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Quantum Efficiency Measurements in Oxygen-Containing Gallium Lanthanum Sulphide Glasses and Fibers doped with Pr^{3+}

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Abstract

The quantum efficiency of Pr^{3+} emission at 1.3μm from the $^1G_4$ - $^3H_5$ transition is measured in Gallium Lanthanum Sulphide (GLS) glass containing varying quantities of lanthanum oxide. The variation of quantum efficiency with host composition is described, and the variation of quantum efficiency with pump wavelength in oxide-containing hosts is compared to a model of the effect of the addition of oxygen on the spectroscopy of the Pr ion. Oxide-containing GLS glasses can show quantum efficiencies of up to 84% of that of pure GLS, while retaining considerably better thermal and glass-forming properties. No degradation of quantum efficiency is seen when GLS glass is pulled into fiber form.

Introduction

Pr^{3+} is the most likely ion to be used in an efficient optical amplifier for the 1.3 μm telecommunication window[1]. To achieve a high efficiency Pr^{3+} amplifier, the glass host for the ion needs to be engineered such that the radiative quantum efficiency of the transition $^1G_4$ to $^3H_5$ is maximised, while the glass also allows ease of fibre manufacture. The radiative quantum efficiency (RQE) of the transition is the best indicator of the potential efficiency of an amplifier based on a particular glass host. So far sulphide-based chalcogenide glasses seem most suited to the role of a glass host[2,3,4] since they exhibit a low peak phonon energy, and therefore allow high RQE for the transition of interest. In particular, gallium lanthanum sulphide (GLS) is a strong candidate for a fibre host for Pr-based amplifiers. Fibres made of this glass have recently been reported[5], and its phonon energy is sufficiently low that multiphonon decay from the $^1G_4$ level does not dominate the emission properties[6]. Achieving production of GLS glass which is free from oxygen impurities is a difficult task - however, the presence of oxygen considerably improves the glass-forming properties of GLS[7]. The presence of oxygen also changes the spectroscopy of the Pr ion[8].

In order to make measurements of the RQE of Pr^{3+} in a particular glass host, use can be made of a recently-reported self-calibrating measurement technique devised by Quimby et al.[9]. This technique eliminates many errors and uncertainties in other techniques. In this letter we report on recent RQE measurements of Pr^{3+} in both pure and oxide-modified $Ga_{(1-x)}La_{(x)}S$ glasses in bulk and fiber form. The results show that the RQE of oxide-substituted GLS can be up to 85% of that of pure GLS, and has a strong pump wavelength dependance with a reduction of up to 17% from its peak value with change of pump wavelength. We will also comment on the effects of oxide impurities on the RQE and on the measurement technique itself.

Procedure:

Bulk-glass samples were prepared with the compositions given in Table I. All samples were doped with 500 ppm Pr_2S_3, measured by weight. This dopant level was chosen such that ion-ion interactions could be kept minimal while insuring a large emission signal.

Table I: Bulk glass compositions

Sample number.	Composition in molar ratios.
1 (155)	70% Ga_2S_3-30% La_2S_3
2 (150)	70% Ga_2S_3-30% La_2S_3 : 5% La_2O_3 substituted
3 (169)	55% Ga_2S_3-45% La_2S_3 : 5% La_2O_3 substituted
4 (178)	70% Ga_2S_3-30% La_2O_3
5 (Fibre)	70% Ga_2S_3-30% La_2O_3 (Pulled into a fibre)

The fibre sample (5) is a core-cladding structure with a core made from bulk sample number 4.

Figure 1 shows the transitions involved in the RQE measurement. Emission from the transition ${}^1G_4$-${}^3H_5$ at ~1.3μm (transition 1) was detected with an InGaAs detector for various pump wavelengths, 970-1010nm from a cw Ti:Sapphire laser. The ${}^1D_2$ level can be pumped directly with a cw R6G dye laser with a range of pump wavelengths. The emission from the two transitions

$^1D_2$-$^1G_4$ at ~1.5μm (transition 2) and $^1G_4$-$^3H_5$ was again detected using an InGaAs detector. Calculation of the RQE requires separating the luminescence from these two transitions. This can be achieved by comparing direct 1μm-pumped $^1G_4$-$^3H_5$ emission spectra for specific pump wavelengths to the combined $^1D_2$-$^1G_4$ and $^1G_4$-$^3H_5$ spectra produced by pumping the $^1D_2$ level. Analysis of residuals after subtraction of the spectra can be used to discern which direct-pumped $^1G_4$ emission spectra best fit the 1.3μm emission peak of the spectra obtained when pumping $^1D_2$ directly. It can be shown[9] that the RQE of the amplifying transition of interest is simply the total photon rate of transition 1 divided by the total photon rate of transition 2. The spectra are recorded with the same detection apparatus so the normalisation is the same for all the spectra and is independent of the pump scheme involved. Since the transitions total photon rates are divided, any collection efficiency or calibration coefficient for the apparatus is not needed since it will cancel. For each $^1D_2$ pump wavelength, a decay measurement was also taken to insure the oscillator strength of the $^1D_2$ level did not vary with pump wavelengths and several pump powers were used to check for power dependance of the emission.

Results:

In figure 2 it can be seen that as the pump wavelength is adjusted the emission peaks change their relative intensities, implying in this case a change in the RQE, and indicating a degree of site selectivity at room temperature[8]. After normalisation and scaling, the emission spectra were analysed as described above. The quality of the fit of transition 1 direct-pumped spectra to transition 1 of the indirect-pumped spectra is shown in figure 2 for the two pump wavelengths of interest (1000nm and 1010nm). The photon rate into each transition is separated by subtraction and the calculation of the RQE is trivial. Figure 3 shows RQE for the different samples at the two pump wavelengths. As a check of the oscillator strength of the transitions, the $^1D_2$ lifetime was measured at the corresponding (595 or 605 nm) pump wavelengths. The decay lifetime is seen to be approximately 50μs and shows only small differences with respect to change in excitation wavelengths. Therefore we can assume that the oscillator strength is constant and no other pump wavelength-dependent effects are creating population in $^1G_4$.

Subtraction of the two spectra in many cases does not perfectly resolve the two transitions, and this imperfect matching of the respective spectra because of their overlap is the main cause of errors in the RQE values. The error in each measurement is large in absolute terms (±10%), but for the individual samples the two efficiencies have much smaller relative error (±2%).

Sample 1, which contains no lanthanum oxide, exhibits a quantum efficiency of ~64%, which agrees well with previously-reported measurements. The samples containing 5% La_2O_3 show quantum efficiencies as high as 54%. The pure GLS samples show no wavelength dependance of the RQE. All the glasses containing lanthanum oxide, however, do display some dependence of RQE on pump wavelength. In all cases, there is a reduction in RQE with shorter pump wavelength. Of particular interest are the differences between samples 2 and 3. Although they contain equal amounts of lanthanum oxide (5% substituted into the glass) they have different lanthanum sulphide to gallium sulphide ratios and this causes a change in the pump wavelength dependance of their RQE.

Comparison of the fibre core (sample 5) with the equivalent bulk glass (sample 4) shows that the RQE does not change when the glass is drawn into a fibre core and that the RQE is still pump wavelength dependant. The equivalence of the results for fibre core and bulk is important, as it shows there is no degradation of optical properties when the fibre is drawn.

These results imply that the addition of lanthanum oxide into GLS glass reduces the RQE and introduces pump wavelength dependance. Our model of this system is based on the idea that La_2O_3 substituted into the glass matrix creates new sites for the rare earth ion, which has been previously put forward to explain the spectral properties of the system[x]. The new sites cause large inhomogeneous broadening via the nephelauxetic effect, and this allows room temperature site selectivity, as seen in figure 1. In the pure GLS glass the rare earth ions replace lanthanum, and are bonded to sulphur. In the oxide-modified glass there are rare earth ions coordinated into oxygen- and sulphur-related sites. Ions at these oxygen-related sites have shorter absorption wavelengths, and exhibit faster non-radiative decay than those at sulphide sites. (The oxygen-related site is also the preferred site for the Pr^{3+} ion and so the effects of lanthanum oxide addition are readily seen.) This model agrees well with our results, since increasing the pump energy implies more oxygen-related Pr^{3+} is excited and due to the faster non-radiative de-excitation of these sites the RQE is decreased.

The fluorescence lifetime of the $^1G_4$ level in oxide-containing GLS is modified, and shows two separate exponential components, one from each of the two sites. Because of this, at shorter pump wavelengths the averaged lifetime given by fitting a single exponential can be as short as 150μs, compared to ~300 for pure GLS. Quantum efficiency calculations based on this lifetime will be misleading, as the lifetimes are non-exponential and pump wavelength dependant.

The value of RQE measured in GLS glass systems by the method described in this paper is only valid for a particular pump wavelength. Errors in the measurement are small when the fluorescence peaks from the two transitions of interest are easily separable. The errors in the measurement become large when the emission from the two transitions of interest overlaps spectrally, and the emission spectra peaks become more difficult to separate.

Conclusion:

It has been shown that the RQE of the $^1G_4$-$^3H_5$ transition of Pr^{3+} in an oxide-substituted GLS glass can be up to 85% of the value for pure GLS glass, and is pump-wavelength dependant. This RQE makes oxide-substituted GLS an attractive host for Pr^{3+}, given the improvement in fiber drawing properties that oxygen addition provides over pure GLS. The RQE in oxide-substituted GLS can be reduced by up to 17% from its peak value by pump wavelength changes. We have also reported the RQE of Pr in a GLS fiber, which, at 12%, shows no degradation compared to the equivalent bulk glass, and is larger than in a ZBLAN host[1]. We have shown that although this particular technique used to find the RQE value is useful, care must be taken when applying such a technique to transitions with large inhomogeneous broadening, as site selective excitation at room temperature mean that results can be strongly pump-wavelength dependant.

Acknowledgements

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Figure captions:

1: Level structure of Pr^{3+}, showing the transitions of interest.

2: Fluorescence spectra of two different Pr sites within the glass. The solid line in each case is the spectrum pumping into the $^1D_2$ level. The dashed lines show the spectrum of transition 2 pumped into the $^1G_4$ level, and the dotted lines show the subtraction of the two spectra, which is equivalent to the spectrum of transition 1. The ratio of the integrals of the two peaks gives the quantum efficiency.

3: Quantum efficiencies for the $^1G_4$ - $^3H_5$ transition in different hosts, pumped at two different wavelengths. Solid bars are for 1010nm pump, shaded bars are for 1000nm pump.

References

1. BECKER, P.C., BROER, M.M., LAMBRECHT, V.G., BRUCE, A.J., and NYKOLAK, G.: 'Pr^{3+}:La-Ga-S glass: A promising material for 1.3µm fibre amplification' Tech. Dig. Topical Meeting Optical Amplifiers and their Applications, 1993, (Optical Society of America, Washington, D.C.), Post-deadline paper PDP5

2. HEWAK, D.W., MEDEIROS, J.A., SAMSON, B., BROWN, R.S., JEDRZEJEWSKI, P., WANG, J., TAYLOR, E., LAMING, R.I., WYLANGOWSKI, G., PAYNE, D.N. : 'Quantum Efficiency of praseodymium-doped Ga:La:S glass for 1.3µm optical fiber amplifiers', *IEEE Photonics Technol. Lett.*, 1994, **6**, pp. 609-612

3. WEI, K., MACHEWIRTH, D.P., WENZEL, J, SNITZER, E, and SIGEL, G.,: 'Pr^{3+}-doped Ge-Ga-S glasses for 1.3micron optical fibre amplifiers', *Opt. Lett.*, 1994, **19**, pp. 904-907

4. BROCKLESBY, W.S., AND PEARSON, A., ' A Spectroscopic Study of Praseodymium-doped Gallium-Lanthanum-Sulphide Glass'. *J. Lumin.*, 1994, **59**, pp.333-340

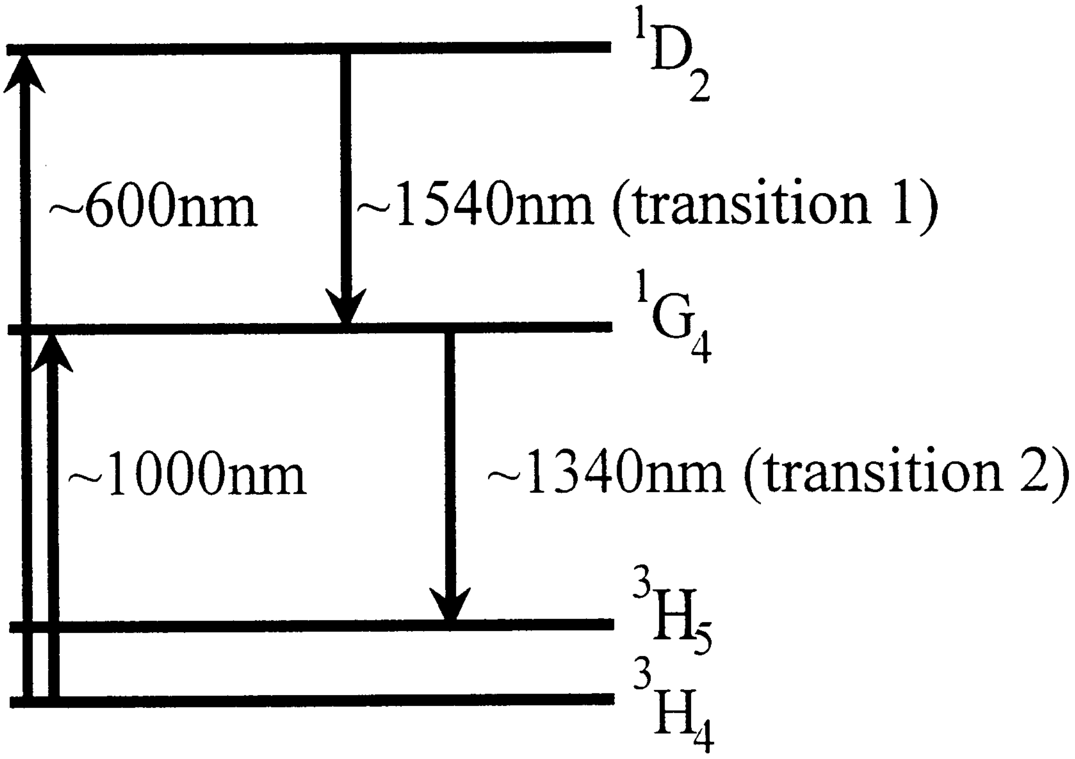
5. HEWAK, D.H, MOORE, R.C., SCHWEITZER, T., WANG, J., SAMSON, B., BROCKLESBY, W.S., PAYNE, D.N., and TARBOX, E.J.: Gallium Lanthanum Sulphide optical fibre for active and passive applications'. *Electron. Lett.*, 1995, **32**, pp. 384-385

6. HEWAK, D.W., DEOL, R.S., WANG, J., WYLANGOWSKI, G., NETO, J.A.M., SAMSON, B.N., LAMING, R.I., BROCKLESBY, W.S., PAYNE, D.N., JHA, A., POULAIN, M., OTERO, S., SURINACH, S., BARO, M.D: 'Low Phonon-Energy Glasses for Efficient 1.3µm optical-fiber amplifiers', *Electron. Lett.*, 1993, **29** pp.237-239

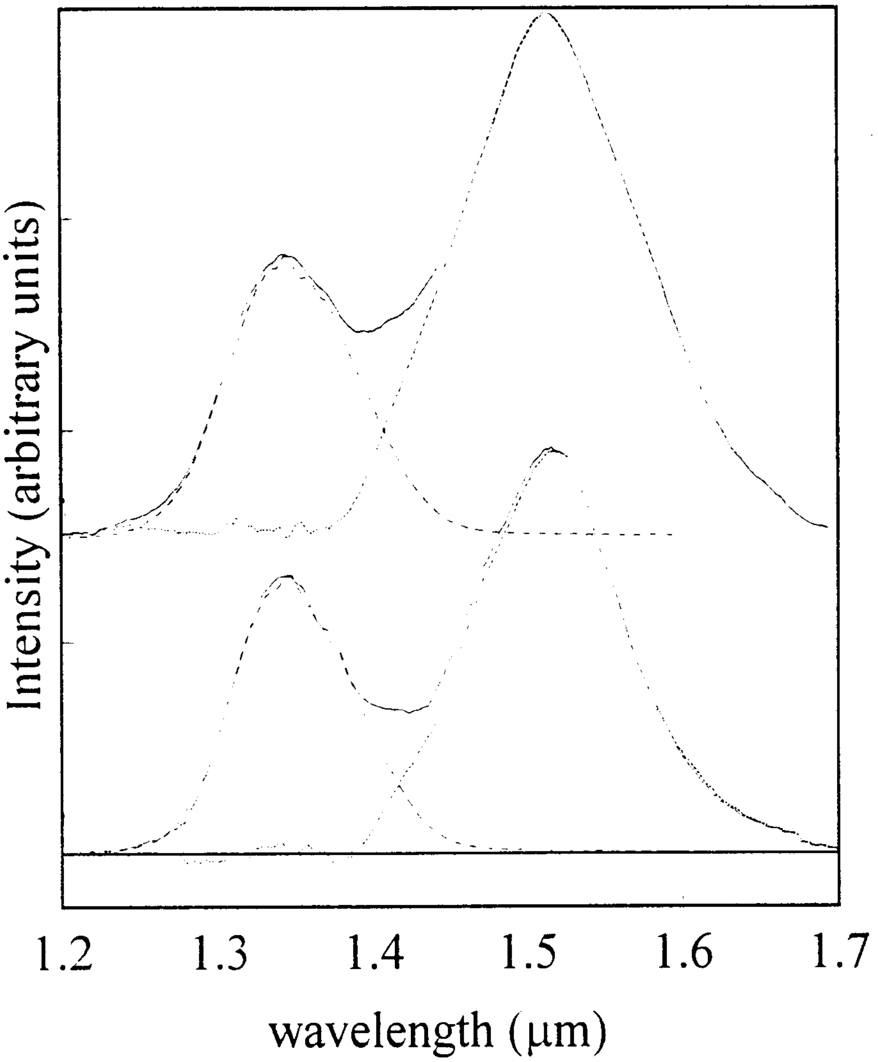
7. KUMTA, P.N., and RISBUD, S.H.: 'Review: Rare-earth chalcogenides - an emerging class of optical materials', *J. Mat. Sci.*, 1994, **29**, pp. 1135-1158

8. BROWN, R.S., BROCKLESBY, W.S., HEWAK, D.W., and SAMSON, B.N.: 'The effect of oxide on the spectroscopic properties of the praseodymium 1.3µm transition in gallium-lanthanum sulphide glass', *J. Lumin.*, 1996, in press.

9. QUIMBY, R.S., GAHAGAN, K.T., AITKEN, B.G., and NEWHOUSE, M.A., 'Self-calibrating quantum efficiency measurement technique and application to Pr^{3+}-doped sulphide glass', *Opt. Lett.* 1995, **20**, pp. 2021-2023



$^1D_2$
~600nm
~1540nm (transition 1)
$^1G_4$
~1000nm
~1340nm (transition 2)
$^3H_5$
$^3H_4$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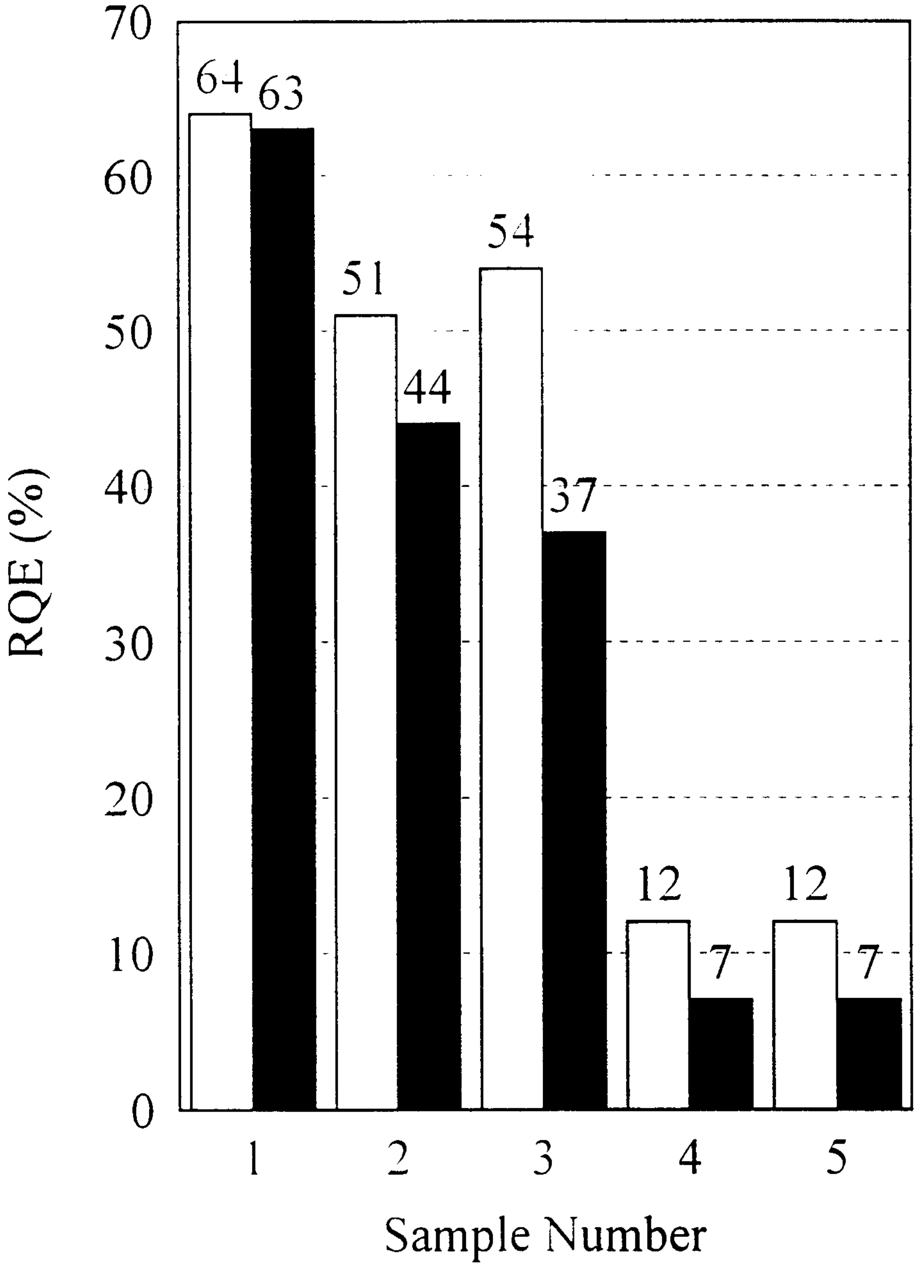
1.3
1.4
1.5
1.6
1.7
wavelength (μm)



RQE (%)
70
60
50
40
30
20
10
0
64
63
51
44
54
37
12
7
12
7
1
2
3
4
5
Sample Number