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"SENSITIZATION OF Nd^{+3} LASER GLASS AND FARADAY ROTATOR GLASSES"

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Introduction

Subsequent to approval by the contract monitors, considerable time and expense was incurred during this contract period, repairing and rebuilding the melter used to produce the optical quality glasses being studied. The repairs were rendered necessary as a result of a stirrer-bar separation which perforated the crucible wall....causing a slow leak. Only those repair charges directly involving government-owned materials are being charged to the contract. Items such as thermal insulation and furnace windings replacement are considered normal overhead expenses.

However, in addition to the repairs, we were also able to continue the Faraday Rotator Glass investigation, making use of hand melting techniques in a high temperature furnace. Furthermore, additional sensitization melts, made prior to the furnace shutdown, are reported upon.

As per a request by Dr. M. Weber of Lawrence Livermore Laboratory, this bi-monthly report will contain a synopsis of all work accomplished to-date under this contract. Therefore, this report will be repetitious for those who received earlier segments.

Synopsis of Previous Reports

Faraday Rotator Glasses

Background

The Faraday effect is composed of two parts...a diamagnetic (positive rotation) and a paramagnetic (negative rotation) component. The diamagnetic component is due to Zeeman splittings of the excited states (filled electronic configurations) associated with most network modifier ions in glasses. The paramagnetic component is associated with the unfilled shells of ions within the glass matrix and derives contributions from the splittings of the excited energy levels plus splittings of the ground state. This latter contribution gives rise to a temperature dependence of the paramagnetic Verdet constant.

Obviously, then, a maximum paramagnetic Verdet constant is achieved in a glass with a low diamagnetic component and vice-versa. In the paramagnetic case, this prognosis is fortuitous, since glasses with a low diamagnetic component also tend to have low dispersion¹ and a low non-

¹See H. Cole, J. Soc. Glass Technol 34, 220 (1950).

linear index of refraction....all contributing to the figure of merit. The one caveat that remains is the index of refraction...which tends to vary directly with the dispersion.

The problem, therefore, is to determine the trade-offs between the various parameters which will produce the best figure of merit per dollar. Initially, this study concentrated on the paramagnetic ions since they showed the most promise. (In the diamagnetic case, although Verdet values of 0.19 min./Oe-cm. at 6328^o and corresponding n_d values of 2.35 have been cast....the dispersion and resulting n_2 values are in the range of 6.0 to 8.0×10^{-13} esu. The high n_2 value is very discouraging.)

Two attractive candidate ions selected for this study were Cerium,

(because of its low cost) and Terbium (because of its high Verdet constant and excellent transmission). The first glass-type studied was the fluorophosphate glasses because of their low non-linear index of refraction.

The important first step of this study was to determine the absolute density of paramagnetic ions that one can achieve in fluorophosphate glasses. This number, limited by the solubility of the paramagnetic ion in the molten glass, along with the density of the glass, determines the maximum Verdet value of that glass/ion combination. Presently available Terbium-Silicate glasses have the following pertinent parameters:

<u>Glass</u>	<u>Density</u>	<u>Ions/cc</u>	<u>Verdet @ 1060 nm</u>
EY-1	3.46	47×10^{20}	-.04 min/Oe-cm
FR-5	4.26	76×10^{20}	-.08 min/Oe-cm

In both cases, the Verdet constant represents the maximum solubility of the Terbium ion in the respective composition. Although it appears that solubility of Terbium in FR-5 is 60% greater than in EY-1, the real difference is only 31% when you take into account the difference in densities between the two glasses. In the cases exhibited above, these concentrations of Terbium (in the form of Tb_2O_3) represent solubilities of approximately 40 and 50 weight percent respectively (9 and 11 Mol percent). Therefore, in order to achieve comparable Verdet constants, the glasses investigated should have solubilities of Tb_2O_3 and Ce_2O_3 of at least 10 Mol percent. These solubilities should be achievable, since both Cerium and Terbium metaphosphate glasses have been made² with ion densities of 60 and 54×10^{20} ions/cm³ respectively.

²Berger et al, Phy. Rev. 133 3A A723 (1964).

Work to Date:

Several representative fluorophosphate glass compositions were mixed sans Terbium or Cerium. From this base mixture, 20-gram samples were doped with Tb_2O_3 , TbF_3 , Ce_2O_3 and CeF_3 in 5 wt. % steps. The samples were then melted down in platinum crucibles. The extent of solubility was determined by the presence or absence of undissolved material in the bottom of the crucible. The fluorophosphate glass compositions used in these initial experiments were all low index (1.44 to 1.45) glasses, with estimated Abbe values in the 80 to 90 range. In order to achieve the large Verdet constants desired, the solubility of CeF_3 and TbF_3 will have to be as high as 50 weight percent in these glasses.

Results in Fluorophosphate Glasses:

Seven different fluorophosphate glass compositions were doped with Cerium and Terbium. Initial results indicated that these glasses, as they stood, had only a limited ability to dissolve the rare earth ions. A series of melt modifications was attempted to improve the solubility. It was found that the addition of 3 to 5 Mol percent of PbF_2 to these compositions increased the solubility substantially. However, the solubility limit was still only about 20-30 weight percent...approximately three-fifths of our target doping.

The addition of Ce_2O_3 to any of the fluorophosphate melts resulted in violent foaming and extreme difficulty in melting down even the smallest amounts. In an attempt to circumvent this problem, the Ce_2O_3 was combined with P_2O_5 to form Cerium Orthophosphate, $(CePO_4)$. $CePO_4$ behaved much better and permitted an orderly experiment. CeF_3 and both the oxide and fluoride of Terbium were relatively trouble-free. As one would suspect, however, regardless of the method of introduction of Cerium and/or Terbium into the melt, the solubility of the respective ions remained approximately the same, for a given composition. Also, the presence of Ce^{+4} ion is especially troublesome, causing the glass to turn yellow-green. Additions of compounds like Antimony to the glass may be necessary to suppress the Ce^{+4} ion.

Further excursions into the phosphate and fluorophosphate glass compositions have so far failed to yield solubility and/or devitrifications limits which can sustain Tb^{+3} or Ce^{+3} concentrations approaching the target level of 50×10^{20} ions/cc.

The following phosphate and fluorophosphate composition families have been covered:

P ₂ O ₅	P ₂ O ₅	P ₂ O ₅	P ₂ O ₅
RF	B ₂ O ₃	PbF ₂	PbF ₂
RF ₂	RF	RF	RF
AlF ₃	RF ₂	RF ₂	RF ₂ AlF ₃

Where: RF is an alkali fluoride and RF₂ is an alkaline earth fluoride.

The maximum concentration of Tb⁺³ we have achieved in a fluorophosphate glass is 20 x 10²⁰ ions/cc....indicating a Verdet constant @1060 nm of about .02 min/Oe-cm (assuming a low diamagnetic component). Attempts to dissolve Ce⁺³ in this same glass resulted in severe devitrification at concentrations an order of magnitude lower.

During the next period, after the rather disappointing experience with the fluorophosphate glasses with regards to Tb⁺³ and Ce⁺³ concentration levels, we elected to investigate the borates. These glasses are not considered ideal for Neodymium laser glasses due to the quenching effect that B₂O₃ has upon the Nd⁺³ fluorescence. However, nothing rules them out as candidate Faraday Rotator glasses.

Simple borate and alumina-borate glasses were used as hosts for the following ions: Tb⁺³, Eu⁺², Ce⁺³, and Nd⁺³. (The Neodymium was used in both a phosphate and borate glass as an indication of solubility). Of the ions covered, only Ce⁺³ refused to make a glass at reasonably high concentration levels.

The data is presented in the table below:

<u>Ion</u>	<u>Glass</u>	<u>Mol%</u>	<u>Ion/cc x 10²⁰</u>	<u>n_D</u>
Tb ⁺³	Alumina Borate	20	75	1.68
Eu ⁺²	Borate	22	83	1.72
Nd ⁺³	Borate	25	94	1.74
Nd ⁺³	Phosphate	22	80	1.61

Although Eu₂O₃ in a phosphate glass results in Eu⁺³ ions...in the borate glass used, no characteristic red fluorescence was observed. This leads one to assume that the vast majority (88%) ended up in the glass as Eu⁺². (This result was not unexpected...see M.W. Shafer and T.C. Suits, J. Am. Ceramic Soc., 49, 261, 1966). The doping level of Eu₂O₃ was 25 Mol%.

In summary, we were able to surpass our target concentration level of 50 x 10²⁰ ions/cc for all the ions tested except Ce⁺³. Of the successful

candidates, Tb^{+3} and Eu^{+2} have the highest Verdet constant per ion. Eu^{+2} is particularly attractive since, at first glance, it appears that higher concentrations are possible and it exhibits less tendency to devitrify the glass.

Sensitizers

Background

The sensitization of Neodymium has been an active subject of investigation for over a decade. Most of the work accomplished entailed either measurements of the increased fluorescence of Neodymium versus the addition of the sensitizing ion or the change in lifetime and intensity of the emission of the sensitizing ion with concentration of Neodymium. Some of the sensitizing ions which have shown energy transfer to Neodymium include UO_2^{+2} (4), Tb^{+3} (3), Mn^{+2} (5), Ce^{+3} (6), and Cr^{+3} (7) among others. In addition, Eu^{+3} (8)(9) also appears interesting and was specifically suggested by M. Weber for study. The sensitizing ions initially chosen for study include UO_2^{+2} , Tb^{+3} , Eu^{+3} and Ce^{+3} .

The objective of this contract is not to repeat the basic sensitization research on these and other candidate sensitizers, but rather to incorporate promising sensitizers into existing laser glasses and measure the resulting changes (if any) in gain versus an unsensitized control.

Optical quality melts of a standard phosphate laser glass doped with Nd_2O_3 are sensitized with one or more doping levels of a promising sensitizer ion. From these melts, one or more $1/4" \times 3 1/4"$ laser rods are fabricated. The relative gain of these rods are then measured at different flashlamp-current densities.

We elected to initiate our sensitization study with the Cerium and Uranyl ions....primarily because of some recent work at Lawrence Livermore Laboratories regarding Ce^{+3} (in which potential improvements in pumping efficiencies of up to 40% are predicted), and because of reported self Q-switching in the case of UO_2^{+2} . We later continued with melts of Europium and Terbium sensitized glasses.

Test Procedure:

The various laser rods are tested in a liquid cooled, close-coupled laser cavity utilizing silver plated reflectors. No U.V. shielding exists within the cavity.

The mirrors are 99.9 percent and 65 percent dielectrics. All rods are

run at 1.3 pulses per second with input energies up to 40 joules per pulse. The flashlamp pulse width is 120 microseconds and the lamp bore is 4mm.

The output of the laser is monitored on a Tektronics 505A oscilloscope using an EEG photo-diode as a pick-up. The energy is measured via a calibrated thermopile and a digital read-out micro-voltmeter.

Ce³⁺

Recent work by R.R. Jacobs et. al. indicate that improvements in optical pumping efficiency in Neodymium lasers of up to 40% should be possible through optimized sensitization with Ce³⁺. Although the work was performed on silicate glasses, no reason is apparent why similar projected improvements should not be expected in phosphate glasses. In fact, bearing in mind that the Ce³⁺-Nd³⁺ energy transfer is increased by increasing the Nd³⁺ concentration, some phosphate glasses should benefit more, since they permit significantly higher Neodymium concentrations than silicates with less tendency for concentration quenching.

To test this thesis, optical quality melts of a phosphate laser glass were prepared which covered the following doping levels:

<u>Melt</u>	<u>Nd₂O₃</u>	<u>Ion/cc</u>	<u>CeO₂</u>	<u>Ion's/cc</u>
1	4.8 wt.%	4.2×10^{20}	0.0 wt.%	-----
2	4.8 wt.%	4.2×10^{20}	0.1 wt.%	8.0×10^{18}
3	4.8 wt.%	4.2×10^{20}	0.2 wt.%	16.0×10^{18}

Laser rods were fabricated from each melt and the gain of these rods compared with an unsensitized or control rod of equivalent Neodymium doping. Figure 1 displays the relative output of the three melts at different energy inputs....corresponding to different current densities. (The flashlamp pulse width was constant). At current densities of approximately 4000 Amp./cm², the 0.1 wt.% Cerium doped sample does show significantly higher output (about 11%). Otherwise, at other current densities, the output of the two materials are within experimental error of each other. The 0.2 wt.% material had consistently lower output throughout the entire region.

A second series of phosphate melts was prepared with the following Neodymium and Cerium concentrations:

<u>Melt</u>	<u>Nd₂O₃</u>	<u>CeO₂</u>	<u>Ion/cc</u>
3	3.0 wt.%	0.5 wt.%	4.0×10^{19}
4	3.0 wt.%	0.0 wt.%	0

The optical density of Ce³⁺ absorption at 0.1 wt.% is approximately 5mm...which in this case is the same order of magnitude as the rod diameter (7.6mm). The optical density of the Nd³⁺ absorption at 4.8 wt.%

— Milligrades Out →

is approximately 6mm....roughly equivalent to the Ce^{3+} absorption. Therefore, one should expect that fairly optimum conditions exist for the anticipated improvement output of a Cerium sensitized material. The results, however, indicate that in general, the gains of the sensitized and unsensitized materials are equivalent....except for a possible improvement at around 4000 Amp./cm² current density. One caveat remains, however, in order to prevent solarization, the U.V. cut-off of these glasses is usually brought down to around 350 nm. This absorption would in effect shield the Cerium and prevent any useful energy transfer properties. In the glasses studied herein, the U.V. absorption edge is at 200 nm....permitting full exposure of the Cerium.

UO₂2+

The literature is replete with data concerning the use of Uranyl ions not only as a sensitizer, but also as a saturable absorber or "brightener" for self Q-switching. A list of publications describing this work can be found in Report #2.

A Phosphate laser glass was doped with .03, 0.3 and 1.0 weight percent UO₃. (Experiments using starting materials of both UO₂ and UO₃ resulted in no detectable difference in the spectroscopic and performing properties of the resulting glass). The color of the doped glasses ranged from blue-green to dark green in color. (The Uranyl-only doped glasses are characteristically yellow in color). The gain of laser rods fabricated from these materials was very low. Even the lightly doped sample (.03 wt.%) exhibited severely degraded gain. The heavily doped sample (1.0 wt.%) would not lase at all at the pumping energies available in our system.

It appears that the induced absorption of the Uranyl ion is sufficiently dominant so that any energy transfer is negated by the robbing of the Nd³⁺ pump bands between 460 nm and 620 nm. In addition, no evidence of self Q-switching was observed in the samples which did lase.

The following table lists the concentrations of the Neodymium and Uranyl ions:

<u>Melt</u>	<u>Nd³⁺</u>	<u>UO₂2+</u>
1	2.1 x 10 ²⁰ ion/cc	.18 x 10 ¹⁸ ion/cc
2	2.1 x 10 ²⁰ ion/cc	1.8 x 10 ¹⁸ ion/cc
3	2.1 x 10 ²⁰ ion/cc	6.0 x 10 ¹⁸ ion/cc

Eu⁺³

The doping of phosphate glasses with Eu₂O₃ results in a preponderance of Eu⁺³ and little or no Eu⁺². The reduction process necessary to obtain the Eu⁺² ion in this glass matrix, in general, quenched the Neodymium and, possibly, destroys the platinum crucible. (According to M. Weber, Eu⁺² is the more desirable sensitizer candidate...fluorescing in the blue rather than at the Eu⁺³ deep red emissions between 580 and 695 nm). In any case, Eu⁺³ also seems a good radiation transfer candidate with its strong emission at 580 nm. corresponding with the strong Nd⁺³ absorption at 582 nm. In addition, Eu⁺³ also shows no concentration quenching effects up to 5 wt.% and had an attractive absorption spectra for a sensitizer ion. Melts analogous to the Tb⁺³ melts were made and the lasing results were as indicated on Figure 2. The data indicates some improvement in pumping efficiency for the lower doped case. One would expect further improvements at higher Neodymium concentrations.

Admittedly, the choice of doping concentration levels was a "shot in the dark," and further melts are needed to map the energy transfer characteristics of both Tb⁺³ and Eu⁺³.

Tb⁺³

A relatively recent publication, "Energy Transfer From Tb⁺³ to Nd³⁺ in Sodium Borate Glass" by T. C. Pant et. al., Journal of Luminescence, 10 (1975) 323-330, reports both radiative and migration modes of energy transfer operative in the Tb-Nd system.

Previous publications have reported the energy transfer as radiative, dipole-dipole, and electrostatic dipole-quadrupole. Pant et. al. finds all three modes operating...depending upon the Neodymium concentration. (The study is based on the measurement of change in lifetime and intensity of Tb⁺³ emission with concentration of Nd⁺³). However, since the Tb⁺³ concentration used in the study is limited to 2 wt.% and the Neodymium concentrations range from 0 to 1.7 wt.%...little guidance is obtained in the "proper" concentrations to use in our studies. We have, therefore, arbitrarily chosen a 3 wt.% Neodymium doping level as standard and two widely varying Tb⁺³ levels. The data is shown in Figure 1A.

The Tb⁺³ sensitized rod shows a distinct over-all improvement in pumping efficiency versus the control. The data also indicates a strong sensitivity to doping concentration ratios.

Realizing that quenching effects are inherently part of any energy-transfer scheme, we have arbitrarily chosen sensitizer doping concen-

○ - Melt 3 3.0 wt% Nd_2O_3

✦ - Melt 4 3.0 wt% Nd_2O_3 + 0.5 wt% CeO_2

FIGURE 2

Melt 1	0 No Fe_2O_3	3.0% Ni_2O_3
Melt 2	A 1.0% Fe_2O_3	3.0 Ni_2O_3
Melt 3	X 0.3% Fe_2O_3	3.0% Ni_2O_3

1300 Amps/cm²

2650 Amps/cm²

3900 Amps/cm²

5200 Amps/cm²

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FIGURE 1A

trations relative to a representative Neodymium concentration to ascertain the dominant features at that level. Therefore, the data we presented does not rule out the possibility that at other Neodymium-sensitizer ion doping levels and/or ratios, a net improvement in gain might result.

Work Accomplished This Period

As is mentioned in the introduction, a majority of the work during this contract period was performed accomplishing the repairing of government-owned equipment and rebuilding and replacing elements of the experimental melting facility. The repair of the Platinum parts necessitates returning them to the manufacturer....incurring the usual transportation delays in addition to the rework time.

Sensitizer melts accomplished prior to the shutdown include a Tb_4O_7 series at different doping levels. Particular attention is being given to the lower Neodymium concentration levels (less than 1 wt.%).

The following doping levels were melted and evaluated:

	<u>Wt.%</u>	<u>Wt.%</u>
Melt 1	No Tb_4O_7	0.4 Nd_2O_3
Melt 2	0.3 Tb_4O_7	0.4 Nd_2O_3
Melt 3	No Tb_4O_7	0.7 Nd_2O_3
Melt 4	0.035 Tb_4O_7	0.7 Nd_2O_3

The results are shown on Figure 3.

Paraday Rotator glass melts were made using the Europium Borate compositions reported earlier. The purpose of these melts is to obtain optical quality samples for measurements of Verdet constants. These samples will be sent to M. Weber at Lawrence Livermore Laboratory. A series of melt modifications was necessary to improve glass forming properties and control the amount of B_2O_3 which is lost during the melt-down.

One of the better glass-making compositions and its relevant properties is as follows:

<u>Oxide</u>	<u>Mol %</u>
B ₂ O ₃	65
Al ₂ O ₃	10
BaO	9
Eu ₂ O ₃	16

index: $(n_d) = 1.65$

density: 3.65 gm/cc

ions/cc Eu⁺⁺: 56×10^{20}

Samples of this glass will be evaluated. Further work on this composition family will be continued next period to increase the concentration of Europium ions plus develop the Terbium analogue. (The Cerium equivalent appears unobtainable at this time.)