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Cr^{3+}–Tm^{3+} energy transfer in alkali silicate glasses

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Abstract

Optical absorption and emission spectra of alkaline silicate glasses doped with Cr^{3+} and Tm^{3+} ions show overlap of the Cr^{3+} emission with the Tm^{3+} absorption, indicating the possibility of energy transfer processes between these ions. Radiative and non-radiative energy transfer from optically excited Cr^{3+} to Tm^{3+} has been studied in three different alkaline disilicate glasses as a function of Tm^{3+} concentration. The energy transfer parameter C_{DA} and the transfer efficiency η_t involved in the non-radiative energy transfer process have been obtained in the 13–300 K temperature range from the analysis of the Cr^{3+} emission decay curves. The existence of a site distribution for Cr^{3+} ions causes non-exponential decay curves even in glasses without Tm^{3+} ions. These curves have been fitted to a modified Inokuti–Hirayama model considering a Gaussian distribution for the Cr^{3+} ions. The results obtained are consistent with an electric dipole interaction mechanism. High transfer efficiencies, close to one, have been found in glasses codoped with 0.1 mol% Cr^{3+} and 2 mol% Tm^{3+}.

Keywords: Cr–Tm; Silicate glasses; Energy transfer

1. Introduction

The Cr^{3+} ion is widely used in the research and development of solid-state lasers. It is incorporated in the solid matrix as a sensitiser of rare earth ions emission in order to increase the optical pumping efficiency [1]. The Cr^{3+} ion is especially interesting as a donor in energy transfer based devices. On one hand, the existence of two broad and intense absorption bands in the visible region allows the efficient absorption of energy from excitation lamps. On the other hand, the emission of the Cr^{3+} ions in the red–NIR region can be used in codoped samples, i.e. with lanthanides, to induce energy transfer processes.

Alkaline silicate glasses are an interesting host for Cr^{3+} ions because of the high emission efficiency observed in lithium silicate glasses [2]. In this work, a study of the energy transfer processes in glasses codoped with Tm^{3+} is presented. The radiative energy transfer is analysed from the emission spectra whereas the non-radiative transfer is analysed using a generalization of the Inokuti–Hirayama model previously proposed by the authors [3,4].

2. Experimental

Samples used in this work were prepared with starting composition (in mol%) $(66-y/2)$ SiO_2, $(33-y/2)$ M_2O (M stands for Li, Na or K), 1 As_2O_3 with 0.1 Cr_2O_3 and yTm_2O_3 ($y=0.1$, 0.5 and 2) [5]. The reason to add As_2O_3 was to reduce Cr^{6+} to Cr^{3+}, also with this purpose an argon atmosphere was used in the furnace and the glasses were annealed in a graphite mold. The glasses will be denoted DSM (M=Li, Na or K). Absorption spectra were measured with a Perkin-Elmer Lambda 9 double spectrophotometer. For time resolved emission spectra and decay curves a tuneable dye laser operating with DCM dye, pumped at 532 nm by Q-switched frequency doubled Nd-YAG laser, was used. Fluorescence was detected through a Spex 0.25 m double monochromator with a photomultiplier. The sample temperature was varied between 13 and 300 K with a helium continuous flow cryostat.

3. Results and discussion

The occurrence of energy transfer processes from Cr^{3+} to Tm^{3+} ions is expected due to the overlap observed

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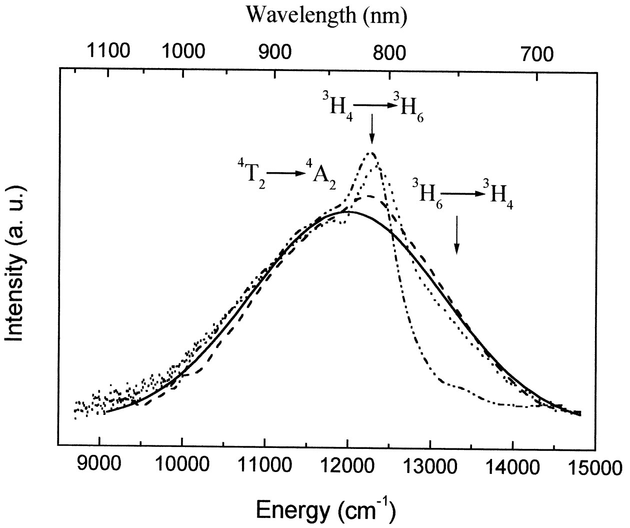

Fig. 1. Emission spectra of DSLi glasses with 0.1 mol% Cr_2O_3 and different concentrations of Tm_2O_3 (——— 0 mol%; – – – 0.1 mol%; · · · 0.5 mol% and – · · – · · – 2 mol%) exciting the Cr^{3+} ions at 15 625 cm^{-1} (640 nm) at room temperature.

between the emission band $^4T_2(t_2^3e) \rightarrow {}^4A_2(t_2^3)$ of the Cr^{3+} ion and the absorption band $^3H_6 \rightarrow {}^3H_4$ of the Tm^{3+} ions. Radiative and non-radiative contributions to the energy transfer will be considered.

3.1. Radiative energy transfer

The radiative energy transfer can be analysed from the emission spectra of the Cr^{3+} ions in the codoped glasses (Fig. 1). In these spectra a decrease of the Cr^{3+} emission can be observed at the energy range from 12 500 cm^{-1} (800 nm) to 14 300 cm^{-1} (700 nm), where the $^3H_6 \rightarrow {}^3H_4$ absorption of the Tm^{3+} ions occurs. Moreover, the emission about 12 350 cm^{-1} (810 nm), due to the $^3H_4 \rightarrow {}^3H_6$ emission of the Tm^{3+} ions, increases with the concentration of these ions. Thus, these results can be interpreted considering a radiative energy transfer process in which Tm^{3+} ions are excited by absorption of photons emitted by Cr^{3+} ions. The percentage of photons emitted by Cr^{3+} ions which is absorbed by Tm^{3+} ions has been calculated from the ratio of the decrease in the Cr^{3+} emission spectrum ($^4T_2 \rightarrow {}^4A_2$) in the codoped glass, due to the Tm^{3+} absorption ($^3H_6 \rightarrow {}^3H_4$), to the total Cr^{3+} emission, obtained from the single Cr^{3+} doped glass; the values obtained are presented in Table 1. Results for the samples codoped with 2 mol% of Tm_2O_3 are relatively high, 20% of the Cr^{3+} emission is absorbed by the Tm^{3+} ions, but the effect is appreciable even at a low concentration of 0.1 mol% of Tm_2O_3. It would be remarked that these results are only estimative because they depend on the geometry of the sample and the experimental excitation and detection set-up.

Table 1
Percentage of photons emitted by Cr^{3+} ions that is absorbed by Tm^{3+} ions in codoped glasses

	Tm_2O_3 (mol%)		
	0.1	0.5	2
DSLi	3	9	18
DSNa	2	12	20
DSK	2	6	–

3.2. Non-radiative energy transfer

The existence of non-radiative energy transfer $Cr^{3+} \rightarrow Tm^{3+}$ is evidenced by the comparison of the Cr^{3+} emission decay curves of glasses codoped with different Tm^{3+} concentration. In Fig. 2, the mean lifetime of Cr^{3+} ions (the decays are non-exponential) in the three studied disilicate glasses as a function of temperature and Tm_2O_3 concentration is shown; measurements were made detecting the emission of the Cr^{3+} ions at about 850 nm. The decay rate increases with temperature and with Tm_2O_3 concentration.

The energy transfer parameter C_{DA} has been calculated using two independent methods, the Dexter formula [6] and the generalised Inokuti–Hirayama model, fitting the decay curves assuming a distribution of sites for the Cr^{3+} ions [4], results are shown in Fig. 3. In both cases, a dipole–dipole mechanism for the interaction between Cr^{3+} and Tm^{3+} ions has been assumed, the transfer probability

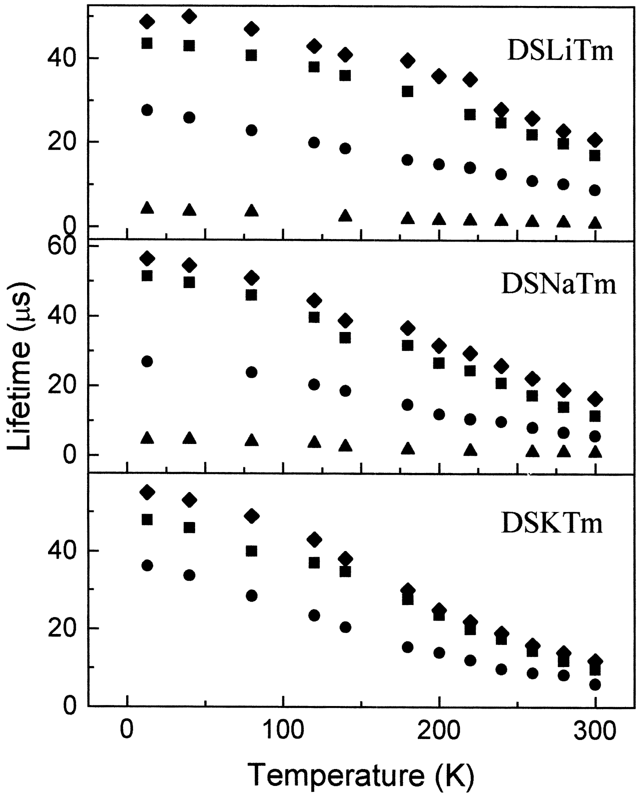

Fig. 2. Mean lifetime of Cr^{3+} emission as a function of temperature for different concentrations of Tm_2O_3 (♦ 0%, ■ 0.1%, ● 0.5% and ▲ 2%) for codoped alkaline disilicate glasses.

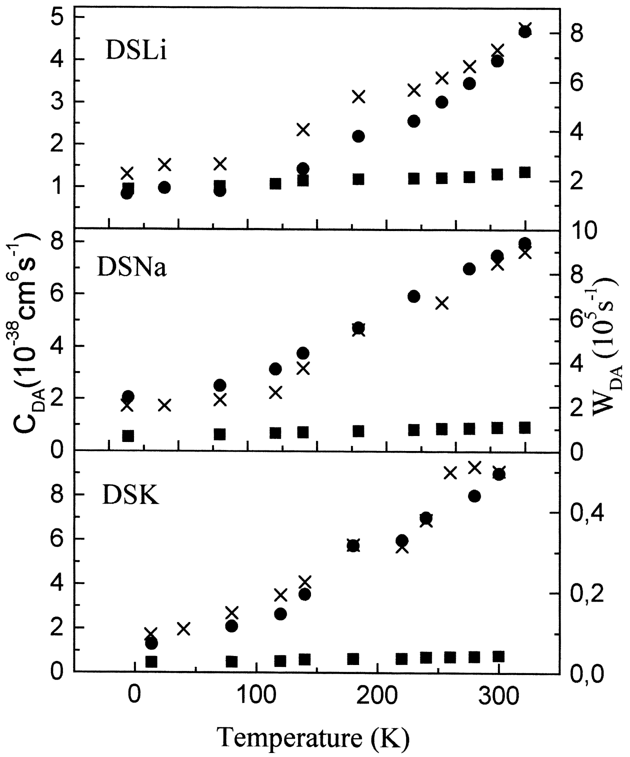

Fig. 3. Transfer efficiency W_{DA} (x) and energy transfer parameter C_{DA} as a function of temperature for alkaline disilicate glasses codoped with 0.1 mol% Cr_2O_3 and 2 mol% Tm_2O_3 calculated from the expression of Dexter (■) and from the generalised Inokuti–Hirayama model (●).

between two ions separated at a distance R is then given by

$$W_{DA}(R) = \frac{C_{DA}}{R^6} \quad (1)$$

The mean value of the transfer probability W_{DA} can be calculated from the experimental mean lifetimes by

$$W_{DA} = \frac{1}{\tau_{Cr-Tm}} - \frac{1}{\tau_{Cr}} \quad (2)$$

where τ_{Cr-Tm} is the mean lifetime in the codoped glasses and τ_{Cr} in the single doped ones. Results as a function of temperature are included in Fig. 3 for comparison with the temperature dependence of the energy transfer parameter C_{DA}.

The values obtained for the energy transfer parameter C_{DA} from the fitting of the decay curves to the generalised Inokuti–Hirayama model are similar to those from the Dexter formula at low temperatures but they are appreciably higher from 100 K to room temperature (Fig. 3). The results of the fitting present a temperature dependence similar to the mean transfer probability W_{DA}.

From the energy transfer parameter C_{DA} and the transfer probability W_{DA}, the donor–acceptor mean distance $\langle R \rangle$ can be obtained by

$$\langle R \rangle = \left(\frac{C_{DA}}{W_{DA}}\right)^{1/6} \quad (3)$$

whereas, the critical radius R_0, defined as the distance for which the transfer probability equals the inverse of the intrinsic lifetime τ_{Cr} [6], is given by

$$R_0 = (C_{DA} \cdot \tau_{Cr})^{1/6} \quad (4)$$

Values obtained for the Li, Na and K disilicate glasses at room temperature are presented in Table 2, using the energy transfer parameters calculated from the Dexter formula and the fits of the decay curves to the generalised Inokuti–Hirayama model. These results show that the critical radius R_0 is similar to the donor–acceptor mean distance for 0.5 mol% Tm_2O_3, predicting an efficient energy transfer $Cr^{3+} \rightarrow Tm^{3+}$ for higher concentration that is in agreement with the experimental observation. For DSK glass, R_0 is slightly higher, indicating probable lower transfer efficiency compared to the other glasses.

On the other hand, it is useful to calculate the non-radiative transfer efficiency η_t for the Cr–Tm system given by

$$\eta_t = W_{DA} \cdot \tau_{Cr-Tm} \quad (5)$$

The behaviour of this parameter with temperature is shown in Fig. 4. There is no important variation because the transfer probability W_{DA} increases with temperature in the same way τ_{Cr-Tm} decreases. Results show that the non-radiative transfer efficiency increases with the concentration of Tm_2O_3, reaching values close to one for glasses doped with 2 mol% Tm_2O_3. For the DSK glass

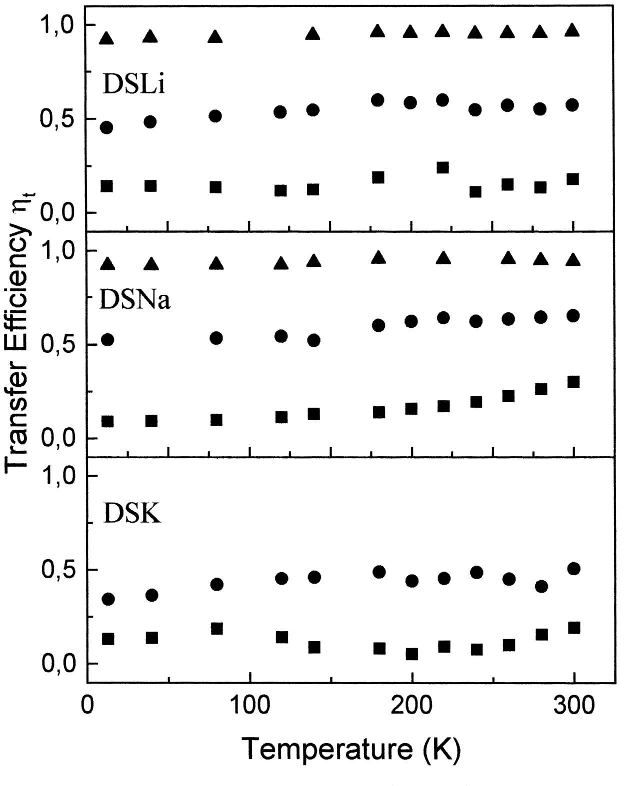

Fig. 4. Non-radiative transfer efficiency η_t $Cr^{3+} \rightarrow Tm^{3+}$ as a function of temperature for alkaline disilicate glasses codoped with 0.1 (■), 0.5 (●) and 2 mol% (▲) Tm_2O_3.

Table 2
Donor–acceptor mean distance (Å) for different alkaline disilicate codoped glasses calculated from Eq. (3) using the values of C_{DA} obtained from the Dexter formula (R_{Dex}) or from the fits of the decay curves to the generalised Inokuti–Hirayama model (R_{Inok}). The critical radii are also shown

TA	Tm_2O_3 (mol%)	R_{Dex} (Å)	R_{Inok} (Å)	$R_{0\text{-Dex}}$ (Å)	$R_{0\text{-Inok}}$ (Å)
DSLi	0.1	10.9	14		
	0.5	7.8	9.9	8.0	9.7
	2	4.8	6.1		
DSNa	0.1	12.2	17.4		
	0.5	6.8	9.6	7.3	10.1
	2	4.7	6.6		
DSK	0.1	11.8	17.6		
	0.5	7.0	9.7	6.9	9.3

with a concentration of 0.5 mol% Tm_2O_3, η_t is lower than in the other corresponding glasses; this result would be expected from data in Table 2.

Finally, it would be taken into account that, although the transfer efficiency increases with Tm^{3+} concentration, the appearance of energy transfer processes between Tm^{3+} ions for high concentration, such as diffusion and cross relaxation, decreases the emission from the $^3H_4$ level while the $^3F_4 \rightarrow {}^3H_6$ emission at 1800 nm increases [7].

4. Conclusions

The system Cr–Tm has high transfer efficiency in alkaline disilicate glasses, with radiative and non-radiative contributions. For 0.1 mol% Cr^{3+}, with a moderate concentration of 2 mol% Tm^{3+}, a transfer efficiency close to one is reached. The dynamics of the transfer process is well described by a generalization of the Inokuti–Hirayama model proposed by the authors that takes into account the site distribution of the Cr^{3+} ions.

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