

## Electronic Spectra Of Pr<sup>3+</sup> Doped Mixed Alkali Borate Glasses

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*An investigation of the optical absorption spectra of 1mol% Pr<sub>2</sub>O<sub>3</sub> in mixed alkali borate glasses of the type xNa<sub>2</sub>O.(30-x)K<sub>2</sub>O.69B<sub>2</sub>O<sub>3</sub>.1Pr<sub>2</sub>O<sub>3</sub> (x=5, 10, 15, 20 and 25) is presented. The glasses were obtained by quenching melts consisting of Na<sub>2</sub>CO<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub>, H<sub>3</sub>BO<sub>3</sub> and Pr<sub>2</sub>O<sub>3</sub> (850°C-1000°C, 1.5-2h) between brass plates. Spectroscopic parameters like Racah (E<sup>1</sup>, E<sup>2</sup> and E<sup>3</sup>) and spin-orbit (ξ<sub>ij</sub>) interaction parameters and Judd-Ofelt intensity parameters (Ω<sub>2</sub>, Ω<sub>4</sub> and Ω<sub>6</sub>) have been calculated as a function of x in the glass matrix. Radiative and non-radiative transition rates (A<sub>T</sub> and W<sub>MPR</sub>), radiative lifetimes (τ<sub>R</sub>), branching ratios (β) and integrated absorption cross sections (Σ) are reported for certain excited states of Pr<sup>3+</sup> in all the glasses studied. All these parameters versus composition variations are discussed in terms of the covalency and of changes into the crystalline field around the Pr<sup>3+</sup> ions by structural changes of the glass matrix.*

The optical absorption spectra of Pr<sup>3+</sup> doped mixed alkali borate glasses are studied. Though the recorded spectra appear similar in shape, the intensities of the corresponding bands change with environment. The experimental and calculated energies and the other spectroscopic parameters are determined for all five Pr<sup>3+</sup> doped mixed alkali borate glasses. It is observed that the hydrogenic ratios, E<sup>1</sup>/E<sup>3</sup> and E<sup>2</sup>/E<sup>3</sup> in all these glasses are about 10.5 and 0.04 respectively. This suggests that the radial properties of the Pr<sup>3+</sup> ion remain unperturbed. The spectral intensities of the eight excited J levels of Pr<sup>3+</sup> i.e., <sup>3</sup>H<sub>4</sub> to <sup>3</sup>F<sub>2</sub>, <sup>3</sup>F<sub>3</sub>+<sup>3</sup>F<sub>4</sub>, <sup>1</sup>D<sub>2</sub>, <sup>3</sup>P<sub>0</sub>, <sup>3</sup>P<sub>1</sub>+<sup>1</sup>I<sub>6</sub> and <sup>3</sup>P<sub>2</sub> for all the mixed alkali borate glasses are calculated. Energies and spectral profiles of some of the transitions represent their co-ordination<sup>(1)</sup>. It is observed that except for <sup>3</sup>P<sub>2</sub> band, there is a good agreement between measured and calculated spectral intensities for all the bands. The spectral intensities of the observed band <sup>3</sup>H<sub>4</sub>→<sup>3</sup>P<sub>2</sub> deviate too much from the predicted value. The intensity of this transition depends strongly on the neighboring atoms but it is not pseudo-quadrupolar<sup>(2)</sup> like all other known hypersensitive transitions.

The calculated Judd-Ofelt<sup>(3,4)</sup> intensity parameters (Ω<sub>2</sub>, Ω<sub>4</sub> and Ω<sub>6</sub>) are presented in Table 1. Normally Ω<sub>2</sub> parameter is an indicator for covalent bonding and Ω<sub>4</sub> and Ω<sub>6</sub> are indicators for viscosity. It is observed that Ω<sub>2</sub> is larger in the mixed alkali borate glasses (particularly at x=15-20 mol%) as compared to the value in the binary borate glass i.e. addition of second alkali seems to increase covalency in these glasses. Among the five mixed alkali borate glasses, Ω<sub>2</sub> parameter is larger for x=15-20 mol% in the glass matrix which indicates high covalency (low ionicity) between praseodymium cation and oxygen anion or to a relatively low symmetry of the local surrounding of the praseodymium ion in this glass. The results of earlier studies on borate glasses indicate that in an alkali borate glass, at x=15-20 mol%, concentration of tetraborate groups is maximum and boroxol groups disappear. From x=20 mol%, diborate formation takes place. For x>30 mol%, the formation of non-bridging oxygen starts and increases in concentration with the introduction of modifying oxides into the glass-forming network. This reduces the average chemical bond strength, leading to a lower covalency. The order of magnitude of intensity parameters is Ω<sub>2</sub><Ω<sub>6</sub><Ω<sub>4</sub> for all the mixed alkali borate glasses. It is observed that Ω<sub>2</sub> value slightly increases and ΣΩ<sub>λ</sub> increases more for x=5

and 10 mol%, compared to their values in binary sodium/potassium borate glasses. Similarly they decrease for x=25 mol%. But when two alkalis are in comparable concentration (x=15-20), the  $\Omega_2$  parameter is large and do not show significant change. It can be observed that  $\Omega_2$  is mainly dependent on  $\Xi$  ( $t, \lambda$ )(covalency) rather than  $A_{i,p}$  (symmetry) at x=15-20 mol%. At x=5 and 25 mol%,  $\Omega_2$  exhibits lower values which indicate high symmetry of the local surrounding of the praseodymium ion and hence at this composition  $A_{i,p}$  contribution seems to increase.

Electric dipole linestrengths ( $S_{ed}$ ), radiative transition probabilities ( $A_{rad}$ ), branching ratios ( $\beta$ ) and integrated absorption cross-sections ( $\Sigma$ ) for the excited states  $^3P_1, ^3P_0, ^1D_2$  and  $^3F_3$  of  $Pr^{3+}$  ion have been calculated. Radiative lifetimes ( $\tau_R$ ) of all the above excited states of  $Pr^{3+}$  are more with x = 5 mol% and less for x=20 mol%. Branching ratios ( $\beta$ ) and integrated absorption cross sections ( $\Sigma$ ) for certain transitions are obtained. It is observed that the branching ratios of the transitions  $^3P_1 \rightarrow ^1H_5, ^3P_0 \rightarrow ^3H_4$  and  $^3F_3 \rightarrow ^3H_4$  are higher when compared with other transitions. Among all the five glasses studied, x=25 in the glass matrix (sodium rich glass) shows larger values of branching ratios for all the transitions and the integrated absorption cross sections also higher for all the transitions except  $^1D_2 \rightarrow ^3H_4$  and  $^3F_3 \rightarrow ^3H_4$ . These two transitions have higher values at x=20mol%. Normally the magnitudes of branching ratios would be higher for the lasing transitions than those for the other transitions. From the above data, it can be concluded that the two transitions i.e.  $^3P_0 \rightarrow ^3H_4$  and  $^3F_3 \rightarrow ^3H_4$  of 25 mol% of  $Na_2O$  glass are found suitable for laser excitation.

The average predicted non-radiative transition rates for the excited state multiplets  $^3P_2, ^1I_6, ^3P_1, ^3P_0, ^1D_2, ^1G_4, ^3F_4, ^3F_3$  and  $^3F_2$  are calculated. From the table, it is observed that the energy gap between  $^1D_2 \rightarrow ^1G_4$  is large, therefore the rate of multiphonon emission is negligible. Thus for the  $^1D_2$  level, the total radiative lifetime is completely dominated by radiative decay only. In the present work, it is observed that  $W_{MPR}$  varies between 1.8 to 2.1 for x=5, 10, 15, 20 and 25 mol%. The remaining excited states posses short lifetimes due to high multiphonon relaxation rates.

Table 1

Parameter	x=5	x=10	x=15	x=20	x=25
$\Omega_2 \times 10^{20}$	3.58±0.23	4.07±0.24	12.31±1.74	12.71±1.29	2.93±0.25
$\Omega_4 \times 10^{20}$	39.58±3.17	46.37±4.73	44.14±4.92	57.03±5.12	59.70±5.93
$\Omega_6 \times 10^{20}$	10.30±1.73	11.96±1.24	13.68±1.73	17.60±1.30	12.79±1.55

#### References

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