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

FINAL REPORT

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"Sensitization of Nd⁺³ Laser Glass and Faraday Rotator Glasses"

by

John D. Myers

Introduction and Summary

This is the final report summarizing work accomplished in a research program conducted by Kigre, Inc. under ERDA Contract #EY-76-C-02-4028.*000. The work commenced on June 1, 1976 and continued through February, including deliveries of "A" size sensitized and unsensitized "control" laser discs plus samples of Faraday Rotator Glasses to the contract monitor.... Dr. M. Weber of Lawrence Livermore Laboratories.

This work was conducted under the direction of John D. Myers, principle investigator. Melts and melt samples were prepared by C.S. Vollers, W. Paulson, and J. Drayton with the help of other Kigre, Inc. personnel as needed.

This report is divided into two sections covering the sensitization research and Faraday Rotator research, respectively. Each section can be considered independent of the other and is essentially a compilation of the interim progress reports with composition and melting details added.

Sensitizers of Neodymium Laser Glasses

Abstract

Five different sensitizer ions were incorporated into a Neodymium-doped phosphate laser glass at up to five different dopant levels. The resulted gains were then measured relative to an undoped control. Each of the sensitizer ions had previously been shown to transfer energy to the Neodymium ion in a glass matrix. Of the sensitizer ions used (including Ce^{+3} , UO_2^{+2} , Eu^{+2} , Tb^{+3} and Cr^{+3}) only the addition of Tb^{+3} resulted in a significant improvement in gain.

Review

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 $UO_2^{2+(1)}$, $Tb^{3+(2)}$, $Mn^{2+(3)}$, $Ce^{3+(4)}$, and $Cr^{+3(5)}$ among others. In addition, $Eu^{2+(6)(7)}$ 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} .

References

- ¹N.T. Melamed, Appl. Phys. Let. 6, 3 1965, 43-45.
- ²T.C. Pant, Jour. Luminescence, 10(1975)323-330.
- ³S. Parke, Phys. and Chem. of Glasses, Vol. 12, No. 5, Oct 1971, 125.
- ⁴R.R. Jacobs, Jour. Appl. Phys., Vol. 47, May 1976, 2020.
- ⁵N.J. Weber, Jour. Appl. Phys., Vol. 44, No. 9, September 1973, 4053-4064.
- ⁶Toru KOMIYAMA, J. of Non-Crystalline Solids 18(1975), 107-118.
- ⁷R.A. Velapoldi, Phys. and Chem. of Glasses, Volume 14, No. 6, December 1973, 101-106.

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. These laser rods are fabricated with plane parallel ends and are equal to or better than normal optical quality grade. 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 585A 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.

Ce⁺³

Recent work by R.R. Jacobs et. al.⁽¹⁾ indicate that improvements in optical pumping efficiency in Neodymium lasers of up to 40% could be possible through optimized sensitization with Ce⁺³. 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 Ce⁺³--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

¹R.R. Jacobs, et. al., J. Appl. Phy., 41 11 2020 (1976).

The absorption coefficient of Ce^{3+} (0.1 wt.% Ce_2O_3) at 300nm is approximately 5mm....which in this case is the same order of magnitude as the rod diameter (7.6mm). The averaged absorption coefficient of the Nd^{3+} at 4.8 wt.% 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.

UO_2^{2+}

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 is as follows:

- 1) Energy Transfer in Triply Activated Glasses, H.W. Gandy, et. al., Applied Physics Letters, Vol. 6, No. 3 (1965)
- 2) Laser Oscillations and Self Q-Switching in Triply Activated Glass, H.W. Gandy, et. al., Applied Physics Letters, Vol. 7, No. 9 (1965)
- 3) Laser Action In Uranyl-Sensitized Nd-doped Glass, N.T. Melamed, et. al., Applied Physics Letters, Vol. 6, No. 3 (1965)
- 4) A Study of "Induced Absorption" in Uranyl Solutions and Glass; L. Cross, Dissertation, University of Michigan, Ph.D., 1966, Physics, general.

A phosphate laser glass was doped with .03, 0.3 and 1.0 weight percent UO_3 . (Experiments using starting materials of both UO_2 and UO_3 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 Nd^{+3} pump bands between 460nm and 620nm. 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>Nd^{3+}</u>	<u>UO_2^{2+}</u>
1	2.1×10^{20} ion/cc	$.18 \times 10^{18}$ ion/cc
2	2.1×10^{20} ion/cc	1.8×10^{18} ion/cc
3	2.1×10^{20} ion/cc	6.0×10^{18} ion/cc

Eu^{+3}

The doping of phosphate glasses with Eu_2O_3 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 quenches the Neodymium and, at times, 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.) Although Eu^{+3} in silicate glasses has been shown¹ to quench the Neodymium fluorescence, no such quenching is observed in the phosphate glass studied here. Doping levels up to 5 wt.% have shown no Neodymium-quenching effects. Therefore, in this case, Eu^{+3} seems a good radiation transfer candidate with its strong emission at 580 nm corresponding with the strong Nd^{+3} absorption at 582 nm. 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

¹ E.J. Sharp, M.J. Weber, G. Cleek, J. Appl. Phys. 41 364(1970)

the dark," and further melts are needed to map the energy transfer characteristics.

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 3.

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.

The following Tb⁺³ sensitized melts were tested:

<u>Melt</u>	<u>Tb₄O₇ (wt.%)</u>	<u>Nd₂O₃ (wt.%)</u>
1	----	3.0
2	1.0	3.0
3	0.3	3.0
4	0.15	3.0
5	----	0.7
6	0.35	0.7
7	----	0.4
8	0.3	0.4

The test results are shown in Figures 3 & 4.

In addition, "A" size discs were manufactured of Q-88 and Q-88 plus sensitizer, and forwarded to M. Weber of Lawrence Livermore Laboratory for testing. One difference which must be noted is that of an addition of an anti-solarant to the disc melts which does not appear in the previous test melts. Initial results indicate "shielding" of the sensitizers by the anti-solarant. Doping levels of these discs are as follows:

<u>Q-88 + sensitizers</u>	<u>Q-88</u>
Nd_2O_3 - 3.3 wt. %	Nd_2O_3 - 3.3 wt. %
Tb_4O_7 - 0.15 wt. %	

Recommendations For Future Work

There are a number of other ions in addition to those we have investigated, which may provide net improvements in gain for Neodymium laser glasses. These ions include $\text{Mn}^{+2(1)}$, $\text{Ag}^{+1(2)}$, $\text{Yb}^{+3(3)}$ plus others which either by themselves or in conjunction with another ion have shown energy transfer. Furthermore, the Europium doped samples have shown a remarkable lack of any concentration quenching effects. This fact plus the strong fluorescence at 580 nanometers suggests that Europium should be effective at higher doping levels than those used in this study. Also, a more complete investigation into the interaction of Tb^{+3} and Nd^{+3} is clearly in order.

We would therefore recommend the following:

1. Explore more extensively the interaction between Tb^{+3} and Nd^{+3} .
2. Investigate higher doping levels of Eu^{+3} and possible radiation transfer to Nd^{+3} .
3. Measure effects (if any) of sensitizing with Mn^{+2} , Ag^{+1} , and Yb^{+3} .
4. Investigate sensitizing effects of known multiple ion schemes.

¹S. Parke and E. Cole, Phys. and Chem. of Glasses 12 5 125(1971)

²E. Nakazawa, preprint 1963 meeting of Physical Society of Japan (obtained from M. Weber)

³J.E. Miller and E.J. Sharp, J. Appl. Phys. 41 11 4718(1970)

FIGURE 1

○ - Melt 3 3.0 wt.% Nd_2O_3
 + - Melt 4 3.0 wt.% Nd_2O_3 +
 0.5 wt.% CeO_2

FIGURE 2

FIGURE 3

Melt 5 $\odot$ - No Tb_4O_7 , 0.7 wt.% Nd_2O_3
Melt 6 $\times$ - .035 wt.% Tb_4O_7 , 0.7 wt.% Nd_2O_3
Melt 7 Δ - No Tb_4O_7 , 0.4 wt.% Nd_2O_3
Melt 8 $\square$ - 0.3 wt.% Tb_4O_7 , 0.4 wt.% Nd_2O_3

1300 Amps/cm²

2500 Amps/cm²

3900 Amps/cm²

5200 Amps/cm²

1-1

Faraday Rotator Glasses

Abstract

Various low-index fluorophosphate glass compositions are doped with Cerium and Terbium ions to determine the maximum ion concentration and Verdet constant achievable with those glass-ion combinations. In addition, Europium, Neodymium and Terbium borate compositions, plus a Neodymium phosphate composition, are melted which show relatively high concentrations of the respective paramagnetic ion.

Review

The Faraday effect is composed of two parts...a diamagnetic (positive rotation) and 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-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

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

showed the most promise. (In the diamagnetic case, although Verdet values of 0.19 min./Oe-cm. at 6328° and corresponding n_d values of 1.35 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 10 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 made¹ with ion densities of 60 and 54×10^{20} ions/cm³ respectively.

In addition to Terbium and Cerium, Europium is also included in this study in view of its high Verdet constant per ion, its good transmission in the visible, plus its reported high solubility in borate glasses.²

¹Berger et. al., Phy. Rev. 133 3A A723 (1964).

²M.W. Shafer and J.C. Suits, J. Am. Ceramic Soc. 49, 261, 1966.

Rationale

The first step in this study involved the search for a candidate fluorophosphate glass with a low n_2suitable for use as a host for the paramagnetic ion. Since, in any given glass family, n_2 varies as n , the study involves the search for a suitable lowest index fluorophosphate glass. From these glasses, a number of compositions were chosen and doped with Cerium and Terbium ions to determine maximum solubility or ions/cc possible.

Experimental Melting Procedures:

Raw Materials

The raw materials used in the experimental melts were all analytical grade chemicals....at best 99.9% pure. The following list includes the chemical formula of each constituent. All but SrHPO_4 were anhydrous.

LiF	CaF_2	$\text{Al}(\text{PO}_3)_3$	BPO_4	TbF_3
KF	MgF_2	AlF_3	B_2O_3	CeF_3
NaF	PbF_2	ZnPO_4	Tb_4O_7	NdF_3
	BaF_2	SrHPO_4	Ce_2O_3	CePO_4
			Eu_2O_3	ZnCl_2

Melting Procedures

The majority of the melting was accomplished in quartz crucibles except for the borate melts which use platinum crucibles due to the higher melting temperatures. The amount of SiO_2 pick-up from the quartz crucibles is considered negligible. After some experimentation with atmospheres, all melting was essentially open to the atmosphere. No appreciable difference in properties was observed between the open-air melting and the "closed" melting in the compositions melted. The maximum melt size was 600 gm. Most of the melts were of 25 gm. size or smaller.

Melting temperatures of the fluorophosphates were below 2000°F while the melting temperatures of the borate glasses were in the range of 2500°F . After melting, the glasses were poured out on a metal plate to cool, or cast in 1" by 1" by 4" molds depending upon the size of the melt. The index of refraction of the melts was measured using index matching fluids. The solubility of Terbium and/or Cerium was determined by examining the crucible and glass for undissolved material. The ion density was determined by measuring the density of the glass and calculating from Mol percentages.

Candidate Glasses -- Fluorophosphates

A synopsis of the glass candidates is given below...classified according to index of refraction.

Glasses With Index Between 1.44 and 1.45 (N_D)

	1.	2.	3.	<u>Mol%</u>	4.	5.	6.
LiF	--	46.6	54.3	30.2	30	31.6	
KF	46	--	--	28.4	25	26.3	
MgF ₂	40	36.2	27.7	8.2	10	(5.2 BaF ₂)	
CaF ₂	--	--	--	8.2	10	10.5	
AlF ₃	--	7.7	10.0	14.1	15	15.9	
Al(PO ₃) ₃	13	9.5	8.0	6.3	10	10.6	

Glasses With N_D Less Than 1.44

No.	<u>N_D</u>	<u>NaF</u>	<u>KF</u>	<u>LiF</u>	<u>CaF₂</u>	<u>MgF₂</u>	<u>BaF₂</u>	<u>AlF₃</u>	<u>Al(PO₃)₃</u>	<u>BPO₄</u>	<u>B₂O₃</u>
7	1.43 - 1.44	9.7	8.4	47.1	3.9	2.9	1.7	15.4	4.0	3.3	3.6
8	1.42 - 1.43	10	8.7	49.1	4.1	3.0	1.7	15.8	4.1	3.5	---
9	1.42 - 1.43	11	9.7	43.5	4.4	3.3	1.9	17.7	4.6	3.9	---
10	1.42 - 1.43	--	13.1	59.3	5.2	4.5	2.7	9.0	6.2	---	---
11	1.42 - 1.43	--	13.2	60.1	5.3	4.7	1.3	9.1	6.3	---	---
12	1.41 - 1.42	--	14.0	63.6	5.6	---	1.4	9.7	5.7	---	---

Melt numbers and compositions of glasses melted in this study are given in Table No. 1.

The compositions chosen for doping were numbers 2, 5, 6, 7, 10, plus two higher index compositions using PbF₂....numbers 13 and 14, as follows:

No.	<u>N_D</u>	<u>LiF</u>	<u>MgF₂</u>	<u>CaF₂</u>	<u>Al(PO₃)₃</u>	<u>AlF₃</u>	<u>PbF₂</u>
13	1.47 - 1.48	50	---	20	10	15	5
14	1.46 - 1.47	57	30	---	10	---	3

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}

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 PbF₂ 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 Ce₂O₃ 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 Ce₂O₃ was combined with P₂O₅ to form Cerium Orthophosphate, (CePO₄). CePO₄ behaved much better and permitted an orderly experiment. CeF₃ 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 failed to yield solubility and/or devitrification 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_2O_5	P_2O_5	P_2O_5	P_2O_5
RF	B_2O_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 RF_2 is an alkaline earth fluoride.

The maximum concentration of Tb^{+3} we have achieved in a fluorophosphate glass is 20×10^{20} 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.

Results in Borate Glasses:

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 B_2O_3 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 a 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 summarized in the table below:

<u>Ion</u>	<u>Glass</u>	<u>Mol%</u>	<u>Ion/cc x 10^{20}</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 Eu_2O_3 in a phosphate glass results in Eu^{+3} ions...in the borate glass used, very little of the 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 Eu_2O_3 was 25 Mol%.

In summary, we were able to surpass our target concentration level of 50×10^{20} 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.

Recommendations For Future Work on Faraday Rotator Glasses

This study in possible low n_2 glasses suitable as hosts for high concentrations of paramagnetic ions has been severely limited due to the insolubility of rare earth ions in the glasses covered. The only notable

exception included in this study involved Neodymium phosphate (B series melt No. 119), which resulted in a relatively low index of refraction (1.61-1.62) for a glass containing 22 Mol% Nd_2O_3 . However, two facts emerge:

1. A mechanism for improving the solubility was indicated by the lead fluoride additions to the fluorophosphate compositions.
2. There exists a family of fluoride glasses utilizing lead fluoride which reportedly has indices of refraction between 1.4 and 1.5 with Abbe values in the neighborhood of 95. (See U.S. Patent 2,466,509 patented Apr. 5, 1949, by Kuan-Han Sun.)

Therefore, we would recommend that the fluoride glasses with relatively high lead fluoride content be investigated as possible Faraday Rotator Glasses.

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<u>P Series</u> <u>felt No.</u>	<u>Index</u>	<u>NaF</u>	<u>LiF</u>	<u>KF</u>	<u>CaF₂</u>	<u>MgF₂</u>	<u>BaF₂</u>	<u>AlF₃</u>	<u>Al(PO₃)₃</u>	<u>Others</u>	<u>Result</u>
101	1.46 - 1.47	--	46.6	--	18.1	18.1	--	7.7	9.5	--	0
102	1.48 - 1.49	--	45.6	--	17.1	17.1	--	6.7	8.5	ZnCl ₂ -5.0	0
103	1.50 - 1.51	--	36.6	--	18.1	18.1	--	7.7	9.5	SrHPO ₄ -10.0	0
104	1.49 - 1.50	--	45.4	--	15.4	15.6	--	6.6	8.2	" 8.7	0
105	1.48 - 1.49	--	42.0	--	14.8	14.8	--	12.5	7.7	" 8.2	0
106	1.46 - 1.47	--	37.3	--	13.2	--	13.2	22.3	6.8	" 7.2	0
107	1.47 - 1.48	--	36.3	--	12.7	--	12.7	21.6	9.7	" 7.0	0
108	1.47 - 1.48	--	42.2	--	11.6	--	11.6	19.6	8.7	" 6.3	0
109	1.47 - 1.48	--	38.8	7.9	10.7	--	10.7	18.1	8.0	" 5.8	0
110	1.46 - 1.47	--	36.0	14.6	9.9	--	9.9	16.7	7.4	" 5.5	0
111	1.45 - 1.46	--	33.4	21.2	9.1	--	9.1	15.4	6.8	" 5.0	0
112	1.44 - 1.45	--	30.2	28.4	8.2	--	8.2	14.1	6.3	" 4.6	0
113	1.44 - 1.45	--	30.0	25.0	10.0	--	10.0	15.0	10.0	--	0
114	1.44 - 1.45	--	32.4	27.0	10.8	--	2.7	16.2	10.9	--	0
115	1.44 - 1.45	--	31.6	26.3	10.5	--	5.2	15.9	10.6	--	0
116	1.43 - 1.44	--	31.9	26.6	10.6	--	2.6	23.0	5.3	--	0
117	1.45 - 1.46	--	19.0	31.4	12.5	--	3.1	21.5	12.5	--	0
118	1.44 - 1.45	--	41.0	27.8	9.1	--	2.2	15.7	9.2	--	0
119	1.43 - 1.44	--	52.3	18.4	7.4	--	1.8	12.7	7.4	--	0
120	1.42 - 1.43	--	58.8	15.8	6.4	--	1.6	11.0	6.4	--	0
121	1.41 - 1.42	--	63.6	14.6	5.6	--	1.4	9.7	5.7	--	0
122	1.42 - 1.43	--	63.0	13.8	5.6	--	1.4	9.6	6.6	--	0
123	1.42 - 1.43	--	60.1	13.2	5.3	4.7	1.3	9.1	6.3	--	0
124A	1.42 - 1.43	--	59.3	13.1	5.2	4.5	2.7	9.0	6.2	--	0
124B	1.44 - 1.45	--	56.3	12.4	5.0	4.3	2.5	8.6	5.9	BPO ₄ -5.0	0
125	1.42 - 1.43	11.0	43.5	9.7	4.4	3.3	1.9	17.7	4.6	" 3.9	0
126A	1.43 - 1.44	12.6	49.0	10.8	5.0	3.7	2.0	7.5	5.1	" 4.3	0
126B	1.42 - 1.43	10.0	49.1	8.7	4.1	3.0	1.7	15.8	4.1	" 3.5	0
127	1.42 - 1.43	11.5	45.5	10.1	4.6	3.5	2.0	14.0	4.7	" 4.1	0

FP Series Melt No.	Index	NaF	LiF	KF	CaF ₂	MgF ₂	BaF ₂	AlF ₃	Al(PO ₃) ₃	Others	Result
128	1.43 - 1.44	9.7	47.1	8.4	3.9	2.9	1.7	15.4	4.0	BPO ₄ -3.3	0
										B ₂ O ₃ -3.6	
129	1.45 - 1.46	10.2	50.1	8.9	4.1	3.1	1.7	7.1	7.5	BPO ₄ -3.6	0
										B ₂ O ₃ -3.7	
130	1.47 - 1.48	--	64.7	--	11.1	4.6	--	8.1	9.3	CeF ₃ -2.2	0
131		--	50.0	--	30.0	--	--	--	10.0	" 10.0	0
132	1.51 - 1.52	--	55.6	--	22.2	--	--	--	23.2	--	0
134	1.43 - 1.44	--	5.7	7.8	--	--	--	--	--	--	0
140	1.44 - 1.45	--	54.3	--	--	27.7	--	10.0	8.0	--	0

B Series Melt No.	Index	B ₂ O ₃	Al ₂ O ₃	Na ₂ O	BaO	Tb ₄ O ₇	Eu ₂ O ₃	CeO ₂	Nd ₂ O ₃	Result
101	---	75.0	---	---	---	25.0	---	---	---	●
102	1.68	70.0	10.0	---	---	20.0	---	---	---	0
103	---	60.9	8.7	13.0	---	17.4	---	---	---	●
104	1.70	75.0	---	---	---	---	25.0	---	---	●
105	---	75.0	---	---	---	---	---	25.0	---	●
106	---	80.0	---	---	---	---	---	---	---	●
107	1.70	60.0	---	---	---	---	---	---	25.0	0
108	---	60.0	15.0	---	---	---	25.0	---	---	●
109	---	46.3	11.6	---	11.3	---	19.3	---	---	●
110	1.70	65.0	9.6	---	9.4	---	16.0	---	---	0
111	---	58.6	8.7	---	14.0	---	18.8	---	---	●
112	---	61.0	8.2	---	13.2	---	17.7	---	---	●
113	---	63.2	7.7	---	12.4	---	16.7	---	---	●

B Series Melt No.	Index	<u>B₂O₃</u>	<u>Al₂O₃</u>	<u>Na₂O</u>	<u>BaO</u>	<u>Tb₄O₇</u>	<u>Eu₂O₃</u>	<u>CeO₂</u>	<u>Nd₂O₃</u>	<u>P₂O₅</u>	Result
114	>1.70	61.9	9.4	---	12.4	---	16.4	---	---	---	0
115	>1.70	62.4	13.2	---	4.3	---	20.1	---	---	---	0
116	>1.70	63.4	13.3	---	2.9	20.4	---	---	---	---	0
117	>1.70	56.4	11.8	---	3.6	27.3	---	---	---	---	0
118	>1.70	62.4	13.2	---	4.3	20.1	---	---	---	---	0
119	1.61 - 1.62	---	---	---	---	---	---	---	22.0	78.0	0
120	1.65 - 1.66	65.0	10.0	---	9.0	---	16.0	---	---	---	0

*
 0 -- Clear
 ○ -- Partial Devitrification
 ● -- Total Devitrification