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LAWRENCE LIVERMORE LABORATORY

University of California/Livermore, California

PROSPECTS FOR GASEOUS RARE EARTH LASERS

W. F. Krupke

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The advantages and disadvantages of Nd:glass as a gain medium for multikilojoule, subnanosecond lasers have been placed in sharp relief with the development of large lasers for fusion research. Most notable of Nd:glass liabilities are: 1) small ratio of optical damage fluence (1 j/cm^2 ; 100 psec) to saturation fluence (5 j/cm^2), necessitating operation in the small signal gain region. Thus, although 500 j/liter can be stored in Nd:glass, one typically can extract only about 10 j/liter in 100 psec pulses; 2) requirement for large surface area transverse to optical beam, and 3) high unit volume cost. On the other hand, the Nd(3+) ion provides an energy level structure conducive to production of a four level population inversion at room temperature. Nd:glass provides large spectral bandwidth ($\approx 200 \text{ cm}^{-1}$) and coherent radiation at the relatively short wavelength of 1.06 microns. It is an interesting (and potentially profitable) exercise to explore alternative Nd(3+) host media which do not suffer from the liabilities of Nd:glass while exhibiting other properties necessary for efficient amplification of subnanosecond pulses. Other solid state hosts have been most seriously considered in the past (crystals, alternative glass compositions, ceramics, etc.). To the extent that the nonlinear index of refraction of a solid scales as some high power of the linear index, solid state hosts will always be limited to fluences of about one j/cm^2 at 100 psec. Nd:liquid lasers have received only limited attention. The excited $4F(3/2)$ upper laser level of Nd(3+) ions undergo rapid radiationless relaxation in most liquids. This process is due to high energy vibrations of bonds involving light atoms, particularly hydrogen.

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Successful Nd liquid lasers have utilized liquid systems which have no atoms lighter than oxygen (SeOCl_2 , POCl_3 , etc.). Solubility of neodymium in the oxychlorides can be greatly increased with inclusion of metal chlorides acting as Lewis acids. It will be of some importance to us later to note that aluminum chloride (AlCl_3) and zirconium chloride (ZrCl_4) are commonly used for this purpose. Nd:liquid lasers have not found wide utility for high energy, short pulse applications because of the onset of stimulated Raman processes at relatively low fluences.

The general features and requirements of a gaseous host for Nd(3+) ions will be treated here. It should be remarked at the outset that the assessment of a gaseous Nd(3+) laser applies generally to most of the lanthanide and actinide ions because of their similar atomic structures. Perhaps the most attractive feature of a gaseous host is its potential for propagating energy fluences an order of magnitude greater than that of glass, e.g. $\approx 10 \text{ j/cm}^2$ at 100 psec. Of course, gas media generally are available at low unit-volume cost. Thus, gases offer the potential for overcoming the major disadvantages of Nd:glass. It remains to identify rare-earth-ion-bearing vapors manifesting appropriate radiative and nonradiative transition probabilities as well as acceptable physiochemical properties.

The electronic configurations of the lanthanide rare earth atoms consist of the xenon core ($1s^2 2s^2 2p^6 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6$) plus $5d^1 6s^2$ valance electrons and a number of 4f electrons. The 4f electrons

are spatially buried within the closed $5s^2 6p^6$ electron shells of the core and are well shielded from the external environment. The three $5d^1 5s^2$ electrons are chemically active and permit formation of simple molecules containing triply ionized rare earth ions, $RE(3+)$, such as $(RE)X_3$, where $X = Cl, F, I, Br$ or a singly charged radical. More complex molecular species may also be of interest for a gas phase RE laser. In molecules of the form $(RE)X_3$, the $RE(3+)$ ion is necessarily coordinated in a position lacking inversion symmetry. The ligand fields of the cations will thus induce electric dipole transitions among the electronic levels of the ground $4f^n$ electronic configurations. In solid state hosts successfully used for lasers, the RE ions are also situated in lattice sites lacking inversion symmetry, suggesting that $(RE)X_3$ molecules might indeed be suitable for gaseous RE lasers.

To assess RE lasers for short pulse laser action a number of rate constants will have to be known. These can be identified through reference to Figure 1 which shows the energy levels of the $Nd(3+)$ ion in a molecule (schematic). Because of 4f shielding, the centers-of-gravity of the electronic energy levels will not be shifted significantly from those of the free ion. These levels are labeled in the conventional Russell-Saunders notation $|[SL]J\rangle$ and are also designated by level number, e. Each electronic J-manifold will be split into a number of Stark components (as in solids) by the ligand fields of the other atoms in the molecule (not shown). Energy may also be taken up by the

Figure 1. Energy level structure (schematic) of Nd(3+) Ion in a molecular vapor.

molecule in the form of vibrations. Vibrational energy levels, associated with a single vibrational mode of the molecule, are designated by the vibrational quantum number v , for each electronic level. The molecule may also rotate, providing additional energy level structure as shown for the $v = 1$ vibrational level of the ground electronic state. As in solids, we anticipate that electronic-vibrational interaction will be very small and that optical spectra of RE vapors will be due to purely electronic transitions. However, from the point of view of using these systems for lasers, and in particular for short pulse lasers, it is important to know the characteristic rotational and vibrational equilibration times since energy will be stored in these degrees of freedom. For Nd(3+) lasers, pumping of the $4F(3/2)$ upper laser level generally occurs via the transitions from the $4I(9/2)$ ground level to the levels lying above $11,000 \text{ cm}^{-1}$. In solids these manifolds relax rapidly via excitation of lattice vibrations to the $4F(3/2)$ level. Because of the relatively large energy gap between the $4F(3/2)$ manifold and the next lower lying manifold, $4I(15/2)$, the $4F(3/2)$ manifold generally decays radiatively. In a RE vapor laser, we require relaxation of the pumped transitions to the $4F(3/2)$ manifold in a time short compared to the radiative lifetime of the $4F(3/2)$ level. At the same time the $4F(3/2)$ manifold must be stable against nonradiative de-excitation over the same interval. Energy stored in vibrational and rotational modes of excited molecules must also be available to $4F(3/2)$ electronic level in a time short compared to the width of the pulse to be amplified. (We are all familiar with rotational-level uncoupling in CO_2 lasers in the nsec range). A necessary, although not sufficient condition to achieve

such a dynamic response is that the fundamental vibrational modes of the molecule are relatively low in energy (say $\sim 300 \text{ cm}^{-1}$, as shown in Figure 1). Vibrational relaxation of the $4F(3/2)$ manifold then requires an unlikely excitation of high order overtones while relaxation of the pump levels requires more probable excitation of relatively low order overtones.

A search of the literature was conducted and three interesting classes of vapors were identified:

- RE - trihalides
- RE - aluminum - chloride complexes
- RE - chealates

The RE-trihalides are the simplest of these vapors. Gruen and DeKock [1] have determined the pressure-temperature functions for NdBr_3 and NdI_3 vapors as well as absorption intensities in their optical spectra. Their studies were directed toward understanding the mechanisms responsible for so-called "hypersensitive" transitions ($\Delta J = 2$ selection rule) noted in RE(3+) solid state and liquid spectra [2]. They report extremely intense hypersensitive 5800 Å transitions in NdBr_3 and NdI_3 along with "normal" transition intensities in the other spectral bands. The vapor pressure vs temperature expressions for these vapors are [1]

$$\begin{array}{l} \text{NdBr}_3 \\ -2.303 \text{ RT } \log P = 72025 + 32.24 \text{ T } \log T - 144.77\text{T} \end{array} \quad (1)$$

$$\begin{array}{l} \text{NdI}_3 \\ -2.303 \text{ RT } \log P = 70884 + 32.24\text{T } \log T - 145.69\text{T} \end{array} \quad (2)$$

where P is the vapor pressure in atm and T is the temperature (°K).

Figure 2 shows plots of NdBr_3 and NdI_3 number densities as a function of temperature. Temperatures of about 1200 °K (900 °C) are required to achieve one torr ($\approx 10^{16}$ molecules/cc). If one could excite half the vapor molecules to the $4F(3/2)$ upper J-manifold of $\text{Nd}(3+)$, the available stored energy density for laser action at 1.06 microns follows immediately (Figure 2). Temperatures of 1400 °K are required to attain 10 joules/liter, a storage comparable to present CO_2 short pulse lasers. As the temperature is raised to increase the gas number density, the thermal population in the lower laser manifold, $4I(11/2)$, increases exponentially. This effect has been included in calculating the stored energy density curves of Figure 2.

Let us ignore for the moment, the problems posed by the high temperatures and chemical reactivity of the vapors, and inquire about the spectral properties for laser action. It turns out that the Judd [3]-Ofelt [4] model of induced electric dipole transitions in the $4f^n$ ground configurations of the RE (3+) ions, recently applied [8] to Nd laser glasses, is applicable to the gas phase spectra as well. The absorption intensities of Pr, Nd, Er, and Tm-bromides and iodides have been measured by Gruen, DeKoch, and McBeth [5] and by Gruen [6]. The absorption intensities have been characterized in terms of three phenomenological intensity parameters, Ω_t , which can be used to calculate the radiative $4F(3/2) \rightarrow 4I(\bar{J})$ transition probabilities, the $4F(3/2)$ radiative lifetime, and the cross-section for stimulated emission near

Figure 2. Number density and stored energy density in the $4F(3/2)$ J-manifold of NdI_3 and NdBr_3 vapors as functions of temperature.

1.06 microns. (The τ_t parameters employed by Gruen, et al. [5] are simply related to the Ω_t parameters used in solid state work [7,8] by $\Omega_t = \frac{3h}{8\pi^2 mc} \tau_t = 9.03 \times 10^{-12} \tau_t$.) Figure 3 shows the measured absorption spectra of NdBr_3 and NdI_3 [5]. The visible spectral region is dominated by the intense hyper-sensitive 5850 Å band ($4I(9/2) \rightarrow 4G(5/2)$; $\Delta J = 2$ transition). These bands are about two orders of magnitude stronger per Nd atom than in low site symmetry solids. Since the number density of Nd ions in a gaseous laser will be at least an order of magnitude less than typical densities in solids ($\rho \sim 10^{20}/\text{cc}$), these anomalously intense bands will be pivotal in the design of gas RE lasers. Table I lists the Ω_t intensity parameters for several Nd bearing vapors [5] and for several Nd doped solids utilized as lasers. Table II gives the calculated transition linestrengths for all absorption transitions of NdI_3 vapor. We note immediately, that all the Ω_2 parameters of the vapors are considerably greater than those of the solids, reflecting for the anomalously strong 5850 Å bands in the vapor phase [5]. Using the Ω_t values for NdI_3 (similar results would be obtained for NdBr_3), we can calculate the radiative properties of $4F(3/2) \rightarrow 4I(J)$ transitions which will be important for laser action. Table III gives the transition linestrengths, transition probabilities, and branching ratios for the $4F(3/2)$ J-manifold. For purposes of comparison, analogous quantities for ED-2 laser glass are listed in Table IV. First we note that the radiative transition linestrengths for NdI_3 are about twice as large as those of ED-2. The transition probabilities for NdI_3 are, however, somewhat less than those of ED-2 [The calculated radiative lifetimes are 645 μsec (NdI_3) and 372 μsec (ED-2).] This difference occurs because of

Figure 3. Spectral Absorbance of NdI_3 and NdBr_3 vapors
[Taken from ref. 5].

TABLE I
Judd-Ofelt Intensity Parameters
for Several Nd Vapors and Solids

<u>Form</u>	<u>Host</u>	<u>*Ω_2</u>	<u>*Ω_4</u>	<u>*Ω_6</u>	<u>Reference</u>
vapor	NdBr ₃	1.8E-18	9.0E-20	9.0E-20	5
vapor	NdI ₃	2.7E-18	9.0E-20	9.0E-20	5
vapor	Nd(thd) ₃	~6.E-19	3.0E-20	3.0E-20	5
vapor	Nd(A ₂ C ₂) ₃	1.8E-19	4.8E-20	3.9E-20	10
glass	Nd:ED-2	3.3E-20	4.7E-20	5.2E-20	7
crystal	Nd:YAG	0.2E-20	2.7E-20	5.0E-20	8

*Units of cm²

TABLE III
Radiative Properties of 4F(3/2)
J-Manifold in NdI₃

<u>Terminal Level</u>	<u>$\bar{\lambda}(\mu)$</u>	<u>$S_f(10^{-20} \text{ cm}^2)$</u>	<u>$A(\text{sec}^{-1})$</u>	<u>β_c</u>
⁴ I(9/2)	0.88	2.60	664	.428
⁴ I(11/2)	1.06	4.94	740	.477
⁴ I(13/2)	1.35	2.00	140	.090
⁴ I(15/2)	1.88	0.25	7	.005
			<u>1551</u>	<u>1.000</u>

ELECTRIC DIPOLE TRANSITION PROBABILITIES

ND : 13

INTENSITY PARAMETERS 2.70000E-18 9.00000E-20 9.00000E-20

REFRACTIVE INDEX RANGE 1.0000 1.0000

INITIAL STATE ENERGY= .0 (CM-1) 4I 4.5

FINAL STATE ENERGY (CM-1)	WAVE LENGTH MICRON	SL	J	SQUARED U(2)	MATRIX U(4)	ELEMENTS U(6)	LINE STRENGTH (CM2)	TRANSITION RATE (SEC-1)
1869.00	5.3505	4I	5.5	.0194	.1074	1.1652	1.6703E-19	
3854.00	2.5947	4I	6.5	.0001	.0136	.4556	4.2406E-20	
5916.00	1.6903	4I	7.5	.0	.0001	.0452	4.0779E-21	
11260.00	.8881	4F	1.5	.0	.2296	.0563	2.5739E-20	
12300.00	.8130	4F	2.5	.0008	.2355	.3977	5.9240E-20	
12518.00	.7988	2H2	4.5	.0091	.0076	.1171	3.5872E-20	
13285.00	.7527	4F	3.5	.0010	.0424	.4245	4.4627E-20	
13374.00	.7477	4S	1.5	.0	.0024	.2337	2.1253E-20	
14578.00	.6860	4F	4.5	.0010	.0094	.0398	7.0021E-21	
15814.00	.6324	2H2	5.5	.0001	.0026	.0103	1.3175E-21	
16961.00	.5896	4G	2.5	.8970	.4094	.0353	2.4620E-18	
17088.00	.5852	4G	3.5	.0740	.1863	.0310	2.1889E-19	
18842.00	.5307	2K	6.5	.0068	.0002	.0312	2.1202E-20	
18853.00	.5304	4G	3.5	.0566	.1612	.0557	1.7239E-19	
19295.00	.5183	4G	4.5	.0046	.0505	.0405	2.1505E-20	
20821.00	.4803	2K	7.5	.0	.0053	.0144	1.7721E-21	
20887.00	.4788	2G1	4.5	.0010	.0153	.0141	5.4067E-21	
21058.00	.4749	2D1	1.5	.0	.0196	.0092	1.7864E-21	
21297.00	.4695	4G	5.5	.0000	.0054	.0081	1.2270E-21	
22958.00	.4356	2P	.5	.0	.0098	.0	3.5806E-21	
23655.00	.4227	2D1	2.5	.0000	.0002	.0070	1.9135E-22	
26017.00	.3844	2P	1.5	.0	.0016	.0008	2.1197E-22	
27806.00	.3596	4D	1.5	.0	.1959	.0170	1.9161E-20	
27983.00	.3574	4D	2.5	.0001	.0570	.0279	7.9075E-21	
28292.00	.3535	2I	5.5	.0049	.0146	.0033	1.4732E-20	
28373.00	.3524	4D	.5	.0	.2554	.0	2.2582E-20	
28391.00	.3461	2L	7.5	.0	.0247	.0006	3.0829E-21	
29664.00	.3371	2I	6.5	.0001	.0013	.0017	6.4285E-22	
30330.00	.3330	4D	3.5	.0000	.0037	.0030	1.0540E-21	
30361.00	.3294	2L	8.5	.0	.0010	.0012	1.9969E-22	
31977.00	.3127	2H1	4.5	.0001	.0005	.0000	1.0430E-21	
33029.00	.3028	2D2	1.5	.0	.0102	.0011	1.0159E-21	
33367.00	.2997	2H1	5.5	.0001	.0001	.0002	3.0079E-22	
34141.00	.2929	2D2	2.5	.0005	.0005	.0030	1.9375E-21	
38998.00	.2564	2F2	2.5	.0028	.0043	.0031	7.9660E-21	
48299.00	.2481	2F2	3.5	.0001	.0005	.0007	2.8858E-22	
49479.00	.2152	2G2	4.5	.0001	.0015	.0001	2.7090E-22	
47355.00	.2112	2G2	3.5	.0005	.0023	.0002	1.4732E-21	
60391.00	.1502	2F1	3.5	.0000	.0002	.0005	9.0847E-23	

Table IV

Radiative Properties of the $4F(3/2)$

J-manifold in Nd:ED-2 Laser Glass [8]

Terminal Level	$\lambda(\mu)$	$S_f(10^{-20} \text{ cm}^2)$	$A(\text{sec}^{-1})$	β_c
4I(9/2)	0.88	1.23	1030	0.380
4I(11/2)	1.06	2.77	1380	0.51
4I(13/2)	1.35	1.10	272	0.10
4I(15/2)	1.88	0.15	<u>12</u>	<u>0.004</u>
			2694	1.00

Table VI

Radiative Properties of the $4F(3/2)$

J-manifold in Nd-Al-Ce Vapor Complex

Terminal Level	$\lambda(\mu)$	$S_f(10^{-20} \text{ cm}^2)$	$A(\text{sec}^{-1})$	β_c
4I(9/2)	0.88	1.32	339	.458
4I(11/2)	1.06	2.25	338	.457
4I(13/2)	1.35	0.82	60	.081
4I(15/2)	1.88	0.11	<u>3</u>	<u>.004</u>
			740	1.000

the greatly different bulk indices of refraction and the local field corrections for the vapor ($n = 1$) and the solid ($n = 1.555$). This is a clear advantage for the vapor, other things being equal, since one has a longer radiative storage time for the same stimulated emission cross-section, σ_p . We can make an estimate of for σ_p for NdI_3 using expression

$$\sigma_p = \frac{\lambda^2}{8\pi c n^2} \frac{A(\text{sec}^{-1})}{\Delta \tilde{\nu} \text{ eff}} \quad (3)$$

where $\Delta \tilde{\nu} \text{ eff}$ is the effective linewidth taking the emission lineshape into account [8]. For the $4F(3/2) \rightarrow 4I(11/2)$ transition at 1.06 microns, we can write

$$\sigma_p [\text{cm}^2] = 1.10 \times 10^{-17} / \Delta \tilde{\nu} \text{ eff } (\text{cm}^{-1}) \quad (4)$$

The spectral fluorescence for NdI_3 (if it is not quenched) has not been recorded. To the extent that absorption linewidths mirror emission linewidths we can estimate σ_p values. Taking $\Delta \tilde{\nu} \text{ eff} \sim 350 \text{ cm}^{-1}$, we calculate $\sigma_p \sim 3.1 \times 10^{-20} \text{ cm}^2$ which is to be compared with $\sigma_p = 2.9 \times 10^{-20} \text{ cm}^2$ for ED-2 [8]. The point of this crude estimate is that NdI_3 (and NdBr_3) exhibit spectral radiative properties very similar to Nd:glass , and are therefore viable candidates for high energy storage lasers.

As to spectral homogeneity or inhomogeneity of the gain line and the quenching rate of the $4F(3/2)$ manifold, only general comments can be offered. First, a simple estimate of the NdI_3 rotational constant, B , gives $B \sim 0.01 \text{ cm}^{-1}$ (compared to $B \sim 0.4 \text{ cm}^{-1}$ in CO_2). This will result in a very dense rotational spectrum and a relatively fast thermalization time (at least gas kinetic). The RE trihalides are known [9] to have very low Debye

temperatures (maximum optical phonon energy $\leq 350 \text{ cm}^{-1}$). Because the I atoms are relatively heavy, we would also expect only vibrational modes of low energy in the gas phase. All of this suggests that electronic-vibrational radiationless relaxation of the $4F(3/2)$ manifold will be improbable (e.g. NdI_3 should fluoresce). Electronic-electronic relaxation via collisions of the type

is nominally a resonance process, but should be moderately ineffective due to 4f electronic shielding and the necessarily low partial pressures of NdI_3 available. At the same time, it is questionable that relaxation of pump levels to the $4F(3/2)$ manifold will be sufficiently rapid in a pure NdI_3 vapor. Clearly one must consider the use of additional gases as selective collision partners. Although a number of these come to mind, the inquiry will not be carried further here. From the preceding commentary, NdI_3 is seen to offer many of the characteristics required for a RE vapor laser. However, the need to operate at temperatures in excess of, say, 1000°K is a formidable restriction, and higher vapor-pressure systems are desirable.

The remarkable physiochemical properties of the rare-earth-metal chloride vapor complexes discovered by Øye and Gruen [10] appear to overcome the high temperature constraint while exhibiting spectral properties comparable to the pure RE trihalides. By providing a vapor of Al_2Cl_6 molecules over solid NdCl_3 , the vapor pressure of Nd-bearing molecules is increased by 7 to 13 orders of magnitude (!!) in the temperature range from 800 to 600°K . The studies of Øye and Gruen [10] suggest that

the Nd ions appear as monomers in the vapor with two possible stoichiometries

and

In these molecules, the $(\text{AlCl}_4)^-$ and $(\text{Al}_2\text{Cl}_7)^-$ radicals replace the single halide atom in the RE trihalides, resulting in similar $4f \rightarrow 4f$ optical spectra. The lower molar absorptivity of the Nd-Al-Cl complex (see below) compared to the pure trihalides suggests a more ionic bonding in the complex. The thermodynamic and optical data of Øye and Gruen [10] are interpreted here for the vapor laser application. Figure 4 (a blow-up of Figure 3 in [10]) shows the spectral molar absorptivity of the Nd-Al-Cl complex at a temperature of 762°K (Experiment G [10]). The broad absorption background curve increasing to shorter wavelength is due to light scattering from damaged cell windows [10], and is not Al_2Cl_6 absorption. This is reasonable since the Al^{3+} ion has a closed $1s^2 2s^2 2p^6$ electron configuration. The partial pressure of the complex is 83.7×10^{-3} atm ($\rho = 8.86 \times 10^{17}$ molecules/cc). J-O intensity parameters were not given in [10], so we measured and fit the spectral intensities of Figure 4. The calculated linestrengths are given in Table V. The J-O parameters are listed in Table I and are seen to be midway between the pure trihalides and the solids. Using these parameters, the radiative properties of the $4F(3/2)$ manifold were calculated (Table VI). The fluorescence linestrengths of the complex are very similar to those of ED-2, but the radiative lifetime is 1.05 msec (unity index of refraction, again). The peak 1.06 micron cross-section, σ_p is given by

Figure 4. Spectral Absorbance of Nd-Al-Cl₂ Complex
[Taken from ref. 10]

ELECTRIC DIPOLE TRANSITION PROBABILITIES
ND :ALCL

INTENSITY PARAMETERS 1.78000E-19 4.77000E-20 3.87000E-20
REFRACTIVE INDEX RANGE 1.0000 1.0000

INITIAL STATE ENERGY= .0 (CM-1) 41 4.5

FINAL STATE ENERGY (CM-1)	WAVE LENGTH MICRON	SL	J	SQUARED U(2)	MATRIX U(4)	ELEMENTS U(6)	LINE STRENGTH (CM2)	TRANSITION RATE (SEC-1)
1869.00	5.3505	4I	5.5	.0194	.1074	1.1652	5.3676E-20	
3854.00	2.5947	4I	6.5	.0001	.0136	.4556	1.9291E-20	
5916.00	1.6903	4I	7.5	.0	.0001	.0452	1.7541E-21	
11260.00	.8881	4F	1.5	.0	.2296	.0563	1.3135E-20	
12300.00	.8130	4F	2.5	.0008	.2355	.3977	2.6773E-20	
12518.00	.7988	2H2	4.5	.0091	.0076	.1171	6.5206E-21	
13285.00	.7527	4F	3.5	.0010	.0424	.4245	1.8624E-20	
13374.00	.7477	4S	1.5	.0	.0024	.2337	9.1604E-21	
14578.00	.6860	4F	4.5	.0010	.0094	.0398	2.1611E-21	
15814.00	.6324	2H2	5.5	.0001	.0026	.0103	5.3350E-22	
16961.00	.5896	4G	2.5	.8970	.4094	.0353	1.8057E-19	
17088.00	.5852	4G	3.5	.0740	.1803	.0310	2.2974E-20	
18842.00	.5307	2K	6.5	.0068	.0002	.0312	2.4295E-21	
18853.00	.5304	4G	3.5	.0566	.1612	.0557	1.9924E-20	
19295.00	.5183	4G	4.5	.0046	.0605	.0405	5.2710E-21	
20821.00	.4803	2K	7.5	.0	.0053	.0144	8.0941E-22	
20887.00	.4788	2G1	4.5	.0010	.0153	.0141	1.4645E-21	
21058.00	.4749	2D1	1.5	.0	.0196	.0002	9.4485E-22	
21297.00	.4695	4G	5.5	.0000	.0054	.0081	5.6931E-22	
22958.00	.4356	2P	.5	.0	.0398	.0	1.8977E-21	
23655.00	.4227	2D1	2.5	.0000	.0002	.0020	8.3825E-23	
26017.00	.3844	2P	1.5	.0	.0016	.0008	1.0521E-22	
27806.00	.3596	4D	1.5	.0	.1959	.0170	1.0003E-20	
27983.00	.3574	4D	2.5	.0001	.0570	.0279	3.8177E-21	
28292.00	.3535	2I	5.5	.0049	.0146	.0033	1.6933E-21	
28373.00	.3524	4D	.5	.0	.2554	.0	1.2181E-20	
28891.00	.3461	2L	7.5	.0	.0247	.0096	1.5480E-21	
29664.00	.3371	2I	6.5	.0001	.0013	.0017	1.5275E-22	
30030.00	.3330	4D	3.5	.0000	.0037	.0030	4.8622E-22	
30361.00	.3294	2L	8.5	.0	.0010	.0012	9.4687E-23	
31977.00	.3127	2H1	4.5	.0001	.0085	.0000	4.2379E-22	
33029.00	.3028	2D2	1.5	.0	.0102	.0011	5.2877E-22	
33367.00	.2997	2H1	5.5	.0001	.0001	.0002	3.0356E-23	
34141.00	.2929	2D2	2.5	.0006	.0006	.0030	2.5092E-22	
38998.00	.2564	2F2	2.5	.0028	.0038	.0001	6.8496E-22	
40299.00	.2481	2F2	3.5	.0001	.0005	.0007	6.2900E-23	
46479.00	.2152	2G2	4.5	.0001	.0015	.0001	8.1070E-23	
47353.00	.2112	2G2	3.5	.0005	.0023	.0002	2.0373E-22	
66591.00	.1502	2F1	3.5	.0000	.0002	.0005	3.1409E-23	

$$\sigma_p = 6.08 \times 10^{-18} / \Delta \nu_{\text{eff}}^2 \quad [\text{cm}^2] \quad (7)$$

Estimating the effective linewidth as 350 cm^{-1} , we calculate $\sigma_p = 1.7 \times 10^{-20} \text{ cm}^2$.

From the pressure/temperature data of [10], we can estimate energy storage for the complex. Figure 5 shows the stored energy in the Nd-Al-Cl complex, $\text{Nd}(\text{AlCl}_4)_3$ as a function of temperature (experimental conditions G [10]), compared with the pure NdI_3 vapor. This calculation assumes that half of the vapor molecules are in the $4F(3/2)$ manifold. Usefully large energy storages ($> 10 \text{ j/liter}$) are attained at temperatures below $600 \text{ }^\circ\text{K}$ in the complex. Figure 6 illustrates another aspect of the problem. It shows the Al_2Cl_6 background pressure and the $4F(3/2)$ energy storage as a function of temperature. Note the relatively high background pressure of 6 to 7 atm which might have profound (good and/or bad) effects on the energy dynamics of the complex molecules. Figure 7 shows how energy storage varies with background pressure for two temperatures. If pressures as high as 8 atm and temperatures as high as $800 \text{ }^\circ\text{K}$ can be tolerated, stored energies in excess of 100 j/liter may be possible. It turns out that the higher temperatures $T \sim 800 \text{ }^\circ\text{K}$ will be required, not only for energy storage, but to provide a reasonable optical thickness for medium pumping. For example, at $T = 762 \text{ }^\circ\text{K}$, the peak absorption coefficient for the strong $5850 \text{ }^\circ\text{A}$ band is only 0.06 cm^{-1} , and the IR bands are about 5 times weaker. This circumstance will obviously drive the pump geometry in unfamiliar ways. Also, for half the molecules in the $4F(3/2)$ manifold at $T = 762^\circ\text{K}$, the small signal gain coefficient (1.06μ) is estimated to be $1.5\%/ \text{cm}$, or well below that of ED-2 glass.

Figure 5. Comparison of stored energy densities for Nd-Al-Cl Complex and NdI_3 vapor as a function of temperature.

Figure 6. Stored energy density in $4F(3/2)$ J-manifold of Nd-Al-Cl vapor complex and pressure of Al_2Cl_6 vapor as a function of temperature.

Figure 7. Partial pressure and stored energy density of Nd-Al-Cl complex as a function of Al_2Cl_6 pressure for two temperatures [ref. 10].

Finally, chelated RE ion vapors can be assessed for RE vapor lasers. A number of studies on high vapor pressure lanthanide chelates [11] were performed in the mid 60's. Of particular interest are the gaseous 2, 2, 6, 6 - tetramethyl - 3, 5 - Heptanedionates, abbreviated RE(thd)₃. The vapor pressures of these systems are comparable to those of the Nd-metal complex and thus will have similar energy storage potential. Øye and Gruen have estimated the JO intensity parameters for these vapors [10] (See Table I). While the Ω_2 value is larger for Nd(thd)₃ than Nd-Al-Cl₂, yielding a more intense 5800 Å band, the Ω_4 and Ω_6 parameters are smaller. This implies a lower stimulated emission cross-section in Nd(thd)₃ for equal line widths. The spectrum of Nd(thd)₃ is shown in Figure 8 (Spectrum B) [10]. Note the broad background absorption of the molecule in the visible and the intense ultraviolet absorption below 4000 Å. The stability of these class of molecules under intense visible and UV irradiation will have to be assessed. Fluorescence emission from Tb (thd)₃ has also been reported in the literature [11].

Figure 8. Spectral Absorbance of Nd(thd)_3 . Curve B.
 [Taken from ref. 10].

SUMMARY

We have seen that many of the characteristics of the RE-trihalides, RE-Al-Cl complexes, and RE(thd)₃ systems are supportive of laser action. There are still many unknowns and plenty of places for things to go wrong, but it would appear that some experiments are in order. Moreover, consideration should not be limited to Nd(3+) alone, since dynamically, other ions radiating in the visible (Ce, Eu and Tb) with low lying 4f → 5d pump bands may succeed where Nd fails. One should probably investigate the Nd-Al-Cl complexes first, since they seem reasonably tractable. Furthermore, as noted earlier, AlCl₃ additives to liquid phosphor oxychloride did not deactivate the 4F(3/2) manifold, and presumably will act similarly in the vapor phase. Other metal halides can also be utilized, (for example, GaCl₃ has lower melting and boiling points than AlCl₃) perhaps providing greater optical transition strengths, greater RE vapor pressures at a given temperature, or lower background pressures for a given storage.

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Dr. Dieter Gruen
Argonne National Laboratory
9700 South Cass Avenue
Argonne, Illinois 60439

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