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Comments and Addenda

The section Comments and Addenda is for short communications which are not appropriate for regular articles. It includes only the following types of communications: (1) Comments on papers previously published in **The Physical Review** *or* **Physical Review Letters**. *(2) Addenda to papers previously published in* **The Physical Review** *or* **Physical Review Letters**, *in which the additional information can be presented without the need for writing a complete article. Manuscripts intended for this section must be accompanied by a brief abstract for information-retrieval purposes. Accepted manuscripts follow the same publication schedule as articles in this journal, and page proofs are sent to authors.*

Multiphonon relaxation of rare-earth ions in beryllium-fluoride glass*

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Relaxation of excited electronic states of rare-earth ions by multiphonon emission was investigated in a beryllium-fluoride glass. Decay rates were measured from the transient fluorescence following pulsed laser excitation of selected states. The multiphonon emission rates exhibit an approximately exponential dependence on the energy gap to the next-lower state and are in general agreement with the phenomenological treatment of multiphonon processes.

Recently relaxation of excited electronic states of trivalent rare earths by multiphonon emission was studied in a series of oxide glasses.[1] Measurements of the temperature dependences of multiphonon emission rates, combined with vibrational frequencies determined from Raman spectra, demonstrated that the high-frequency vibrations in each glass were the dominant cause of relaxation. These vibrations are generally those associated with motion of ions in the glass network-forming units; that is, molecular groups such as SiO_4, BO_3, and TeO_6. Changes in the ligands and the vibrations of the glass are expected to affect the strength of the ion-phonon coupling. To investigate this and to compare the behavior in oxide versus halide glasses, we have studied the multiphonon relaxation of rare earths in a beryllium-fluoride-based glass.

Halide glasses can be prepared with various network-former compounds[2] including BeF_2, $ZnCl_2$, AlF_3, and, as described recently, ZrF_4.[3,4] Many properties of fluoroberyllate glasses are well established. In particular, the optical spectra of rare earths in such glasses have been surveyed by Kolovkov and Petrovskiy.[5] Fluorescence is observed from more rare-earth levels in fluoroberyllate glasses than in oxide glasses such as silicates, phosphates, and borates. This, as we shall show, is a consequence of the decreased rate of multiphonon emission in the beryllium fluoride glasses and is evidence of smaller ion-phonon coupling.

Because of the distribution of bond angles and interatomic separations in glasses, there are differences in the local fields at individual rare-earth sites in glass. This accounts for the broad inhomogeneous optical linewidths and nonexponential radiative decays observed from rare earths in glasses.[6] The strength of the ion-phonon coupling is also expected to vary with site due to differences in the strength of the crystal fields and in the local vibrational modes. Thus, a range of multiphonon decay rates should be present. This has been observed for Nd^{3+} in silicate laser glass,[7] for Mo^{3+} in phosphate glass,[8] and also in the experiments reported below.

Rare-earth ions studied were Nd^{3+} and Er^{3+}. The host glass composition was (mol%): 49 BeF_2, 27 KF, 14 CaF_2, 10 AlF_3; the rare-earth fluoride dopant concentrations were 0.2 mol%. Measurements of multiphonon emission rates were made at 295 °K by monitoring the transient fluorescence following pulsed optical excitation into selected J states. For Nd^{3+}, the rise time of the $^4F_{3/2} \rightarrow {}^4I_{9/2} + {}^4I_{11/2}$ fluorescence was measured following excitation (i) at 532 nm using the second harmonic and (ii) at 355 nm using the third harmonic of a YAlG:Nd laser. The rise time is a measure of the rate-limiting step in the cascade from the initial excited state to $^4F_{3/2}$. For Er^{3+}, the $^2H_{11/2}$ state was excited using the 532-nm second-harmonic YAlG:Nd laser output; subsequent fluorescence from the $^4S_{3/2}$, $^4F_{9/2}$, and $^4I_{11/2}$ lower states was observed. Additional details of the apparatus

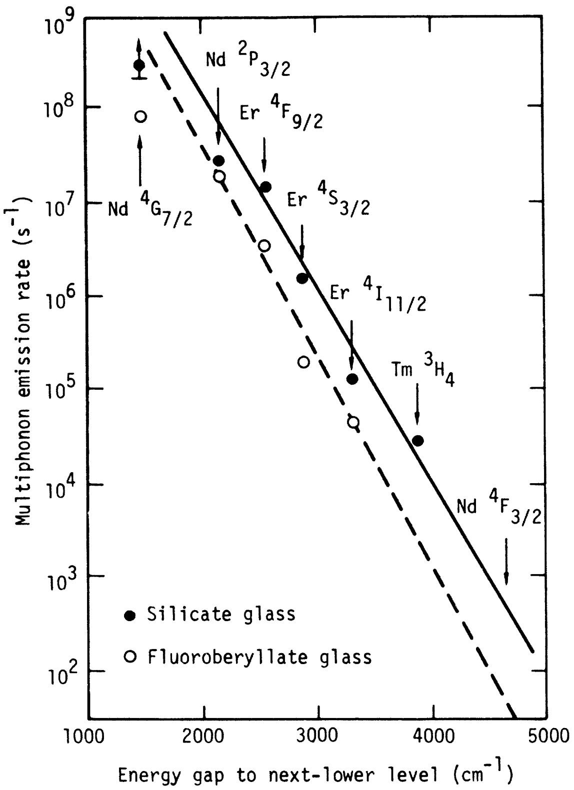

FIG. 1. Comparison of the rates of multiphonon emission from rare-earth ions in silicate and fluoroberyllate glasses plotted as a function of energy gap to the next-lower level. Data recorded at 295 °K.

and experimental techniques are given in Ref. 1. In all cases, the laser pulse duration was very short compared to the multiphonon emission times. In addition, the rate of multiphonon emission was very much greater than the rate of radiative decay. The latter were estimated using the Judd-Ofelt intensity parameters.[9]

The rates of multiphonon emission for rare earths in crystals and oxide glasses[1] have been found to exhibit an approximately exponential dependence on energy gap ΔE to the next-lower level of the form

$$W_{\mathrm{MP}} = W_0 e^{-\alpha \Delta E}, \tag{1}$$

where W_0 and α are phenomenological parameters. Data for five different rare-earth electronic states in fluoroberyllate glass are plotted as a function of energy gap in Fig. 1 and are seen to exhibit a similar dependence. (The measured rates are an effective average over the different sites.) The dashed straight line in Fig. 1 corresponds to Eq. (1) with $W_0 = 9 \times 10^{11}$ s^{-1} and $\alpha = 6.3 \times 10^{-3}$ cm^{-1}. As observed previously,[1] for excited states where the energy ΔE can be conserved by only ≤ 2 phonons (e.g., the $^4G_{7/2}$ state of Nd^{3+}), the data deviates from the simple exponential dependence derived from averaging of higher-order processes.

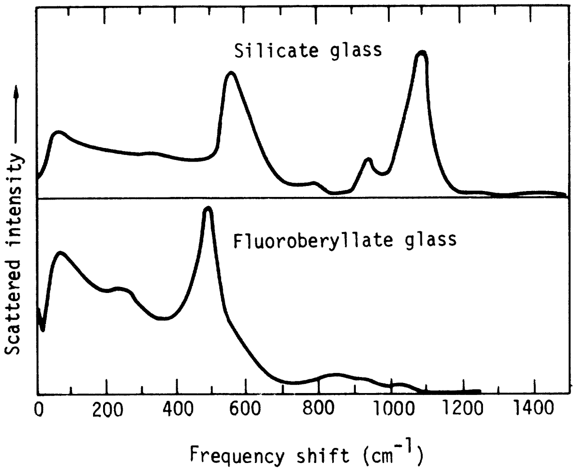

FIG. 2. Polarized Raman spectra at 295 °K of a silicate and a fluoroberyllate glass.

For all excited states studied, the relaxation was predominantly by multiphonon emission. Therefore, for nonselective excitations the time dependence of the decays should reflect the range of multiphonon emission rates present. This was clearly evident from the Er^{3+} $^4S_{3/2}$ fluorescence decay which was nonexponential. The decay rates ranged from 4 to 10 μs for the initial and fifth e-folding times. Although the laser excitation linewidth was narrow, ~1 cm^{-1}, the homogeneous linewidths of Stark levels of the $^2H_{11/2}$ manifold are probably sufficiently broad at 295 °K so that several different ion sites with different decay rates were initially excited.

For comparison, data[1] on multiphonon relaxation for rare earths in a silicate glass [composition (mol %) = 67 SiO$_2$, 15 Na$_2$O, 18 BaO] is also included in Fig. 1. The energy gaps between rare-earth J states in the silicate and fluoroberyllate glasses are approximately equal. Thus, the differences in multiphonon emission rates are attributed to different vibrational spectra and/or crystal-field strengths. The ranges of vibrational frequencies for the two glasses are evident from the Raman spectra shown in Fig. 2. The highest frequency vibrations are associated with Si–O and Be–F bond stretching modes of the glass former groups—SiO$_4^{4-}$ and BeF$_4^{2-}$. Although the Raman scattering intensities differ, the ranges of vibrational frequencies in the silicate and fluoroberyllate glasses are very similar. This was also found in a recent comparison of the Raman spectra of vitreous SiO$_2$ and BeF$_2$.[10]

The difference in multiphonon emission rate for a given energy gap in Fig. 1 may, therefore, be due to the strength of the ion-phonon coupling. The local fields at rare-earth sites in oxide glasses are stronger than in fluoride glasses because of the larger charge, and the bonding is more covalent. In addition, the nature of the effective vibrations at the rare-earth sites is also different (note that there is a reversal of the cation to anion mass ratio for SiO_2- and BeF_2-based glasses).

Beryllium fluoride glasses have recently been considered for high-power laser applications because their nonlinear refractive index is predicted to be small, thereby reducing the effects of self-focusing.[11] Consider laser action from the $^4F_{3/2}$ level of Nd^{3+}. The energy gap to the next-lower state is $\approx 4700\ cm^{-1}$. Extrapolating the results of Fig. 1 to this gap yields a multiphonon emission rate of $\sim 50\ s^{-1}$ at 300 °K. The calculated average radiative decay rate is $1.6\times 10^3\ s^{-1}$. Therefore, nonradiative losses by multiphonon emission are very small and the radiative quantum efficiency of the $^4F_{3/2}$ level of Nd^{3+} at low Nd concentrations is approximately unity. This is consistent with other measurements which show that the relative radiative quantum efficiency from the $^4F_{3/2}$ state of Nd^{3+} in a fluoroberyllate glass is constant, independent of site.[7]

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