ELSEVIER

Journal of Alloys and Compounds 275–277 (1998) 430–434

Journal of ALLOYS AND COMPOUNDS

Saturation effect on multiphonon relaxation rates

F. Pellé[a,b,*], N. Gardant[a,b], F. Auzel[a,b], Groupe d'Optique des Terres Rares

[a]*LPCM - UPR 211 (CNRS), 1 Pl. A. Briand F 92195 Meudon cedex, France*
[b]*DTD-BAG CNET, 196 Av. H. Ravera 92225 Bagneux, France*

Abstract

Fluorescence decay time of resonantly excited RE multiplets were recorded as a function of excitation power density in different glass hosts. The multiphonon nonradiative relaxation rates are reduced at high excited state concentration for large energy gaps. The results are analysed in a statistical approach and the observed phonon bottleneck effect related to an accepting mode saturation. At high excited state density, several ions lying in the phonon diffusion volume simultaneously fill the common accepting mode set of the host. The critical distance below which excited ions share a common phonon bath is related to the phonon diffusion length l_c in the host. Theoretical fit of experimental data allows the deduction of l_c. The results are compared with the phonon mean free path in the host independently derived from sound velocity measurements and estimation of thermal conductivity and heat capacity of the investigated glasses. © 1998 Elsevier Science S.A.

Keywords: Multiphonon; Glasses; Rare Earth ions; Processes

1. Introduction

The different nonradiative pathways of electronic excitation and especially nonradiative relaxation by multiphonon processes in Rare-Earth (RE) doped systems are quite well understood and several theories based on different approaches have been developed to solve the N^{th}-phonon nonradiative decay probability. Except for small energy gaps, the well-known exponential gap law [1] can describe the multiphonon relaxation rates dependence with the process order in a given host. However, excitation through high peak power laser sources providing high excited state concentrations allows the observation of the new aspects of multiphonon relaxation processes. As an example, generation of laser-like short emission pulses has recently been obtained above a pumping threshold with $NdCl_3$ hydrated powders [2]. In this experiment, the observed radiative rate exceeds the nonradiative one by two orders of magnitude. Nonlinear effects have been ruled out; this behaviour seems then to be related to the high excited state density provided by the excitation source. On the other hand, for high excitation powers, we have already observed a saturation effect in the multiphonon process in an Yb^{3+} doped borate glass [3,4] and other ions in germanate glass have been presented. A model was proposed to analyse, in a statistical approach, the observed effect [5]. In this paper, a study of the excited state population density effect on multiphonon radiationless processes of RE excited multiplets for different glasses with different highest phonon energy is reported. The model we propose for this kind of bottleneck effect seems quite general in glasses. Furthermore, our model should give enlightenment to the laser-like emission of $NdCl_3$ hydrated powder.

2. Experimental results

To investigate the effect of excited state population density on the exponential energy gap law, fluorescence decay of Er^{3+} ($^4S_{3/2}$), Er^{3+} ($^4I_{11/2}$), Tm^{3+} ($^3H_4$) and Nd^{3+} ($^4F_{3/2}$) states has been recorded as a function of excitation power. These measurements were performed for each selected multiplet in several glass hosts whose compositions were chosen in order to change the phonon cut-off frequency which determines the multiphonon order (N): ZBLAN ($\hbar\omega \approx 500$ cm^{-1}), tellurite ($\hbar\omega \approx 800$ cm^{-1}), germanate ($\hbar\omega \approx 900$ cm^{-1}), phosphate ($\hbar\omega \approx 1100$ cm^{-1}). To avoid contribution from interactions or energy transfers between RE ions to the total decay rate of the excited multiplet, the RE concentration was kept at a low level (<0.2 at.%) for all glasses except phosphate which exhibits a high phonon cut-off frequency resulting in a low radiative quantum efficiency of studied multiplets. In this case, experimental results were obtained with 2 at.% doped

*Corresponding author.

PII: S0925-8388(98)00362-4

glasses and will only be considered in a qualitative way. The nonradiative decays were obtained, as usual, by subtracting the radiative part (calculated from absorption and Judd Ofelt theory) from the experimental decay rate. All measurements were performed on thin samples to prevent lengthening of experimental decays by trapping effects. Each multiplet was resonantly excited by a frequency doubled YAG laser or a YAG pumped Ti–sapphire laser. Optical attenuators were used to avoid saturation of detectors. The excited state density has been calculated from concentration, absorption cross-section at the excitation wavelength of the RE, excitation power and beam diameter measured at the entrance face of the sample.

When increasing the excitation power, a shortening of decays is observed for multiplets separated from the next lower level by an energy gap which requires less than 3 phonons (i.e. Er^{3+} ($^4S_{3/2}$) in all glasses except ZBLAN) otherwise lengthening is obtained. Two examples are represented on Fig. 1. Measured variations in decay time values, over all the excitation power range are, in all cases, well above the experimental accuracy (<3%). These results cannot be explained by amplified spontaneous emission, saturation, photon trapping or other nonlinear effects since emission spectra are the same whatever the excitation power and no narrowing can be observed (Fig. 2). As an example, the multiphonon relaxation rates for the Nd^{3+}($^4F_{3/2}$) multiplet in tellurite, germanate and phosphate glasses are plotted in Fig. 3 as a function of the excitation population density. In ZBLAN, due to the large gap between the $^4F_{3/2}$ multiplet and the next lower one (≈4300 cm^{-1}) and the low phonon cut-off frequency of the host, the multiphonon process is negligible at low excitation power and cannot be further reduced. As shown in Fig. 3, the multiphonon process from the Nd^{3+}($^4F_{3/2}$) multiplet is almost completely suppressed at high excited state density in tellurite and germanate glasses. In the case of phosphate, the multiphonon process and interactions

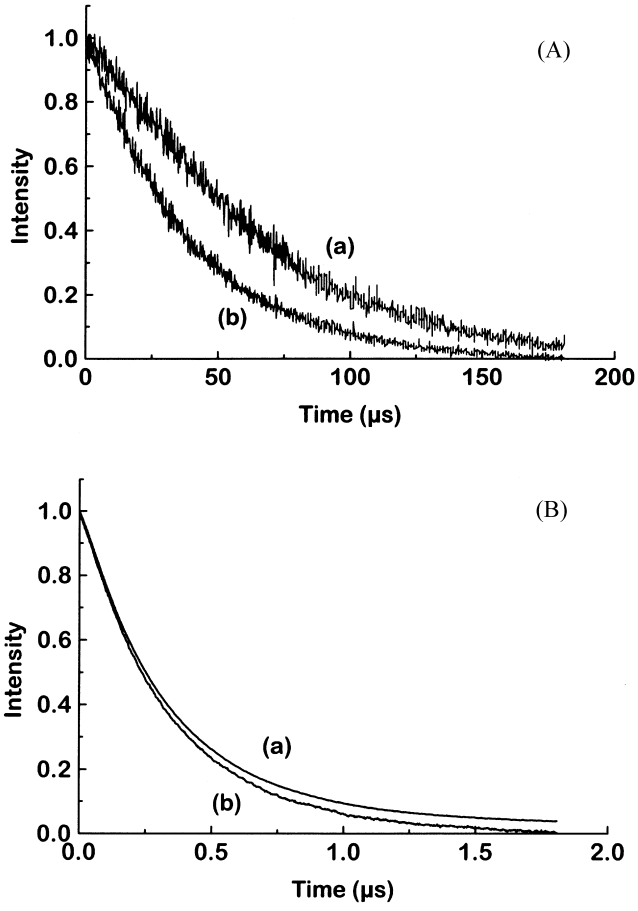

Fig. 1. (A) Er^{3+}($^4S_{3/2}$) fluorescence transients recorded at low and high excitation power in germanate glass (a) $N_{exc}=10^{17}$ cm^{-3}; (b) $N_{exc}=1.2\times10^{18}$ cm^{-3}. (B) Nd^{3+}($^4F_{3/2}$) fluorescence transients recorded at low and high excitation power in germanate glass (a) $N_{exc}=2\times10^{18}$ cm^{-3}; (b) $N_{exc}=1.5\times10^{19}$ cm^{-3}

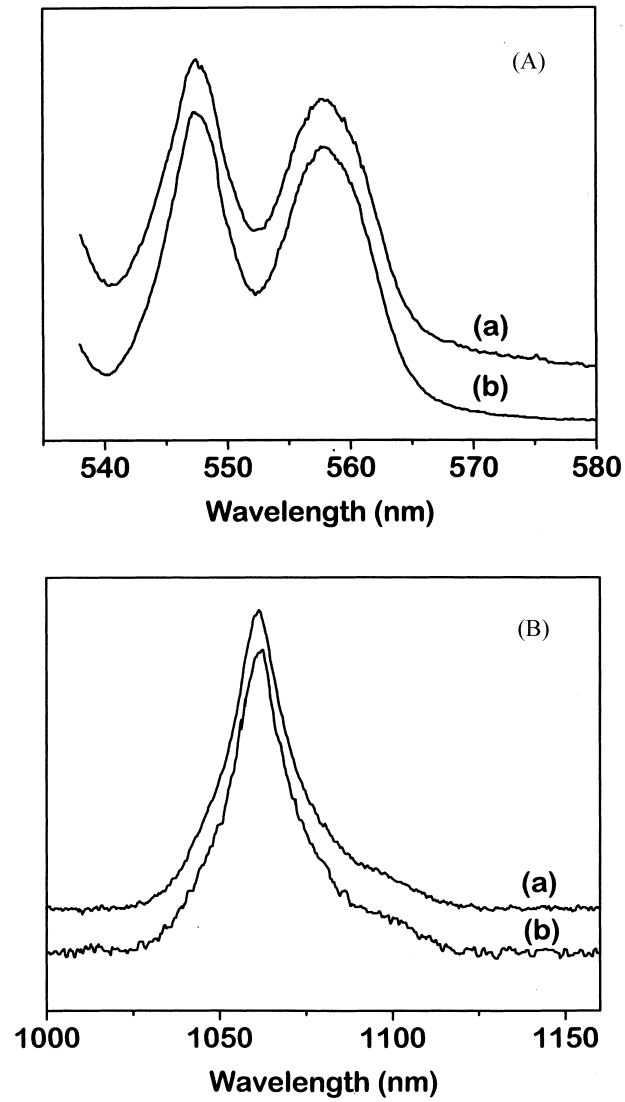

Fig. 2. (A) $^4S_{3/2}\rightarrow{}^4I_{15/2}$ emission spectrum at low and high excitation power in germanate glass (a) $N_{exc}=10^{17}$ cm^{-3}; (b) $N_{exc}=1.2\times10^{18}$ cm^{-3}. (B) $^4F_{3/2}\rightarrow{}^4I_{11/2}$ emission spectrum at low and high excitation power in germanate glass (a) $N_{exc}=2\times10^{18}$ cm^{-3}; (b) $N_{exc}=1.5\times10^{19}$ cm^{-3}.

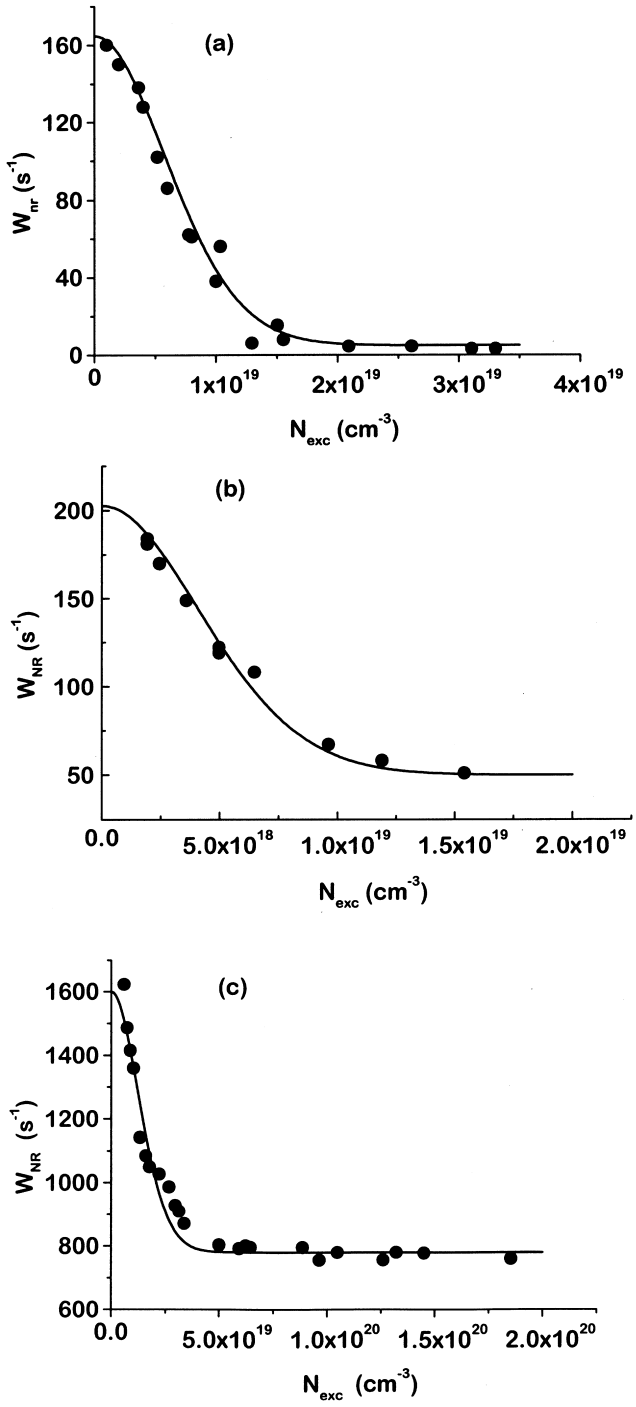

Fig. 3. Multiphonon relaxation rates of Nd^{3+} ($^4F_{3/2}$) excited state versus excited state population density: (a) tellurite glass, (b) germanate glass and (c) phosphate glass. Theoretical fit of experimental data, plotted as solid lines, were obtained using Eq. (2) with a phonon diffusion length of 17 Å (a), 24 Å (b) and 15 Å (c).

between ions contribute to the nonradiative part of the decay since experiments have been performed on more concentrated samples. The nonradiative relaxation rate saturates to a constant value which is ascribed to the contribution from interactions or energy transfers.

Multiphonon nonradiative rates of all considered levels are plotted as a function of multiphonon order in a semilogarithmic scale in Fig. 4 for tellurite and germanate glasses, each set of points stands for a fixed excited state population density (N_{exc}). The normalisation procedure by the absorption cross-section and the excitation intensity results in a weak scattering of the experimental results for a fixed excited state density compared to previously reported results. The obtained lines cross at the same point. Such a crossing point has already been predicted [6] and experimentally observed [7] when considering the multiphonon relaxation rate dependence with the process order for different glasses and crystals. This rotation point occurs at about 2.6 and is related to the promoting modes [6]. Our experimental results are consistent with this theory and show that if the nonradiative part of the decay corresponding to the filling of the promoting modes is constant whatever the excited state density, the contribution due to

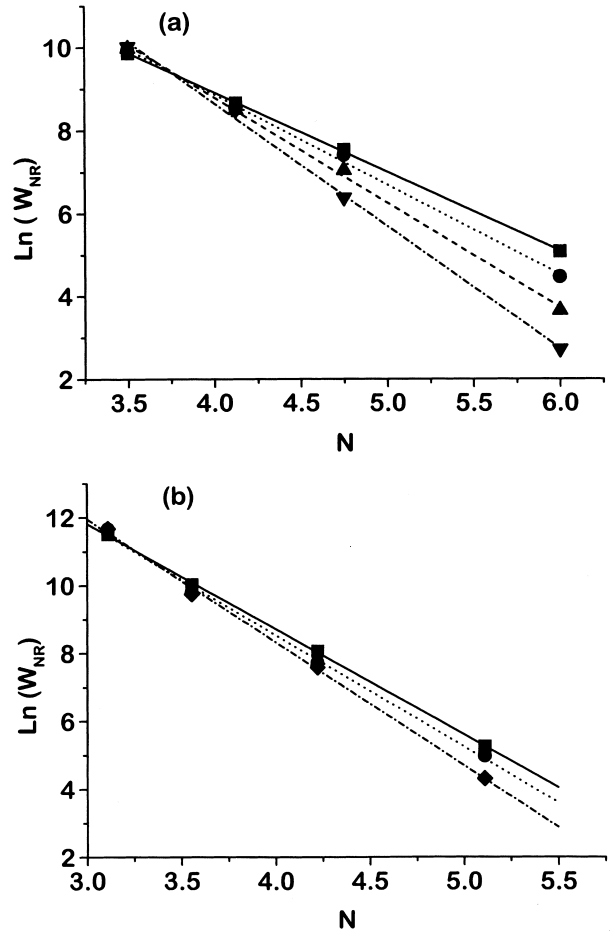

Fig. 4. Variation of the exponential gap law versus the multiphonon order for different excited state densities. Theoretical fit (solid lines) are obtained through Eq. (2): (a) tellurite glass [(■) $N_{exc}=10^{18}$ cm^{-3}; (●) $N_{exc}=6\times10^{18}$ cm^{-3}; (▲) $N_{exc}=8\times10^{18}$ cm^{-3}; (▼) $N_{exc}=1.5\times10^{19}$ cm^{-3}]; (b) germanate glass [(■) $N_{exc}=10^{17}$ cm^{-3}; (●) $N_{exc}=4\times10^{18}$ cm^{-3}; (♦) $N_{exc}=10^{19}$ cm^{-3}].

the filling of the remaining energy gap, i.e. the accepting modes, will be saturated with an increase in the excited state density. So, multiphonon processes requiring a number of phonons higher than the number of the promoting modes will saturate with an increase in the excited state density. This, in turn, explains the behaviour of the multiphonon relaxation rate obtain for Er^{3+} ($^4S_{3/2}$) in ZBLAN.

3. Saturation process: model and application to the experimental results

In the nonadiabatic approach, the multiphonon nonradiative relaxation probability as given by the Fermi golden rule is expressed as the product of an electronic factor (the promoting term) by Frank Condon integrals (the accepting term) [6]. Among the different methods developed to calculate the last term, the most usual expression for W_{nr} in the case of RE ($N>>S_0$) ions is derived from a modified Huang and Rhys's treatment [8] including the promoting term [6]:

$$W_{nr} \propto \frac{S_0{}^N}{N!}\left(\frac{N_p}{S_0}\right)^2. \quad (1)$$

The exponential gap law is then obtained using the Stirling approximation.

From the effect on the excited state density on the multiphonon relaxation rate (Fig. 4), we suggest that only the accepting term will be affected when increasing the excited ion concentration. Now the microscopic process for the saturation will be the following: by increasing the excitation power density, the probability for excited ions to lie in a phonon diffusion volume increases. These ions will share a common phonon bath and will simultaneously contribute to the filling of the common set of accepting modes of the host. This is quite equivalent to increase the order of the process and then, explains the reduction of the multiphonon relaxation rate with the excited state density. Let l_c be the phonon diffusion length in the host, v_l the volume for phonon diffusion, the averaged number of excited ions ($\bar{x}$) in v_l around one excited ion is a function of N_{exc} [5]. In this process, $(1+\bar{x})$ ions will simultaneously fill the N common accepting modes instead of 1, the modified expression for the multiphonon relaxation rate will be the following:

$$W_{nr} = W_0 e^{-S_0(2\bar{n}+1)}(\bar{n}+1)^{(1+\bar{x})N}\frac{S_0^{(1+\bar{x})N}}{[(1+\bar{x})N]!}\left(\frac{N_p}{S_0}\right)^2. \quad (2)$$

Experimental multiphonon relaxation rates obtained for each multiplet, i.e. for fixed energy gap ($N>3$) as a function of the excited state density have been fitted using Eq. (2) with l_c through $\bar{x}$ as the only free parameter. In each case, the calculated curves are in good agreement with experimental values. As examples, the least square fit of experimental data obtained for Nd^{3+} ($^4F_{3/2}$) are represented in Fig. 3 by solid lines. The phonon diffusion length as determined by least square fit of experimental values ranges from 22, 15 and 17 Å for Er^{3+} ($^4I_{11/2}$), Tm^{3+} ($^3H_4$) and Nd^{3+} ($^4F_{3/2}$) states, respectively, in tellurite glass and from 28 Å for Er^{3+} ($^4I_{11/2}$) to 24 Å for Tm^{3+} ($^3H_4$) and Nd^{3+} ($^4F_{3/2}$) in germanate glass. In phosphate glass, 14 Å was obtained for Er^{3+} ($^4I_{11/2}$) and Nd^{3+} ($^4F_{3/2}$), and 12 Å for Tm^{3+} ($^3H_4$).

Furthermore, Eq. (2) is able to describe the W_{nr} dependence with the multiphonon order N at fixed excited state density. The least square fit results of experimental values obtained in tellurite and germanate set using Eq. (2) are plotted in semilogarithmic scale in Fig. 4 by continuous lines. As shown, we obtained straight lines in good agreement with experimental results showing that Eq. (2) is still equivalent to the exponential gap law but with an exponential coefficient depending on N_{exc}. Applying the Stirling approximation to Eq. (2), the exponential parameter is given by:

$$\alpha = \frac{(1+\bar{x})}{\hbar\omega}\left[\left(1-\frac{2}{N(1+\bar{x})}\right)\mathrm{Log}\left(\frac{N}{S_0}\right)+ \mathrm{Log}(1+\bar{x})-1\right]. \quad (3)$$

Finally, slopes of theoretical lines obtained through Eq. (2) are plotted in Fig. 5 as function of N_{exc} in comparison with the fit obtained using Eq. (3) with l_c as the only free parameter. The best results were obtained with a phonon diffusion length of 22 and 29 Å for tellurite and germanate glass, respectively. These results are in quite good agreement with those determined for individual multiplets.

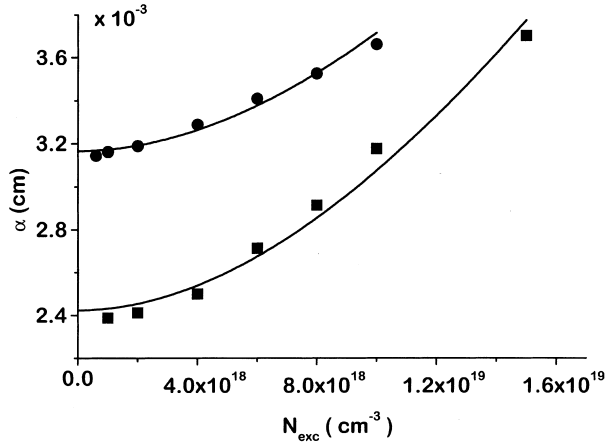

Fig. 5. Exponential parameter (α) versus excited state density. Solid lines result from the least squares fit of data using Eq. (3). Best fits are obtained for l_c=29 Å [germanate glass (■)] and 22 Å [tellurite glass (●)].

4. Comparison between the phonon diffusion length and the phonon mean free path

At high excited state density, multiphonon relaxation will result in an excess of phonon localised in a small volume and a local heating. Phonons generated during this process will propagate in order to dissipate this excess and restore a thermal equilibrium. This phonon of high energy cannot propagate over long distances and will break into lower energetic modes due to anharmonic interactions within the lattice. The phonon mean free path is related to the thermal conductivity κ, the heat capacity C_v and the sound velocity v_s in the host through the relation [9]:

$$\kappa = \frac{1}{3} C_v l_c v_s. \quad (4)$$

The thermal conductivity and heat capacity of the investigated glass hosts were calculated using additive formula [10,11] since this method allows us to obtain such quantities with a relatively good accuracy (about 10%). Sound velocities were measured by classical echo method. All the calculated and measured values are summarised in Table 1. Applying Eq. (4), the phonon mean free path equals 22 and 29 Å in tellurite and germanate glasses, respectively. These values are in quite good agreement with phonon diffusion lengths optically determined. In the case of phosphate, shorter distances are obtained from optical data. This can be related to the high concentration of the RE ions in the glass reducing l_c as observed in Yb^{3+} doped glasses [4].

Table 1
Calculated thermal conductivity and heat capacity, measured sound velocity and phonon mean free path deduced from Eq. (4)

	κ (cal cm^{-1} deg^{-1} s^{-1})	c_v (cal cm^{-3} deg^{-1})	v_s (cm s^{-1})	l_c (Å)
Tellurite	1.38×10^{-3}	0.852	2.40×10^{5}	20
Germanate	1.64×10^{-3}	0.445	3.81×10^{5}	29
Phosphate	2.38×10^{-3}	0.549	4.01×10^{5}	32

5. Conclusion

The effect of the excited state population density on multiphonon relaxation rates for RE multiplets in different glasses is clearly demonstrated. The reduction of the multiphonon decay probability at high excited state concentration is related to a saturation of the accepting modes. A statistical approach of the microscopic process allows us to propose a theoretical model which is validated by a good agreement between the phonon diffusion length deduced from optical data and the phonon mean free path length independently derived from a thermodynamic approach.

Acknowledgements

We would like to thank D. Morin and M. Genotelle for synthesis, density and refractive index measurements.

References

[1] L.A. Riseberg, H.W. Moos, Phys. Rev. 174 (1968) 429–438.
[2] C. Gouedard, D. Husson, C. Sauteret, F. Auzel, A. Migus, J. Opt. Soc. Am. B 10 (1993) 358–2363.
[3] F. Auzel, F. Pellé, C.R. Acad. Sci. Paris IIb (1996) 835–841.
[4] F. Auzel, F. Pellé, J. Lumin. 69 (1996) 249–255.
[5] F. Auzel, F. Pellé, Phys. Rev. B 55 (1997) 11006–11009.
[6] F. Auzel, in: B. Di Bartolo (Ed.), Multiphonon Interaction of Excited Luminescent Centers in the Weak Coupling Limit: Non-radiative Decay and Multiphonon Side Bands, Plenum, New York, 1978 p. 67–113.
[7] J.M.F. Van Dijk, M.F.H. Schuurmans, J. Chem. Phys. 78(9) (1983) 5317–5323.
[8] K. Huang, A. Rhys, Proc. R. Soc. London A 204 (1950) 406–423.
[9] C. Kittel, Introduction to Solid State Physics, J. Wiley, New York, 1971.
[10] E.H. Ratcliffe, Glass Technol. 4 (1963) 113–128.
[11] H. Scholze, GLAS, Natur, Struktur und Eigenschaften, Springer Verlag, Berlin/Heidelberg, 1977.