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## Visible emission from rare earth ions in nanocrystal-containing glasses

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### Abstract

Rare earth-doped glasses are of great interest for their optical and fluorescence properties. However, phonon-mediated non-radiative transitions are a major obstacle to their use and the quantum efficiencies are sensitive to the environment of the rare earth ion. Recently, complex glasses containing fluorides have been developed in which fluoride crystallites can be made to form with a high solubility for rare earth ions. We have performed a study of the visible emission of  $\text{Pr}^{3+}$  in these glasses and have identified three groups of fluorescence lines coming from transitions between the P and the H levels. The phonons play an important role, both in up-conversion as well as in non-radiative decay between levels in these two sets. This effect is illustrated by the temperature dependence of the fluorescence spectra measured from 295 K to 4 K and for three different wavelengths, 514 nm, 488 nm and 476 nm in the quenched glasses and in the heat-treated or crystallite-containing glasses. Comparison of fluorescence spectra from glasses containing either  $\text{Pr}^{3+}/\text{Y}^{3+}$  or  $\text{Pr}^{3+}/\text{Gd}^{3+}$  also reveal an energy transfer between praseodymium that is increased by the presence of yttrium. © 1997 Elsevier Science B.V.

### 1. Introduction

The development of optical telecommunications has created a need for low loss optical amplifiers at both 1.3 nm and 1.5 nm. At 1.3 nm,

$\text{Pr}^{3+}$  is an active element of choice. However, one of the obstacles to the use of rare earth (RE) ions can be the life time of the excited states and non-radiative decay paths which depend on the local environment of the ion and on the phonon energies [1]. This is a problem in silica glasses which are otherwise attractive because of their high degree of transparency mediates their usefulness. From the point of view of the life time and the non-radiative decay, fluoride glasses offer

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a useful alternative because their phonon energies are lower. In addition, they possess a higher RE solubility [2]. On the negative side, fluoride glasses are not as easily prepared into fibers. Recently a hybrid solution has been found. It has been possible, with the addition of fluorides and another element such as yttrium, gadolinium or lutetium, to induce in aluminosilicate glasses the formation of fluoride nanocrystals in which the RE tend to be preferentially located [3]. These ceram-glasses have generated much interest because they combine the transparency of the silicates with the low phonon energies of the fluoride glasses. The resulting glasses also possess convenient processing properties and durabilities.

Because of the importance of the electron-phonon interactions in the radiative or non-radiative processes of the excited RE ions, we have performed a study of the visible emission from  $\text{Pr}^{3+}$  ions in these nanocrystal-containing glasses.

## 2. Experimental

The composition of the glass ceramic host for the samples studied was  $30\text{SiO}_2-15\text{Al}_2\text{O}_3-29\text{CdF}_2-17\text{PbF}_2-5\text{ZnF}_2-4\text{XF}_3$  with X being yttrium or gadolinium. Most of the glass samples were doped with 300 ppm of  $\text{Pr}^{3+}$  except for one sample with 25 ppm of  $\text{Pr}^{3+}$ . Two samples of each glass were prepared, one quenched from high temperature and the other subsequently annealed between 390 and 470°C from 45 min to 4.5 h.

The fluorescence measurements were taken with a high resolution Raman spectrometer (ISA U1000). The excitation was provided by an argon ion laser. The input power incident on the samples was consistently 100 mW and the three main lines of the laser were successively used, 514 nm, 488 nm and 476 nm. The integration time was typically 0.5 s per point and the resolution, set by the slit width, was  $2\text{ cm}^{-1}$ . It is important to note that, because all the fluorescence spectra presented in this paper were taken with a Raman spectrometer, the frequencies appearing on the horizontal axes of the graphs are relative frequencies which should be subtracted from the frequency of the laser to obtain the actual transition

frequencies. Consequently, energies increase to the right of the horizontal axis and negative frequencies correspond to energies that are higher than the excitation laser frequency.

## 3. Results

In the present study, the three main lines of the argon laser were used to excite the  $\text{Pr}^{3+}$  ion. As we show below, the comparison of the spectra obtained from each of these three lines was found to be useful. It first allowed us to resolve Raman and fluorescence spectral features and it also allowed us to detect the role of phonons in up-conversion to higher excited states and non-radiative decay to lower excited states.

Fig. 1 shows the spectrum obtained on an annealed sample containing  $\text{Y}^{3+}$  and 300 ppm of  $\text{Pr}^{3+}$  measured with the 514 nm excitation. The two largest peaks are the well known Raman Stokes and anti-Stokes Boson peaks found in many glasses and due to internal vibrations in the glass. The smallest peak is also a Raman peak, the origin of which is not known. The Raman origin of these spectral features is established by the fact that the frequency of the scattered light is always shifted by the same amount from the frequency of the incident laser light, irrespective of the absolute frequency/wavelength of the laser. This fact is why it is usually convenient to plot the results on a relative scale with the zero corresponding to the incident laser frequency.

When exciting with a higher laser frequency, the spectrum is clearly different. In Fig. 2 we have superposed the spectra obtained with the three main lines of the laser, 514 nm, 488 nm and 476 nm. In this figure, however, the horizontal scale is an absolute frequency scale and the spectral amplitudes have been adjusted for an easier comparison. As expected for fluorescence spectra, corresponding lines appear at the same absolute frequency even though they have been measured using different excitation frequencies/wavelengths. It is interesting to note that the spectrum measured with 514-nm incident light also clearly contains the same fluorescence lines even though they were hardly visible on the previous graph because of the scale. All samples containing  $\text{Pr}^{3+}$

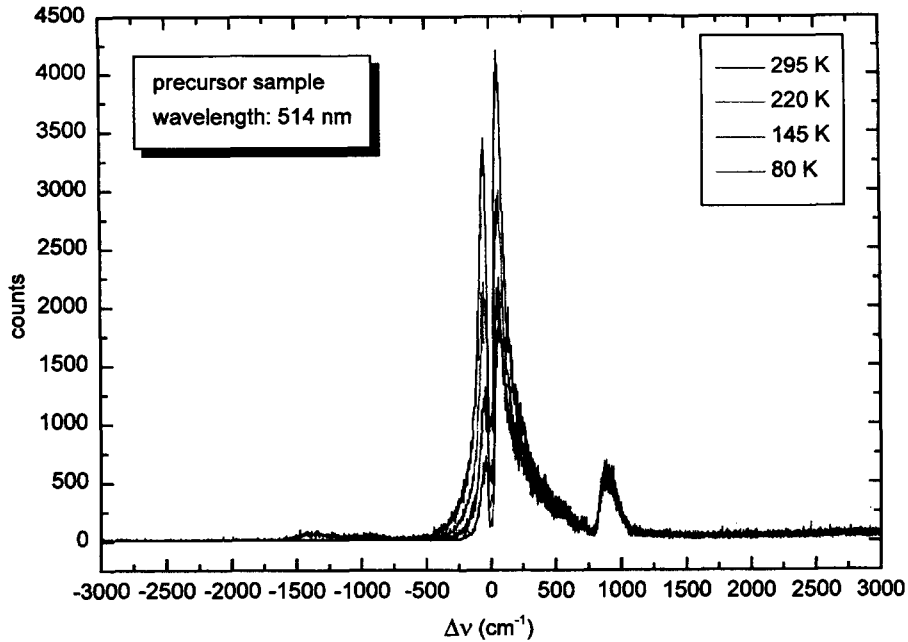


Fig. 1. Fluorescence spectra from a  $\text{Pr}^{3+}/\text{Y}^{3+}$  ceramglass excited at 514 nm. The two most prominent peaks are the anti-Stokes and the Stokes 'Boson' peaks and the smaller peak, an as yet non-identified Raman peak.

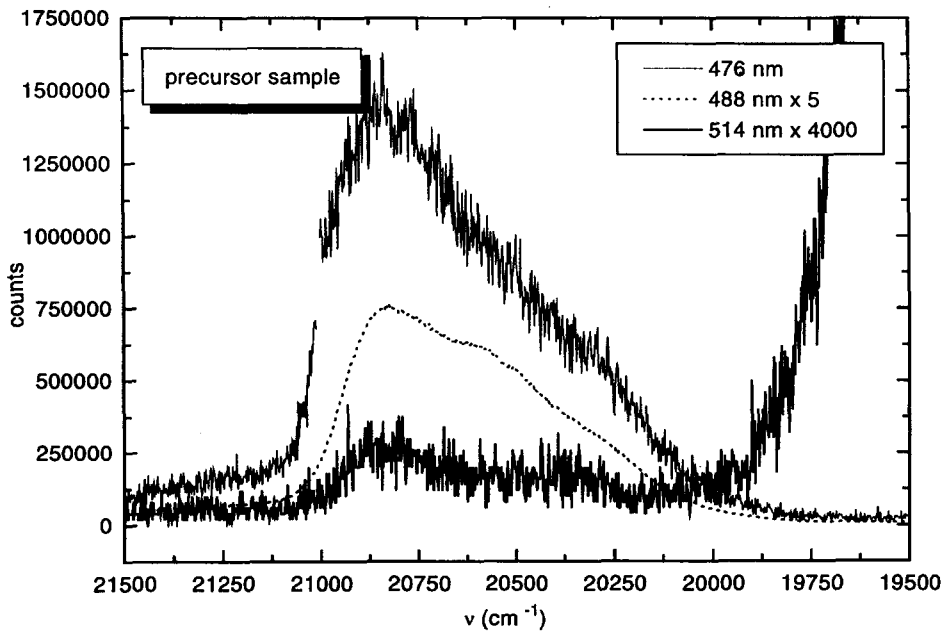


Fig. 2. Fluorescence spectra at three different excitation wavelengths, 514 nm, 488 nm and 476 nm. The perfect correspondence of the three spectra, on an absolute frequency scale, confirms that these are fluorescence spectra.

displayed the same distinct fluorescence spectrum within the observed range of  $21500\text{ cm}^{-1}$  to  $14000\text{ cm}^{-1}$ . Another relevant observation is the large width of these lines. As discussed below, this width can be attributed to an energy transfer between  $\text{Pr}^{3+}$  ions which is increased by the presence of  $\text{Y}^{3+}$ .

In contrast with the samples cerammed with  $\text{Y}^{3+}$ , samples prepared with  $\text{Gd}^{3+}$  have much narrower fluorescence lines as shown in Fig. 3. The two spectra presented in this figure were obtained on two samples containing gadolinium and 300 ppm and 25 ppm of  $\text{Pr}^{3+}$ , respectively. Despite the large difference in  $\text{Pr}^{3+}$  concentration both have narrower fluorescence lines. Following the above explanation, we conclude that  $\text{Gd}^{3+}$  does not enhance the energy transfer between  $\text{Pr}^{3+}$  ions. The origin of this difference between  $\text{Y}^{3+}$  and  $\text{Gd}^{3+}$  is given in the next paragraph. Analysis revealed that the spectra of  $\text{Pr}^{3+}$  in the cerammed glasses were similar to those of  $\text{Pr}^{3+}$  in Pb/Cd fluoride crystals [4].

The atomic energy levels of  $\text{Pr}^{3+}$  are presented in Fig. 4. The ground state is  $^3\text{H}_4$  and the rele-

vant excited states for visible emission are  $^3\text{P}_0$ ,  $^3\text{P}_1$ ,  $^1\text{I}_6$  and  $^3\text{P}_2$ . Because of their proximity in energy, the  $^3\text{P}_1$  and  $^1\text{I}_6$  may not be resolved. Next to the energy level diagram, we also list the different transitions and the corresponding letters that allow their identification on the spectra of Fig. 3. There are three main groups of fluorescence lines in the spectrum associated with transitions from the three main excited states. The L line at  $4000\text{ cm}^{-1}$  ( $\sim 16500\text{ cm}^{-1}$  absolute) is special since it falls at the position of two possible transitions,  $^3\text{P}_0$  to  $^3\text{H}_6$  and  $^1\text{D}_2$  to  $^3\text{H}_4$ .

When examining the energy level diagram, it is important to realize that, starting from the ground state, the 514 nm excitation falls almost  $1300\text{ cm}^{-1}$  below the  $^3\text{P}_0$  level. This explains why the fluorescence lines are comparatively weak for this excitation frequency. The 488 nm excitation also falls short of the  $^3\text{P}_0$  level but only by  $260\text{ cm}^{-1}$  and the fluorescence lines are quite intense for this excitation frequency (see in particular lines B and L). Finally, the 476 nm excitation falls between the  $^3\text{P}_0$  and the  $^3\text{P}_1$  and the fluorescence spectra are also very intense. In the same man-

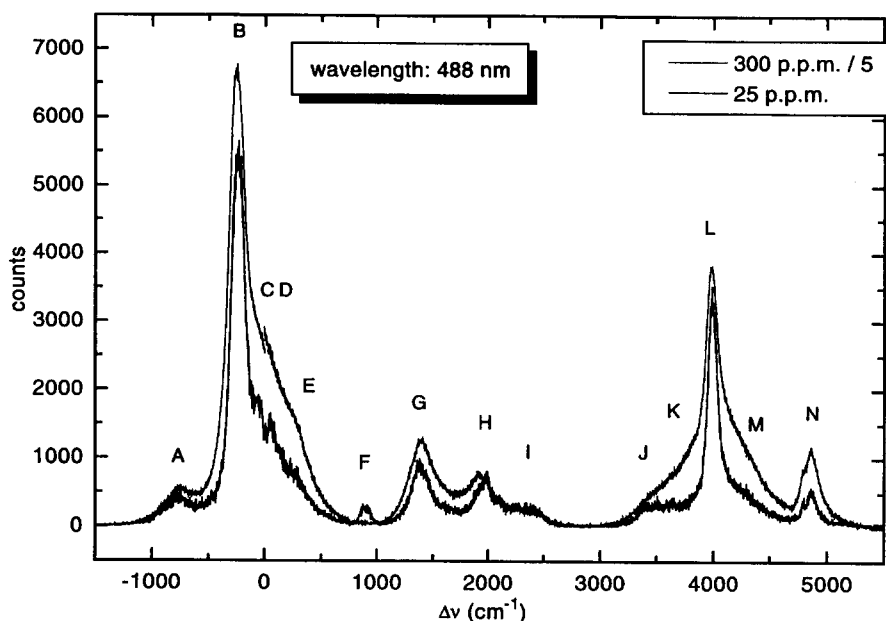


Fig. 3. Spectra from two glasses with gadolinium: the upper spectrum with  $\sim 300\text{ ppm Pr}^{3+}$  and the lower spectrum with  $\sim 25\text{ ppm Pr}^{3+}$ . Note: the widths of the lines are comparable in the two spectra and also much narrower than the corresponding widths in the  $300\text{ ppm Pr}^{3+}/\text{Y}^{3+}$  glass.

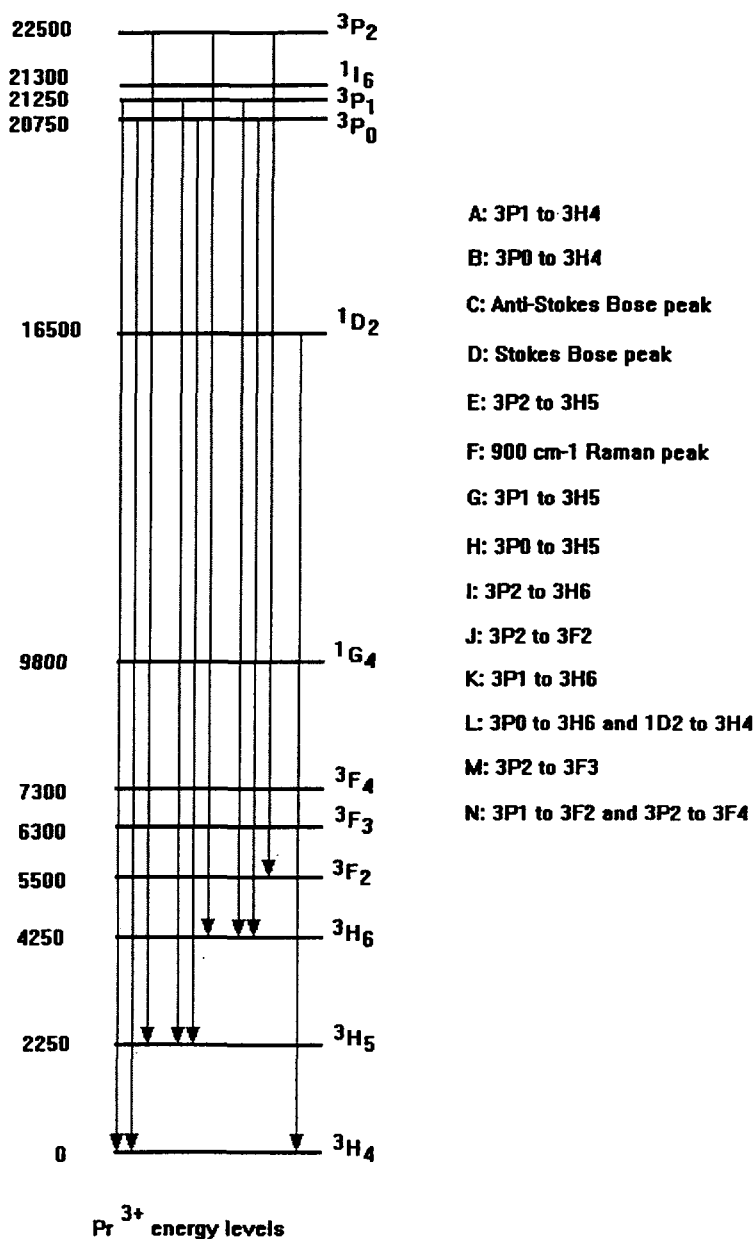


Fig. 4. Energy diagram and line indexation of the fluorescence spectra. The letters identify the lines in the spectra shown on the previous figure.

ner, despite the fact that all excitation frequencies used are less than the  $^3P_1$  and  $^3P_2$  levels, fluorescence lines (e.g. A and E) are nevertheless observed for transitions from these levels. All these observations indicate an efficient up-conversion of the incident photons to higher energy

levels, particularly when the frequency of the exciting photons falls within  $500\text{ cm}^{-1}$  of a given energy level. The drop in up-conversion efficiency as a function of the frequency difference between the exciting photon and a given energy level can be estimated by comparing, for instance, the rela-

tive intensities of the fluorescence lines A, B in Fig. 3. Both of these lines, which appear at negative relative energies, correspond, as we explained above, to transitions from higher frequencies than the excitation laser frequency at zero. With the contribution of the phonon energy, the incident photons at 488 nm are able to excite the  $\text{Pr}^{3+}$  ions up to the  $^3\text{P}_1$  level, but much less efficiently than to the  $^3\text{P}_0$  level.

In the next figure, Fig. 5, we compare spectra obtained from an as-quenched (precursor) sample and from a heat-treated (annealed or cerammed) sample at room temperature. The two spectra are identical but for a slight difference in intensity. As we discuss below, we suggest that the local structural environment of the  $\text{Pr}^{3+}$  ion is the same in both glasses. The temperature dependence of this intensity, shown in Fig. 6, is however different in the two samples and suggests that the coupling to phonons, and therefore the vibrational environments of the  $\text{Pr}^{3+}$  ion, differ.

In the precursor sample, the amplitudes of all the lines decreases monotonically with temperature. By contrast, in the heat-treated sample, the

amplitudes of the B line first increases while that of the A line decreases monotonically. There appears to be a transfer of amplitude from one line to the other. This temperature dependence is also stronger in the spectra measured with the 476 nm excitation than in those measured with 488 nm. In the former, the B line increases in amplitude down to 145 K while, in the latter, it begins to decrease below 220 K. The second group of three lines, G, H, I, seems to display a similar temperature dependence, with an initial transfer of amplitude from G to H in the annealed sample.

#### 4. Discussion

The fluorescence results reported above illustrate the importance of up-conversion and the existence of various decay paths that depend on temperature and therefore point to the essential role of phonons [5–7].

The up-conversion processes necessarily depend on the phonon population and are no longer possible at low temperatures. This explains why,

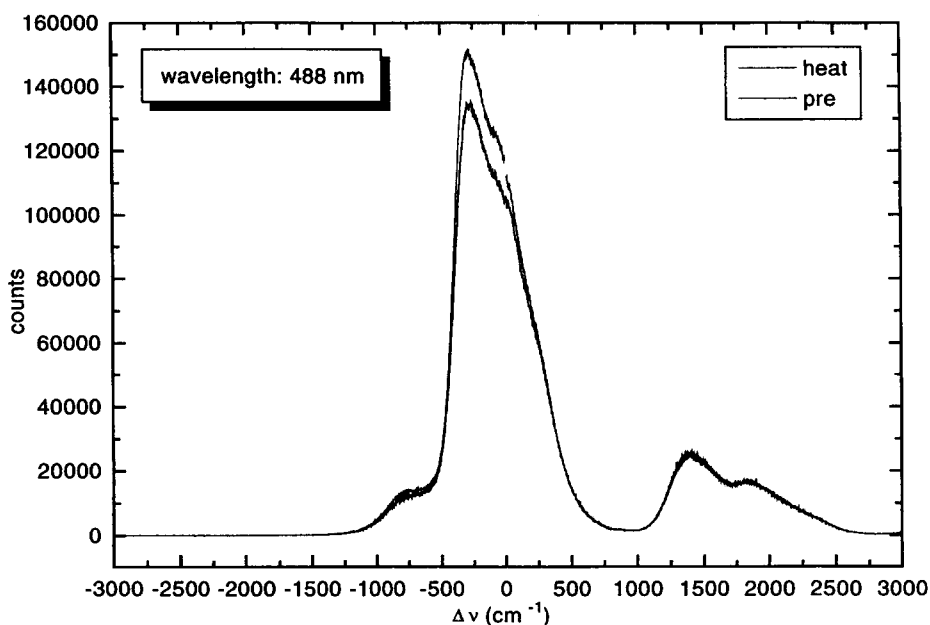


Fig. 5. Comparison of spectra from precursor and heat-treated glass. It would appear that the immediate environment of the  $\text{Pr}^{3+}$  ion is the same in both quenched and cerammed glass (i.e. same short range environment).

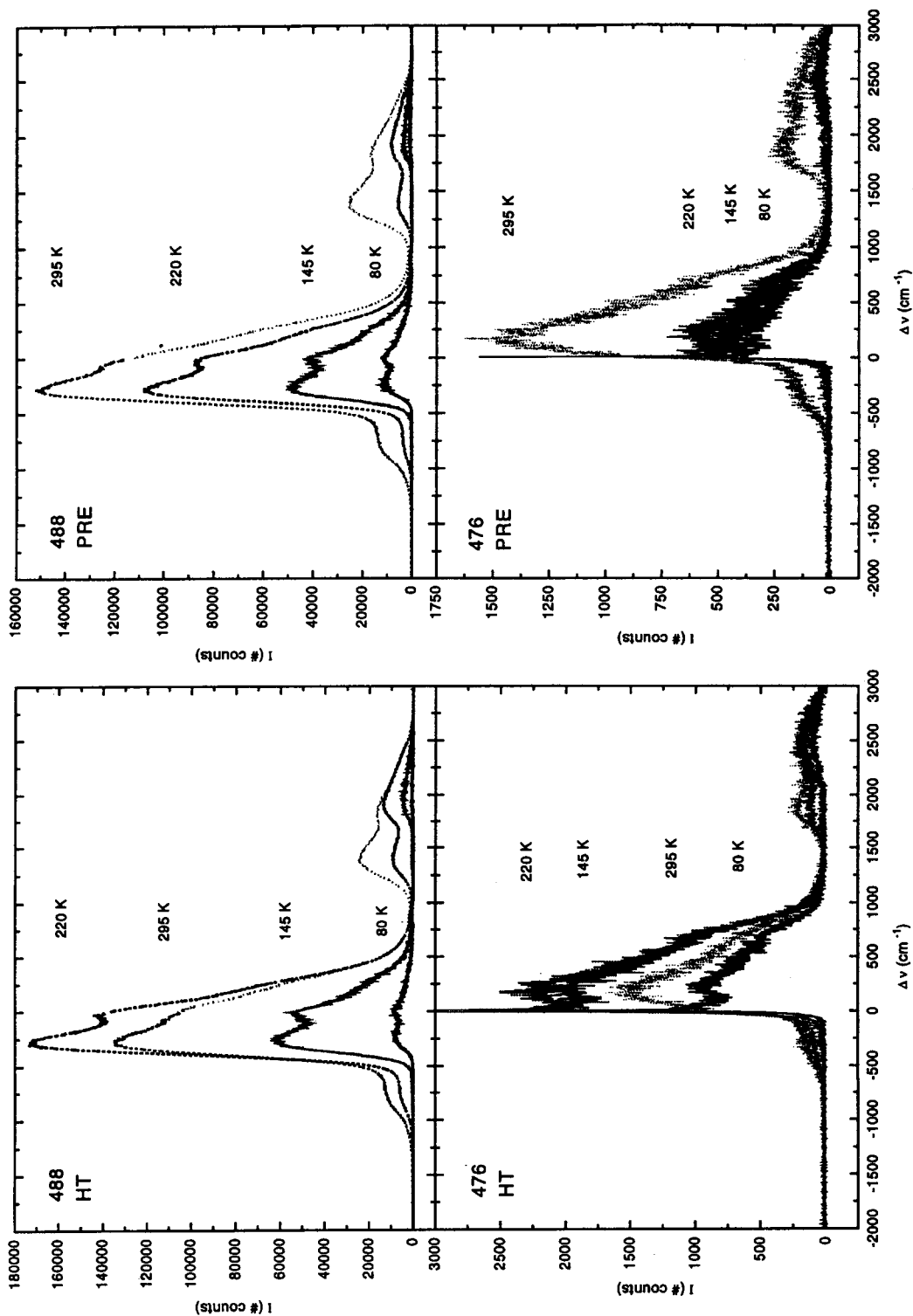


Fig. 6. Temperature dependence of the main fluorescence lines in the precursor and heat-treated glasses measured with 488 nm and 476 nm excitation wavelengths. Note: although the lineshapes are approximately the same in both at 295 K, their temperature dependencies are significantly different.

in Fig. 6c and d, the intensity of the spectra decreases monotonically with temperature. The evolution of the up-conversion processes with temperature also has an effect on the decay path of the excitations because the latter depends upon the initial excited state of the  $\text{Pr}^{3+}$  ion. Changes in decay path explains the changes observed in the relative intensities of the different fluorescence lines. In particular, this is the case for the A and B lines and for the G and H lines in the spectra of the heat-treated sample. For example, as the temperature decreases, there are fewer high energy phonons that can up-convert the incident phonons to the  $^3\text{P}_1$  level. Fewer atoms therefore decay from that level and, instead, more decay from the  $3\text{P}_0$  level resulting in a loss of intensity of the A line and gain of the B line. As the temperature is further decreased, the B line also begins to lose intensity. When exciting with 488-nm light, the decrease in intensity of the B line occurs below 220 K whereas, when exciting with 476-nm light, it only begins below 145 K. This observation is simply due to the fact that the 488 nm excites the  $\text{Pr}^{3+}$  ions just below the  $^3\text{P}_0$  level while the 476 nm light is capable of exciting them above it.

Another aspect of the results that calls for comments is the width of the fluorescence lines. These are smaller in glasses cerammed with gadolinium than in those cerammed with yttrium. As shown in Fig. 3, even for a concentration of 300 ppm of  $\text{Pr}^{3+}$ , the B and L lines are still relatively narrow compared to the corresponding lines in Fig. 5. There are two possible explanations for this observation: (a) the first one has to do with the respective ionic radii of  $\text{Y}^{3+}$  and  $\text{Gd}^{3+}$  and the local deformation caused by these two ions; (b) the second is due to the position of the energy levels of the two ions. Although this question is not settled, the second explanation is likely to be significant because the first excited state of  $\text{Gd}^{3+}$  is very far above the excited states of  $\text{Pr}^{3+}$  that are responsible for the fluorescence spectra shown here.

## 5. Conclusions

Mixed fluoride nanocrystals containing  $\text{Pr}^{3+}$

can be formed in aluminosilicate glasses by ceramming (annealing). The  $\text{Pr}^{3+}$  ions, preferentially located in these, give rise to an intense and characteristic fluorescence spectrum. In this spectrum, we have identified three main groups of three lines each which correspond respectively to optical transitions from the  $^3\text{P}_0$ ,  $^3\text{P}_1$  and  $^3\text{P}_2$  excited energy levels. Our indexation is in agreement with that given for  $\text{Pr}^{3+}$  in other glasses and in mixed fluoride crystals. Comparison of the fluorescence spectra obtained with different excitation laser frequencies reveals the importance of up-conversion processes.

The close similarity that exists between the spectra from as-quenched and annealed (cerammed) samples suggest that the local environment of the  $\text{Pr}^{3+}$  ions is the same in both. However the temperature dependence of the line intensities differ in the two types of samples indicating that the coupling to phonons differs. In the annealed sample, the temperature dependence of the line amplitudes reveals changes in the decay path that correspond to changes in the thermal population of phonons that are active in the up-conversion processes while, in the quenched glass, the line intensities all decay monotonically.

Finally, comparison of the fluorescence linewidths indicates that  $\text{Y}^{3+}$  increases the energy transfer between  $\text{Pr}^{3+}$  ions.

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