Glass Properties, Calculated and Observed, in the Na_2O-B_2O_3-GeO_2 (SiO_2) System based on the Sub-system Concept

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1. Introduction

Computation of glass properties of multi-component system from its chemical composition is particularly difficult and offers quite an interesting problem at the same time. Especially it is true in cases where constituent atoms, such as boron B, germanium Ge and aluminum Al, would change their coordination number with chemical composition of glass including alkali metal oxides or alkali earth metal oxides. We have proposed a method to calculate glass properties based on the sub-system concept [1-3], wherein change of coordination state is taken into consideration.

2.Calculation of glass properties by the sub-system concept

According to the sub-system concept a multi-component system, Na_2O-B_2O_3-GeO_2 for example, is supposed to consist of some mixtures of binary systems: Na_2O-B_2O_3 and Na_2O-GeO_2 (sub-systems). The essential presumption made in this concept states that in the multi-component system sub-systems are thermodynamically equilibrated. The activity of an component, Na_2O for instance in this system, shared among the sub-systems must be equal. The activity of Na_2O itself would vary with composition. To determine the concentration of the Na_2O component in each sub-system, value of activity coefficient γ must be considered. The absolute values of γ are not necessary. Instead relative ratio γ_1/γ_2 is essential, where 1 and 2 denote the sub-system; Na_2O-B_2O_3 and Na_2O-GeO_2, respectively. The activity coefficient ratio was inferred from the Raman spectra measured in the Na_2O-B_2O_3-GeO_2 system. Partial fraction of B_2O_3 in this system was substituted for GeO_2. The change of Raman spectra with the substitution showed that 770cm^{-1} peak allocated to four-fold coordinated boron group BO_4Na increased with B_2O_3 -> GeO_2 substitution, meanwhile 803cm^{-1} peak allocated to three-fold coordinated BO_3 group in the boroxol ring decreased. The relative change in the peak intensity was interpreted as implying affinity between Na_2O and B_2O_3 much stronger than between Na_2O and GeO_2. Therefore it might be speculated that γ_1 should be smaller than γ_2. The relative ratio γ_2/γ_1 was set tentatively at 2. Another clue to evaluate the relative value of the activity coefficient is provided from the electromotive measurement in the molten salts of binary systems including Na_2O-B_2O_3, Na_2O-GeO_2 and Na_2O-SiO_2 as a function of Na_2O concentration. Na_2O activity $\log a^*(Na_2O) = -\log O$ in the Na_2O-SiO_2 system lies on the same level of the Na_2O-GeO_2 system and at much higher level compared with the Na_2O-B_2O_3 system. It is apparent from this measurement that γ_2/γ_1 stays at somewhat constant value in the range 1.5 to 2.5. It may be reasonable to assume a constant value 2 for γ_2/γ_1 as a first approximation irrespective Na_2O concentration. Suppose the Na_2O-B_2O_3-GeO_2 system of following chemical composition. $sNa_2O+m_1B_2O_3+m_2GeO_2$ is decomposed into two sub-systems: Na_2O-B_2O_3 and Na_2O-GeO_2 of certain Na_2O concentrations, s_1 and s_2, as given below. Then

$s\mathrm{Na_2O}+m_1\mathrm{B_2O_3}+m_2\mathrm{GeO_2} = (s_1\mathrm{Na_2O}+m_1\mathrm{B_2O_3}) + (s_2\mathrm{Na_2O}+m_2\mathrm{GeO_2})$ (1). Since activity a^* is a product of activity coefficient γ and its concentration $s_1/(s_1+m_1)$ or $s_2/(s_2+m_2)$, $a^*_1=\gamma_1 s_1/(s_1+m_1)$ (2) and $a^*_2=\gamma_2 s_2/(s_2+m_2)$ (3). At equilibrium $a_1^* = a_2^*$ (4). And $s_1+s_2=s$ (5), $s+m_1+m_2=1$ (6). From equations (1) through (6) one can obtain the values of s_1 and s_2 for a given set of s, m_1 and m_2. In case where $\gamma_2/\gamma_1= 2$ is assumed, it means that the $\mathrm{Na_2O}$ concentration in the $\mathrm{Na_2O}$-$\mathrm{B_2O_3}$ sub-system is simply double as much as that in the $\mathrm{Na_2O}$-$\mathrm{GeO_2}$ sub-system. In the present study density or molar volume, thermal expansion coefficient, viscosity, glass transition temperature and glass forming regions under given cooling rates were computed from its composition in the $\mathrm{Na_2O}$-$\mathrm{B_2O_3}$-$\mathrm{GeO_2}$ ($\mathrm{SiO_2}$) system. There are some experimental data that can be compared with the theoretical values.

3.Results and discussion

3.1 Molar volume in the $\mathrm{Na_2O}$-$\mathrm{B_2O_3}$-$\mathrm{GeO_2}$ system

The molar volume V of glass in the $\mathrm{Na_2O}$-$\mathrm{B_2O_3}$-$\mathrm{GeO_2}$ system was computed from the molar volumes V_1 of the $\mathrm{Na_2O}$-$\mathrm{B_2O_3}$ system and V_2 the $\mathrm{Na_2O}$-$\mathrm{GeO_2}$ system by $V= x_1V_1+ x_2V_2$ (7), where $x_1 =s_1+m_1$ and $x_2=s_2+m_2$ are the molar fractions of the sub-system 1 and 2, respectively. We need of course molar volumes V_1 and V_2 for the sub-system as a function of $\mathrm{Na_2O}$ content. V_1 decreases with $\mathrm{Na_2O}$ but meets a small bump at 50mol% $\mathrm{Na_2O}$. V_2 decreases with $\mathrm{Na_2O}$ and has a minimum at 19mol% $\mathrm{Na_2O}$. Figure1 shows the molar volume isotherms in the $\mathrm{Na_2O}$-$\mathrm{B_2O_3}$-$\mathrm{GeO_2}$ system. Experimental data are few in this system. In the $\mathrm{Na_2O}$ fixed composition series observed values have shown an excellent agreement with the theoretical ones [1] .

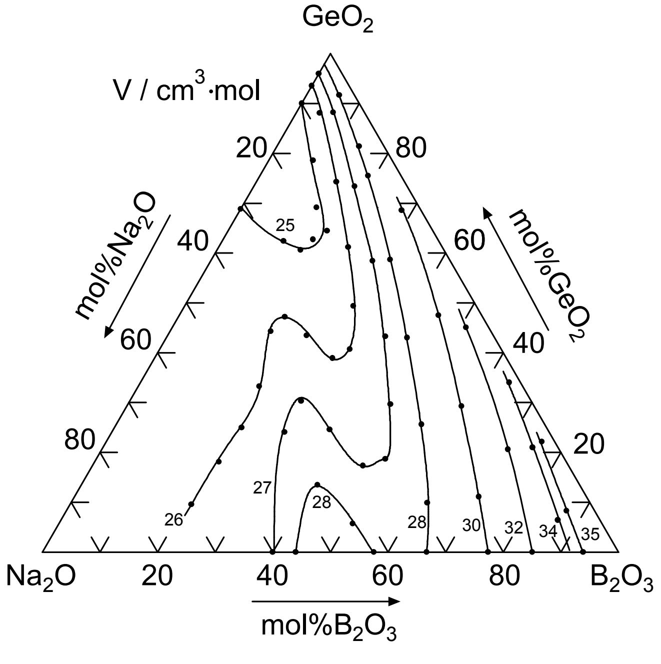
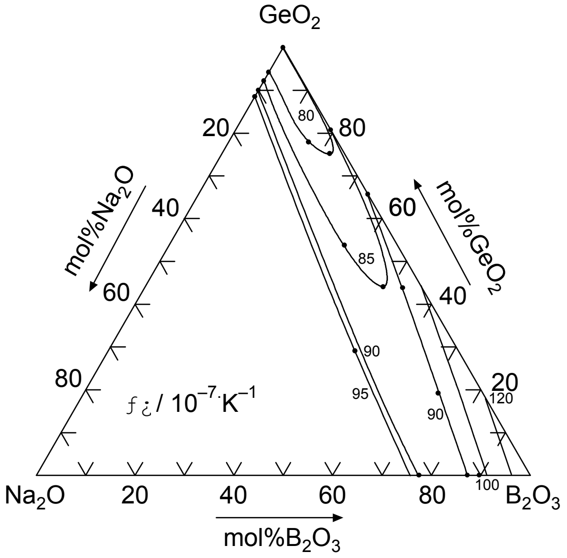


Figure 1

Volume isotherms in the $\mathrm{Na_2O}$-$\mathrm{B_2O_3}$-$\mathrm{GeO_2}$ system in the range V=25-35cm^3/mol.

3.2 Thermal expansion in the Na_2O-B_2O_3-GeO_2 system

To calculate the thermal expansion coefficient α of the system needed are Youngs' moduli E_1 and E_2 together with thermal expansion coefficients α_1 and α_2 of the sub-systems 1 and 2, respectively as a function of Na_2O content. $\alpha = (x_1E_1\alpha_1 + x_2E_2\alpha_2)/(x_1E_1+x_2E_2)$ (8). E_1 increases with Na_2O and reaches a maximum at 33mol% Na_2O. E_2 shows a maximum at 17mol%Na_2O. On the other hand α_1 decreases with Na_2O and reaches a minimum at 17mol% Na_2O. α_2 falls until 2mol% Na_2O is attained and after that α increases steadily. Combining these data, thermal expansion isotherms of α =80x10^{-7}-120x10^{-7} K^{-1} were obtained as shown in Fig.2.



Thermal expansion isotherms in the Na_2O-B_2O_3-GeO_2 system in the range α= 80x10^{-7} - 120x$10^{-7}K^{-1}$

3.3 Isothermal viscosity in the Na_2O-B_2O_3-SiO_2 system[2]

Isothermal viscosity η of the Na_2O-B_2O_3-SiO_2 system was calculated from the isothermal viscosities η_1 and η_2 of the sub-systems Na_2O-B_2O_3 and Na_2O-SiO_2, respectively, by eq.(9). $\log\eta = x_1\log\eta_1 + 0.967x_1x_2|\log\eta_1 - \log\eta_2| + x_2\log\eta_2$ (9), η_1 exhibits rather irregular compositional change with Na_2O content. At temperatures lower than 900°C it shows a maximum at around 20mol% Na_2O and at other temperatures it decreases monotonously. η_2 simply decreases with Na_2O. The isothermal viscosities at 1000°C in the range $\log\eta$/Pas=0-10 are shown in Fig.3. Strong influence of boron anomaly in the Na_2O -B_2O_3 sub-system is remained in the Na_2O-B_2O_3-SiO_2 system .

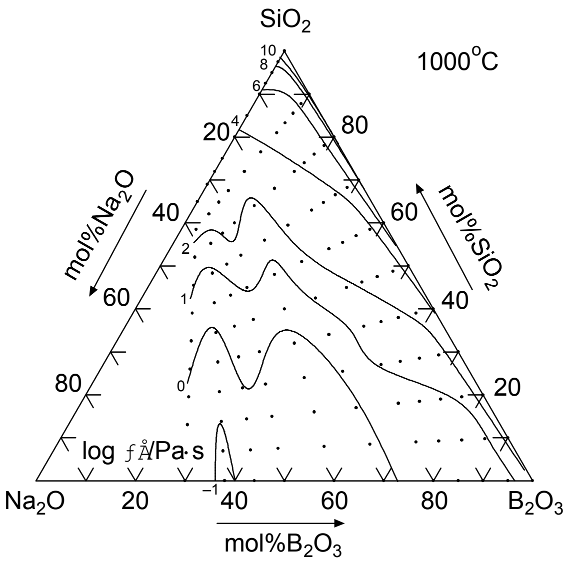


Figure 3 Isothermal viscosities of the Na_2O-B_2O_3-SiO_2 system at 1000°C in the range $\log\eta$/Pas=0-10

3.4 Glass transition point *Tg* in the Na_2O-B_2O_3-GeO_2 system[3]

Andrade type equation (10) applies at higher viscosity region $\log\eta$/Pas=9-13. $\log\eta = C + D/T$ (10), where T is temperature, and C and D are constants. Assuming the additive law among the characteristic constants C_1 and C_2, D_1 and D_2, intrinsic to the sub-system 1 and 2, respectively, C and D values are computed by $C=x_1C_1+x_2C_2$ (11) and $D=x_1D_1+x_2D_2$ (12). Tg, characteristic temperature of $\log\eta$/Pas=12, was computed from eq. (10) by $Tg=D/(12-C)$ (13). Fairly good agreement was obtained in the Na_2O fixed series.

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[1] R.Ota, J.Fukunaga and T.Wakasugi, in *Borate Glasses, Crystals & Melts*, edited byA.C.Wright, S.A.Feller and A.C.Hannon, The Society Glass Technology, 1997, pp.199-206.

[2] R.Ota, T.Wakasugi and K.Tanaka, Abstracts of Proc. XIXICG 2001,Edinburgh, Phys. & Chem. Glasses, in press.

[3] R.Ota and T.Wakasugi, Materials Science Research International, 6, [6], 9-14(2000).