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U^{3+} doped fluoride glass emission at 2.5 μm

J. LAMBARD*, A.M. JURDYC, B. JACQUIER, M.F. JOUBERT and R. MAHIOU**

URA 442 du CNRS, Université Lyon I, Bd du 11 Novembre 1918, 69622 Villeurbanne cedex, France

* CEA Saclay, SCM Bât. 125, 91191 Gif-sur-Yvette cedex, France

** URA 444 du CNRS, Université Blaise Pascal, Clermont II, 63177 Aubière cedex, France

ABSTRACT

Fluorescence dynamics of trivalent uranium in ZBLAN or BATY glasses and ZBLAN fiber has been investigated at various temperatures. A careful fluorescence analysis of all these systems allows to identify some of the crystal field components of the ground level $J=9/2$. Fluorescence decays of the 2.5 μm emission have been recorded using an infrared nanosecond pulsed laser indicating an average lifetime of hundred of milliseconds at low concentration. The non exponential behavior of the decay increases with concentration.

INTRODUCTION

Fluoride glasses are greatly investigated for their potential use as low loss fibers, optical amplifiers or laser sources either in the infrared range or in the visible because of the low phonon frequency of the glass net. Among the already studied rare earth doped fluoride fibers [1-3], no ion has been found suitable for amplifying and lasing near 2.55 μm where the fluoride glass fiber minimum loss is to occur. Laser effects in this wavelength range were only reported with trivalent uranium ions doped into BaF_2 , CaF_2 or SrF_2 crystals [4-6]. Recently, one of us reported the use of irradiation techniques to introduce successfully U^{3+} ions in fluoride glasses [7] which is well suitable for high quality glass as compared to glass preparation under reducing atmosphere [8]. The first results of optical absorption, fluorescence and electron paramagnetic resonance (EPR) measurements were presented.

In this paper, fluorescence measurements and decay times were recorded on bulk and fiber materials for different concentrations of trivalent uranium showing the effect of energy transfer between excited ions.

EXPERIMENTAL PROCEDURE

Two types of fluoride glasses of compositions ZBLAN ($53ZrF_4$, $20BaF_2$, $4LaF_3$, $3AlF_3$, $20NaF$) and BATY ($20BaF_2$, $30AlF_3$, $30ThF_4$, $20YF_3$) were prepared using conventional techniques. Tetravalent uranium ions were introduced in UF_4 powder with high purity anhydrous fluorides (from 200 ppm to 1000 ppm). After glass melting at 850-900°C under N_2/O_2 atmosphere inside a dry box and casting into brass moulds, the reduction of U^{4+} to U^{3+} ions was ensured by submitting glass samples to highly ionizing radiations (^{60}Co). After reduction, the U^{3+} ion molar concentration is within 160-600ppm. It is noticed that a best reduction efficiency is reached for low doping [7]. A ZBLA/ZBLAN doped preform (35 ppm U^{4+} in the core glass) was also manufactured and partly drawn into a 15 μm core diameter and a cladding of 100 μm , the fiber being single mode at wavelength greater than 0.9 μm .

Low temperature fluorescence and decay time measurements were performed on bulk materials and the back scattered light of the input of the fiber was analysed when samples are excited using the infrared radiation of a tunable Ti:S cw laser or a nanosecond pulsed laser from a tunable dye laser the frequency of which was downshifted by stimulated raman scattering in a high pressure gaseous H_2 cell.

RESULTS

As expected, comparative low temperature absorption measurements on irradiated and non irradiated samples show the presence of U^{3+} , the levels of which are also known on doped fluoride crystals [9] and recently reported in fluoroaluminate glass [8] (see left side of fig.1).

Fluorescence

The bulk samples were excited at 876.6 nm where more than 94% of the absorption is due to U^{3+} ions with respect to the unreduced tetravalent uranium. Low temperature fluorescence measurements show a line narrowing of the emission bands (fig.2) which allows to identify some of the Stark components of the ground multiplet as depicted on the right side of fig.1, the first excited component being included in the broadening of the first peak. No appreciable changes can be detected between the two glass compositions, either at room temperature or 4.4 K. Figure 3 shows a comparison of the room temperature emission spectra of the same excited fiber recorded with different experimental conditions. As reported before [7], the maximum of longitudinal fluorescence (see curves 2 and 3 of figure 3) is shifted towards the short wavelengths as the fiber is shortened. Assuming that our back scattering light output emission analysis (curve 1) corresponds to a sample shorter than the above ones because of the strong absorption of the laser light (more than 90% in 30 cm), it follows the trend defined previously. However, it should be noticed that the excitation wavelength and the pumping power were not identical in the two measurements.

Decay measurements

Fluorescence decays of bulk samples doped with various concentrations were measured at different temperatures. U^{3+} ions were pumped at 894.2 nm where almost no U^{4+} absorption is expected after reduction. All the decays are non exponential at all temperatures. This non exponentiality changes slightly with concentration, as shown in figure 4 for the BATY composition. It is to be noted that the decay profile is very sensitive to the density of excitation. A similar trend was measured for the ZBLAN composition with the same order of magnitude of decay times. This behaviour indicates the existence of an efficient energy transfer which may quench the quantum yield of the U^{3+} 2.5 μ m emission. At low temperatures, the change of the decay profile with concentration is not significative but the temperature dependence of the profile is indicative of a phonon assisted energy transfer mechanism.

DISCUSSION

Efficient fluorescence of U^{3+} ions in fluoride glasses has been observed at 2.5 μ m. Low temperature data allow to confirm the assignment of the $^4I_{11/2} \rightarrow ^4I_{9/2}$ transition by comparing with fluoride crystals or glasses [8, 9]. The Stark splitting of the ground multiplet in the two systems seems very close. As a consequence, we notice that the glass composition (ZBLAN or BATY) has a reasonably small influence on the crystal field acting on U^{3+} ions. Tuning the excitation wavelength will provide a similar information for the excited states which is already under way at the laboratory. However, the presence of U^{4+} due to incomplete reduction may complicate the spectra. Indeed, for many transitions in the near infrared, there is a quite good overlap between absorptions of U^{4+} and U^{3+} . This may also cause some effects in the fluorescence dynamics of the 2.5 μ m emission.

The most puzzling question concerns the behaviour of the fluorescence of the fiber which tends to appear at shorter wavelength as the length decreases. This can be easily explained by a reabsorption process at the resonance (2.23 μ m) which is favored by increasing the length of the fiber (comparison of curves 2 and 3 of figure 3). However, the curve 1 of figure 3 is not understood at the present time, except that the input power was higher than in the previous experiment which may point out the role of excited state absorption (ESA) losses or favor some amplified spontaneous emission (ASE). Indeed, a quick look of the energy level diagram

Fig. 1: U^{3+} energy level diagram in fluoride glasses.

Fig. 2 Fluorescence spectra of doped ZBLAN at room temperature (1) and at 12 °K (2).

Fig. 3 Fluorescence spectra of a doped fibre: 1 back scattered light from input, 2 and 3 longitudinal output of 0.4m and 1.5m fiber lengths respectively from ref. 7.

Fig. 4 Fluorescence decay curves at 300 °K of U^{3+} doped BATY: left, 160 ppm and right, 600 ppm; the full lines represent theoretical fits with Inokuti and Hirayama's formula.

of figure 1 shows unambiguously the great number of possible coincidences between down transitions and absorption transitions from the first excited state $^4I_{11/2}$.

At room temperature, the average long decay time of the low concentrated materials is about 120 μs while, at higher concentrations, a long time behaviour of 90 μs is estimated. Using an Inokuti and Hirayama type energy transfer process, the decay profiles are well reproduced as shown on figure 4. However, the significance of the obtained parameters is far from evident since it leads to a variation of the lifetime with concentration. It is likely that the energy transfer process is a multistep process which contributes to limited diffusion mechanism and trapping to sinks. These sinks may be related to the presence of U^{4+} ions, the energy levels of which are closely resonant to the first excited state of U^{3+} ions.

CONCLUSION

Fluorescence of ZBLAN and BATY fluoride glasses doped with trivalent uranium has been recorded versus temperature and concentration. Furthermore, fluorescence dynamics has been investigated at different temperatures which points out the existence of an energy transfer process between trivalent uranium ions; tetravalent uranium ions are supposed to act as traps. The spectral behaviour of the fluorescence of the fiber is still a puzzling question. Investigations of very low concentrated materials would be useful in relation with a quasi complete reduction of the tetravalent uranium and for the feasibility of an amplifier at 2.5 μm .

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