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Optical properties of pure, Nd^{3+}-doped and Pr^{3+}-doped fluoroindate glasses *

C.X. Cardoso, Y. Messaddeq, L.A.O. Nunes and M.A. Aegerter
Institute of Physics and Chemistry of São Paulo, University of São Paulo, 13560-970 São Carlos, SP, Brazil

Fluoroindate glasses doped with Pr^{3+} or Nd^{3+} are promising materials for the development of fluoride fibers, amplifiers and lasers. The optical properties of an InF_3–SrF_2–BaF_2–ZnF_2–GdF_3–NaF composition pure and doped up to 3 mol% have been systematically studied. The extended UV transmission of this glass allows the identification of most of the $^8S \rightarrow {}^6P$ and $^8S \rightarrow {}^6I$ transitions of Gd ions. The optical transitions of Pr^{3+} and Nd^{3+} have been identified in absorption between 250 and 10000 nm. Fluorescence and excitation spectra and lifetime have been measured at 300 K. Most of the transitions have been identified.

1. Introduction

There is an increasing interest in the determination of the optical properties of heavy metal fluoride glasses doped with rare-earth ions. Devices with excellent characteristics have been recently reported using ZrF_4 [1] and InF_3-based glass [2,3]. This paper presents the optical properties, including absorption, fluorescence and decay times, of Nd^{3+}- and Pr^{3+}-doped InSBZnGdN glasses.

2. Experimental

Glasses of compositions $(40-x)InF_3$–$20SrF_2$–$16BaF_2$–$20ZnF_2$–$2GdF_3$–$2NaF$–xMF_3, M being Nd or Pr with $0 < x < 3$ mol%, called hereafter InSBZnGdN, have been fabricated in a dry box under controlled Ar atmosphere. Absorption spectra were measured with a Cary 17 and Bomem IR DAS spectrometer over the spectral range 0.25–10 μm. The fluorescence properties were determined at 300 K up to $\lambda = 1.5$ μm. The emission spectra have been measured by a conventional optical set-up; the excitation light source was either a coherent 5W argon laser or a high intensity Oriel monochromator illuminator (model 7340) equipped with Xe and quartz halogen lamp. The luminescence was analyzed by a 50 cm Jarrell–Ash monochromator and detected by an EMI 9684 QB-SI photomultiplier (UV–visible) or Judson Ge J16-D detector (near infrared); the signal was amplified by a lock-in EG&G Par 5204. The decay times were measured by time resolution spectroscopy exciting the samples at 350 nm by a 5 ns light pulse provided by the third harmonic of a Quanta Ray DCR 1A Nd:YAG laser (5 kW peak power and 10 Hz repetition rate). The complete rejection of laser radiation was done by employing color filters. The signal was detected by an ITT FW 130 photo-multiplier, amplified by an Ortec preamplifier and analyzed by a home-made computerized data acquisition system (Box Car).

3. Results

Figure 1 shows the transmission spectrum of pure InSBZnGdN glass compared with those of

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Correspondence to: Dr M.A. Aegerter, Institute of Physics and Chemistry of São Paulo, University of São Paulo, 13560-970 São Carlos, SP, Brazil. Tel: +55-162 74 92 06. Telefax: +55-162 71 36 16.

Table 1
Pr^{3+} absorption bands in InSBZnGdN doped with 3 mol% Pr measured at 300 K and identification of the electronic levels reached from the $^3H_4$ ground state

E (cm^{-1})	Level	E (cm^{-1})	Level
22573	$^3P_2$	6963	$^3F_4$
21367	$^3P_1$	6519	$^3F_3$
20877	$^3P_0$	5146	$^3F_2$
17015	$^1D_2$	4254	$^3H_6$
9865	$^1G_4$	2428	$^3H_5$
		2134	

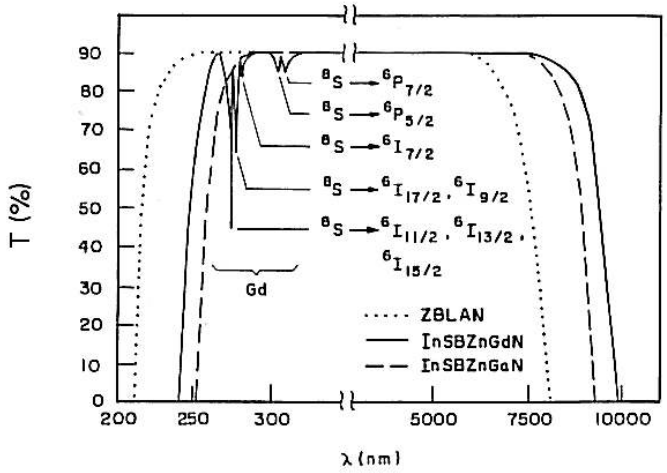

Fig. 1. Transmission spectrum of undoped InSBZnGdN glass compared with ZBLAN and InSBZnGaN glasses.

ZrF_2–BaF_2–LaF_3–NaF (ZBLAN), InF_3–SrF_2–BaF_2–ZnF_2–GaF_3–NaF (InSBZnGaN) also prepared in our laboratory.

The absorption spectra and the electronic levels of InSBZnGdN glasses doped with Pr^{3+} and Nd^{3+} are shown in figs. 2 and 3 and in table 1 and 2, respectively.

The Pr^{3+} fluorescence spectrum excited in the $^3H_4 \rightarrow {}^3P_0$ transition by 476.6 nm laser light is shown in fig. 4. The energy of the emission bands and the corresponding electronic transitions are presented in table 3.

Table 2
Nd^{3+} absorption bands in InSBZnGdN doped with 3 mol% Nd, measured at 300 K and identification of the electronic levels reached from the $^4I_{9/2}$ ground state

E (cm^{-1})	Level	E (cm^{-1})	Level
38535	$^2F_{5/2}$	19138	$^4G_{9/2}$, $^4G_{7/2}$, $^2K_{13/2}$
34542	$^2D_{5/2}^2$	17349	$^2G_{5/2}$, $G_{7/2}$
33501	$^2D_{3/2}^2$	15998	$^2H_{11/2}$
30441	$^4D_{7/2}$	14708	$^4F_{9/2}$
29329	$^2L_{15/2}$	13475	$^4F_{7/2}$, $^4S_{3/2}$
28902	$^4D_{1/2}$	12540	$^2H_{9/2}$, $^4F_{5/2}$
28288	$^4D_{3/2}$, $^4D_{5/2}$, $^2I_{11/2}$	11509	$^4F_{3/2}$
26316	$^2P_{3/2}$	5843	$^4I_{15/2}$
23310	$^2P_{1/2}$, $^2D_{5/2}$	4004	$^4I_{13/2}$
21231	$^2D_{3/2}$, $^2G_{9/2}$, $^4G_{11/2}$, $^2K_{15/2}$	1984	$^4I_{11/2}$

Table 3
Energy and transition of Pr^{3+} emission bands of InSBZnGdN doped with 3 mol% Pr excited in the $^3P_0$ level (476.5 nm), measured at room temperature

E (cm^{-1})	Transition	E (cm^{-1})	Transition
20790, 20513	$^3P_0 \rightarrow {}^3H_4$	14749	$^3P_0 \rightarrow {}^3F_3$
		14357	$^1D_2 \rightarrow {}^3H_5$
19084, 18726, 18215	$^3P_0 \rightarrow {}^3H_5$	13927	$^3P_0 \rightarrow {}^3F_4$
16963	$^3P_0 \rightarrow {}^3H_6$, $^1D_2 \rightarrow 3H_4$	11286, 11111, 11001	$^3P_0 \rightarrow {}^1G_4$
16556	$^3P_0 \rightarrow {}^3H_6$	9833	$^1D_2 \rightarrow {}^3F_4$, $^1G_4 \rightarrow {}^3H_5$
15711, 15492	$^3P_0 \rightarrow {}^3F_2$	7564	$^1G_4 \rightarrow {}^3H_5$

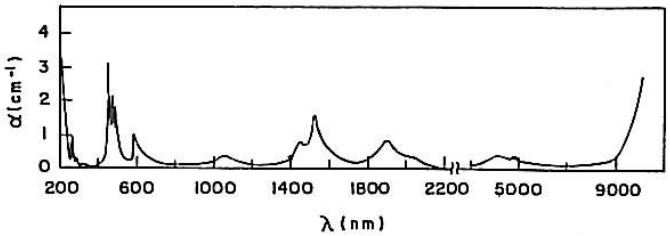

Fig. 2. Absorption spectra of InSBZnGdN glass doped with 3 mol% Pr.

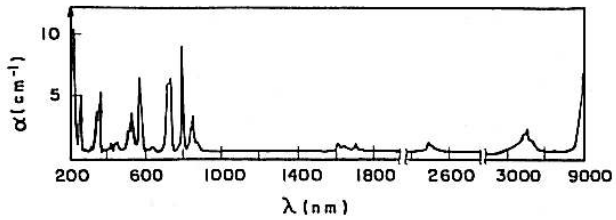

Fig. 3. Absorption spectra of InSBZnGdN glass doped with 3 mol% Nd.

The Nd^{3+} fluorescence spectra excited at 350 nm by the monochromator illuminator in the $^4D_{3/2}$, $^4D_{5/2}$, $^4D_{1/2}$ states and at 514.5 nm by the laser light in the $^4G_{7/2}$, $^4G_{9/2}$ $^2K_{13/2}$ states are shown in fig. 5. The energy and electronic transitions of the respective emission bands are presented in table 4.

The decay times have been measured as a function of neodymium concentration following a 5 ns pulse excitation of the $^4D_{3/2}$ level. Most of the observed transitions originate from the $^2P_{3/2}$ level which is reached by fast non-radiative transition. A typical result is shown in fig. 6 for a 0.1 mol% doped sample and all experimental data are summarized in table 5.

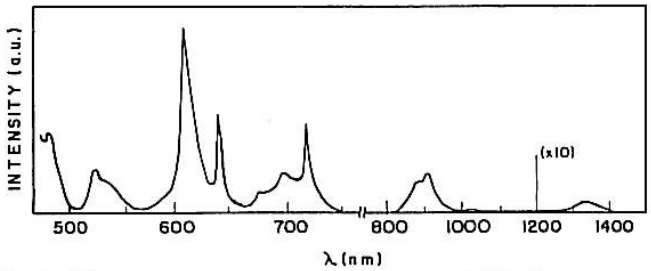

Fig. 4. Fluorescence spectrum of InSBZnGdN:Pr measured at 300 K after excitation of the $^3H_4$ level (476.5 nm).

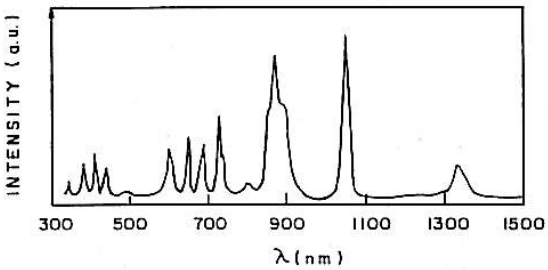

Fig. 5. Fluorescence spectrum of InSBZnGdN:Nd measured at 300 K after excitation of the levels $^4D_{3/2}$, $^4D_{5/2}$, $^4D_{1/2}$ (350 nm). The fluorescence spectrum obtained by excitation of the levels $^4G_{7/2}$, $^4G_{9/2}$, $^2K_{13/2}$ (514.5 nm) is identical for $\lambda > 750$ nm and emission bands are observed between 514 and 750 nm.

4. Discussion

The new composition InSBZnGdN has one of the largest transmission ranges of the fluoride glasses and is a good candidate to prepare optical fibers to be coupled to CO laser with emission at ~ 5 μm for light power delivery. The shift of the multiphonon edge toward lower wavelengths is due to the lower energy of the phonons of this material. The sharp bands observed in the UV

Table 4
Energy and transition of Nd^{3+} emission bands in InSbZnGdN doped with 3 mol% Nd excited in $^4D_{3/2}$ level (350 nm), measured at room temperature

E (cm^{-1})	Transition	E (cm^{-1})	Transition
27933	$^4D_{3/2} \rightarrow {}^4I_{9/2}$	14727, 14577	$^4D_{3/2} \rightarrow {}^4F_{7/2}, {}^4S_{3/2}$ $^2P_{3/2} \rightarrow {}^4F_{3/2}$
26178	$^4D_{3/2} \rightarrow {}^4I_{11/2}, {}^2P_{3/2} \rightarrow {}^4I_{9/2}$	13680	$^2P_{3/2} \rightarrow {}^4F_{5/2}, {}^2H_{9/2}$
23866	$^4D_{3/2} \rightarrow {}^4I_{13/2}, {}^2P_{3/2} \rightarrow {}^4I_{11/2}$	13459	$^4D_{3/2} \rightarrow {}^4F_{9/2}$
22271	$^4D_{3/2} \rightarrow {}^4I_{5/2}, {}^2P_{3/2} \rightarrow {}^4I_{13/2}$	12570	$^4F_{5/2}(^2H_{9/2}) \rightarrow {}^4I_{9/2}$
19880	$^2P_{3/2} \rightarrow {}^4I_{15/2}$	11614, 11534, 11325, 11229	$^4F_{9/2} \rightarrow {}^4I_{9/2}$
16806, 16708	$^4D_{3/2} \rightarrow {}^4F_{3/2}$	9489	$^4F_{3/2} \rightarrow {}^4I_{11/2}$
15625	$^4D_{3/2} \rightarrow {}^4F_{5/2}, {}^2H_{9/2}$	7576	$^4F_{3/2} \rightarrow {}^4I_{13/2}$

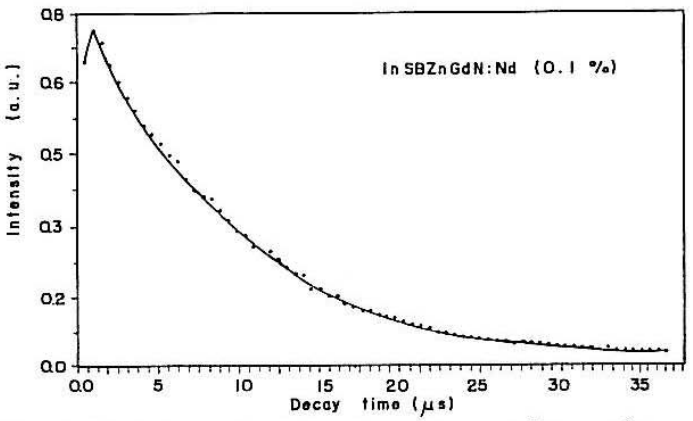

Fig. 6. Typical result of the decay time of $^2P_{3/2} \rightarrow {}^4F_{5/2}$ emission of InSBZnGdN glass doped with 0.1% Nd measured at 300 K by pulse excitation of the $^4D_{3/2}$ level. The line is drawn through the data symbols as a guide for the eye.

range at 272.5, 275.5, 278.5, 305 and 311 nm correspond to the transitions $^8S \rightarrow {}^6I$ and $^8S \rightarrow {}^6P$ of Gd ions.

Glasses doped with Nd^{3+} and Pr^{3+} present absorption properties very similar to those found in fluorozirconate compositions [4–6]. All the transitions have been identified following Adams and Sibley [4]. The small shift in the positions of the absorption bands compared for instance with those found in ZBLAN are due to the different structure and ions coordination number between these compositions [7] but no change in positions have been observed for doping up to 3 mol%. It is interesting to note that the absorption band of Nd doped glasses are in general slightly narrower than those of ZBLAN and InSBZnGaN [8] (where for this composition Gd has been substituted by Ga). Consequently some of the Stark transitions such as $2L_{15/2}$, $2D_{5/2}$, $2G_{7/2}$ and $2G_{5/2}$, $4S_{3/12}$ and $4F_{7/2}$, $4I_{14/2}$, $4I_{13/2}$, $4I_{11/2}$ have been better resolved.

Table 5
Decay time of InSBZnGdN glass doped with Nd; $\lambda_{exc} = 350$ nm

Concentration of Nd^{3+} (mol%)	τ (μs)		
	$^2P_{3/2} \rightarrow {}^4F_{5/2}$	$^2P_{3/2} \rightarrow {}^4I_{15/2}$	$^2P_{3/2} \rightarrow {}^4I_{13/2}$ $^4D_{3/2} \rightarrow {}^4I_{15/2}$
0.05	3.9; 11.5	92.5	5.2; 76
0.1	5.7	63	3.4; 69
1.0	5.3	46.5	3.9; 56.5
3.0	3.5	5.9; 22	4.8; 25

The emissions observed in Pr- or Nd-doped InSBZnGdN glasses are also similar to those found in fluorozirconate compositions and the slight shifts reflect again the different structure and coordination number of the ions; the positions of the bands however do not shift as a function of the ions concentration. The intensities of the emissions are strongly dependent of the Pr and Nd concentrations and a quenching is observed over 0.1%.

The infrared emission of Nd^{3+}-doped glasses corresponding to the final $4F_{3/2} \rightarrow 4I_{13/2}$ transition is of great interest for telecommunications. In this composition, the band is slightly shifted to higher energy as compared with ZBLANP and BIZYT glasses and peaks at room temperature at 1.315 μm, which is a good promise for its use as amplifying fibers.

The emission spectrum excited in the $^4G_{7/2}$, $^4G_{9/2}$, $^2K_{13/2}$ bands is identical to that excited in the 4 D multiplet for $\lambda > 750$ nm. No emission is found between 525 and 750 nm indicating that the emissions observed in this range originate from the $^4D_{3/2}$ and possibly from the $^2P_{3/2}$ levels as indicated in table 4.

The emission spectrum of Pr^{3+} presents interesting features. Several transitions are better resolved than in ZBLAN as for instance $^3P_0 \rightarrow {}^3H_4$ (~ 485 nm), $^3P_0 \rightarrow {}^3H_5$ (~ 540 nm) and $^3P_0 \rightarrow {}^1G_4$ (~ 900 nm). The 1.3 μm emission corresponding to the $^1G_4 \rightarrow {}^3H_5$ transition, of great importance for telecommunications, is broad with its maximum at 1.322 μm, practically at the same position at that of ZBLAN. Its intensity (when excited in the $^3P_0$ level) is low.

The decay times of Nd-doped glasses are of the same order of magnitude as those observed for the transition $^2P_{3/2} \rightarrow {}^4I_{11/2}$ for PMG : Pr glass [9] but much smaller than those of the emissions originating from the $^4F_{3/2}$ measured in ZBLANP : Pr [5] and BIZYT [10]. For 1% and 2% Nd^{3+}-doped samples, the $Nd^{3+} \rightarrow Nd^{3+}$ interaction becomes apparent, resulting in the quenching of the luminescence. Supermigration is observed at higher concentration of neodymium (3% Nd^{3+}).

Samples doped with praseodymium have also been measured as a function of concentration (0.1, 1 and 2 mol%). The decay time of the level $^3P_0 \rightarrow {}^3H_6$ is about 47 μs, independent of the Pr concentration. This result is in good agreement with calculated values [4].

5. Conclusion

The transmission spectrum of pure fluoroindate glass has one of the largest transparency spectral range of fluoride glasses: 260 nm up to 10000 nm. In the UV region, five absorption peaks are observed and have been identified as $^8S \rightarrow {}^6I$ and $^8S \rightarrow {}^6P$ transitions of Gd ions. The absorption and emission spectra of Pr^{3+} and Nd^{3+} have been measured at room temperature and are found similar to those of fluorozirconate glasses. The decay times of the transitions originating from the $^2P_{3/2}$ of Nd^{3+} are shorter than the decay time of the transition $^4F_{3/2} \rightarrow {}^4I$. The decay time of the $^3P_0 \rightarrow {}^3H_6$ transition of Pr^{3+} is 47 μs, independent of the concentration. Research is underway to obtain data at lower temperature.

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