Liquid Lasers. Preparative Techniques for Selenium Oxychloride Based Laser Solutions

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Abstract: Liquid laser solutions based on neodymium(III) selenium oxychloride are prepared by dissolving neodymium oxide in mixtures of selenium oxychloride with tin tetrachloride or with antimony pentachloride. Hydrogen-containing compounds which quench the Nd^{3+} fluorescence are removed with a solvent component at elevated temperatures. Deeply colored reduction products of selenium oxychloride formed at these temperatures are oxidized to colorless noninterfering products with potassium chlorate which is found to be a powerful oxidant in the aprotic acid solutions.

In a previous paper of this series it was shown that selenium oxychloride meets a set of criteria that define a desirable solvent for Nd^{3+}-based inorganic liquid lasers.[1] Neodymium oxide, halides, and selenite are bases in this solvent. Their solubilities are enhanced by acidifying the solvent. An analysis of the requirements from the acids suggested that tin tetrachloride and antimony pentachloride are particularly suitable for these liquid laser systems.[1] This paper describes the problems encountered in making the laser liquids and the current solutions to these problems. It outlines detailed procedures for the preparation of laser-active liquids.

Experimental Section

Materials. Neodymium Oxide. Neodymium oxide (99.999%) was purchased from the Rare Earth Division of American Potash and Chemical Corporation, West Chicago, Ill. (Catalog No. 629.92). The oxide absorbs water and carbon dioxide from the atmosphere and must be fired (at 950°) to constant weight prior to use.

Selenium Oxychloride. Technical grade selenium oxychloride is available from J. T. Baker Chemical Co., Phillipsburg, N. J. The material, which greatly varies in purity from batch to batch, is contaminated with hydrogen-containing compounds (such as the HCl adduct of selenium oxychloride), with selenium dioxide and with selenium monochloride (Se_2Cl_2), as well as with inert light-scattering particles. The solvent may be purified by double distillation at reduced pressure. Since the material is toxic, all operations must be carried out in a hood. The operator should wear rubber gloves and safety glasses. The material is also highly corrosive, and therefore all-glass apparatus must be used. Cold glass joints may be lubricated with Kel-F grease to obtain a tight seal, but Teflon sleeves must be used for joints which become hot. Also if Kel-F contamination is to be avoided in the preparation of the laser solution, Teflon sleeves are preferred.

Oil rather than water pumps should be used in the vacuum distillation, and these pumps should be protected by two consecutive traps at liquid nitrogen temperature. Also, rather than using a capillary gas inlet to prevent bumping, the selenium oxychloride should be stirred during the distillation with a Teflon-coated magnetic stirring bar.

Distillation at higher temperatures ($\sim$100°) leads to more effective removal of the hydrogen-containing compounds (as hydrogen chloride). However, at higher temperatures selenium oxychloride starts to decompose to chlorine, selenium dioxide, and selenium monochloride, which is deep brown. For this reason a first distillation at approximately 90° is recommended to remove the bulk of the hydrogen-containing compounds, followed by a second distillation at 40° in which the deeply colored reduction product is separated. The brown selenium monochloride boils at a lower temperature than selenium oxychloride, while colorless selenium dioxide sublimes substantially higher. The distilled selenium oxychloride is a light, straw-colored liquid. The solvent should be stored in all-glass flasks with Teflon sleeves on the joints in a desiccator with magnesium perchlorate ("Anhydrone") or should, preferably, be kept in a drybox under a dry nitrogen atmosphere.

Tin Tetrachloride. Reagent grade tin tetrachloride ("stannic chloride") is available from J. T. Baker Chemical Co., Phillipsburg, N. J. The material typically has a stated purity of 99.5%. The most troublesome impurities in the liquid are hydrates and adducts between the tetrachloride and hydrochloric acid. These decompose in distillation to recombine in the distillate. For this reason, purification by distillation or fractionation is difficult to achieve.

One way to reduce the concentration of the hydrogen-containing compounds is to pass the nonpolar tin tetrachloride through a column of basic alumina (Grade I, Woelm). The polar adducts are preferentially absorbed.

Antimony Pentachloride. Reagent grade antimony pentachloride is available from J. T. Baker Chemical Co., Phillipsburg, N. J. The purity of the material is generally stated to be 100.0%. The compound can be purified by distillation; however, purification is generally not required.

Potassium Chlorate. Analytical grade potassium chlorate is available from most chemical houses. The material is used without further purification.

Apparatus. The laser solutions are prepared in a standard all-glass distillation apparatus, with vacuum-tight Teflon sleeves in all joints. A Teflon-coated magnetic stirring bar is used in the reaction flask. The receiving end of the distillation apparatus is connected through a three-way valve to the pump (*via* two traps cooled with liquid nitrogen) and to the atmosphere (through a drying tube filled with anhydrous magnesium perchlorate).

Preparation of Laser Solutions. Acid Solutions with Tin Tetrachloride. The following is a typical procedure for preparation of a 0.3 *N* neodymium solution. To 1.51 g (0.045 mole) of neodymium oxide, 7 ml of tin tetrachloride is added. The mixture is stirred to form a suspension. To the suspension, 23 ml of selenium oxychloride is added (in a single batch). An exothermic reaction (formation of the selenium oxychloride–tin tetrachloride adduct) takes place. The mixture is heated with stirring (at 80–100°) until all the neodymium oxide dissolves. When the dissolution is complete, 3 ml of the solvent is distilled off at atmospheric pressure. The boiling range of the distilled liquid is 100–114°. During the distillation the neodymium solution turns brown. As soon as the distillation is completed and while the stirred mixture is hot (90–100°), a crystal of potassium chlorate is added. The crystal decomposes in a rapid reaction, and the solution becomes lighter in color. Crystals are added until a color change is no longer observed. The solution is allowed to cool room temperature, the valve to the atmosphere is closed, and solution is pumped on. Pumping is continued until the bubbling stops (20 min). The resulting solution has the blue-violet color typical of Nd^{3+}.

Neutral Solutions with Tin Tetrachloride. A 0.3 *N* Nd^{3+} solution is prepared as previously described, using 30 ml of selenium oxychloride and 5 ml of tin tetrachloride. Rather than distilling out a controlled amount of the solution at atmospheric pressure, the distillation is continued until the boiling point reaches 125°. Potassium chlorate is added as previously. After the pressure is reduced, the distillation is continued until 2 ml of selenium oxychloride distils over. The resulting solution has the blue-violet color typical of Nd^{3+}.

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[1] A. Heller, *J. Mol. Spectry.*, in press.

Acid Solutions with Antimony Pentachloride. A 0.3 *N* Nd^{3+} solution is prepared as follows: 1.51 g (0.0045 mole) of neodymium oxide is suspended in 27 ml of selenium oxychloride, 6 ml of antimony pentachloride is added slowly to the stirred suspension, and the mixture is heated at 80–100° until all the neodymium oxide dissolves. The pressure in the system is then partially reduced to obtain a boiling point of 80–90° for the liquid; 3 ml of selenium oxychloride is allowed to distil over at this temperature. A crystal of potassium chlorate is added to the brown solution which is kept at 80–90°. The crystal decomposes and the solution becomes lighter in color. The procedure is repeated until no further change is observed in the color of the solution. The stirred solution is then cooled to room temperature and subjected to the full vacuum obtainable from the oil pump until the bubbling stops (approximately 20 min). The solution has the blue-violet color typical of Nd^{3+}, but may have an added yellowish tint so that thick samples will appear to be brown-violet.

Storage and Handling. The prepared laser solutions may be stored in sealed ampoules. Sealing should be done while the ampoule is protected from atmospheric humidity by an attached drying tube. The solution may also be stored in all-glass stoppered flasks with Teflon sleeves in a desiccator (over magnesium perchlorate) or in a drybox (under a dry inert gas such as nitrogen).

Handling of the laser solutions should be limited to a drybox.

Results and Discussion

The most undesirable impurities in the laser solutions of the present type are hydrogen-containing compounds, the removal of which is essential to the performance of lasers of the present type.[1] To eliminate these compounds, one may start with extremely pure solvents or one may separate them in the preparative procedure. Since the extreme purification processes required are tedious, the present study approaches the problem by the second path. Traces of hydrogen-containing compounds are removed along with part of the solvent by distillation.

The solvent component distilled in preparations involving tin tetrachloride is dominantly the tetrachloride, as seen from the boiling point of the mixture. This is possible because the complex between tin tetrachloride and selenium oxychloride is not extremely strong or, in other words, tin tetrachloride still has a substantial pressure above its mixtures with selenium oxychloride. Hydrogen-containing compounds are presumably removed as the tin tetrachloride adduct with water or one of the hydrogen chloride adducts of tin tetrachloride. For this reason, colorless crystals are observed in the distillate.

In the preparation involving antimony pentachloride, the dominant solvent component in the distillate is selenium oxychloride.

Since selenium oxychloride forms stable adducts with hydrogen chloride, the distillation must be carried out at a temperature sufficiently high to assure the decomposition of the adducts. Antimony pentachloride presumably forms a stronger compound with selenium oxychloride, as suggested by the fact that the distillate from the mixtures is mainly composed of selenium oxychloride.

The acid formation, the Nd_2O_3 dissolution, and the hydrogen-eliminating steps can be described by the following equations.

$$SnCl_4 + 2SeOCl_2 \rightleftarrows SnCl_6{}^{2-} + 2SeOCl^+ \text{(solv)}$$

$$SbCl_5 + SeOCl_2 \longrightarrow SbCl_6{}^- + SeOCl^+ \text{(solv)}$$

$$6SeOCl^+ \text{(solv)} + Nd_2O_3 \longrightarrow 2Nd^{3+} \text{(solv)} + 3SeOCl_2 + 3SeO_2$$

$$SnCl_4 \cdot nHCl \xrightarrow{110^\circ} SnCl_4 + HCl$$

$$SnCl_4 \cdot nH_2O \xrightarrow{110^\circ} SnCl_4 + H_2O$$

$$SeOCl_2 \cdot HCl \xrightarrow{90^\circ} SeOCl_2 + HCl$$

$$SeO_2 \cdot 2HCl \xrightarrow{90^\circ} SeOCl_2 + H_2O$$

The elevated temperatures required for the decomposition of the complexes involve also a loss of chlorine from selenium oxychloride. The resulting mixture is deep brown because of the presence of reduction products such as Se_2Cl_2 (selenium monochloride) or selenium dissolved.

$$2SeOCl_2 \rightleftarrows SeO_2 + SeCl_4$$

$$2SeCl_4 \longrightarrow Se_2Cl_2 + 3Cl_2$$

$$Se_2Cl_2 \longrightarrow 2Se + Cl_2$$

The brown compounds, which interfere with the optical pumping of the laser solutions, are eliminated by oxidation with acid potassium chlorate

$$ClO_3{}^- + SeOCl^+ \longrightarrow SeOCl_2 + 3O$$

$$ClO_3 + SeOCl^+ \longrightarrow SeO_2 + ClO_2 + Cl$$

or

$$Se_2Cl_2 + 2O \longrightarrow 2SeOCl_2$$

$$Se_2Cl_2 + ClO_2 \longrightarrow 2SeOCl_2 + Cl$$

$$Se_2Cl_2 + 4Cl \longrightarrow 2SeCl_4$$

Selenium may be oxidized in a similar fashion. The selenium dioxide, tetrachloride, or oxychloride that is formed does not absorb in the spectral region used for optical pumping.

The solutions obtained after the chlorate treatment contain yellow dissolved gases (chlorine or chlorine dioxide). Removal of these under vacuum results in solutions which have only the typical absorption bands of Nd^{3+} down to 4200 Å in the tin tetrachloride containing solutions, and down to 4500 Å in the solutions containing antimony pentachloride.

The laser solutions prepared by the present techniques have typical thresholds of 6–10 joules. In better cavities thresholds as low as 2.0 joules have, however, been obtained. Their emittance in the $^4F_{3/2} \rightarrow {}^4I_{11/2}$ peak (at 10,560–10,580 Å) equals or exceeds the emittance of better neodymium-doped sodium-compensated calcium tungstate laser crystals. The exponential decay times of the fluorescence for the solutions made with tin tetrachloride reach 230 μsec, while the decay times of the antimony pentachloride containing solutions reach 260 μsec. Neither of the values is believed to be the true radiative lifetime, indicating further room for improvement.

As pointed out in a previous paper,[1] the "neutral" solutions are less viscous than the acid solutions. Because of the lower viscosity, which is of advantage in circulating liquid lasers, diffusion-assisted quenching processes are also enhanced. For this reason, or because of the enhanced self-quenching due to chloride bridges between the Nd^{3+} ions,[1] the lifetimes obtained in the neutral solutions do not exceed 180 μsec. In addition to being less viscous, the neutral solutions are less corrosive than the acid ones.

To conclude, we wish to point out that the methods considered in this paper are only those based on the chemical elimination of interfering impurities, rather than on their complete exclusion from the starting materials. Techniques for preparing starting materials of high purity are being developed at the present in the author's laboratory by Charles Brecher and Kenneth French.

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