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

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Introduction:

Work on the contract was started on June 1, 1976 with a review of previous work on Faraday Rotator glasses in light of more recent developments in low-index phosphate and fluorophosphate glasses. (As per discussions with Dr. M. Weber of Lawrence Livermore Laboratory, work on sensitization is delayed pending evaluation of sensitized samples submitted prior to the contract period).

A cursory view of the constraints bounding this study can be seen by examining the implications of the figure-of-merit of Faraday Rotator materials for use in laser fusion systems.

The figure of merit for Faraday Rotator materials is described by M. Weber as being directly proportional to the Verdet value and the index of refraction of the material and inversely proportional to its non-linear refractive index. In general terms, then, the figure of merit is essentially proportional to the density of the ions involved¹ and inversely proportional to the dispersion of the glass matrix.

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 the 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.

¹See N.F. Borrelli, J. of Chem. Phy. 41, 11 3289, (1964).

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 dispersion² 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 will concentrate on the paramagnetic ions since they show the most promise. (In the diamagnetic case, although Verdet values of 0.19 min/Oe-cm. at 6328Å⁰ 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 x 10⁻¹³ esu. The high n_2 value is very discouraging.)

Two attractive candidate ions selected for this study are Cerium, (because of its low cost) and Terbium (because of its high Verdet constant and excellent transmission). The first glass-type studied will be the fluorophosphate glasses because of their low non-linear index of refraction.

Rationale:

The important first step of this study is 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, will determine the maximum Verdet value for that glass/ion combination. Presently available Terbium-Silicate glasses have the following pertinent parameters:

²See H. Cole, J. Soc. Glass Technol 34, 220 (1950).

<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 made³ with ion densities of 60 and 54×10^{20} ions/cm³ respectively.

Procedure:

The experimental procedure was as follows:

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_5 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:

Seven different fluorophosphate glass compositions were doped with

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

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.

Problems:

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.

Future Work:

During the next period, further modifications will be made to both phosphate and fluorophosphate glass compositions to increase the solubility of the earth ions. Also, other methods of introduction of both Cerium and Terbium will be evaluated.

The sensitization work will also begin next period.