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Pr³⁺ -doped fluoride glass for a 589 nm fibre laser

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13. ABSTRACT (Maximum 200 words) This report results from a contract tasking University of Leeds as follows: The contractor will identify the preferred fluoride glass host for the 589nm Pr+3-doped fiber laser, carry out a full optical and spectroscopic characterization of the Pr+3-doped glass, model the lasing behaviour at 589nm, and produce a small number of glass rods suitable for fibre drawing and gain measurements.				
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1. INTRODUCTION

We have undertaken to investigate a range of Pr-doped fluoride glasses with the aim of identifying a suitable glass host for a 589 nm laser. Pr-doped fluorozirconate ZBLAN glass is known to lase at 601-618 nm¹, but lasing at 589 nm cannot be achieved in this host.

In preliminary experiments with different Pr-doped fluoride glasses we observed that the emission spectrum of Pr³⁺ depends strongly on the host glass. Figure 1 shows the energy levels of Pr³⁺. When excited with blue and violet lines of Ar⁺ laser, Pr³⁺ emits red fluorescence, as shown in Figure 2. The red emission spectrum consists of two peaks, ³P₀→³H₆ at 603 nm and ³P₀→³F₂ at 635 nm, which both originate from the ³P₀ level and therefore compete. In ZBLAN glass the two peaks have equal strength. However, we found that the ³P₀→³F₂ transition is hypersensitive and varies greatly among different glass hosts. As a result, we found that in some glasses the ³P₀→³H₆ transition is greatly enhanced relative to the ³P₀→³F₂ transition. Moreover, the width of the 603 nm peak, and hence the amount of emission at 589 nm, also varies considerably. Therefore it is possible to design a glass host where the ³P₀→³H₆ transition will be sufficiently dominant and broad to make possible lasing at 589 nm. The work of the project was thus mainly devoted to identifying the criteria and designing host glass having an enhanced ³P₀→³H₆ transition.

2. EXPERIMENTAL

The glass families studied were Pr³⁺ doped fluorides: fluoroaluminate, fluoroindate and fluorozirconate. Fluoroaluminate and fluoroindate glass samples were especially prepared for the purposes of this work; whilst fluorozirconate glasses had been made in the course of a previous unrelated project. Over 60 fluoroaluminate and fluoroindate glass compositions were prepared, and altogether over 80 glass samples were examined. The glass hosts were chosen for the high solubility of Pr³⁺ ions (up to 1-5 mol%) and for good glass stability. Moreover, all examined glass families are capable of large compositional variation by network modifiers. Relatively low phonon energy glasses, such as fluorides, must be used, since the ³P₀ level is quenched by multiphonon relaxation in high phonon energy hosts such as silica.

Luminescence from the ³P₀ level was excited by blue and violet lines of an Ar⁺ laser, and was clearly observed as a bright pink track in the sample along the pump beam. The spectra were measured by a double-grating monochromator and a Si-photodetector. The optical path through the sample to the detector was maintained at approximately 1 mm, to minimize the effect of GSA at 587 nm. The refractive indices were determined by an Abbe refractometer at λ=589 nm. Absorption spectra were measured by a UV-VIS spectrophotometer.

3. RESULTS AND CONCLUSIONS

Figure 2 shows measured emission spectra from the 3P_0 level of Pr^{3+} in fluoroindate (inf), fluoroaluminate (alf) and fluorozirconate (zrf) glasses. The spectra are normalized with respect to the $^3P_0 \rightarrow ^3H_6$ peak, since the oscillator strength of this transition is less sensitive to the host. It is clearly seen that the relative strength of the $^3P_0 \rightarrow ^3F_2$ peak varies greatly among different hosts. In fluoroaluminate glass the 603 nm peak is significantly broader due to the multiple dopant sites in this glass host, resulting in a relatively higher emission at 589 nm.

The branching ratio of the two transitions, $^3P_0 \rightarrow ^3F_2 : ^3P_0 \rightarrow ^3H_6$, is defined as the ratio of their peak heights and represents their relative strengths. The branching ratios for a variety of glass hosts are plotted in Figure 3 against material polarizability α , calculated by the Clausius-Mossotti formula as $\alpha \sim (n^2 - 1)/(n^2 + 2)$. The data separate into three distinct groups, lying on different slope lines, according to the glass family: fluoroaluminate, fluoroindate and fluorozirconate. It is seen that in all three examined glass families the branching ratio is proportional to host polarizability, the solid lines showing linear least-squares fits to the data.

Our results demonstrate that the $^3P_0 \rightarrow ^3F_2 : ^3P_0 \rightarrow ^3H_6$ branching ratio is determined by two factors, host polarizability and dopant site symmetry. Figure 3 shows that in all three fluoride glass families the branching ratio increases linearly with host polarizability $\alpha \sim (n^2 - 1)/(n^2 + 2)$, i.e. the strength of the host lattice field. The steepness of the branching ratio-polarizability slope reflects the degree of symmetry of the dopant sites, a steeper slope indicating lower symmetry sites. Consequently, two primary criteria for a 589 nm laser glass host are high dopant site symmetry and low refractive index (low polarizability).

Of all examined glass families, fluoroindate glasses have by far the lowest branching ratios and the shallowest slope of the polarization dependence. Fluoroaluminate glasses have substantially higher branching ratios than fluoroindates. Fluorozirconate glasses have the highest branching ratios, often > 1 , with the 635 nm emission predominating. The glass compositions in Figure 3 generally span the glass-forming regions of the respective glass families. For example, it is not possible to reduce the refractive index of fluorozirconates or fluoroaluminates sufficiently to achieve branching ratios comparable with fluoroindates. The refractive index of fluoroindates can be reduced further; however, gains in the branching ratio will be insignificant due to the shallow slope of the branching ratio-polarization relationship.

In all emission spectra, the observed peak at 603 nm contains a small contribution from the 3P_1 level. As seen in Figure 1, the 3P_0 and 3P_1 levels lie sufficiently close together (580 cm^{-1}) to be thermalized; at room temperature the population of the 3P_1 level is around 6%. The $^3P_1 \rightarrow ^3F_2$ emission is approximately at 585 nm; the shoulder at 585 nm in Figure 2 is ascribed to this transition². The $^3P_1 \rightarrow ^3F_2$ emission can therefore contribute significantly to the 589 nm laser. To investigate this possibility, glass samples were heated in situ to around 140°C , and Pr^{3+} emission spectra were measured. A strong thermal enhancement of the 589 nm emission was observed. Figure 4 shows that heating the glass from 20°C to 140°C

resulted in an increase of the 589 nm emission by a factor of over 2. In fluoroaluminate glass a slight beneficial decrease in the branching ratio was also observed. The experiment indicates that 589 nm emission can be increased further by raising the glass temperature higher. Fluoroindate and fluoroaluminate glasses can be safely heated to respectively 250°C and 400°C; our present heating equipment, however, is limited to around 140°C.

We examined a large number of glass hosts in three glass families in order to identify the host parameters which determine the Pr^{3+} emission at red wavelengths, and to enable us to design a glass host capable of lasing at 589 nm. Fluorozirconate glasses are clearly unsuitable for this purpose, having branching ratios of >1 . Fluoroaluminate glasses have much lower branching ratios, 0.6-0.9, and broad emission peaks offering more emission at 589 nm. In addition, fluoroaluminate glasses have the highest glass transition temperatures, and so may be more amenable to thermal enhancement of the 589 nm emission. Some of the low-refractive index fluoroindate compositions have branching ratios as low as <0.5 , offering increased ${}^3\text{P}_0 \rightarrow {}^3\text{H}_6$ emission, but with a narrower peak than fluoroaluminates. The width of emission in fluoroaluminate glasses arises from multiple dopant sites in this glass. It is possible that by including additional constituents in fluoroindate compositions broader emission can be achieved without sacrificing the low branching ratio. Moreover, thermal enhancement may overcome the differences in peak widths.

Both fluoroindate and fluoroaluminate glasses appear to be highly promising hosts for the 589 nm Pr-doped laser. Both glasses have good stability and are suitable for thermal enhancement and for fibre fabrication. However, fluoroindate glasses have an immediate advantage in that fibre drawing technology for low-loss fluoroindate fibres is well-developed and commercially available (La Verre Fluore, Hoya and NTT produce fluoroindate fibres, especially for Pr-doped 1.3 μm amplifiers).

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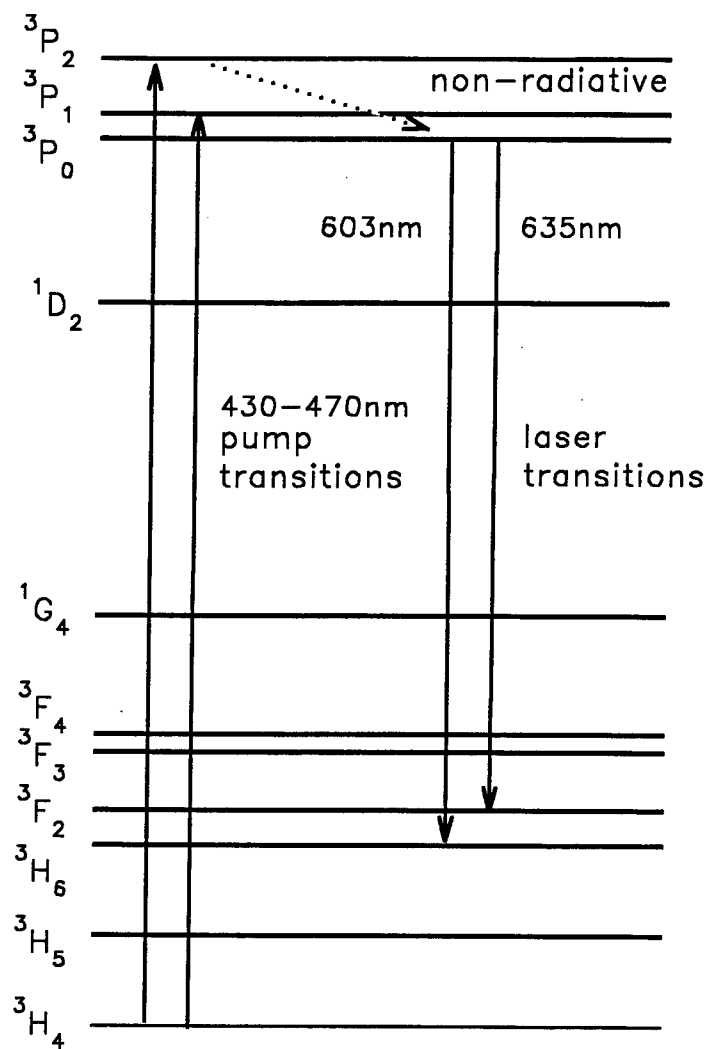


Figure 1. Energy levels of Pr^{3+} .

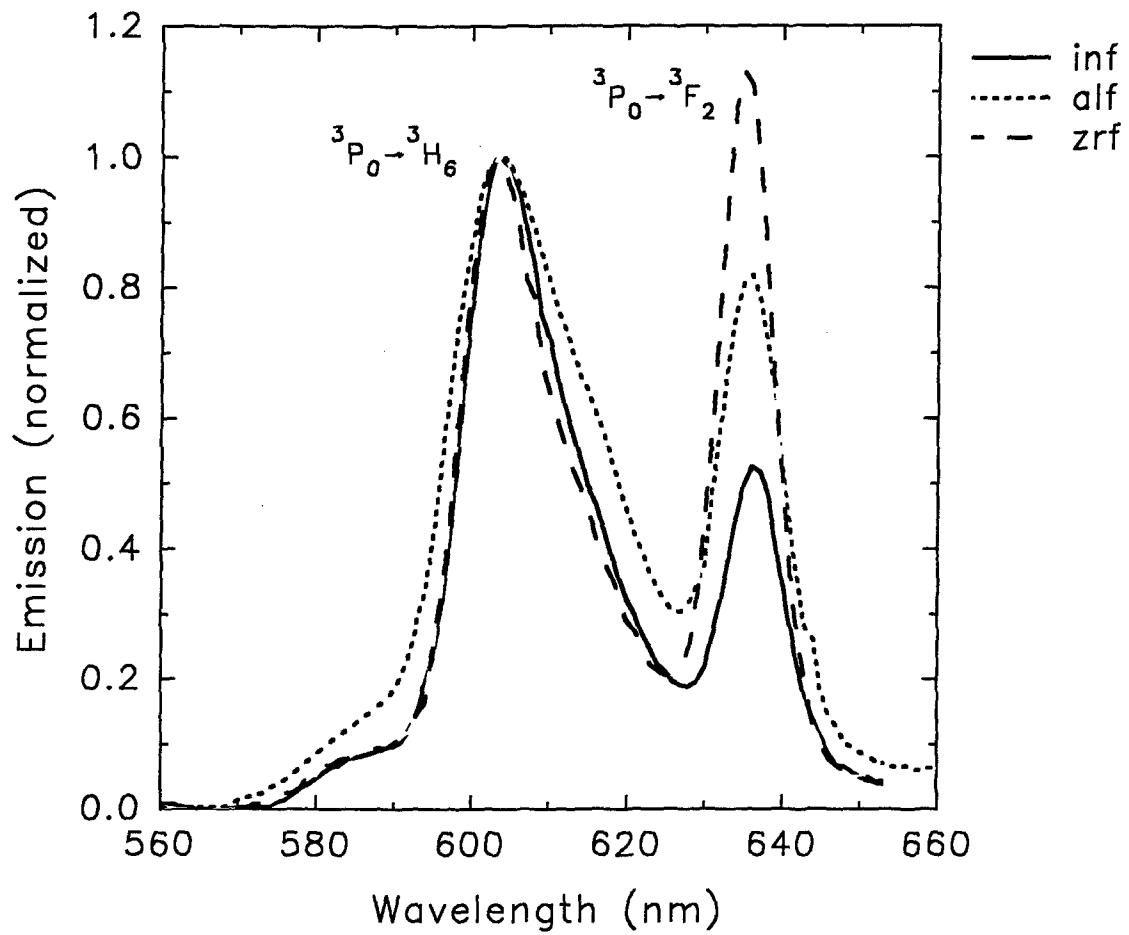


Figure 2. Red emission spectra in Pr-doped glasses:
 inf - fluoroindate, alf - fluoroaluminate, zrf - fluorozirconate.

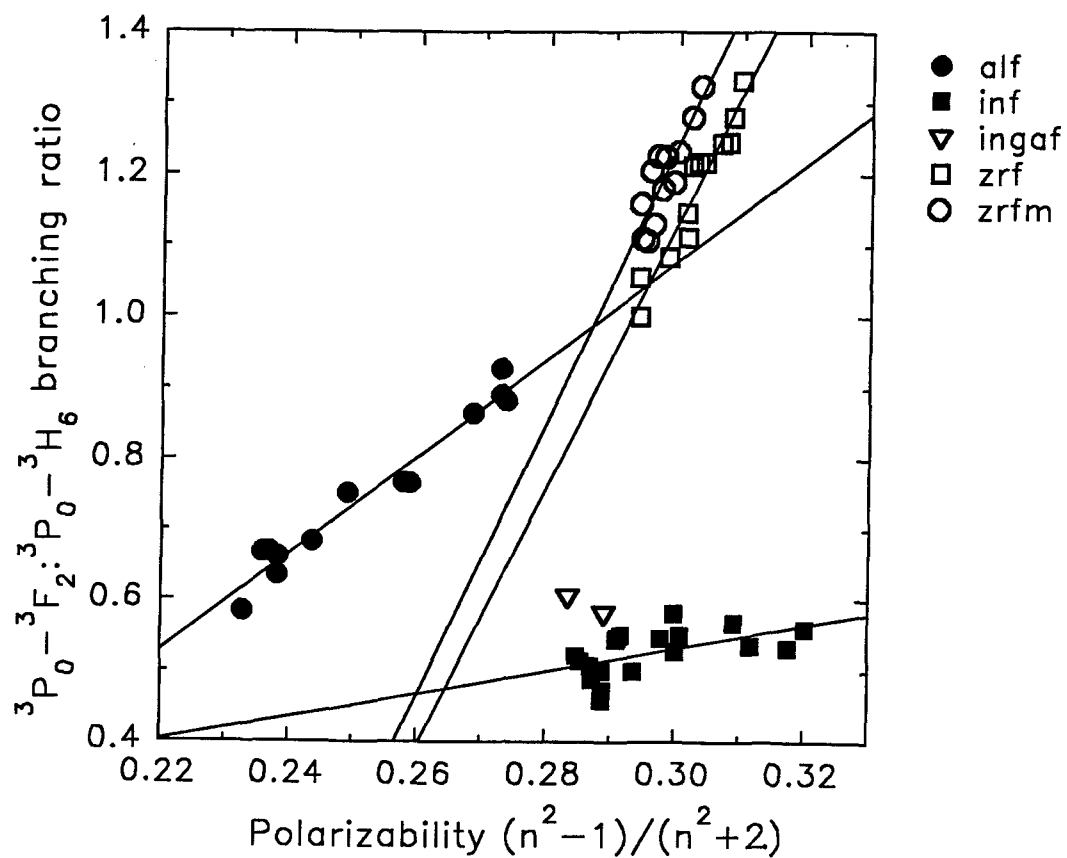


Figure 3. ${}^3P_0 \rightarrow {}^3F_2: {}^3P_0 \rightarrow {}^3H_6$ branching ratios versus host polarizability in Pr-doped glasses: alf - fluoroaluminate, inf - fluoroindate, ingaf - fluoro-indo-gallate, zrf - fluorozirconate, zrfm - modified fluorozirconate.

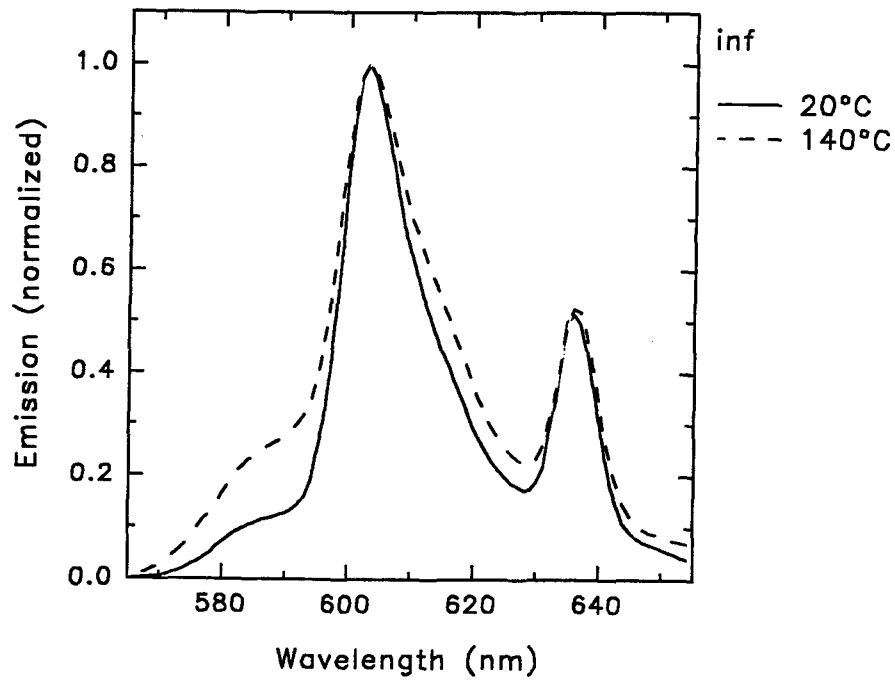
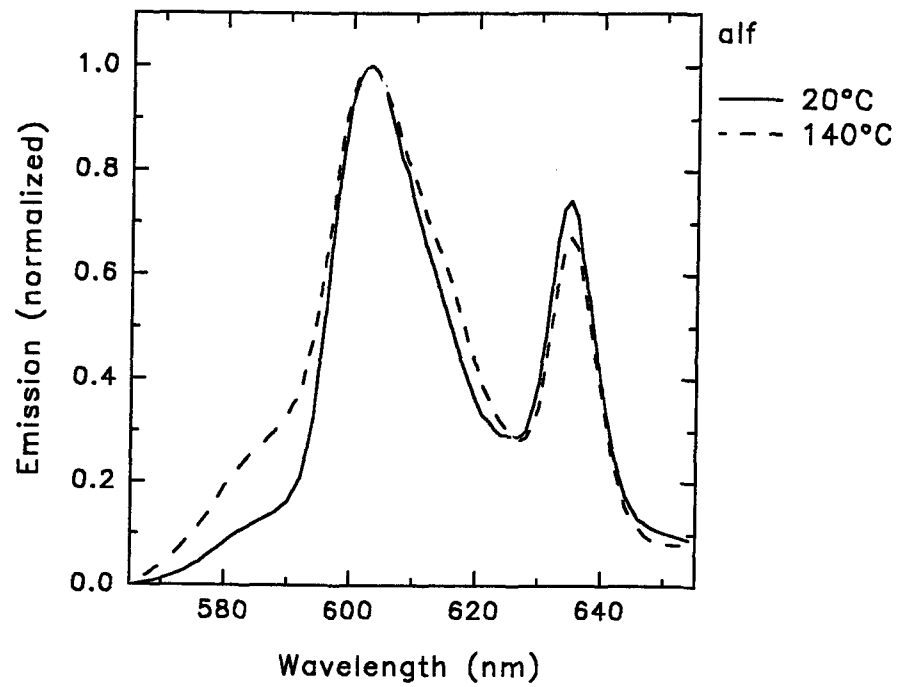


Figure 4. Pr^{3+} emission in fluoroaluminate (alf) and fluoroindate (inf) glasses: solid - at 20°C, dashed - at 140°C.