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The optical properties of Nd^{3+} ions have been investigated in fluorophosphate glasses of composition $Al(PO_3)_3$-BaF_2-CaF_2-MgF_2-AlF_3 with different fluorine to oxygen ratios by using steady-state and time-resolved laser spectroscopy. Judd-Ofelt parameters were derived from the absorption spectra and used to calculate the $^4F_{3/2} \rightarrow {}^4I_{11/2}$ stimulated emission cross section and the $^4F_{3/2}$ radiative lifetime. The effective linewidth of the $^4F_{3/2} \rightarrow {}^4I_{11/2}$ fluorescence spectra narrows as the fluorine to oxygen ratio increases. The experimental lifetimes, ranging from 472 to 494 μs, show a linear dependence with the fluorine content.

I. INTRODUCTION

Fluoride phosphate glasses are potential candidates for applications in high performance optics and laser technology. For laser applications the fluorophosphate glasses are attractive in terms of their small refractive index non-linearity. The structure and properties of these glasses mainly depend on the relation between fluorides and phosphates (1). A knowledge of the most important laser parameters requires a detailed spectroscopic study of the optical properties of paramagnetic ions, which are influenced by the glass structure. It is known that large variations in laser parameters are possible by varying the chemical composition of the host glass (2).

The aim of this work is to establish a correlation between glass-matrix composition and Nd^{3+} spectral properties in fluorophosphate glasses of composition ($Al(PO_3)_3$-BaF_2-CaF_2-MgF_2 -AlF_3) with different oxygen to fluorine ratios.

II. EXPERIMENTAL

Fluorophosphate glass samples were obtained with the composition ($xAl(PO_3)_3$-$23.44BaF_2$-$18.75CaF_2$-$14.06MgF_2$-$yAlF_3$) in wt% and doped with 1 wt% of Nd_2O_3. We have studied five samples with fluorine to oxygen ratios (F/O) 4, 4.82, 6.04, 6.88 and 8. For convenience the samples have been labelled as glasses A, B, C, D and E respectively. They were prepared by melting the precursor mixture in platinum crucibles in an electric furnace heated up to 1200 °C under a controlled atmosphere. Then the melt was poured into a brass mould and annealed at 500°C. Finally, the samples were cut and polished for optical measurements.

Conventional absorption spectra were performed with a CARY 5 spectrophotometer. The emission measurements were made using an Argon laser as exciting light, which was chopped at 200Hz. The fluorescence was analyzed with a 0.22m SPEX monochromator, and the signal was detected by a Hamamatsu R7102 extended IR photomultiplier and finally amplified by a standard lock-in technique.

Lifetime measurements were performed by exciting the sample with a tunable dye laser (1ns pulse width), pumped by a pulsed nitrogen laser, and detecting the emission with a Hamamatsu R7102 photomultiplier. The data were processed by a EGG-PAR boxcar integrator.

III. RESULTS AND DISCUSSION

a) Absorption properties

The absorption spectra were obtained at 295K for the five samples studied. For each one, nine absorption bands lying between 400 and 950 nm were integrated, and these data, along with the values for the Nd^{3+} concentration ($1.31x10^{20}$ ions/cm^3) and the refractive index were fitted by a computarized least squares program to yield the best fit values for the Judd-Ofelt (JO) parameters Ω_t. The JO parameters are displayed for the five samples in Table I. Ω_2 is the most sensitive to local structure and host composition, and its value is indicative of the amount of covalent bonding. As can be seen in Table I, the Ω_2 value is higher for the sample with the higher amount of phosphates, which has a more covalent bonding character.

Table I. Judd-Ofelt parameters (10^{-20} cm^2) and spectroscopic quality factor calculated from the absorption spectra for Nd^{3+} (1wt%).

	Glass A	Glass B	Glass C	Glass D	Glass E
Ω_2	2.33	2.19	2.12	1.83	1.84
Ω_4	2,78	2.80	2.79	2.84	2.84
Ω_6	4.43	4.38	4.46	4.33	4.32
Ω_4/Ω_6	0.63	0.64	0.62	0.66	0.66

The radiative transition probabilities and branching ratios for the fluorescence from the $^4F_{3/2}$ state to the ^4I_J states were calculated for the five samples from the JO parameters. The fluorescence branching ratios, together with the total spontaneous emission probability (W_R) are listed in Table II. According to Jacobs and Weber (4), the intensity of the $^4F_{3/2}\rightarrow{}^4I_{11/2}$ laser transition is only dependent on the Ω_4 and Ω_6 parameters. For a large cross section, Ω_4 and Ω_6 are required to be as large as possible. Since Ω_2 does not enter the branching ratios for the $^4F_{3/2}$ fluorescence, it can be expressed in terms of Ω_4/Ω_6. To maximize the fluorescence intensity to $^4I_{11/2}$ one wants $\Omega_4 << \Omega_6$. From the values obtained for these samples the spectroscopic quality factor is slightly higher for samples with a higher content of fluorine ions. (See Table I)

Table II.-Branching ratios and spontaneous emission probability (W_R) for the $^4F_{3/2}\rightarrow{}^4I_J$ (J=9/2, 11/2, 13/2, 15/2) transitions of Nd^{3+} (1wt%) in the five studied samples.

$^4F_{3/2}\rightarrow$	$^4I_{9/2}$	$^4I_{11/2}$	$^4I_{13/2}$	$^4I_{15/2}$	W_R (s^{-1})
Glass A	0.366	0.521	0.106	0.0056	1835
Glass B	0.369	0.519	0.106	0.0055	1808
Glass C	0.366	0.521	0.107	0.0056	1802
Glass D	0.372	0.517	0.105	0.0055	1767
Glass E	0.373	0.516	0.105	0.0055	1748

b) Fluorescence properties

The $^4F_{3/2} \rightarrow {}^4I_{11/2}$ steady-state spectra were obtained at 295K by exciting the samples with the 514 nm line of an Argon laser. As an example Figure 1 shows the spectrum for glass C. For all samples studied the emission bands are inhomogeneously broadened, due to the site-to-site variations in the local ligand field, and the wavelength of the fluorescence peak only shows a small variation ranging from 1052 to 1054nm. Since the emission bands are also asymmetric, an effective linewidth was determined by integrating the fluorescence lineshape and dividing by the intensity at the peak fluorescence emission wavelength (5). It is known (2), that the effective linewidth is narrowed by using monovalent halide rather than divalent oxide anions. As can be seen in Table III, the narrowest effective linewidth corresponds to the sample with the highest content of fluorine ions.

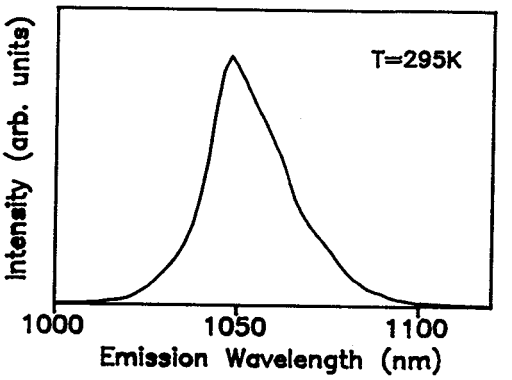

Figure 1.- Room temperature fluorescence spectrum of the $^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition for Nd^{3+} in glass C.

The radiative transition probability for emission together with the recorded luminescence spectra makes it possible to evaluate the stimulated emission cross section of $^4F_{3/2} \rightarrow {}^4I_{11/2}$ for the five samples (5). The values obtained are displayed in Table III.

Table III.- Room temperature emission properties of Nd^{3+} (1wt%) in the five studied samples.

	Glass A	Glass B	Glass C	Glass D	Glass E
$\Delta\lambda_{eff}$ (nm)	28.50	27.94	27.84	27.73	27.70
$\sigma_p(10^{20}cm^2)$	2.56	2.57	2.60	2.52	2.53
$\tau_R(\mu s)$	545	553	555	566	572
$\tau_{exp}(\mu s)$	472	476	482	489	494

c) Lifetime results

The decays of the $^4F_{3/2} \rightarrow {}^4I_{11/2}$ laser transition were performed with a narrow band tunable dye laser (1ns pulse width), and exciting the samples at the $^4I_{9/2} \rightarrow {}^4G_{5/2}$ absorption band (575nm). The radiative lifetime, calculated from the absorption parameters and measured fluorescence lifetimes of the five samples with 1wt% of Nd^{3+} are also given in

Table III. The decays were found to be single exponentials for all samples. Figure 2 shows the experimental lifetimes as a function of the fluorine to oxygen ratio. As can be observed the lifetimes linearly increase when the fluorine to oxygen ratio increases.

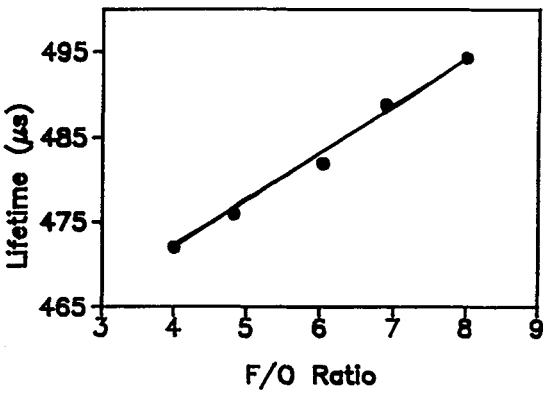

Figure 2.- Experimental lifetimes obtained by exciting the samples at 575nm and collecting at the $^4F_{3/2} \rightarrow {}^4I_{11/2}$ emission peak.

The concentration dependence of the decays between 0.5 and 5wt% Nd_2O_3 were obtained as a function of temperature in the 4.2K-300K temperature range for glass C. As the concentration raises a decrease of the experimental lifetimes are observed even at helium temperature. The quenching of the Nd^{3+} fluorescence by $Nd^{3+} \rightarrow Nd^{3+}$ interactions is already present at concentrations higher than 1 wt%.

IV. CONCLUSIONS

From the steady-state optical absorption measurements the JO parameters were derived and used to calculate the $^4F_{3/2} \rightarrow {}^4I_{11/2}$ stimulated emission cross section and the $^4F_{3/2}$ radiative lifetime. The values obtained were similar for all samples. The Ω_2 parameter decreases when the fluoride content increases, according with the weakest covalent bonding for the sample with the lowest amount of phosphates. This behaviour is in agreement with the decrease of the effective linewidth when the fluorine content increases, since it is known that fluoride glasses have narrower emissions. The lifetime values of the $^4F_{3/2}$ state were found to be linearly dependent on the F/O ratio. In spite of this, the quantum efficiency is similar in all samples studied.

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REFERENCES

1.- D. Ehrt and W. Seeber, J. Non-Cryst. Solids **129**, 19 (1991).
2.- M.J. Weber, J. Non-Cryst. Solids **123**, 208 (1990).
3.- C.K. Jorgensen and R. Reisfeld, J. Less-Common Met. **93**, 107 (1983)
4.- R.R. Jacobs and M.J. Weber, IEEE J. of Quantum Electron. **QE-12**, 102 (1976).
5.- M.J. Weber, D.C. Ziegler, and C.A. Angell J. Appl. Phys. **53**, 4344 (1982).