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Spectroscopic properties of Nd^{3+}-doped heavy metal fluoride glasses

G. Amaranath and S. Buddhudu
Department of Physics, S.V. University, Tirupati-517 502, India

F.J. Bryant
Department of Physics, University of Hull, Hull, UK

Luo Xi, B. Yu and S. Huang
Changchun Institute of Physics, Changchun, PR China

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Indium trifluoride based multicomponent glasses of the composition: $30InF_3$–$30BaF_2$–$10ThF_4$–$9ZnF_2$–20RF, (RF = LiF, NaF and KF) with Nd^{3+} (1 M%) were prepared and an investigation was carried out on the significant effects of RF on the physical properties, the absorption spectra, the photoluminescence spectra and the decay times (μs) of the laser emission transition $^4F_{3/2} \rightarrow {}^4I_{11/2}$ (1.05 μm) at 300 and 77 K, by using an argon ion laser as the source of excitation. To understand the laser efficiency of these materials, the values of the spectroscopic quality factor (Ω_4/Ω_6) and the quantum efficiency (η) obtained from the measured and computed lifetimes of the $^4F_{3/2} \rightarrow {}^4I_{11/2}$ have been estimated and it is found that glass A could be suggested as a suitable lasing material.

1. Introduction

The zirconium fluoride free glass systems have attracted a great deal of attention among the different research scientists in several laboratories, because of their larger transmission range extended up to the IR region [1]. These glasses have been used for the preparation of several optical components namely, IR domes, lenses, filters, laser windows and laser host materials [2]. The superior nature of InF_3 over ZrF_4, in the glass making as well as the transmission ability has been thoroughly investigated in different binary, ternary and multicomponent systems without any dopants by Bouaggad et al. [1] at the CNRS laboratories in F[illegible] also ZrF_4-free optical laser glasses with Ho^{3+}, Eu^{3+}, Tb^{3+} and Pr^{3+}, ions as the luminescent centers [3–8].

In this paper, we report the preparation and the important results from our systematic study on the physical-, the absorption-, and the luminescence properties of Nd^{3+}-doped glasses with the alkali fluorides as the glass-network modifiers (NWM).

2. Experimental

Three newly formed Nd^{3+} (1 M%) doped opti-[illegible] the prepared glasses have been labelled as glass A, glass B and glass C, respectively. In the above composition, the three glasses contain both alkali and alkaline earth fluorides to control the crystallization phenomenon and subsequently to obtain good transparency. For all these glasses, the ratio between the number of anions and the cations remains constant. These glasses carry a good number of polarizable cations, that are expected to display significant differences in their physical and optical properties [9]. The glasses selected in the present study have been prepared by employing the quenching technique described earlier [10,11]. Before putting the chemical mix into a platinum crucible, the mix has been crushed in an agate morter to have fine powder particles in the chemical composition. The collected melts from the crucible are quenched between two brass plates and allowed to cool down to room temperature, to produce a few circularly shaped optical glasses with good transparency.

Pure chemicals such as In_2O_3, ThO_2, BaO and alkali oxides were purchased from M/s. Johnson Mathey Chemicals Ltd., Cheshire, UK. With our collaboration from both the physics and chemistry departments of University of Hull, the glasses could be prepared by converting the oxides into fluorides with the addition of excess NH_4HF_2. The chemical mix has been pre-heated for 20 min at 400 °C for the fluorination reaction. Surplus NH_4HF_2 still present in the container has been removed on evaporation at a temperature of 400 °C. Because of the change of alkali cations among the three glasses, the melting temperature varies between 850 and 1000 °C.

By considering procedures that are already known [4–6], the refractive indices and the densities of Nd-doped glasses have been measured to examine the effects of the chemical composition on these physical parameters and also on the other related physical properties. The absorption spectra of Nd-glasses have been recorded at room temperature in the wavelength range from 920 to 320 nm on a Perkin Elmer 551 spectrophotometer. The excitation and photoluminescence spectra of these glasses have been recorded at the laboratories of the Changchun Institute of Physics, Changchun, PR China. The lifetime of the Nd^{3+}-laser excitation state $^4F_{3/2} \rightarrow {}^4I_{11/2}$ has been measured both at room and the liquid nitrogen temperatures, using the line $\lambda = 488$ nm of an argon ion laser. The lifetime (μs) of this emission level has been measured by the use of a Biomation 610B Transient Recorder and a Nicholet 1070 Signal Averager, coupled to the fluorescence spectrophotometer.

Table 1
Physical properties of Nd^{3+}-doped heavy metal fluoride glasses with alkali fluorides (LiF, NaF and KF) as the network modifiers (NWM).

Property	Glass A	Glass B	Glass C
Density d ($g \cdot cm^{-3}$)	4.970	4.952	4.938
Refractive index (n_d) at $\lambda = 589.3$ nm	1.585	1.590	1.593
Average molecular weight ($\bar{M}$ in g)	151.45	154.66	157.88
Nd^{3+}-ion concentration ($N \times 10^{-19}$ ions cm^{-3})	0.800	0.786	0.772
Mean atomic volume V ($g \cdot cm^{-3}$ at^{-1})	9.206	9.436	9.660
Dielectric constant ($\epsilon = n_d^2$)	2.512	2.528	2.538
Reflection losses R (%)	5.1	5.2	5.2
Molar refractivity R_M (cm^{-3})	10.21	10.54	10.83
Polaron radius r_p (nm)	2.02	2.03	2.04
Interionic distance r_i (nm)	5.00	5.03	5.06
Electronic polarizability ($\alpha_e \times 10^{20}$ cm^3)	1.000	1.025	1.048

3. Results and discussion

3.1. Physical properties

The data presented in table 1 show that an increase in the average molecular weight ($\bar{M}$) significantly influences both the density and refractive index and also various other physical parameters such as the mean atomic volume (V), polaron radius (r_p) inter-ionic distance (r_i), the electronic polarizability factor (α_e) dielectric constant (ϵ) and the Nd^{3+}-concentration (N) to be affected.

Table 3
Radiative properties of Nd^{3+}-doped heavy metal fluoride glasses with alkali fluorides (LiF, NaF and KF) as network modifiers (NWM).

Transition $^4F_{3/2} \rightarrow$	Glass A		Glass B		Glass C	
	$A(s^{-1})$	β_R	$A(s^{-1})$	β_R	$A(s^{-1})$	β_R
$^4I_{15/2}$	72	0.004	41	0.006	111	0.004
$^4I_{13/2}$	1399	0.086	793	0.111	2155	0.072
$^4I_{11/2}$	7651	0.469	3774	0.529	12510	0.420
$^4I_{9/2}$	7188	0.441	2529	0.354	14985	0.504
$A_T = \sum_{J=9/2}^{15/2} A$	16310		7137		29761	

3.4. Laser characteristics

The results presented in table 4 describe the measured lifetime (T_m in μs), both at room and liquid nitrogen temperatures for $^4F_{3/2} \rightarrow {}^4I_{11/2}$ of Nd-glasses along with the computed radiative lifetimes (T_R) obtained from the absorption measurements. The quantum efficiency (η) has been estimated only for the room temperature measurement. The stimulated emission cross-section value of $^4F_{3/2} \rightarrow {}^4I_{11/2}$ has been evaluated from the expression [4],

$$\sigma_P = \frac{\lambda_P^4}{8\pi C n_d^2 \, \Delta\lambda_P} A\left({}^4F_{3/2} \rightarrow {}^4I_{11/2}\right).$$

The different parameters in this equation have their standard meanings. The induced emission cross-section is an important factor for devices as it determines the laser gain for a given inversion of population as explained by Tanimura et al. [16] earlier.

Table 4
Laser emission characteristics of Nd^{3+}-doped heavy metal fluoride glasses with alkali fluorides (LiF, NaF and KF) as network modifiers.

Properties	Glass A	Glass B	Glass C
Radiative lifetime			
T_R (μs)	61	140	34
Measured lifetime			
T_m (μs) at 300 K	47	63	48
at 77 K	56	71	64
Quantum efficiency			
at 300 K ($\eta = T_m/T_R$)	0.77	0.45	0.71
Stimulated emission cross-section ($\sigma_P \times 10^{20}$ cm^2)	22.33	10.95	36.14

4. Conclusions

To examine the effects of alkali fluorides, three newly synthesized Nd^{3+}-doped InF_3 based glasses were undertaken and characterized for their physical and absorption properties at 300 K. The integrated absorption coefficient of the five absorption levels resulted in a good agreement between the experimental and computed spectral intensities of f–f transitions. The photoluminescence recordings at 77 K show an intense laser emission at 1.05 μm, for the glasses studied. The Judd–Ofelt theory combined with the recorded photoluminescence spectra has made it possible to measure the stimulated emission cross-section of $^4F_{3/2} \rightarrow {}^4I_{11/2}$ for the three Nd-glasses. According to Jacobs and Weber [17], the luminescence characteristic parameters of $^4F_{3/2} \rightarrow {}^4I_{15/2, 13/2, 11/2, 9/2}$ of Nd^{3+}-doped materials could be defined only through a couple of J–O parameters namely Ω_4/Ω_6 (fig. 3). With regard to Ω_2, it becomes independent in characterizing these four transitions because these emission levels have all zero values for their tensor operator $\| U^2 \|^2$. By examining the results from tables 2 and 4, the spectroscopic quality factor (Ω_4/Ω_6) and the quantum efficiency (η) of the laser emission level $^4F_{3/2} \rightarrow {}^4I_{11/2}$, it could be observed that glass A possesses better values compared to the other two glasses (B and C). It is therefore suggested that glass A could be consid-

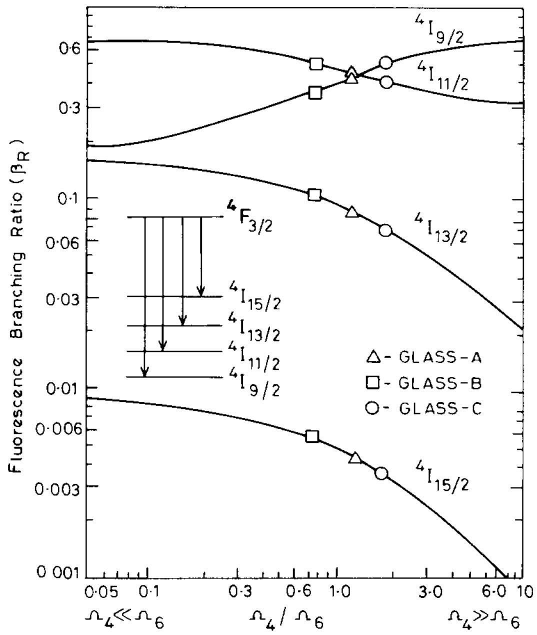

Fig. 3. Fluorescence branching ratios versus the magnitudes of the spectroscopic quality factor (Ω_4/Ω_6) for the $^4F_{3/2} \rightarrow {}^4I_J$ ($J=\frac{15}{2}, \frac{13}{2}, \frac{11}{2}, \frac{9}{2}$) of Nd^{3+}-doped HMF glasses.

ered as a good optical system for generating a strong laser emission at $\lambda \approx 1.05$ μm.

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