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**Cr<sup>3+</sup>-doped vibronic laser in fluoride glass**

**University of Leeds**

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## 1. INTRODUCTION

$\text{Cr}^{3+}$ -doped vibronic lasers are known in a number of host crystals, such as alexandrite,  $\text{LiCaAlF}_6$  and  $\text{LiSrAlF}_6$ . We undertook to examine a range of  $\text{Cr}^{3+}$ -doped glasses with the aim of developing a glass fibre analogue of these crystal-based lasers, and if possible improving the tuning range. The wavelength and tuning range of the  ${}^4\text{T}_2$ - ${}^4\text{A}_2$  vibronic lasing transition of  $\text{Cr}^{3+}$  are strongly affected by the dopant site environment, and consequently vary greatly among different host crystals. Glass hosts offer a much larger variation in composition and properties than is possible in crystals; therefore  $\text{Cr}^{3+}$ -doped glasses could potentially provide a greater range of wavelengths than crystals.

Vibronic  $\text{Cr}^{3+}$ -doped glass lasers have been considered by a number of workers. Many different types of  $\text{Cr}^{3+}$ -doped glass have been investigated in detail, including: sodium silicate<sup>[1,2]</sup>; Ca-Ga-Ge-O<sup>[3]</sup>; fluorophosphate<sup>[4]</sup>; fluorides Ba-In-Zn-Y-Th-Ga-F<sup>[5]</sup>, Pb-Ba-Ga-F and Pb-Zn-Ga-F<sup>[6,7,8]</sup>, Zr-Ba-F-based<sup>[9]</sup>, In-Ga-Ba-F-based<sup>[10]</sup>. The most wide-ranging study, by Rasheed et al<sup>[2,11]</sup>, investigated  $\text{Cr}^{3+}$  luminescence in fluorozirconate, fluoride, phosphate, lithium borate, potassium borate and tellurite glasses. A strong relationship between the host ligand field and wavelength was observed:  $\text{Cr}^{3+}$  absorption and emission lines were seen to shift to shorter wavelengths and the Stokes shift was reduced in hosts with strong ligand fields. However, in all examined glasses, but especially in fluorides, the quantum efficiency of  $\text{Cr}^{3+}$  emission was unacceptably low, with strong thermal quenching. Indeed, in many fluoride glasses no emission could be observed at room temperature.

As shown in Figure 1, low quantum efficiency is due to phonon-assisted nonradiative crossover between the  ${}^4\text{T}_2$  and  ${}^4\text{A}_2$  states, where the activation energy equals the distance from the lowest point of the  ${}^4\text{T}_2$  curve to the crossover point. In dopant sites where the weak ligand field makes the  ${}^4\text{T}_2$  parabola shallower (e.g. fluorides), the activation energy is reduced, and the nonradiative relaxation rate increases. Configurational coordinates for the  ${}^4\text{T}_2$  and  ${}^4\text{A}_2$  states have been calculated for some glasses (e.g. [6], [9]), and were in agreement with quantum efficiency measurements. Large electron-phonon coupling and high phonon energy of the host also promote increased nonradiative rate; however, the dominant factor is the effect of the ligand field on the energy level overlap. At present, therefore, the key problem in obtaining a  $\text{Cr}^{3+}$ -doped glass laser is to increase its quantum efficiency, which is determined largely by the host glass structure and dopant site configuration.

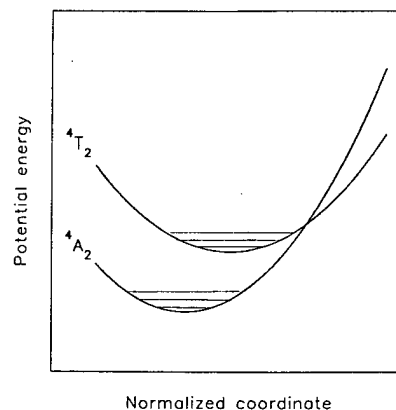


Figure 1. Schematic diagram of energy levels of  $\text{Cr}^{3+}$  involved in the vibronic transition.

## 2. EXPERIMENTAL

The aim of the project was to investigate glass analogues of Cr-LiSAF, therefore we concentrated our work on fluoride and high-fluorine fluorophosphate glasses. Several Cr<sup>3+</sup>-doped glass samples were prepared. Table 1 below lists the glass compositions.

Cr<sup>3+</sup> absorption spectra were measured by UV-VIS-NIR spectrophotometer (Perkin-Elmer Lambda-19). Emission was excited by 150 mW at 700 nm from a Ti-Sapphire laser, and was observed by a monochromator and a silicon photodetector. Observations of emission were carried out at room temperature.

Table 1: Compositions of Cr<sup>3+</sup>-doped glasses.

Glass	Composition mol%
cb01	34.5PbF <sub>2</sub> :24.5ZnF <sub>2</sub> :35.5GaF <sub>3</sub> :2.2AlF <sub>3</sub> :3.1YF <sub>3</sub> :0.2CrF <sub>3</sub>
cb05	39.8InF <sub>3</sub> :20ZnF <sub>2</sub> :20BaF <sub>2</sub> :5SrF <sub>2</sub> :15PbF <sub>2</sub> :0.2CrF <sub>3</sub>
cb06	34PbF <sub>2</sub> :24ZnF <sub>2</sub> :35GaF <sub>3</sub> :2.2AlF <sub>3</sub> :3.1YF <sub>3</sub> :1.5NaPO <sub>3</sub> :0.2CrF <sub>3</sub>
cb08	39.8AlF <sub>3</sub> :22CaF <sub>2</sub> :6MgF <sub>2</sub> :5SrF <sub>2</sub> :20BaF <sub>2</sub> :10LiF:10NaF:3NaPO <sub>3</sub> :0.2CrF <sub>3</sub>
cb10	22.9Al(PO <sub>3</sub> ) <sub>3</sub> :40BaF <sub>2</sub> :18.9SrF <sub>2</sub> :18AlF <sub>3</sub> :0.2CrF <sub>3</sub>

## 3. RESULTS

Figure 2 shows Cr<sup>3+</sup> absorption spectra in the examined glasses. All five spectra are broadly similar; however, it is seen that the dip shifts to longer wavelengths with the addition of increasing amounts phosphate (see Table 1). Phosphate in glass composition gives rise to stronger ligand fields; therefore the shift in the dip may be attributed to the strengthening of the short-wavelength component of the absorption peak. This interpretation is also supported by the observed changes in the relative heights of the two humps.

Cr<sup>3+</sup>-doped glasses were excited by at 700 nm. Room-temperature emission was observed in all glasses with the exception of cb05, indicating a relatively high quantum efficiency in these glasses. However, the emission level was too weak to measure the spectrum, so only qualitative results were obtained. Emission maximum was around 880 nm in all glasses. Emission appeared to extend from approximately 950 nm down to 750 nm, where it became impossible to observe due to pump interference. The emission range therefore appears to be similar to Cr-LiSAF (760-920 nm). Emission was very weak in glasses cb01 and cb06, was somewhat stronger in cb08, and increased dramatically (approximately tripled) in cb10. This confirms the effect of phosphate in generating strong ligand fields, and as a result increasing the quantum efficiency.

No emission was observed in glass cb05, which is a fluoroindate composition similar

to those investigated in Refs 5 & 10, and is known to have a low quantum efficiency. This glass was chosen for examination because Cr<sup>3+</sup> emission in this host is significantly red-shifted compared with other fluorides, due to its weak ligand fields which also cause its low quantum efficiency.

#### 4. CONCLUSIONS

Room-temperature broad emission in the Cr<sup>3+</sup> vibronic band was observed in four fluoride and fluorophosphate glasses. The emission maximum was at 880 nm and the emission band appeared to be similar to Cr-LiSAF. Observation of Cr<sup>3+</sup> emission at room temperature indicates a relatively high quantum efficiency. The strongest emission signal was observed in the highest-phosphate glass composition.

The family of high-fluorine fluorophosphate glasses, such as cb10, appears to offer the best prospects of a Cr-glass vibronic laser similar to Cr-LiSAF. Further work is necessary to increase the quantum efficiency of Cr<sup>3+</sup>-doped glass and to establish its spectroscopic properties.

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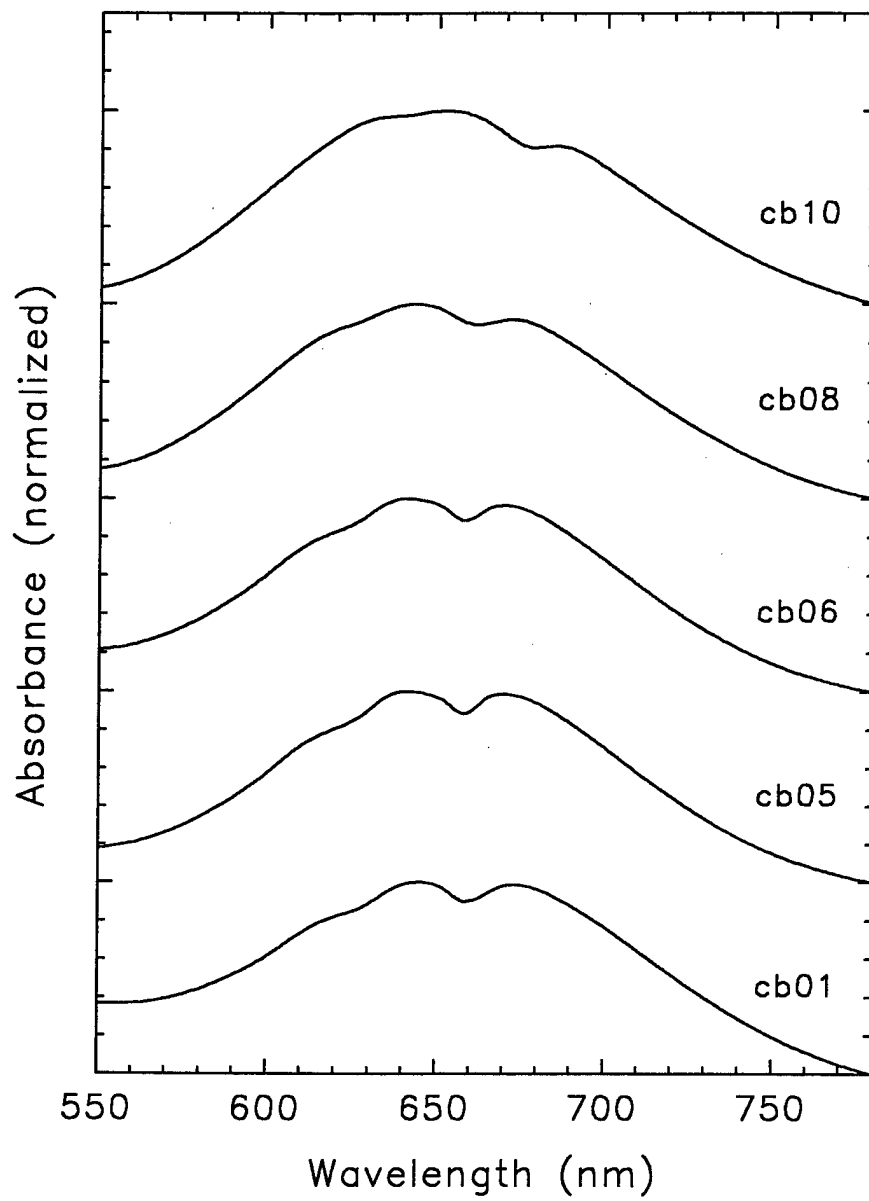


Figure 2. Cr<sup>3+</sup> absorption spectra in examined glasses