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Spectra of Nd^{3+} Doped Boro-Tellurite Glasses

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This paper reports the preparation and the absorption spectra of Nd^{3+} doped B_2O_3-BaO-TeO_2-RF (R = Li, Na or K) glasses. Both physical and optical properties such as energy-level structure, bonding, oscillator-strength and radiative life times have been computed and the effects of the change in the alkali cations (Li, Na and K) in the glass chemical composition were verified.

INTRODUCTION

In the last five years, a great deal of work has been carried out in the production and analysis of some rare-earth-ion-doped glasses based on heavy metal fluorides[1–4], fluoroborates[5, 6] and fluorophosphates[7–10]. Now, we bring out yet another new glass system of B_2O_3 mixed with TeO_2 in order to understand the effects of the glass network modifiers (LiF, NaF and KF) both on physical and absorption spectral properties of the dopant rare earth (Nd^{3+}) ions. In the present work, we report energy level structure, bonding, band intensities and radiative properties of the Nd-glasses from their absorption spectra.

EXPERIMENTAL

Following are the three optical glasses prepared by employing the quenching technique[1–6].

Glass-A: $65B_2O_3 + 2TeO_2 + 12BaO + 20LiF + 1NdF_3$

Glass-B: $65B_2O_2 + 2TeO_2 + 12BaO + 20NaF + 1NdF_3$

Glass-C: $65B_2O_3 + 2TeO_2 + 12BaO + 20KF + 1NdF_3$

These glasses were prepared by using the pure chemicals H_3BO_3, TeO_2, $BaCO_3$, LiF, NaF, KF and NdF_3. The melts (at 950°C) were quenched as was described in our earlier papers[1–6] in obtaining the glasses in circular discs (1–2 cm diameter) with a uniform thickenss of 0.254 cm. The prepared glasses had excellent transparency and with an extended IR transmission ability. These glasses were also found to be moisture resistant due to TeO_2 content availability in the B_2O_3-BaO-RF (R = Li, Na and K) composition. These glasses are in violet-pink colour due to the homogeneous mixing up of dopant (Nd^{3+}) ions in them.

RESULTS AND DISCUSSION

Physical properties such as refractive indices (n_d), densities (d) and dopant (Nd^{3+}) ion concentration (N) of the glasses examined are presented in Table-1.

TABLE-1
PHYSICAL PROPERTIES OF Nd^{3+}-DOPED BORO-TELLURITE GLASSES

Physical properties	Glass-A	Glass-B	Glass-C
Average molecular weight (Mg)	74.260	77.470	82.650
Refractive index (n_d) (at 5893 Å)	1.477	1.466	1.471
Density (d) (g/cm^3) (300 K)	1.999	2.089	2.073
Dopant ion conc. (N × 10^{22} ions/cm^3)	1.621	1.624	1.510

Glass-A was transmitting UV radiations up to 350 nm, glass-B up to 360 nm and glass-C up to 370 nm respectively. This variation was attributed to the change of cations (Li^+, Na^+, K^+) in these glass systems. Absorption spectra of these Nd-glasses were measured on a Perkin-Elmer 551 Spectrophotometer in the wavelength range of 350–920 nm. Due to the non-availability of necessary facilities, the photoluminescence spectra of these glasses could not be measured at 1.06 μm, where a strong lasing emission ($^4F_{3/2} \rightarrow {}^4I_{15/2}$) exists. Actually, the available facilities do provide photoluminescence spectra only up to a maximum

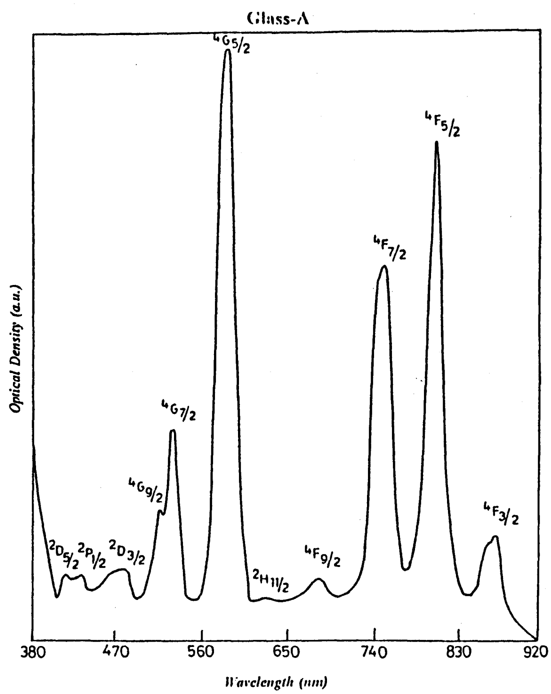

Fig. 1. Absorption spectra of Nd^{3+}: boro-tellurite glass (with 20 M% LiF)

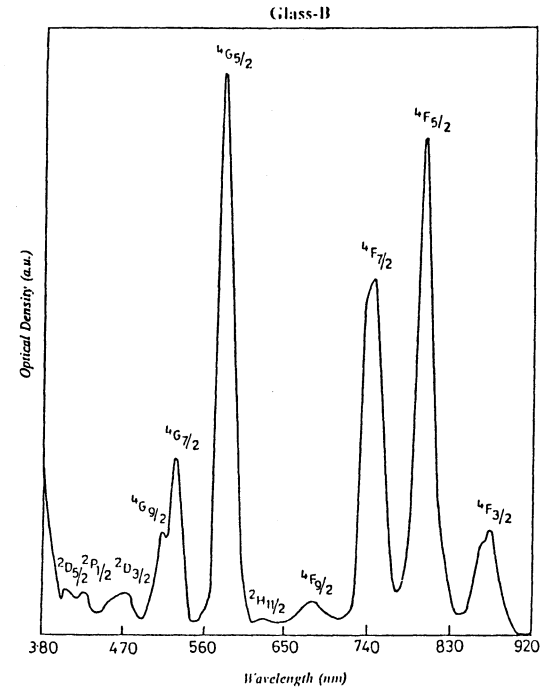

Fig. 2. Absorption spectra of Nd^{3+}: boro-tellurite glass (with 20 M% NaF)

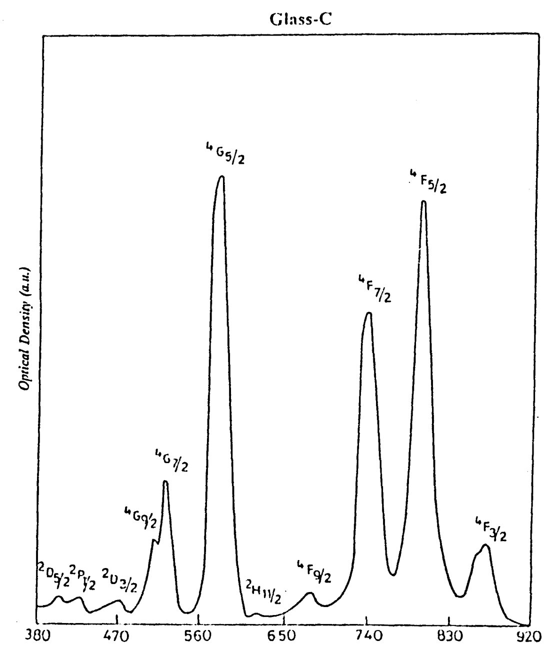

Fig. 3. Absorption spectra of Nd^{3+}: boro-tellurite glass (with 20 M% KF)

wavelength about 0.8 μm. As has been established by taking relevant expressions from literature[10–15], the computation of radiative property parameters of the emission transitions ($^4F_{3/2} \rightarrow {}^4I_{15/2}$, $^4I_{13/2}$, $^4I_{11/2}$ and $^4I_{9/2}$) was carried out systematically, through the estimation of the Judd-Oflet intensity parameters from their absorption spectra (Fig. 1–3). Absorption spectra of these Nd^{3+} glasses have shown eleven absorption bands and are labelled appropriately to the concerned electronic transitions. Based on the measured band energies, the energy level structure characterising parameters such as Racah (E^1, E^2, E^3), spin-orbit (ξ_{4f}), bonding (β, δ) were calculated by performing a least square fit analysis[16]. The results given in Table-2 show that both the experimental and the theoretical energies have satisfactorily been correlated with r.m.s. deviation of ±84, ±134 and ±144 cm^{-1} in glass-A, B and C respectively. Table-3 presents the values of optical densities (OD), oscillator strengths (f_{ed}) of the bands and also the spectral intensity characterizing Judd-Ofelt (Ω_λ) parameters and these are found to be in the following trend in all three Nd-glasses:

$$\Omega_6 > \Omega_2 > \Omega_4$$

TABLE-2

ENERGIES (E in cm^{-1}), r.m.s. DEVIATION (σ), ENERGY LEVEL STRUCTURE RACAH (E^1, E^2 AND E^3), SPIN-ORBIT (ξ_{4f}), NEPHELAUXETIC RATIO (β) BONDING (δ%) PARAMETERS OF Nd^{3+} DOPED BORO-TELLURITE GLASSES

Absorption bands	Glass-A		Glass-B		Glass-C	
	E_{expt}	E_{cal}	E_{expt}	E_{cal}	E_{expt}	E_{cal}
$^4I_{9/2} \rightarrow {}^4F_{3/2}$	11504	11432	11465	11471	11485	11501
$\rightarrow {}^4F_{5/2}$	12497	12450	12473	12402	12497	12453
$\rightarrow {}^4F_{7/2}$	13401	13429	13401	13361	13419	13423
$\rightarrow {}^4F_{9/2}$	14702	14678	14702	14588	14724	14660
$\rightarrow {}^2H_{11/2}$	15945	15897	15970	16149	16073	16183
$\rightarrow {}^4G_{5/2}$	17163	17116	17163	17203	17252	17245
$\rightarrow {}^4G_{7/2}$	18863	19022	18916	19167	19006	19220
$\rightarrow {}^4G_{9/2}$	19412	19434	19412	19435	19526	19511
$\rightarrow {}^2D_{3/2}$	20915	21067	21136	21265	21136	21286
$\rightarrow {}^2P_{1/2}$	23035	22917	23249	23069	23249	23106
$\rightarrow {}^2D_{5/2}$	23860	23817	24443	24248	24443	24274
σ_{rms} (cm^{-1})	±84		±136		±144	
E^1 (cm^{-1})	4721		4830		4822	
E^2 (cm^{-1})	23		21		22	
E^3 (cm^{-1})	489		495		495	
ξ_{4f} (cm^{-1})	860		802		816	
β	0.993		0.997		0.999	
δ%	0.693		0.256		0.018	

Table-3 clearly shows that in glass-A the Judd-Ofelt parameters have their maximum values compared to the glasses B and C. The oscillator strength of the hypersensitive transition ($^4G_{5/2} \leftarrow {}^4I_{9/2}$) has been in more prominence with a brighter intensity over the other remaining ten bands of the Nd-glasses investigated.

TABLE-3
OPTICAL DENSITY (OD IN ARBITRARY UNITS), OSCILLATOR STRENGTH ($f_{ed} \times 10^6$) AND JUDD-OFELT INTENSITY ($\Omega_\lambda \times 10^{20}$ cm^2) PARAMETERS OF Nd^{3+}-DOPED BORO-TELLURITE GLASSES

Absorption bands from the ground state $^4I_{9/2}$	Glass-A		Glass-B		Glass-C	
	OD	fed	OD	fed	OD	fed
$^4F_{3/2}$	0.206	0.620	0.123	0.524	0.123	0.450
$^4F_{5/2}$	0.839	3.595	0.750	3.012	0.682	2.597
$^4F_{7/2}$	0.636	2.157	0.530	1.808	0.495	1.557
$^4F_{9/2}$	0.154	0.434	0.029	0.363	0.047	0.313
$^2H_{11/2}$	0.126	0.116	0.060	0.099	0.057	0.008
$^4G_{5/2}$	0.969	9.157	0.837	7.753	0.718	6.662
$^4G_{7/2}$	0.389	1.496	0.215	1.270	0.196	1.092
$^4G_{9/2}$	0.260	0.672	0.135	0.566	0.147	0.487
$^2D_{3/2}$	0.167	0.031	0.040	0.027	0.040	0.023
$^2P_{1/2}$	0.152	0.061	0.033	0.052	0.043	0.044
$^2D_{5/2}$	0.156	0.034	0.037	0.029	0.044	0.025
Ω_2	3.646		3.183		2.718	
Ω_4	0.497		0.436		0.372	
Ω_6	4.650		4.059		3.466	

Among the eleven observed bands, ($^4G_{5/2} \leftarrow {}^4I_{9/2}$) has been the only one hypersensitive transition that follows the selection ruels[17]:

$$\Delta J \leq \pm 2, \quad \Delta L \leq \pm 2 \quad \text{and} \quad \Delta S = 0$$

such a band has been an environmental sensitive (spectral intensity of such a band, which satisfies the above conditions, changes significantly depending upon the glass chemical composition, hence it is considered as an environmental sensitive band) as shown more clearly in Fig. 1 and in Table-3 respectively. The computated radiative properties namely transition probability (A), relaxation rate (A_T) and radiative lifetimes (T_R) of the Nd^{3+} glasses, are given in Table-4. Looking at the results, it is noticed that the glass-A, in which the band energies have been more satisfactorily correlated with an r.m.s. deviation ($\sigma = \pm 84$ cm). In respect of the other physical quantities and optical results, it was in glass-A only that the results are found to be more encouraging. Thus among the three Nd-glasses, one glass (A) with 20LiF, could be suggested as a better optical material.

TABLE-4
TRANSITION PROBABILITY (A in sec^{-1}), TOTAL TRANSITION PROBABILITY (A_T in sec^{-1}) AND RADIATIVE LIFE TIME (T_R in μs) OF Nd^{3+} BORO-TELLURITE GLASSES

Emission transitions	Glass-A	Glass-B	Glass-C
	A	A	A
${}^4F_{3/2} \rightarrow {}^4I_{15/2}$	11	9	8
$\rightarrow {}^4I_{13/2}$	217	187	160
$\rightarrow {}^4I_{11/2}$	878	755	647
$\rightarrow {}^4I_{9/2}$	298	257	220
$A_T = \Sigma A$	1406	1208	1035
$T_R = (A_T)^{-1}$	711	827	966

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