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# Luminescence quenching by OH groups in highly Er-doped phosphate glasses

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## Abstract

Highly (up to 4 mol%  $\text{Er}_2\text{O}_3$ ) Er-doped phosphate bulk glasses have been prepared by common glass-melting techniques. Afterwards, a heat treatment was performed on the as-melted samples. The photoluminescence lifetime of Er ions for the  $^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2}$  transition increases substantially, typically from 3 ms up to 7 ms for a sample doped with 2 mol%  $\text{Er}_2\text{O}_3$ , due to the heat treatment. The increase of the lifetime is ascribed to a decrease in concentration of hydroxyl groups incorporated in the glass, which is confirmed by IR absorption spectroscopic measurements. The photoluminescence peak intensity also increases because of drying by a factor of 3 to 7 depending on glass composition. Based on electric dipole–dipole interaction theory, the luminescence concentration quenching mechanism by hydroxyl groups is modelled. The model predicts that more than half of the hydroxyl groups in the glass is coupled to Er ions. The influence of the glass structure and role of  $\text{Al}^{3+}$  on the  $\text{Er}^{3+}$  luminescence is studied by infrared spectroscopy.

## 1. Introduction

Recently, much attention has been given to the research and development of 1.5  $\mu\text{m}$  optical amplifiers for long-distance communication systems [1]. Glass fibre amplifiers with a low  $\text{Er}^{3+}$  concentration have been demonstrated to be quite efficient for this application [2]. Parallel to the development of a fibre amplifier having a length of several meters, there is a strong interest in developing planar waveguide amplifiers with small dimensions of around a few centimetres [3–5]. Planar waveguide amplifiers have potential applications in optical telecommunication

and signal processing systems as integrated devices [5].

For planar optical waveguide amplifiers, a high Er concentration and a high pump power density are needed to obtain sufficient optical amplification gains because the optical interaction path is shorter. At high Er concentration, however, the luminescence will be quenched by energy transfer processes due to ion–ion interactions [1,6] and, besides, another cooperative upconversion process occurs if a high pump power is applied at the same time [1]. These two luminescence quenching processes strongly influence the amplifier efficiency of planar waveguide amplifiers [1]. Efforts have been made to optimize Er-doped hosts including glasses and crystals [5].

Er-doped phosphate glasses have proved to be good optical glasses and the  $^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2}$  transi-

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tion around 1.5  $\mu\text{m}$  has been used for laser action in bulk glasses for many years [7]. Thus, phosphate glasses were selected as Er hosts in this study and  $\text{Er}^{3+}$  luminescence quenching processes in highly doped phosphate glasses was studied. Hydroxyl groups are serious quenchers [7–9] for the  $\text{Er}^{3+}$  lasing transition at 1.5  $\mu\text{m}$  and are thus the objective of the present glass optimization. By decreasing the OH concentration,  $\text{Er}^{3+}$  photoluminescence (PL) peak intensity and PL lifetime increase substantially. It appears that the upconversion quenching process does not occur at the present pump power for glass samples studied here.

Three types of Er-doped phosphate glass have been studied. Heat treatments were conducted on as-melted samples. Luminescence spectrum and lifetime were measured for both as-melted and dried samples. UV/VIS transmission and absorption spectra were measured. Infrared spectroscopy provides information about the structure of these glasses. The role of hydroxyl groups and the influence of glass structure on  $\text{Er}^{3+}$  lifetime are discussed and modelled.

## 2. Experimental procedure

### 2.1. Preparation of glass

The batch compositions of the melted glass and the corresponding abbreviations are listed in Table 1. For preparation of the glass batches, an 89% solution of pure orthophosphoric acid was used. Analytical reagent grade carbonates or oxides provided the other components. All the powders were well mixed and put in a platinum crucible. Next, orthophosphoric acid was added to the crucible at room temperature. The batch was allowed to stand overnight and then

dried at a low temperature from 100 to 500°C, with a controlled low heating rate to remove most of the water inside the batch. This process promotes the gradual formation of phosphates and their dehydration.

The dehydrated batches were put into a normal electrical furnace at  $\sim 750^\circ\text{C}$  and gradually heated. The melting temperature was 1100–1450°C depending on the composition. The melt was kept for about 6 h at the melting temperature. The as-melted glass was poured into a graphite crucible and annealed at 390–450°C.

### 2.2. Controlled heat treatments

Several methods have been reported for further decreasing the OH concentration in the as-melted glasses [8,9] including drying in vacuum, dry oxygen gas bubbling, increasing the glass melting temperature and re-melting of the glasses under water-vapour-free atmosphere. The last method has been selected here for re-melting the glass, since it is an easy method and offers good results.

Part of a sample was put in a glassy carbon crucible in a silica tube under pure argon atmosphere ( $\text{H}_2\text{O} < 15$  ppm) and re-melted by RF-inductive heating. In preliminary experiments, re-melted samples were found to turn black. This change was attributed to contamination by the carbon wall and subsequent reduction of metal oxides. Therefore 99.7% pure alumina crucibles inside a vitreous carbon crucible were used to prepare samples for these experiments. The heating temperature was chosen to avoid selective evaporation of glass components and the contamination of the silica tube. The re-melting processes lasted for 1–2 h at a temperature of 1100–1200°C depending on glass composition. The liquids were allowed to cool in the argon atmosphere, and then were taken out and annealed in a normal furnace in air. The resulting samples were cut and polished for further uses.

### 2.3. Photoluminescence lifetime and spectral measurements

$\text{Er}^{3+}$  PL spectrum and PL lifetime of the 1.5  $\mu\text{m}$  transition were measured using polished glass samples with a thickness of 1 mm. PL spectra were

Table 1  
Glass compositions (in mol%)

| Glass | $\text{P}_2\text{O}_5$<br>( $\pm 1$ ) | $\text{Na}_2\text{O}$<br>( $\pm 2$ ) | $\text{Li}_2\text{O}$<br>( $\pm 2$ ) | $\text{Al}_2\text{O}_3$<br>( $\pm 2$ ) | $\text{BaO}$<br>( $\pm 0.5$ ) |
|-------|---------------------------------------|--------------------------------------|--------------------------------------|--|-------------------------------|
| PBL   | 50                                    | –                                    | 26–30                                | 3–3.5                                  | 16                            |
| P424  | 38–40                                 | 38–40                                | –                                    | 20–21.6                                | –                             |
| PJB   | 31                                    | 42–44                                | –                                    | 20–22.6                                | 2                             |

The Er dopant levels include: 0.02, 0.2, 1.0, 2.0, 4.0 mol%  $\text{Er}_2\text{O}_3$ , respectively.

recorded at room temperature. The 514.5 nm line of an argon ion laser was used as pumping source, which matches the  $^4H_{11/2}$  manifold of  $Er^{3+}$ . The excited  $Er^{3+}$  ions decay non-radiatively to the metastable state  $^4I_{13/2}$  and then radiatively decay to the ground state  $^4I_{15/2}$ . The luminescence signals were analyzed by a 48 cm monochromator in combination with a liquid-nitrogen-cooled Ge detector and recorded by a lock-in amplifier. The system resolution was  $\sim 1$  nm.

For the PL lifetime measurements, the pumping beam was chopped at 15 Hz with a power of 100 mW and was focused onto the sample surface in an  $\sim 0.15$  mm diameter spot. The pump pulse duration was  $\sim 1$  ms with a cutoff edge of  $< 100$   $\mu$ s. Luminescence decay curves were recorded and averaged by a digital oscilloscope system. The influence of pump power density on  $Er^{3+}$  PL lifetime was examined by varying the pump power from 100 mW to 2.5 W.

Room temperature transmission and absorption measurements were performed both in the UV/VIS range 0.2–2.5  $\mu$ m (Perkin Elmer Lambda 9 Spectrophotometer) and in the IR range 2.5–5  $\mu$ m (PE-883 IR Spectrophotometer). Chemical analysis of the melted samples by energy dispersive analysis of X-rays (EDAX) was carried out to check the glass compositions.

### 3. Results

#### 3.1. EDAX measurement

The glass compositions measured by EDAX agree well with the corresponding batch compositions (see Table 1), within 2 mol%.

#### 3.2. $Er^{3+} \ ^4I_{13/2} \rightarrow \ ^4I_{15/2}$ PL spectrum and lifetime

Photoluminescence spectra of the PBL and P424 glasses doped with 2 mol%  $Er_2O_3$ , both as-melted and dried, are shown in Fig. 1. These PL spectra were measured at the same conditions. The effects of the heat treatment are clearly shown in Fig. 1. The PL intensities increase strongly for dried samples, which is about seven times for the PBL glass and about three times for the P424 glass. The peak

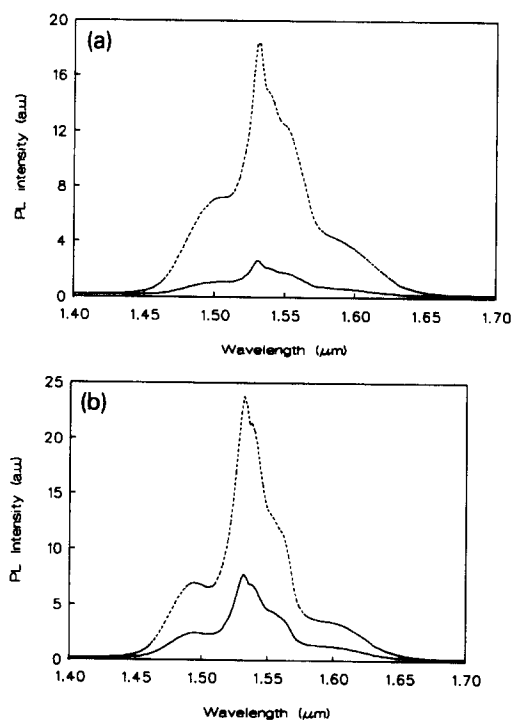


Fig. 1. Room temperature photoluminescence spectra for the corresponding as-melted and dried glasses doped with 2 mol%  $Er_2O_3$ . The  $^4I_{13/2} \rightarrow ^4I_{15/2}$  manifold transitions is centered at 1.534  $\mu$ m. The solid lines are for as-melted samples and dashed lines for dried samples. All curves in this figure are measured at the same conditions. (a) PBL glass. (b) P424 glass.

wavelength of the  $Er^{3+} \ ^4I_{13/2} \rightarrow \ ^4I_{15/2}$  transition is located at 1.534  $\mu$ m for all glass samples, including PJB glasses (data not shown). Also, the heat treatment does not change the peak wavelength.

Fig. 2 shows the PL lifetime as a function of  $Er^{3+}$  concentration in different samples. The PL decay curves for determining the  $1/e$  decay time are exponential within errors of measurement even for samples doped with 2 mol%  $Er_2O_3$ ; a typical curve is shown in Fig. 3 (in logarithmic format). In Fig. 2(a), the PL lifetime for as-melted PBL samples decreases with increasing  $Er^{3+}$  concentration. The other as-melted samples in Figs. 2(b) and (c) show the same effect of PL lifetime decrease with increasing  $Er^{3+}$  concentration, however to a less extent. After heat treatment, PL lifetimes for all samples increased. For PBL and P424, lifetimes measured with a pumping density of  $\sim 0.3$  kW/cm<sup>2</sup> were as high as 7 ms even for a concentration of 2 mol%

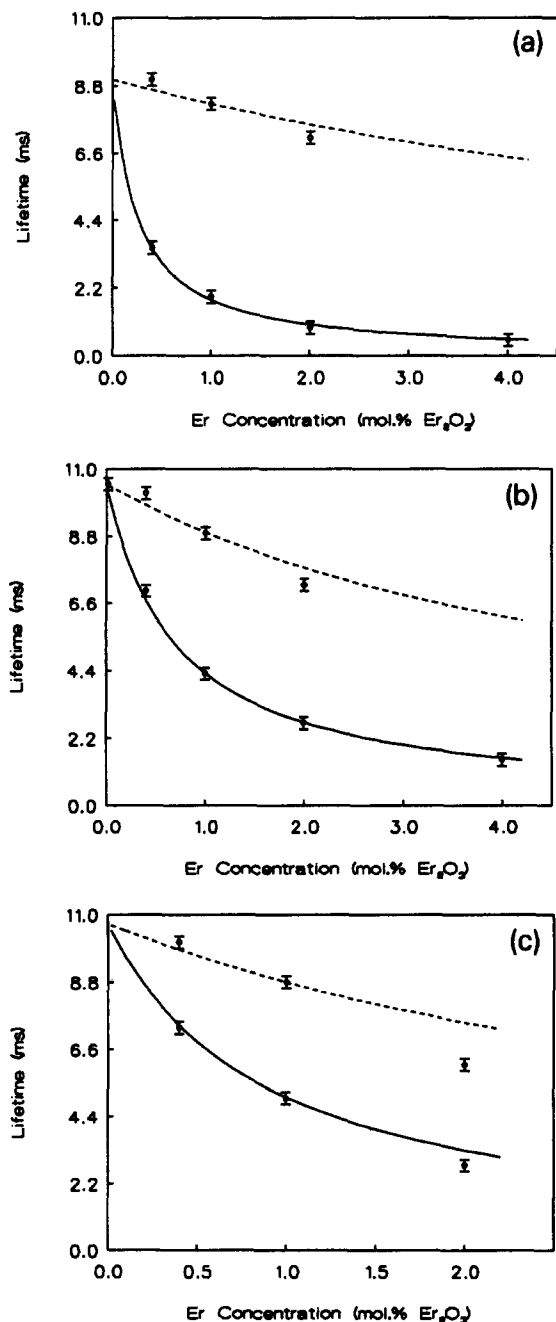


Fig. 2. Photoluminescence  $^4\text{I}_{13/2}$  lifetime as a function of Er concentration. Experimentally measured data are depicted in data-points (measuring error within  $\pm 0.2$  ms). The fitting lines are based on the proposed Er photoluminescence quenching model. The solid lines are for the as-melted samples and the dashed lines for dried samples. (a) PBL glass. (b) P424 glass. (c) PJB glass.

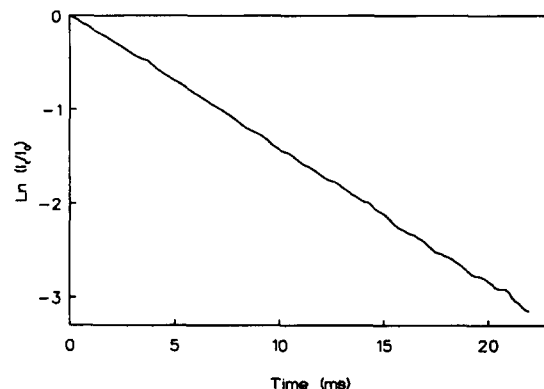


Fig. 3. Photoluminescence decay curve for the dried P424 glass doped with 2 mol%  $\text{Er}_2\text{O}_3$ .  $I_t$  and  $I_0$  represent the photoluminescence intensity at  $t$  ms and 0 ms. The corresponding luminescence lifetime is  $7.1 \pm 0.2$  ms. A laser pump power of 100 mW is used corresponding to a launched power density  $\sim 0.3$  kW/cm $^2$ .

$\text{Er}_2\text{O}_3$ . As explained below, the increase in lifetime after the heat treatment is due to a decrease of the OH content.

The influence of pump power density on the  $\text{Er}^{3+}$  PL lifetime in the P424 glass is depicted in Fig. 4. For thin glass samples, a pump power density as high as  $\sim 7$  kW/cm $^2$  is reached, at which the PL decay curve is still exponential or linear in a logarithmic format within errors of measurement. This dependence shows that no strong quenching effect occurs up to this pump power density. The PBL and PJB glasses show a slight lifetime reduction similar

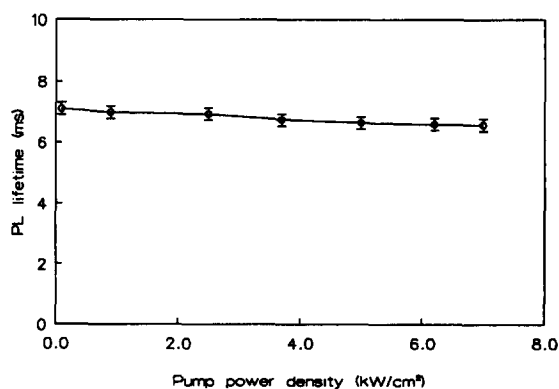


Fig. 4. Er photoluminescence lifetime of the dried P424 (2 mol%  $\text{Er}_2\text{O}_3$ ) glass as a function of pumping density. The line serves as a guide for the eye. The maximum launched pump power density is 7 kW/cm $^2$ .

to the P424 glass in Fig. 4. It is expected that a cooperative upconversion process occurring at high pump powers and high Er concentrations would lead to light emission at  $0.98\ \mu\text{m}$  [1]. No luminescence at  $0.98\ \mu\text{m}$  is observed in the present study. So, it appears that the upconversion quenching process does not occur at the present pump power for these glass samples.

### 3.3. UV/VIS and infrared spectroscopy

From UV/VIS transmission spectral measurements (data not shown), the spectral absorption coefficient,  $\alpha_{\text{abs}}$ , can be determined. The integrated absorption cross-sections,  $K_a$ , for the  $\text{Er}^{3+}\ ^4\text{I}_{13/2} \rightarrow\ ^4\text{I}_{15/2}$  transition can be written as [1]

$$K_a = \int \sigma_{\text{abs}}(\nu) d\nu = \int \frac{\alpha_{\text{abs}}(\nu)}{N_{\text{Er}}} d\nu. \quad (1)$$

For the P424 glass doped with 2 mol%  $\text{Er}_2\text{O}_3$ , as an example,  $K_a$ , calculated from the measured data, was  $4.6 \times 10^{-8}\ \text{cm}^2/\text{s}$ . This value is used below.

The infrared transmission spectra for the as-melted samples are depicted in Fig. 5. This figure shows the broad OH absorption band in the near IR. For the PBL and P424 samples, this band is located at  $\sim 2910\ \text{cm}^{-1}$  ( $3.44\ \mu\text{m}$ ). For PJB samples, this band is shifted to  $3450\ \text{cm}^{-1}$  ( $2.90\ \mu\text{m}$ ). The increase of Er concentration has little influence on the IR absorption band. In Fig. 6, infrared spectra for as-melted and dried P424 samples are compared. By

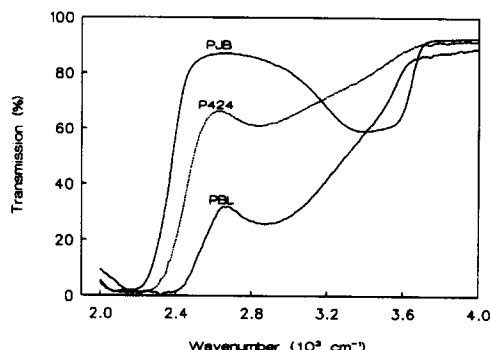


Fig. 5. Infrared transmission spectra showing OH IR absorption bands. The sample thickness is 1 mm. For PBL, P424 and PJB, the absorption band is located at 2910, 2860 and  $3450\ \text{cm}^{-1}$ , respectively.

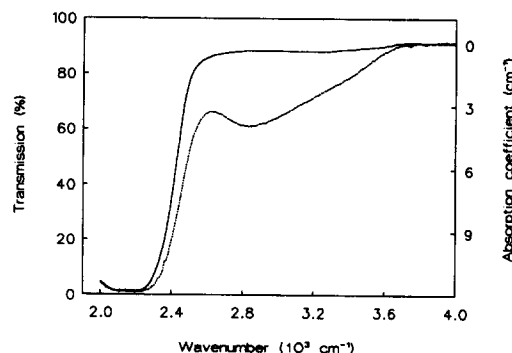


Fig. 6. Infrared transmission spectra for the as-melted (dashed line) and dried (solid line) P424 glass. The sample thickness is 1 mm. The corresponding absorption coefficients are labelled in the right Y axis from top to bottom.

drying, the OH content decreases and the OH absorption peak almost vanishes.

The IR absorption coefficient for P424 samples is also depicted in Fig. 6, which shows that the absorption coefficients at  $2910\ \text{cm}^{-1}$  are  $4.0$  and  $0.5\ \text{cm}^{-1}$  for as-melted and dried samples, respectively. In Ref. [10], extinction coefficient data at  $2910\ \text{cm}^{-1}$  for a glass similar to P424 were presented. An OH concentration of  $360 \pm 100\ \text{ppm}$  absorption gives an absorption of  $\sim 2.8\ \text{cm}^{-1}$  [10]. By comparison, it is estimated that the as-melted P424 glass has an OH concentration of  $\sim 530\ \text{ppm}$  or  $9.54 \times 10^{19}\ \text{cm}^{-3}$  and the dried P424 glass  $\sim 70\ \text{ppm}$  or  $1.26 \times 10^{19}\ \text{cm}^{-3}$ . So, with the present relatively simple setup for heat treatment, the OH content was effectively reduced.

## 4. Discussion

### 4.1. Glass structures and $\text{Er}^{3+}$ luminescence properties

The glass host can influence the luminescent properties of rare-earth ions such as  $\text{Er}^{3+}$ , which is observed in the PL lifetime of the  $^4\text{I}_{13/2} \rightarrow\ ^4\text{I}_{15/2}$  transition of excited  $\text{Er}^{3+}$  ions. Among other factors, the PL lifetime of  $\text{Er}^{3+}$ -doped glasses is influenced by the OH content in the glass [7]. IR absorption spectroscopy can provide more information about these OH groups in the glass. It is known [11] that the presence and bonding state of OH groups in glass

matrices is closely related to the relative number of non-bridging oxygens in the glass.

Infrared absorption spectra of silicate glasses have been studied extensively [12]. The fundamental stretching vibrations of OH groups experiencing different degrees of hydrogen bonding give rise to three absorption bands. The band at 2.7–2.9  $\mu\text{m}$  is due to free OH groups, whereas the bonded or associated OH groups cause peaks to occur at 3.3–3.8  $\mu\text{m}$  and at  $\sim 4.2$   $\mu\text{m}$ . Addition of  $\text{Al}_2\text{O}_3$  to alkali silicate glasses brings about a decrease of non-bridging oxygens, which leads to a decrease of associated OH groups.

In phosphate glasses, OH groups can be present at different positions on the phosphate chain, which gives rise to different  $-\text{OH}\cdots\text{O}-$  associations. This difference results in a number of overlapping absorption bands, which combined to give a broad band. This OH absorption band extends from  $\sim 2500$  to  $3600\text{ cm}^{-1}$  (2.7–4  $\mu\text{m}$ ), due to the fundamental stretching vibration of OH groups, as in silicate glasses [13].

In Fig. 5, the PBL glasses rich in alkali and alkaline earth ions, having a relative high number of non-bridging oxygens, mainly show associated OH groups which have a peak around  $2800\text{ cm}^{-1}$ . P424 and PJB glasses both have a high  $\text{Al}_2\text{O}_3$  content, leading to a much lower concentration of non-bridging oxygens and thus most of the OH groups in these as-melted samples are expected to be present in a free bonding state, similar to the case of aluminosilicate glasses. An OH absorption band is indeed observed for the PJB glass at around  $3500\text{ cm}^{-1}$ . It is interesting to note that the absorption band for as-melted P424 glass having a similar amount of  $\text{Al}_2\text{O}_3$  as in the PJB glass is located at a different position and has a different band shape, although the intensities of the two peaks are similar. The OH absorption band of the P424 glass is similar to the band of the PBL glass and is located at almost the same position, only having a lower intensity. We suggest that these observations show that the P424 and PJB glass have different glass structures in spite of similar  $\text{Al}_2\text{O}_3$  contents.

The complex role of  $\text{Al}_2\text{O}_3$  in phosphate glasses has been discussed recently [14]. It is shown that in sodium aluminophosphate glasses there is a structure change at the pyrophosphate stoichiometry (overall

Table 2  
Structural characteristics of studied phosphate glasses

| Glass | $\text{Al}_2\text{O}_3$ content (mol%) | O/P molar ratio | Non-bridging oxygens | OH bonding state |
|-------|--|-----------------|----------------------|------------------|
| PBL   | $\sim 3$                               | 3.07            | rich                 | associated       |
| P424  | $\sim 20$                              | 3.75            | less                 | associated       |
| PJB   | $\sim 20$                              | 4.34            | less                 | free             |

O/P ratio = 3.5), and it is also suggested that a second change occurs at the orthophosphate stoichiometry (O/P = 4). In Table 2, the structural characteristics of our phosphate glasses are listed. As shown in Table 2, O/P is 3.75 for P424 glasses and 4.34 for PJB glasses. The observation that phosphate glasses having different values of O/P give different OH infrared absorption bands supports the above-mentioned predictions.

Linking the IR absorption spectra to the measured values of the  $^4\text{I}_{13/2}$  PL lifetime of  $\text{Er}^{3+}$  ions, the following observations can be made. The P424 and PJB glasses incorporate OH groups with different bonding states but have similar absorption peak intensities. The PL lifetimes for both glasses are similar. On the other hand, the P424 and PBL glass having really different absorption peak intensities give different PL lifetimes. The smaller the infrared absorption peak, the higher the lifetime of Er ions. The general conclusion is that  $\text{Er}^{3+}$  PL lifetime is influenced mainly by the amount of OH content in the glass, rather than by the specific OH bonding state.

#### 4.2. Modelling of $\text{Er}^{3+}$ luminescence quenching by hydroxyl groups

It has been suggested by several authors that OH groups are serious quenchers of the photoluminescence of Er ions in phosphate glasses [7,8]. In a luminescence study on Er-doped alkali silicate glasses [9], a similar conclusion is reached that  $\text{Er}^{3+}$  PL lifetime reduction has a combined rather than a separate dependence on both the  $\text{Er}^{3+}$  and OH concentrations. A possible two-phonon quenching mechanism by OH groups is suggested [9]. Based on this suggestion, a simplified energy transfer and quench-

ing model is described here to explain the observed  $\text{Er}^{3+}$  luminescence quenching quantitatively.

A general theory of concentration quenching was proposed by Förster and Dexter [6]. According to this theory, the energy transfer probability per unit time between two nearby  $\text{Er}^{3+}$  ions by the electric dipole–dipole interaction is equal to

$$P_{\text{dd}} = \frac{3h^4 c^4}{64\pi^5 n^4} \frac{Q_a}{\tau_0 R^6} \int \frac{f_a(E)f_e(E)}{E^4} dE$$

$$= \left(\frac{R_0}{R}\right)^6 \frac{1}{\tau_0}, \quad (2)$$

where  $n$  is the refractive index,  $c$  is the velocity of light in vacuum,  $h$  is the Planck constant,  $\tau_0$  is the  $\text{Er}^{3+}$  PL lifetime without energy transfer,  $R$  is the separation of the two neighbouring  $\text{Er}^{3+}$  ions and  $Q_a$  is the integrated absorption cross-section of the  $\text{Er}^{3+}$  ions ( $Q_a = \int \sigma(E) dE = hK_a$ ;  $K_a$  is from Eq. (1)).  $f_a(E)$  and  $f_e(E)$  are normalized shape functions of the absorption and emission spectra, and  $\int f(E) dE = 1$ .  $R_0$  is a critical distance at which  $P_{\text{dd}}$  equals  $1/\tau_0$  ( $\text{Er}^{3+}$  transition probability without energy transfer). Let  $N_0 = (4\pi R_0^3/3)^{-1}$ ;  $N_0$  is a critical concentration.

The Förster–Dexter theory [6] deals with the microscopic case of two ions interacting with one another. Concerning the macroscopic case with many ions, the energy transfer process in a glassy matrix can be treated as an energy diffusion process [15]. The concentration dependent lifetime,  $\tau$ , can be written as

$$(1/\tau) = (1/\tau_0) + (1/\tau_D), \quad (3)$$

where  $\tau_0$  is the lifetime without experiencing energy transfer as in Eq. (1).  $1/\tau_D$  is the quenching rate due to energy transfer by electrical dipole–dipole interactions, and is dependent on both the  $\text{Er}^{3+}$  and OH concentrations. The exact form of  $\tau_D$  is described below.

Three assumptions are proposed to build the present Er concentration quenching model. (i) The OH quenching centres are only coupled efficiently to a fraction of Er ions. (ii) The amount of  $\text{Er}^{3+}$  ions coupled to OH groups is dependent on the OH concentration in the glass,  $N_{\text{Er-OH}} = \alpha N_{\text{OH}}$  ( $0 < \alpha <$

1). (iii) Non-radiative quenching occurs after the excited energy is transferred to Er ions coupled to OH groups, possibly via a two-phonon mechanism. Thus, with an increasing Er concentration (above the critical concentration predicted by Eq. (2)), energy transfer between excited Er ions and ground state Er ions increasingly takes place. The excited energy will be lost whenever it is transferred to an  $\text{Er}^{3+}$  ion coupled to an OH quenching centre.

Taking into account these assumptions, the activators (Er ions) and quenchers (Er ions coupled to OH groups) are essentially identical as far as energy transfer is concerned, and one has a simplified formula for  $1/\tau_D$  in Eq. (3) [15],

$$\frac{1}{\tau_D} = k N_{\text{Er}} N_{\text{Er-OH}} = \frac{9}{2\pi} \frac{N_{\text{Er}} (\alpha N_{\text{OH}})}{\tau_0 N_0^2}, \quad (4)$$

with  $k = 8\pi R_0^6/\tau_0$  or  $k = (9/2\pi)(\tau_0 N_0^2)^{-1}$ , and  $N_{\text{Er-OH}} = \alpha N_{\text{OH}}$ .  $\tau_0$ ,  $R_0$  and  $N_0$  are from Eq. (2).

Applying this model to P424 glasses as an example, the following input parameters for Eq. (2) have been used:  $E = 0.81$  eV for the  $^4I_{13/2} - ^4I_{15/2}$  transition;  $n = 1.50$  (measured by Abbe refractometer);  $Q_a = 1.9 \times 10^{-22}$  cm<sup>2</sup> eV;  $\tau_0 = 10.5$  ms (measured lifetime for a P424 glass doped with 0.02 mol.%  $\text{Er}_2\text{O}_3$ );  $\int f_a(E)f_e(E) dE \approx 1$  (eV)<sup>-1</sup> (assuming a maximum overlap between  $f_a(E)$  and  $f_e(E)$ ). One obtains  $R_0 = 12.1$  Å, and  $N_0 = 1.35 \times 10^{20}$  cm<sup>-3</sup>. Further,  $N_{\text{Er}} = 6.08 \times 10^{20}$  cm<sup>-3</sup> for 2 mol.%  $\text{Er}_2\text{O}_3$  doped P424 glass,  $N_{\text{OH}} = 9.54 \times 10^{19}$  cm<sup>-3</sup> for the as-melted P424 glass and  $1.26 \times 10^{19}$  cm<sup>-3</sup> for the dried one.

Combining Eqs. (3) and (4), we obtain  $\tau$  as a function of  $N_{\text{Er}}$ . Fitting this relation with measured PL lifetime values as shown in Fig. 2(b), we obtain  $\alpha \sim 60\%$  for both as-melted and dried P424 glasses. This value indicates that more than half of the OH groups inside the P424 glass is coupled to the  $\text{Er}^{3+}$  ions, which causes the PL quenching. In Fig. 2(b), it can be seen that the fitting curve for the dried glass deviates from the data. The fitting curve lies below the data at a low Er concentration and above the data at a high Er concentration. Apparently, the energy transfer between Er ions is less severe with a low Er concentration, which leads to less quenching. We suggest that the lower PL lifetime than predicted at a high Er concentration is due to additional quenchers



other than OH groups becoming effective in quenching  $\text{Er}^{3+}$  luminescence for the dried glass.

For PBL and PJB glasses, similar fitting processes are carried out as shown in Figs. 2(a) and (c), and similar conclusions about the coupling of OH groups to Er ions in the glass are reached. As can be seen from Figs. 2 (a) and (c), the model predicts correct lifetime reduction trends for as-melted PBL and PJB glasses. Again the predicted values for the dried samples deviate somewhat from the data, due to the same reasons as explained for the P424 glass.

The high  $\text{Er}^{3+}$  PL lifetime at relatively high Er concentrations is attractive for practical purposes. It is expected that efficient planar optical waveguide amplifiers at 1.5  $\mu\text{m}$  can be realized in thin films of the highly  $\text{Er}^{3+}$ -doped phosphate glasses. Currently, thin films of these  $\text{Er}^{3+}$ -doped phosphate glasses are being deposited by the authors, using laser ablation and RF-sputtering techniques.

## 5. Conclusions

$\text{Er}^{3+}$  1.5  $\mu\text{m}$  luminescence quenching in phosphate glasses at high Er concentrations is examined. For as-melted phosphate glasses, the  $\text{Er}^{3+}$  PL lifetime decreases rapidly upon increasing  $\text{Er}^{3+}$  doping levels. This decrease is attributed to a combined concentration quenching process depending on both the  $\text{Er}^{3+}$  dopant concentration and the OH concentration in the glass. A concentration quenching model is proposed and it shows that more than half of the OH groups in the glass is coupled to the  $\text{Er}^{3+}$  ions. The controlled heat treatment decreases the OH concentration and results in an increase of the  $\text{Er}^{3+}$  PL lifetime for different Er concentrations. PL intensities also increase along with the increase of the lifetime. The heat treatment is effective for all three types of glass although there is a pronounced difference in the glass structure.

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