

SPECTROSCOPIC PROPERTIES OF Pr^{3+} -DOPED MULTICOMPONENT
FLUORIDE GLASSES

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ABSTRACT

A new family of five optical glasses of the following chemical composition with 1M% PrF_3 were prepared to examine the effects of alkali fluorides both in mixed and unmixed form: $30\text{InF}_3\text{-}30\text{BaF}_2\text{-}10\text{ThF}_4\text{-}9\text{ZnF}_2\text{-}20\text{RF}$, where $\text{RF}=\text{LiF}$, NaF , KF , NaF-KF and KF-LiF . Significant results have been obtained from the physical characterization of the fluoride glasses. Both the absorption and photoluminescence spectra of these glasses were also measured. Laser emission properties of these glasses were examined both at room and liquid nitrogen temperatures by using an Ar^+ ion laser. The fluorescent lifetime (in μs) of the emission state $^1\text{D}_2+^3\text{H}_4$ ($\lambda=0.59 \mu\text{m}$) was measured at both 300 K and 77 K. The stimulated emission cross-section of different observed luminescent states of these Pr-doped glasses were measured by the use of Judd-Ofelt theory with the recorded photoluminescence spectra.

MATERIALS INDEX: praseodymium, fluorides, glasses, rare earths

Introduction

Rare-earths doped fluorozirconate optical glasses have in recent years attracted considerable attention as potential materials for mid-IR optical fibers, as well as for laser glass development (1-3). Three years ago, for the first time, zirconium-free glasses based primarily on indium trifluoride (InF_3) and barium fluoride (BaF_2) were prepared at the CNRS laboratories in France (4). Guery et al. (5) have reported that InF_3 -based heavy metal fluoride (HMF) glasses were identified as better devices compared with the zirconium fluoride-based glasses for laser efficiency properties.

At present, our group has actively been involved in the research and development of alkali mixed, HMF-based glasses with the rare-earths as luminescent centers to understand their laser emission characteristics. Earlier, we

carried out systematic studies on the Ho^{3+} , Eu^{3+} and Tb^{3+} ions as dopants in alkali mixed HMF glasses (6-9). Now we report on the preparation and characterization of the Pr^{3+} -doped, alkali-mixed, multicomponent HMF glasses, by the measurement of both the absorption and fluorescence spectra.

Experimental

An attempt has been made for the first time to prepare a new family of Pr^{3+} -doped, InF_3 -based, multicomponent HMF glasses with the alkali contents as the glass network modifiers. The chemical compositions used for these glasses are as follows: $30\text{InF}_3 - 30\text{BaF}_2 - 10\text{ThF}_4 - 9\text{ZnF}_2 - 20\text{RF} - 1\text{PrF}_3$, where RF carries the alkali content (20LiF , 20NaF , 20KF , $10\text{NaF}-10\text{KF}$ and $10\text{KF}-10\text{LiF}$). For our convenience, these glasses were labelled as Glasses A, B, C, D and E, respectively. Although we could also prepare another glass with $10\text{LiF}-10\text{NaF}$ content, that has not exhibited sufficient transparency. Therefore, we have excluded this particular glass for characterization. Because of the availability of a large quantity of alkali and alkaline-earth fluorides, crystallization phenomenon has been considerably reduced, resulting in good transparency. By following the procedures given by Poulain et al. (10), the glasses were prepared by the quenching technique in between two brass plates, and the quenched melts were allowed to cool down to laboratory temperature. The required chemicals were purchased from M/s. Johnson Matthey Company Ltd., Cheshire, UK. The oxides were converted into fluorides with the addition of excess NH_4HF_2 and preheated for 20 minutes at 400°C to achieve the fluorination reaction. Thus, the excess NH_4HF_2 was eliminated by evaporation at a maximum temperature of 800°C . The temperature and the time of melting were between $850-1000^\circ\text{C}$ and 1-3 hours, depending on the glass composition. The prepared glasses have dimensions of 1-2 cm in diameter with a uniform thickness of 1-2 mm. The formation of the glass was confirmed by making an observation through both polarising microscopy and XRD analysis.

For all these glasses, densities and refractive indices were measured by using the standard procedures. The visible absorption spectra of Pr^{3+} doped glasses were recorded on a Perkin Elmer 551 Spectrophotometer from 420-620 nm. With regard to the NIR spectra ($1300-3000\text{ cm}^{-1}$) of these glasses, these were carried out on a Carl Zeiss 51 Specord Spectrophotometer.

The fluorescence spectra of these glasses were measured at the Changchun Institute of Physics, Changchun, P.R. China. The lifetime of the laser emission state $^1\text{D}_2 \rightarrow ^3\text{H}_4$ of Pr^{3+} -doped glasses was measured at both room and liquid nitrogen temperatures by using an Argon ion laser (478 nm) fitted with the other essential accessories such as a Biomation 610B Transient Recorder and a Nicolet 1070 Signal Averager.

Results and Discussion

Physical Properties

With the measurement of densities and refractive indices of these glasses we have estimated the values of several other physical parameters to understand the optical efficiencies of these devices by using the relevant expressions given in the literature (9). The determined values of different physical parameters of Pr^{3+} -doped glasses are given in Table 1.

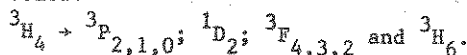
Absorption Properties

Eight absorption states have been identified from the measured absorption

TABLE 1
Various physical properties of Pr^{3+} -doped HMF glasses mixed with alkali fluorides.

Parameters	Glass A	Glass B	Glass C	Glass D	Glass E
Density (gm/cm^3)	4.251	4.260	4.266	4.273	4.280
Refractive index (at 589.3 nm)	1.573	1.565	1.559	1.560	1.548
Average molecular weight	151.4	154.6	157.9	156.2	154.6
Pr^{3+} ion concentration ($\text{Nx}10^{-19}$ (ions/ cm^3))	0.94	0.91	0.89	0.90	0.91
Mean atomic volume ($\text{gm/cm}^3/\text{at}^{-1}$)	10.76	10.97	11.18	11.05	10.92
Dielectric constant (ϵ)	2.474	2.449	2.431	2.434	2.396
Reflection losses R (%)	8.6	8.6	8.5	8.5	8.4
Molar refraction R_M (cm^3)	11.74	11.82	11.95	11.84	11.47
Polaron radius r_p (nm)	1.91	1.93	1.94	1.94	1.93
Inter ionic distance r_i (nm)	4.75	4.78	4.82	4.80	4.79
Electronic polarizability (α) $\times 10^{21}$ cm^3	8.40	8.51	8.62	8.56	8.33
<u>J-O intensity parameters</u>					
$\Omega_2 \times 10^{20}$ (cm^2)	5.64	1.11	-0.37	-0.11	2.20
$\Omega_4 \times 10^{20}$ (cm^2)	13.32	13.98	13.19	14.56	17.27
$\Omega_6 \times 10^{20}$ (cm^2)	4.15	3.44	3.61	4.41	6.93

spectra of Pr^{3+} -doped glasses in the wavelength region of VIS-NIR. The spectral lines this measured are assigned to the appropriate electronic transitions as mentioned below:

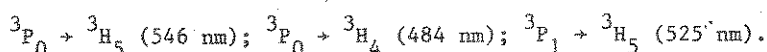
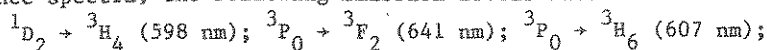


Following the reported results of Tanimura *et al.* (1), the Judd-Ofelt theory has been applied to measured spectral intensities as an ideal model. According to these authors, the Judd-Ofelt model explains satisfactorily the luminescence characteristics and the influence of glass compositions on these properties. In view of this, we have combined the J-O parameters (Ω_λ) with the measured photoluminescence spectra of the Pr-doped glasses to have an insight into the effective laser emission characteristics from these optical devices. Since the half-band-width of $^3\text{H}_6$ absorption level could not be measured, as it appears very weak in all the five glasses. Therefore, the fitting was carried out only with the seven levels. The application of J-O theory to the measured seven absorption band oscillator strengths for each of the five glasses has resulted in a set of best fit intensity parameters through the least squares fit method. These J-O parameters are also accommodated in Table 1 for a comparison in five glasses. The value of Ω_2 has become negative in two glasses (C and D), due to the f-d mixing. Similar such observations have been made earlier on Pr^{3+} -doped in several other inorganic glasses (12-14). The unit tensor operators $||U^\lambda||^2$ for the absorption and emission levels of Pr^{3+} ion are already available in the literature (15,16). On the substitution of Weber's (16) energy level parameters in the Taylor-series expansion, the eigen values for different states have been obtained for their use in the estimation of radiative properties of the glasses studied.

Fluorescence Properties

The measurement of photoluminescence spectra of Pr^{3+} -doped glasses was carried out at room and liquid nitrogen temperatures. From the recorded photo-

luminescence spectra, the following emission levels have been identified:



Among these six luminescent states, $^1D_2 \rightarrow ^3H_4$ for all the glasses studied has been very intense; therefore, the lifetime measurement was carried out both at 300 K and 77 K for this particular state. However, the radiative properties for all the observed emission states have been characterised by the use of Judd-Ofelt intensity parameters (Table 1) obtained from the absorption measurements. The spontaneous emission probability value from these observed emission states to their next lower lying states was estimated from (5):

$$A = \frac{64\pi^4 e^2 v^3}{3h(J+1)} \left[\frac{n(n^2+2)^2}{9} \right] S$$

This equation describes only the forced electric-dipole emission probability. The total transition probability for each of these six emission levels was computed from the expression (5):

$$A_T = \Sigma A$$

This value was estimated in order to make a comparison between the measured lifetimes at 300 K and 77 K and the Judd-Ofelt theory for this emission state. The quantum efficiency factor for this emission state was calculated from (6):

$$\eta = (T_{\text{measured}} / T_{\text{radiative}})$$

The fluorescence branching ratio is considered to be another important factor in understanding the strength of the laser potentiality of the prepared materials. Therefore, this factor was determined for all the observed emission states by using the formula (5):

$$\beta_R = (A/A_T)$$

The calculated values of emission level peak position λ_p , band-width $\Delta\lambda_p$, spontaneous emission probability (A), total transition probability (A_T), and the branching ratio β_R for different emission levels were tabulated in Table 2. An examination of the data presented in this table confirm that $^3P_0 \rightarrow ^3H_4$ has got the maximum β_R value and the minimum for $^3P_0 \rightarrow ^3H_6$. It has already been established that an emission level with the β_R value near 0.5 becomes a laser emission transition (1). In the case of $^1D_2 \rightarrow ^3H_4$ the magnitude of β_R in five different glasses is in between 0.198 (for glass A) and 0.316 (for glass C). Because β_R value is better in the C-glass for all emission levels (Table 2), this system could be identified as a suitable one for laser action.

From the photoluminescence spectral profiles, the stimulated emission cross-section σ_p for the observed emission states was evaluated from the relation (6):

$$\sigma_p = \frac{\lambda_p^4}{8\pi C n^2 \Delta\lambda_p}$$

Where λ_p is the wavelength of the transition, $\Delta\lambda_p$ is the bandwidth obtained by integrating the intensity of the luminescence shape and dividing by the intensity of this wavelength (λ_p). This stimulated emission cross-section is an important parameter for laser gain of the materials, as it determines the laser gain for a given population of inversion (18). The values of σ_p for various

TABLE 2

The radiative properties for the emission levels of Pr^{3+} -doped HMF glasses mixed with alkali fluorides.

Transition	Parameter	Glass-A	Glass-B	Glass-C	Glass-D	Glass-E
$3\text{P}_0 \rightarrow 3\text{F}_2$	$\lambda_p(\text{nm})$	642.1	641.9	642.1	641.0	641.0
	$\Delta\lambda_p(\text{nm})$	5.4	4.9	6.0	4.9	6.2
	$A(\text{s}^{-1})$	15414	29940	---	---	5717
	$A_T(\text{s}^{-1})$	76791	65729	57723	64947	82416
	β_R	0.201	0.045	---	---	0.069
	$\sigma_p(10^{20}\text{cm}^2)$	26.19	5.57	---	---	8.65
$3\text{P}_0 \rightarrow 3\text{H}_6$	$\lambda_p(\text{nm})$	607.9	607.9	607.9	607.9	608.3
	$\Delta\lambda_p(\text{nm})$	11.1	11.8	11.0	12.0	8.4
	$A(\text{s}^{-1})$	3052	2495	2583	3163	4848
	$A_T(\text{s}^{-1})$	76791	65729	57723	64947	82416
	β_R	0.040	0.040	0.045	0.049	0.059
	$\sigma_p(10^{20}\text{cm}^2)$	2.02	1.56	1.73	1.96	4.40
$1\text{P}_2 \rightarrow 3\text{H}_4$	$\lambda_p(\text{nm})$	598.8	598.8	599.0	598.4	598.8
	$\Delta\lambda_p(\text{nm})$	15.6	14.7	14.9	17.2	17.2
	$A(\text{s}^{-1})$	985	896	868	1007	1356
	$A_T(\text{s}^{-1})$	4965	3400	2747	3196	4672
	β_R	0.198	0.264	0.316	0.315	0.290
	$\sigma_p(10^{20}\text{cm}^2)$	0.44	0.43	0.41	0.41	0.56
$3\text{P}_1 \rightarrow 3\text{H}_5$	$\lambda_p(\text{nm})$	525.2	524.9	525.5	524.9	524.9
	$\Delta\lambda_p(\text{nm})$	6.4	7.2	7.5	6.1	6.9
	$A(\text{s}^{-1})$	22805	23120	21716	24215	28817
	$A_T(\text{s}^{-1})$	72442	62337	55025	61974	78724
	β_R	0.315	0.371	0.395	0.391	0.366
	$\sigma_p(10^{20}\text{cm}^2)$	14.65	13.26	12.13	14.49	17.55
$3\text{P}_0 \rightarrow 3\text{H}_4$	$\lambda_p(\text{nm})$	484.5	484.4	484.4	484.3	483.8
	$\Delta\lambda_p(\text{nm})$	8.7	8.1	8.9	8.6	9.1
	$A(\text{s}^{-1})$	46817	48357	45065	49827	57680
	$A_T(\text{s}^{-1})$	76791	65729	57723	64947	82416
	β_R	0.610	0.736	0.781	0.767	0.700
	$\sigma_p(10^{20}\text{cm}^2)$	15.89	17.82	15.16	17.41	19.16

emission levels of Pr^{3+} glasses are shown in Table 2. Because of the fact that β_2 the parameter for both C and D glasses has a negative sign, the estimated values of A , β_R and σ_p could not therefore be listed in this table. Hence, this situation is indicated with dashes. It may be noticed from Table 2 that the transition $3\text{P}_0 \rightarrow 3\text{H}_5$ is not at all discussed. It was because the $\|\langle v\lambda \rangle\|^2$ for this transition have their values as zeros. Therefore, no mention of this level has been made in that table. Again, σ_p further confirms the suitability of the glass C as σ_p values for different levels are in the minimum magnitudes compared with the other remaining glasses.

In Table 3, a comparison between the measurement and predicted lifetimes of $1\text{D}_2 \rightarrow 3\text{H}_4$ of Pr-glasses was made. The quantum efficiency factor for $1\text{D}_2 \rightarrow 3\text{H}_4$ is better in glass C, compared with the others. Based on the magnitude of η from Table 3, the glasses are arranged as follows:

Glass C > Glass D > Glass B > Glass E > Glass A.

TABLE 3

Comparison between the lifetimes (both measured and predicted) of the laser transition $^1D_2 \rightarrow ^3H_4$ of Pr^{3+} doped HMF glasses.

Parameters	Glass-A	Glass-B	Glass-C	Glass-D	Glass-E	
Radiative lifetime $T_R(\mu s)$	201	294	364	313	214	157 (ref. 19)
Measured lifetime $T_m(\mu s)$ (i) at 300 K	120	231	305	251	160	110
(ii) at 77 K	154	245	316	270	187	150 (ref. 1)
Quantum efficiency $\eta = (T_m/T_R)$	0.60	0.79	0.84	0.80	0.75	0.60 (ref. 16)

Conclusions

Five newly synthesised Pr^{3+} -doped multicomponent HMF glasses were characterised for their physical, absorption and emission properties as a function of the alkali metal content. The Judd-Ofelt theory of electric-dipole transition combined with the photoluminescence band-shapes has provided a convenient way to determine the laser properties of Pr^{3+} -doped fluoride glasses. From the absorption intensities, the J-O parameters were derived and, in turn, were used to evaluate the radiative lifetimes to compare the measured lifetimes of $^1D_2 \rightarrow ^3H_4$. The laser efficiency factors, namely β_R , η and σ_p , have confirmed that among the five glasses studied here, one (namely glass-C) could be identified as a suitable optical device for laser emission characteristics.

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