

Brief Reports

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Vibronic spectrum of Gd^{3+} in BeF_2 glass

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Vibronic sidebands associated with the ${}^6P_{7/2} \rightarrow {}^8S_{7/2}$ transition of Gd^{3+} in BeF_2 glass are observed with the use of line-narrowed fluorescence techniques. Comparison of the relative intensities of peaks in vibronic, polarized Raman, and infrared (ϵ_2) spectra demonstrate that different selection rules are operative. No variation of vibronic spectra with laser excitation wavelength was detected.

In a recent paper¹ we reported on the vibronic fluorescence spectra of Gd^{3+} in a series of metaphosphate glasses having modifier cations of different mass and charge, observed using laser-induced fluorescence line-narrowing techniques. Comparison of the vibronic spectra with polarized Raman and infrared (ϵ_2) spectra revealed the strong effect of selection rules on the different spectroscopies with vibronic selection rules being remarkably similar to those of *HV* Raman scattering. The frequencies and relative intensities of peaks in the vibronic spectra change slightly with respect to corresponding peaks in the *HV* Raman spectra when the Gd^{3+} probe is a large mass or charge defect, implying that the vibrations of the host are perturbed by the presence of the rare earth. We have now extended these studies to BeF_2 glass to (1) investigate vibronic spectra in a fluoride glass system, (2) compare cases where the cation-to-anion mass ratio of the glass network former is less than unity (BeF_4^{2-}) and greater than unity (PO_4^{3-}), and (3) search for possible variations of vibronic spectra with excitation frequency analogous to observed variations of transition frequencies, homogeneous linewidths, and transition probabilities in glass.²

Beryllium fluoride glass doped with 0.5 mol% GdF_3 was prepared by melting $(NH_4)_2BeF_4$ powder in a graphite crucible under a CO_2 atmosphere, yielding polished samples with typical dimensions of $10 \times 5 \times 5$ mm³. Vibronic spectra were recorded using the same apparatus and technique described previously.¹

The ${}^6P_{7/2} \rightarrow {}^8S_{7/2}$ fluorescence spectrum of Gd^{3+} : BeF_2 glass at 293 K, excited in the middle of

the ${}^8S_{7/2} \rightarrow {}^6P_{7/2}$ absorption band with the second harmonic of the flashlamp-pumped dye laser, is shown in Fig. 1. It consists of a narrow peak resonant with the laser, a broad zero-phonon fluorescence band, and very weak vibronic sidebands extending out to ≈ 320 nm. The width of the zero-phonon band in BeF_2 glass is 110 cm⁻¹ compared to 210 cm⁻¹ in $Ba(PO_3)_2$ glass; the fluorescence lifetimes for the two glasses are 10.0 and 4.2 ms, respectively. These results reflect the weaker fields and interactions at rare-earth sites due to monovalent halide ligands as compared to divalent oxide ligands.³

Low-temperature (≈ 20 K) ${}^6P_{7/2} \rightarrow {}^8S_{7/2}$ fluores-

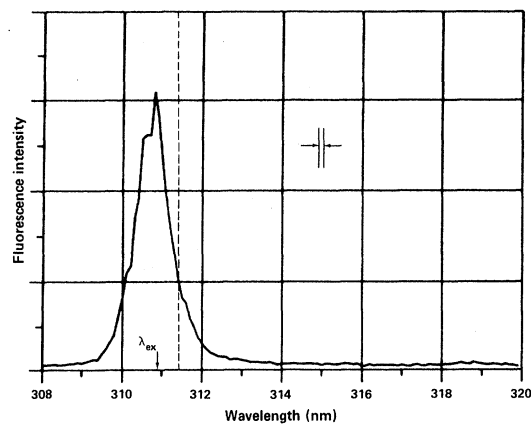


FIG. 1. ${}^6P_{7/2} \rightarrow {}^8S_{7/2}$ fluorescence spectrum of Gd^{3+} in BeF_2 glass at 293 K. Laser excitation wavelength: 310.8 nm.

cence, excited with laser wavelength $\lambda_{\text{ex}} < 311.4$ nm (indicated by the dashed line in Fig. 1), consists of a sharp line-narrowed zero-phonon line accompanied by a broad, less intense zero-phonon background on the long-wavelength side of λ_{ex} , and the weak vibronic sidebands. With excitation wavelengths ≥ 311.4 nm, line narrowing was more complete and the background was not observed. An example of the associated vibronic spectrum ($\lambda_{\text{ex}} = 311.4$ nm) is shown in Fig. 2 where the abscissa represents the frequency shift of the phonon-assisted fluorescence from the peak of the sharp zero-phonon line.

Vibronic spectra of BeF_2 and the metaphosphate glasses are similar, with each exhibiting a dominant high-frequency peak and less intense structure at lower frequencies. As discussed in Ref. 1, the in-

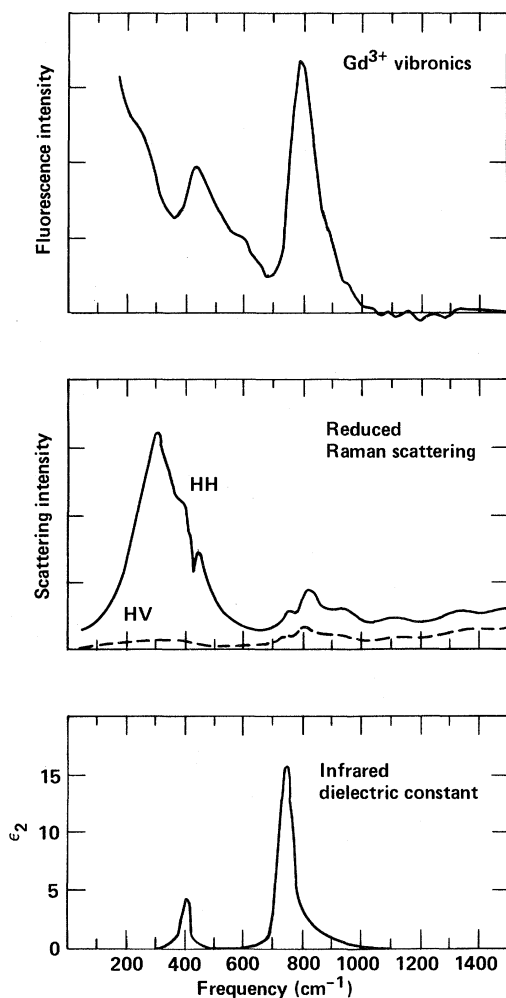


FIG. 2. Comparison of the Gd^{3+} vibronic spectrum, HH and HV polarized Raman spectra, and dielectric constant spectrum of BeF_2 glass. The Raman and ϵ_2 spectra are from Ref. 6.

crease in vibronic intensity below ≈ 300 cm^{-1} is the result of the superposition of the vibronic signal and the tail of the more intense zero-phonon line (observed with spectrometer slit width such that the reciprocal linear dispersion is ≈ 30 cm^{-1}). There is also a contribution at low frequencies from ions excited via vibrationally assisted absorption. The intensity of the zero-phonon fluorescence from these ions is comparable to fluorescent vibronic transitions. High-frequency features in vibrational spectra are generally associated with stretching motions of the glass former. The frequencies of the dominant peak in BeF_2 (800 cm^{-1}) and in the metaphosphate glasses (e.g., 1225 cm^{-1} for barium metaphosphate) are consistent with this qualitative association since the force constant of the P-O bond is known to be greater (~ 4 times) than that of the Be-F bond.^{4,5}

Also plotted in Fig. 2 are the reduced polarized Raman and dielectric constant spectra of undoped vitreous BeF_2 reported by Galeener, Lucovsky, and Geils.⁶ Vibronic, HH Raman, and ϵ_2 spectra all show bands centered about 400 and 800 cm^{-1} but relative intensities, widths, and precise peak frequencies vary. The extremely weak HV Raman spectrum does not allow detailed comparison with the vibronic spectra as was done in the case of the metaphosphate glasses.

We also searched for variations in vibronic spectra from subsets of ions with energy levels resonant with different excitation wavelengths. In these experiments we restricted λ_{ex} to wavelengths ≥ 311.4 nm to avoid exciting ions by absorption to other than the lowest-energy Stark state of the ${}^6P_{7/2}$ manifold. At low temperatures, ions excited in this manner relax to their lowest-energy ${}^6P_{7/2}$ states (at various energies above the ground state) before fluorescing. This type of accidental coincidence, in which higher Stark states are at equal energies but lowest Stark states are not, is the origin of the broad long-wavelength zero-phonon background in the 20-K spectra, and results in vibronic spectra which are a superposition of sidebands shifted from different zero-phonon lines. When $\lambda_{\text{ex}} < 311.4$ nm, vibronic structure are not shifted from the exciting laser frequency but appear at fixed absolute frequencies. The peaks in the vibronic spectra are also wider than when $\lambda_{\text{ex}} > 311.4$ nm; e.g., the dominant 800 - cm^{-1} peak has a full width at half maximum of 128 ± 5 cm^{-1} when $\lambda_{\text{ex}} = 311.1$ nm as compared to 98 ± 5 cm^{-1} when $\lambda_{\text{ex}} = 311.4$ nm.

With excitation in the low-energy wing of the ${}^8S_{7/2} \rightarrow {}^6P_{7/2}$ band, absorption is possible only via transitions to the lowest-energy Stark state; line narrowing is more complete and vibronic sidebands "track" the exciting laser frequency. Vibronic spectra recorded with λ_{ex} from 311.4 to 311.85 nm were identical within a spectral resolution of 30 cm^{-1} and spectral accuracy of 5 cm^{-1} . The absence of any observable differences in vibronic spectra obtained by

selective excitation of different subsets of ions may be (1) because the variations are less than the experimental resolution used, (2) a consequence of the long-range nature of the ion-phonon interaction, or (3) the result of accidental coincidences of resonant transitions. If the rare-earth probe ion interacts with atoms in its second or third coordination shell (Be and next-nearest neighbor F, respectively), it will be influenced by vibrations of a significant volume of the glass. The total effect on the probe will therefore be from vibrations of many local structures that average variations, resulting in a similar dynamic crystal field at each ion site. The long-range nature of the interaction may be especially important in BeF_2 , compared to oxide glasses, as a result of a "reduced-mass" effect if the motion of the light beryllium ion in the second coordination shell accounts for most of the total motion of Gd-F-Be vibrations. This explanation was used by Brecher *et al.*⁷ to justify a decreased site-to-site dependency in the phonon-mediated nonradiative decay rate of Nd^{3+} in borate glass (boron at. wt = 11) as compared to silicate glass (silicon at. wt = 32). The influence of the anion motion would be even more pronounced with the light, doubly charged beryllium.

Another plausible explanation for the identical spectra, irrespective of the range of interaction, is that the subset of ions excited by the laser has a wide variety of environments. This would result in spectra that are superpositions of sidebands from sites with different vibrational modes, even though the sites all have electronic energy levels separated by the same

frequency. Intuitively, ions with the same energy levels should have similar local structure. However, calculations of the energy eigenvalues of Eu^{3+} in different BeF_2 environments predicted from Monte Carlo⁸ and molecular dynamics⁹ simulations have shown this need not be true. Hence one can have line narrowing, in which a subset of sites resonant with the laser are selected, without having complete structural site selectivity.

The proposed explanations are not mutually exclusive. Identical spectra may result from a combination of these effects or from other, unknown effects. The conclusion that must be drawn from the data is that vibronic spectra of Gd^{3+} in BeF_2 do not exhibit large differences with excitation wavelength—differences known to exist in glass from measurements of frequencies, linewidths, and transition probabilities. This frustrates the use of vibronic spectra as a tool to verify local structures in BeF_2 from their characteristic vibrational frequencies and intensities, but does not negate its value as a probe of vibrations in glass that are governed by selection rules which are different from the more conventional spectroscopies.

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