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A spectroscopic study of praseodymium-doped gallium-lanthanum-sulphide glass

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Abstract

Fluorescence spectra of Pr^{3+}-doped gallium-lanthanum sulphide (GLS) chalcogenide glass at 300 and 1.9 K are presented. Energy-selective spectroscopy is performed for the $^1D_2$ and $^3P_0$ levels at both temperatures, and the results show that there is strong correlation between the inhomogeneous profiles of ground and excited states, a situation which does not normally occur in rare-earth doped glasses. This is explained in terms of the relative contributions to the broadening from the nephelauxetic effect and crystal field broadening in this system. Its implication for the 1.3 μm amplifier based on Pr^{3+} in this host is assessed.

1. Introduction

Pr^{3+}-doped glasses are a good candidate for an optical 1.3 μm amplifier for telecommunications applications. Optical fibres doped with Nd^{3+} and Pr^{3+} have been put forward as candidates [1,2], but the efficiency of the Nd^{3+} amplifier is limited by excited state absorbtion and 1.06 μm emission, and Pr^{3+} doped into silica glass shows no 1.3 μm emission because of fast multiphonon emission. Low-phonon energy glasses, for example tellurite [3] and fluoride glasses [4,5] are likely to be a more useful host for amplifiers based on Pr. Amplification in Pr-doped fluoride has already been demonstrated [6-8]. Unfortunately the quantum efficiency for the 1.3 μm transition of Pr^{3+} is low, limiting the usefulness of amplifiers based on this system [9].

In order to increase the QE of 1.3 μm emission from Pr, glasses with lower-phonon energies than the fluorides, such as chalcogenide and chalcohalide glasses, can be used as hosts. Fibre development in these glasses has previously been centred on their use as transmission fibres for CO_2 lasers [10], in the mid-infrared [11] and in terms of photoinduced effects [12]. Little study has been given to the effect of these hosts on dopant ions other than to note a large red shift of emission spectra [13] and few studies have assessed their applications to devices [14].

The Pr^{3+} ion seems especially suited to this glass and much work is being put into producing a glass that can be made into fibres. We present here a detailed spectral study of one possible chalcogenide glass and assess how its spectral properties could affect its operation as an optical amplifier.

2. Experimental details

The sample used was of the composition $70Ga_2S_3 \cdot 29.9La_2S_3 \cdot 0.01Pr_2S_3$ with a resulting

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Pr^{3+} concentration of ~30 ppm. The low dopant level ensures that concentration effects are not a factor in this work. It was prepared in an evacuated and sealed ampoule, melted at 1150°C for 2 h and rapidly quenched in water [15]. Detection of fluorescence was performed using a Stanford photon counting system running a photomultiplier mounted on a 1 m spectrometer connected to a PC, which was used to collate the data and control the photon counter. The laser output was chopped using an optoacoustic modulator. Lifetime data were collected using the system as a box-car averager, and gated detection was used during spectrum acquisition, in order to record signals with the laser on and with the laser off. All the observed lifetimes were non-exponential decays and the values given for the results are fits to the first two e-folds. To observe resonant fluorescence, a second mechanical chopper before the spectrometer entrance slit was used in anti-phase to block laser scatter. Fluorescence spectra were recorded at room temperature, and at 1.9 K using a pumped helium cryostat. Excitation was either by a Coherent CR599 Rhodamine 6G dye laser for the $^1D_2$ level, or using the single lines of an argon laser for the ^3P multiplet.

The experiments consisted of studies of fluorescence, including fluorescence decays and line narrowing, from two multiplets, the $^3P_0$ and the $^1D_2$ level, at about 480 and 580 nm, respectively. These levels are not directly involved in the construction of devices at 1.3 μm, and spectroscopy of the levels directly related to device production has been carried out by Becker et al. [16]. However, the detailed spectroscopy of the $^3P_0$ and $^1D_2$ levels shows common characteristics between the two which are unusual in a glass, principally the fact that line narrowing is seen on non-resonant transitions. Sections 3 and 4 detail the measurements on the two multiplets. The discussion of these results follows in Section 5.

3. Fluorescence from the $^1D_2$ level

With excitation into either the $^1D_2$ or $^3P_0$ levels, it is immediately obvious that in comparison to Pr^{3+} in other glasses, i.e. ZBLAN, there is a large (~20 nm) shift to lower energies of the visible fluorescence lines, as noted in previous studies [13]. This immediately brings into question whether the required 1.3 μm emission has been shifted out of the telecommunications window. However, it appears that whilst the excited state energy levels are lowered relative to the ground state, their relative energy splittings remain almost unchanged.

3.1. Room temperature emission

The lifetime of the $^1D_2$ level is 55 μs, a reduction by a factor of ~5 on that observed in ZBLAN. This lifetime is not affected by multiphonon emission, as the gap from $^1D_2$ to $^1G_4$ is ~6000 cm^{-1}, which implies that the transition has a larger oscillator strength which increases the rate of radiative decay. This correlates with the higher degree of covalency in the glass.

Fig. 1 shows how the emission varies as the dye laser is tuned across the inhomogeneous profile of the transition. When pumping in the high-energy wing of the absorbtion, two components exist, at 605 and 620 nm. As the pump wavelength is increased, the wavelengths of these components converge until only one peak exists, at ~608 nm, as the pump approaches 595 nm.

The change from two peaks to one can be explained by the process of site selection. When pumping at short wavelengths all of the inhomogeneous profile is excited, because different Stark levels of different sites may be excited, as is illustrated in Fig. 1(a). As the excitation wavelength is decreased, eventually only a single site is excited (Fig. 1(b)), and thus site-selection is possible, resulting in the changed fluorescence spectrum seen in the lower section of Fig. 1. As the laser frequency is increased still further, the only transitions in resonance with the laser are those from thermally excited Stark levels in the ground state, and the site-selectivity observed when the laser is in resonance with the transition from lowest Stark level to lowest Stark level is again lost.

This line-narrowing effect will only be observed if the splitting between the lowest Start level in the excited state and the other levels is large, as illustrated in Fig. 1. For the $^1D_2$ state this splitting

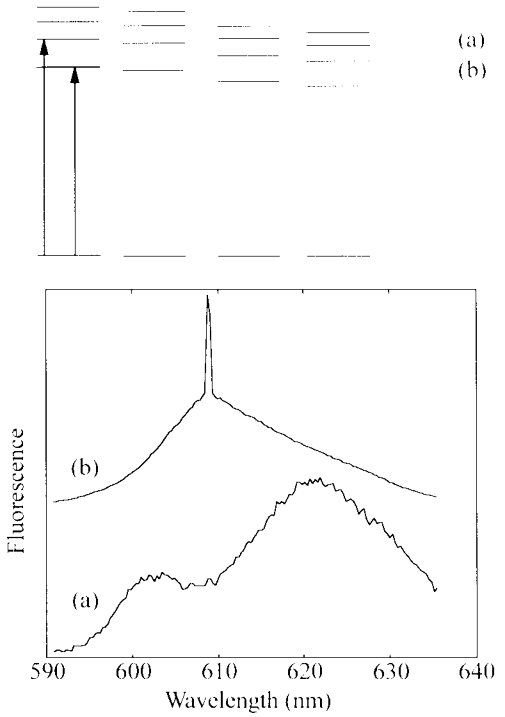

Fig. 1. Dye laser pumped room temperature $^1D_2$ emission spectra of Pr^{3+} in GLS glass. At wavelength (a), non-resonant excitation of many sites is possible via higher-lying Stark levels. At wavelength (b), only resonant excitation of particular energies within the inhomogeneous profile of the lowest Stark level is possible. The effect of this is shown in the two spectra . The bottom spectrum is excited at a wavelength equivalent to (a), and the top spectrum equivalent to (b).

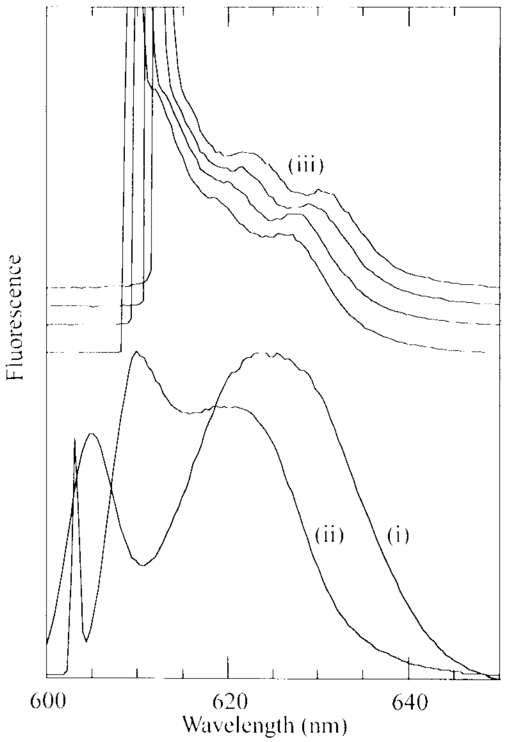

Fig. 2. 1.9 K $^1D_2$ emission spectra. Resonant fluorescence: (i) pumping at 580 nm, showing little change compared to the room temperature equivalent, (ii) laser at 603 nm showing a resonant peak and the loss of all other ground state emission and (iii) pumping in the wing with the laser between 610 and 614 nm giving the Stark components and showing how they remain stationary compared to the laser and each other.

is ~400 cm^{-1} and thus comparable with kT at 300 K.

3.2. *Fluorescence at 1.9 K*

Fig. 2 shows the results of selective laser excitation of the $^1D_2$ level at 1.9 K. When pumping at high energies, it appears that the spectra at 1.9 and 300 K are nearly identical. The high-energy peak at 300 K has a broader profile because of thermalization of the ions in the excited state. The shift in the peak of the emission for transitions from $^1D_2$ to the upper Stark levels of the ground state of around 150 cm^{-1} corresponds well to kT at 300 K of ~200 cm^{-1}.

As soon as the excitation wavelength enters the resonant regime at ~590 nm, the profile changes drastically as site selection begins to take place. All the emission from the excited state is from the lowest Stark level because thermalization to higher Stark levels is negligible at this temperature. This results in a narrow fluorescence peak resonant with the laser for the transition to the lowest Stark component in the ground state. Accidental degeneracy, however, means that the rest of the ground state Stark levels do not become clear until the laser wavelength is long enough to pump only a small subset of ions.

The Stark structure becomes clear for excitation at around 608 nm. This confirms that the component seen at 608 nm for shorter pump wavelengths is due to the non-resonant excitation of the transition between the lowest Stark levels in the excited and ground states. To allow the Stark structure to be resolved, virtually all the sites excited have to be resonant. The figure shows that there are a total of three transitions. For pumping from 608 nm to the edge of the absorbtion at 613 nm, the components retain the same shape and separation. This differs from the typical case where for different excitation energies the separation and relative positions of the Stark levels vary [17].

Figs. 3(a) and (b) show an unexpected result. The non-resonant transitions from $^1D_2$ to $^3H_5$, $^3H_6$ and $^3F_2$ all mirror the effects seen for the resonant excitation scheme. The high-energy wing due to transitions between the lowest Stark components of the energy levels when pumping the high-energy side of the absorbtion is clearly visible for these transitions, just as it was for $^1D_2$ to $^3H_4$. In the same way, the wing disappears as the laser is tuned to longer wavelengths and site selection occurs. Most striking, however, is the appearance of a narrow peak, analogous to the FLN peak which is seen in the resonant case. This peak appears for the same pump wavelength as for the resonant peak in the case of the transition to $^3H_5$ and at slightly longer wavelengths for that to $^3H_6$. In the $^3H_4$ case especially, the appearance of this peak coincides with Stark components becoming visible in the emission at ~ 710 nm.

Using an extended range PMT it was also possible to monitor the fluorescence from $^1D_2$ to $^3F_3$ and $^3F_4$. Whilst not showing the narrow FLN peak, they did narrow and move to lower energies as the excitation wavelength became longer.

In addition to the narrow emission lines due to the Pr, a broad background fluorescence between ~ 650 and 850 nm was observed which was not seen in the room temperature spectra. This could be excited by wavelengths not resonant with any Pr^{3+}-absorbtion band and was thus attributed to fluorescence by the glass. This has been seen previously in AsSe chalcogenides [18], where defects are assumed to be the cause. However, in contrast to the fluorescence seen due to the UV absorbtion edge (see Section 4.2), the lifetime of this emission was long compared to the ion lifetime, being of order 250 μs. The spectra shown have this background removed.

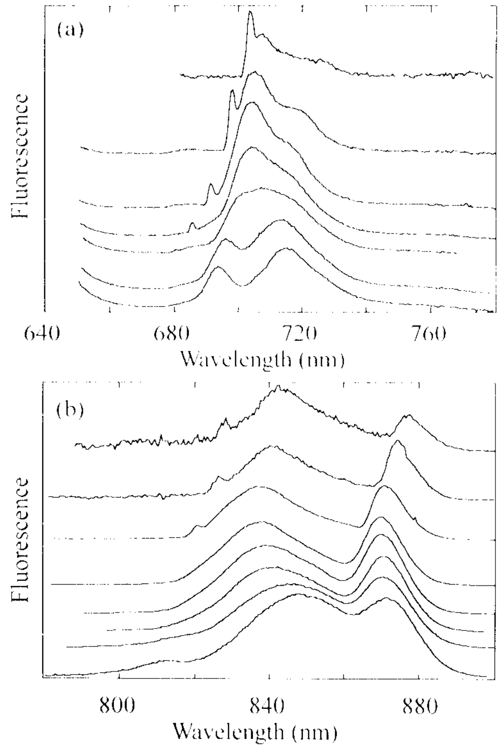

Fig. 3. Non-resonant emission to (a), $^3H_5$ and (b) $^3H_6$ and $^3F_2$ for laser pumping between 580 nm (bottom of each figure) and 610 nm (top), showing the same effect on shape as seen for the resonant case. Note especially the appearance of a narrowed component and Stark structure.

4. $^3P_0$ Emission

The closely split $^3P_2$, $^3P_1$ and $^3P_0$ multiplet can be selectively excited using the discrete lines produced by an argon ion laser, whose wavelengths range between 457.9 and 496.5 nm. The observed fluorescence from the ^3P multiplet changes drastically with excitation wavelength at room temperature (Fig. 4) and at 1.9 K (Fig. 5). The lack of a continuously tunable source means that the complex spectra are hard to interpret, but very similar effects to those seen in fluorescence from the $^1D_2$ level can be seen. These pump wavelengths are well within

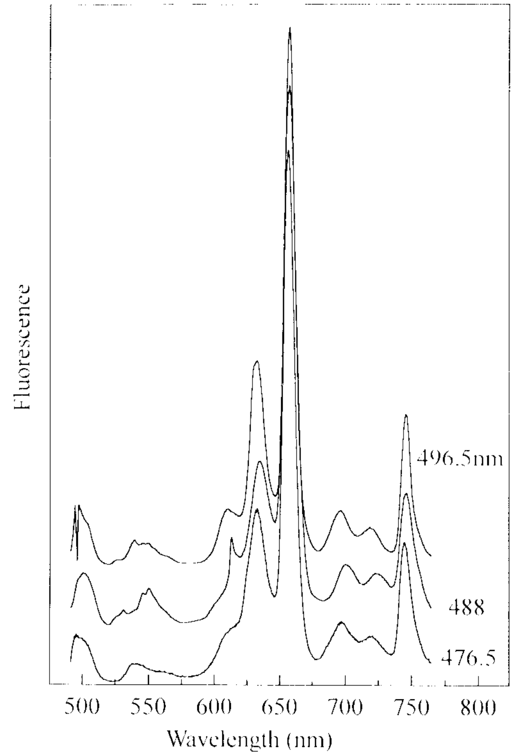

Fig. 4. Argon laser pumped room temperature emission spectra (pump wavelengths as indicated). These consist of a combination of $^3P_0$, $^3P_1$ and $^1D_2$ lines. The emission at ~550 nm is complicated by Er^{3+} emission for the longer pump wavelengths (see text). The spectra show changes of position and shape with pump wavelength, especially in the 600–650 nm region.

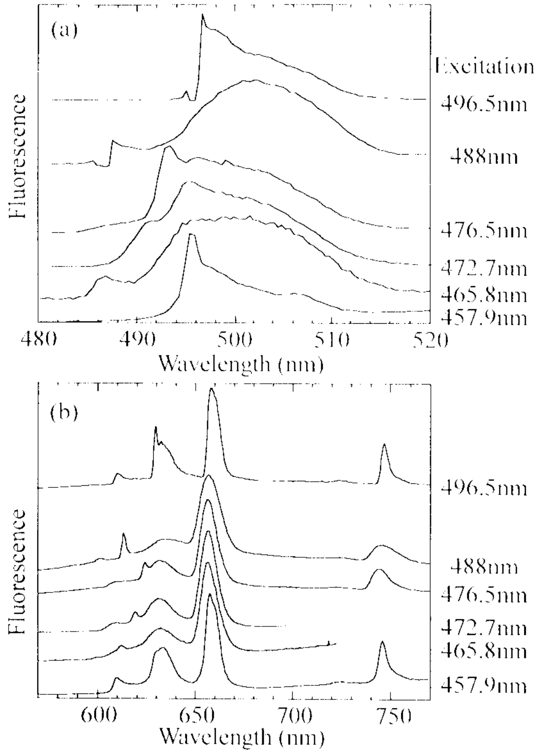

Fig. 5. 1.9 K $^3P_0$ emission spectra. (a) Resonant fluorescence. The different Argon laser wavelengths excite into the ^3P multiplet but all emission is from $^3P_0$. Note that exciting into the low energy wing of any component of the multiplet, i.e. 457.9 nm pumping, is equivalent to resonant $^3P_0$ pumping at 496.5 nm and the same for the high energy wing with 488 nm and 465.8 nm pumping. (b) Non-resonant fluorescence showing narrowing for low-energy wing pumping and extra components for high energy wing pumping, as seen for $^1D_2$ pumping. The 457.9 nm case shows narrowing despite two non-radiative transitions ($^3P_2$ to $^3P_1$ then to $^3P_0$) then a radiative transfer not to the ground state.

the intrinsic absorption of chalcogenide glasses, so laser powers had to be kept low to avoid heat damage to the samples. In addition the glass was contaminated with erbium, which has an absorption at 490 nm and emits in a band at ~550 nm. This 550 nm emission obscures the $^3P_0$ to $^3H_5$ emission, which is already very weak in comparison to the other emission lines.

4.1. *Room-temperature emission*

Room-temperature emission spectra pumped at 496.5, 488 and 476.5 nm are shown in Fig. 4. The argon laser line at 476.5 nm absorbs into the centre of the $^3P_1$ level, whilst that at 488 nm is exciting into the high energy wing of the $^3P_0$ level and 496.5 nm is into the centre of the same level. The emission due to 476.5 nm pumping is the only one without erbium fluorescence at 550 nm, instead showing that of Pr^{3+} from $^3P_1$ and $^3P_0$ to $^3H_5$. Thermalization to $^3P_1$ gives additional lines at ~540 and ~700 nm.

4.2. *Fluorescence at 1.9 K*

Absorption into the band edge of the glass when pumping in the blue causes a strong broad-band emission from the chalcogenide glass at 1.9 K. The lifetime of this is less than 1 μs. The spectra shown in Fig. 5 were taken by gating the detection electronics to collect the fluorescence 2 μs after the laser was switched off, to allow observation of only the long-lived Pr^{3+} fluorescence.

Figs. 5(a) and (b) show the fluorescence (a) resonant with the laser, and (b) in the region 600–750 nm, when pumping with different Ar lines. The very small energy gap between the ^3P levels, which allows multiphonon decay within the ^3P multiplet, and negligible thermalization mean that fluorescence is only observed from the $^3P_0$ level.

Fig. 5(a) shows that the fluorescence from the $^3P_0$ level still shows the effects of line narrowing for different pump wavelengths even though the $^3P_0$ level is being populated by non-radiative decay from $^3P_1$ and $^3P_2$. In particular, the emission when pumped at 465.8 nm shows typical off-resonance pumping, where a broad line is excited, and emission pumped at 457.9 nm, absorbing into the $^3P_2$ band, shows line narrowing on the $^3P_0$–$^3H_4$ transition. This indicates clearly that there is strong correlation between the inhomogeneous broadening of different ^3P levels.

Fig. 5(b) shows the fluorescence from Pr^{3+} in the spectral region 600–750 nm when pumped in the ^3P multiplet. As in the case of the $^1D_2$ fluorescence, line-narrowed spectra can be seen from transitions which are to other electronic levels apart from the ground state. The degree of line-narrowing depends on how close the particular pump wavelength is to resonance with a particular energy level. A clear example can be seen in the top trace of Fig. 5(b), pumped at 496.5 nm. Here, a line-narrowed component at 630 nm can be clearly seen, corresponding to the transition from $^3P_0$ to $^3H_6$.

Fluorescence from the Er^{3+} contamination in this sample can be seen at 550 nm for 488 nm pumping (Fig. 6). It is interesting to note we see exactly the same effects as for pumping the Pr^{3+}, with site selection and Stark structure apparent in transitions to levels other than the ground state.

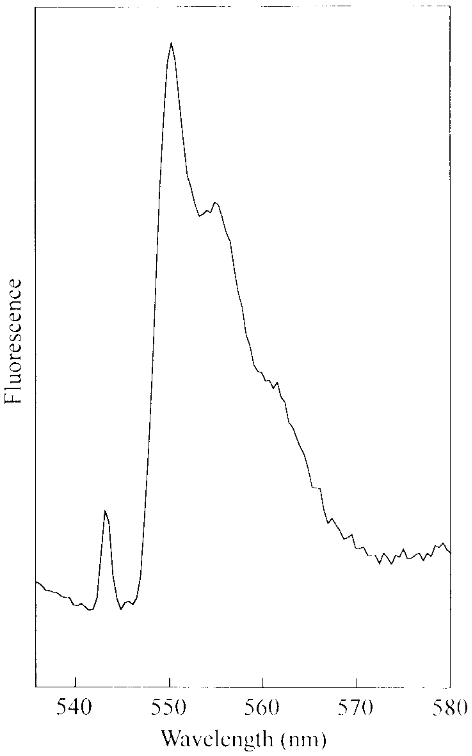

Fig. 6. Erbium fluorescence at 1.9 K when pumping at 488 nm showing Stark structure and a narrowed component.

5. Discussion

Site-selection at room temperature, especially to the degree observed here, is very unusual in a rare-earth-doped glass. The observation of equivalent large scale changes in fluorescence from the excited state to lower lying energy levels, including site-selection, for both $^1D_2$ and the ^3P multiplet demonstrates that the strong correlation in inhomogeneous broadening occurs for all the energy levels observed.

At cryogenic temperatures, the structure of the $^1D_2$ resonant fluorescence as a function of pump wavelength does not change once the effect of accidental degeneracy is lost at longer pump wavelengths. This shows that the Stark splittings in the $^3H_4$ state remain equally spaced within the inhomogeneous profile and indicates that the crystal field parameters are constant and not a strong function of the energy relative to the ground state.

The fact that the Stark splitting is apparently independent of position within the inhomogeneous profile correlates well with the other surprising feature of this work, i.e. the appearance of line-narrowed peaks in transitions not resonant with the exciting laser. These line-narrowed peaks, which occur in transitions from $^1D_2$ to $^3H_5$ and $^3H_6$, and from the ^3P multiplet to $^3H_4$ and $^3H_6$ indicate that there is strong correlation of the inhomogeneous broadening between different levels. This is once more in sharp contrast to the situation normally found in RE-doped glasses.

In order to understand the origin of inhomogeneous broadening and splitting in this system, it is necessary to consider the mechanisms which produce splitting of RE levels in solids. The free-ion effects, such as the residual Coulomb interaction and the LS coupling, are modified by the change in the centrally-symmetric field caused by the host (the nephelauxetic effect) and the crystal field splitting. In a silicate glass, the crystal field is normally expected to be the dominant contributor to inhomogeneous broadening. The crystal field acts very differently on levels with different angular momentum and there is little correlation of a particular chromophore's position within the inhomogeneous profile in different electronic multiplets. This results in little or no line-narrowing effects on transitions to non-resonant electronic levels, or even to other Stark levels within the same multiplet [19]. In the chalcogenide system under study here, we see much line narrowing, and little variation in Stark levels from site to site. From these results we infer that in our system the nephelauxetic effect provides the dominant contribution to inhomogeneous broadening. This can explain most of the results contained in this paper, and also has significant repercussions for the production of useful devices from this material.

The observation of three Stark components (including the resonant transition) suggests that the ion site has a high degree of symmetry. Completely raising the degeneracy, the case for a random site around the ion, would give nine levels. The site symmetry would typically be probed more effectively using the Eu^{3+} ion [19] but in this situation a problem arises. If we assume that the dopant ion substitutes for lanthanum ions, as the glass composition suggests, it becomes a glass former. Rare earth-ions have been shown to drastically affect the glass forming properties of chalcogenides [20] and hence must have a strong influence on their surroundings. This depends directly on the ion size and hence the larger Eu^{3+} ion may well see a very different local structure compared to the Pr^{3+} ion, as their sizes are significantly different.

6. Application to device properties

As mentioned earlier, this glass system is one of the main prospects for the 1.3 μm fibre amplifier. Our results imply that there may well be differences in the way that such devices will work due to the spectroscopic properties of the host. The results we have observed for the ^3P and $^1D_2$ transitions are very similar, indicating that similar effects will be seen for the $^1G_4$ transition involved in the amplifier.

In the erbium amplifier system, there is no correlation between inhomogeneous broadening on pump and signal transitions. Thus, the degree of inhomogeneity of the amplifier transition is determined by the material parameters. The degree of site-selectivity observed at room temperature in this system means that the degree of inhomogeneity of the amplifier transition will depend on how broad-band the pump is. A narrow-bandwidth pump will result in a more homogeneous amplifier, and a broad-band pump will result in an increase in the inhomogeneity of the amplifier characteristics.

The site-selection will also reduce the proportion of ions actually excited by a narrow-bandwidth pump, resulting in an apparently lower concentration of Pr^{3+} ions. However, the amplifier gain will be increased compared to normal systems because the reduction in the inhomogeneous broadening will decrease the width of the transition, increasing the effective cross-section.

7. Conclusion

This work has shown that doping gallium–lanthanum sulphide glasses with rare earth ions has a strong influence on the fluorescence properties of the ion. Site-selection is observed at room temperature in both resonant emission and emission to other electronic multiplets. This is shown to be an important consideration for device applications. At cryogenic temperatures, resolving the Stark structure indicates that the inhomogeneous broadening, rather than being dominated by crystal field shifts which are uncorrelated from level to level, is strongly correlated between levels resulting in line-narrowing on non-resonant transitions. This suggests that the nephelauxetic effect is strong in these systems, and provides the largest contribution to the inhomogeneous broadening. This radical difference in spectroscopic properties will affect the behaviour of any amplifier devices made using this host.

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