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PARAMETERS IN Nd GLASSES

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ABSTRACT

Laser-induced fluorescence line-narrowing has revealed that the emission properties of Nd^{3+} in various glasses are strongly dependent on the nature of the site. In a mixed anion glass, the multiplicity of ligand combinations causes additional complications. The spectral and kinetic manifestations of these are presented and discussed.

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The structural disorder inherent in glassy systems has been a major obstacle in the characterization of their spectroscopic properties. These properties are a superposition of contributions from ions residing in a multiplicity of environments, and only with the recent development of the techniques of laser-induced fluorescence line-narrowing^{1,2} has it been possible to extract the behavior of specific subsets within the total ensemble. Many features of the fluorescence of rare earth ions in glasses have been found to show a strong and systematic dependence on the nature of the site.³ Studies of various Eu^{3+} -doped oxide⁴ and fluoride⁵ glasses by means of laser-induced fluorescence line-narrowing have shown that the emission properties can be correlated with structural parameters involving the relative distances of coordinating anions. We have investigated similar glasses doped with Nd^{3+} and have shown that both the radiative and nonradiative transition rates can vary widely over the ensemble of ionic sites.^{6,7} In all but one of these cases, however, the glasses are characterized by only a single anion, such as silicate, phosphate, or fluoroberyllate; the details of these studies are discussed elsewhere.⁷ It is the purpose of this paper to discuss the complications that may ensue when more than one type of anion is present in the glass and the embodiment of these complications in a specific fluorophosphate glass.

The presence of more than one type of anion inserts an additional dimension into the usual structural disorder inherent in a glass. Upon the normal range of variation of the coordination structure another variable - the identity of the coordinating species itself - becomes superimposed. This variation may have two different effects. One is the purely statistical effect of replacing a specified number of one type of anion by another without materially altering the geometry of the first coordination shell, and makes itself felt through the different electronegativities of the anions and the strengths of their respective bonds with the central ion. The other, arising from differences in the ionic radii of the two ions, causes variations not only in the geometry of the coordination structure but also in the coordination number itself. Since fluoride and oxide ions have almost identical radii, the latter effect is negligible in the fluorophosphate, and may be disregarded.

Most of the optical properties of Nd^{3+} in the fluorophosphate glass appear to reflect the chemical nature of the bulk. For example, the $^4\text{I}_{9/2} - ^2\text{P}_{1/2}$ absorption at 4°K (Fig. 1) lies between the limits delineated by the pure phosphate and pure

fluoride (fluoroberyllate) glasses. The position within this range is purely a function of the fluorine-oxygen ratio; at the composition of the particular glass indicated (F:O ratio ≈ 7.5) the absorption is nearly at the limiting wavelength for fully fluorided glass, but at other compositions may in fact occupy any position up to the long wavelength limit indicated by the pure phosphate. The smooth monotonic dependence of absorption wavelength with F:O ratio, and the fact that no significant change is observed in the absorption profile, tend to support the assumption of direct substitution with no major change in coordination number.

In the emission from the Nd^{3+} ion similar behavior is observed. As shown in Fig. 2, the ${}^4\text{F}_{3/2}$ - ${}^4\text{I}_{11/2}$ fluorescence from the fluorophosphate again occupies a position between those for the pure fluoride and pure oxide glasses, and is completely adjustable between these limits. In this case, however, a change is observed in the line shape, with a shoulder on the long wavelength side of the peak becoming increasingly more prominent as the F:O ratio is increased. This suggests that the distribution of fluoride and oxide ions among the various sites may not be completely random, but rather tend to favor coordinations that are preponderantly one or the other.

Studies using fluorescence line-narrowing techniques give extremely striking results. Measurements of the site-dependent decay times (Fig. 3) show that in both the phosphate (pure oxide) and the fluoroberyllate (pure fluoride) glasses the decay times range about 10% above and below their mean values, although in the fluoroberyllate, as is typical in fluoride hosts, that mean value is some 75% greater. In the fluorophosphate, however, while the average decay time is intermediate between those of the other two glasses, the range of variation - almost 200 μsec - is nearly three times greater. Moreover, the longer decay times occur at the shorter excitation wavelengths, largely overlapping the fluoroberyllate, while the shorter decay times occur at the longer excitation wavelengths characteristic of the phosphate. Indeed, when the decay time is corrected for the differences in index of refraction for the glasses,⁷ we find that the values in the fluorophosphate span the full range between those typical of the pure fluoride and pure oxide glasses. Thus, these measurements give strong indications of a considerable degree of site segregation in the mixed anion glass, with those sites having predominantly fluoride coordination excited at the shorter wavelengths, and the predominantly oxidic sites excited at the longer wavelengths.

Measurements of the site-dependent fluorescent intensity tend to corroborate this assertion. By recording the total fluorescent emission at any given excitation wavelength and normalizing it in terms of a constant number of photons actually absorbed by the specimen, it is possible to derive a site-dependent relative quantum efficiency,⁷ and, with the independent measurements of total decay time, to extract the site dependence of both radiative and nonradiative decay rates (Fig. 4). We find in the case of the fluorophosphate that the average nonradiative decay rates calculated for sites on the short wavelength side of the excitation range ($< 100 \text{ sec}^{-1}$) are consistent with multiphonon relaxation rates typical of fluoride hosts, while those on the long wavelength side ($\approx 400 \text{ sec}^{-1}$) correspond to rates in oxidic hosts, again indicating a segregation of sites.

The spectra themselves, however, indicate that this site segregation is far from complete. Both the phosphate and fluoroberyllate show line-narrowed spectra (Fig. 5) typical of relatively well ordered glasses, with clean well-resolved Stark components that can be followed systematically across the excitation range.⁷ In the fluorophosphate, however, the Stark components are quite broad and poorly resolved at all excitation wavelengths. Not even at the short and long excitation wavelength extremes, where the decay time data indicate the sites to be predominantly fluoride or oxide, do the spectra sharpen up to resemble those of the pure single anion host. Thus while the behavior of the decay time indicates a segregation of the sites by excitation energy, the spectra show that even those sites that contain preponderantly fluoride or oxide coordinators still have enough of the other type to limit the site selection process. Measurements on other ions (notably Eu^{3+}) may help confirm the nature of such mixed anion glasses, and are currently in progress.

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FIGURE CAPTIONS

- Fig. 1 Absorption profile of the $^4I_{9/2} \rightarrow ^2P_{1/2}$ transition of Nd^{3+} in the phosphate, fluorophosphate, and fluoroberyllate glasses at 4 K.
- Fig. 2 Emission profile of the $^4F_{3/2} - ^4I_{11/2}$ transition of Nd^{3+} in the phosphate, fluorophosphate, and fluoroberyllate glasses at 300K.
- Fig. 3 Site variation of the fluorescence decay times of Nd^{3+} in the phosphate, fluorophosphate, and fluoroberyllate glasses (at 4 K) under tuned laser excitation.
- Fig. 4 Site variation of the radiative and nonradiative transition rates of Nd^{3+} in the fluorophosphate glass (at 4 K), under tuned laser excitation.
- Fig. 5 Site variation of the emission spectrum of Nd^{3+} in the fluorophosphate glass (at 4 K) when excited at 426 nm (bottom) and 429 nm (top). The broken curves show the spectra of Nd^{3+} in the fluoroberyllate (bottom) and the phosphate (top) at the same excitation wavelengths.

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Fig. 2

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Fig 4