net effect is that the laser solution has a peak emittance which exceeds by a factor of 1.2 that of our best CW, neodymium-doped, sodium-compensated calcium tungstate laser crystal under identical excitation conditions. This suggests a high quantum efficiency of fluorescence in the liquid.

The characteristics of the neodymium ion in solution approximate those of the ion in crystalline lattices rather than in glasses as indicated by the rigorously exponential decay (110 μsec) and by the laser characteristics.[2]

The laser solutions were prepared by dissolving neodymium oxide in selenium oxychloride containing 500 g/liter tin tetrachloride and bringing the solution to a boil, allowing a small amount of the liquid to distill off. The preparation and handling require safety precautions (hood, gloves) as the solvent is highly corrosive and toxic.

Stimulated emission has been observed over the $0.02N$–$75N$ neodymium concentration range. The upper limit is due to the increase in the viscosity with the neodymium concentration: Above $0.75N$ the solutions are excessively viscous for handling at room temperature. The properties of the Nd^{+3}:$SeOCl_2$ laser which are reported in the following Letter,[2] indicate that the gain of this material is unusually high.

Selenium oxychloride is transparent at least up to 3 μ, with the highest reported vibration at 955 cm^{-1} (1.05 μ).[15] Thus, the present study opens the way for the investigation of the fluorescence and laser characteristics of solutions of other visible- and infrared-emitting ions and their cross-sensitized systems.

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CHARACTERISTICS OF THE Nd^{+3}:$SeOCl_2$ LIQUID LASER

(rm temp; inorganic liquid; output to 10 J; linewidth <1 Å; E)

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This Letter describes the performance characteristics of a new room-temperature liquid laser utilizing the Nd^{+3}:$SeOCl_2$ system described in the previous Letter.[1]

The laser cells, made of quartz tubing with optically flat windows fused at each end, were filled with a $0.5N$ solution of Nd^{+3}:$SeOCl_2$ and then sealed off. Silver or dielectric mirrors were deposited on the external surfaces of the windows. Cells with bore diameters of 4 and 6 mm and of lengths ranging between 2 and 6 in. were used. The experiments were performed with the arrangement shown on