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Specific heat and transport "anomalies" in mixed alkali glasses

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We show that changes in the relative mole fractions of Li_2O and Na_2O in alkali metaphosphate glasses lead to "anomalies" in the specific heat and structural relaxations. The heat capacity change between the liquid and glassy states, $\Delta c_p(T_g)$, at the calorimetric glass transition temperature, T_g, exhibits a minimum when the mole fractions of Li_2O and Na_2O are comparable. Moreover, systematic changes in the temperature dependence of the viscosity, η, i.e., changes in the "fragility" of the system, accompany these changes in mole fraction. This observed dependence of the "fragility" on the mixed alkali ion composition occurs in the absence of apparent changes in the covalent network connectivity which normally accounts for this behavior in glasses. © *1998 American Institute of Physics.* [S0021-9606(98)51342-6]

INTRODUCTION

The three-dimensional covalent network structure, and hence the melt flow characteristics, of inorganic glass formers, like SiO_2, GeO_2 or P_2O_5, can be modified with the addition of alkaline earth or alkali oxides. The effect of an alkali oxide, M_2O, is to depolymerize the long-range covalent glass network by converting oxygens that bridge neighboring network forming cations into nonbridging oxygens (NBO), now charge-compensated by the alkali ions, M^+. As the alkali oxide mole fraction increases, and the fraction of NBOs increases, the three-dimensional network becomes more depolymerized while the short-range tetrahedral structure of the network forming cations is generally preserved.

The temperature dependence of the viscosity changes in a predictable manner with these changes in the network connectivity. The well documented classification scheme developed by Angell and co-workers[1–7] identifies the behavior of the three-dimensional covalent network glass formers as "strong" because their viscosity-temperature relations are Arrhenius. The viscosity-temperature relation of a "strong" glass becomes increasingly non-Arrhenius with an increase in the fraction of NBO's. In the other extreme limit, the viscosity, η, of liquids like calcium potassium nitrate, $2Ca(NO_3)_2 \cdot KNO_3$, which are characterized by nondirectional ionic bonding, exhibit highly non-Arrhenius temperature dependencies. This behavior is classified as "fragile." The temperature dependence of the viscosities of polymers, small molecule organic liquids, and alkali modified oxide glasses are well described by the Vogel–Fulcher equation

$$\log \eta = A + \frac{B}{(T - T_0)}, \qquad (1)$$

where A, B, and T_0 are constants. The behavior of these substances is generally intermediate between that of the "strong" covalent network formers and the very "fragile" CKN glasses. Inorganic glasses are particularly interesting because their "fragilities" can readily be tailored. In the case of alkali modified oxide glasses, the "strong–fragile" behavior has been correlated with an increase in the magnitude of the heat capacity change, $\Delta c_p(T_g)$, between the liquid and glassy states at T_g. SiO_2 and GeO_2, for example, have vanishingly small values of $\Delta c_p(T_g)$. The value of $\Delta c_p(T_g)$ increases with the fraction of NBO's. The classification scheme, as discussed by Angell,[1–6] therefore refers to the ease with which the short and intermediate range structure of the glass can be broken down to accommodate flow.

In addition to changing the "fragility" of the glass by a "depolymerization" of its three-dimensional network structure, the same result might be achieved by taking advantage of changes in the coordination structure. For example, lanthanum borates ($La_2O_3 \cdot 3B_2O_3$) exhibit extremely "fragile" viscosity temperature behavior.[4] This is believed to be the result of changes in the coordination states of boron and of lanthanum in the glass melt.

In this paper we show that the "fragility" of alkali phosphates of the general form $1/2[(1-x) \cdot Na_2O + x \cdot Li_2O] + 1/2(P_2O_5)$ changes with the relative composition, x, of Na and Li ions while the total alkali content remains fixed. It is noteworthy that these changes in the $\eta - T$ behavior with x occur in the absence of changes in the covalent network connectivity, generally expected in oxide glass melts. We show that this behavior is correlated with minima in the specific heat capacity and with the ratio T_0/T_g, where T_g is the glass transition temperature. An apparent failure of the Adam–Gibbs theory,[8] which has provided a good description of the behavior of single alkali oxide modified glasses, to provide

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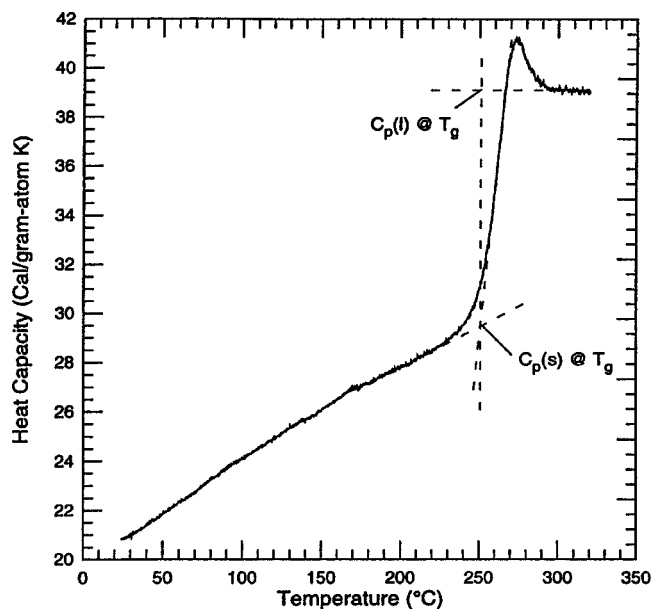
FIG. 1. A plot of heat capacity as a function of temperature is shown here for a mixed alkali metaphosphate glass of $x=0.4$.

TABLE I. The glass transition temperatures and Vogel–Fulcher parameters, T_0 and B, for different mixed alkali compositions, x, are shown here.

x	T_g(DSC)	T_g(visc)	T_0	B
1.0	606	595	488±5	2103±160
0.8	562	527	422±3	1774±80
0.6	531	496	348±4	2877±114
0.5	519	494	310±7	3687±256
0.4	521	492	328±4	3159±117
0.2	534	508	390±4	2246±105
0	560	550	442±20	2547±670

an accurate assessment of the general experimental results in this mixed alkali oxide glass is noted.

EXPERIMENT

The metaphosphate glasses were prepared by melting appropriate mixtures of reagent grade $NH_4H_2PO_4$, $NaPO_3$, and Li_2CO_3 in platinum crucibles after calcining at 220 °C and 550 °C to remove NH_3 and CO_2, respectively. Dry oxygen was subsequently bubbled through the melt at 900 °C for 1 h, after which the glasses were cast into steel molds, then annealed for hours at T_g.

Temperature dependent heat flow traces were obtained using a Perkin–Elmer DSC-7. In order to ensure that all the glasses had the same thermal history, each glass was first heated at a fixed rate, (e.g., 10 °C/min) to well above T_g (but below T_c) and held for a specified period of time then subsequently cooled at a fixed rate (e.g., 10 °C/min) below T_g and held. The samples were then reheated at a fixed rate of (~5 deg/min) while the data were collected. The temperature dependent heat capacities of the samples were determined by referencing the heat flow of the glass sample to the heat flow of sapphire. The methods used in Ref. 9 were followed in order to determine the heat capacities. Figure 1 shows a typical heat capacity trace for a glass containing 20% lithium ($x=0.4$). The values of the heat capacity in the liquid and glassy states, together with the T_g, are indicated on the graph.

Viscosities in the range from 4×10^{14} to 10^{10} Poise were determined using a theta beam bending viscometer while those in the range 10^6-10^9 Poise were determined by parallel plate rheometry using a Perkin–Elmer TMA7.[10] The standard protocol for measuring the viscosity of glasses was used to conduct the measurements. Table I shows the values of the Vogel–Fulcher parameters obtained from these data using a nonlinear regression analysis based on the Marquardt–Levenberg algorithm in the program Sigma-Plot.

RESULTS AND DISCUSSION

As discussed in the Introduction, $\Delta c_p(T_g)$ for a network glass former whose structure is modified by the addition of a single type of alkali oxide can be correlated with changes in "fragility." [2–8,11] The covalently bonded network formers, like SiO_2, exhibit vanishingly small changes in $\Delta c_p(T_g)$. The magnitude of $\Delta c_p(T_g)$ increases as the network becomes more depolymerized. Accompanying such an increase in "fragility" is a decrease in T_g. Our heat capacity measurements of the mixed alkali metaphosphates, Fig. 2, show that $\Delta c_p(T_g)$ exhibits a minimum when the number of unlike alkali cations is comparable, i.e., the fraction of Li_2O, $x \approx 1/2$. This minimum suggests that the glasses are "strongest" in the middle of the composition regime. It is interesting to contrast this behavior with that of mixed alkali tellurites. Mixed alkali tellurites exhibit no changes in $\Delta c_p(T_g)$ with composition.[12]

The results of a detailed analysis of the viscosity temperature relations for each of the metaphosphate glasses also reveal that the "fragility" of these glasses varies with composition and that the glasses are least "fragile" in the middle of the composition regime. Figure 3(a) shows the temperature dependence of the viscosity for three glass compositions, $x=0$, 0.4, and 0.8, plotted as a function of T_g/T. These glasses clearly have different temperature dependencies; the compositions at $x=0$ and 0.8 exhibit more "fragile" behavior than the composition at $x=0.4$. In this figure, the glass transition temperature is chosen to be the temperature at which the viscosity, η, is 10^{13} Poise in order to be consistent with the "fragility" plots generally used to illus-
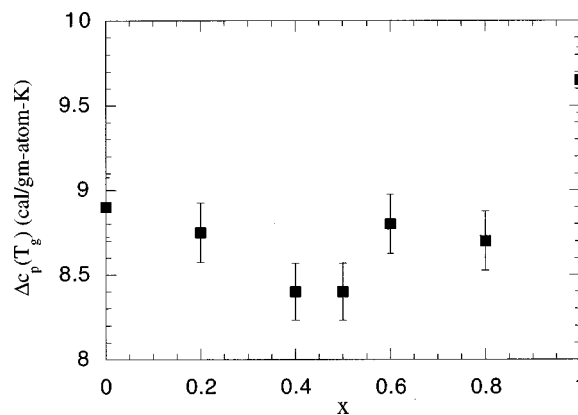

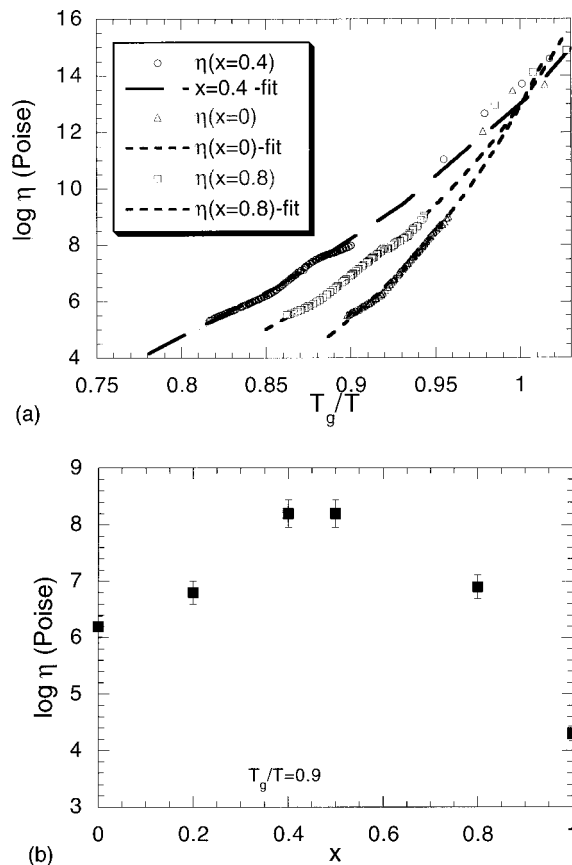FIG. 2. The dependence of $\Delta c_p(T_g)$ on x is depicted here.

FIG. 4. A plot of T_g vs x is shown here. T_g was obtained using two different procedures, as explained in the text.

FIG. 3. (a) The temperature dependencies of the viscosities of three metaphosphate glass compositions, $x=0$, 0.4, and 0.8 are shown here. The lines drawn through the data are fits using Eq. (1). The values of the fitting parameters, B and T_0, are shown in Table I. (b) The dependence of the viscosity underconditions of $T_g/T=0.9$ is shown here.

glasses approach that of the pure analogs (i.e., values of x $=0$ and 1).

A further analysis of this data will require revisiting Eq. (1) and recasting it in a new form:

$$\log \frac{\eta}{\eta(T_g)} = -(1-\alpha)m\left[\frac{(1-T_0/T_g)}{(1-\alpha T_0/T_g)}\right]. \qquad (2)$$

In this equation, $\eta(T_g)$ is the viscosity at T_g and α $=T_g/T$. The so-called fragility index is identified as

$$m = \frac{BT_g}{[T_g(1-T_0/T_g)]^2}. \qquad (3)$$

The temperature dependence of the slope of the $\eta-T$ relation at T_g has been formally identified as the fragility index $m=E_\eta/2.3T_g$ and $E_\eta=d\eta/d(T_g/T)$. It is well accepted that m is a measure of the ''fragility'' of the glass; a larger value of m denotes a larger degree of ''fragility.''[7] Using the values of T_0, T_g, and B from Table I, the fragility index was calculated for each glass composition. It is clear from these data in Fig. 6 that m approaches a minimum near $x\approx0.5$. This is consistent with the foregoing discussion that the behavior of the glasses becomes more fragile as x approaches 0 or 1. Moreover, the maximum which the viscosity exhibits at $x\approx1/2$, as shown in Fig. 3(b), is driven primarily by the minimum in m.

trate ''strong-fragile'' behavior in glasses.[1–7] This choice is rationalized on the basis that, as discussed by Angell, a large number of inorganic oxide melts have viscosities of approximately 10^{13} Poise at T_g. Of course, the more accurate, and generally accepted, means by which the glass transition temperature of any material is determined is by differential scanning calorimetry (DSC). A comparison of T_g's obtained using DSC and those obtained using the viscosity criterion is shown in Fig. 4. While the glass transition temperatures obtained using both techniques exhibit the same dependence on composition, the T_g's obtained using DSC are higher. Throughout the remainder of this paper we will use the T_g's measured using DSC. It should be noted, however, that the general conclusions drawn from these results remain the same, regardless of the set of T_g's used.

The parameters obtained by fitting Eq. (1) to the temperature dependent viscosity measurements using a nonlinear regression analysis, based on the Marquardt–Levenberg algorithm, are shown in Table I. Further insight into the behavior of these glasses can be obtained by examining the parameter T_g/T_0. Figure 5 shows that T_g/T_0 exhibits a minimum at $x\approx1/2$. The ratio T_g/T_0 should approach unity for fragile glasses.[2,3,5] These data clearly show that the glasses become more fragile as the composition of the
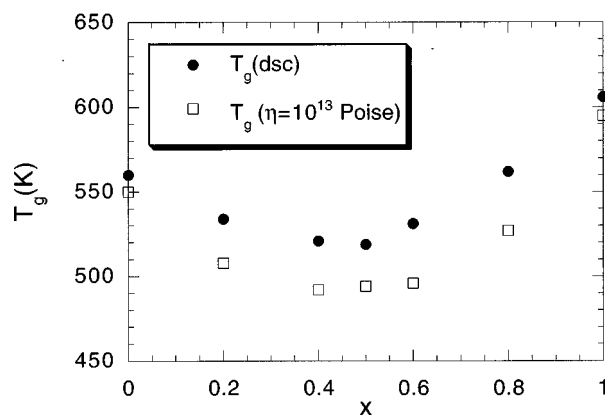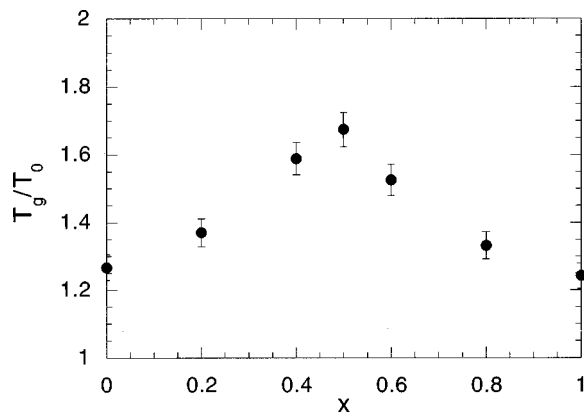

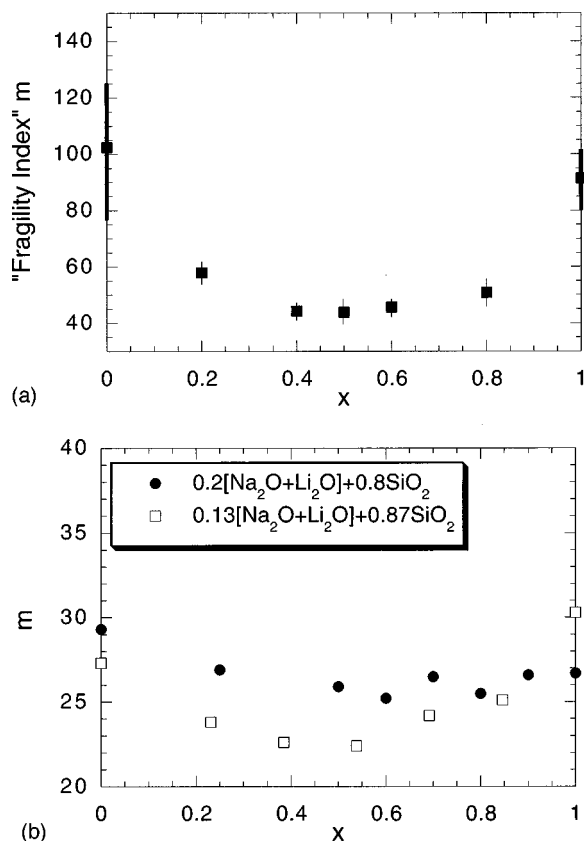FIG. 5. The compositional dependence of T_g/T_0 is shown here.

FIG. 6. (a) The fragility index, m, calculated using Eq. (3) and the experimentally determined parameters, is shown to exhibit a minimum at $x \approx = 0.5$. (b) The dependence of M on the composition of mixed alkali silicates is shown here. These values of m were determined from an analysis of the data in Refs. 23 and 24. These data sets also show that T_g exhibits a minimum.

It is worthwhile to examine the molecular structure of these glasses. A combination of flow birefringence and spectroscopic measurements indicate that the metaphosphate structure is chainlike,[13–16] composed of P–O–P chains. Each structural unit of the chain comprises a tetrahedral arrangement of oxygen anions around a phosphorus cation and the "chain" is formed by the linkage of two corners of each tetrahedron through the so-called bridging oxygens. The remaining two nonbridging oxygens are neutralized by the alkali ions. Further, the alkali metaphosphate glasses exhibit no distinct changes in the phosphate network (with the exception of changes in the average bond lengths and angles), either with different alkali ions or when the glass is heated through T_g; viz., a metaphosphate chain topology is retained. Consequently, there is no way to rationalize this behavior in terms of obvious structural changes involving changes in the network connectivity.

Mixed alkali borates and mixed alkali tellurites have recently been shown to exhibit changes in the fragility (changes in the η–T dependence) as one cation is substituted for another.[12,14–19] This behavior, however, has been shown to be the result of changes in the network connectivity. Accordingly, the ratio of BO_3 and BO_4 units in alkali borates[18] and the ratio of TeO_4 and TeO_3 units in alkali tellurites[12,20] have been shown to depend on the relative con-

centrations of alkali ions. Both borate and tellurite networks change as the glass is heated through T_g. These additional network contributions evidently do not seem to contribute to the dynamics in the metaphosphates. It is noteworthy that in silicate glasses, for example, the relative concentrations of Si tetrahedra with 2, 3, and 4 bridging oxygens depends on field strength of the alkali counterion[20,21] and these site distributions change when the glasses are heated above T_g.[22] We have analyzed the relevant data of mixed alkali silicates. There are clear, yet less pronounced, changes in the "fragility" of mixed alkali silicates.[23] Our analysis of viscosity data[23,24] for Na_2O and Li_2O mixed alkali silicates reveal that m exhibits a minimum in the middle of the composition regime, Fig. 6(b). Like the metaphosphates, the glass transition temperature of the mixed alkali silicates also exhibits a minimum.[23,24] Clearly, differences in the polarizabilities between bonds formed by Na and Li ions appear to have a nontrivial effect on the glass properties. In the case of the metaphosphates changes in the bond angles and bond lengths are documented,[14–16] whereas more significant changes in the structure of borates, silicates, and tellurites are observed. These changes in the intermediate range structure caused by relative changes in the mixed alkali ion mole fraction have a significant influence on the fragility of the glasses.

One might examine these observations in light of the Vogel–Fulcher equation and the work of Adam and Gibbs.[8] The Adam–Gibbs model has provided important guidance for understanding the correlations between the heat capacity changes at T_g and the viscosities of the glasses.[1,3,5–7] They proposed that if the mechanism of viscous flow occurs by the cooperative dynamics of groups, or clusters of particles, and that if each group relaxed independently of each other then the relation between the relaxation time of the minimum sized group and the configurational entropy, S_c, is

$$\log \tau = \log \tau_0 + \frac{K}{TS_c}. \tag{4}$$

Here K is a constant related to the free energy barrier which must be surmounted by each group of particles. Note that the viscosity $\eta = G_\infty \tau$, where G_∞ is the modulus which can be obtained from stress relaxation measurements, and $1/\tau_0$ might be identified as an attempt frequency. The configurational entropy, S_c, can be expressed in terms of the heat capacity

$$S_c = \int_{T_0}^{T} \frac{\Delta c_p(T)}{T'} \, dT'. \tag{5}$$

By taking advantage of a commonly used empirical relationship for glasses,[1,5] $\Delta c_p(T) = \Delta c_p(T_g) T_g / T$, the Vogel–Fulcher relation is obtained,

$$\log \tau = \text{const} + \frac{J}{T - T_0}, \tag{6}$$

a well known result.[6] In this equation, J should correspond to the parameter B in Eq. (1). This analysis provides a means by which one might be able to determine the compositional dependence of the constant J in terms of measurable parameters. From the above analysis
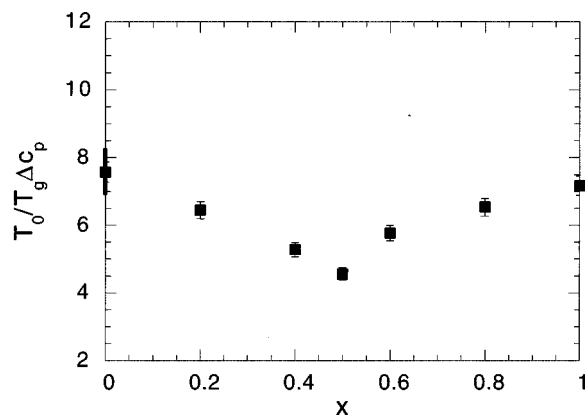
FIG. 7. The parameter $T_0/T_g \Delta c_p(T_g)$ is shown to exhibit a minimum at $x \approx 1/2$.

$$J \propto \frac{T_0}{T_g \Delta c_p(T_g)}. \tag{7}$$

We encounter a curious contradiction when we plot the compositional dependence of the parameter $T_0/T_g \Delta c_p(T_g)$ and compare it with B. Figure 7 shows that J, or equivalently $T_0/T_g \Delta c_p(T_g)$, exhibits a minimum, whereas Fig. 8 shows that B, obtained from the viscosity temperature relations (Table I) exhibits a maximum. The compositional dependence of T_g/T_0 has a strong influence on J, considerably larger than that of $\Delta c_p(T_g)$. Considering the η vs T behavior which clearly shows that these glasses become more fragile as x approaches 0 or 1, these results raise interesting questions about the applicability of the Adam–Gibbs model in this case.

The differences between ''strong'' and ''fragile'' glasses are generally believed to be related to the ease with which the glass can flow. In oxide glasses this is commonly identified as the ease with which the structure is ''broken down'' to accommodate flow. For example, small values $\Delta c_p(T_g)$ are measured for SiO_2, whereas larger values are found for more fragile glasses. The structure of these systems is clearly characterized by the three-dimensional covalent network where flow is facilitated by the breaking of covalent and ionic bonds and subsequent bond-interchange mechanisms.[25] 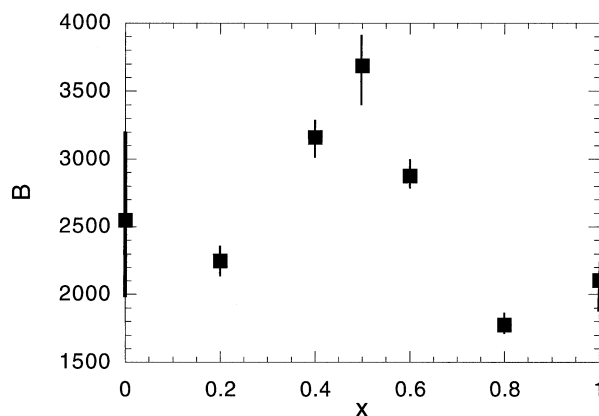In the case of the mixed alkali metaphosphates, flow is dominated to a lesser extent by the breaking of covalent bonds since the covalent structure is chainlike. Ionic bonds play a considerably greater role in the flow processes.

It is worthwhile to address this unusual behavior of these mixed alkali glasses in terms of a historical context.[26–32] Below the glass transition temperature there exists a well documented transport ''anomaly'' in structurally disordered mixed alkali conductors. Here the ionic conductivity, σ, in glassy ionic conductors of the general form, $y[x \cdot M_2O + (1-x)M_2'O] + (1-y) \cdot$ (network former, i.e., SiO_2, P_2O_5), where $M_2'O$ is a second alkali oxide, exhibit deep minima in the regime where the number of unlike cationic species is comparable.[30–33] The minimum in the conductivity is orders of magnitude below the values of their single alkali counterparts. This effect increases as the disparity in size of the alkali ions increase and it decreases with increasing temperature. It is noteworthy that relaxations due to these cations can account for as much as a 30% decrease in the elastic modulus of the glass at temperatures just below T_g.[31,32] The prevailing spectroscopic studies suggest that the unlike cations are distributed homogeneously throughout the network and that each type of cation creates and maintains a distinct environment.[33–35] Despite much work on this topic, there is still no generally accepted theoretical explanation of the conductivity ''anomaly.'' Recently, however, computer simulations based on a model in which each mobile ion creates and maintains its own distinct environment after each displacement, i.e., a memory effect, have had success at shedding some light on this phenomenon.[26,27]

CONCLUDING REMARKS

We showed that the substitution of Li with Na ions in a mixed alkali metaphosphate glass had an important effect on the ''fragility'' of the material. Specifically, we showed that the heat capacity change which occurred as the temperature of the material decreased from the liquid to the glass state, $\Delta c_p(T_g)$, underwent a minimum when the mole fractions of Li_2O and Na_2O were comparable. Experimental parameters, independently determined from the viscosity temperature relations, strongly indicate that the glasses became more ''fragile'' as the composition approached that of the pure single alkali oxide modified analogs. The change in fragility of the mixed alkali modified glasses with composition appears to be quite general, particularly in light of the fact that other glass systems, silicates, borates, and tellurites, show minima in m. It is noteworthy that these changes in ''fragility'' are independent of structural details of the systems. The metaphosphate glass is unique since the ''fragility'' was manipulated in the absence of apparent changes in the covalent network topology which usually accounts for this behavior. We also show a failure of the Adam–Gibbs theory to fully account for this interesting ''mixed alkali'' phenomenon.

ACKNOWLEDGMENTS

FIG. 8. The dependence of B on x is shown here.

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