

## Emission spectra of $Tb^{3+}$ : $Bi_2O_3$ - $B_2O_3$ - $R_2O$ ( $R = Li, Na \& K$ ) glasses

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Heavy metal oxide glasses based on  $Bi_2O_3$  have attracted a great deal of attention due to their interesting properties such as high density, high refractive index, low bond strength, high polarisability, long infrared cut-off wavelength, high nonlinear optical susceptibility and also capability to accept large amounts of luminescent rare earth ions. In particular, their highly nonlinear optical properties make them potential materials for use as ultra-fast optical switches, couplers in optical data processing devices, and as laser waveguides for applications in optical communications and optoelectronics [1–3]. Bismuth based heavy metal oxide glasses have demonstrated wide and flat gain emission bands like in the case of tellurite glasses as potential optical systems in the wavelength division multiplexing (WDM) networks [4]. A systematic study has been carried out on glass formation range in the binary  $Bi_2O_3$ - $B_2O_3$  and ternary  $Bi_2O_3$ - $B_2O_3$ - $R_2O$  systems [5]. In the present paper, the objective is to investigate the effects of the alkali on the emission spectra of  $Tb^{3+}$ :  $75Bi_2O_3$ - $21B_2O_3$ - $4R_2O$  ( $R = Li, Na \& K$ ) glasses. Terbium ( $Tb^{3+}$ ) (1 mol%) doped alkali (Li, Na & K) bismuth-borate glasses in the composition  $75Bi_2O_3$ - $21B_2O_3$ - $4RO_2$  were prepared using the conventional quenching technique. The raw chemicals were  $Bi_2O_3$ ,  $H_3BO_3$ ,  $Tb_2O_3$  and carbonates of Li, Na and K (Aldrich). About 10 g batches of the raw chemicals were thoroughly mixed and melted in Pt crucibles at 800–950 °C in an electric furnace for an hour. The glass melts were quenched between smooth surface brass plates to produce 1 cm diameter optical glass discs of 0.3 cm thickness. These were annealed at temperature 400 °C for one hour and then slowly cooled to room temperature in order to remove the residual stresses that exist in the glasses. The excitation and photoluminescence spectra of three  $Tb^{3+}$  (1 mol) doped alkali (Li, Na, K) bismuth borate glasses labeled as  $Tb^{3+}$ : Glass-Li, Na & K, respectively, were recorded at the room temperature on a SPEX Fluorolog3-21 spectrophotometer. The excitation source was a 450 W CW Xenon arc lamp, mounted vertically in an air-cooled housing; electromagnetic radiation collection and focusing were by means of an off-axis mirror for source with a flash duration of 3  $\mu s$  (FWHM) for a resolution of 0.01 m. The average lifetimes ( $\tau$ ) of the emission transitions were computed from the experimental data by means of a

double exponential as described in ref [6–8]. Excitation spectrum of  $Tb^{3+}$  doped lithium-bismuth-borate glass is shown in Fig. 1. Monitoring the green emission transition ( $^5D_4 \rightarrow ^7F_5$ ) at 550 nm reveals the existence of a group of excitation bands in the wavelength region 300–400 nm. These bands are assigned to the relevant transitions from the ground state ( $^7F_6$ ) to the higher closely packed energy levels such as  $^5H_7$  or  $^5D_{0,1}$  (318 nm);  $^5G_2$  or  $^5L_6$  (337 nm);  $^5L_9$  or  $^5G_4$  (352 nm);  $^5L_{10}$  (370 nm);  $^5G_6$  or  $^5D_3$  (377 nm). Of these, an intense peak at 377 nm ( $^5D_3$ ) has been chosen in obtaining the emission spectra of  $Tb^{3+}$  doped alkali bismuth-borate glasses. Two emission peaks arising from  $^5D_3$  to the lower levels of  $^7F_5$  and  $^7F_4$  in the blue wavelength region are observed only for the  $Tb^{3+}$ : Glass-Li as shown in Fig. 2. The emissions from  $^5D_3$  excited level of  $Tb^{3+}$  ions have not been obtained earlier in the several other hosts in the literature [9, 10], it has possibly been due to the cross relaxation (CR) process or it might be because of the non-radiative relaxations that occur from the high energy lattice phonons of the host matrix. The cross relaxation takes place between the transitions of  $^5D_3$ - $^5D_4$  and  $^7F_6$ - $^7F_0$  within the same ions or involves the two neighboring ions, as their energy level difference approximately matches ( $\Delta E \approx 5800 \text{ cm}^{-1}$ ). Both the cases support that there are radiative transitions down to the ground states

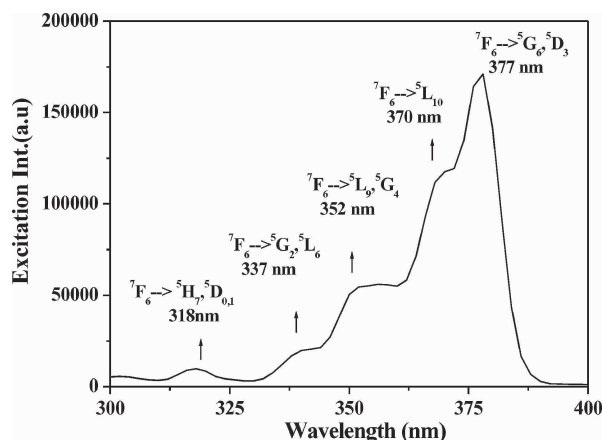


Figure 1 Excitation spectrum of  $Tb^{3+}$  (1 mol):  $75Bi_2O_3$ - $21B_2O_3$ - $4Li_2O$  with green emission  $\lambda_{emis} = 546 \text{ nm}$  ( $^5D_4 \rightarrow ^7F_5$ ).

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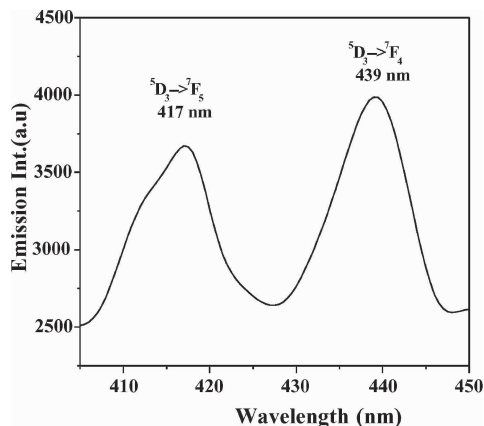


Figure 2 Blue emission from  $Tb^{3+}$ : Glass-Li at  $\lambda_{exc} = 377$  nm ( ${}^7F_6 \rightarrow {}^5G_6, {}^5D_3$ ).

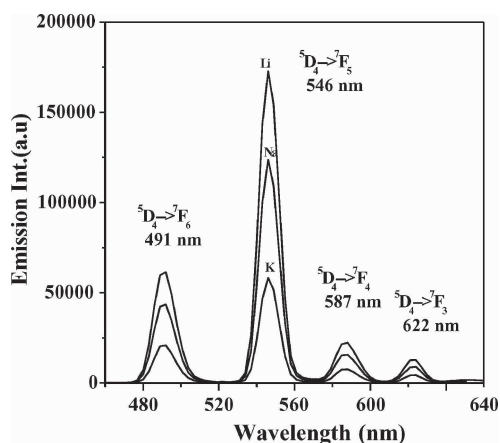


Figure 3 Emission spectra of  $Tb^{3+}$ : Glasses-Li, Na & K at  $\lambda_{exc} = 377$  nm ( ${}^7F_6 \rightarrow {}^5G_6, {}^5D_3$ ).

from the excited  ${}^5D_4$  level. All the three  $Tb^{3+}$ -alkali bismuth-borate glasses have revealed four emission transitions in the wavelength range 460–640 nm which are assigned to  ${}^5D_4 \rightarrow {}^7F_6$  (491 nm),  ${}^5D_4 \rightarrow {}^7F_5$  (546 nm) and  ${}^5D_4 \rightarrow {}^7F_4$  (587 nm),  ${}^5D_4 \rightarrow {}^7F_3$  (622 nm) transitions as shown in Fig. 3. The partial energy level scheme of  $Tb^{3+}$  ions showing the radiative

transitions from excited  ${}^5D_3, {}^5D_4$  levels to the ground states along with a possible cross relaxation (CR) mechanism  $\{({}^5D_3 \rightarrow {}^5D_4) \rightarrow ({}^7F_6 \rightarrow {}^7F_0)\}$  is represented in the Fig. 4. In the present alkali bismuth-borate glass system, the multiphonon assisted nonradiative relaxations from  ${}^5D_3$  to  ${}^5D_4$  level are also very much expected due to the higher energy phonons ( $\sim 1300$   $cm^{-1}$ ) of B–O bonds in the host matrix. Among the measured four emission transitions, the transition  ${}^5D_4 \rightarrow {}^7F_5$  obeys the selection rule of a magnetic dipole (MD) transition with  $\Delta J = \pm 1$  at 546 nm showing a bright green luminescent color from these  $Tb^{3+}$  doped glasses. Fig. 3 clearly reveals the significant influences of alkali ions on the  $Tb^{3+}$  emission characteristics with a decreasing trend in their fluorescence richness and bandwidths as function of the availability of alkali ( $Li^+, Na^+, K^+$ ) ions. The glass containing  $Li^+$  has demonstrated bright green color emitting performance compared to the Na- and K-ion containing glasses, which could be due to the reduction in the overall interaction strength with the host. The interaction strength depends on the molar polarisabilities and magnetic susceptibilities of the alkali compounds [11].

It is known that the negative values of diamagnetic susceptibilities of alkali oxide increase from  $Li_2O$  to  $K_2O$ , which for lanthanides could be larger and positive, indicating a strong paramagnetic nature of these lanthanide oxides [12]. The bismuth containing glasses could well be compared with those of tellurite glasses because the trivalent bismuth ( $Bi^{3+}$ ) is isoelectronic with tetravalent tellurium ( $Te^{4+}$ ), in which the rare earth ions take the structural sites [13, 14]. Hence in the bismuthate glasses the rare earth ions take the structural sites of  $Bi^{3+}$  as the alkali modifiers. When the alkali ions replace the  $Bi^{3+}$ , the structure becomes less close packed with the formation of non-bridging oxygen [15]. The combined multipole O–RE–O–R ( $R = Li, Na \& K$ ) at the non-bridging sites in the bismuth borate glasses has therefore a strong paramagnetic coupling, which increases from potassium ion to lithium ion. It is because of a strong paramagnetic interaction

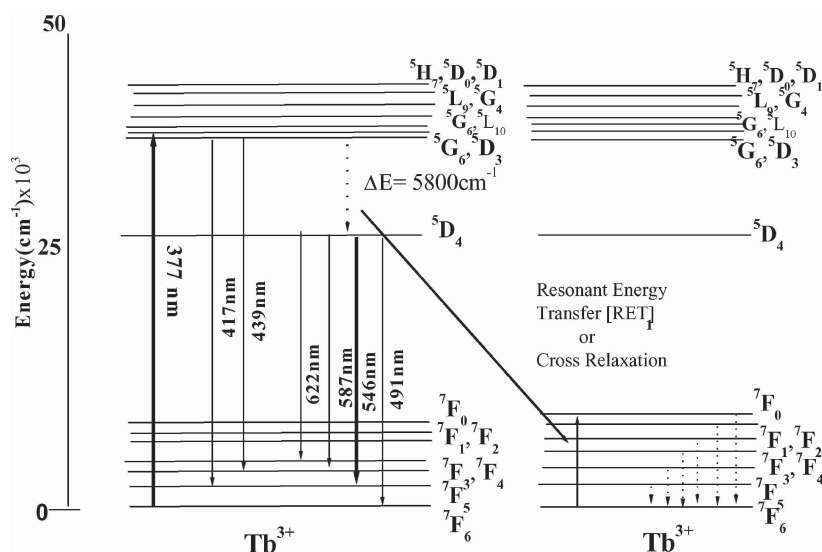


Figure 4 Energy level scheme of the emission process in  $Tb^{3+}$  (1 mol%):  $75Bi_2O_3-21B_2O_3-4R_2O$  ( $R = Li, Na \& K$ ) glasses at  $\lambda_{exc} = 377$  nm ( ${}^7F_6 \rightarrow {}^5G_6, {}^5D_3$ ).

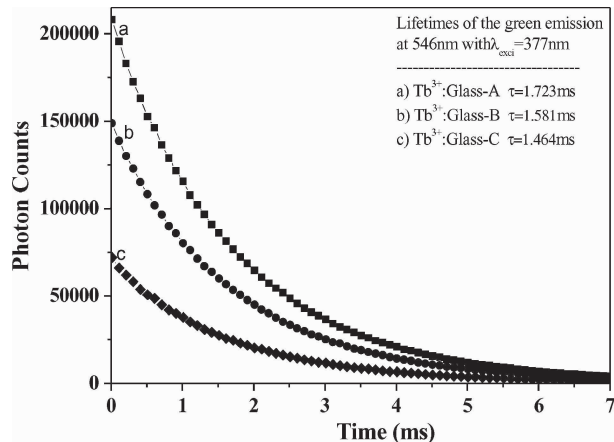


Figure 5 Green emission decay curves of  $Tb^{3+}$ : Glasses–Li, Na & K at  $\lambda_{exc} = 377$  nm ( ${}^7F_6 \rightarrow {}^5G_6, {}^5D_3$ ).

that the values of the intensity for different alkali-containing glasses decrease from  $Li^+$  to  $K^+$ , hence there is significant variation in the FWHM values of the emission bands. The lifetime values of the intense emission transition  ${}^5D_4 \rightarrow {}^7F_5$  for three alkali bismuth-borate glasses have been measured and their decay curves along with the lifetimes ( $\tau$  ms) are presented in Fig. 5. Because of the fact that  $Tb^{3+}$ : Glass-Li with co-dopant  $Li^+$  has demonstrated an intense green luminescence, the lifetimes of the other remaining emission bands such as  ${}^5D_3 \rightarrow {}^7F_{5,4}$  and  ${}^5D_4 \rightarrow {}^7F_{6,5,4,3}$  were also measured and decay curves are shown in Figs 6 and 7 respectively along with the average lifetime values. In conclusion, we have successfully developed  $Tb^{3+}$  (1 mol%) doped  $75Bi_2O_3-21B_2O_3-4R_2O$  ( $R = Li, Na \& K$ ) glasses and studied their emission properties. All three glasses have revealed four emission transitions originating from  ${}^5D_4 \rightarrow {}^7F_{6,5,4,3}$  when excited to ( ${}^5G_6, {}^5D_3$ ) levels of  $Tb^{3+}$  ions at  $\lambda_{exc} = 377$  nm. The effects of different alkali ions on the emission characteristics of  $Tb^{3+}$  have also been examined, a better green emission performance is observed with  $Li^+$  ion co-doped glass compared to the  $Na^+$  and  $K^+$  ions doped glasses. The blue emission bands arising from the excited  ${}^5D_3$  level to  ${}^7F_{6,5}$  ground state manifolds have also been recorded at 417 and 436 nm respectively for the  $Tb^{3+}$

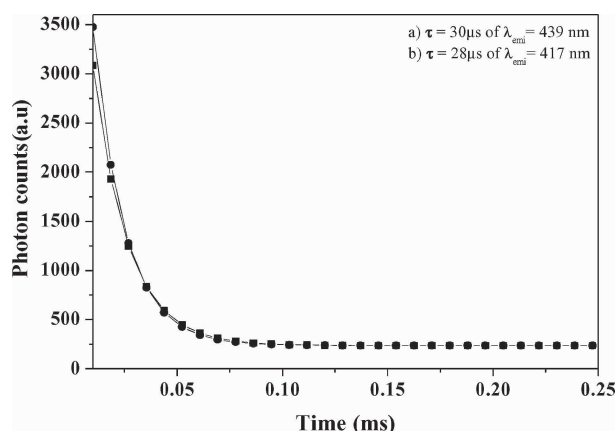


Figure 6 Decay curves of the blue emissions of  $Tb^{3+}$ : Glass–Li at  $\lambda_{exc} = 377$  nm ( ${}^7F_6 \rightarrow {}^5G_6, {}^5D_3$ ).

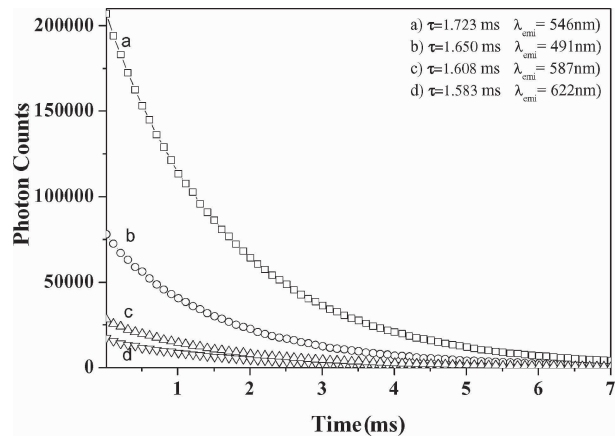


Figure 7 Decay curves of emission transitions of  $Tb^{3+}$ : Glass–Li at  $\lambda_{exc} = 377$  nm ( ${}^7F_6 \rightarrow {}^5G_6, {}^5D_3$ ).

doped Lithia-bismuth-borate glass. The lifetimes of the emission transitions have been measured for all the  $Tb^{3+}$  doped alkali bismuth-borate glasses. The emission mechanism has been explained in terms of an energy level scheme.

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