

## Photoluminescence quenching by OH in Er- and Pr-doped glasses for 1.5 and 1.3 $\mu\text{m}$ optical amplifiers

A.J. Faber, D.R. Simons, Y. Yan, H. de Waal

TNO Institute of Applied Physics, P.O. Box 595, NL-5600 AN Eindhoven

### ABSTRACT

In this paper we report on the effect of hydroxyl (OH) groups on the photoluminescence in the near IR (1.5 and 1.3  $\mu\text{m}$ ) in rare earth (Er, Pr)-doped glasses. The 1.5  $\mu\text{m}$  emission of Er-doped phosphate glasses was studied, before and after a special heat treatment. The luminescent lifetime of the 1.5  $\mu\text{m}$  emission increases substantially, typically from 3 ms up to 7.2 ms for a 2 mole%  $\text{Er}_2\text{O}_3$ -doped phosphate glass, due to the controlled heat treatment. The increase in lifetime is ascribed to a decrease in OH-concentration, which is confirmed by IR-absorption spectroscopy. The quenching by OH is described by a simplified quenching model, which predicts the 1.5  $\mu\text{m}$  emission lifetime as a function of Er-concentration with the OH-concentration as parameter. It appears that the larger part of the OH groups is coupled to Er ions and thus acts as quenching centre.

Photoluminescence quenching by OH groups is also reported for the 1.3  $\mu\text{m}$  emission of Pr in  $\text{GeS}_2$ -glasses: In pure OH-free  $\text{GeS}_2$  glass the 1.3  $\mu\text{m}$  emission lifetime is as high as 350  $\mu\text{s}$ , for a 400 ppm dopant level. In  $\text{GeS}_2$  glasses containing only small amounts of OH (approximately 100 ppm), this lifetime is less than 200  $\mu\text{s}$ .

Both examples demonstrate that for the fabrication of efficient glass optical amplifiers at the telecommunication windows 1.3 and 1.5  $\mu\text{m}$ , the OH-impurity level of the host glass must be kept as low as possible.

**Keywords:** glasses, rare earths, optical amplifiers, photoluminescence quenching, hydroxyl groups

### 1. INTRODUCTION

Currently, advanced rare earth-doped glasses receive much attention in view of application in either fibre or planar waveguide optical amplifiers<sup>1</sup>. For the fabrication of efficient amplifier devices, several challenges are encountered, including the development of a highly Er-doped planar amplifier at 1.5  $\mu\text{m}$  and a Pr-doped low phonon glass fibre amplifier at 1.3  $\mu\text{m}$ .

For planar optical amplifiers at 1.5  $\mu\text{m}$  a high Er-concentration of typically 1 at% is needed to obtain sufficient optical amplification in a few cm's optical waveguide. However, at high Er-concentrations the 1.5  $\mu\text{m}$  luminescence will be quenched by energy transfer mechanisms like upconversion processes, due to ion-ion interaction<sup>1</sup>.

In this paper an other luminescence quenching mechanism in glasses is described, namely quenching by transfer of excitation energy to hydroxyl (OH) groups, which may be present as impurities. The fundamental vibrations of OH-groups give rise to absorption bands in the near IR, between 2500 and 3600  $\text{cm}^{-1}$  (2.7 - 4  $\mu\text{m}$ ). The overtones of these OH-vibrations are overlapping with the 1.5  $\mu\text{m}$  emission band of Er. This overlap can result in serious luminescence quenching, as will be illustrated for the case of Er-doped phosphate glasses. A simplified photoluminescence quenching model by OH-groups will be presented.

For the case of Pr-doped glasses, the main quenching mechanism of the 1.3  $\mu\text{m}$  ( $^1\text{G}_4 - ^3\text{H}_5$ ) radiative transition is multiphonon relaxation from the  $^1\text{G}_4$  to the  $^3\text{F}_4$  level, e.g. non-radiative energy transfer to mostly highly energetic glass phonons. Therefore, a host glass composition with a low phonon energy spectrum is required for efficient 1.3  $\mu\text{m}$  emission. In this paper, photoluminescence characteristics of Pr-doped chalcogenide  $\text{GeS}_2$  glasses will be presented. In these low phonon glasses, the 1.3  $\mu\text{m}$  emission can be very efficient. However, it will be demonstrated that also in this case, OH-impurities in  $\text{GeS}_2$  glass can degrade the luminescence efficiency to a large extent.

## 2. Er-DOPED PHOSPHATE GLASSES

### 2.1 Experimental

#### Glass preparation and heat treatment

Different phosphate glasses were prepared, including the compositions listed in Table 1. Analytical reagent grade chemicals were melted for about 6 hours at around 1100°C ~ 1450°C depending on glass composition. The as-melted glasses were poured into graphite crucibles and annealed at 390°C ~ 450°C.

Table 1 Glass Compositions (in mole%)

Glass	P <sub>2</sub> O <sub>5</sub>	Na <sub>2</sub> O	Li <sub>2</sub> O	Al <sub>2</sub> O <sub>3</sub>	BaO
PBL	50	-	26~30	3~3.5	16
P424	38~40	38~40	-	20~21.6	-
PJB	31	42~44	-	22.6	2

The Er dopant levels include: 0.02, 0.2, 1.0, 2.0, 4.0 mole% Er<sub>2</sub>O<sub>3</sub>, respectively.

In order to decrease the OH concentration in the as-melted glasses, part of the glass was re-melted under pure argon atmosphere (H<sub>2</sub>O < 15 ppm) by RF-inductive heating. The heating temperature was well chosen to avoid selective evaporation of glass components. The re-melting processes lasted for 1 ~ 2 hours at about 1100 ~ 1200°C. The melts were allowed to cool down in the argon atmosphere, and then taken out and annealed in a normal furnace in air.

#### Optical characterization techniques

Photoluminescence (PL) spectra were recorded at room temperature, using an Argon ion laser as excitation source and lock-in techniques for detection. PL decay curves were also recorded to enable determination of emission lifetimes. Room-temperature transmittance and reflectance measurements were performed in the IR range (2.5 - 50 μm) by a Perkin Elmer 883 model spectrophotometer.

### 2.2 Results

#### Optical characterization of bulk glasses

Typical Er<sup>3+</sup>-PL spectra are shown in figure 1 for a phosphate glass doped with 2 mol% Er<sub>2</sub>O<sub>3</sub>, both as-melted and dried. This figure clearly demonstrates the effect of the heat treatment, which results in a strong increase in PL intensity. The peak wavelength of the Er <sup>4</sup>I<sub>13/2</sub> → <sup>4</sup>I<sub>15/2</sub> transition is located at 1.53 μm for all glass samples and the heat-treatment does not change the peak wavelength. Figure 2 shows the PL lifetime of Er<sup>3+</sup> at 1.53 μm as a function of Er<sup>3+</sup>-concentration in the 3 phosphate glasses under study, both as-melted and dried. Obviously, the PL lifetime decreases upon increasing the Er<sup>3+</sup> concentration. However, after heat treatment the PL-lifetime values for all glass compositions and Er<sup>3+</sup> concentrations increase substantially. This increase in lifetime after heat treatment is due to a decrease of the number of OH-quenchers, as will be explained below.

To evaluate the OH-concentration in the glasses before and after the heat treatment, the IR transmission spectra of the as-melted and dried glasses have been measured. As an example, the IR transmission spectra of the as-melted and dried P424 glasses are compared in figure 3. After drying, the OH absorption peak at 2910 cm<sup>-1</sup> has almost disappeared. On the basis of figure 3 and literature data on the OH-absorption coefficient<sup>2</sup>, it is estimated that the as-melted P424 glass has an OH concentration of about 530 ppm and the dried P424 glass about 70 ppm.

### 2.3 Model of Er<sup>3+</sup> PL-quenching by OH-groups

Recently, a possible two phonon quenching mechanism of the PL of Er<sup>3+</sup> by OH groups has been suggested<sup>3</sup>. Based on this suggestion, a simplified energy transfer and quenching model is described here to explain the observed Er<sup>3+</sup> luminescence quenching quantitatively. In this model, energy transfer by electric dipole - dipole interaction between excited Er<sup>3+</sup> ions and ground state Er<sup>3+</sup> ions takes place increasingly at higher Er concentrations. It is assumed that the excitation energy will be lost whenever it is transferred to an Er<sup>3+</sup> ion coupled to an OH group. Summarizing, the basic assumptions of the model include:

(i) The OH groups are only coupled efficiently to a certain amount of Er ions; this amount of Er-OH quenching centres ( $N_{\text{Er-OH}}$ ) is dependent on the OH concentration ( $N_{\text{OH}}$ ) inside the glass according to:  $N_{\text{Er-OH}} = \alpha N_{\text{OH}}$  ( $0 < \alpha < 1$ ), and  $\alpha$  is referred to as a coupling coefficient.

(ii) Quenching occurs after the excitation energy is transferred to Er ions coupled to OH groups, possibly via a two phonon mechanism.

For the macroscopic case with many Er ions, the energy transfer process in a glassy matrix can be treated by an energy diffusion process<sup>4</sup>. Taking into account above assumptions, the activators (Er ions) and quenchers (Er ions coupled to OH groups) are essentially identical as far as energy transfer is concerned. The concentration dependent lifetime  $\tau$  can then be written as<sup>4</sup>:

$$1/\tau = 1/\tau_0 + kN_{\text{Er}}N_{\text{Er-OH}} \quad (1)$$

where:

$\tau_0$  = Er<sup>3+</sup> PL-lifetime without energy transfer (at very low Er<sup>3+</sup>-concentration)

$k$  =  $8\pi R_0^6/\tau_0$ , with  $R_0$  the critical distance for energy transfer between neighbouring Er<sup>3+</sup> ions according to Förster-Dexter<sup>5</sup> (for  $R_0$  the nonradiative energy transfer probability equals  $1/\tau_0$ )

$N_{\text{Er-OH}} = \alpha N_{\text{OH}}$  according to assumption (i)

Applying this model to P424 glasses as an example, the model parameters for Eq.1 are as follows:

$\tau_0 = 10.5$  ms (Measured lifetime for a P424 glass doped with 0.02 mol.% Er<sub>2</sub>O<sub>3</sub>)

$R_0 = 12.1$  Å

$N_{\text{OH}} = 9.54 \times 10^{19}$ cm<sup>-3</sup> for the as-melted P424 glass and =  $1.26 \times 10^{19}$ cm<sup>-3</sup> for the dried one.

Fitting the  $\tau \sim N_{\text{Er}}$  relation from Eq. 1 with measured PL lifetime values as shown in Fig. 2<sup>a</sup>, we get the coupling coefficient  $\alpha \sim 60$  % for both the as-melted and the dried P424 glass. This indicates that the larger part of the OH groups inside the P424 glass is coupled to the Er<sup>3+</sup> ions, which causes the PL lifetime quenching. For PBL and PJB glasses, similar fitting processes are carried out with similar results (cf. Fig 2).

Apparently, the model predicts correct lifetime reduction trends for all the phosphate glasses under study.

## 3. Pr-DOPED GeS<sub>2</sub> GLASSES

### 3.1 Experimental

#### Glass preparation

Several GeS<sub>2</sub> glasses, doped with Pr were melted, starting from 5N-6N (metals basis) high purity Ge and S elements. Pr was added in the form of Pr<sub>2</sub>S<sub>3</sub>. The starting materials were handled in a glovebox, with an Ar atmosphere and levels of less than 1 ppm H<sub>2</sub>O and O<sub>2</sub>, and batched into silica ampoules. Special attention was paid to prior cleaning of the ampoules to prevent ampoule wall impurities from devitrifying the glass. The ampoules were sealed off with an oxyfuel flame under a vacuum of 10<sup>-3</sup> to 10<sup>-4</sup> mbar.

The ampoules were rotated at the melting temperature of 1000 °C for several hours, quenched in air and subsequently annealed at 265 °C.

### Optical characterization techniques

The same experimental equipment as for the characterization of Er-doped phosphate glasses was used.

## 3.2 Results and discussion

### Spectrophotometry

In figure 4 the IR transmittance spectra of two Pr-doped GeS<sub>2</sub> glasses, differing in hydroxyl content, are shown. The H-OH and Ge-OH absorption bands are located at 7.5 μm and 2.8 μm, respectively and the SH band is at 4 μm<sup>6</sup>. If we assume a molar extinction factor of 70 l.mol<sup>-1</sup>.cm<sup>-1</sup> for the Ge-OH band (like for Si-OH in silicate glass<sup>7</sup>) the OH<sup>-</sup> content of the hydroxyl-rich GeS<sub>2</sub> glass is estimated to be 100 ppm. The OH-overtone around 1.4 μm overlaps with the high wavelength tail of the 1.3 μm <sup>1</sup>G<sub>4</sub> - <sup>3</sup>H<sub>5</sub> emission and thus OH is a possible luminescence quencher. The other glass does not show an absorption band at 2.8 μm, so is virtually hydroxyl-free (and denoted as such). The difference in hydroxyl-content is due to a difference in Ge quality as starting material.

### Photoluminescence

Figure 5 shows the energy level diagram for Pr. The PL spectrum of hydroxyl-free 400 ppm Pr-doped GeS<sub>2</sub> glass is shown in figure 6; the various emission bands are assigned. The maximum PL signal for the <sup>1</sup>G<sub>4</sub> - <sup>3</sup>H<sub>5</sub> transition is centered at 1.34 μm, with a FWHM of 100 nm. The PL decay curve of the Pr<sup>3+</sup> <sup>1</sup>G<sub>4</sub> state, depicted in figure 7, is purely exponential and the emission lifetime is 350 ± 30 μs. This lifetime compares favourably to the measured 337 μs in Ge-As-S glass<sup>9</sup>; as in the latter glass the only possible quenching mechanism for the <sup>1</sup>G<sub>4</sub> - <sup>3</sup>H<sub>5</sub> luminescence in GeS<sub>2</sub> glass is multiphonon relaxation since the Pr dopant level is too low for effective concentration quenching.

In figure 8 the PL spectra for OH-containing 50 ppm and 200 ppm Pr-doped GeS<sub>2</sub> glass are compared. The different emission bands are assigned. Clearly, in the 200 ppm-doped sample the <sup>1</sup>G<sub>4</sub> emission is quenched with respect to the <sup>1</sup>D<sub>2</sub> emission more than in the 50 ppm-sample. The PL decay curves of the <sup>1</sup>G<sub>4</sub> state for both samples are non-exponential. When fitted with a double-exponential the emission lifetime has a short component of less than 200 μs and a tail in the order of 300 to 400 μs. Next to multiphonon relaxation, there is thus also OH-quenching since the emission lifetime is shortened with respect to the OH-free sample. There is also a change in the PL emission band intensities as the Pr-dopant level changes, apparently because the <sup>1</sup>G<sub>4</sub> level is more sensitive to hydroxyl quenching than the <sup>1</sup>D<sub>2</sub> level.

## 4. CONCLUSIONS

Er<sup>3+</sup> 1.5 μm luminescence in highly doped phosphate glasses is examined. For as-melted phosphate glasses, the Er<sup>3+</sup> PL lifetime decreases rapidly upon increasing Er<sup>3+</sup> doping level. This is attributed to a combined quenching process, depending on both the Er<sup>3+</sup> dopant concentration and the OH concentration in the glass. A quenching model is proposed, which shows that the major part of the OH groups is coupled to Er<sup>3+</sup>-ions. By a controlled heat treatment of the phosphate glass melts, most of the OH-groups can be removed. This results in a considerable increase in the Er<sup>3+</sup> PL efficiency as demonstrated by PL intensity and PL lifetime measurements.

The <sup>1</sup>G<sub>4</sub> - <sup>3</sup>H<sub>5</sub> PL spectrum of Pr-doped GeS<sub>2</sub> glass is centered at 1.34 μm. The emission lifetime of the Pr<sup>3+</sup> <sup>1</sup>G<sub>4</sub> state in hydroxyl-free glass is 350 ± 30 μs and the PL decay is single-exponential. Hydroxyl has been shown to be a serious <sup>1</sup>G<sub>4</sub> luminescence quencher.

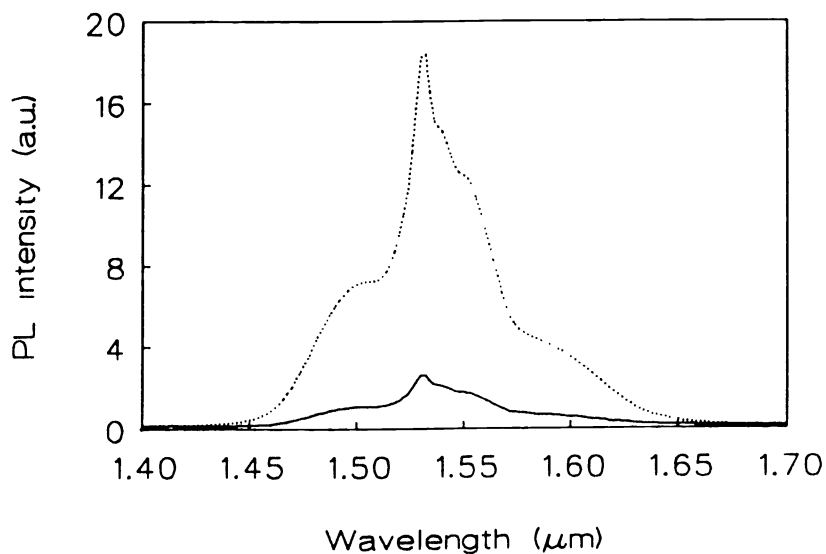
It is concluded that in view of efficient photoluminescence in Er- and Pr-doped glasses at 1.5 and 1.3 μm respectively, an OH-free glass host is a prerequisite.

## 5. ACKNOWLEDGEMENTS

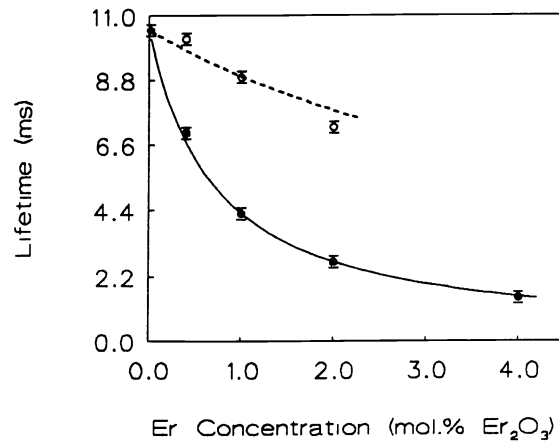
The financial support of the IC Technology Programme (IOP Electro-Optics) of the Dutch Ministry of Economic Affairs and of the Technology Foundation (STW) is gratefully acknowledged. The FOM Institute for Atomic and Molecular Physics, Amsterdam, is thanked for assistance with the photoluminescence measurements.

## 6. REFERENCES

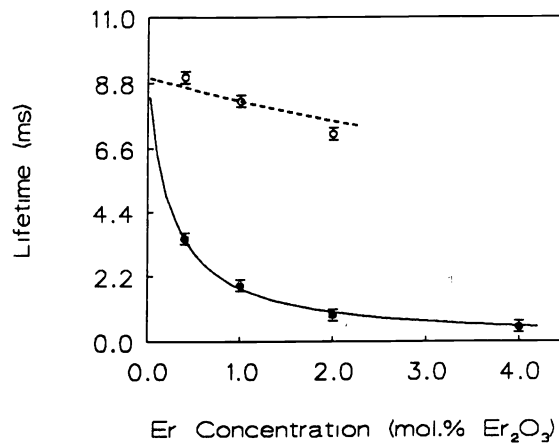
1. W.J. Miniscalco, *J. Lightwave Technol.* 9 (1991) 234
2. D.E. Day and J.M. Stevels, *J. Non Crystalline Solids* 14 (1974), 165 - 177
3. A.J. Bruce et al., *Mater. Res. Soc. Symp. Proc. Vol. 244* (1992) 157
4. F. Auzel, "Radiationless Processes", (B. Di Bartolo, ed.), Plenum Press (1979) 213
5. D.L. Dexter and J.H. Schukman, *J. Chem. Phys.* 22 (1954) 1063
6. A.M. Reitter et al., *J. Non. Cryst. Solids* 139 (1992) 121
7. R. Brückner, H. Hessenkemper, *Glastech. Ber.* 66 (1993) 245
8. K. Wei et al., *Fundamentals of Glass Science and Technology - ESG 1993 Proc. Suppl. to Vol. 23* (1993) 303



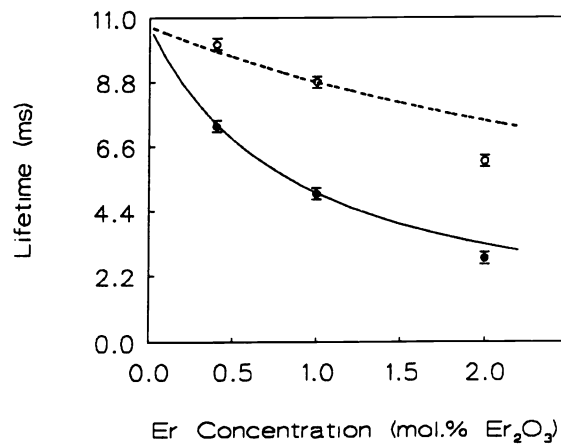
**Figure 1** Room-temperature PL spectra (measured at the same conditions) for as-melted (solid line) and dried (dashed line) PBL glasses (2 mole %  $\text{Er}_2\text{O}_3$ ).



(a) P424 glasses



(b) PBL glasses



(c) PJB glasses

Figure 2 PL-lifetime as a function of Er concentration. The fitted lines are based on the proposed Er PL quenching model.

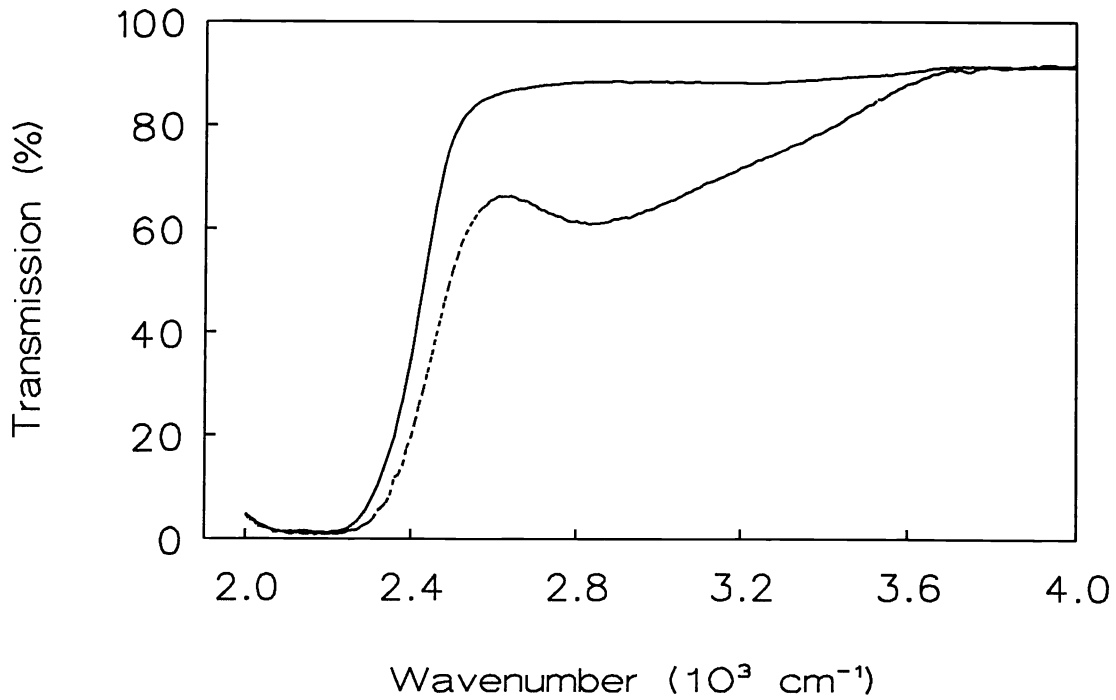


Figure 3 IR transmittance spectra for the as-melted (dashed line) and dried (solid line) P424-glass.

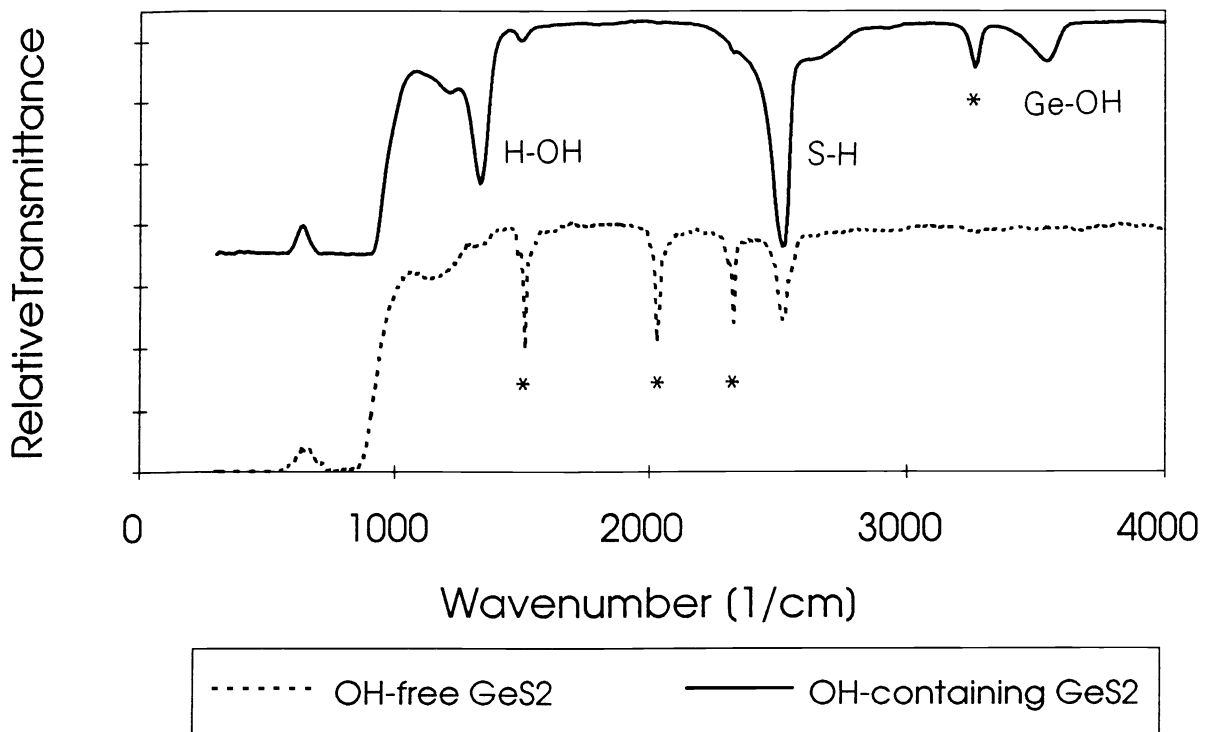


Figure 4 IR transmittance spectra of Pr-doped  $\text{GeS}_2$  glasses with a different OH-content. Absorption bands denoted with an asterisk have not been assigned.

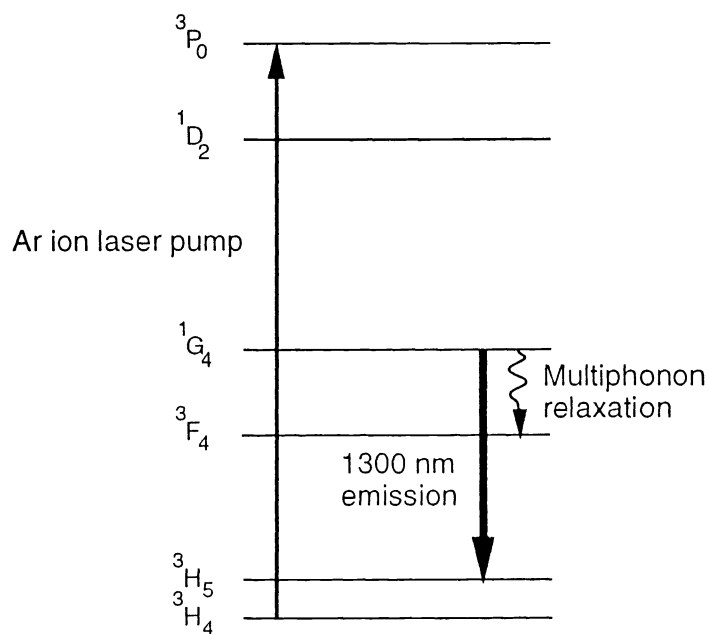


Figure 5 The energy level diagram of Pr<sup>3+</sup>. Also shown are the pump absorption, the emission gain and the multiphonon relaxation transition.

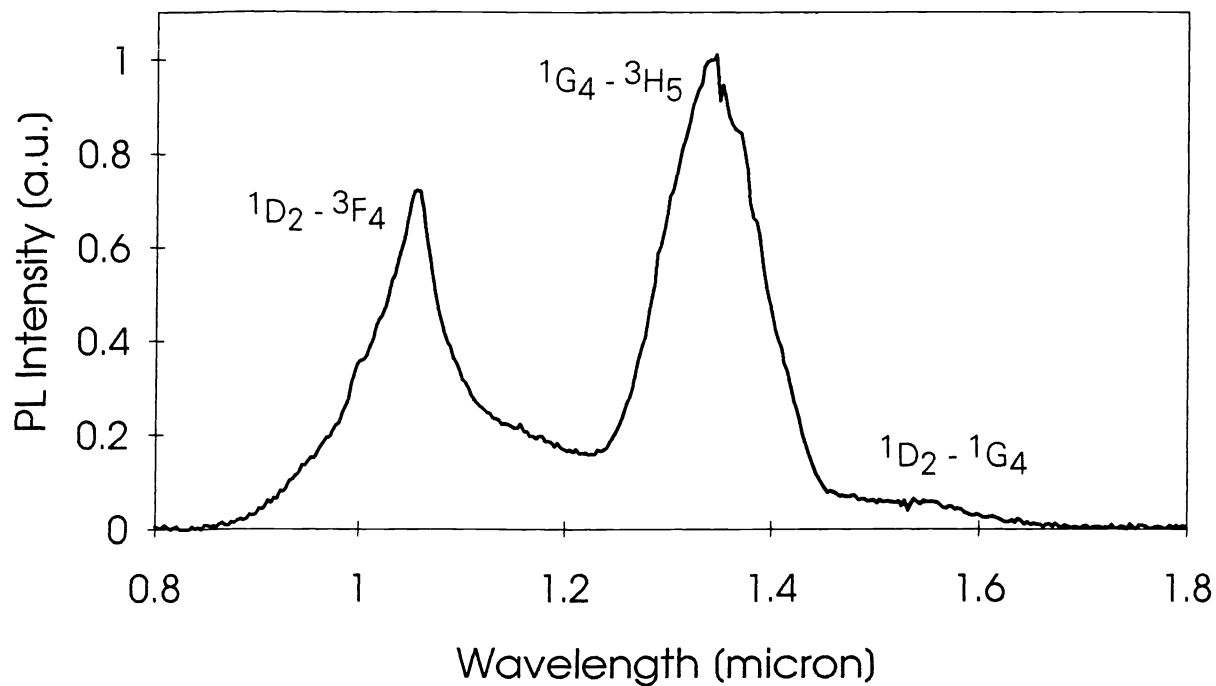


Figure 6 PL spectrum of OH-free 400 ppm Pr-doped GeS<sub>2</sub> glass. The various emission bands are assigned.



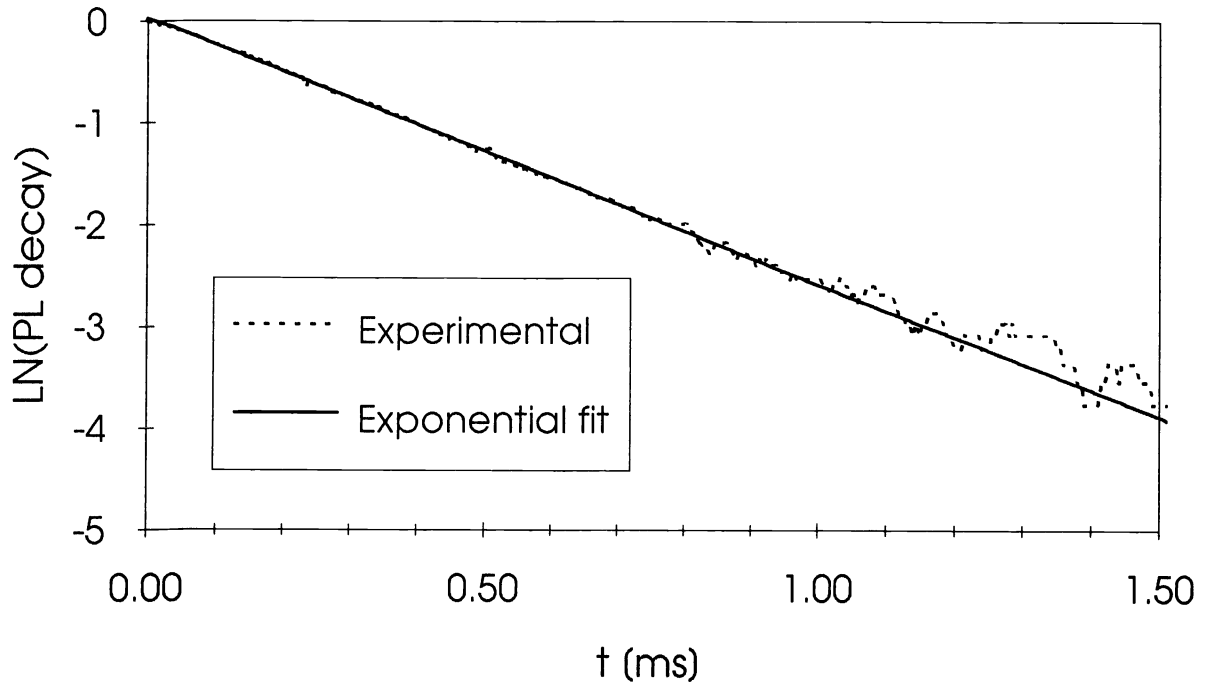


Figure 7 The natural logarithm of the PL decay curve of the  $\text{Pr}^{3+} \ ^1\text{G}_4$  state in OH-free  $\text{GeS}_2$ ; the emission lifetime is  $350 \pm 30 \ \mu\text{s}$ .

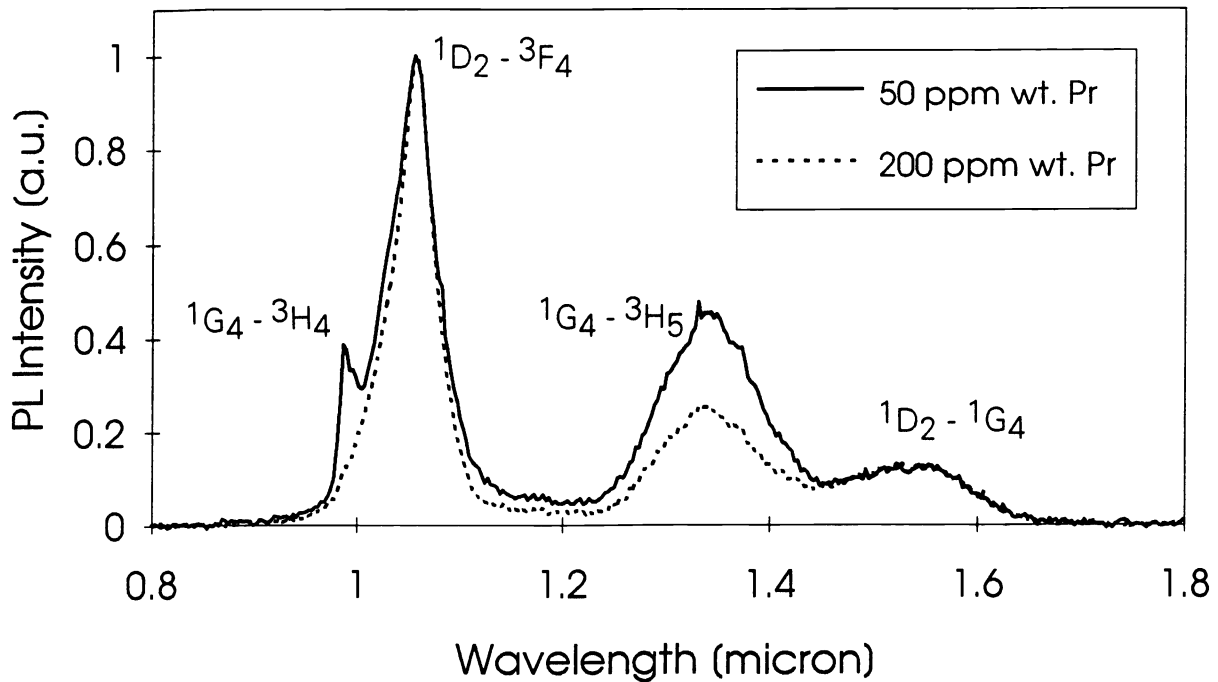


Figure 8 PL spectra of OH-containing Pr-doped  $\text{GeS}_2$  glass. The various emission bands are assigned.