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Judd-Ofelt Analysis and Multiphonon Relaxations of Rare Earth Ions in Fluorohafnate Glasses

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The optical properties of fluorohafnate glasses doped with Pr^{3+}, Nd^{3+}, Sm^{3+}, Dy^{3+}, Ho^{3+}, Er^{3+}, and Tm^{3+} have been studied. From optical absorption measurements and using Judd–Ofelt theory, JO parameters Ω_2, Ω_4, and Ω_6 have been obtained. The Ω_2 values indicate that fluorohafnate glasses present a less ionic character than fluorozirconates. Multiphonon emission probabilities for several levels of Er^{3+} and Ho^{3+} ions were determined by the difference between the measured rates and the calculated radiative transition probabilities. The results are almost the same as those found in fluorozirconates. Multiphonon emission probabilities are in agreement with the energy-gap law followed by rare-earth ions in crystals and glasses.

Introduction

Heavy-metal fluoride glasses have received great attention since their discovery because of their potential applications and their importance from a basic research viewpoint. A number of investigations have characterized the structure and optical, mechanical, and electrical properties of these materials. Rare-earth (RE) and transition metal ions can be easily incorporated into fluorozirconate glasses and in the last years a considerable effort has been devoted to the characterization of the optical properties of zirconium fluoride glasses doped with RE ions (*1–9*). The interest in spectroscopy of rare earths in these materials is increasing continuously especially in conection with laser research and related applications. In fact, laser action has already been proved in fluorozirconate glasses doped with Nd^{3+}, Ho^{3+}, Er^{3+}, and Tm^{3+} (*10–13*). Although hafnium seems to behave in the same way as zirconium, there is no systematic study of the spectroscopic properties of RE ions in glasses based on hafnium fluoride. Recently a few works on energy transfer and energy up-conversion of different rare earth ions have appeared (*14–17*). The purpose of this work is to obtain some spectroscopy data of Pr^{3+}, Nd^{3+}, Sm^{3+}, Dy^{3+}, Ho^{3+}, Er^{3+}, and Tm^{3+} ions in fluorohafnate glasses and compare them with zirconium fluoride-based glasses.

Experimental Methods

The samples used in this study were prepared in our laboratory by methods described in Ref. (*18*). The starting composition (in mol%) of the glasses was 52 HfF_4,

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18 BaF_2, 3 LaF_3, 2 AlF_3, and 25 CsBr. This composition was slightly modified in order to get samples with 2 and 0.2 mol% of the corresponding RE for absorption and lifetime measurements, respectively.

Optical absorption measurements were performed on a Hitachi U3400 spectrophotometer. Emission spectra were obtained by exciting the samples with light from a 150-W Xe arc lamp passed through a 0.25-m Bausch & Lomb monochromator. Fluorescence was detected with a Hamamatsu R-928 photomultiplier tube placed at the exit slit of a 0.5-m Jarrell-Ash monochromator. Lifetime measurements were carried out by modulating the beam with a light chopper and using a Tektronix 2430 digital storage oscilloscope controlled by an IBM personal computer. This system allowed lifetimes as short as 10 μsec to be measured. Low temperature measurements were performed in an Oxford Instruments CF-104 continuous flow cryostat.

Experimental Results and Discussion

Absorption and Emission Measurements

The absorption spectra of the 2.0 mol% samples were measured in the range from 250 to 2600 nm. The oscillator strengths of the absorption transitions were calculated using the expression:

$$f = \frac{mc^2}{\pi e^2 N} \int \frac{\mathrm{OD}(\lambda) \times 2.303}{d \times \lambda^2}\, d\lambda, \qquad (1)$$

where m and e are the electron mass and charge, respectively, c is the light velocity, OD(λ) the optical density as a function of wavelength λ, and d the thickness of sample. N is the number of absorbing ions in the unit volume and it has been taken to be equal to the starting RE concentration.

The experimental f values have been used to calculate the Ω_t values corresponding to the Judd–Ofelt theory (*19*, *20*). Using this theory the electric dipole line strength S_{ed} can be found using the expression

$$S_{\mathrm{ed}}(aJ, bJ') = e^2 \sum_{t=2,4,6} \Omega_t (\langle f^n[\alpha SL]J \| U^{(t)} \| f^n[\alpha' S' L']J' \rangle)^2, \qquad (2)$$

where Ω_2, Ω_4, Ω_6 are three parameters (JO parameters) to be obtained from a comparison with the experimental results. It is known that the reduced matrix elements of the unit tensors $U^{(t)}$ ($t = 2, 4, 6$) are almost insensitive to the ion environment. We have used the values of these parameters as given in Ref. (*21*).

Some of the electronic transitions within the $4f^n$ ground configuration of the RE^{3+} ions have a small magnetic dipole contribution which is given by (see, e.g., Ref. (*3*))

$$S_{\mathrm{md}}(aJ, bJ') = \frac{e^2 \hbar^2}{4m^2c^2} (\langle f^n[\alpha SL]J \| L + 2S \| f^n[\alpha' S' L']J' \rangle)^2. \qquad (3)$$

The values of S_{md} are usually small and not sensitive to the host.

The oscillator strength $f(aJ, bJ')$ of the $|aJ\rangle \rightarrow |bJ'\rangle$ transition (at a mean frequency ν) is given by

$$f(aJ, bJ') = \frac{8\pi^2 m\nu}{3h(2J + 1)e^2 n^2} [X_{\mathrm{ed}} S_{\mathrm{ed}} + X_{\mathrm{md}} S_{\mathrm{md}}], \qquad (4)$$

where n is the refractive index of the host at the mean frequency of the transition, $X_{\mathrm{ed}} = n(n^2 + 2)^2/9$ and $X_{\mathrm{md}} = n^3$.

The JO parameters found at least-squares fitting of the calculated f values given by Eq. (4) to the experimental ones are given in Table I with those found for the same ions in fluorozirconate glasses and given in the literature. It can be seen that the JO parameters are larger in fluorohafnate than in fluorozirconate glasses except for the Sm^{3+} ions, which are lower. Jorgensen and Reisfeld noted that the Ω_2 parameter is indicative of the amount of covalent bonding, while the Ω_6 parameter is related to the rigidity of the host (*22*). From Table I it can be concluded that fluorohafnate glasses are

TABLE I

JUDD–OFELT PARAMETERS FOR SEVERAL RE^{3+} IONS IN FLUOROHAFNATE GLASSES (FIGURES IN BRACKETS ARE FOR FLUOROZIRCONATE GLASSES)

$\Omega_t (\times 10^{-20}\ cm^2)$	2	4	6	Ref.
Pr	0.212	5.82	6.68	
	(0.067)	(5.05)	(6.92)	(*5*)
Nd	2.36	4.48	4.72	
	(1.89)	(3.69)	(4.22)	(*1*)
Sm	1.44	2.87	1.44	
	(2.37)	(4.24)	(2.99)	(*8*)
Dy	3.12	2.07	2.48	
	(2.70)	(1.80)	(2.00)	(*9*)
Ho	3.30	2.22	1.93	
	(2.28)	(2.08)	(1.73)	(*4*)
Er	3.20	1.65	1.23	
	(2.54)	(1.39)	(0.965)	(*3*)
Tm	2.81	2.07	0.96	
	(2.80)	(1.91)	(1.01)	(*6*)

slightly less ionic in character than fluorozirconates but still more ionic than oxide glasses, which present larger Ω_2 values.

On the other hand, in the JO theory those transitions in which intensity is dominated by the Ω_2 parameter were called hypersensitive transitions by Jorgensen and Judd (*23*). Those transitions obey the selection rules $|\Delta J| \leq 2$, $|\Delta L| \leq 2$, and $\Delta S = 0$. The room temperature (RT) visible absorption spectra of Nd^{3+} and Ho^{3+} ions in fluorohafnate and fluorozirconate glasses are given in Figs. 1 and 2, respectively. Although all absorption bands are larger in fluorohafnate glasses, this increase is even larger in the hypersensitive transitions ($^4I_{9/2} \rightarrow {}^4G_{5/2}$ for Nd^{3+} and $^5I_8 \rightarrow {}^5G_6$ in the case of Ho^{3+} ions), which show more covalent bonding for fluorohafnate glasses.

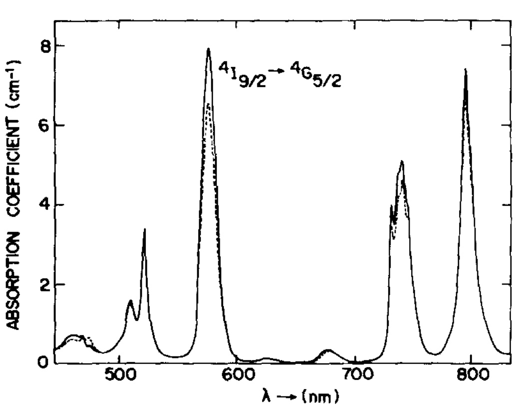

FIG. 1. Absorption spectra at RT in the range 445–835 nm of 2 mol% Nd^{3+} ions in: (—) fluorohafnate and (---) fluorozirconate glasses.

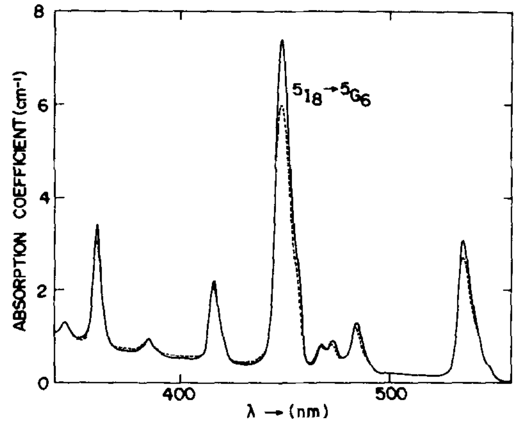

FIG. 2. Absorption spectra at RT in the range 340–560 nm of 2 mol% Ho^{3+} ions in: (—) fluorohafnate and (---) fluorozirconate glasses.

It can be interesting to compare graphically the Ω_t values with those obtained in the case of RE^{3+} ions in fluorozirconate glasses. Peacock (*24*) has pointed out that a representation of Ω_t (for the same host) as a function of the number n of f electrons of RE^{3+} ions is expected to be a monotonic curve if the electric dipole contributions to the absorption bands are mainly due to a static crystal field effect. Examples of this behavior in the case of the Ω_6 parameter are given in Peacock's paper. This author indicates that the Ω_4 parameter also presents a parallel behavior while the Ω_2 values, which are usually poorly determined, show a more scattered behavior. In Fig. 3 the values for Ω_2, Ω_4, and Ω_6 given in Table I are displayed as

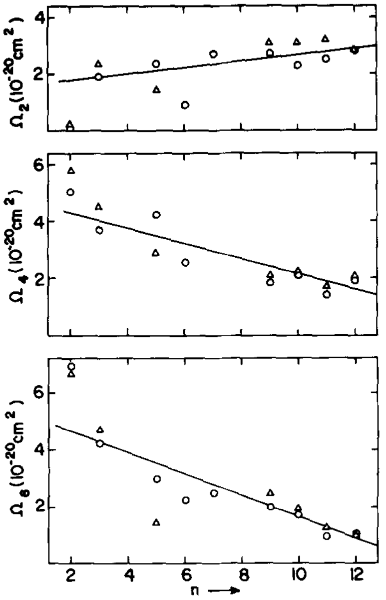

FIG. 3. Judd-Ofelt Ω_2, Ω_4, and Ω_6 parameters as a function of the number n of f electrons for different RE^{3+} ions in: (○) fluorozirconate and (△) fluorohafnate glasses. The solid line only shows the data trend.

a function of the number of f electrons n. The Ω_t values for Pr^{3+} have been included although, as reported in Ref. (*24*), they usually show a singular behavior. In the case of Ω_4 and Ω_6 a similar linear decreasing trend is observed while the Ω_2 values slightly increase with the number of f electrons.

The Ω_t values found with the absorption measurements have also been used to calculate the spontaneous emission probabilities $A(aJ, bJ')$ of the different electronic transitions, which are given by the expression (see, e.g., Ref. (*3*))

$$A(aJ, bJ') = \frac{64\pi^4\nu^3}{3(2J+1)hc^3}[X_{\text{ed}}S_{\text{ed}} + X_{\text{md}}S_{\text{md}}] \quad (5)$$

and are related to the radiative lifetime τ_R of an excited state a by

$$\frac{1}{\tau_R} = \sum_b A(a, b), \quad (6)$$

where the summation is over electric and magnetic dipole transitions to all terminal states b.

Because the JO parameters in the fluorohafnate glasses are larger than in the fluorozirconates, the spontaneous emission probabilities are also slightly larger in the fluorohafnate glasses. In Fig. 4 are shown the emission spectra of Pr^{3+} ions in fluorohafnate and zirconate glasses when the ions are excited to the $^3P_2$ level. It is seen that the hypersensitive transition $^3P_0 \rightarrow {}^3F_2$ is relatively larger in fluorohafnates as happened in the Nd^{3+} and Ho^{3+} absorption measurements (see Figs. 1 and 2).

Multiphonon Relaxations

Finally the multiphonon relaxation rates of RE ions in fluorohafnate glasses have been studied. The multiphonon relaxation rates W_{NR} (NR means nonradiative) from a given level a to the next lower level, in absence of energy transfer, may be obtained using the relation

$$W_{\text{NR}} = \frac{1}{\tau_{\text{exp}}} - \frac{1}{\tau_R}, \quad (7)$$

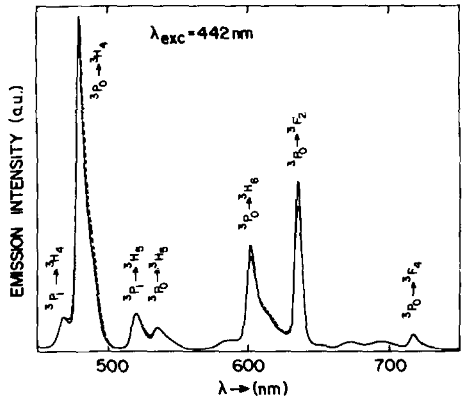

FIG. 4. Emission spectra at RT of Pr^{3+} ions in: (—) fluorohafnate and (---) fluorozirconate glasses, under excitation to the $^3P_2$ level. The spectra are not corrected for instrument response.

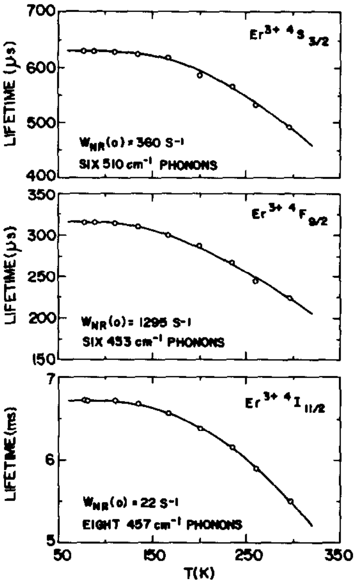

FIG. 5. Temperature dependence of the $^4S_{3/2}$, $^4F_{9/2}$, and $^4I_{11/2}$ Er^{3+} emission lifetimes.

where $\tau_{\exp}$ is the experimental lifetime of the level *a* at the particular temperature.

In Figs. 5 and 6 are shown the experimental lifetimes (from LNT up to RT) of $^4S_{3/2}$, $^4F_{9/2}$, and $^4I_{11/2}$ levels for Er^{3+} ions and $^5S_2$, $^5I_6$, and $^5F_5$ levels for Ho^{3+}, respectively, in samples of fluorohafnate glasses containing 0.2 mol% of dopant ion. At this concentration, energy transfer between ions can be considered negligible. The W_{NR} values at LNT for the mentioned levels have been obtained from expression (7) by using the measured lifetimes and the radiative rates calculated by the JO theory. On the other hand the temperature dependence of the multhiphonon relaxation between the electronic levels of RE in glasses may be adequately described by the single frequency model developed by Riseberg and Moos (*25*), through the expression

$$W_{NR}(T) = W_{NR}(0)\left[\frac{\exp(\hbar\omega/kT)}{\exp(\hbar\omega/kT) - 1}\right]^p, \quad (8)$$

where $\hbar\omega$ is the energy of the active phonons in the transition, $p = \Delta E/\hbar\omega$ is the number of phonons which must be emitted to span the energy gap (ΔE) between adjacent levels, and $W_{NR}(0)$ is the low temperature multiphonon emission rate. Due to inhomogeneous broadening, the energy gaps are not definitely known; nevertheless it is possible to obtain reasonable limits for the gap values from absorption and emission measurements. From the relation $p = \Delta E/\hbar\omega$, initial values of p and $\hbar\omega$ were substituted into Eq. (8). These values, along with the value of $W_{NR}(0)$ were adjusted to give the best fit to the observed multiphonon relaxation rates. The final values for these parameters are shown in Figs. 5 and 6. With these calculated multiphonon rates and the radiative ones, the calculated lifetimes were obtained. They are shown as solid lines in Figures 5 and 6. It must be taken into account that the radiative rate of the $^5S_2$ Ho^{3+} level is temperature dependent due to thermalization with the $^5F_4$ level, and the effective radiative rate for the two levels was calculated

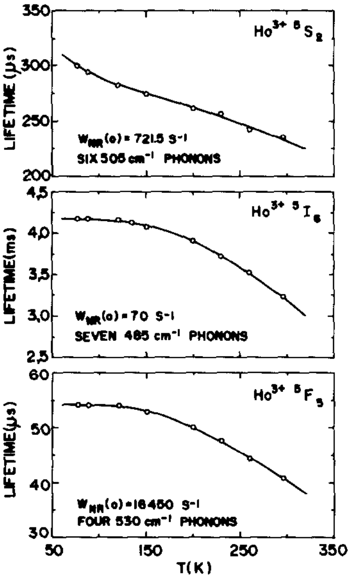

FIG. 6. Temperature dependence of the $^5S_2$, $^5I_6$, and $^5F_5$ Ho^{3+} emission lifetimes.

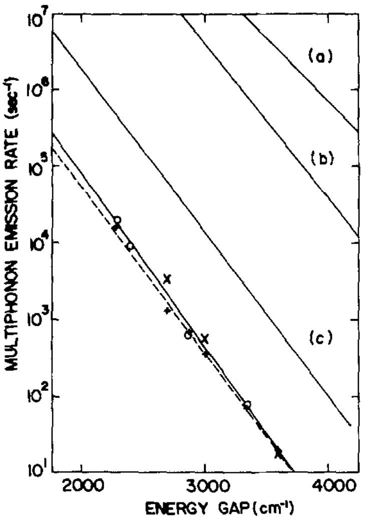

FIG. 7. Multiphonon emission rates of RE^{3+} ions in (a) borate, (b) phosphate, and (c) germanate glasses. (○) Ho^{3+} and (×) Er^{3+} in fluorozirconate glasses, (+) Ho^{3+} and Er^{3+} in fluorohafnate glasses.

TABLE II

PARAMETERS OF NONRADIATIVE RELAXATION IN SEVERAL MATRICES

Matrix	C (sec^{-1})	α (cm)	$\hbar\omega$ (cm^{-1})
Hafnate	1.3×10^9	5.0×10^{-3}	490
Zirconate	2.8×10^9	5.2×10^{-3}	472
Germanate[a]	3.4×10^{10}	4.9×10^{-3}	900
Phosphate[a]	5.4×10^{12}	4.7×10^{-3}	1200
Borate[a]	2.9×10^{12}	3.8×10^{-3}	1400

[a] Ref (*27*).

using the appropriate relation (see Eq. (13) of Ref. (*4*)). This is the reason for the different temperature dependence of the calculated lifetime of $^5S_2$ Ho^{3+} level with respect to the others levels.

Some authors (*26, 27*) have observed that in crystals and glasses multiphonon emission rates show an exponential dependence on energy gap to the next lower level when the number of phonons involved is more than two. This relationship can be expressed as

$$W_{NR} = C \exp(-\alpha \Delta E), \qquad (9)$$

where C and α are positive constants characteristic of the host.

A semilogarithm graph of the observed LNT multiphonon emission rates for the levels mentioned above versus the energy gap (ΔE) to the next lowest level is shown in Fig. 7. The values found for the same levels in fluorozirconate glasses (*3, 4*) are also plotted. A least-squares fit of these observed data to Eq. (9) is portrayed in the figure as well as straight lines corresponding to the mentioned fits for borates, phosphates, germanates, and fluorozirconates. The values of the parameters C and α obtained from the fits for fluorohafnate and fluorozirconate glasses, as well as those values given in the literature (*27*) for the others matrices mentioned, are shown in Table II. It has to be noted that parameters C and α given in Table II for fluorozirconate glasses are slightly different from those reported in (*3*) because in that work only the Er^{3+} levels were taken into account while in the present fit, both the Er^{3+} and Ho^{3+} levels have been considered. From Fig. 7 it can be concluded that the multiphonon emission rates in fluorohafnate glasses are very much like those in zirconate glasses and much lower than that found in oxide glasses.

Finally the last column of Table II contains the energy ($\hbar\omega$) of the phonons active in the nonradiative transitions in the different glasses. In fluorohafnate glasses $\hbar\omega$ is an average value obtained from the parameters given in Figs. 5 and 6, and this value is in accordance with that found (~500 cm^{-1}) by Almeida *et al.* (*28*) for the energy of the stretching vibrations of the glass network in binary flurohafnate glasses using infrared and Raman data. From the values of $\hbar\omega$ in Table II for the different glasses and those of W_{NR} plotted in Fig. 5 it can be said that the lower the energy of the stretching frequencies of the glass former is, the lower the multiphonon decay rates from a given level to the next lower level are obtained since a large number of phonons is needed to make the nonradiative transition.

Conclusion

In conclusion it can be said that RE-doped fluorohafnate glasses present oscillator strengths and JO parameters slightly larger than those of fluorozirconate glasses. The Ω_2 parameter indicates a more covalent bonding in fluorohafnate glasses. Multiphonon relaxation rates of electronic transitions are almost the same in both type of glasses and much lower than oxide glasses. These results show that hafnium fluoride-based glasses can be considered, as zirconate glasses, good hosts for laser applications.

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