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Optical properties of Ni^{2+} in fluoride investigated by time-resolved spectroscopy

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The optical properties of Ni^{2+}-doped barium-indium-gallium-based (BIGaZYT) and lead-based (PBI) fluoride glasses have been investigated. Absorption and luminescence measurements performed over a wide temperature range indicate that the dopant ion occupies a site of nearly-octahedral symmetry. We observe three luminescence transitions (green, red and NIR) which are assigned to the $^1T_2(^1D)\rightarrow{}^3A_2(^3F)$, $^1T_2(^1D)\rightarrow{}^3T_2(^3F)$ and $^1T_2(^1D)\rightarrow{}^3T_1(^3F)$ transitions of the Ni^{2+} ion. Steady-state emission spectra and luminescence decay times as a function of temperature have been measured to determine the presence and extent of nonradiative transitions. In order to correlate glass-matrix composition with emission spectral properties, detailed time resolved measurements have been performed.

1. INTRODUCTION

Much of the present interest about the spectroscopy of the nickel ion is centred in the search and development of nickel-doped materials as active media for tunable infrared lasers. Among laser host material, fluoride glasses have received much attention because of their large transparency and facility to dissolve rare-earth or transition-metal ions[1,2]. However, there have been only a few studies on the optical properties of Ni^{2+} in fluoride glasses[3,4] because of the low efficiency and thermal quenching of the emission. In recent works[5-7], the authors discussed the strong thermal quenching of the $^4T_2\rightarrow{}^4A_2$ Cr^{3+} luminescence in fluoride glasses. These studies also provided a first insight into a possible site distribution of Cr^{3+} in these glasses.

The aim of this work is to characterise the optical properties of Ni^{2+} in two fluoride glasses (BIGaZYT and PBI) and to study the influence of the glass composition on its spectral and temperature behaviour.

2. MATERIALS AND TECHNIQUES

Barium-indium-gallium-based (BIGaZYT) fluoride glass was prepared at the Mineral Chemistry Laboratory of the Rennes University (France). Lead-based (PBI) fluoride glass sample was prepared at the University of Maine, Le Mans, France. Samples were obtained by adding 0,5 wt.% NiF_2 to mixtures with the composition in mol%:

$30BaF_2$-$18InF_3$-$12GaF_3$-$20ZnF_2$-$10YF_3$-$10ThF_3$ (BIGaZYT)
$20PbF_2$-$25BaF_2$-$50InF_3$-$5ZnF_2$-$5YF_3$-$2AlF_3$ (PBI)

The experimental method for preparing these fluoride glasses has been well described in the literature[8-10].

The sample temperature was varied between 4.2 and 300K with a continuous flow cryostat. Conventional absorption spectra were performed with a CARY 5 spectrophotometer. The emission measurements were made using the 457Å Ar^+ laser line as exciting light. The fluorescence was analysed with a 0.22-m SPEX monochromator, and the signal was detected by a Hamamatsu R7102 extended IR photomultiplier and finally amplified by a standard lock-in technique. The system response was calibrated with a standard tungsten-halogen lamp to correct the emission spectra.

Lifetime measurements and time-resolved spectroscopy were performed with a tunable dye laser (1-ns pulse width). The spectra were processed by a EGG-PAR boxcar integrator.

3. EXPERIMENTAL RESULTS

A. Absorption and emission spectra

The absorption spectra of BIGaZYT:Ni^{2+} and PBI:Ni^{2+} were recorded at room temperature. These spectra are very similar to those found in other fluoride glasses[3,4,11-13] and are consistent with Ni^{2+} ions occupying octahedral sites. Figure 1 shows, as an example, the absorption spectrum of Ni^{2+} in BIGaZYT. Table 1 shows for comparison the observed and calculated energy levels using Sugano et al.[14] matrix elements for all the $3d^n$ electron systems.

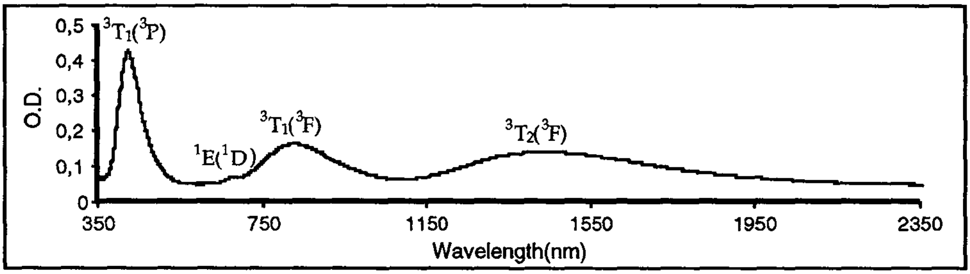

Figure 1 Absorption spectrum of Ni^{2+} in BIGaZYT glass recorded at room temperature.

Table 1 Comparison of the experimentally observed (at room temperature) and predicted energy levels for Ni^{2+} in BIGaZYT and PBI glasses.

	BIGaZYT				PBI			
	Observed	Calculated			Observed	Calculated		
Level	cm^{-1}	cm^{-1}			cm^{-1}	cm^{-1}		
$^3T_2(^3F)$	6940	6940	Dq=	694cm^{-1}	7143	7143	Dq=	714cm^{-1}
$^3T_1(^3F)$	12121	11793	B=	966cm^{-1}	12346	12100	B=	954cm^{-1}
$^1E(^1D)$	14815	14829	C/B=	4,04	14903	14903	C/B=	4,17
$^3T_1(^3P)$	23529	23517	Dq/B=	0,72	23641	23641	Dq/B=	0,75

The emission measurements were made under excitation in the $^3T_1(^3P) \leftarrow {}^3A_2(^3F)$ absorption band using the 457nm line of an Ar^+ laser. Luminescence occurs from $^1T_2(^1D)$ giving rise to a green, red and NIR bands. The band assignments and lifetimes at the emission wavelengths observed for Ni^{2+} in BIGaZYT and PBI are listed in Table 2. The integrated emission intensity (Figure 2 a)) decreases as temperature increases, which is due to increasing nonradiative processes[3].

Table 2 Emission properties of Ni^{2+} in BIGaZYT and PBI glasses at 77K.

				BIGaZYT	PBI
Emission	Band $^1T_2(^1D) \rightarrow$	Assignment	λ_{em} (nm)	Lifetime (µs)	Lifetime (µs)
green		$^3A_2(^3F)$	530	20	17
red		$^3T_2(^3F)$	780	14	12
NIR		$^3T_1(^3F)$	1080	10	

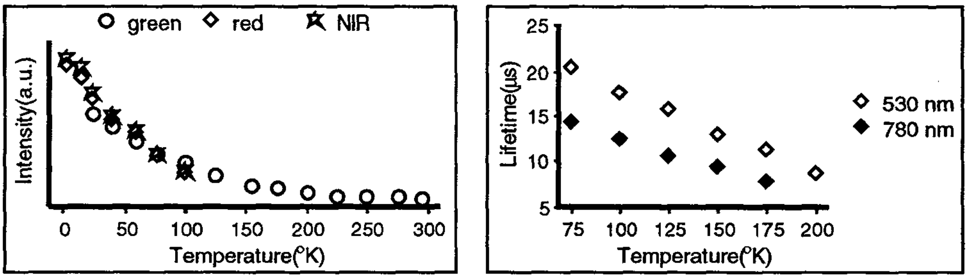

Figure 2 a) Thermal quenching of the green red and NIR emissions of Ni^{2+} in BIGaZYT.
b) Lifetimes of Ni^{2+} in BIGaZYT as a function of the temperature for the green and red emissions.

B. Emission lifetime results

The decay kinetics of the three luminescence emissions were studied as a function of temperature and emission wavelength, under pulsed laser excitation along the $^3T_1(^3P)\leftarrow{}^3A_2(^3F)$ absorption band. For practical purposes we use the "average lifetime" defined by equation $\bar{\tau}=\int tI(t)dt/\int I(t)dt$. The temperature dependence of lifetimes is the same for the three emissions (Figure 2 b)). This is consistent with the fact that these transitions originate at the same $^1T_2(^1D)$ excited state[15]. The qualitative similarity of the temperature dependence of the lifetimes and integrated intensities suggests that the lifetime decrease is due to thermal quenching[3]. Fluorescence decay measurements have been carried out at 77K for the three bands at different emission wavelengths for an excitation wavelength of 437nm (Figure 3). Table 2 contains the decay times at the peak positions of the three emissions. The lifetime is almost constant along the red emission band. Nevertheless the decays for the green and NIR emissions are faster for the lower detection energies and are non exponential. Figure 4 a) shows the logarithmic plot of the decay monitored at 530nm for the BIGaZYT:Ni^{2+}. A short-lived component of the experimental decay of almost 6μs can be appreciated.

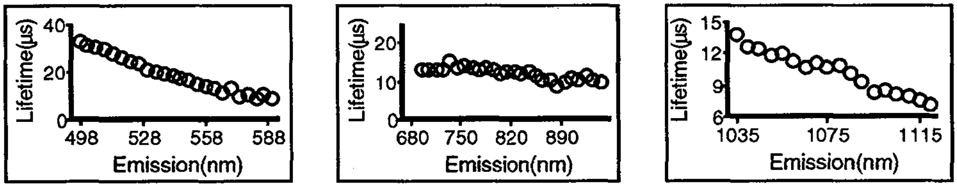

Figure 3 Lifetimes of Ni^{2+} in BIGaZYT at different emission wavelengths for an excitation wavelength of 437nm recorded at 77K.

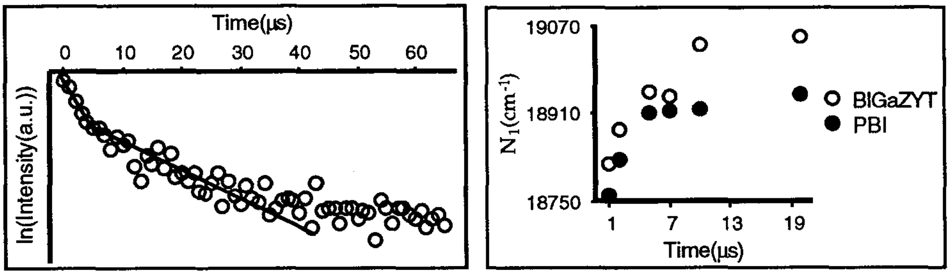

Figure 4 a) Logarithmic plot of the decay monitored at 530nm for Ni^{2+} in BIGaZYT.
b) Time dependence of the first moment for the green emission of Ni^{2+} in BIGaZYT and PBI glasses recorded at 77K.

C. Time resolved spectra

Time-resolved emission spectra (see Figure 5) were obtained at 77K after exciting the samples with a tunable laser at the peak position of the $^3T_1(^3P)\leftarrow{}^3A_2(^3F)$. For the green and NIR emissions there is a shift to higher energies and a narrowing of the emission band as time increases between 1μs and 20μs. Figure 4 b) displays the time dependence of the first moment (peak position) calculated from the TR emission spectra of the green band for BIGaZYT:Ni^{2+} and PBI:Ni^{2+}. It can be seen that for both glasses the shift of the peak is more pronounced at a time that corresponds with the values for the short-lived components of the decays.

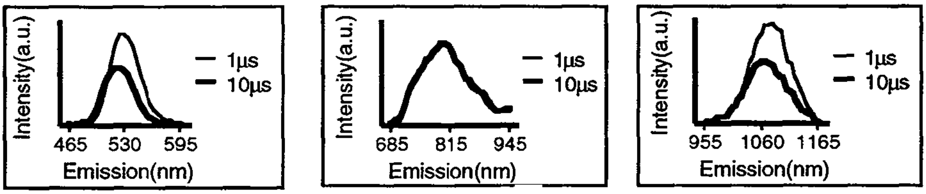

Figure 5 Time resolved spectra for the three emissions of Ni^{2+} in BIGaZYT glass recorded at 77K under 437nm excitation.

4. DISCUSSION

The preceding spectroscopic data show that in BIGaZYT and PBI fluoride glasses the Ni^{2+} ion tends to occupy sites that have nearly octahedral symmetry. For both glasses the red emission presents neither any significative temporal evolution in the time resolved emission spectra nor any wavelength dependence for the lifetimes. These results are in agreement with the predictions of the Tanabe-Sugano diagram for the $^1T_2(^1D)\rightarrow{}^3T_2(^3F)$ transition, as the crystal field energy curves of the levels involved in this transition are almost parallel. So, a change of the crystal field does not result in a change of the transition energy between these levels. In contrast, the green and NIR emission show faster decays for the lower detection energies. In addition, the time resolved emission spectra present a shift to higher energies and a narrowing as time increases. For both glasses the shift of the peak is more pronounced at a time that corresponds with the values for the short-lived components of the decays. These data can be explained by assuming some sort of distribution of Ni^{2+} ions with different energy levels and transition probabilities. At short time delays the time resolved emission spectra correspond to the characteristic fluorescence of the whole distribution of ions. When time increases, the ions with shorter lifetimes have decayed and make no contribution to the delayed fluorescence. As a consequence a blue shift and a narrowing should appear. Moreover our data show that the blue shift undergoes an abrupt change in the time interval that covers the short lived component of the experimental decays for both glasses. These results are consistent with the existence of two kinds of site distributions for Ni^{2+} ions.

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