ROLE OF MANGANESE ON GLASS FORMING ABILITY, HARDNESS, FRAGILITY, GLASS ACTIVATION ENERGY AND STABILITY OF SODIUM-ALUMINO-SILICATE GLASSES

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Abstract: Differential thermal analysis (DTA) under non-isothermal conditions, density and Vicker's hardness techniques have been employed to investigate the effect of different MnO₂ contents on the thermal transitions data, hardness, Hv, glass-forming ability, GFA, stability, GS, fragility, Fi and activation energy of glass transition, E_g of 40SiO₂5Al₂O₃55Na₂O glass. The dependence of the characteristic temperatures “glass transition temperature” (T_g), the crystallization onset temperature (T_c) and the crystallization temperature (T_x) on the heating rate (β) were utilized in the determination of the activation energy for the glass transition (E_g), the glass thermal stability (K_H and γ_m) and the fragility, F_i. Three approaches were used to analyze the dependence of glass transition temperature on the heating rate (β) and another two were used to calculate the fragility parameter (F_i). The composition dependence of the T_g, density, E_g, H_v, GFA and Fi were discussed in the light of different oxidation states of manganese ions and its influence on the structure of the glasses. The indicative parameters of GFA, ΔT_x, Trg, K_H, γ_m and Hv were increased with the addition of MnO₂ up to 0.4 mol%, and decreased beyond 0.4 mol% MnO₂. The glass activation energies had lower values in MnO₂ content up to 0.4 mol% which are in good agreement with the fragility parameter Fi values. Then the addition of low amount of MnO₂ up to 0.4 at% MnO₂ in 40SiO₂5Al₂O₃55Na₂O glass at the expense of Na₂O may improve the glass-forming ability, thermal stability, the rigidity of the glass network and the glass sample S3 is the best GFA and stability with higher Hv and kinetically strong-glass forming (KS).

Keywords: density; glass-forming ability, fragility, activation energy of glass transition, Vicker's hardness, non-isothermal DTA.

1. Introduction

Many 3d-transition metals can exist in more than one oxidation state in glasses [1-3]. PbO–Nb₂O₅–P₂O₅ glasses containing different concentrations of MnO ranging from 0 to 2.5 mol% had been studied [4]. The results had been analyzed in the light of different oxidation states of manganese ions. The analysis indicates that when the concentration of MnO is around 1.0 mol%, manganese ions mostly exist in Mn²⁺ state, occupy network forming positions with MnO₄ structural units and increase the rigidity of the glass network. When MnO is present in higher concentrations, these ions seem to exist mostly in the Mn³⁺ state and occupy modifying positions. Lee et al. investigated the fragility of sodium silicate glasses, Na₂O-SiO₂, on the basis of the viscosity and thermal properties, and found that the fragility of Na₂O-SiO₂ glasses monotonically increases as the Na₂O content increases [5]. In such a case, the coordination number of silicon atom is constant to be four but non-bridging oxygen atoms increased with an increase in the alkali oxide contents. Aniya has also proposed the extended model of the fragility, in which not only the coordination number but also the bond strength is considered, and it has been shown that the degrees of both fluctuations relate to the fragility [6]. In order to evaluate the level of glass stability for the glass samples, different simple quantitative methods had been used [7–11]. Most of these methods are based on
characteristic temperatures such as the glass transition temperature, $T_g$, the crystallization temperature, $T_c$, or the melting temperature, $T_m$. [10, 11]. In the present work, the role of replacing Na$_2$O by MnO$_2$ on sodium-alumino-silicate glasses was investigated by applying non-isothermal DTA, density, Vicker's hardness techniques and calculating the activation energy of glass transition to study the dependence of $T_g$ on the heating rate by using different methods. The fragility index (Fi) was determined to see whether these glass samples are obtained from kinetically strong-glass forming (KS) or kinetically fragile–glass–forming (KF) liquids. The code and glass composition are shown in Table 1.

2. Experimental Work

A series of glass samples of [40 SiO$_2$ + 5Al$_2$O$_3$+ \{55–x\} Na$_2$O + xMnO$_2$] where $x$ =0.05, 0.2, 0.4, 0.6, 0.8 and 1 mol % MnO$_2$ were prepared by using raw materials all of these are chemically pure and were finally pulverized. The details of the compositions chosen for the present study are given in Table 1.

<table>
<thead>
<tr>
<th>Code</th>
<th>SiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>Na$_2$O</th>
<th>MnO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>40</td>
<td>5</td>
<td>54.95</td>
<td>0.05</td>
</tr>
<tr>
<td>S2</td>
<td>40</td>
<td>5</td>
<td>54.8</td>
<td>0.2</td>
</tr>
<tr>
<td>S3</td>
<td>40</td>
<td>5</td>
<td>54.6</td>
<td>0.4</td>
</tr>
<tr>
<td>S4</td>
<td>40</td>
<td>5</td>
<td>54.4</td>
<td>0.6</td>
</tr>
<tr>
<td>S5</td>
<td>40</td>
<td>5</td>
<td>54.2</td>
<td>0.8</td>
</tr>
<tr>
<td>S6</td>
<td>40</td>
<td>5</td>
<td>54</td>
<td>1</td>
</tr>
</tbody>
</table>

The homogeneous mixture was melted in porcelain crucible in an electrically programmable heated furnace, type UAF 15/10 Lenton thermal Designs, equipped with automatic temperature controller. The samples were melted at about (1100 ± 20)°C for two hours with heating rate 30°C/min. The molted material were quenched in air and poured at room temperature between two steel plates. The quenched samples were annealed at 300°C for 20 min. The as-made glasses were immediately stored in vacuum desiccators until used for measurements. The samples were examined by using Philips analytical X-ray diffraction system, type PW 3710 based with Cu tube anode, which confirms the amorphous nature of the investigated glass samples. The measurements were carried out using different techniques:

1) glass density measurements were made at room temperature using the standard “Archimedes principle” with toluene as the immersion fluid of stable density (0.866 g / cm$^3$). The experimental error was about ±0.003 g/cm$^3$.The molar volume [$V_m$] was calculated from molecular weight [M] and density.
2) Differential thermal analysis measurements [DTA] were carried out using a SHIMADZU DTA-50 ANALYZER. The measurements were carried out between 25°C to 1100°C [in N₂ gas using Al₂O₃ powder as a reference material], at different heating rates β = 15, 25, 35 and 40 K / min.

3) The Vicker's hardness was measured by using a Zwick-3270 micro hardness tester with a Vicker's indenter. The surfaces of the glass samples were cleaned in 10% HF aqueous solution for 30 sec. The applied load and the loading time were 4.9 N and 30 sec, respectively. The indentations of the glass samples were observed by using a microscope at room temperature.

3. Results, Calculations and Discussions

3.1. XRD investigations

The glass samples \{40 \text{ mol\% SiO}_2+5 \text{ mol\% Al}_2\text{O}_3+ (55 – X) \text{ mol\% Na}_2\text{O} + x \text{ mol\% MnO}_2\} with \(x = 0.05, 0.2, 0.4, 0.6, 0.8\) and \(1 \text{ mol\% MnO}_2\) were examined by XRD as shown in Figure 1 S1, S3, S5 and S6 glass samples. It shows a broad halo which characteristic of the amorphous structure at around diffraction angles \((2\theta) \approx 32°\) to be fully amorphous indicating that these glass samples are composed of glassy phase as shown in Figure 1. This indicates the absence of long range of atomic arrangement and also the periodicity of the three-dimensional network in the quenched materials [12]. The glass samples have been investigated using differential thermal analysis, density, molar volume and Vicker’s hardness.

![Fig. 1. The XRD of the investigated glass samples.](image)

3.2. Density and Molar volume

Density is a powerful tool able to capable the changes in the structure of glasses which is affected by the structural softening/compactness, change in geometrical configuration, coordination...
number, cross-link density and dimension of interstitial spaces of the glasses. Figure (2) shows the dependence of the density and molar volume of the glass system: 40 mol% SiO₂ + 5 mol% Al₂O₃ + (55 – x) mol% Na₂O + x mol% MnO₂ on manganese content where x = 0.05, 0.2, 0.4, 0.6, 0.8 and 1 mol% MnO₂. The glass density shows an opposite trend to the molar volume for all glass samples, i.e., gradually the density is increased and the molar volume is decreased as the mol% of MnO₂ is increased over the studied range from x = 0.05 to 0.2 mol% followed by a sharp increases in the density and a sharp decreases in the molar volume up to 0.4 mol% MnO₂. Beyond 0.4 mol% MnO₂ the density is rapidly decreased and the molar volume is increased rapidly as the mol% of MnO₂ is gradually increased. The variation of density and molar volume with MnO₂ mol% can be interpreted in terms of the structural changes which take place in the silicate networks upon replacing Na₂O by MnO₂ due to the effect of the different oxidation states of manganese ions [4], since the SiO₂/ Al₂O₃ ratio is constant in all the glass samples and the ratio of SiO₂/ Na₂O depends on the manganese concentration. Then the variation of the density and the molar volume with manganese content below 0.4 mol% MnO₂ may be due to the manganese ions mostly exist in Mn²⁺ state [13], and occupy network forming positions with Increasing MnO₂ at the expense of Na₂O up to 0.4 mol% MnO₂, results in decreasing the content of Na₂O as a modifier in the glass network. This will decrease the matrix occupation by Na²⁺ ions and the no. of (SiNBOs) decreases which consolidates their structure and increases their density. Beyond 0.4 mol% MnO₂, the manganese ions may be changed from Mn²⁺ to Mn³⁺ state and occupy modifying positions [4, 13]. In turn the no. of silicon ions associate with one or more nonbridging oxygens (SiNBOs) increases because of the excess of modifier ions able to associate with silicon. This leads to decrease in the polymerization of the silicate network and expands (opened up) the structure of the glass network and in turn, leads to an increase in the molar volume [14]. Also the decrease in density beyond 0.4 mol% MnO₂ supported that the network is weakened as manganese oxide is accommodated in the glass inducing a rearrangement of the network.

![Graph of density and molar volume](image)

**Fig. 2.** The density and molar volume of the investigated glass samples.
3.3. Non-isothermal DTA

DTA investigations of the glass transition temperature, \( T_g \), are useful in suggesting structural changes that achieve by composition changes.

The DTA curves from the different stoichiometries have been measured at heating rate 25 K/min. They have exhibited an endothermic peak, which is characteristic of glass transition region \( \{T_{gon}, T_{gend} \text{ and } T_g\} \), followed by an exothermic peak at higher temperature characteristic of crystallization region \( \{T_x \text{ and } T_c \text{ onset and peak crystallization temperatures, respectively}\} \). The exothermic peak is followed by a sharp peak exactly before the onset melting temperature, \( T_m \), which may be the eutectic point of the glass samples and \( T_m \) followed by the offset melting temperatures, \( T_l \). Effect of \( x \text{ mol}\% \text{ MnO}_2 \) content on the thermal transitions data for the investigated glass samples is shown in Figure 3a–c as determined from the DTA traces at heating rate 25 K/min. The values of glass transition temperature, \( T_g \), of the investigated glass samples are seen to increase gradually as the manganese oxide content is increased up to 0.4 mol.\% \text{ MnO}_2 followed by a rapid decrease beyond 0.4 mol.\% \text{ MnO}_2 as shown in Figure 3a. Then the variations of \( T_g \) with manganese content have two regions of affect: one up to 0.4 mol.\% \text{ MnO}_2 and another one beyond 0.4 mol.\% \text{ MnO}_2 exactly like the density and the molar volume results. The maximum \( T_g \), was observed for a glass composed of low content of \text{ MnO}_2 (\leq 0.4 \text{ mol }\%). The investigated glass samples contain a high amount of sodium which is varied with the manganese content, while the amounts of aluminium and silicon are constant in all glass samples. Then before adding the manganese, the glass samples have a modified network and the effect of \text{ Al}_2\text{O}_3 in a modified silicate glass results in a lowering of the concentration of non-bridging oxygens with the formation of corner-linked, negatively charged \([\text{AlO}_4/2]^{-1}\) tetrahedral unit that is charge-balanced by the modifier alkali [12]. In contrast to glasses containing \text{ MnO}_2 up to 0.4 \text{ mol}\%, the manganese ions \text{ Mn}^{2+} occupy network forming positions [13] and in turn decreases the matrix occupation by \text{ Na}^{2+} ions plus the effect of \text{ Al}_2\text{O}_3 which increases the polymerization of the network in modified silicate glasses and results in an increase in the \( T_g \) [12] at this region of manganese concentrations. Beyond 0.4 mol.\% \text{ MnO}_2 the manganese ions changed to \text{ Mn}^{3+} ions which enter the glass network as a modifier and more addition of network modifying ions into \text{ SiO}_2 breaks up the connectivity of bridging oxygens corner linking the \text{ SiO}_4 tetrahedra with the creation of ‘non-bridging’ oxygens that are linked to only one \text{ Si} atom where each alkali introduces one non-bridging oxygen [12]. Then as compositions beyond 0.4 mol.\% \text{ MnO}_2 become more modified, the silica network is gradually depolymerized, with dramatic reductions in the glass transition \( T_g \) indicating weakening of the glass structure as supported by density results. Effect of \( x \text{ mol}\% \text{ MnO}_2 \) content on \( T_c \) and \( T_l \) (the peak crystallization and the liquidus temperatures respectively) is shown in Figure 3b and c. They have the same trend to the glass transition temperature. Meanwhile, \( T_l \) increases with increasing the manganese oxide content.
content up to 0.4 mol% and then rapidly decreases. Such a behavior has been observed [15-17] in other glasses and may be attributed to the stability.

**Fig. 3.** Effect of MnO₂ content on the thermal transitions data for the investigated glass samples as determined from DTA curves, (a) – the glass transition temperature, \( T_g \); (b) – the peak crystallization temperature, \( T_p \); (c) – the liquidus temperature, \( T_l \).

### 3.4 Dependence of \( T_g \) on the heating rate

The glass transition temperature is known to depend on several independent parameters such as the band gap, bond energy, effective molecular weight, the type and fraction of various structural units formed and the average coordination number [18, 19]. Then the non-isothermal DTA measurements for 40 mol% SiO₂ + 5 mol% Al₂O₃ + (55 – \( x \)) mol% Na₂O + \( x \) mol% MnO₂ where \( x = 0.05, 0.2, 0.4, 0.6, 0.8 \) and 1 mol% MnO₂ glasses at four different heating rates 15, 25, 35 and 40 K/min were obtained. Figure 4 shows the DTA thermogram for the glass sample S4 as an example recorded at the chosen heating rate. The glass transition temperature represents the strength or rigidity of the glassy structure of the glass samples. Then three approaches were used to analyze the dependence of glass transition temperature on the heating rate (\( \beta \)). The first is the empirical relationship that can be written in the following form:

\[
T_g = A + B \ln \beta,
\]

where \( A \) and \( B \) are constants for a given glass composition [20, 21] and \( \beta \) is the rate of heating. The plot of \( T_g \) vs. \( \ln \beta \) gives a straight line, the slope of which gives \( B \) and the correlation coefficients \( r \) of the plots is all greater than 0.99 indicating good linear relationships. The results shown in Fig. 5a indicate the validity of Eq. (1) for the investigated glass samples. However, it was reported [21] that the slope \( B \) is related to the cooling rate of the melt, the lower the cooling rate of melt, the lower the value of \( B \). This signifies that \( B \) is related with the response of the construction changes within the
glass transition region. The obtained values of A and B are given in Table 2. The second approach
is the dependence of the glass transition temperature on the heating rate, $\beta$, by using Kissinger’s
formula [22] in the form

$$\ln \left( \frac{\beta}{T_g^2} \right) = -\frac{E_g}{RT_g} + \text{const},$$

where $R$ is the gas constant. This equation was derived for phase transformation from amorphous to
crystalline phase, and it may also be valid for glass to amorphous transformation used for evaluation
of glass transition activation energy, $E_g$, from the dependence of $T_g$ on the heating rate and has been
widely used [16, 21, 23]. The plot of $\ln \left( \frac{\beta}{T_g^2} \right)$ vs. $1000/T_g$ gives a straight line the slope of which
gives $E_g$ (glass transition activation energy). Figure 5b shows such a plot for the investigated glass
samples where the correlation coefficients $r$ of the plots is all greater than 0.99 indicating good linear relationships and the obtained values of the glass activation energy are given in Table 2. It is
reported [16, 21, 23] that $E_g$ is responsible for the molecular motion and rearrangement of the atoms
around $T_g$ and the glass with lower $E_g$ is the most stable. The third approach is the dependence of
the glass transition temperature on the heating rate according to Moynihan and co-workers [24-26],

$$\ln \beta = -\frac{E_g}{RT_g} + \text{const},$$

where $R$ is the gas constant. The plot of $\ln \beta$ versus $1000/T_g$ yields a straight line the correlation coefficients $r$ of the plots is all greater than 0.99 indicating good linear relationships, the slope of which gives the activation energy of the glass transition. Figure 5c shows such a plot for the investigated glass samples and the obtained values are given in Table 2. From this table, it is
observed that the activation energy for the glass transition has been calculated using the above models in good agreement with each other and the difference is within the experimental errors. The average values of obtained values of the glass transition activation energy $E$ (average) from the above models are shown in Fig. 5d. It is found that the activation energy for the glass transition, increases comparatively in the glass samples containing $0 < x \leq 0.4$ mol% MnO$_2$, then shows the dramatic change step-wisely in $x > 0.4$ mol% MnO$_2$ which is in accordance with the density and $T_g$ results. From the energy point of view, the state of an amorphous system in the glass samples containing $0 < x \leq 0.4$ mol% MnO$_2$, which has the lowest energy, is the best stable and is the best GFA as we will see below. Larger activation energy for the glass samples beyond 0.4 mol% MnO$_2$ is accountable for the molecular motion and rearrangement of the atoms around $T_g$ and corresponds to larger fragility parameter ($F_i$) as we will see below. The behavior of these results is in accordance with our previous results [27] and lie within the observed values for glasses [1, 23, 28].
Fig. 4. The DTA traces in the endothermic and exothermic directions at different heating rate for the glass sample S4, as an example.
Fig. 5. (a) the plot of $T_g$ vs. $\ln \beta$; (b) the plot of $\ln(T_g/\beta)$ versus $1000/T_g$; (c) $\ln \beta$ versus $1000/T_g$; (d) the average glass transition activation energy, $E$ (average) which deducted from the different models.

Table 2. The glass transition temperature $T_g$, the parameters A and B of Eq. (1) and the glass transition activation energy $E_g$ [kJ/mol].

<table>
<thead>
<tr>
<th>Code</th>
<th>$T_g$ (K)</th>
<th>The values of A &amp; B, K</th>
<th>Glass transition activation energy ($E_g$) (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>15 K/min</td>
<td>25 K/min</td>
<td>S1</td>
</tr>
<tr>
<td></td>
<td>35 K/min</td>
<td>40 K/min</td>
<td>A</td>
</tr>
<tr>
<td>S1</td>
<td>722.4</td>
<td>728.76</td>
<td>675.8 ±0.5</td>
</tr>
<tr>
<td>S2</td>
<td>736.56</td>
<td>744.75</td>
<td>691.1 ±1.2</td>
</tr>
<tr>
<td>S3</td>
<td>743.8</td>
<td>752.44</td>
<td>698.1 ±1.5</td>
</tr>
<tr>
<td>S4</td>
<td>716.92</td>
<td>723.82</td>
<td>677.5 ±1.1</td>
</tr>
<tr>
<td>S5</td>
<td>712.72</td>
<td>717.84</td>
<td>680.4 ±1.4</td>
</tr>
<tr>
<td>S6</td>
<td>708.25</td>
<td>712.71</td>
<td>680.8 ± 1.4</td>
</tr>
</tbody>
</table>

3.5. The fragility index and Vicker's hardness

3.5.1 Fragility index

There are several methods to quantifying the ‘fragility index’ among which the fragility parameter ($F_i$) is often used. In this article two approaches were used.
The first one was determined by calculating the kinetic fragility index, $F_i$, because it is a measure of the rate at which the relaxation time decreases with increasing temperature around $T_g$ and is given by the expression [29,30]:

$$F_i = \frac{E_\eta}{RT_g \ln \beta}$$

where $R$ is a gas constant and $E_\eta$ is the activation energy of viscous flow occurring around glass transition and was calculated using the equation [23, 31]

$$\ln \left( \frac{T_g^2}{\beta} \right) = \frac{E_\eta}{RT_g + \text{const}}$$

where, \( \beta \) is the heating rate, the plot of \( \ln \left( \frac{T_g^2}{\beta} \right) \) vs. \( 1000/T_g \) shown in Fig. 6 which gives a straight lines, the slope of which gives $E_\eta$ (the activation energy of viscous flow around $T_g$). The activation energy of viscous flow occurring around glass transition and liquid fragility of each glass has been calculated in order to understand the change in the local structures under cooled liquids with the compositions to calculate the fragility parameter ($F_i$) and shown in Fig. 6. The calculated values of the fragility are shown in Fig. 6a. The second approach for calculating the fragility index is the dependence of the fragility on the glass transition temperature, $T_g$. Then the fragility index of the glass, in the temperature range of glass transition, can be approximately evaluated [32] as the ratio

$$F_i \approx 2.1T_g / \left( T_{g_{\text{end}}} - T_g \right).$$

The dependence of this quantity on the glass composition is shown in Fig. 6a. It shows that the first model has slightly higher values of $F_i$ in comparison to the second model but they have a same trend. This difference results from the different employed methods or measurement accuracy. Investigating the two methods, it is found that the fragility slightly changes (or about to be constant) with increasing MnO$_2$ content up to 0.4 at%, at which has the lowest activation energy. This significant change may reflect its GFA and stability increase as we will see below. Behind 0.4 mol% MnO$_2$ the fragility shows the dramatic change step-wisely at which has larger activation energy. Behind 0.4 mol% MnO$_2$, the glass compositions are become more modified and the silica network is gradually depolymerized, and in turn increases the fragility. The behaviour of these results is in accordance with above and our previous results [27]. According to Vilgis [33], glass-forming liquids that exhibit an approximate Arrhenius temperature dependence of their relaxation times are defined as strong and specified with low value of $F_i$ ($F_i \approx 16$), while the limit for fragile glass-forming liquids is characterized by a high value of $F_i$ ($F_i \approx 200$) [34]. However, considering that the values of $F_i$ from both models are within the above mentioned limit, it is reasonable to state that the investigated glass samples are obtained from strong glass-forming liquids.
Fig. 6. the plot of $\ln\left(\frac{T_g}{\beta}\right)$ versus $1000/T_g$.

Fig. 6a & Fig. 6b. (a) the fragility of the investigated glass samples versus MnO$_2$ content; (b) Vicker's hardness, $H_v$, versus MnO$_2$ content.

3.5.2 Vicker's hardness

Figure 6b represents the measured values of Vicker's hardness of the investigated glasses as a function of the MnO$_2$ content. It is found that the value of the Vicker's hardness is increased gradually as the manganese oxide content is increased up to 0.4 mol.% MnO$_2$ and rapidly is
decreased beyond 0.4 mol% MnO2. The increasing values of Vicker's hardness in the concentration region ≤ 0.4mol% MnO2 may be due to the manganese ions mostly existing in Mn²⁺ state, occupy network forming positions with MnO₄ structural units and increase the rigidity of the glass network [4 & 13]. While above 0.4 mol% MnO₂, the values of Vicker's hardness is decreased, may be due to the manganese ions change to Mn³⁺ state and occupy modifying positions with increasing the manganese content [13]. In turn, the number of NBOs increases which weakened the glass structure and reduces the rigidity of the glass structure.

3.5.3 Relation between fragility and Vicker's hardness

There have been attempts of correlating the fragility with mechanical properties, Hv, of the corresponding glass, deducing that both should signify the resistance to shear either of the melt or of the glassy solid [35]. Such correlation, which would have linked a property of the liquid to another one of the glass, is shown in Fig. 7a. It shows the variation of the fragility index Fi with the Vicker's hardness of the investigated glass samples. It is obvious that the glass samples with higher value of fragile have a lower value of hardness and vice versa. This relation may be applicable to explain both the fragility and hardness of the investigated glasses. Increasing MnO₂ at the expense of Na₂O results in decreasing the content of Na₂O as a modifier in the glass network, this will decrease the matrix occupation by Na²⁺ ions. It is known that in silica all Si atoms are surrounded by four bridging oxygens but in silicate glasses Si atoms can have one, two, three or four non-bridging oxygens as nearest neighbors, depending on the concentration of the modifiers. Then the number of bridging oxygen atoms per silicon tetrahedron (Si–O–Si; BOs) increases as alkali oxide Na₂O content decreases and nonbridging oxygen atoms (Si–O; NBOs) decrease [14]. Also, a constant tetrahedral network formers like Al are established into a modified silicate glass composition. They predominantly form negatively charged (AlO₄₋) units that charge compensated by the modifying cations and the concentration of non-bridging oxygens is reduced in proportion [12]. In contrast to glasses containing MnO₂ up to 0.4 mol%, manganese ions mostly exist in Mn²⁺ state [4, 13], occupy network forming positions with MnO₄ structural units. Since the coordination number of silicon atom is constant to be four, the number of bridging oxygens per silicon tetrahedron increases and (SiNBOs) decreases which increases the rigidity of the glass network and decreases the fragility of the glasses [13] and higher the resistance of the supercooled liquid against transformation into crystalline [35,36]. Beyond 0.4 mol% MnO₂, the alkali oxide Na₂O content decreased and manganese ions increased and changed to Mn³⁺ state which occupies modifying positions [13]. In turn the no. of silicon ions associated with one or more nonbridging oxygens (SiNBOs) increases and (Si–O–Si; BOs), the number of bridging oxygens per silicon tetrahedron systematically decreases. This leads to decrease in the polymerization of the silicate network and
expands the structure of the glass network and reduces the rigidity of the glasses, which in turn gives rise to weakening of the glass structure and increases the fragility of these glass samples [14] at which the resistance decreases to shear of the melt and kinetically fragile–glass–forming (KF) liquids [35, 36].

![Graph](image)

**Fig. 7.** (a) the variation of the fragility $F_i$ with Vicker's hardness $H_v$ of the studied glass samples; (b) the variation of Vicker's hardness $H_v$ with the glass transition temperature, $T_g$, of the studied glass samples.

4. Glass-forming ability and the glass stability:

4.1 Glass-forming composition region

To assess GFA of the glass samples, the first parameter is defined as $T_{rg} = T_g / T_m$ [7] (the reduced glass transition temperature) was calculated and plotted as a function of MnO$_2$ content and shown in Fig. 8a. The calculated values of $T_{rg}$ are increased by increasing the MnO$_2$ content and it has a maximum value at about 0.4 mol% MnO$_2$, and then decreased beyond 0.4 mol% MnO$_2$ as shown in Fig. 8a. Then the investigated glass samples have a higher GFA in the low manganese oxide content up to 0.4 mol% MnO$_2$ than in high MnO$_2$ content and the best GFA at the glass sample 0.4 mol% MnO$_2$. The second parameter to calculate the glass forming ability is expressed by $\Delta T_s = T_s - T_g$ which called the width of the supercooled liquid region SCL [8], the temperature difference observed during heating between the onset crystallization temperature $T_s$ and the glass
transition temperature, $T_g$. Usually, unstable glasses show crystallization peak close to the glass transition temperature. Therefore, the temperature difference $T_x - T_g$ between the two temperatures is a good indication of thermal stability because the higher the value of this difference, the more the delay in the nucleation process [8]. The calculated values of SCL increase by increasing the MnO$_2$ content with a maximum value at about 0.4 mol% MnO$_2$ indicating high GFA, and then decreased beyond 0.4 mol% MnO$_2$ indicating low GFA as shown in Fig. 8b. Then the result of SCL for the investigated glass samples shows a good correlation between $\Delta T_x$ and the GFA. Then the reduced glass transition temperature $T_{rg}$ and the SCL $\Delta T_x$ have a higher value at about 0.4 mol% MnO$_2$ content glass sample indicating that the concentration region of ($0 \leq x \leq 0.4$ mol % MnO$_2$) is the best glass forming ability composition region and this result has supported from above discussion. Then the glass sample of 40 mol% SiO$_2$ + 5 mol% Al$_2$O$_3$ + 54.6 mol% Na$_2$O + 0.4 mol% MnO$_2$ is the best GFA. Increasing density up to 0.4 mol% MnO$_2$, increase the stability of the under cooled melt, resulting in the enhancement of the GFA.

![Fig. 8.](image)

**Fig. 8.** (a) the reduced glass transition temperature, $T_{rg} = T_g / T_m$ versus MnO$_2$ content; (b) the supercooled liquid region SCL $\Delta T_x = T_x - T_g$, versus MnO$_2$ content.

### 4.2 Glass stability

Hrubý [11] has introduced a parameter $K_H$, which combine the nucleation and growth aspects of phase transformation as an indicator of the GS and is given by: $K_H = \left( T_x - T_g \right) \left( T_m - T_x \right)$. The parameter $K_H$ is often used to estimate glass stability, GS. The large of the $K_H$ values, the greater the stability of the glass against devitrification. The calculated values of $K_H$ are shown in Fig. 9a. It is observed that the values of $K_H$ are increased with increasing the manganese content up about 0.4 mol% MnO$_2$ indicating increase of GS and GFA. Beyond 0.4 mol% MnO$_2$ the values of $K_H$ decreased indicating the decrease in GS and GFA. It has the same trend as the GFA parameters $T_{rg}$ and $\Delta T_x$. So, a strong correlation between GS parameter $K_H$, and the GFA indicators is concluded. The second parameter to assess GS is expressed by
The calculated values of $\gamma_m$, are shown in figure (9b). It is observed that the values of $\gamma_m$, have the same trend as $K_H$, indicating that glass stability and GFA of the investigated glass samples increase in low content of manganese up to 0.4 mol% and decrease beyond 0.4 mol% MnO$_2$. In conclusion, the parameters $K_H$ and $\gamma_m$ exhibited an excellent correlation with the GFA [10]. Then the glass sample of 40 mol% SiO$_2$ + 5 mol% Al$_2$O$_3$ + 54.6 mol% Na$_2$O + 0.4 mol% MnO$_2$ has a higher GFA and thermal stability.

![Figure 9](image_url)

**Fig. 9.** (a) Hrubý parameter $K_H$ versus MnO$_2$ content; (b) the calculated values of the glass stability parameter, $\gamma_m$, versus MnO$_2$ content

### 4.3 Relationship of mechanical and thermal properties with density:

From all above, there have been attempts of correlating the thermal and mechanical properties of the corresponding glasses. It is well established that mechanical properties of glasses are correlate with the glass transition temperature [37, 38]. The variation of glass transition temperature, $T_g$, with the hardness of the studied glass samples is shown in Fig. 7b. The hardness shows the same trend like the glass transition temperature ($T_g$), i.e. the lowest value of $T_g$ corresponding to the lowest value of hardness and the higher value of the hardness corresponding to the higher value of $T_g$. Since the higher the glass transition temperature and hardness, the easier it is to produce glasses on cooling and the more stable they are upon reheating. Then $T_g$ and Hv are in good correlation and, hence, glasses have a high glass formers and stability in low manganese oxide content. Since the effect of manganese oxide content on $T_g$ with density is seen to increase gradually in low manganese oxide content up to 0.4 mol.% MnO$_2$ and decreased beyond 0.4 mol% MnO$_2$. Also, the fragility is in accordance with the $E$ (average) were slightly increased with increasing MnO$_2$ content up to 0.4 at% and rapidly increased beyond 0.4 mol% MnO$_2$. Beyond 0.4
mol% MnO$_2$ the number of NBOs increases which weakens the glass structure and reduces the rigidity of the glass structure causing a decrease in $T_g$ and density at this region of concentrations. Therefore, as compositions become more modified, the silica network is gradually depolymerized, with dramatic reductions in the glass transition, $T_g$ and increases in the fragility. A strong correlation is found between the GFA and the glass stability, GS parameters. Both they have a higher values at about 0.4 mol% MnO$_2$ glass sample which has a lower glass activation energy as shown in Fig. 5d. This indicates that the glass sample containing 0.4 mol% MnO$_2$ is the best GFA and higher thermal stability demonstrating that concentration region of (0< $x$ ≤ 0.4 mol % MnO$_2$) is the higher glass forming ability and stability composition region. Then the glass sample S3 is the best GFA and stability. This result is correlated well with the results of density, hardness, and fragility. Figure 10 shows the variation of hardness and fragility of the investigated glass samples with the supercooled liquid region, SCL, $\Delta T_x$ which is a good pointer for the thermal stability. It is obvious that the higher value of fragility corresponds to the lowest value of both the (SCL), $\Delta T_x$, and the hardness which confirmed that the more fragile glass-forming substances should have a low thermal stability and rigidity, inducing a rearrangement of the glass network at this region of manganese content. Since the high hardness values correspond to the high values of $\Delta T_x$ then the glass samples of higher rigidity have a higher thermal stability and good GFA verifying that the glass samples with a higher GFA are stronger glass formers with a lower fragility index $F_i$ [39].

![Fig. 10. The variation of Vicker's hardness Hv and the fragility index $F_i$ with the supercooled liquid region, SCL, $\Delta T_x$.](image)

Hence the stable glass with higher GFA requires less activation energy for glass transition process [8] which is in accordance with the above results. In conclusion, at low manganese content glass samples (0< $x$ ≤ 0.4 mol %), manganese oxide is accommodated in the glass structure improving the thermal stability, rigidity and the GFA of the investigated glasses which are in accordance with the results of the fragility and activation energy for the glass transition. Beyond 0.4 mol% MnO$_2$, the
increasing of MnO₂ content will result in a lower density and in turn less viscosity. Low viscosity accelerates the crystallization kinetics on cooling and then depresses the GFA of the samples [40]. Thus, beyond 0.4 mol% MnO₂, the investigated glass samples have a high fragility and glass activation energy and in turn lower GFA. Then there is a good correlation of the glass transition temperature and density results with mechanical properties of 40 mol% SiO₂ + 5 mol% Al₂O₃ + (55 – x) mol% Na₂O + x mol% MnO₂ where x = 0.05, 0.2, 0.4, 0.6, 0.8 and 1 mol% MnO₂ glasses. Hence, the density results have supported the \( T_g \) data and both of them have supported the hardness and the fragility results. Also the hardness and fragility results are in accordance with both of the GFA and stability results. Thus, in general, it can be said that the glasses with lower \( T_g \), lower density and lower hardness could provide higher fragility and glass activation energy and in turn lower stability and GFA. Then from all above the direct correlation between \( T_g \), density, hardness, GFA and GS results and all they are in indirect relation with both the fragility and the glass activation energy results while the fragility is correlated directly with the activation energy of the glass transition.

5. Conclusions

The effect of MnO₂ content on \( T_g \), density, hardness, glass-forming ability, stability, fragility and activation energy of glass transition of 40SiO₂5Al₂O₃55Na₂O has been investigated. The indicative parameters of GFA, \( \Delta T_x \), \( T_{rg} \), KH and \( \gamma_m \) show an increasing tendency with the addition of MnO₂ up to 0.4 mol%, and decreasing beyond 0.4 mol% MnO₂. The glass transition kinetic studies show that the glass activation energies have lower values in MnO₂ content up to 0.4 mol%. The fragility parameter \( F_i \) values of the investigated glass samples have been evaluated using two different methods indicating that the present glass system is a strong glass former according to Angell’s classification scheme. The experimental results show that addition of MnO₂ up to 0.4 at% MnO₂ in 40SiO₂5Al₂O₃55Na₂O glass may improve the glass-forming ability and thermal stability with increasing the hardness and the glass sample of 40 SiO₂ 5 Al₂O₃ 54.6 Na₂O 0.4 MnO₂ at the expense of Na₂O is the best GFA and stability.

REFERENCES