Pressure-induced energy transfer processes between Sm^{3+} ions in lithium fluoroborate glasses

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Fluorescence decay curves for the $^4G_{5/2} \rightarrow {}^6H_{7/2}$ transition of Sm^{3+} ions in lithium fluoroborate glasses for different lanthanide concentrations have been measured as a function of pressure up to 21 GPa at room temperature. At ambient conditions, for 0.2 mol % of Sm^{3+}, a single exponential completely describes the fluorescence decay curve. On the contrary, in the case of 2 mol % of Sm^{3+}, a distinct nonexponential behavior is observed, indicating that energy transfer processes only occur for higher concentrations in fluoroborate glasses. With increasing pressure the fluorescence decays show a more pronounced nonexponential behavior, even for the sample with low concentration, accompanied by a fast decrease of the lifetimes. Cross relaxation between Sm^{3+} ions can explain the energy transfer processes, for which migration does not play a relevant role. A generalized Yokota-Tanimoto model has been used to explain this behavior. For the first time, the lifetime and the energy transfer parameter have been obtained and analyzed independently as a function of pressure. Moreover, their contributions to the luminescence intensity also have been analyzed.

I. INTRODUCTION

Research on glasses doped with lanthanide ions have focused a great deal in the last 30 years on the design of new optical devices,[1] due to their similar optical properties and easier fabrication compared to crystalline matrices. The interest in fluoroborate glasses is due to their high ionic conductivity,[2] the short-range order around network-forming borons, the ''anomalous'' dependence of their structure on the molar fraction of oxide modifiers,[3] and the particular role of the fluoride ions in the formation of the three-dimensional network[4,5] and in the local structure of the lanthanide ions.[6]

Two main changes in the optical properties of the lanthanide ions can be induced by applying pressure to the matrix. On one hand, a red shift of the transition between multiplets of the $4f^N$ ground configuration, associated with a decrease in the lanthanide free-ion atomic parameters, and, on the other hand, an increase in the fine Stark splitting of these multiplets, related to the enhancement of the crystal-field interactions with the $4f$ electrons of the lanthanide ion. The former can be correlated with an expansion of the $4f$-electron wave functions with increasing covalency, while the latter is ascribed to a change in the sum of various interactions such as covalency, overlap or Coulomb interactions between the $4f$ electrons and their ligands. These contributions can be modulated by changing the distances and bond angles under pressure.[7,8] Similarly, from the point of view of the interaction processes between lanthanide ions, the diminishing of the matrix volume changes the distances among ions in the matrix and, hence, plays an important role in the energy transfer processes. Actually, decreasing distances can even produce a complete quenching of the emission of the lanthanide ions.

The Sm^{3+} ion is one of the most interesting cases to analyze energy transfer processes since its lowest emitting level $^4G_{5/2}$ has a relatively high quantum efficiency and shows different quenching emission channels. The concentration quenching of the $^4G_{5/2}$ fluorescence has been analyzed for different glasses, such as germanate,[9] borate,[10] fluorozincate[11] or fluoroborate,[12] and crystals.[13] Several cross relaxation processes between Sm^{3+} ions have been invoked to explain the temporal evolution of this fluorescence.

Despite the exhaustive study of the fluorescence of crystals doped with Sm^{2+} (Refs. 14–16) and Sm^{3+} ions[17–20] as pressure calibrators, only two recent works are devoted to analyze the effects of pressure on the fluorescence of Sm^{3+} ions in glasses, both focusing on fluoroborate glasses.[21,22] Moreover, very few works were concerned with energy transfer processes under pressure, i.e., Hayes and Drickamer[23] studied the energy transfer between ligands and lanthanides (Eu^{3+}, Sm^{3+},...) in molecular chelates by analyzing their luminescence and, more recently, Wamsley and Bray[24] applied the Inokuti and Hirayama model[25] to describe the energy transfer in Cr^{3+}:Tm^{3+}:YAG (yttrium aluminum garnet) under pressure. However, to our knowledge, this is the first work that studies the energy transfer processes between Sm^{3+} ions under pressure by analyzing the evolution of the fluorescence decays. The decay curves and the emission intensities of the $^4G_{5/2}$ level in fluoroborate glass doped with 0.2 and 2 mol % of Sm^{3+} ions has been measured and analyzed as a function of pressure up to 12 and 21 GPa, respectively.

II. THEORY

When the interactions between optically active ions are negligible, the decay of the fluorescence curves can be fitted to a single exponential and the lifetime can be calculated straightforwardly. However, when the concentration is large enough the interaction between optically active ions becomes important and energy transfer processes from a donor (excited lanthanide ion) to an acceptor (nonexcited lanthanide ion) have to be taken into account. In this situation the fluorescence decay, which is proportional to the probability that a donor is still excited after pulsed excitation at $t=0$, is given by

$$I(t)=I(0)\exp\left\{-\frac{t}{\tau}\right\}\prod_{K=1}^{N_A}\exp\{-tW_{DA}(R_K)\}, \quad (1)$$

where τ is the lifetime (including radiative and multiphonon deexcitations), N_A is the number of acceptors, and $W_{DA}(R_K)$ is the energy transfer probability between a donor and an acceptor separated by a distance R_K.

The situation described by Eq. (1) allows the donor to decay via intrinsic deexcitation (characterized by τ) and via transfer processes to acceptors.

If a multipolar interaction between donors and acceptors is considered, the energy transfer probability can be expressed by[25]

$$W_{DA}(R_K)=\frac{C_{DA}^{(S)}}{R_K^S}, \quad (2)$$

where $S=6$, 8 or 10 depends on whether the dominant mechanism of the interaction is dipole-dipole, dipole-quadrupole or quadrupole-quadrupole, respectively, and the process is characterized by the microscopic parameter $C_{DA}^{(S)}$.

From Eq. (1), and considering a small number of excited ions compared to the total number of active ions, Inokuti and Hirayama[25] obtained

$$I(t)=I(0)\exp\left\{-\frac{t}{\tau}-Qt^{3/S}\right\}, \quad (3)$$

where Q is the energy transfer parameter and is given by

$$Q=\frac{4\pi}{3}C_A\Gamma\left(1-\frac{3}{S}\right)(C_{DA}^{(S)})^{3/S}, \quad (4)$$

where C_A is the concentration of acceptors, which practically coincides with the total concentration of lanthanide ions and $\Gamma(x)$ is the gamma function.

Taking into account also the migration processes (transfer between donors, as shown in Fig. 1 for Sm^{3+} ions), Martín *et al.*[26] obtained a generalization of the Yokota-Tanimoto expression[27] for the emission intensity versus time for any kind of multipolar interaction, i.e.,

$$I(t)=I(0)\exp\left[-\frac{t}{\tau}-Qt^{3/S}\left(\frac{1+a_1X+a_2X^2}{1+b_1X}\right)^{(S-3)/(S-2)}\right], \quad (5)$$

TABLE I. Values for the Padé approximant coefficients in Eq. (5) for different multipolar interactions (after Ref. 26).

S	a_1	a_2	b_1
6	10.866	15.500	8.743
8	17.072	35.860	13.882
10	24.524	67.909	20.290

where a_1, a_2, and b_1 are the Padé approximant coefficients that depend on the multipolar character of the interaction (see Table I) and

$$X=DC_{DA}^{-2/S}t^{1-2/S}, \quad (6)$$

where D is the diffusion coefficient that characterizes the energy transfer processes between donors.

From Eq. (5), assuming a dipole-dipole interaction ($S=6$) the Yokota-Tanimoto expression is reproduced, whereas the Inokuti-Hirayama expression is obtained when the migration between donors is negligible ($D=0$).

In the models given by Eqs. (3) and (5), energy transfer due to cross relaxation processes between ions (as shown in Fig. 1 for Sm^{3+} ions) are well described, regardless of whether these processes are assisted or not by phonons (nonresonant and resonant processes, respectively). Usually, in energy transfer processes assisted by phonons the value for the C_{DA} parameter, and hence the transfer probability and the Q parameter, are much more lower than those in the resonant situation. Moreover, if the distance between optically active ions decrease (due to an increase in the pressure or in the doping concentration) then one may expect an increase in the Q parameter and, as a consequence, faster fluorescence decays.

On the other hand, in the generalized model given by Eq. (5) the energy transfer processes between donors, characterized by the parameter D, are also taken into account. If these processes are efficient, the energy could migrate among the donors until a nearby acceptor is reached and may result in an increase in the transfer efficiency. Even in samples with only one type of lanthanide ion, playing the roles of donors and acceptors, the cross relaxation and the migration processes could compete.

It is worth noting that the Eqs. (3) and (5) are only valid for the special case of pulsed excitation and a random distribution of optically active ions (donors and acceptors) in the sample. It is so because there is not enough time during the exciting laser pulse (of the typical order of ns) for the donors to transfer to other ions (donors or acceptors), so they are still kept randomly distributed. However, in other experiments the decay curves are obtained once the system has reached a steady state after a long period of excitation, instead of a pulsed one. Such a situation is given, for example, if the excitation is carried out using a continuous laser and a chopper. In the steady state, the probability of finding a donor near an acceptor is less than the probability of finding a donor with an acceptor farther away, and hence the donors are not randomly distributed. Thus the temporal evolution of
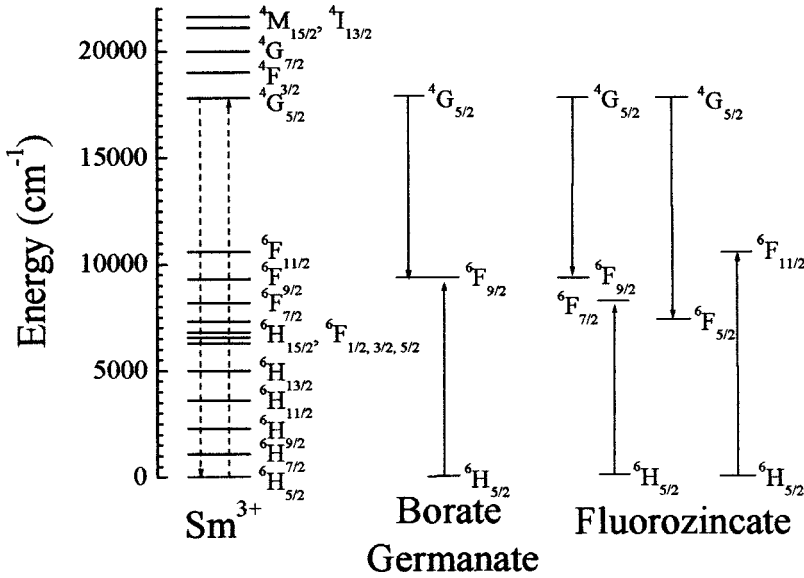
FIG. 1. Part of the free Sm^{3+} ion energy level diagram and the most important channels for cross relaxation in germanate,[9] borate,[10] and fluorozincate[11] glasses at ambient conditions. The channel for the migration of energy is also shown (dashed lines).

the emission intensity must be modified according to the Eisenthal and Siegel expression,[28] i.e.,

$$I_{exp}(t) = \frac{\int_0^t I(t')dt'}{\int_0^\infty I(t')dt'}, \tag{7}$$

where $I(t')$ is given by Eq. (5).

Finally, for continuous excitation, it is also interesting to analyze the dependence of the emission intensity on the energy transfer efficiency. This intensity is proportional to the concentration of excited ions N^*, which can be expressed as a function of the quantum yield of the luminescence η/η_0, i.e.,[28]

$$N^* \propto \tau \frac{\eta}{\eta_0}, \tag{8}$$

where the quantum yield of luminescence is defined by[28,29]

$$\frac{\eta}{\eta_0} = \frac{1}{\tau} \int_0^\infty I_{exp}(t)dt \tag{9}$$

and η and η_0 represent the donor quantum yield with and without acceptors, respectively. Thus, η/η_0 becomes unity when energy transfer to acceptors is negligible.

III. EXPERIMENT

The composition (in mol %) of the glasses studied in the present work was $(50-x/2)$ LiF$+(50-x/2)$ H$_3$BO$_3$ $+x$Sm$_2$O$_3$, with $x=0.1$ and 1. Details of the preparation method has been given in a previous paper.[21] The fluorescence of the Sm^{3+} ions was excited by the 476 nm line of an Ar ion laser and recorded using a 0.85 m double grating monochromator equipped with a cooled photomultiplier. Decay curves were obtained using a mechanical chopper with a multichannel scalar interfaced to a personal computer that recorded and averaged the signal. For measurements at pres-

sures up to 21 GPa the sample was inserted in a diamond-anvil cell. A methanol-ethanol-water mixture (16:3:1) was used as a hydrostatic transmitting medium, and pressure determination was performed using the SrFCl:Sm^{2+} fluorescence.[15]

IV. RESULTS AND DISCUSSION

The absorption and emission spectra of Sm^{3+} ions in lithium fluoroborate glass at ambient conditions have been presented in a previous paper.[21] According to the free Sm^{3+} ion energy level diagram (Fig. 1), the luminescence spectra originate from transitions between the $^4G_{5/2}$ level and the ^6H_J ($J=5/2$, 7/2, 9/2, 11/2, and 13/2) levels. The absence of emission starting from any other level above $^4G_{5/2}$ is due to the high-energy phonons found in fluoroborate glasses. The vibronic spectra of the Eu^{3+} ion in the same matrix show two broad phonon side bands associated with vibrational modes with phonon energies of about 1000 and 1400 cm^{-1}.[6] Thus, when the Sm^{3+} ions are excited to any level above the $^4G_{5/2}$ multiplet, a fast and efficient nonradiative multiphonon relaxation to the $^4G_{5/2}$ multiplet occurs.

The decay of the $^4G_{5/2} \rightarrow {}^6H_{7/2}$ fluorescence after switching off the excitation has been measured for different concentrations of Sm^{3+} ions (0.2 and 2 mol %) at ambient conditions as well as under pressure. For the sample with 0.2 mol % of Sm^{3+} ions at ambient pressure a very good fit of the decay curve to a single exponential is achieved, as shown in Fig. 2. The obtained lifetime is 3.0 ms, slightly higher than that calculated using the Judd-Ofelt theory.[21] Moreover, an imperceptible temperature dependence of the lifetime between room temperature and 2K for the sample with low concentration[21] points to an almost unity quantum emission efficiency for the $^4G_{5/2}$ level and thus to a purely radiative decay of the excited Sm^{3+} ions. The pure radiative decay is due to the large energy gap of about 7000 cm^{-1} to the lower-lying $^6F_{11/2}$ level (see Fig. 1), preventing an appreciable multiphonon relaxation probability. Any nonexponential behavior of the fluorescence decay from this level can thus be
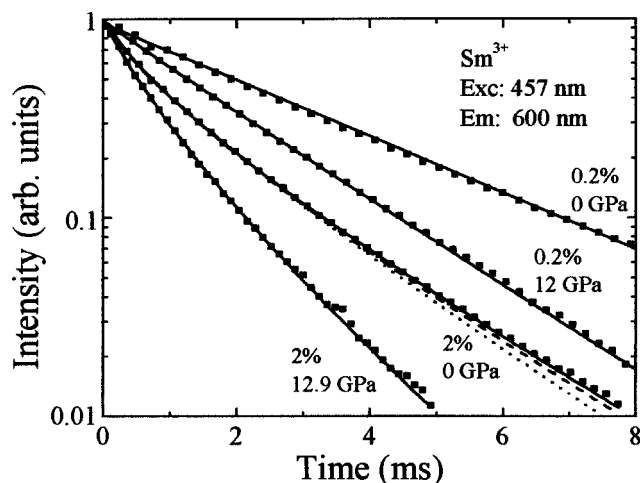
FIG. 2. Fluorescence decays in fluoroborate glasses doped with 0.2 and 2 mol % of Sm^{3+} at different pressures at room temperature. Lines correspond to the best fits of the experimental results using the equations indicated in the text. For 2 mol % of Sm^{3+} at ambient conditions the fits of the decay curve to a dipole-dipole ($S=6$) (dotted line), dipole-quadrupole ($S=8$) (dashed line), and quadrupole-quadrupole ($S=10$) multipolar (solid line) interactions are included for comparison.

FIG. 3. Lifetime of the $^4G_{5/2}$ level (□) and energy transfer parameter Q (■) versus pressure obtained from the fits of the fluorescence decays in a fluoroborate glass doped with 2 mol % of Sm^{3+}.

related to energy transfer processes, as it is the case for the sample doped with 2 mol % of Sm^{3+} already at ambient pressure (see Fig. 2).

Under pressure, all decay curves clearly show nonexponential features, including the samples with the lower concentration of only 0.2 mol % of Sm^{3+} ions. In order to determine the mechanisms of the energy transfer involved, the decays of the $^4G_{5/2}$ fluorescence in the fluoroborate glass doped with 2 mol % of Sm^{3+} ions under pressure have been fitted according to Eq. (7) by using the generalized Yokota-Tanimoto model given by Eq. (5). From these fits the values for the τ, D, and Q parameters were obtained considering $S=6$, 8, and 10. Best fits of the experimental decays are obtained for $S=10$ without taking into account migration processes ($D=0$), as shown in Fig. 2. If migration processes are also included, the root-mean-square deviation clearly increases.

We thus conclude that in this case the dominant interaction for the cross relaxation of the $^4G_{5/2}$ level is quadrupole-quadrupole for the whole range of pressures with a negligible influence due to the migration processes. As an example, the fits for the dipole-dipole ($S=6$) and dipole-quadrupole ($S=8$) interactions for the 2 mol % sample at ambient conditions also have been included in Fig. 2. The best fit corresponds to $S=10$ with a root-mean-square deviation better than those obtained for $S=6$ and $S=8$, respectively. The most important channels for these cross relaxation processes in different glasses at ambient conditions are shown in Fig. 1. Identical results have been obtained at ambient conditions by Mahato, Rai, and Rai[12] for oxyfluoroborate glasses, by Chang and Powell[30] for $CaWO_4$ crystals, and by Ozawa[31] for powdered phosphor. In contrast to this result, in other glasses also dipole-dipole and dipole-quadrupole interactions have been proposed.[9–11]
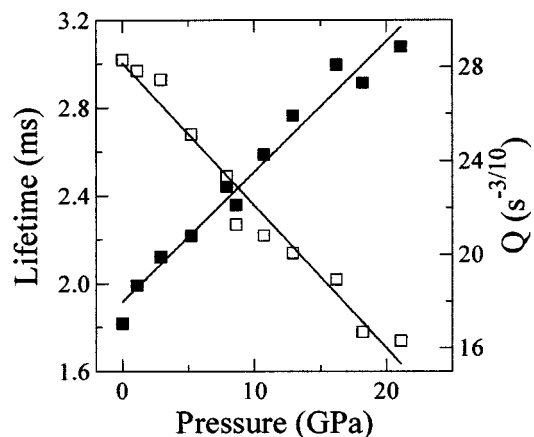
One option that has been discarded in the fitting processes is to fix the value of the lifetime τ. This is evident from the fluorescence line narrowing measurements in an Eu^{3+}-doped fluoroborate glass at ambient conditions.[6] Results indicate the existence of a relatively wide distribution of local structures for the lanthanide ion in the glass, for which the fluoride ions play a fundamental role. Each environment is characterized by different excitation and emission energies and line profiles and also by a particular lifetime. Thus, since under pressure a change in the local structure is expected, one cannot assume one and the same value for the lifetime at different pressures.

The lifetime of the $^4G_{5/2}$ level and the transfer parameter Q obtained from the fitting process for the 2 mol % sample under pressure are given in Fig. 3. It is worth noting that the lifetime obtained for the sample with 2 mol % at ambient conditions is rather close to the value obtained for the sample with the low concentration (about 3 ms), for which no transfer processes occur. This shows that the theoretical model applied here can correctly grasp the energy transfer situation in the case of the sample with higher concentration.

As already mentioned, also for the 0.2 mol % doped sample the decay curves become nonexponential when the pressure is increased. These decay curves are well fitted to Eq. (7), using the generalized Yokota-Tanimoto model given by Eq. (5) and considering $S=10$ and $D=0$. From these fits, the lifetime τ and the transfer parameter Q have been obtained. On one hand, in the pressure range of up to 12 GPa the lifetime τ shows a decrease that is similar to that found for the 2 mol % doped sample (see Fig. 3). On the other hand, since for the 0.2 mol % sample a negligible energy transfer except at very high pressures is expected, the values obtained for the transfer parameter Q from the fits are not conclusive at low pressures and the only reliable values are obtained at high pressures. As an example, for the decay curve obtained at 12 GPa values of 2.3 ms for the lifetime and 2.8 $s^{-3/10}$ for the Q parameter have been determined from the fit. In this range of pressures, the lifetime is similar to that obtained for the 2 mol % (see Fig. 3) whereas the Q

parameter is about an order of magnitude lower than that obtained for the 2 mol % sample in similar conditions. The latter result exactly fits to what could be expected of the linear dependence of Q on the Sm^{3+} concentration according to Eq. (4).

With increasing pressure, the lifetime decreases almost linearly. Such a decrease could be explained either by an increase in the multiphonon deexcitation probabilities or by an increase in the electronic transition probabilities. The latter effect could be explained by stronger crystal fields as a result of changes in the Sm^{3+} local structure under pressure. As a consequence, a stronger mixing of opposite parity configurations with the $4f^5$ configuration due to the odd crystal-field Hamiltonian and an increase in the transition probabilities may occur. Such a behavior has been observed in the case of Sm^{3+} and other lanthanide ions in crystals.[32]

On the other hand, Lochhead and Bray[33] related the decrease in the lifetime and in the overall fluorescence intensity of the Eu^{3+} $^5D_0$ level in Na silicate glasses with pressure to an enhancement of the electron-phonon coupling, and hence in the nonradiative deexcitation. However, according to IR and Raman studies in different crystals and glasses under pressure, the energies of the vibrational modes do not show a unique behavior. Depending on the matrix, the energies either increase, decrease, or the modes may even disappear.[34-38] Moreover, the measurement of the vibronic spectra under pressure, which could give information about the $4f$ electron-phonon coupling, are rather difficult to perform and, to our knowledge, they have not yet been performed in glasses. In those cases where the maximum energies of the vibrational modes increased, the change was not large enough to induce a drastic variation in the multiphonon relaxation probabilities. Therefore, it seems unlikely that a drastic change in the multiphonon relaxation can be made responsible for the observed lifetime decrease shown in Fig. 3.

If it is assumed that the decrease in the lifetime is not due to an enhancement of the multiphonon relaxation, an increase in the electronic transition probability must be responsible. As discussed, such an increase could be explained by enhanced configuration interactions, which in turn can be caused by stronger crystal fields. Indeed, the emission spectra of the Sm^{3+} ions in lithium fluoroborate glasses under pressure give some evidence for the increasing crystal fields. The spectra have been measured previously by Jayasankar et al.[21] In particular, they observed a red shift (~ -5 cm^{-1}/GPa) and a broadening (~ 2.6 cm^{-1}/GPa) of the fluorescence lines under pressure up to 9 GPa. The former effect is due to an increase in the covalency in the Sm^{3+}-ligand bonds as they are shortened by compression, whereas the latter effect is due to the fluctuation of the local fields, accompanied by the formation of strong crystal-field environments for the Sm^{3+} ions as a consequence of the increasing distortion of the glass network with the pressure, that modulate the bond angles and lengths.[39] Therefore, it is possible that the configuration interactions also increase under pressure, which could explain a decreasing lifetime.

According to Fig. 3, the behavior of the transfer parameter Q with pressure is contrary to that of the lifetime. This observation could be explained by the increase of the effective concentration of lanthanide ions with the reduction of the matrix volume under pressure, the change in the transition probabilities and the variation of the overlap integral of the normalized line-shape functions of the donor emission and acceptor absorption for $S = 10$.[40] As already pointed out, experimental evidences for the latter effect have been found in the increase of the full width at half maximum of the emission line profiles with pressure in this matrix.[21]

In order to analyze the contribution of the variation in matrix volume with pressure in the effective Sm^{3+} concentration, and hence in the transfer parameter Q, the equation of state of Murnaghan[41] at constant temperature has been used as a well-defined expression that easily relates volume and pressure in a solid,

$$\frac{V}{V_0} = \left(1 + (p - p_0) \frac{B'_0}{B_0} \right)^{-1/B'_0}, \qquad (10)$$

where V_0 is the volume, B_0 is the bulk modulus (inverse of the isothermic compressibility modulus K), both at a reference pressure p_0, and $B'_0 = (dB_0/dp)_{p=p_0}$. Usually, p_0 is set to the ambient pressure value and a value of around 4 can be used for B'_0. B_0 may range from 40 to 400 GPa depending on the matrix under consideration. From the values obtained by Kumar and Veeraiah[42] for the Young's modulus and the Poisson's ratio in lanthanide-doped lithium fluoroborate glasses, and taking into account the isotropic character of the glass, it has been possible to extrapolate a value for the bulk modulus around 68 GPa for the Sm^{3+}-doped fluoroborate glass. For this value of B_0 and for the pressures applied in the present work, the volume of the matrix may decrease by not more than 20%. Such a decrease can cause a variation in the Sm^{3+} concentration and the proportional transfer parameter Q [see Eq. (4)] by a factor of about 1.25. Thus, the change in the matrix volume alone is clearly insufficient to explain the large variation of the transfer parameter Q observed here (see Fig. 3). Therefore, changes in the transition probabilities and/or the overlap integral must be also taken into account in order to explain the behavior of the transfer parameter Q.

The competition of the two effects, radiative deexcitation and the energy transfer, gives rise to a decrease in the $^4G_{5/2}$ fluorescence intensity by a factor of 4 when pressure is increased from ambient conditions to 21 GPa (Fig. 4). A similar behavior has been reported also by Souza-Filho et al.[22] in lead fluoroborate glasses.

According to Eq. (8), the luminescence intensity, proportional to the concentration of excited ions N^*, depends on the lifetime and the luminescence quantum yield. Using Eq. (9) and taking into account a linear dependence of the lifetime τ and the energy transfer parameter Q according to Fig. 3, the pressure dependence of the luminescence quantum yield shown in Fig. 4 has been obtained. From Figs. 3 and 4 it is obvious that both the luminescence quantum yield and the lifetime τ decrease by about a factor of 2 from ambient conditions to 21 GPa. Combining these results, Eq. (8) predicts a decrease in the luminescence intensity by a factor of 4 in the pressure range studied. A good agreement between the
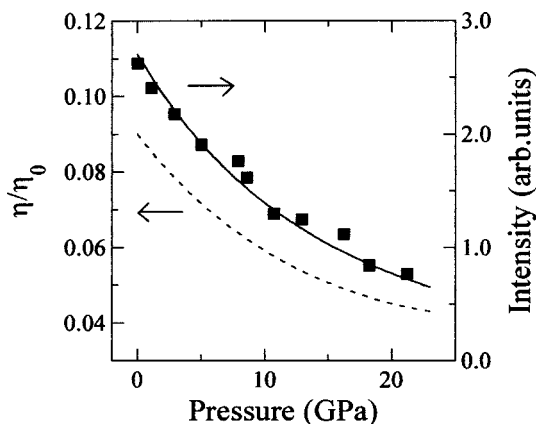
FIG. 4. Luminescence intensity (■) versus pressure obtained in a fluoroborate glass doped with 2 mol % of Sm^{3+}. The solid line corresponds to the dependence obtained from Eq. (8), whereas the dashed line is the luminescence quantum yield obtained from Eq. (9).

calculated and experimental results is shown in Fig. 4, where the luminescence intensity versus pressure calculated from Eq. (8) completely coincides with the normalized experimental results.

V. CONCLUSIONS

At ambient conditions, energy transfer processes are observed for a concentration of 2 mol % Sm^{3+} ions in fluoroborate glasses, while they are negligible for a concentration of 0.2 mol %. Pressure induces energy transfer processes between the Sm^{3+} ions also for the sample with low concen-

tration. A generalized Yokota-Tanimoto model is used in order to analyze the transfer dynamics. The best fits are obtained for $S=10$ and $D=0$ for both concentrations of Sm^{3+} ions and for all pressures. Thus, a quadrupole-quadrupole interaction for the cross relaxation of the $^4G_{5/2}$ level can be determined as the dominant mechanism, while migration was shown to play a negligible role in the transfer processes for fluoroborate glasses.

From the analysis of the luminescence decays, the behavior of the lifetime and the transfer parameter are obtained independently as a function of pressure. As for the result, both parameters showed a strong variation by a factor of ~ 2 up to 21 GPa. The decrease in the lifetime with an increasing pressure could be explained by an increase in the electronic transition probabilities as a consequence of stronger crystal fields felt by the Sm^{3+} ions. On the other hand, the increase in the energy transfer efficiency, which produces a decrease in the luminescence quantum yield, can be attributed to various contributions: an effective increase in the Sm^{3+} concentration, changes in the transition probabilities, and changes in the line profiles of the involved transitions.

It has been shown that the decrease in lifetime as well as the decrease found in the quantum yield can quantitatively explain the experimentally observed decrease in the luminescence intensity under pressure.

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