

Time-resolved luminescence data on the 1060 nm transition in Nd³⁺-doped zinc tellurite glasses

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2000 J. Phys.: Condens. Matter 12 7303

(<http://iopscience.iop.org/0953-8984/12/32/314>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.221

The article was downloaded on 16/05/2010 at 06:39

Please note that [terms and conditions apply](#).

Time-resolved luminescence data on the 1060 nm transition in Nd³⁺-doped zinc tellurite glasses

N Jaba†, A Kanoun†, H Mejri†, H Maaref† and A Brenier‡

† Laboratoire de Physique des Semiconducteurs, Département de Physique, Faculté des Sciences, 5019, Monastir, Tunisia

‡ Laboratoire de Physico-Chimie des Matériaux Luminescents, UMR 5620 CNRS, Université Lyon 1, France

E-mail: hassen.maaref@fsm.rnu.tn

Received 5 April 2000

Abstract. We report time-resolved luminescence data for the ${}^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition in Nd³⁺-doped zinc tellurite glass. The photoluminescence (PL) shows nonexponential decay and the associated decay time depends on ion concentration. PL results are analysed and discussed using the stretched exponential function, commonly used to describe disordered systems. The nonexponential behaviour has been explained as due to a multi-configurational distribution of luminescent ions in a disordered medium. The dipole–dipole interactions remain at the origin of the PL decay time shortening.

1. Introduction

Analysis of the luminescence decay provides information about the dynamics of the recombination processes. Theoretically, this decay has been discussed using Dexter [1] and/or Inokuti–Hirayama [2] models in the case of electric multipolar interactions of rare earth (RE) ions in crystals and glasses [3–6]. It is shown that the dipole–dipole interaction is the main process responsible for the shortening of the luminescence lifetimes in heavily doped samples [7]. The effects of the disorder on the dynamics of luminescence have not been, however, considered in studies based on these models.

The latter aspect has stimulated a great deal of interest in analysing the transport and PL properties of disordered systems [8–10], such as porous silicon [11–13]. It was found that transport and relaxation in disordered solids are governed by a long-tailed waiting-time distribution called ‘dispersive’ because many time scales coexist [8]. Scale-invariant dynamic phenomena are seen in a wide variety of disordered materials. Dispersive motion can account quantitatively for many of the universal characteristics seen in transport and relaxation measurements in these materials, which include amorphous semiconductors and insulators, polymer films, molecular solid solutions and glasses [8]. Several decay laws are often encountered in these disordered systems and are considered a consequence of the dispersive diffusion of photoexcited carriers. In the case of PL measurements, the disorder has been suggested to be at the origin of the observed nonexponential decay profiles [10, 11]. The nonexponential character of the luminescence decay has been well described by an empirical law called the ‘stretched exponential function’ [8–14].

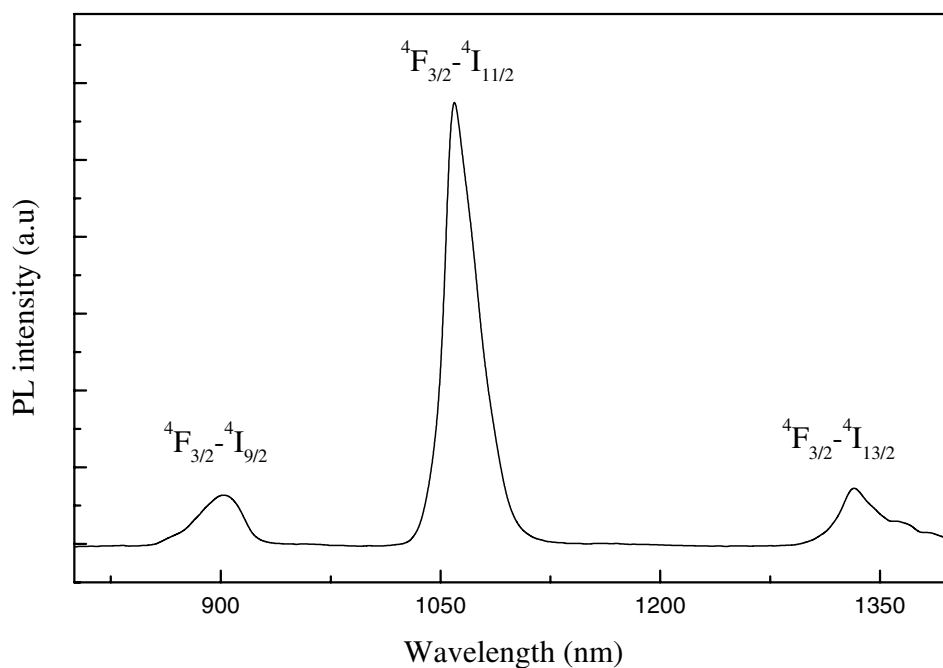


Figure 1. Typical PL spectrum of Nd^{3+} in $70\text{TeO}_2\text{-}30\text{ZnO}$ glass at room temperature.

In this paper, PL decay measurements, obtained on Nd^{3+} -doped zinc tellurite glasses will be presented. A quantitative analysis of these data has been possible using the stretched exponential function. Two main observations are revealed: (i) the PL decay is not a single exponential even in samples with low neodymium concentrations, (ii) the PL decay time becomes shorter as the Nd^{3+} ion concentration increases. An attempt to assign this behaviour to an energy transfer process, induced by a RE ion concentration effect in a disordered host glass, will be presented. It was also confirmed that this energy transfer originates from a dipole–dipole interaction, according to the Dexter model.

2. Experiment

Glasses were prepared from oxide powders of TeO_2 , ZnO and Nd_2O_3 as starting materials using the conventional melt-quenching method. The amount of the dopant was varied between 0.2 to 3.0 at.% Nd^{3+} . Luminescence was excited by a 514.5 nm line. Time-resolved PL spectra are recorded by exciting the samples at 514.5 nm with a BM Industries Nd-YAG laser pumping a Laser Analytical Systems dye laser. The pulse duration is 8 ns at a repetition rate of 500 Hz. The light has been focused on a 0.6 m Jobin–Yvon HR S2 spectrometer. The detection was performed using an R 1767 Hamamatsu photomultiplier and an oscilloscope averaged Lecroy 9410. All the measured spectra were corrected for apparatus response.

3. Results and discussion

Figure 1 shows a typical PL spectrum of the Nd^{3+} ion in $70\text{TeO}_2\text{-}30\text{ZnO}$ glass. This spectrum is composed of three distinct emission bands centred around 900, 1060 and 1330 nm respectively.

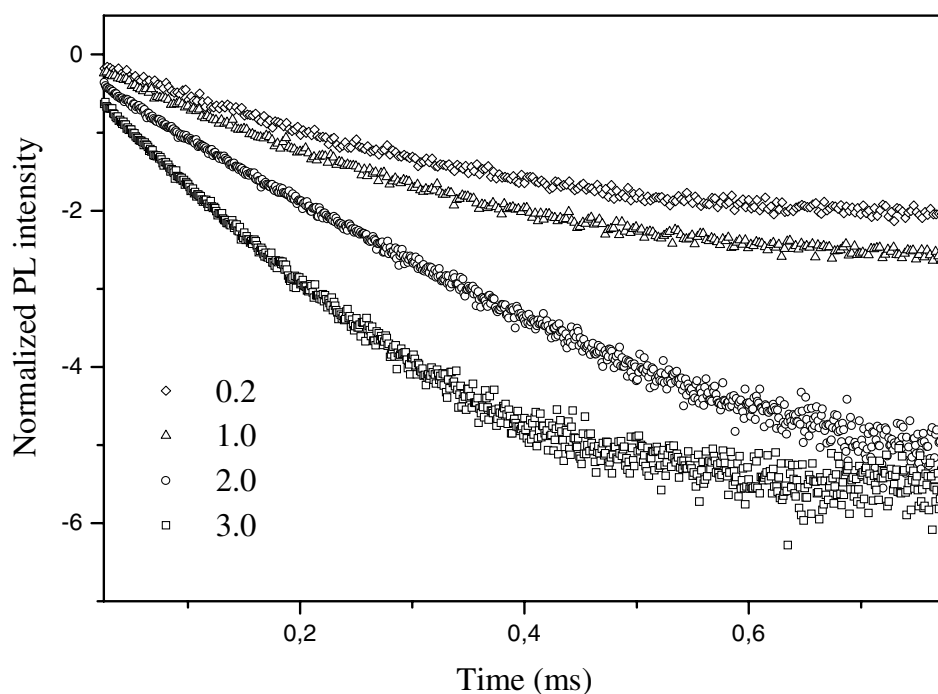


Figure 2. Logarithm of the PL decay calculated for different Nd³⁺ ion concentrations ranging from 0.2 to 3.0 at. %.

The assignment of the PL lines to the electronic transitions is indicated in the plot. It can be noticed that the ${}^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition is the most intense and has an effective width of 24 nm. We have studied the effects of the Nd³⁺ ion concentration on the luminescence intensity of the latter transition. It was found that this intensity shows a quenching behaviour beyond a critical Nd³⁺ ion concentration, that is on average 0.5 at. %. This quenching in luminescence intensity may be attributed to an Nd³⁺-Nd³⁺ cross relaxation energy transfer and/or an energy transfer from Nd³⁺ ions to unintentionally introduced impurities in the network. We have investigated, on the other hand, the luminescence decay of the ${}^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition in order to analyse the dynamics of this energy transfer. Figure 2 depicts the PL decay profiles of Nd³⁺, measured for different ion concentrations. The decay curves show a nonexponential behaviour with ion-concentration-dependent time constant. High ion concentration levels, indeed, speed up the luminescence decay significantly. To analyse these data, we have adopted the stretched exponential function [10, 11]:

$$I(t) = I_0 \exp[-(t/\tau)^\beta] \quad (1)$$

where β is the dispersive factor and τ is the total lifetime. A method to determine the parameters β and τ consists of plotting $[-dI(t)/dt]/I(t)$ against t in a log-log scale. This plot can be performed using the equation:

$$\ln \left[-\frac{dI(t)/dt}{I(t)} \right] = (\beta - 1) \ln(t) + \ln \left(\frac{\beta}{\tau^\beta} \right). \quad (2)$$

According to the latter equation, the dispersive parameter β is given from the slope of the log-log plot of $[-dI(t)/dt]/I(t)$ against t . The total lifetime τ can be deduced from the ordinate at the origin of this plot. Using PL decay data, we have calculated the function

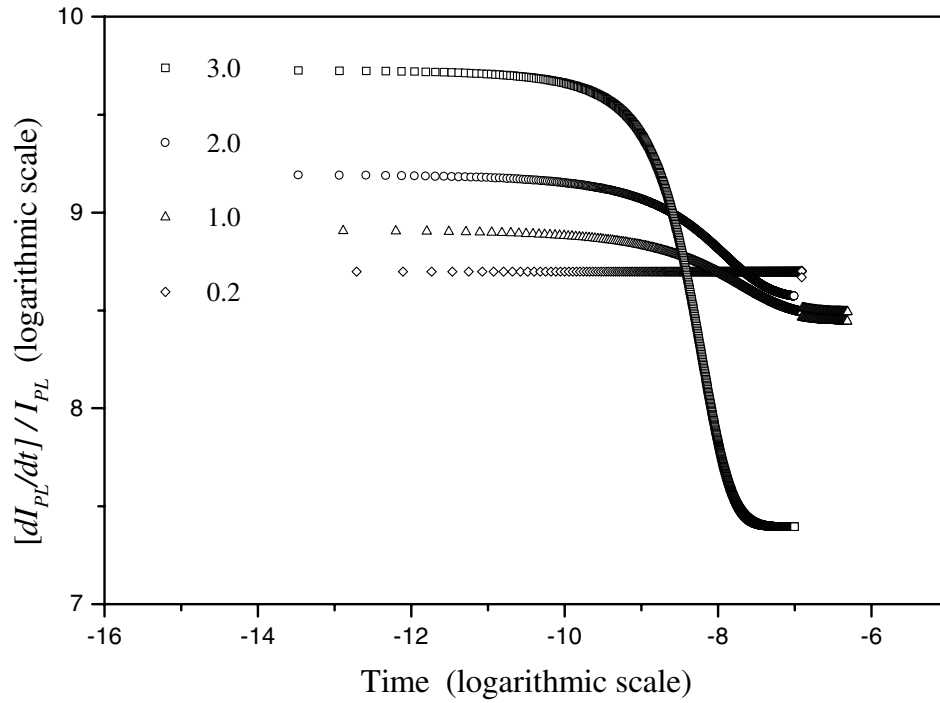


Figure 3. PL decay of Nd^{3+} at room temperature, plotted according to equation (2) for the different concentrations investigated.

Table 1. Values of the dispersive factor β and the total lifetime τ , deduced from PL decay data using equation (2).

Concentration (at.%)	β	τ (μs)
0.2	0.998	166
1.0	0.989	141
2.0	0.983	105
3.0	0.976	62

$[\ln[-[dI(t)/dt]/I(t)]]$ for the different Nd^{3+} ion concentrations investigated. The results are summarized in figure 3. As clearly seen, the curves show a linear variation in the time range 1–100 μs . It has to be noticed, in addition, that the slope as well as the ordinate at the origin of the plots vary with increased Nd^{3+} ion concentration. Such a result evidences the effects of the disorder on the non-radiative recombination. This aspect will be analysed and discussed later. In table 1 are listed the values of the parameters β and τ , obtained from the fit of PL decay data with use of equation (2) in the time range mentioned above. For the 0.2 at.% ion concentration, β is close to unity, indicating that luminescence decay is nearly a single exponential. This implies that there is one radiative-recombination pathway for excited ions. This proposal is supported by the fact that energy transfer between excited ions can be ignored in the case of a low ion concentration [15]. The energy transfer is neglected; the total decay time can be written in the form

$$\frac{1}{\tau} = \frac{1}{\tau_r} + \frac{1}{\tau_p} \quad (3)$$

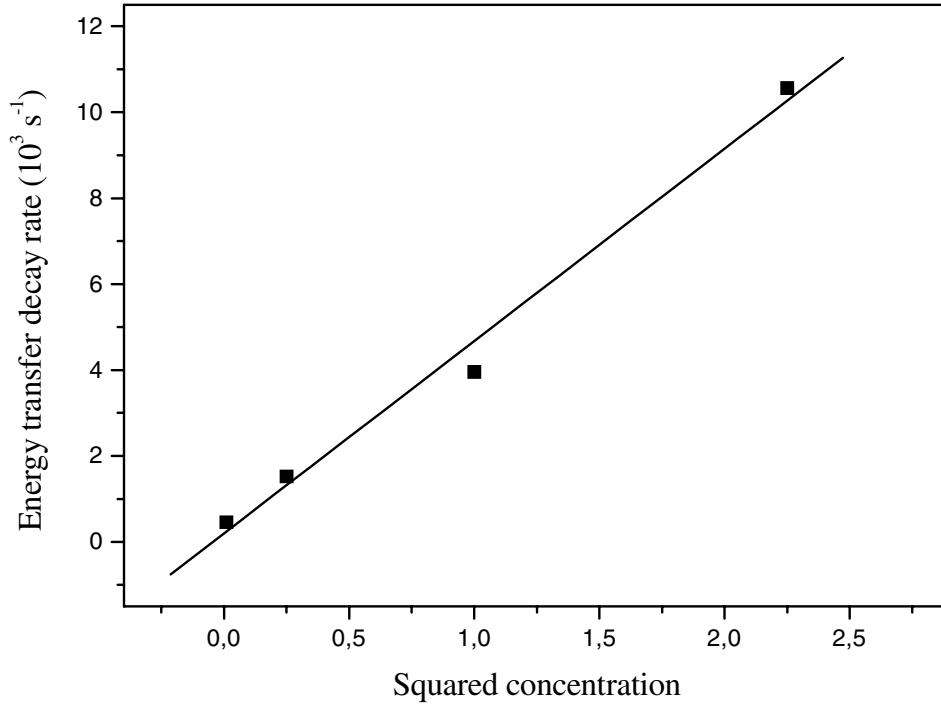


Figure 4. Variation of the energy transfer decay rate against the squared Nd³⁺ ion concentration.

where τ_r and τ_p are the radiative and the multiphonon decay times of the emitting level ${}^4F_{3/2}$. To evaluate the first decay rate, the intensity parameters $\Omega_{t=2,4,6}$ have been calculated using the Judd–Ofelt formulae [16, 17]. The obtained value for this lifetime is 203 μs with $\Omega_2 = 1.15$, $\Omega_4 = 4.59$ and $\Omega_6 = 2.70 \times 10^{-20} \text{ cm}^2$. The lifetime τ_p has been computed using the model of multiphonon relaxation proposed by Riseberg and Moos [18], in which the multiphonon decay time is given by the relationship:

$$\frac{1}{\tau_p} = C_p \exp(-\alpha \Delta E) \left(1 - \exp\left(-\frac{\hbar\omega}{K_B T}\right) \right)^{-p} \quad (4)$$

where C_p and α are non-radiative parameters which depend on the host material, ΔE represents the energy gap between ${}^4F_{3/2}$ and ${}^4I_{13/2}$ levels. $p = \Delta E/\hbar\omega$ is the number of phonons emitted through the relaxation process. The value of τ_p , evaluated from equation (4) at $T = 300 \text{ K}$, is of magnitude $1.55 \times 10^4 \text{ s}$. The parameters used for this calculation are: $\Delta E = 7400 \text{ cm}^{-1}$, $\alpha = 4.7 \times 10^{-3} \text{ cm}$, $C_p = 6.3 \times 10^{10} \text{ s}^{-1}$ and $\hbar\omega \approx 750 \text{ cm}^{-1}$ respectively [19]. The multiphonon relaxation channels involving ${}^4I_{11/2}$ and ${}^4I_{9/2}$ levels have not been considered in the τ_p calculation. In fact, the energy gaps of ${}^4F_{3/2} \rightarrow {}^4I_{11/2}$ and ${}^4F_{3/2} \rightarrow {}^4I_{9/2}$ transitions are much longer than the energy gap of the ${}^4F_{3/2} \rightarrow {}^4I_{13/2}$ transition. We will, now, study the effects of the Nd³⁺ ion concentration on the total decay time τ . When this concentration increases, the energy transfer takes place. Thus, the decay time characterizing this process must be considered in the calculation of τ . We have labelled this decay time τ_{et} . Then, equation (3) will be rewritten as:

$$\frac{1}{\tau} = \frac{1}{\tau_r} + \frac{1}{\tau_p} + \frac{1}{\tau_{et}} \quad (5)$$

Using the latter equation, we can deduce the energy transfer rate $1/\tau_{et}$ from the PL intensity measurements. The relevant values of τ_{et} are depicted in figure 4. As seen, this decay rate shows a linear variation with the square of the Nd^{3+} ion concentration. The linear behaviour indicates that energy transfer process is induced by a dipole–dipole interaction in Nd^{3+} – Nd^{3+} pairs. In fact, according to the Dexter model [1], the energy transfer rate occurring by an electric dipole interaction is proportional to the inverse of the sixth power of the distance separating the two ions and consequently to the squared concentration. This model supposes that Nd^{3+} ion pairs are homogeneously distributed in the host lattice. This assumption is valid when the ion concentration is not large enough. In case of a relatively high ion concentration, the distribution of distances between ions in the pairs is not homogeneous. Thus, the energy transfer process will not be characterized by a single relaxation time. Additionally, if the host lattice is disordered, as is the case in glass systems, the energy transfer can be affected by the disorder even at low ion concentration levels. In such a case, the energy transfer will be described by a distribution of decay times. Experimental evidence of the disorder effect is given by the non-exponential behaviour of PL decay observed in the sample doped with 0.2 at.% Nd^{3+} (see figure 2). Both the random distribution of separating distances of ions in pairs and environmental disorder influence the PL decay profiles of luminescent ions. The stretched exponential function, used in this analysis, can account well for the dispersive character of the PL response. Particularly, the measurement of the parameter β gives information about the effects of the spatial distribution of RE ions on their luminescence properties. In evaluating the factor β , we have found that this parameter decreases as Nd^{3+} ion concentration increases (see table 1). This dispersion does not mean that several processes different in nature govern the shortening of the PL decay. It is due probably to a mixing of single-exponential decay signals having different relaxation times, which are of dipole–dipole interaction nature. This mixing can be understood as resulting from the multi-configurational distribution of luminescent ions in a disordered host lattice.

4. Summary

Time-resolved PL measurements have been performed on Nd^{3+} -doped zinc tellurite glasses at room temperature. It was found that the PL decay was not a single exponential. Moreover, an increase in Nd^{3+} ion concentration shortens the PL decay time. These results were analysed and discussed using the stretched exponential function. Two main conclusions were derived from this analysis: (i) the shortening of luminescence decay is due to an energy transfer that is induced by a dipole–dipole interaction in a disordered host lattice, (ii) the disorder arises from the multi-configurational distribution of luminescent ions in the glass system studied.

References

- [1] Dexter D L 1962 *Phys. Rev.* **126** 1962
- [2] Inokuti M and Hirayama F 1965 *J. Chem. Phys.* **43** 1978
- [3] Kanoun A, Alaya S and Maaref H 1990 *World Renewable Energy Congress (Reading 1990)*
- [4] Bettinelli M and Ingleto G 1989 *J. Lumin.* **43** 115
- [5] Ajithkumar G and Unnikrishnan N V 1997 *Solid State Commun.* **104** 29
- [6] Ajroud M, Haouari M, Ouada H B, Maaref H, Brenier A and Garapon C 2000 *J. Phys.: Condens. Matter* **12** 3181
- [7] Savoini B, Santiuste J E M and Gonzalez R 1997 *Phys. Rev. B* **56** 5856
- [8] Scher H, Shlesinger M F and Bendler J T 1991 *Phys. Today* **41** 26 and references therein
- [9] Chen X, Henderson B and O'Donnell K P 1992 *Appl. Phys. Lett.* **60** 2672
- [10] Sawada S, Hamada N and Ookubo N 1994 *Phys. Rev. B* **49** 5236

- [11] Pavesi L and Ceschini M 1993 *Phys. Rev. B* **48** 17 625
- [12] Kanemitsu Y 1994 *Phys. Rev. B* **49** 16 845
- [13] Mihalcescu I, Vial J C and Romestain R 1996 *J. Appl. Phys.* **80** 2404
- [14] M'ghaeth R, Maaref H, Mihalcescu I and Vial J C 1999 *Phys. Rev. B* **60** 4450
- [15] van der Ziel J P, Van Uitert L G, Grodkiewicz W H and Mikulyak R M 1986 *J. Appl. Phys.* **60** 4262
- [16] Judd B R 1962 *Phys. Rev.* **127** 750
- [17] Ofelt G S 1962 *J. Chem. Phys.* **37** 511
- [18] Riseberg L A and Moos H W 1968 *Phys. Rev.* **174** 429
- [19] Wang J S, Vogel E M and Snitzer E 1994 *Opt. Mater.* **3** 187