Evidence for erbium-erbium energy migration in erbium(III) bis(perfluoro-p-tolyl)phosphinate

Tan, RHC; Pearson, JM; Zheng, Y; Wyatt, PB; Gillin, WP

Evidence for erbium-erbium energy migration in erbium(III) bis(perfluoro-*p*-tolyl)phosphinate

R. H. C. Tan,[1] J. M. Pearson,[2] Y. Zheng,[2] P. B. Wyatt,[2] and W. P. Gillin[1,a)]

[1]*Department of Physics, Queen Mary, University of London, London E1 4NS, United Kingdom*
[2]*School of Biological and Chemical Sciences, Queen Mary, University of London, London E1 4NS, United Kingdom*

Photoluminescence lifetime measurements of the erbium decay in samples of erbium(III) bis(perfluoro-*p*-tolyl)phosphinate, $Er[(p\text{-}CF_3C_6F_4)_2PO_2]_3$, as a function of erbium concentration have been made. It has been found that for concentrations greater than 50%, the lifetime could be fitted with a stretched exponential function, which is indicative of erbium-erbium energy migration to quenching sites, most likely at the surface of the finely divided powder. At concentrations below 50%, the decay was single exponential with a maximum lifetime of ~ 700 μs. © *2008 American Institute of Physics.* [DOI: 10.1063/1.2896105]

Erbium-doped glasses are widely used for telecommunications due to the sharp intra-atomic $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition in the 4f orbital, which results in an emission at ~ 1.5 μm, which is the low loss window for a silica optical fiber. If erbium is incorporated into organic hosts, then the organic ligands can act as photosensitizers, resulting in much higher absorption cross sections, with broader absorption bands than those for the free Er^{3+} ion.[1–4] However, ligands and coordinated solvent molecules usually contain C–H and O–H bonds that can cause vibrational quenching of electronically excited erbium; this limits any application of such complexes in infrared emitting devices. Deuteration or fluorination of hydrogen-containing ligands, together with exclusion of coordinated water, can extend the lifetime of infrared luminescence from lanthanide complexes.[5] We recently quantified the role of CH oscillators in the quenching of erbium by deuterating the $[Cs][Er(HFA)_4]$ (H-HFA is 1,1,1,5,5,5-hexafluoro-2,4-pentanedione) system, which has only one C–H bond per ligand, and we showed that any hydrogen within 20 Å of an erbium ion acts as an efficient quenching center.[6,7] Mancino *et al.*[8] have shown that an evaporated thin film of $Er(F\text{-}tpip)_3$, where F-tpip is perfluorinated imidodiphosphinate $[(C_6F_5)_2P(O)]_2N^-$, has a luminescence lifetime of 224 μs and this system, with no hydrogen, has a lifetime still considerably shorter than that expected for isolated ions. We have recently investigated the perfluorinated diphenylphosphinate system $Er[(C_6F_5)_2PO_2]_3$,[9] which forms a thermally stable but highly insoluble coordination polymer, and found that in the as-grown state, we can obtain luminescence lifetimes of ~ 0.5 ms. Again, this is still significantly worse than might be expected from isolated ions and suggests that other quenching mechanisms are operating.

In order to investigate this, we have measured the radiative lifetimes of a series of closely related rare earth perfluorinated *p*-tolylphosphinate complexes $Er_xY_{1-x}[(p\text{-}CF_3C_6F_4)_2PO_2]_3$ for samples where the erbium concentrations in the polymer were varied from 100 to 0.1 mol % by substituting erbium with yttrium. Y^{3+} has approximately the same ionic radius as Er^{3+} but is optically inert.

$(p\text{-}CF_3C_6F_4)_2PO_2H$ was made by alkaline hydrolysis of $(p\text{-}CF_3C_6F_4)_3PO$, in analogy with the preparation of $(C_6F_5)_2PO_2H$ in Ref. 10; the new tolyl ligand $(p\text{-}CF_3C_6F_4)_2PO_2H$ was fully characterized by CHN microanalysis, IR, ^{19}F and ^{31}P NMR, and high resolution mass spectrometries. Reaction of a solution of $(p\text{-}CF_3C_6F_4)_2PO_2H$ in diethyl ether with aqueous $ErCl_3$ led to the formation of the insoluble $Er[(p\text{-}CF_3C_6F_4)_2PO_2]_3$ at the interface between the two immiscible solvents. To form the diluted materials, a solution of erbium and yttrium chlorides in the required molar concentrations was used in the synthesis. After filtering, the powders were dried at 100 °C and 1 mbar in the presence of P_2O_5 for 3 days. IR spectroscopy and elemental analysis indicated that the products were anhydrous.

Photoluminescence from the complexes was excited using ~ 7 ns pulses, at an excitation wavelength of 520 nm, from a Continuum Panther optical parametric oscillator pumped with a Surelite I laser. This wavelength was chosen to provide direct excitation into the $^4S_{3/2}$ level of the erbium ion which decays to the $^4I_{13/2}$ level. The luminescence was dispersed in a Triax 550 spectrometer and detected using a Hamamatsu R5509-72 infrared photomultiplier tube. Lifetime data for the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition were recorded at the peak of the photoluminescence spectra (1542 nm) at a temperature of 300 K.

Figure 1 shows the luminescence decay curve for the 100% $Er[(p\text{-}CF_3C_6F_4)_2PO_2]_3$ sample. For the 100% sample, the decay is clearly nonexponential, although as the erbium concentration is reduced, the decay process tends toward becoming single exponential, which happens for erbium concentrations less than $\sim 70\%$. For the high concentrations, the data can be fitted using a multiple exponential decay process with three exponentials. However, without a defined number of distinct environments to account for such multiple exponential decay, the fitting of such process is somewhat arbitrary and of limited use in the analysis of data. Given that the luminescence decay becomes single exponential as the erbium concentration is reduced, it seems likely that the nonexponential decay is a consequence of energy migration among the emitting centers where there is a distribution of decay rates. We have therefore fitted our data using the stretched exponential function,
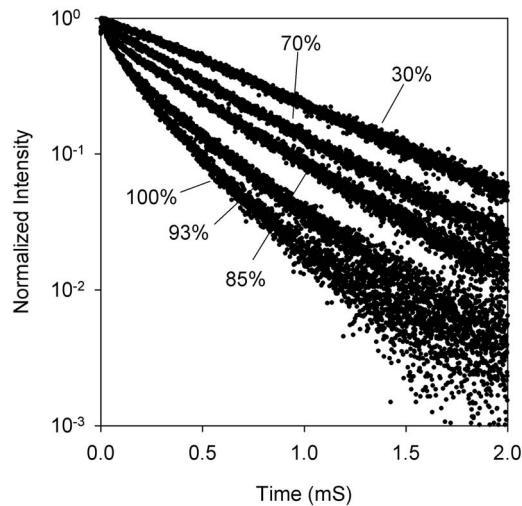
a)Electronic mail: w.gillin@qmul.ac.uk.

FIG. 1. Luminescence decay curves for the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition of erbium at a number of erbium concentrations.

FIG. 2. The average lifetime obtained from the stretched exponential fits as a function of the erbium concentration.

$$I = I_0 + I_1 \exp[-(t/\tau)^\beta], \tag{1}$$

where I_0 is the offset intensity, I_1 is the initial intensity, τ is the lifetime, and β is the stretching function. This is an empirical fit that is widely used to fit nonexponential decay processes, and although there is no well defined physical significance to the fit, it is frequently used to describe a superposition of exponential relaxation times.[11] One justification for its use in this work is that if we had a finely divided powder with quenching sites at the surface, due to adsorbed water or solvent, then there would be a distribution in lifetimes with the ions in the center of the grains having long lifetimes and those at the surface being rapidly quenched. Without energy migration between the erbium ions, the number of ions in the surface region would be relatively small; hence, their contribution to the observed decay would be correspondingly small. However, with energy migration, there is a constant flow of excitation from the ions in the bulk to those at the surface, which is manifested as the distribution in lifetimes. Table I gives the results of the fitting of Eq. (1) to our data. It can be seen that for erbium concentrations less than 50%, the β value for the fits are all unity, which implies a single exponential decay process. Above 50%, the β value decreases to ~0.7. Using this stretched exponential function, it is possible to define a lifetime distribution function and calculate an average relaxation time $\langle\tau\rangle$, where

$$\langle\tau\rangle = \frac{\tau}{\beta}\Gamma\left(\frac{1}{\beta}\right). \tag{2}$$

This average relaxation time is plotted in Fig. 2 as a function of the erbium concentration. From Fig. 2, it can be seen that for concentrations below 30%, the measured lifetime values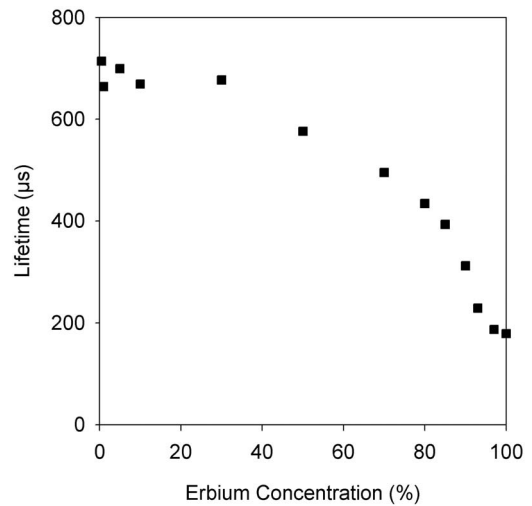 are approximately constant, which suggests that this is the intrinsically limited lifetime in this material and that at this concentration, there is negligible energy migration between neighboring erbium ions. This therefore provides an upper limit to the erbium concentration that can be utilized in a device based upon these materials. At the present time, we have not yet directly measured the absolute lifetime of the erbium in these complexes, but we would expect it to be slightly higher than the values measured for the dilute erbium samples. Our measured lifetimes may well be due to the presence of very small concentrations of residual water or hydrocarbon solvents within the complexes. When we can produce materials which can be sublimed, we should be able to further purify the material and determine if this is the rate limiting process.

We have therefore demonstrated that for fully halogenated ligands coordinated around erbium ions, although the quenching effects of CH and OH oscillators in the ligands can be massively reduced, the concentration of erbium that can be achieved is sufficient for erbium-erbium energy migration to play a role in reducing the lifetime. However, the erbium dilution needed to overcome the quenching induced by this process is relatively modest, and very high erbium concentrations should be achievable. The ligands used in this work have absorption bands in the deep UV, which prohibits excitation of the ions through energy transfer from the ligands. However, we are currently looking to further functionalize these ligands to produce materials which can be pumped using currently available high power light emitting diodes and which could possibly be used to provide electrical excitation of the ions.

TABLE I. The measured lifetimes and stretching parameters of the 1542 nm emission from the Er^{3+} $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition at different erbium concentrations.

	100%	97%	93%	90%	85%	80%	70%	50%	30%	10%	5%	1%	0.5%
τ (μs)	147	146	179	265	353	405	474	576	677	669	699	664	714
β	0.73	0.69	0.69	0.76	0.82	0.87	0.91	1	1	1	1	1	1

[1] L. H. Slooff, A. Polman, M. P. Oude Wolbers, F. C. J. M. van Veggel, D. N. Reinhoudt, and J. W. Hofstraat, J. Appl. Phys. **83**, 497 (1998).

[2] R. J. Curry and W. P. Gillin, Appl. Phys. Lett. **75**, 1380 (1999).

[3] R. J. Curry and W. P. Gillin, Curr. Opin. Solid State Mater. Sci. **5**, 481 (2002).

[4] J.-C. G. Bünzli and C. Piguet, Chem. Soc. Rev. **34**, 1048 (2005).

[5] Y. Hasegawa, Y. Wada, and S. Yanagida, J. Photochem. Photobiol. C **5**, 183 (2004).

[6] L. Winkless, R. H. C. Tan, Y. Zheng, M. Motevalli, P. B. Wyatt, and W. P. Gillin, Appl. Phys. Lett. **89**, 111115 (2006).

[7] R. H. C. Tan, M. Motevalli, I. Abrahams, P. B. Wyatt, and W. P. Gillin, J. Phys. Chem. B **110**, 24476 (2006).

[8] G. Mancino, A. J. Ferguson, A. Beeby, N. J. Long, and T. S. Jones, J. Am. Chem. Soc. **127**, 524 (2005).

[9] J. M. Pearson, Y. Zheng, R. H. C. Tan, W. P. Gillin, and P. B. Wyatt, J. Mater. Sci.: Mater. Electron. (submitted), DOI:10.1007/s10854-008-9662-9.

[10] K. W. Oliver, S. J. Rettig, R. C. Thompson, J. Trotter, and S. Xia, J. Fluorine Chem. **83**, 47 (1997).

[11] C. P. Lindsey and G. D. Patterson, J. Chem. Phys. **73**, 3348 (1980).