Energy transfer between Eu^{3+} ions in calcium diborate glasses

Energy transfer between Eu^{3+} ions in calcium diborate glasses

V Lavín, I R Martín, U R Rodríguez-Mendoza and V D Rodríguez

Departamento de Física Fundamental y Experimental, Universidad de La Laguna, 38206 La Laguna, Tenerife, Spain

Abstract. The evolution of the $^5D_0 \rightarrow \, ^7F_0$ emission of Eu^{3+} ions in calcium diborate glasses has been analysed using time resolved fluorescence line narrowing measurements in order to give a complete view of the energy transfer processes between these ions. At low concentration (2.5 mol% of Eu$_2$O$_3$) and exciting within the high energy side of the inhomogeneous $^7F_0 \rightarrow \, ^5D_0$ absorption band, the luminescence spectrum mainly consists of a narrow resonant peak that repeats the exciting profile, indicating that the migration processes between Eu^{3+} ions within the $^5D_0$ level is not important. However, at higher concentrations (5 to 11.5 mol% of Eu$_2$O$_3$) the luminescence spectrum contains not only a narrow emission but also a broad band due to ions excited by energy transfer (background fluorescence), which for long times well reproduces the inhomogeneous profile. The temporal evolution of the narrow band fluorescence and the shape of the background fluorescence have been analysed using a previously proposed model. The purpose is to understand the dynamics involved in the energy transfer processes caused by the interaction between Eu^{3+} ions and the implications in their luminescence. A very good agreement with the experimental results is found taking into account an energy dependent quadrupole–quadrupole ($S = 10$) non-radiative energy transfer process assisted by a phonon from Eu^{3+} ions at high crystal field sites to ions at low crystal field sites. The temperature dependence of the energy transfer processes is analysed in the range from 13 to 60 K.

1. Introduction

Since the discovery of the laser in the 1960s, spectroscopic research in rare earth doped crystalline and amorphous materials has received great attention due to the possibility of using them in optical fibre communication technology, solid state lasers, light converters, TV phosphors etc [1, 2]. Rare earth doped glasses are of special interest because of the role of the inhomogeneous crystal field in their optical properties [3]. Because of the disordered nature of the media, there are different sites for the rare earth ions in the same matrix that generate broadened luminescence. The particular symmetry of the ion site and the nature of the bonds with the coordinating ions rule the optical properties of these active ions. This inhomogeneity is revealed by the luminescence spectra under site selective excitation [4–8].

On the other hand, when the distance between rare earth ions is short enough the interaction between them induces energy transfer processes. The quasi-resonant energy transfer between ions of the same species is called migration. This process can be analysed by time resolved fluorescence line narrowing (TRFLN), it being possible to obtain information about a particular subset of ions [9–16]. In this technique an inhomogeneously broadened absorption band is excited with a monochromatic pulsed tunable laser. Initially, a narrow emission spectrum is observed coming from ions with excitation energy resonant with the laser. As time goes on, broad background fluorescence can be observed due to ions excited by energy transfer. The

analysis of the fluorescence spectrum evolution in these experiments gives information about the different sites occupied by the ions in the matrix and the interaction between them.

Together with Nd^{3+}, the Eu^{3+} ion is the most frequent choice for a crystal field probe to test the ion–ion and ion–matrix interactions in crystals and glasses [17]. The main advantages are the simplicity of its energy level structure, the sensitivity shown by the luminescence to its surroundings and the fact that the ground state $^7F_0$ and the lowest emitting state $^5D_0$ are not split by the crystal field. Moreover, the relatively long lifetime of the $^5D_0$ level, between 1.6 and 2 ms in calcium diborate glasses [18], allows us to follow the temporal evolution of the fluorescence without difficulty.

The present authors proposed theoretical expressions for the evolution of the fluorescence in TRFLN experiments when there are migration processes assisted by a phonon [16]. These expressions were used to analyse the migration processes between Yb^{3+} ions in fluoroindate glasses. In this work, the energy transfer between different sites occupied by Eu^{3+} ions in calcium diborate glasses is investigated by TRFLN as a function of temperature in the range 13–60 K. Borate glasses are interesting matrices for this study because they present a relatively large broadening of the $^5D_0 \rightarrow \, ^7F_0$ transition, when compared to other oxides [9], resulting in a large energy mismatch between sites.

2. Experimental details

The samples used in this study were prepared with the following composition in mol%: $(66.66 - x/2)$ CaO, $(33.3 - x/2)$ B_2O_3 and x Eu_2O_3, with x equal to 2.5, 5 or 11.5. Reagent grade calcium carbonate and boric acid were heated in a platinum crucible for 12 hours at $900\,°C$. The mix was then crushed and the europium oxide was added. The final glass was obtained by melting at $1150\,°C$ for 2 hours and finally casting the melt into a slab on a stainless steel plate at room temperature.

Broad band emission spectra were obtained by exciting the samples with light from a 250 W incandescent lamp passed through a 0.25 m monochromator. Fluorescence was detected through a 0.25 m double monochromator with a photomultiplier. For TRFLN spectra a tunable dye laser operating with Rhodamine 6G, pumped by a Q-switched 532 nm frequency-doubled Nd-YAG laser, was used. The spectral linewidth was 0.15 cm^{-1} and the pulse width 5 ns. The time resolved fluorescence was recorded using the 0.25 m double grating monochromator with a maximum slit of 50 μm and a photomultiplier. In order to avoid the saturation of the detector by direct laser light, a mechanical chopper synchronized with the Q-switching was inserted between the sample and the monochromator. Finally, a digital storage oscilloscope controlled by a personal computer registered the signal. For low temperature measurements a helium continuous flow cryostat was used in the range from 13 to 60 K.

3. Theoretical background

From TRFLN the ratio $R(t, E_0)$ of the intensity in the narrow band I_R, coming from ions with energy E_0 excited resonantly, to the total intensity, which includes the background fluorescence I_B, can be obtained. This relation can be expressed as

$$R(t, E_0) = \frac{I_R}{I_R + I_B}. \tag{1}$$

Huber and Ching obtained a general theoretical approximation for $R(t)$ considering asymmetric transfer rates and depending on the energy mismatch between ions [19]. They also obtained an expression for the evolution of the background fluorescence.

In a previous paper the present authors evaluated the expressions given by Huber and Ching for the ratio $R(t, E_0)$ and the background fluorescence assuming a multipole interaction assisted by a phonon [16]. In this case, the transfer probability from ions with energy E_0 to ions with energy E is given by

$$W_{0R} = \frac{C_{DA}^{(S)}(E - E_0)}{R^S} \tag{2}$$

where $S = 6, 8, 10, \ldots$ depending on the interaction character (dipole–dipole, dipole–quadrupole, quadrupole–quadrupole, ...), R is the donor–acceptor distance and $C_{DA}^{(S)}(E - E_0)$ is the donor–acceptor energy transfer parameter whose dependence on the energy mismatch $(E - E_0)$ for processes with emission or absorption of a phonon is given by [20]

$$C_{DA}^{(S)}(E - E_0) \propto |E - E_0| \left[\frac{1}{\exp[|E - E_0|/KT]} + 1 \right] \qquad E \leqslant E_0$$

or

$$C_{DA}^{(S)}(E - E_0) \propto |E - E_0| \left[\frac{1}{\exp[|E - E_0|/KT]} \right] \qquad E \geqslant E_0. \tag{3}$$

The solution found by the authors for the quantity $R(t, E_0)$ can be expressed by [16]

$$R(t, E_0) = \exp[-\beta t^{3/S}] \tag{4}$$

with

$$\beta = C_A \frac{4\pi}{3} \Gamma\left(1 - \frac{3}{S}\right) \int [C_{DA}^{(S)}(E - E_0)]^{3/S} W_+^{(3/S)-1} p(E) \, dE \tag{5}$$

where

$$W_+ = 1 + \exp\left(\frac{E - E_0}{KT}\right) \tag{6}$$

and $p(E)$ is the normalized inhomogeneous line shape.

It must be emphasized that if the transfer rate is symmetric and independent of the energy mismatch between ions, the expressions proposed by Huber *et al* [19–21] can be obtained.

4. Results and discussion

The inhomogeneous excitation spectrum of the $^5D_0 \rightarrow {}^7F_0$ transition in calcium diborate glass with 11.5 mol% of Eu_2O_3, obtained detecting at 611 nm ($^5D_0 \rightarrow {}^7F_2$ emission) at 13 K, is presented in figure 1. The emission spectra from $^5D_0$ to the ground state $^7F_0$ with 2.5 and 11.5 mol% of Eu_2O_3 obtained under stationary broad band excitation at 395 nm ($^7F_0 \rightarrow {}^5L_6$ transition) and at 13 K are also shown in figure 1. Although the $^7F_0 \leftrightarrow {}^5D_0$ transitions are completely forbidden in the Judd–Ofelt theory [22, 23], where the intermediate coupling scheme is used, they are allowed if 'J-mixing' between ^7F_J levels becomes important or the symmetry of the crystal field acting on the active ion is low (C_S, C_n or C_{nv} symmetries) [24, 25]. The asymmetric, inhomogeneously broadened profiles observed for these transitions are due to the large variation in the local crystal field acting on the Eu^{3+} ions from site to site. An important shift of the emission band towards longer wavelengths with respect to the excitation spectrum is found. This shift increases markedly with the Eu^{3+} concentration while the width decreases. This effect is due to energy transfer processes towards the Eu^{3+} ions in the lowest crystal field sites, which result to be very efficient in the glass with 11.5 mol% of Eu_2O_3. A similar effect has also been observed in Yb^{3+} doped samples when the concentration was enlarged and radiative energy transfer between these ions was not important [26, 27].
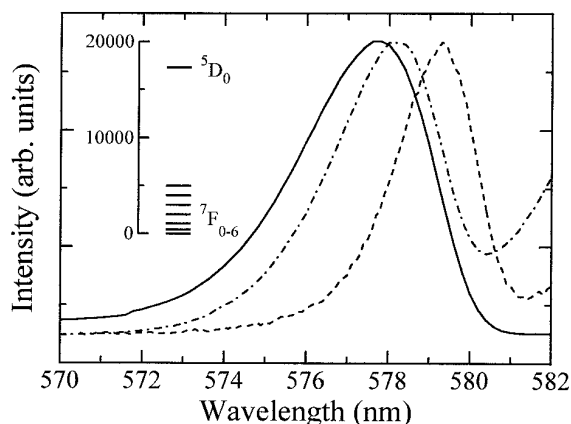
Figure 1. Inhomogeneous excitation (——— 11.5 mol%) and emission (— · — 2.5 mol% and — — — 11.5 mol%) spectra corresponding to the $^7F_0 \leftrightarrow {}^5D_0$ transitions obtained in calcium diborate glasses doped with Eu_2O_3 at 13 K. Low energy level diagram of Eu^{3+} ions.

The TRFLN spectra with a delay of 3 ms after excitation at the high energy side of the $^7F_0 \rightarrow {}^5D_0$ band in calcium diborate glasses with 2.5, 5 and 11.5 mol% of Eu_2O_3 at 13 K are shown in figure 2. For the glass with 2.5 mol% of Eu_2O_3 mainly resonant emission coming from the subset of ions initially excited is observed. This indicates that for this concentration the energy transfer processes between ions are not important. The same conclusion was obtained in the analysis of the energy transfer processes between Eu^{3+} (donors) and Ho^{3+} ions (acceptors) in calcium diborate glasses with 2.5 mol% of Eu_2O_3 [18]. In this codoped sample the luminescence decay curves from the $^5D_0$ level of the Eu^{3+} ions were well fitted to the Inokuti–Hirayama model [28], which does not take into account migration between donors. When the Eu^{3+} ion concentration is increased the background fluorescence becomes important. It can be seen in figure 2 that 3 ms after the laser pulse with 11.5 mol% of Eu_2O_3 the integrated background emission is higher than the resonant one.

TRFLN spectra obtained in calcium diborate glass with 11.5 mol% of Eu_2O_3 at 13 K with increasing delay after laser pulse at 576.55 nm are presented in figure 3. It is noteworthy that the background fluorescence spectra do not coincide with the inhomogeneous excitation spectrum in figure 1. Although the excitation is carried out at 576.55 nm, close to the maximum of the excitation spectrum, the background fluorescence is appreciable only at the long wavelength side of the excitation. Moreover, the maximum of the fluorescence spectra is shifted towards long wavelength with respect to the excitation spectrum. This indicates that the transfer between the Eu^{3+} ions is asymmetric, the processes with emission of phonons are more probable than those with absorption of phonons and the transfer furthermore depends on the energy mismatch between donors and acceptors ions. On these conditions equation (4), proposed by the authors, is expected to be adequate to describe the temporal evolution of the ratio $R(t, E_0)$. On the other hand, when the delay increases a shift towards longer wavelengths of the background fluorescence is observed; this is a consequence of successive energy transfer from the acceptors to other Eu^{3+} ions. As a result, the background fluorescence tends to resemble the $^5D_0 \rightarrow {}^7F_0$ inhomogeneous emission spectrum obtained under stationary broad band excitation. Similar results have been obtained exciting at different wavelengths within the $^7F_0 \rightarrow {}^5D_0$ inhomogeneous band at 13 K. In all the cases the transfer rate is asymmetric and energy dependent.
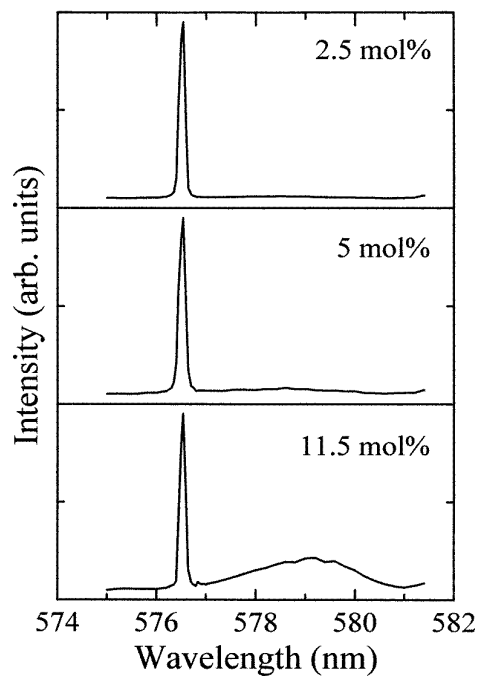
Figure 2. ^{5}D$_0$ → ^{7}F$_0$ TRFLN spectra in calcium diborate glasses doped with 2.5, 5 and 11.5 mol% of Eu$_2$O$_3$ at 13 K with a delay of 3 ms after laser excitation at 576.55 nm.

The ratio $R(t, E_0)$, given by equation (1), has been calculated from TRFLN measurements. The values obtained for this parameter with laser excitation at 576.55 nm are presented in figure 4 as a function of delay time for different temperatures in 11.5 mol% of Eu$_2$O$_3$ doped glass. It is found that values for $R(t, E_0)$ of 0.5 (i.e. the background emission is equal to the
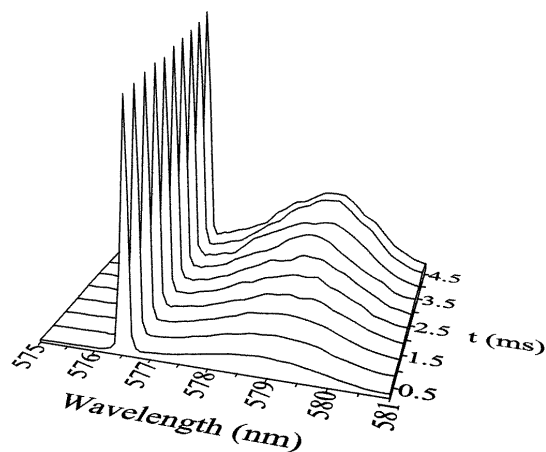

Figure 3. ^{5}D$_0$ → ^{7}F$_0$ TRFLN spectra obtained in calcium diborate glass doped with 11.5 mol% of Eu$_2$O$_3$ at 13 K versus delay after laser pulse at 576.55 nm. Spectra have been normalized to the intensity of the resonant emission.

resonant emission) are obtained 0.5 ms after the laser pulse in the glass with 11.5 mol% of Eu_2O_3 at 13 K. Comparing with results for Yb^{3+} [16], it would be noticed that similar values for $R(t, E_0)$ were obtained with a relatively low concentration of 0.75 mol% of YbF_3. This is due to the low probability of the forbidden $^5D_0 \leftrightarrow {}^7F_0$ transitions, involved in the energy transfer between Eu^{3+} ions, compared with the probability of the transitions $^2F_{7/2} \leftrightarrow {}^2F_{5/2}$ in the Yb^{3+} ions. Therefore, relatively high concentrations of Eu^{3+} ions are necessary in order to study energy transfer between them.
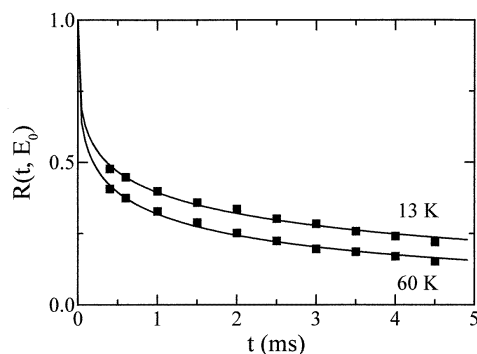

Figure 4. Values obtained for $R(t, E_0)$ as a function of delay time with laser excitation at 576.55 nm at 13 and 60 K in calcium diborate glass doped with 11.5 mol% of Eu_2O_3. The solid lines correspond to the fits to equation (4).

The fits of $R(t, E_0)$ to equation (4) are also included in this figure. The values calculated for S and β from these fits as a function of the temperature exciting at 576.55 nm are included in table 1. All the values obtained for S are close to 10, indicating a dominant quadrupole–quadrupole character for the interaction giving energy transfer in this glass. With different excitation wavelength the best fit was also obtained for a quadrupole–quadrupole interaction. In other glasses a dipole–dipole mechanism has been proposed [9, 12, 15], except in the study of Alimov *et al* [29] that suggested a quadrupolar mechanism.

Table 1. Values obtained for S and β at different temperatures in a calcium diborate glass doped with 11.5 mol% of Eu_2O_3 and laser excitation at 576.55 nm.

T (K)	S	β $(s^{-3/8})$
13	9.6	8.03
20	9.7	8.28
30	10	8.54
40	9.8	8.70
50	10.1	9.06
60	9.9	9.28

In order to understand the quadrupole–quadrupole character of the interaction, it would be taken into account that, when the dipole transitions are forbidden, the dipole–quadrupole or the quadrupole–quadrupole interactions can be dominant in the transfer at enough short distance between ions [30]. This is the case of the $^5D_0 \leftrightarrow {}^7F_0$ transitions of Eu^{3+} ions and, moreover, the energy transfer is analysed in glasses with relatively high concentration of Eu^{3+} ions, i.e. with short separation between them.

The parameter β has been obtained from fits of experimental values of $R(t, E_0)$ to equation (4) for different temperatures and excitation wavelengths. The results in the

temperature range from 13 to 60 K and with excitation at 576.55 nm are presented in figure 5. The fit of the temperature dependence of β to equation (5) is also included in this figure taking $S = 10$, the inhomogeneous line shape $p(E)$ given by the normalized excitation spectrum and considering processes with emission of a phonon with energy $|E - E_0|$. From the fit the energy transfer parameter $C_{DA}^{(S)}(E - E_0)$ is calculated. In order to compare the transfer probability between Eu³⁺ ions with results for other ions, which can have other multipole interaction character, the critical radius can be calculated from the equation

$$\frac{1}{\tau} = \frac{C_{DA}^{(S)}}{(R_C)^S} \tag{7}$$

i.e., the critical radius is the distance between ions for which the energy transfer probability coincides with the radiative decay probability. For a energy mismatch $|E - E_0|$ of 30 cm⁻¹, corresponding to the mismatch between the ions excited at 576.55 nm and the maximum of the excitation band to the ⁵D₀ level, the calculated critical radius is 4.2 Å. Meanwhile, for the couple Eu³⁺–Ho³⁺ the value calculated with data of [18] for the same excitation wavelength is 7.5 Å. For the migration between Yb³⁺ ions with the same energy mismatch of 30 cm⁻¹, from data of [16] a critical radius of 13.7 Å is obtained, using the proposed model. These parameters for energy transfer are summarized in table 2. The relatively low critical radii for migration between Eu³⁺ ions could be expected due to the low probability of the transition among the ⁵D₀ and ⁷F₀ levels.
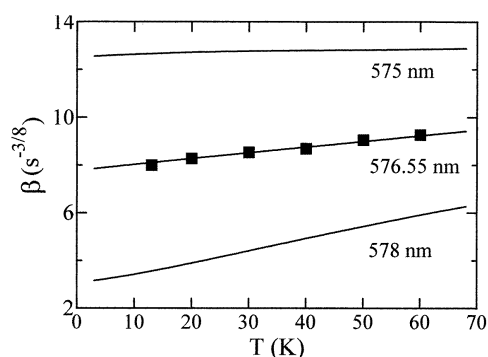

Figure 5. Temperature dependence of β (■) in calcium diborate glass with 11.5 mol% of Eu₂O₃ with laser excitation at 576.55 nm. The solid line corresponds to the fit to equation (5) for $S = 10$. Calculated curves for excitation at 575 and 578 nm are also included to show the expected dependence of β on the excitation wavelength.

Table 2. Energy transfer parameters for different couples of ions. The radiative donor lifetimes are also shown.

	S	τ (ms)	$C_{DA}^{(S)}$ (cm^S s⁻¹)	R_C (Å)
Eu³⁺–Eu³⁺	10	1.8	9.5×10^{-72}	4.2
Eu³⁺–Ho³⁺	6	1.8	1.0×10^{-40}	7.5
Yb³⁺–Yb³⁺	8	1.55	8.1×10^{-53}	13.7

The temperature dependence obtained from the proposed equation (5) for the parameter β under excitation at 575 and 578 nm is also shown in figure 5. With excitation wavelength close to the maximum of the excitation spectrum at 577.5 nm, the energy of the emitted phonons is comparable to KT and then β depends appreciably on T. At shorter excitation wavelengths,
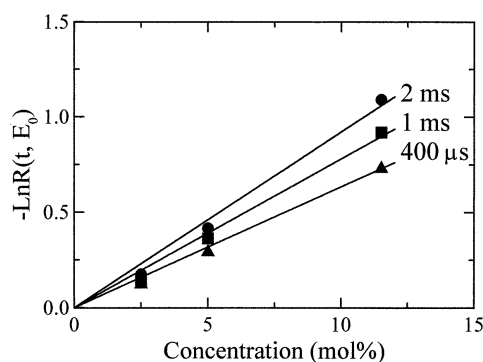
Figure 6. Dependence of $R(t, E_0)$ on the Eu_2O_3 concentration for the indicated delays after excitation pulsed at 576.55 nm.

with $|E - E_0| \gg KT$, a nearly temperature independent transfer rate would be expected as can be seen in figure 5 for excitation at 575 nm. This would be the case of the results obtained by Balda *et al* in fluorophosphate glasses at 77 K [15].

From equation (5) a linear dependence of the parameter β on the concentration is obtained for any kind of multipole interaction. This result is tested in figure 6 where $\mathrm{Ln}[R(t, E_0)]$ is shown as a function of Eu_2O_3 concentration for different fixed delays, obtaining the expected linear behaviour.

5. Conclusions

The energy migration between Eu^{3+} ions after excitation to the $^5D_0$ level has been studied by TRFLN in calcium diborate glasses. From the experimental results it is found that the energy transfer is asymmetric and energy dependent. These results are well fitted by the equations previously proposed by the present authors to analyse this kind of process in Yb^{3+} doped fluoride glasses. The dominant interaction for Eu^{3+} ions is quadrupole–quadrupole while for Yb^{3+} ions it was dipole–quadrupole. As would be expected, a relatively low critical radius for the migration between Eu^{3+} ions is obtained. The transfer rate between Eu^{3+} ions is temperature dependent and the results are well accounted for by the proposed equations for energy mismatch comparable to KT.

Acknowledgments

References

[1] Kaminskii A A 1991 *Ann. Phys. Fr.* **16** 639
[2] Blasse G and Grabmaier B C 1994 *Luminescent Materials* (Berlin: Springer)
[3] Weber M J 1986 *Laser Spectroscopy of Solids* ed W M Yen and P M Selzer (Berlin: Springer) p 189
[4] Brecher C and Riseberg L A 1980 *J. Non-Cryst. Solids* **40** 469
[5] Basiev T T, Malyshev V A and Przhevuskii A K 1987 *Spectroscopy of Solids Containing Rare-Earth Ions* ed A A Kapliansky and R M Macfarlane (Amsterdam: North-Holland) p 303

[6] Capobianco J A, Prouxl P P, Raspa N, Simkin D J and Krashkevich D 1989 *J. Chem. Phys.* **90** 2856
 [7] Balda R, Fernández J, Eilers H and Yen W M 1994 *J. Lumin.* **59** 81
 [8] Lavín V, Rodríguez V D, Martín I R and Rodríguez-Mendoza U R 1997 *J. Lumin.* **72–74** 437
 [9] Motegui N and Shionoya S 1973 *J. Lumin.* **8** 1
[10] Brawer S A and Weber M J 1979 *Appl. Phys. Lett.* **35** 31
[11] Yen W M 1979 *J. Lumin.* **18/19** 639
[12] Morgan J R and El-Sayed M A 1981 *J. Phys. Chem.* **85** 3566
[13] Gang X, Boulon G and Powell R C 1983 *J. Chem. Phys.* **78** 4374
[14] Gang X and Powell R C 1985 *J. Appl. Phys.* **57** 1299
[15] Balda R, Fernández J, Adam J L and Arriandiaga M A 1996 *Phys. Rev.* B **54** 12 076
[16] Martín I R, Rodríguez V D, Rodríguez-Mendoza U R and Lavín V 1998 *Phys. Rev.* B **57** 3396
[17] Görller-Walrand G and Binnemans K 1996 *Handbook on the Physics and Chemistry of Rare Earths* vol 23,
       ed K A Gschneidner Jr and L Eyring (Amsterdam: North-Holland) ch 155, p 121
[18] Rodríguez V D, Lavín V, Rodríguez-Mendoza U R, Martín I R and Nuñez P 1995 *Radiat. Eff. Defects Solids*
       135 105
[19] Huber D L and Ching W Y 1978 *Phys. Rev.* B **18** 5320
[20] Holstein T, Lyo S K and Orbach R 1986 *Laser Spectroscopy of Solids* ed W M Yen and P M Selzer (Berlin:
       Springer) p 39
[21] Huber D L, Hamilton D S and Barnett B 1977 *Phys. Rev.* B **16** 4642
[22] Judd B R 1962 *Phys. Rev.* **127** 750
[23] Ofelt G S 1962 *J. Chem. Phys.* **37** 511
[24] Nishimura G and Kushida T 1991 *J. Phys. Soc. Japan* **60** 683
[25] Porcher P and Caro P 1980 *J. Lumin.* **21** 207
[26] Ageeva L E, Przhevuskii A K, Tolstoi M N and Shapovalov V N 1974 *Sov. Phys.–Solid State* **16** 1082
[27] Savostyanov V A, Malyshev V A, Przhevuskii A K and Troshin A S 1979 *Opt. Spectrosc.* **47** 295
[28] Inokuti M and Hirayama F 1965 *J. Chem. Phys.* **43** 1978
[29] Alimov O K, Basiev T T, Voron'ko Yu K, Gaigerova L S and Dmitryuk A V 1977 *Sov. Phys.–JETP* **45** 690
[30] Di Bartolo B 1984 *Energy Transfer among Ions in Solids in Energy Transfer Processes in Condensed Matter*
       ed B Di Bartolo (New York: Plenum) p 103