Viscosities of Na_2O-SiO_2-B_2O_3 Melts

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ABSTRACT

Viscosities of Na_2O-SiO_2-B_2O_3 ternary melts were determined. Experiments were carried out using graphite crucibles for X_{B2O3} = 0.1 to 0.6 and 920 to 1405 K. The results showed that viscosities of melts decreased with increase in B_2O_3 content at X_{SiO2}/X_{Na2O} = 2.0 and 1.5 and increased at X_{SiO2}/X_{Na2O} = 1.0 at a fixed temperature. For a fixed ratio of X_{SiO2}/X_{Na2O} and at 1317 K, the viscosities of melts decreased from 1.3 poise to 0.32 as the X_{B2O3} in the melt increased from 0.3 to 0.57 respectively. A viscosity model, incorporating structure of the melts has been developed. The predicted viscosity data are in excellent agreement with the experimental data.

1. INTRODUCTION

Many technologically important glasses, such as Vycor and Pyrex Processes as well as coating materials for aerospace technology, are based on sodium borosilicate. Therefore, the viscosities of sodium borosilicate melts are very important for glass manufacturing operations. For glass melting operations, the viscosity should be about 10^2 poise. But several limitations exist, as experimental measurements of viscosities are very difficult to make and time consuming. The only resort in such cases is to come up with a reliable model that will predict viscosities in a self-consistent manner over the entire composition and temperature range. In practice, the glass-forming oxygen polyhedra are triangles and tetrahedra, such as B_2O_3, SiO_2 and cations forming such as polyhedra have been termed as network formers. Alkali ions occupied random position distributed in the structural unit to provide local charge neutrality. These cations are termed as network modifiers. The viscosities of glass melts are affected by structure changing of glass melts. Therefore, the study of viscosity behavior of glass melts can be related with the structure of the melts. A structure based viscosity model, which considers depolymerization effects and related breakdown of the silicate network structure on the addition of metal oxides to the melt, has been developed. Based on this model, a series of successful predictions were made by Hu and Reddy for binary alkaline earth metal oxide and silicate melts [1, 2], Reddy and Hebbar for binary silicate melts [3], Shrivastava and Reddy for B_2O_3-K_2O binary melts [4], Reddy and Yen for B_2O_3- Na_2O binary melts [5, 6]. In this paper we present experimental viscosity data and predicted viscosities of Na_2O-SiO_2-B_2O_3 glass melts as a function of temperature and composition.

2. EXPERIMENTAL METHOD

A Brookfield viscometer (RVT DV-II) was used to measure the viscosity of Na_2O-SiO_2-B_2O_3 melts. This viscometer measures viscosity by rotating a graphite spindle in the fluid. The torque necessary to overcome the viscous resistance to the induced movement, which is indicated by reflection of a spring, is converted to a viscosity value by means of a calibration factor. A continuous digital display of viscosity in centipoise is provided by means of LED.

A detailed description of the experimental procedure is given elsewhere [4]. Hence only a brief description is given below.

The SiC heating element resistance furnace with a solid state controller was used to heat up the samples. Samples of specific melt composition were premixed before heating in the furnace. Boron oxide was premelted before mixing with sodium oxide and silica. The crucible with sample were kept at constant temperature zone of heating furnace for 30 minutes in order to let the mixed sample form homogenous phase before viscosity measurement. Two Pt/Pt-10%Rh thermocouples were used to measure the temperature, one for the furnace controller, and another one for measuring the temperature of the crucible. Argon gas atmosphere was maintained during entire viscosity measurement period. The experimental set-up is shown in Fig. 1.

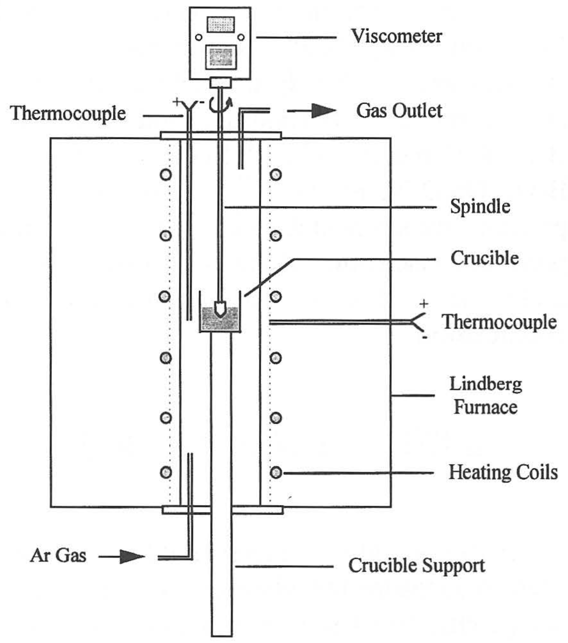

Fig. 1: Experimental Setup

3. EXPERIMENTAL RESULTS

The experimental viscosity data of Na_2O-SiO_2-B_2O_3 glass melts are presented in Fig. 7 to 10. The viscosities of melts decreased with increase in B_2O_3 content at $X_{SiO2}/X_{Na2O} = 2.0$ and 1.5 at a constant temperature. At $X_{SiO2}/X_{Na2O} = 1.0$, viscosities increased with increase in B_2O_3. At $X_{SiO2}/X_{Na2O} = 0.5$, viscosities increased with increase in B_2O_3 for higher temperatures and decreased with increase in B_2O_3 for lower temperatures. For example at a fixed ratio of $X_{SiO2}/X_{Na2O} = 2.0$ and 1317 K, the viscosities of Na_2O-SiO_2-B_2O_3 melts decreased from 1.3 poise to 0.32 as the X_{B2O3} in the melt increased from 0.3 to 0.57 respectively.

4. VISCOSITY MODEL

4.1 Theoretical Consideration

For glass network breakdown, one mole of B_2O_3 glass network need 3 moles of free oxygen. The mole fractions of cations in terms of electrically equivalent fractions of cations, $N_{B^{3+}}$ and $N_{Si^{4+}}$ are given as [7]:

$$N_{B^{3+}} = \frac{3n_{B^{3+}}}{3n_{B^{3+}} + 4n_{Si^{4+}}} \qquad (1)$$

$$N_{Si^{4+}} = \frac{4n_{Si^{4+}}}{3n_{B^{3+}} + 4n_{Si^{4+}}} \qquad (2)$$

where $3n_{B^{3+}}$ and $4n_{Si^{4+}}$ are the numbers of equivalents of the cations B^{3+} and Si^{4+}. If expressed $n_{B^{3+}}$ and $n_{Si^{4+}}$ in terms of X_{B2O3} and X_{SiO2}, then one mole of B_2O_3 consists of 2 moles B^{3+} and one mole SiO_2 consists of one mole Si^{4+}. Thus, $n_{B^{3+}} = 2X_{B_2O_3}$ and $n_{Si^{4+}} = X_{SiO_2}$. Then the equation (1) and (2) can be rewritten as equation (3) and (4) respectively.

$$N_{B^{3+}} = \frac{3(2X_{B_2O_3})}{3(2X_{B_2O_3}) + 4X_{SiO_2}}$$

$$= \frac{3X_{B_2O_3}}{3X_{B_2O_3} + 2X_{SiO_2}} \qquad (3)$$

$$N_{Si^{4+}} = \frac{4X_{SiO_2}}{3(2X_{B_2O_3}) + 4X_{SiO_2}}$$

$$= \frac{2X_{SiO_2}}{3X_{B_2O_3} + 2X_{SiO_2}} \qquad (4)$$

Consideration of ionic liquids containing holes [8], the viscosity can be expressed as equation (5):

$$\eta = \frac{2}{3} N_h R_h (6.28 mKT)^{\frac{1}{2}} \exp(\frac{E}{RT}) \qquad (5)$$

where N_h is the number of holes per unit volume, R_h is the average radius of the holes, m is the mass of an ionic unit, K is Boltzmann constant, T is absolute temperature, E is the energy of ionic unit for viscous flow, R is gas constant.

Calculation of $(6.28mKT)^{1/2}$:

The term $(6.28mKT)^{1/2}$ can be rearranged as :

$$(6.28mKT)^{1/2} = (6.28\,W/R)^{1/2} KT^{1/2} \qquad (6)$$

where W is the molecular weight of an ionic unit. For Na_2O-B_2O_3 melts, molecular weight considered as the weight of BO_3 unit. For Na_2O-SiO_2, the molecular weight considered as the weight of SiO_4 unit. The molecular weight of an ionic unit can be expressed as:

$$W = N_{B^{3+}} W_{BO_3} + N_{Si^{4+}} W_{SiO_4} \qquad (7)$$

where W_{BO3} = 0.059 (Kg/mole) and W_{SiO4} = 0.092 (Kg/mole).

The equation (6) can be rewritten as:

$$(6.28W/R)^{1/2} KT^{1/2} =$$

$$(6.28/R)^{1/2} (N_{B^{3+}}(0.059)$$

$$+ N_{Si^{4+}}(0.092))^{1/2} KT^{1/2}$$

$$= (4.75\times10^{-24}) \left(\frac{X_{B_2O_3} + 1.04X_{SiO_2}}{3X_{B_2O_3} + 2X_{SiO_2}} \right)^{1/2} T^{1/2} \qquad (8)$$

Calculation of R_h:

Fürth [9] have shown that the size of a typical hole in a liquid is roughly the same as the ionic unit and the hole can accommodate an ionic unit. The basic building units are BO_3 triangles and SiO_4 tetrahedron for borate and silicate melts respectively. The radius of BO_3 and SiO_4 unit have been calculated by [4] and [1] respectively. Therefore, the radius of an ionic unit again can be expressed by equation (9):

$$R_h = N_{B^{3+}} R_{h_{BO_3}} + N_{Si^{4+}} R_{h_{SiO_4}} \qquad (9)$$

where R_{hBO3} = 2.94 Å and R_{hSiO4} = 3.4 Å, thus

$$R_h = (8.82\times10^{-10}) \left(\frac{X_{B_2O_3} + 0.77X_{SiO_2}}{3X_{B_2O_3} + 2X_{SiO_2}} \right) \qquad (10)$$

Calculation of N_h:

The number of holes per unit volume was expressed in terms of NO^o, where NO^o is mole fraction of bridging oxygen in melts. This calculation involves the number of holes are equal to BO_3 and SiO_4 units present in the melts and that all the holes are occupied by the ionic species. Thus

$$N_h = NO^o \times A_v = 6.023\times10^{23} NO^o \qquad (11)$$

Substituting $(6.28mKT)^{1/2}$, R_h, and N_h, the following expression can be obtained.

$$\eta = 1.68\times10^{-9}(X_{B_2O_3}+0.77X_{SiO_2})$$
$$(X_{B_2O_3}+1.04X_{SiO_2})^{1/2}(3X_{B_2O_3}+2X_{SiO_2})^{-3/2}$$
$$(NO^{o})T^{1/2}\exp(E/RT) \qquad (12)$$

To estimate viscosity by equation (12), NO^{o} and E are needed to be calculated. The calculation of NO^{o} and E are described below.

4.2 Calculation of NO^{o}:

If B mole of B_2O_3 are mixing with S mole of SiO_2 and M mole of Na_2O, the charge and mass balance can be expressed as equation (13) and (14), respectively as:

$$no^{o} = 3B+2S-1/2no^{-} \qquad (13)$$

$$no^{2-} = M-1/2no^{-} \qquad (14)$$

The total number of anions can be calculated as:

$$no^{o}+no^{-}+no^{2-} = 3B+2S+M \qquad (15)$$

where no^{-} is the number of non bridging oxygen bonded to only one boron or silicon atom. no^{o} is the number of bridging oxygen bonded to two boron or silicon atoms. no^{2-} is the number of free oxygen ions.

The mole fraction of bridging oxygen of total anion can be calculated by using Yokokawa's model [10] and expressed as equation (16).

$$NO^{o} = \frac{no^{o}}{total\ number\ of\ oxygen} = \frac{3B+2S-1/2no-}{3B+2S+M} \qquad (16)$$

Considering the mole fraction in liquid melts, then

$$NO^{o} = \frac{3X_{B_2O_3}+2X_{SiO_2}-1/2no^{-}}{3X_{B_2O_3}+2X_{SiO_2}+X_M} = \frac{3X_{B_2O_3}+2X_{SiO_2}-1/2no^{-}}{2X_{B_2O_3}+X_{SiO_2}+1} \qquad (17)$$

no^{-} further can be calculated by equation (18).

$$(1-\exp(\Delta G^{o}/RT))(no^{-})^2$$
$$-2(2X_{B_2O_3}+X_{SiO_2}+1)no^{-}$$
$$+4(1-X_{B_2O_3}-X_{SiO_2})(3X_{B_2O_3}+2X_{SiO_2}) = 0 \qquad (18)$$

ΔG^{o} is the Gibbs energy of depolymerization reaction. For Na_2O - SiO_2 and Na_2O - B_2O_3 melts, the depolymerization reaction can be described as reactions (19) and (20) respectively.

$$Na_2O(l)+SiO_2(l) = Na_2SiO_3(l) \qquad (19)$$

$$Na_2O(l)+B_2O_3(l) = Na_2B_2O_4(l) \qquad (20)$$

ΔG^{o} can be expressed as

$$\Delta G^{o} = N_{B^{3+}}\Delta G_B^{o}+N_{Si^{4+}}\Delta G_S^{o} \qquad (21)$$

where ΔG_S^{o} and ΔG_B^{o} are the Gibbs energy for reactions (19) and (20) respectively. The calculated NO^{o} are shown in Fig. 2.

4.3 Calculation of E

The energy of ionic unit for viscous flow is function of composition and temperature. SiO_2 is strong acidic oxide and Na_2O is strong basic oxide. As concept of basicity, the ratio of X_{SiO2}/X_{Na2O} and X_{B2O3} were considered to define the composition. The energy term of ionic unit can be considered as the energy of ionic unit to break the bond and move the ionic unit into the holes. The value of energy was calculated from the present experimental data. The calculated energy of ionic units for ratio = 2, 1.5, 1 and 0.5 are shown in Fig. 3, 4, 5 and 6 respectively.

As observed, the energy term can be expressed as equation (22):

$$E = A + BT \tag{22}$$

where A and B are constants and are function of composition. The constants A and B are expressed by polynomial expression which are given by equation (23) and (24).

$$A = k + mX_{B_2O_3} + nX^2_{B_2O_3} + pX^3_{B_2O_3} \tag{23}$$

$$B = \alpha + \beta X_{B_2O_3} + \gamma X^2_{B_2O_3} + \delta X^3_{B_2O_3} \tag{24}$$

where

$$k = -4.10909\times10^5 - 3.16176\times10^5 R + 1.216120\times10^6 R^2 - 5.13104\times10^5 R^3$$

$$m = -1.343160\times10^6 + 1.7586\times10^7 R - 2.2046\times10^7 R^2 + 1.768940\times10^6 R^3$$

$$n = 1.59975\times10^7 - 8.4629\times10^7 R + 9.18343\times10^7 R^2 - 2.76946\times10^7 R^3$$

$$p = -2.15337\times10^7 + 9.79282\times10^7 R - 1.01984\times10^7 R^2 + 2.99583\times10^7 R^3$$

and

$$\alpha = 1557.73 - 2146.51R + 684.746R^2 + 66.530R^3$$

$$\beta = -8493.96 + 8023.87R + 1457.36R^2 - 297.47R^3$$

$$\gamma = 13734.2 + 2565.39R - 22661.9R^2 + 9981.06R^3$$

$$\delta = -7326.2 - 14018.2R + 28442.3R^2 - 10587.9R^3$$

where R is the ratio of X_{SiO2}/X_{Na2O}.

The calculated E and NO^o values were plugged into the equation (11) and the viscosities of several melts are calculated.

5. RESULTS AND DISCUSSIONS

The experimental viscosity data and calculated data for compositions $X_{SiO2}/X_{Na2O} = 2$ are shown in Fig. 7. The calculated results are in excellent agreement with the experimental results. The viscosities decreases with the increase in X_{B2O3}. As can be seen from the figure, the viscosities decrease with the increase in temperature of the melt for the composition of $X_{B2O3} = 0.3$, 0.4, 0.5 and 0.57. From $X_{B2O3} = 0.3$ to 0.4, the viscosities decrease significantly.

Fig. 8 shows the experimental and calculated data for $X_{SiO2}/X_{Na2O} = 1.5$. Again, viscosities decrease with the increase in content of X_{B2O3}. Significant decrease in viscosities can be seen with the increase in X_{B2O3} from 0.375 to 0.444. The viscosities were also decreased with increasing the temperature of the melt.

Fig. 9 shows the experimental viscosity data and calculated data for $X_{SiO2}/X_{Na2O} = 1$. As can be seen, viscosities increase with increase in X_{B2O3}. This is different from that for $X_{SiO2}/X_{Na2O} = 2$ and 1.5. Viscosities of this ratio decrease with increase in temperature of the melt for all four X_{B2O3} compositions.

The experimental data and calculated data for $X_{SiO2}/X_{Na2O} = 0.5$ are shown in Fig. 10. An excellent agreement between experimental data and calculated data can be seen with $X_{B2O3} = 0.57$ at all temperature. For $X_{B2O3} = 0.25$, 0.4 and 0.5, a good agreement can be seen only in higher temperature range. For smaller value of X_{B2O3}, larger deviation was observed at lower temperatures. Further investigation was carried out to study this abnormal behavior. It was found that the deviation is due to the formation of solid particles in the melts [11].

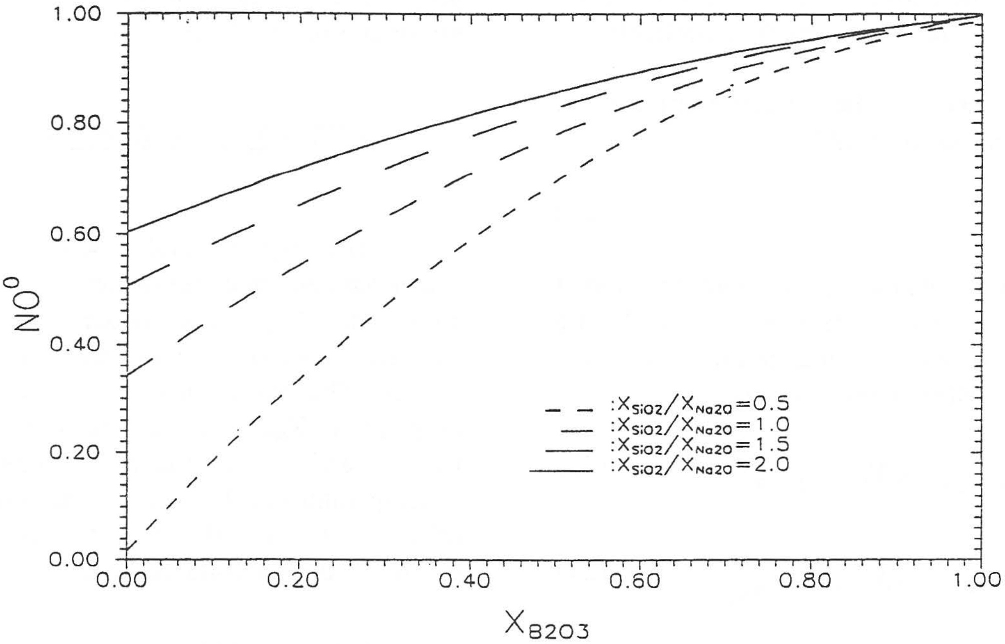

Fig. 2: NO^0 as a function of X_{B2O3} with different X_{SiO2}/X_{Na2O}.

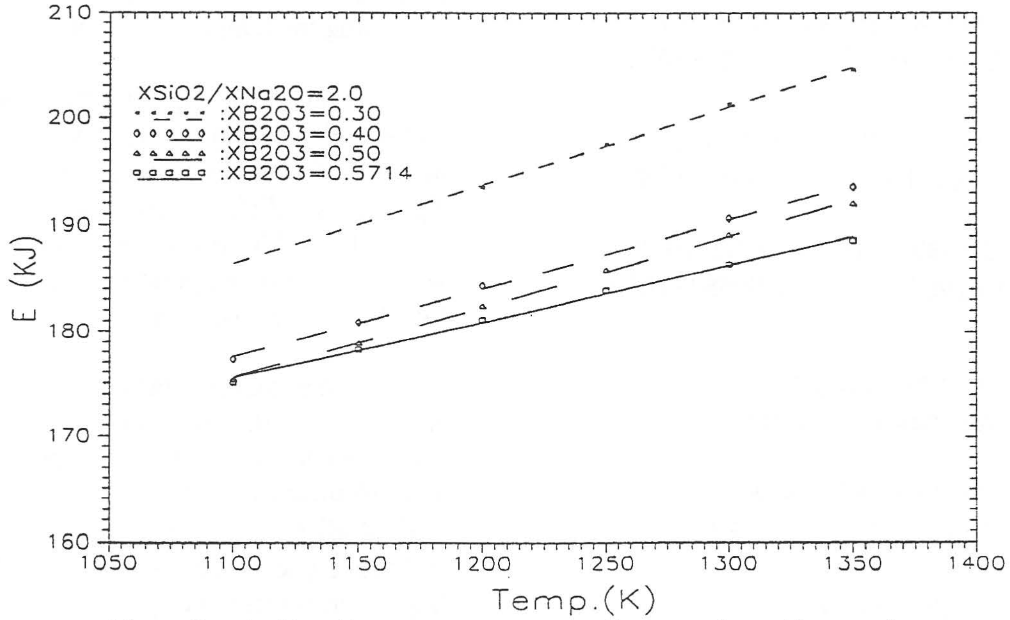

Fig. 3: Activation energy as linear function of temperature (X_{SiO2}/X_{Na2O}=2.0)

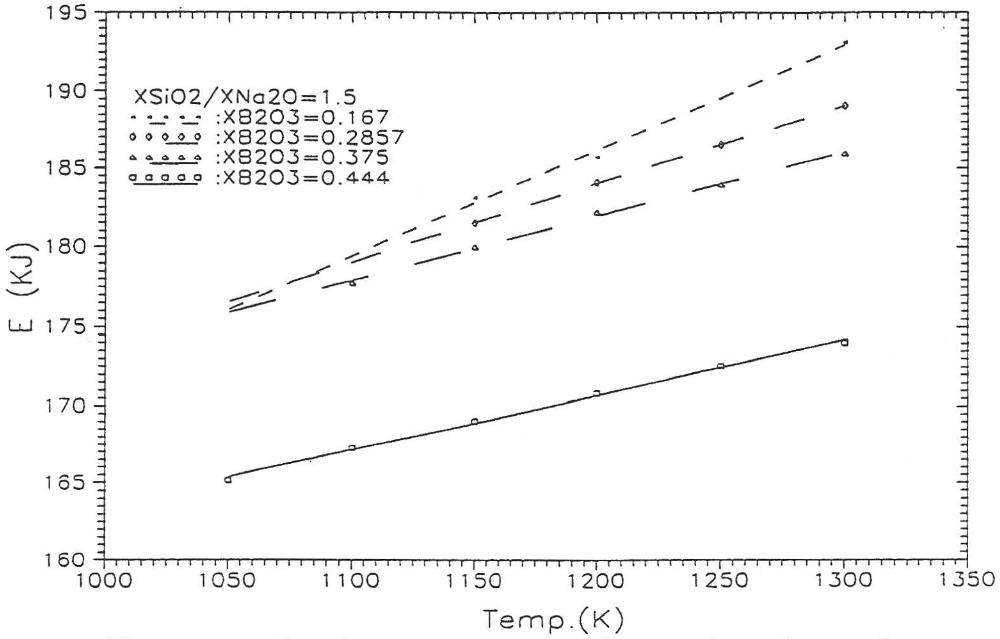

Fig. 4: Activation energy as linear function of temperature ($X_{SiO_2}/X_{Na_2O}=1.5$)

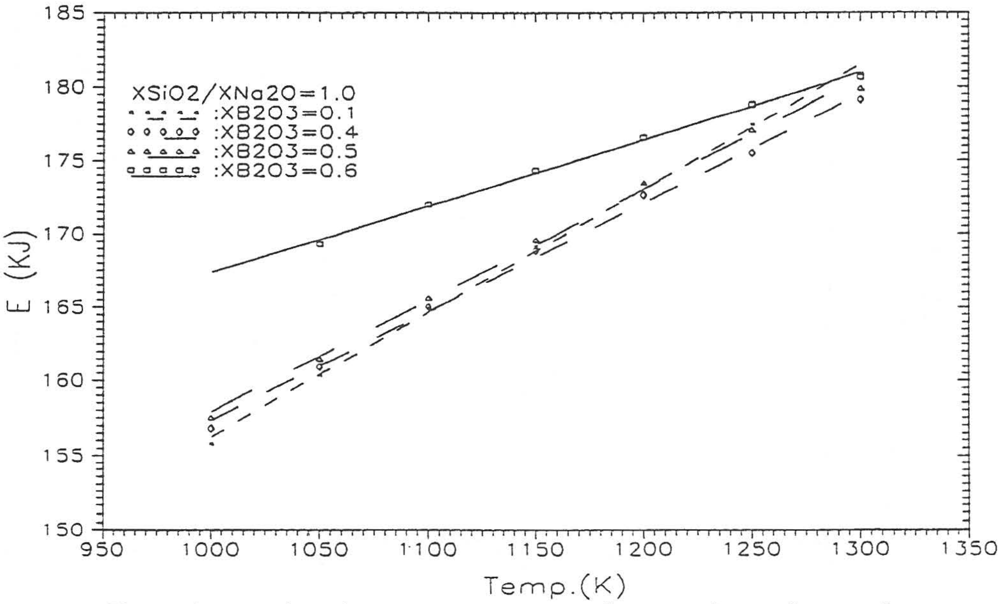

Fig. 5: Activation energy as linear function of temperature ($X_{SiO_2}/X_{Na_2O}=1.0$).

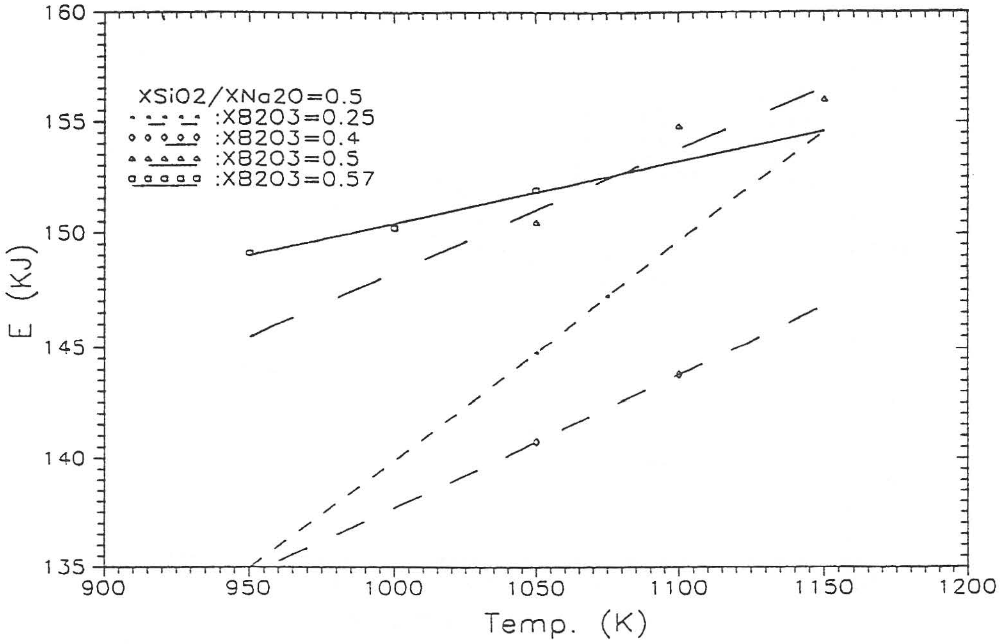

Fig. 6: Activation energy as linear function of temperature (X_{SiO2}/X_{Na2O}=0.5).

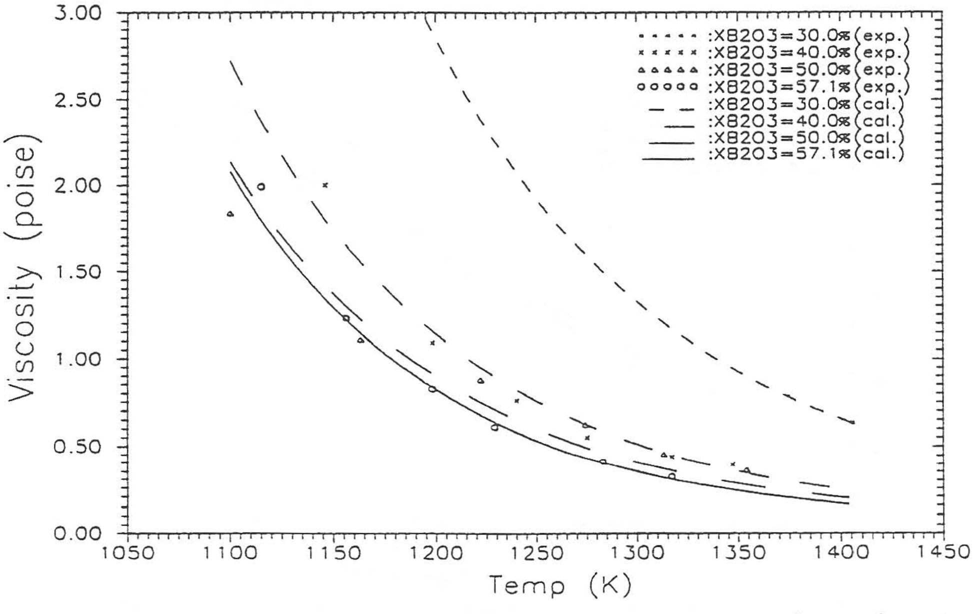

Fig. 7: Viscosities as a function of temperature. (SiO_2/Na_2O=2.0)

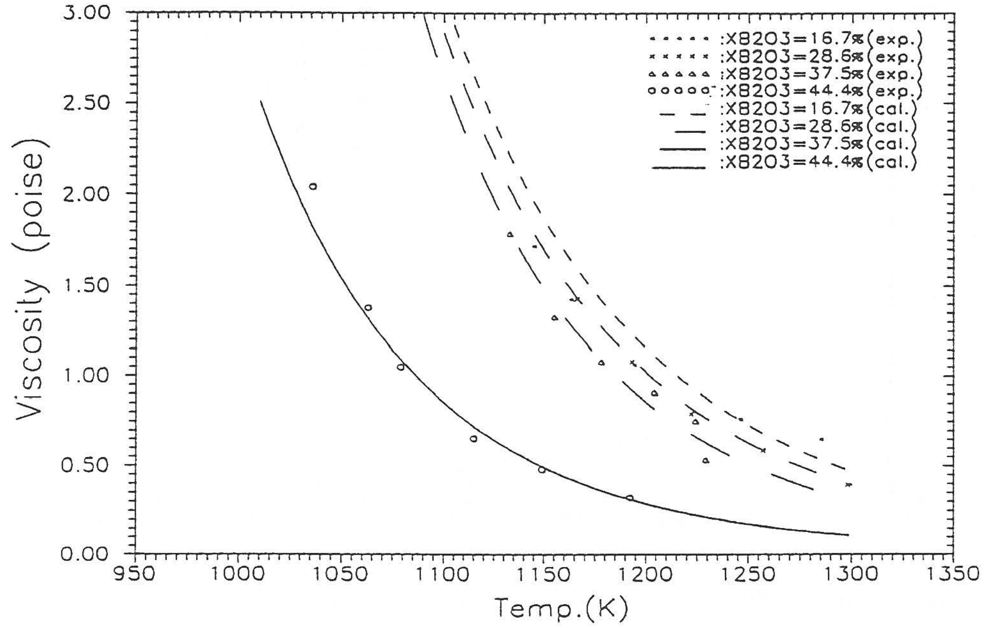

Fig. 8: Viscosities as a function of temperature. ($X_{SiO2}/X_{Na2O}=1.5$)

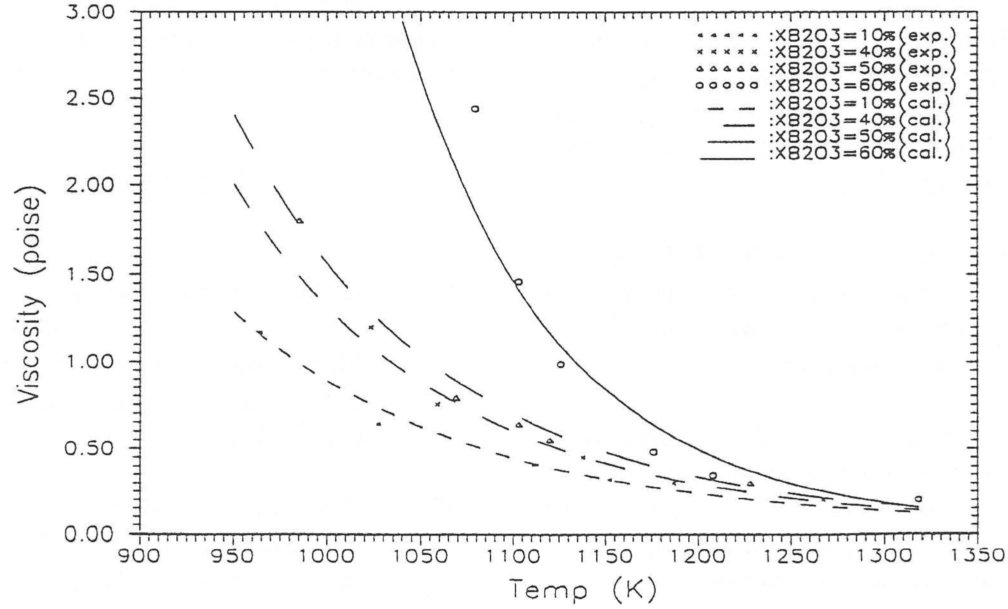

Fig. 9: Viscosities as a function of temperature. ($SiO_2/Na_2O=1$)

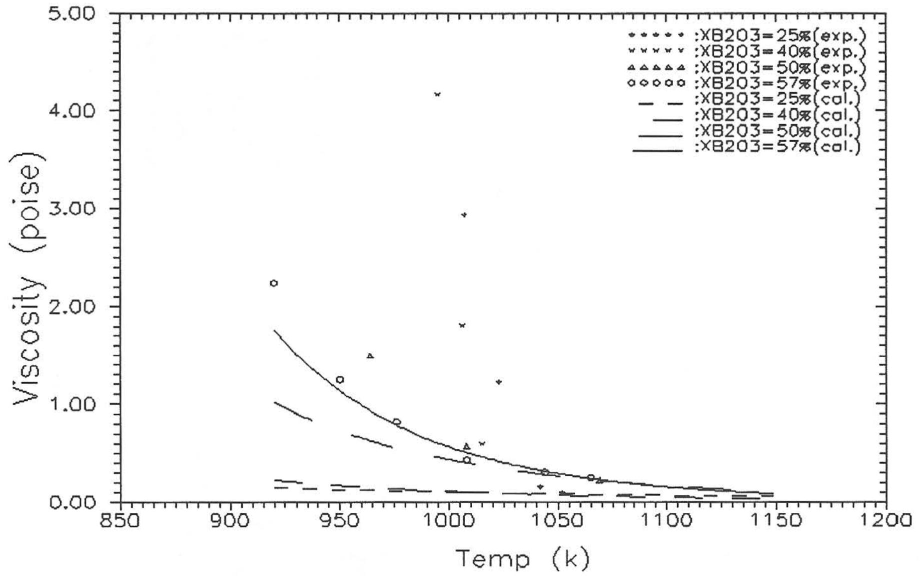

Fig. 10: Visicosities as a function of temperature. ($SiO_2/Na_2O=0.5$)

6. CONCLUSIONS

(1) Viscosities of Na_2O-SiO_2-B_2O_3 melts decrease with increase in X_{B2O3} for X_{SiO2}/X_{Na2O} = 2 and 1.5. For X_{SiO2}/X_{Na2O} = 1 and 0.5, viscosities increase with increasing X_{B2O3}.

(2) Viscosities of Na_2O-SiO_2-B_2O_3 ternary melts decreased with increase in temperature of the melts at all the compositions studied.

(3) A viscosity model, incorporating structure and kinetic aspects has been developed for Na_2O-SiO_2-B_2O_3 ternary system. The calculated data by present model shows an excellent agreement with experimental data for X_{SiO2}/X_{Na2O} = 2, 1.5 and 1. The large deviation is observed for the composition with X_{SiO2}/X_{Na2O} = 0.5. This may be due to the formation of solid particles in the liquid melts.

ACKNOWLEDGMENTS

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