Study on some physical and optical properties of alkaline alumino borate glasses doped with Mn$^{2+}$ ions

1'Mohamad Raheem Ahmed*, 2Md Shareefuddin

1Department of physics, Muffakham Jah College of Engineering and Technology, Osmania University, Hyderabad-500034, India.
2Department of Physics, Osmania University, Hyderabad-500007, India.

*Corresponding Author: E-mail: mdraheem@mjcollege.ac.in, Tel: +91 9948845758

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Abstract: Alkaline alumino borate glasses have composition (30-x) MO-xAl$_2$O$_3$-69.5B$_2$O$_3$-0.5MnO$_2$ (0 ≤ x ≤ 15 mol %) (where MO=SrO, BaO). These glasses were prepared by melt quenching process. For these glasses, density was calculated using Archimedes principle. Variation in the density and molar volume was explained on the base of the bond length of Al-O and B-O. The values of polaron radius increases and field strength (F) decreases are attributed to the open structure. From optical absorption spectra, it was observed that broad absorption peak at 470 nm is due to the transition of Mn$^{2+}$ ions from $^3$E_g→$^5$T$_2$ in the octahedral site. Optical band gap ($E_g$) and Urbach energy ($\Delta E$) were calculated. It results in the creation of non-bridging oxygens (NBO’s) in the present glass system.

Keywords: Alkaline alumino glasses, Borate glasses, Physical properties, Optical properties.

I. INTRODUCTION

In the class of all TM ions, manganese ion is especially fascinating as it exists in several valence states in several glass networks relies on the quantitative properties of modifier and glass formers, the size of ions, their field strength, a mobility of ion in the glass. In this way, low field strength alkaline earth oxides enters in the alkaline glasses, which have generally introduced into the glass network [9]. When alkaline earth metal oxides added to the borate oxide, a part of the boron is modified to tetrahedral coordination to a particular limit after which nonbridging oxygens are formed [7]. A portion of the advantages in utilizing modifiers (alkali/alkaline) in borate glass details are to increase the thermal resistance and mechanical strength, enhanced aqueous capacity to concentrate TM ions, chemical durability and also reduced of melting temperature[8]. Al$_2$O$_3$ enters in the alkaline borate glasses are either AlO$_4$ or AlO$_6$ depend on the ratio of the aluminium and alkaline earth material. If the ratio is less than one it forms AlO$_4$ tetrahedra, a ratio is greater than one it form AlO$_6$ units [9]. Aluminium based alkali/alkaline borate glasses have excellent applications towards the geological and industrial[10]. In the present work, glasses were taken to physical and optical characterization to observe the changes in the glass network and study the effect of aluminium ions in the glass.

II. EXPERIMENTAL

Mn doped strontium alumino borate glasses have been synthesized through a melt quenching process with composition (30-x) MO-xAl$_2$O$_3$-69.5B$_2$O$_3$-0.5MnO$_2$ (0 ≤ x ≤ 15 mol %)(MO=SrO,BaO) (SABM Glasses)(BABM glasses) in an electrical silicon carbide heating element furnace at a temperature 1100°C in the air atmosphere. The chemicals used were analar grade of H$_2$BO$_3$, SrO, BaO, Al$_2$O$_3$ and MnO$_2$. These were weighed according to molar ratio and weighted for 10 gm. This mixture of raw material was filled in platinum crucible and placed in an electrical-heated furnace which took nearly 50-60min to melt and
get complete homogeneous melt. At room temperature, the prepared melt was quenched through pouring it over a preheated (150°C) steel plate. The glasses were then annealed at 300°C for 3 hr to relieve residual internal stress. Shimadzu UV-1800 is used to record the Ultraviolet - Visible spectra in the wave length region 300-700nm.

III. RESULTS AND DISCUSSION

A. Physical analysis

Density measurements of inorganic amorphous solids like glasses stand premier physical property to be investigated. This leads to evaluate different properties of material characterization. From the literature, it is understood that the density of the glass depends on the modifier concentration and additives in the glass composition [11]. It is observed from (Table 1 and Table 2) that the density values are progressively decreasing. With the increase in molar volume the content of Al$_2$O$_3$ increases from 5 to 15 mole percentages by decreasing equal amount of MO (SrO and BaO). The density decrement is as expected since the density of SrO (4.7 g/cm$^3$) and BaO (5.725 g/cm$^3$) much higher than the density of Al$_2$O$_3$ (3.95 g/cm$^3$). From the literature, it is understood that MO acts as a modifier and convert BO$_3$ to BO$_4$ units which in general should decrease molar volume. But in the present case, MO (SrO and BaO) is being replaced by Al$_2$O$_3$ i.e., Al$_2$O$_3$ concentration increases from 5 to 15 mole percentage while MO decreasing keeping other B$_2$O$_3$ and MnO content. Al$_2$O$_3$ consumes some of the oxygens form MO readily converted to AlO$_3$. The remaining aluminium reacts with MnO suppress the process of converting BO$_3$ to BO$_4$ thereby resulting non-binding oxygens (NBO’s) in the form of BO$_3$ units. This suppresses the increase in molar volume and a decrease in density. Another reason is Al-O bond length is increasing compared to nearby B-O bonds in tri or tetragonal borate with an increment of aluminium content [9]. Generally, the Archimedes principle used to estimate density [12]

$$\rho_{Ex} = \frac{W_{Ta}}{W_{Ta} - W_{Tx}} \times \rho_x$$  \hspace{1cm} (1)

Where $W_{Ta}$ weight without liquid i.e., in the air, $W_{Tx}$ weight in liquid i.e., in xylene respectively and $\rho_x$ is 0.863 g/cm$^3$.

$$V_M = \frac{M_W}{\rho_{Ex}}$$  \hspace{1cm} (2)

Equation (2) is used to calculate the molar volume ($V_M$) and corresponding terms in the above equation are mentioned in the reference [12].

To affirm the increase in molar volume the average boron-boron separation $<d_{B-B}>$ calculated [13] by using $V_m^{B} = \frac{V_m}{2(1-X_B)}$ in which $V_m^{B}$ represents the volume that contains one mole of boron within the given structure while $X_B$ is the molar fraction of boron trioxide

$<d_{B-B}> = \frac{V_m^{B}}{N_A}$ where $N_A$ is 6.0221x10$^{23}$ being the Avogadro number. The values of boran-boran distance increases progressively with an increment of Al$_2$O$_3$ (Table 1 and Table 2). The presence of Al$_2$O$_3$ helps to increase average boran-boran distance consequently leads to an increase in molar volume.

The refractive index ($n_d$) of both the glasses has been related to the energy gap ($E_g$) through the relation is given by [14]

$$\frac{(n_d^2-1)}{(n_d^2+2)} = 1 - \frac{E_g}{\sqrt{20}}$$  \hspace{1cm} (3)

where $E_g$ is the energy band gap.

The increment noticed in the values of refractive index ($n_d$) for both the series is a result of the raise in the NBO’s count. The refractive index ($n_d$) and dielectric constant ($\varepsilon$) are related as [14]

$$\varepsilon = n_d^2$$  \hspace{1cm} (4)

The values of $\varepsilon$ and $n_d$ are presented in Table 1 and Table 2. The molar refractivity $R_M$ of the glass samples was evaluated using [14]

$$R_M = \frac{n_{d}^{2} - 1}{n_{d}^{2} + 2} \times V_m$$  \hspace{1cm} (5)

where $n_d$ - refractive index, $V_m$ - molar volume.

In search of understanding the parameters like polaron radius ($r_p$) and inter-ionic separation($r_i$) the need arises for calculation of transition metal (TM) ion concentration per cc. In present glass systems Mn$^{2+}$ being TM ion, its concentration is calculated by the formula [14]

$$N_i = \frac{X(mol\%)}{M} \times \frac{N_A}{d}$$  \hspace{1cm} (6)

where $X(mol\%)$ refers to a transition metal ion, d- density, M- average molecular weight.

The polaron radius ($r_p$) and inter-ionic separation($r_i$) calculated through the following relation [14]

$$r_p = \frac{1}{2} \left( \frac{\pi}{6N_A} \right)^{\frac{1}{3}}$$  \hspace{1cm} (7)

and
The field strength is calculated using the oxidation number (Z) from the following formula [14]

\[ F = \frac{Z}{r_p^2} \]  

(9)

In general polaron radius \( r_p \) and field strength should show the opposite trend which is clearly observed in the present work. The value of \( r_p \) increases are attributed to the open structure caused by Mn\(^{2+} \) addition; the value of field strength (F) decreases also supports the open structure, which resulted in an increase in molar volume [15] as seen earlier. The polaron radius \( r_p \) and interionic distance \( r_i \) results are in tune with each other. The polaron radius in all the glasses (SABM and BAMB glasses) is less than the corresponding interionic distance which in accordance with the usual prediction of the polaron theory that the polaron radius should be smaller than the site separation. [16]

The theoretical optical basicity \( \Lambda_{\text{th}} \) is calculated utilizing the relation is mentioned below [13, 14]

\[ \Lambda_{\text{th}} = X_{\text{B}_{\text{2}O_3}} \Lambda_{\text{B}_{\text{2}O_3}} + X_{\text{Al}_{2}O_3} \Lambda_{\text{Al}_{2}O_3} + X_{\text{B}_{2}O_3} \Lambda_{\text{B}_{2}O_3} + X_{\text{CuO}} \Lambda_{\text{CuO}} \]  

(10)

where \( X_{\text{B}_{2}O_3}, X_{\text{Al}_{2}O_3}, X_{\text{B}_{2}O_3}, X_{\text{CuO}} \) are fractions of present oxides and \( \Lambda_{\text{B}_{2}O_3}, \Lambda_{\text{Al}_{2}O_3}, \Lambda_{\text{B}_{2}O_3}, \Lambda_{\text{CuO}} \) are optical basicity values.

The calculated values of optical basicity for SABM and BAMB glasses are given in Table 1 and 2. This trend shows, decreasing the capability of electron donation of oxide ions to coordinate cations. There is an increment in the refractive index \( n_d \) and molar reactivity \( R_m \) shows more polarizable electrons surrounding the oxygens.

Table 1. Physical and optical parameters of SABM glasses

<table>
<thead>
<tr>
<th>Physical property parameters</th>
<th>X=5 mole%</th>
<th>X=7.5 mole%</th>
<th>X=10 mole%</th>
<th>X=12.5 mole%</th>
<th>X=15 mole%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass code</td>
<td>SABM0</td>
<td>SABM1</td>
<td>SABM2</td>
<td>SABM3</td>
<td>SABM4</td>
</tr>
<tr>
<td>Average molecular weight M(g)</td>
<td>79.822</td>
<td>79.780</td>
<td>79.739</td>
<td>79.697</td>
<td>79.656</td>
</tr>
<tr>
<td>Density ( \rho ) (g/cm(^3))</td>
<td>2.766</td>
<td>2.708</td>
<td>2.601</td>
<td>2.520</td>
<td>2.513</td>
</tr>
<tr>
<td>(Experimental)</td>
<td>2.677</td>
<td>2.601</td>
<td>2.527</td>
<td>2.455</td>
<td>2.385</td>
</tr>
<tr>
<td>Molar volume (cm(^3)/mole)</td>
<td>28.84</td>
<td>29.45</td>
<td>30.65</td>
<td>31.62</td>
<td>31.69</td>
</tr>
<tr>
<td>Average boron-boron distance(d(^{B-B})) (nm)</td>
<td>0.507</td>
<td>0.511</td>
<td>0.518</td>
<td>0.523</td>
<td>0.524</td>
</tr>
<tr>
<td>Transition metal ion concentration (Ni) ( 10^{21}) (ions/cc)</td>
<td>10.437</td>
<td>10.223</td>
<td>9.823</td>
<td>9.521</td>
<td>9.501</td>
</tr>
<tr>
<td>Polaron radius ( r_p ) (Å) ( (\pm0.01) )</td>
<td>2.19</td>
<td>2.20</td>
<td>2.23</td>
<td>2.26</td>
<td>2.26</td>
</tr>
<tr>
<td>Inter-ionic distance ( r_i ) (Å) ( (\pm0.005) )</td>
<td>5.42</td>
<td>5.46</td>
<td>5.53</td>
<td>5.59</td>
<td>5.59</td>
</tr>
<tr>
<td>Field strength (F) ( 10^{15}) cm(^2)) ( (\pm0.01) )</td>
<td>4.17</td>
<td>4.13</td>
<td>4.02</td>
<td>3.92</td>
<td>3.92</td>
</tr>
<tr>
<td>Optical band gap ( E_g ) (eV) ( (\pm0.01) )</td>
<td>3.24</td>
<td>3.17</td>
<td>3.12</td>
<td>3.10</td>
<td>2.95</td>
</tr>
<tr>
<td>Refractive index ( n_d )</td>
<td>2.335</td>
<td>2.352</td>
<td>2.365</td>
<td>2.345</td>
<td>2.410</td>
</tr>
<tr>
<td>Molar Refractivity ( R_m )(cm(^3))</td>
<td>18.932</td>
<td>19.067</td>
<td>19.169</td>
<td>19.012</td>
<td>19.514</td>
</tr>
<tr>
<td>Urbach energy(eV) ( (\pm0.01) )</td>
<td>0.501</td>
<td>0.613</td>
<td>0.634</td>
<td>0.642</td>
<td>0.754</td>
</tr>
<tr>
<td>Dielectric constant ( \varepsilon )</td>
<td>5.452</td>
<td>5.531</td>
<td>5.593</td>
<td>5.499</td>
<td>5.808</td>
</tr>
<tr>
<td>Optical basicity ( \Lambda_{\text{th}} ) ( (\pm0.0001) )</td>
<td>0.618</td>
<td>0.605</td>
<td>0.591</td>
<td>0.578</td>
<td>0.564</td>
</tr>
</tbody>
</table>
Table 2. Physical and optical parameters of BABM glasses

<table>
<thead>
<tr>
<th>Physical property parameters</th>
<th>X=5 mole%</th>
<th>X=7.5 mole%</th>
<th>X=10 mole%</th>
<th>X=12.5 mole%</th>
<th>X=15 mole%</th>
</tr>
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<tbody>
<tr>
<td>Glass code</td>
<td>BABM0</td>
<td>BABM1</td>
<td>BABM2</td>
<td>BABM3</td>
<td>BABM4</td>
</tr>
<tr>
<td>Average molecular weight M(g)</td>
<td>92.249</td>
<td>90.965</td>
<td>89.681</td>
<td>88.396</td>
<td>87.111</td>
</tr>
<tr>
<td>Density ρ(g/cm³) (±0.001)</td>
<td>3.837</td>
<td>3.067</td>
<td>3.053</td>
<td>2.908</td>
<td>2.766</td>
</tr>
<tr>
<td>Theoretical</td>
<td>2.990</td>
<td>2.925</td>
<td>2.863</td>
<td>2.801</td>
<td>2.741</td>
</tr>
<tr>
<td>Molar volume (cm³/mole)(±0.01)</td>
<td>24.037</td>
<td>29.656</td>
<td>29.861</td>
<td>30.390</td>
<td>31.492</td>
</tr>
<tr>
<td>Average boron-boron distance (d^B-B) (nm)</td>
<td>0.478</td>
<td>0.512</td>
<td>0.513</td>
<td>0.516</td>
<td>0.522</td>
</tr>
<tr>
<td>Transition metal ion concentration (Ni) 10²²(ions/cc)(±0.01)</td>
<td>1.25</td>
<td>1.02</td>
<td>1.01</td>
<td>0.99</td>
<td>0.95</td>
</tr>
<tr>
<td>Polaron radius (r_p) (Å) (±0.005)</td>
<td>2.06</td>
<td>2.2</td>
<td>2.21</td>
<td>2.23</td>
<td>2.26</td>
</tr>
<tr>
<td>Inter-ionic distance (r_i) (Å) (±0.005)</td>
<td>5.11</td>
<td>5.46</td>
<td>5.48</td>
<td>5.51</td>
<td>5.59</td>
</tr>
<tr>
<td>Field strength (F) (10¹⁵ cm⁻²)</td>
<td>4.71</td>
<td>4.13</td>
<td>4.09</td>
<td>4.02</td>
<td>3.92</td>
</tr>
<tr>
<td>Optical band gap (E_g)(eV)(±0.01)</td>
<td>3.02</td>
<td>2.72</td>
<td>2.62</td>
<td>2.44</td>
<td>2.25</td>
</tr>
<tr>
<td>Refractive index n_d</td>
<td>2.391</td>
<td>2.476</td>
<td>2.507</td>
<td>2.566</td>
<td>2.635</td>
</tr>
<tr>
<td>Molar Refractivity R_m(cm^3)</td>
<td>14.692</td>
<td>18.713</td>
<td>19.048</td>
<td>19.769</td>
<td>20.928</td>
</tr>
<tr>
<td>Dielectric constant ε</td>
<td>5.716</td>
<td>6.130</td>
<td>6.285</td>
<td>6.584</td>
<td>6.943</td>
</tr>
<tr>
<td>Urbach energy (eV) (±0.001)</td>
<td>0.167</td>
<td>0.368</td>
<td>0.260</td>
<td>0.385</td>
<td>0.507</td>
</tr>
<tr>
<td>Optical basicity Λ_d(±0.001)</td>
<td>0.638</td>
<td>0.623</td>
<td>0.607</td>
<td>0.592</td>
<td>0.576</td>
</tr>
</tbody>
</table>

B. Optical absorption studies

UV-visible absorption of two spectra SABM, BABM glasses were carried out at room temperature and absorption spectra for two series shown in Fig. 1 and Fig. 2. For two series of the glasses, there is only one peak at ~470nm is analysed using crystal field theory and it is observed that the peak is due to the transition of Mn³⁺ ion from $^5E_g \rightarrow ^5E_{2g}$ in the octahedral site[17]. Further analysis of octahedral site is observed that a deformation occurs in site and forms tetrahedral deformation. Generally, manganese exists as two forms i.e., Mn²⁺ and Mn³⁺. In the present work, spin-forbidden lines of Mn³⁺ ion is not observed due to the background absorption band of a strong Mn³⁺ ion. The extra kink observed at ~610nm for BABM glasses is due to the transition $^6A_{1g}(S) \rightarrow ^4T_{1g}(G)$ [18].
C. Optical band gap ($E_g$) and Urbach energy ($\Delta E$)

The indirect transition associated with the energy transformation from the uppermost energy level of the valence band to the lowermost energy level of the conduction band. In the present glass sample production of AlO$_4$ tetrahedra limited up to (Al$_2$O$_3$/MO) $\leq$ 1 (where MO= BaO and SrO); each Al$_2$O$_3$ chemical assimilate with one MO, to create two AlO$_4$. The
remaining MO molecules interact with $\text{B}_2\text{O}_3$ and creating structural basis containing NBOs. Increasing $\text{Al}_2\text{O}_3$ quantity the number of $\text{BO}_4$ decreases in the glass network, whereas the concentration of $\text{BO}_3$ increases [1]. Incorporation octahedrally oriented $\text{Al}^{3+}$ ions depolymerise the glass by promoting defects. This chaotic nature in oxide glasses is radix of the decrease in $E_g$ and increases the NBO’s [19]. The absorption coefficient ($\alpha$) can be measured as a basis of frequency ($\nu$), thickness ($d$) is given by 

$$
\alpha(\nu) = \frac{A}{d} \times 2.303
$$

In above equation absorbance is represented by $A$. The direct and indirect transitions are calculated using the relation[20,21]

$$
\alpha(\nu) = b(h\nu - E_{opt})^{1/2} / h\nu
$$

Where an index($r$) take a value, $r = 1/2$ for indirect allowed transition. The plotted an indirect transition graph for both the series is manifested in Fig.3, Fig.5 and measured values are listed in a Table. The Urbach’s energy ($\Delta E$) in amorphous materials is the provision of important data about the transitions in the forbidden band gap of localized states. Moreover, for obtaining $\Delta E$ values the linear portion is expected to plot a graph between $\ln \alpha(\nu)$ vs $h\nu$ and take a reciprocal of the slope for a fitted straight line to linear portion[15, 22]. The calculated $\Delta E$ values listed in Table for both BABM, SABM glass samples. An increase in $\Delta E$ observed from a higher number of structural disorders in the case of amorphous materials. In the present case, the Urbach energy increases with $\text{Al}_2\text{O}_3$ mole percentage, increment indicates the increase of structural disorders.

![Fig. 3 Tauc’s plot of SABM glasses](image1)

![Fig.4 Urbach plots of SABM glasses](image2)
It was observed from the result of two series (SABM and BABM) the density is decreasing and molar volume is increasing due to the higher density of alkaline earth materials (SrO, BaO) replaced by the lower density of Al₂O₃. In both series, the increase in the values of polaron radius was attributed to the open structure. The decrease in the values of field strength (F) indicates the open structure and supported the increase in molar volume. Optical absorption spectra of glasses were revealed that a

IV. CONCLUSIONS

Fig. 5 Tauc’s plot of BABM glasses

Fig. 6 Urbach plots of BABM glasses
broadband at wavelength 470 nm attributed to ground state $^5E_g$ to excited state $^5T_{2g}$ of Mn$^{3+}$ ion. There was another peak observed at ~610nm in BABM series is due to the transition of $^6A_{1g}(S) \rightarrow ^4T_{1g}(G)$. The decrease in $E_g$ results in an increase of NBOs. It was observed from the optical properties of two series BO$_4$ units are decreasing, whereas the concentration of BO$_3$ increases in the glass network.

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Authors Profile
Mohamad Raheem Ahmed, Ph.D- Reasearch scholar, Department of Physics, Osmania University, Hyderabad-500007, India and working as Assistant professor, Department of Physics, Mufakhamjah college of Engineering and Technology, Banjara hills, Hyderabad, India.

Prof. Md. Shareefuddin, Department of Physics, Osmania University, Hyderabad-500007, India