

## Optical properties and cross relaxation among $\text{Sm}^{3+}$ ions in fluorzincate glasses

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Optical absorption and emission spectra are presented for  $\text{Sm}^{3+}$  ions in  $\text{ZnF}_2$ - $\text{CdF}_2$ -based glasses (0.1, 1.5 and 2.5 mol% of  $\text{Sm}^{3+}$ ). The measured oscillator strengths and branching ratios for several transitions are compared with values obtained with the Judd–Ofelt theory. Energy transfer among  $\text{Sm}^{3+}$  ions has been investigated. The decay curves are nonexponential when the concentration is 1.5 or 2.5 mol%. It can be explained by cross relaxation between ions of  $\text{Sm}^{3+}$ . Energy migration does not play a relevant role in these decay processes.

### 1. Introduction

Heavy metal fluoride glasses based on  $\text{ZrF}_4$  have received great attention since their discovery in 1975 by Poulain et al. [1]. These materials present a very high transparency from the UV to the IR region, they can be easily prepared and a relatively high concentration of transition metals and rare earth ions can be incorporated into the matrix. Their low phonon energies result in weaker non-radiative transitions and higher fluorescence efficiencies than in oxide glasses.

Fluoride glasses based on  $\text{ZnF}_2$ - $\text{CdF}_2$  present higher transparency in the IR than  $\text{ZrF}_4$  glasses. Recently the spectroscopic properties of these glasses doped with  $\text{Ho}^{3+}$ ,  $\text{Er}^{3+}$ ,  $\text{Tm}^{3+}$  [2] and  $\text{Nd}^{3+}$ ,  $\text{Dy}^{3+}$  [3] have been reported and it was found that they present quantum efficiencies comparable to those of fluorzirconates.

In this work the optical properties of  $\text{Sm}^{3+}$  in  $\text{ZnF}_2$ - $\text{CdF}_2$ -based glasses are reported as well as their concentration dependence. From the optical absorption spectrum and applying the Judd–Ofelt theory [4,5], the radiative lifetime of the  $^4\text{G}_{5/2}$  level and the branching ratios for the different emissions have been obtained and compared with the experimental ones. The concentration quenching of the  $^4\text{G}_{5/2}$  fluorescence in different matrices has been reported [6–8] and several cross relaxation processes have been proposed to explain the experimental results. In our case samples with 1.5 and 2.5 mol% of  $\text{Sm}^{3+}$  show nonexponential decays and they are analyzed to determine the mechanisms involved in the quenching of the  $^4\text{G}_{5/2}$  emissions.

### 2. Experimental methods

The samples used in this study were prepared by methods described in ref. [9]. The starting compositions (in mol%) of the glasses were  $32\text{ZnF}_2$ ,

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$28\text{CdF}_2$ ,  $20\text{BaF}_2$ ,  $11\text{LiF}$ ,  $5\text{AlF}_3$ ,  $(4-x)\text{LaF}_3$  and  $x\text{SmF}_3$ , with  $x$  equal to 0.1, 1.5 and 2.5.

Optical absorption measurements were performed on a Perkin Elmer Lambda 9 spectrophotometer. Emission spectra were obtained by exciting the samples with light from a 300 W Xe arc lamp passed through a 0.25 m Spex 1680 double monochromator. Fluorescence was detected through a 0.25 m Spex 1681 monochromator with either a photomultiplier Hamamatsu R758 or a refrigerated PbS New England EM detector. Spectra were corrected for instrument response.

Lifetimes and emission decays were measured by modulating the exciting light with a mechanical chopper and using a Tektronix 2432 digital storage oscilloscope controlled by a personal computer.

### 3. Theoretical introduction

From the absorption spectrum, the oscillator strengths of the electronic transitions can be calculated using the expression:

$$f = \frac{mc}{\pi e^2 N} \int \frac{2.303 \text{OD}(\nu)}{d} d\nu, \quad (1)$$

where  $m$  and  $e$  are the electron mass and charge respectively,  $c$  is the light velocity,  $N$  is the number of absorbing ions in the unit volume,  $\nu$  is the light frequency,  $\text{OD}(\nu)$  is the optical density and  $d$  is the thickness of the sample.

In the Judd–Ofelt theory [4,5] the oscillator strength of the  $aJ \rightarrow bJ'$  transition (at mean frequency  $\nu$ ) is given by:

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

where  $n$  is the refractive index of the host at the mean frequency of the transition,  $X_{\text{ed}} = n(n^2 + 2)^2/9$ ,  $X_{\text{md}} = n^3$ .  $S_{\text{ed}}$  and  $S_{\text{md}}$ , which give the electric and magnetic dipole contributions, can be written:

$$S_{\text{ed}} = e^2 \sum_{t=2,4,6} \Omega_t |\langle aJ | U^{(t)} | bJ' \rangle|^2, \quad (3)$$

$$S_{\text{md}} = \left[ \frac{e}{2mc} \right]^2 |\langle aJ | L + 2S | bJ' \rangle|^2, \quad (4)$$

where the  $\Omega_t$  parameters, known as Judd–Ofelt parameters, are characteristic of each ion–matrix combination. The reduced matrix elements of  $L + 2S$  and of the unit tensors  $U^{(t)}$  are not very sensitive to the ion environment.

The spontaneous emission probabilities  $A(aJ, bJ')$  of the different electronic transitions are given in the Judd–Ofelt theory by:

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

The radiative lifetime of an excited level  $aJ$  is given by:

$$\tau = \frac{1}{\sum_{bJ'} A(aJ, bJ')}, \quad (6)$$

where the sum is extended over all the states at energies lower than  $aJ$ .

The branching ratios for the different emissions with the same initial level are:

$$\beta(aJ, bJ') = \frac{A(aJ, bJ')}{\sum_{bJ'} A(aJ, bJ')}. \quad (7)$$

The relative values of the branching ratios can be obtained from the areas under the emission curves.

When the interactions between luminescent ions are not important the decay of the photoluminescence curves can be fitted to a single exponential. In this way the lifetime of the excited level is obtained. However, when the concentration is large enough, energy transfer appears and the decay curves become nonexponential.

If we consider that the process responsible for the nonexponential decay is cross relaxation, the expression derived by Inokuti and Hirayama [10] and Eisenthal and Siegel [11] for the decay of the luminescence of a system with only donor–acceptor transfer and which is initially in a stationary state can be used. In our case, the acceptors are the nonexcited  $\text{Sm}^{3+}$  ions and that expression is valid

if the number of excited ions is small compared with the total number of active ions. The emission intensity versus  $t$  is given by:

$$\Phi(t) = \frac{\int_t^\infty \exp\left(-\frac{t'}{\tau} - \frac{4\pi}{3} N_A (t' C_{DA}^{(s)})^{3/s} \Gamma\left(1 - \frac{3}{S}\right)\right) dt'}{\int_0^\infty \exp\left(-\frac{t'}{\tau} - \frac{4\pi}{3} N_A (t' C_{DA}^{(s)})^{3/s} \Gamma\left(1 - \frac{3}{S}\right)\right) dt'} \quad (8)$$

where  $S = 6, 8$  or  $10$  depending on whether the dominant mechanism of the interaction is dipole-dipole, dipole-quadrupole or quadrupole-quadrupole, respectively,  $N_A$  is the concentration of acceptor ions,  $\Gamma(x)$  is the gamma function and  $C_{DA}^{(s)}$  is the parameter of the dominant contribution to the donor-acceptor transfer related with the transition probability by:

$$W_{DA} = \frac{C_{DA}^{(s)}}{R^s}, \quad (9)$$

where  $R$  is the distance between ions involved in the transfer.

The parameter of transfer  $C_{DA}^{(s)}$  can also be calculated for dipole-dipole resonant interaction with the expression obtained by Dexter [12]:

$$C_{DA}^{(6)} = \frac{3h^4 c^4}{64\pi^5 n^4} \frac{Q_A}{\tau} S, \quad (10)$$

where  $S$  is the overlap integral of the normalized line shape functions for donor emission and acceptor absorption,  $\tau^{-1}$  is the spontaneous emission probability of the donor transition and  $Q_A$  is the integrated cross section of acceptor absorption.

## 4. Experimental results and discussion

### 4.1. Optical absorption and fluorescence spectra

The room-temperature absorption spectrum of a sample with 2.5 mol% of  $\text{Sm}^{3+}$  is shown in fig. 1. Transitions are assigned by comparison with the energy diagram of the free ions represented in fig. 2. The experimental  $f$  values obtained from eq. (1)

are given in table 1 and they have been used to determine the Judd-Ofelt parameters by a least squares fitting to eq. (2). The reduced matrix elements of the  $U^{(0)}$  and  $L + 2S$  operators given by Carnall and co-workers for  $\text{Sm}^{3+}$  [13,14] have been used in our calculations.

The results obtained for the Judd-Ofelt parameters are  $\Omega_2 = 0.68 \times 10^{-20}$ ,  $\Omega_4 = 3.77 \times 10^{-20}$  and  $\Omega_6 = 2.15 \times 10^{-20} \text{ cm}^2$ , with a RMS of  $4 \times 10^{-7}$ . The oscillator strengths calculated with these parameters are also listed in table 1.

Photoluminescence of  $\text{Sm}^{3+}$  ions has been measured. When any of the levels above  ${}^4G_{5/2}$  is excited there is a quick nonradiative relaxation to this fluorescent level and consequently the same emission spectrum is obtained with any of these excitations. In fig. 3, the complete emission spectrum obtained exciting in the 400 nm region is shown. The branching ratios for the different emissions from the  ${}^4G_{5/2}$  level have been obtained from the relative areas under the emission peaks. These values are given in table 2 together with those calculated using the Judd-Ofelt theory with the  $\Omega_i$  parameters derived from the absorption data. A reasonable agreement is obtained between calculated and experimental values.

The decay of the  ${}^4G_{5/2}$  luminescence after switching the excitation off has been also measured for different concentrations of  $\text{Sm}^{3+}$  (0.1, 1.5 and 2.5 mol%). For samples with 0.1 mol% of  $\text{Sm}^{3+}$ , a very good fitting of the decay curves to a single exponential is achieved, as shown in fig. 4. The obtained lifetime is 5.25 ms, in good agreement with the value calculated using the Judd-Ofelt theory and eq. (6) (5.66 ms). No temperature dependence of the lifetime between room temperature and liquid nitrogen temperature is observed within our experimental accuracy (<2%). This indicates that nonradiative transitions do not contribute to the relaxation of the  ${}^4G_{5/2}$  as expected because the wide energy gap between this level and the next one at lower energies.

### 4.2. Cross relaxation of $\text{Sm}^{3+}$ ions

For samples with 1.5 and 2.5 mol% of  $\text{Sm}^{3+}$ , the decay curves cannot be fitted to single exponentials.

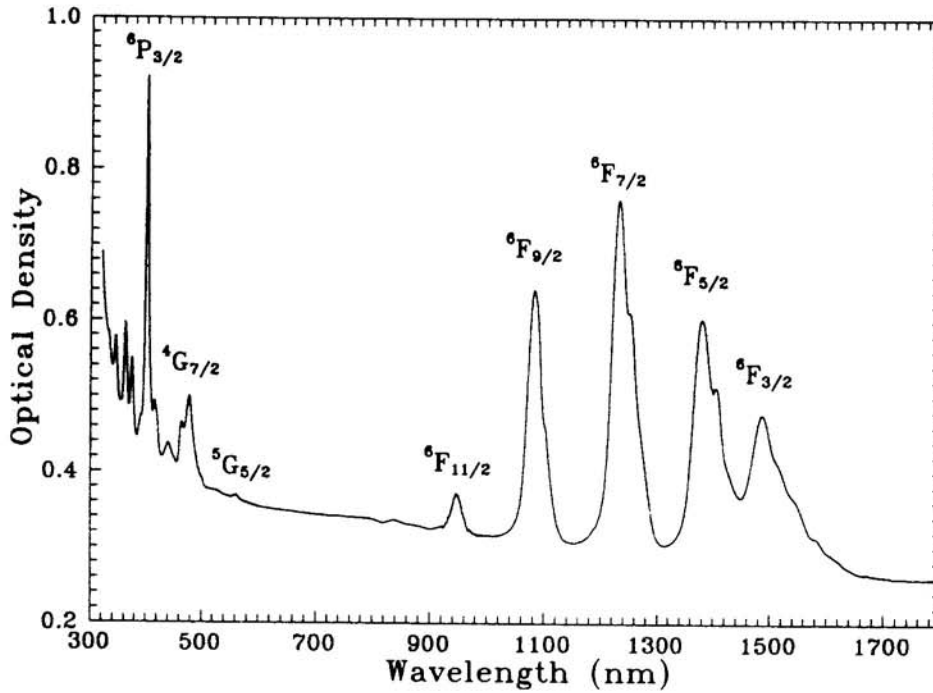


Fig. 1. Absorption spectrum at room temperature of 2.5 mol% of  $Sm^{3+}$  in fluorizincate glass. The transitions are from the  ${}^6H_{5/2}$  to the indicated levels.

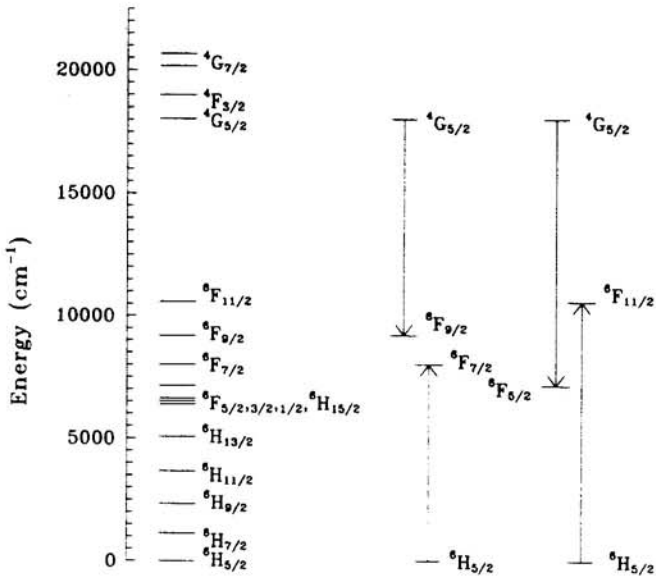


Fig. 2. Energy level diagram and the most important channels of cross relaxation of  $Sm^{3+}$  ions in fluorizincate glasses.

This is because the donor-acceptor energy transfer is important for these ion concentrations.

In order to determine the mechanisms involved, we begin by considering only cross relaxation. The best fits of the experimental decay results to eq. (8) are obtained for  $S = 6$  as shown in fig. 4. From this

Table 1

Experimental and calculated oscillator strengths for  $Sm^{3+}$  ( $10^{-8}$ ). All transitions are from the  ${}^6H_{5/2}$  level

Levels	Spectral region [nm]	$ZnF_2-CdF_2$	
		$f_{exp}$	$f_{cal}$
${}^6H_{15/2}, {}^6F_{1/2}, {}^6F_{3/2}, {}^6F_{5/2}$	1487	316	318
${}^6F_{7/2}$	1233	267	291
${}^6F_{9/2}$	1082	185	184
${}^6F_{11/2}$	948	31	29
${}^4G_{7/2}, {}^4I_{9/2}, {}^4M_{15/2}, {}^4I_{11/2}, {}^4I_{13/2}$	477	190	89
${}^4F_{5/2}, {}^4M_{17/2}, {}^4G_{9/2}, {}^4I_{15/2}$	439	30	13
$({}^6P, {}^4P)_{5/2}, {}^4L_{13/2}, {}^4F_{7/2}, {}^6P_{3/2}, {}^4K_{11/2}, {}^4L_{15/2}, {}^4G_{11/2}$	401	508	506
${}^4D_{1/2}, {}^6P_{7/2}, {}^4L_{17/2}, {}^4K_{13/2}, {}^4F_{9/2}$	373	82	117
${}^4D_{3/2}, ({}^4D, {}^6P)_{5/2}, {}^4H_{7/2}$	361	123	113
${}^4H_{9/2}, {}^4D_{7/2}, {}^4H_{11/2}$	344	60	63
${}^4H_{13/2}, {}^4G_{7/2}, {}^4G_{9/2}, {}^4G_{5/2}$	332	10	8
${}^4G_{11/2}, {}^2L_{15.2}, {}^4P_{3/2}$	317	42	42
${}^4P_{5/2}$	305	10	7

we conclude that in our case the dominant interaction for the cross relaxation of the  ${}^4G_{5/2}$  is dipole-dipole. The same conclusion has been obtained for  $Sm^{3+}$  ions in borate glasses [8] although

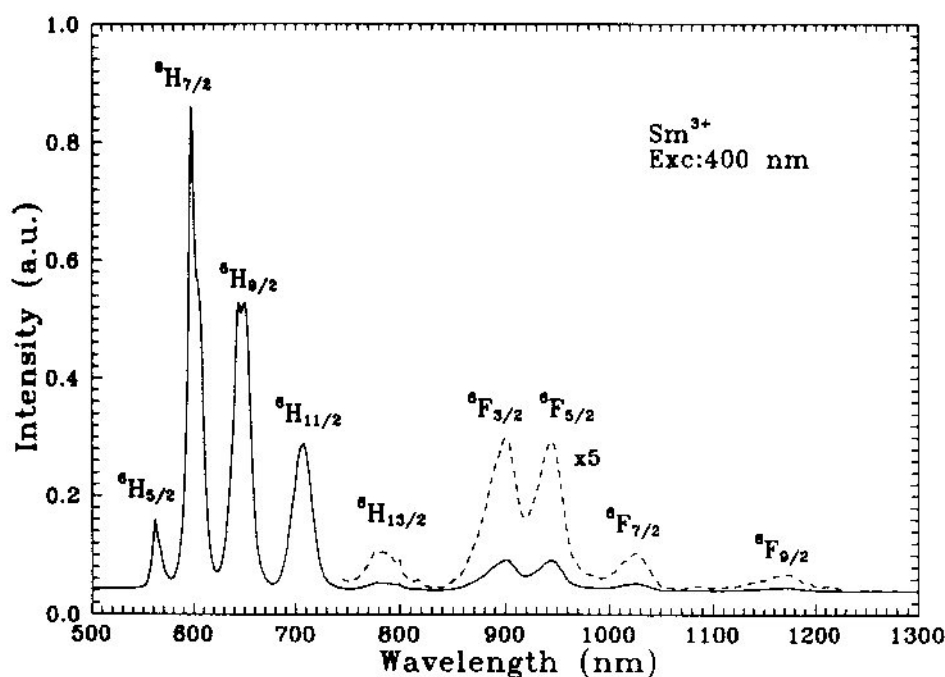


Fig. 3. Emission spectrum of 2.5 mol% of  $\text{Sm}^{3+}$  at room temperature. The transitions are from the  ${}^4\text{G}_{5/2}$  to the indicated levels.

Table 2  
Branching ratios for the  ${}^4\text{G}_{5/2}$  level of  $\text{Sm}^{3+}$  ions

Transition	$\lambda$ [nm]	$\text{ZnF}_2\text{-CdF}_2$	
		$\beta_{\text{cal}}$	$\beta_{\text{exp}}$
${}^4\text{G}_{5/2} \rightarrow {}^6\text{H}_{5/2}$	560	0.076 <sup>a)</sup>	0.044
${}^6\text{H}_{7/2}$	596	0.466	0.377
${}^6\text{H}_{9/2}$	642	0.275	0.312
${}^6\text{H}_{11/2}$	706	0.127	0.162
${}^6\text{H}_{13/2}$	785	0.014	0.011
${}^6\text{F}_{3/2}$	899	0.002	0.042
${}^6\text{F}_{5/2}$	943	0.024	0.036
${}^6\text{F}_{7/2}$	1026	0.012	0.009
${}^6\text{F}_{9/2}$	1163	0.003	0.007

<sup>a)</sup> Magnetic-dipole contribution.

in other cases dipole–quadrupole and even quadrupole–quadrupole interactions have been proposed [7,15,16]. The values obtained for  $C_{\text{DA}}^{(6)}$  in our glasses are  $5.3 \times 10^{-41}$  and  $4.4 \times 10^{-41} \text{ cm}^6 \text{ s}^{-1}$  for 2.5 and 1.5 mol% respectively.

The transfer parameter  $C_{\text{DA}}^{(6)}$  can also be calculated for dipole–dipole interaction using eq. (10) for every channel of cross relaxation from the  ${}^4\text{G}_{5/2}$

Table 3

Overlap integral  $S[(\text{cm}^{-1})^{-5}]$  and transfer parameter  $C_{\text{DA}}$  ( $\text{cm}^6 \text{ s}^{-1}$ ) for every channel of cross relaxation from the  ${}^4\text{G}_{5/2}$  level for  $\text{Sm}^{3+}$  ions

Transitions	$S (10^{-20})$	$C_{\text{DA}} (10^{-42})$
${}^4\text{G}_{5/2}, {}^6\text{H}_{5/2} \rightarrow {}^6\text{F}_{9/2}, {}^6\text{F}_{7/2}$	6.6	5.9
${}^4\text{G}_{5/2}, {}^6\text{H}_{5/2} \rightarrow {}^6\text{F}_{9/2}, {}^6\text{F}_{9/2}$	4.0	2.6
${}^4\text{G}_{5/2}, {}^6\text{H}_{5/2} \rightarrow {}^6\text{F}_{7/2}, {}^6\text{F}_{9/2}$	1.4	1.3
${}^4\text{G}_{5/2}, {}^6\text{H}_{5/2} \rightarrow {}^6\text{F}_{5/2}, {}^6\text{F}_{11/2}$	14.9	8.0

level. In table 3 the values of the overlap integrals and the calculated transfer parameters are given for the most important cross relaxation channels. It can be seen that the cross relaxation channel  ${}^4\text{G}_{5/2}, {}^6\text{H}_{5/2} \rightarrow {}^6\text{F}_{9/2}, {}^6\text{F}_{9/2}$  that has been proposed to be the dominant one in borate and germanate glasses [7,8] is not the most important one in our case, while the main cross relaxation channels seem to be  ${}^4\text{G}_{5/2}, {}^6\text{H}_{5/2} \rightarrow {}^6\text{F}_{5/2}, {}^6\text{F}_{11/2}$  and  ${}^4\text{G}_{5/2}, {}^6\text{H}_{5/2} \rightarrow {}^6\text{F}_{9/2}, {}^6\text{F}_{7/2}$ , they are shown in fig. 2.

The small energy shifts of the  $\text{Sm}^{3+}$  levels in different matrices seem to play an important role in the overlap integrals and consequently in the transfer processes that appear in each case.

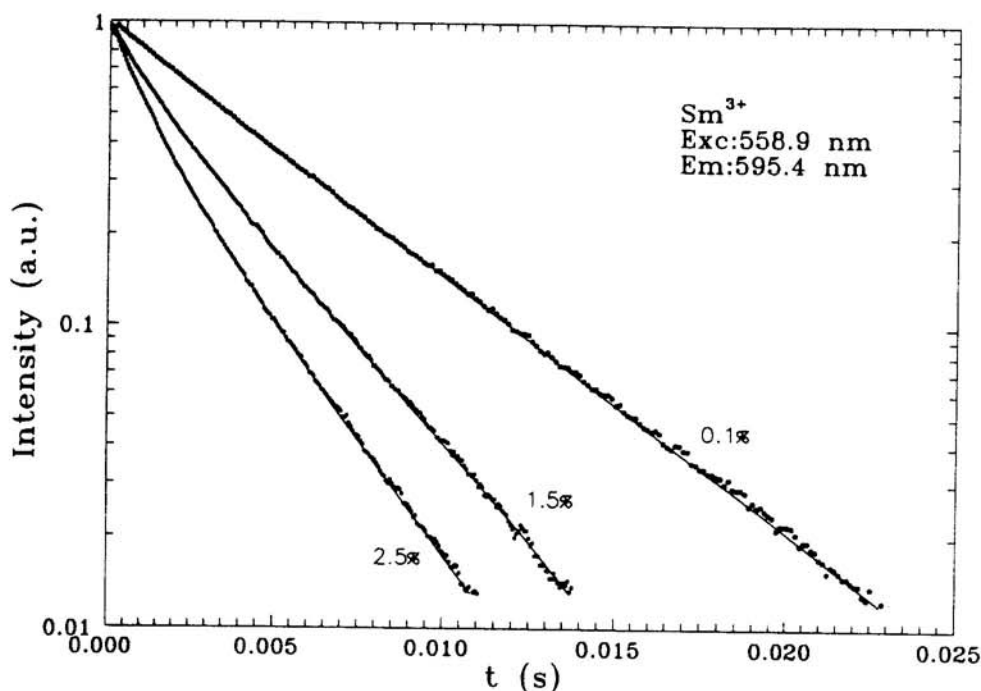


Fig. 4. Luminescence decays at room temperature in fluorizincate glasses with 0.1, 1.5 and 2.5 mol% of  $\text{Sm}^{3+}$ . The lines represent the best fits of the experimental results to eq. (8).

The sum of the transfer parameters (table 3) gives a total value of  $1.8 \times 10^{-41} \text{ cm}^6 \text{ s}^{-1}$  which is comparable with the experimental result obtained from the decay curves.

Finally, concerning the influence of energy migration, we want to mention that a very good fitting is achieved considering only cross relaxation, as shown in fig. 4. Moreover, the transfer parameter for migration  $C_{DD}$  calculated with the eq. (10) is  $9.4 \times 10^{-44} \text{ cm}^6 \text{ s}^{-1}$ . This value is too small as compared with those corresponding to cross relaxation and we can therefore conclude that migration does not play a relevant role in these processes.

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