

# Characterization Of $Tm^{3+}$ Doped Mixed Alkali Borate Glasses - Spectroscopic Investigations

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*The effect of mixed alkalis on the optical absorption spectra of  $Tm^{3+}$  in  $xNa_2O.(30-x)K_2O.70B_2O_3$  ( $x = 5, 10, 15, 20$  and  $25$ ) glasses has been studied. The optical band gap values ( $E_{opt}$ ) for both direct and indirect transitions have been obtained using Davis and Mott theory. Spectroscopic parameters like Racah ( $E^1, E^2$  and  $E^3$ ), spin-orbit ( $\xi_{sp}$ ) and Judd-Ofelt intensity parameters ( $\Omega_2, \Omega_4$  and  $\Omega_6$ ) have been calculated for different  $x$  values. Radiative transition probabilities ( $A_{rad}$ ), radiative lifetimes ( $\tau_R$ ), branching ratios ( $\beta$ ), integrated absorption cross sections ( $\int$ ) and multiphonon relaxation rates ( $W_{MPR}$ ) are calculated for certain excited states of  $Tm^{3+}$  ion. The observed trends in the above parameters as a function of  $x$  in these borate glasses have been discussed keeping in view the effect of mixed alkalis in borate glasses. Certain potential lasing transitions have been identified for laser action among various transitions of  $Tm^{3+}$  in these mixed alkali borate glasses.*

In the present work, from the optical absorption spectra of  $Tm^{3+}$  doped mixed alkali borate glasses, the absorption edges for  $x=5, 10, 15, 20$  and  $25$  mol% glasses are at 400, 394, 362, 355 and 360 nm respectively. It is observed that there is sharp decrease in edge shift for  $x = 15-20$ mol% and the edge shift slightly increases for  $x= 25$  mol%. In other words, as  $x$  increase from 5 to 20, the absorption edge shifts towards shorter wavelengths whereas for  $x=25$ , the edge shifts towards longer wavelength. The sharp decrease in edge shift at  $x=15-20$ mol% indicates structural changes that might have occurred in this region. The study of variation of optical gap with composition gives information regarding the structure and the nature of bonds in the matrix. From the variation of  $(\alpha h\nu)^{1/2}$  and  $(\alpha h\nu)^2$  with  $h\nu$ , optical band gap values ( $E_{opt}$ ) for both direct and indirect transitions of  $Tm^{3+}$  doped borate glasses are obtained using Davis and Mott theory [1]. These values are 2.903, 3.010, 2.905, 2.915 and 2.937 eV for indirect transitions and 2.912, 3.208, 3.018, 3.027 and 3.000 eV for direct transitions for  $x=5, 10, 15, 20$  and  $25$  mol% respectively. It is observed that the optical band gap values for both direct and indirect transitions are lowest and highest in the case of  $x=5$  and  $x=10$  in the above glass matrix respectively.

The spectral intensities for the observed absorption bands, which are often expressed in terms of the oscillator strength ( $f_{meas}$ ), were determined by measuring the areas under the absorption curves. The theoretical oscillator strengths are calculated using Judd-Ofelt [2, 3] theory. The spectral intensities of most of the bands are low in glasses with  $x = 15$  and high in glasses with  $x = 5$  which indicate that non-symmetric component of the electric field acting on  $Tm^{3+}$  is low for  $x=15$  (equal mol% of potassium and sodium content) and is strong for  $x=5$  in the mixed alkali borate glasses. The best set of Judd-Ofelt intensity parameters  $\Omega_2, \Omega_4$  and  $\Omega_6$  are obtained from a least square analysis of the observed oscillator strengths for all the mixed alkali borate glasses and are presented in Table 1. These values depend on the host glass composition [4]. In general,  $\Omega_2$  parameter indicates covalency of the metal ligand bond and  $\Omega_4$  and  $\Omega_6$  are related to the rigidity of the host matrix. In the present work,  $\Omega_2$  exhibits

maximum for  $x=5$  and a minimum for  $x=15$ . It indicates that high covalency (low ionicity) between thulium cation and oxide anion and to a relatively high asymmetry of the local surroundings of the thulium ion in  $x=5$  mol% glass whereas low covalency (high ionicity) and to a relatively low asymmetry of the local surroundings of thulium ion in  $x=15$  mol% glass.  $^3H_6 \rightarrow ^3F_4$ ,  $^3H_6 \rightarrow ^3H_4$  and  $^3H_6 \rightarrow ^1G_4$  are the hypersensitive transitions for  $Tm^{3+}$  ion. These transitions obey the selection rules  $\Delta L \leq 2$ ,  $\Delta L \leq 2$  and  $\Delta S = 0$ . The hypersensitive transition  $^3H_6 \rightarrow ^1G_4$  in all the absorption spectra of  $Tm^{3+}$  doped glasses is split into two peaks by the Stark splitting due to crystal field and the peak to peak separation is 1307, 1663, 1426, 1351 and 1307  $cm^{-1}$  for  $x=5, 10, 15, 20$  and  $25$  in the glass matrix respectively. It is observed that the peak-to-peak separation is same for  $x=5$  and  $25$  mol%. Judd suggested that the spectral profile of the hypersensitive transition is strongly affected by changes in the symmetry of the crystal field acting on the rare earth ion. A difference in the shape of the transition indicates a difference in the environment of the  $Tm^{3+}$  ion. In the present work, the hypersensitive profiles are different for  $x=10, 15$  and  $20$  mol% showing significant differences in the crystal field asymmetries. On the other hand, for  $x=5$  and  $25$  mol%, the hypersensitive profiles are similar which indicate symmetry of the crystal field around  $Tm^{3+}$  ion is similar. The relative intensity ratio between the peaks  $I_L/I_S$ , where  $I_L$  is the intensity of the peak with larger wavelength and  $I_S$  is the intensity of the peak with shorter wavelength, increases with an increase in the covalency of Tm-O bond. The observed peak intensity ratios in the present work are 0.964, 0.951, 0.742, 0.814 and 0.899 for  $x=5, 10, 15, 20$  and  $25$  mol% respectively. It shows that covalency of Tm-O bond decreases with  $x$  upto  $x=15$  and for  $x=20$  and  $25$  mol% covalency increases. Similar trend is observed from the studies of  $\Omega_2$  parameter.

Using the  $\Omega_\lambda$  parameters, the radiative transition probabilities ( $A_{rad}$ ) and radiative lifetimes ( $\tau_R$ ) for the excited states  $^3P_0, ^1D_2, ^1G_4, ^3F_2, ^3F_3, ^3H_4, ^3H_5$  and  $^3F_4$  are estimated for all the glasses studied. It is observed that the lifetimes of all the excited states increase (i.e.,  $A_r$  decrease) up to  $x=15$  and for  $x=20$  and  $25$ , lifetimes decrease. It is observed that the magnitudes of branching ratios are high for the transitions,  $^3P_0 \rightarrow ^3F_2, ^1D_2 \rightarrow ^3F_4, ^3F_2 \rightarrow ^3F_4, ^3H_4 \rightarrow ^3H_6, ^3H_5 \rightarrow ^3H_6$  and  $^3F_4 \rightarrow ^3H_6$ . Among all the transitions  $^3H_4 \rightarrow ^3H_6, ^3H_5 \rightarrow ^3H_6$  and  $^3F_4 \rightarrow ^3H_6$  transitions have larger values of branching ratios. Multiphonon relaxation rates for various transitions of  $Tm^{3+}$  in mixed alkali borate glasses were calculated using the values of  $3.8 \times 10^{-3} cm^{-1}$  and  $c = 2.9 \times 10^{12} sec^{-1}$  reported for borate glasses.

Table 1

Parameter	$x=5$	$x=10$	$x=15$	$x=20$	$x=25$
$\Omega_2 \times 10^{20}$	11.68 $\pm$ 1.12	4.15 $\pm$ 0.42	4.12 $\pm$ 0.39	6.65 $\pm$ 0.62	7.86 $\pm$ 0.70
$\Omega_4 \times 10^{20}$	0.65 $\pm$ 0.07	0.80 $\pm$ 0.07	0.04 $\pm$ 0.005	0.03 $\pm$ 0.003	0.41 $\pm$ 0.03
$\Omega_6 \times 10^{20}$	1.04 $\pm$ 0.12	0.40 $\pm$ 0.03	0.46 $\pm$ 0.05	0.78 $\pm$ 0.08	0.78 $\pm$ 0.08

#### References

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