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Energetics of the Charge-Coupled Substitution $Si^{4+} \rightarrow Na^{+} + T^{3+}$ in the Glasses $NaTO_2$–SiO_2 (T = Al, Fe, Ga, B)

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Heats of solution in molten $2PbO \cdot B_2O_3$ at 973 K are reported for glasses $xNaT^{3+}O_2$–$(1 - x)SiO_2$ for T = Fe, Ga. These measurements, combined with previous data for T = Al, B, give a relative measure of the enthalpy of the charge-coupled substitution $Si^{4+} \rightarrow Na^{+} + T^{3+}$. The heats of solution become more endothermic with increasing x for $x \leq 0.5$ and exhibit a maximum near $x = 0.5$. This indicates an exothermic enthalpy for the substitution and an overall stabilization of the glasses. The degree to which the glasses are stabilized decreases in the order Al > Ga > Fe > B. On the basis of molecular orbital calculations, X-ray scattering, and Raman spectroscopy, it is argued that this trend is primarily due to a decrease in the range of energetically favorable T–O–T bond angles as Al, Ga, Fe, and B are substituted for Si. [Key words: glass, substitution, enthalapy, charge, couplers.]

I. Introduction

In previous studies,[1,2] thermochemical measurements on a series of aluminosilicate glasses examined the interaction of nonframework cations with a fully polymerized aluminosilicate framework. Heats of solution in molten $2PbO \cdot B_2O_3$ near 973 K were measured in glasses $M_{1/n}AlO_2$–SiO_2 (M = Li, Na, K, Rb, Cs, Mg, Ca, Sr, Ba, Pb) giving a relative measure of the enthalpy of the charge-coupled substitution $Si^{4+} \rightarrow Al^{3+} + 1/n\ M^{n+}$. In the present study, we extend this approach to the charge-coupled substitution $Si^{4+} \rightarrow Na^{+} + T^{3+}$ in glasses $NaT^{3+}O_2$–SiO_2 (T = Al, Ga, Fe, B) where Na^{+} is maintained as the nonframework cation while the substituting framework cation is varied. The calorimetric data for T = Al and B were reported previously;[3–5] the data for T = Ga and Fe are presented in this paper. Systematics in the enthalpies of solution and the derived heats of mixing are compared with those of the previous studies, correlated with the results of ab initio molecular orbital calculations,[6,7] and discussed in terms of glass structure and bonding.

II. Experimental Procedure

(1) Sample Preparation

Glass samples $xNaFeO_2$–$(1 - x)SiO_2$ (x = 0.125, 0.25, and 0.33) were obtained from D. Dingwell and their preparation and analysis is described elsewhere.[8] The series $xNaGaO_2$–$(1 - x)SiO_2$ (x = 0.1, 0.25, 0.4, and 0.5) was prepared from reagent-grade SiO_2, Ga_2O_3, and Na_2CO_3, each dried overnight at 400 K. $NaGaO_2$ was first produced from the reaction $Na_2CO_3 + Ga_2O_3 = 2NaGaO_2 + CO_2$. The reactants were mixed manually and then ground in an automatic agate mortar. This mixture was initially heated to 673 K, and was then raised in 100 K steps every hour to 973 K where it remained overnight. The product was confirmed to be $NaGaO_2$ through X-ray diffractometry (XRD). $NaGaO_2$ and SiO_2 were then mixed in the desired proportions and heated in a platinum crucible inside a quench furnace. To minimize Na loss during synthesis, it was desirable to maintain as low a temperature as possible while fusing the samples. The appropriate fusion temperature for each composition was determined by repeatedly grinding, heating, and quenching the samples from various temperatures and examining the products for crystalline phases through both optical microscopy and XRD. Once the fusion temperatures were determined, new samples (typically ~10 g) were ground, fused, and ground again before the final fusion. The final temperatures at which the samples were fused were 1478, 1488, 1729, and 1918 K for x = 0.5, 0.4, 0.25, and 0.1, respectively. No significant weight loss was observed during synthesis, indicating that Na loss was not significant. This was confirmed by electron microprobe analysis (EMA) as described below.

(2) Analysis

Each of the gallosilicate glasses was examined by optical microscopy and XRD and no crystalline material was detected.

EMAs were also made on each of the samples to look for inhomogeneities as well as to confirm the compositions. The measurements were performed on a microprobe† in the Geology Department at Rutgers University using a probe current and probe voltage of 3 nA and 15 kV, respectively. To minimize Na loss during the actual probe measurements, a series of line scans with various collection times were performed on a well-characterized Na-bearing glass.[9] For collection times up to 20 s, no changes in the Na count rate were observed. Furthermore, the line scans on the $x = 0.1$ sample using collection times of 10 and 20 s gave results which were identical within experimental error (~1%).

All of the samples were slightly inhomogeneous with variations in Na, Ga, and Si content on the order of 1% to 2%. The inhomogeneity increased with increasing x. In addition, the $x = 0.1$ sample had a small amount (~1%) of SiO_2 (cristobalite) inclusions. The compositions and standard deviations determined from EMAs are given in Table I with the nominal compositions.

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†Model 8600 Superprobe, JEOL, Ltd., Tokyo, Japan.

Table I. Compositions of $NaGaO_2 \cdot SiO_2$ and $NaFeO_2 \cdot SiO_2$ Glasses

Nominal (mole fraction)			Analyzed (mole fraction)*			
Na_2O	Ga_2O_3	SiO_2	Na_2O†	Ga_2O_3†	SiO_2†	Totals‡
0.05	0.05	0.90	0.054(0.002)	0.055(0.006)	0.891(0.003)	0.995(0.006)
0.125	0.125	0.75	0.123(0.007)	0.123(0.003)	0.755(0.003)	0.997(0.007)
0.20	0.20	0.60	0.203(0.005)	0.193(0.007)	0.604(0.004)	0.987(0.011)
0.25	0.25	0.50	0.255(0.012)	0.233(0.011)	0.512(0.011)	0.982(0.009)
Na_2O	Fe_2O_3	SiO_2	Na_2O†	Fe_2O_3†	SiO_2†	Totals‡
0.0625	0.0625	0.8750	0.0641	0.0649	0.8710	0.9745
0.125	0.125	0.750	0.128	0.127	0.745	1.0070
0.167	0.167	0.667	0.177	0.174	0.649	1.0051

*Electron microprobe analysis (see text for details). †Analyses normalized to 100% for comparison with nominal values. Numbers in parentheses are standard deviations on six determinations. ‡Totals of weight percents of the oxides (oxygen by difference).

(3) Calorimetry

Solution calorimetric measurements in molten $2PbO \cdot B_2O_3$ at 973 K (~30 mg of sample in ~30 g of flux) were performed in a Calvet-type twin calorimeter.[2,10] Prior to dissolution in the lead borate flux, the sample was positioned above the flux at 973 K for 4 to 12 h while the system equilibrated thermally. To check that the glasses did not devitrify during this period, dummy runs were performed in which the sample was removed from the calorimeter after the equilibration period. The product was then examined for crystalline phases by optical microscopy and XRD. Only two compositions, $Na_{0.33}Fe_{0.33}Si_{0.67}O_2$ and $Na_{0.5}Ga_{0.5}Si_{0.5}O_2$ showed evidence of devitrification. The heats of solution of these samples were obtained through a combination of drop solution and transposed-temperature-drop calorimetric measurements. In a drop-solution experiment, the sample is dropped from room temperature into the solvent at 973 K, giving the heat content from room temperature to 973 K plus the heat of solution at 973 K. In a transposed-temperature-drop experiment, the sample is dropped from room temperature into the calorimeter at 973 K with no solvent present, giving the heat content from room temperature to 973 K plus the heat effect associated with any transformations at 973 K. As long as no devitrification takes place on the time scale of a drop experiment (<1 h), the latter contribution is zero, and the difference between the two measurements gives the heat of solution. This was the case for these glasses. Because the Fe-bearing glasses contain essentially all Fe^{3+} and this oxidation state is maintained on dissolving the glasses in molten lead borate in air, oxidation–reduction effects do not complicate the observed enthalpies.

III. Results

The new calorimetric data are presented in Table II and Fig. 1 with the results obtained previously on xNaAlO$_2$–(1 − x)SiO$_2$ and xNaBO$_2$–(1 − x)SiO$_2$.[3-5] The general shape of the enthalpy-of-solution curves are similar for the $M^{n+}_{1/n}$-AlO_2–SiO_2 and $NaTO_2$–SiO_2 systems (see Fig. 1). In all of the glasses, for $x \leq 0.5$, the heats of solution become increasingly endothermic with increasing x and tend to exhibit a maximum near $x = 0.5$, particularly in the Al and B systems. This maximum implies an exothermic heat of mixing for the reaction $x\mathrm{NaTO_2} + (1 - x)\mathrm{SiO_2} = \mathrm{Na}_x\mathrm{T}_x\mathrm{Si}_{1-x}\mathrm{O_2}$. As discussed by Roy and Navrotsky,[2] dissolution of these framework silicate glasses in lead borate breaks up the framework into isolated tetrahedra and alkali cations dissolved in a borate matrix. Thus, a comparison of heats of solution gives a relative measure of the strength of bonding in the glasses. Following the procedure of Roy and Navrotsky,[2] we can define a heat of stabilization for the substitution by

$$-\Delta H_{stab} = (\Delta H_{sol}(\mathrm{SiO_2}) - \Delta H_{sol}(\mathrm{Na}_x\mathrm{T}_x\mathrm{Si}_{1-x}\mathrm{O_2}))/x$$

For $x < 0.5$, where the increase in ΔH_{sol} is approximately linear in x, ΔH_{stab} is essentially the slope of ΔH_{sol} vs x. The values of ΔH_{stab}, given in Table III, increase in the order B, Fe, Ga, Al. We now attempt to understand these systematics in terms of glass structure.

IV. Discussion

In the system $M^{n+}_{1/n}AlO_2$–SiO_2, Roy and Navrotsky[2] found that ΔH_{stab} decreased with increasing electronegativity or decreasing basicity of the M^{n+} cation. ΔH_{stab} varies smoothly with the field strength, z/r, of the M^{n+} cation, where z is the formal ionic charge and r is the Shannon and Prewitt ionic radius.[11] We found that when ΔH_{stab} is plotted versus r/z (see insert to Fig. 2), a linear correlation is obtained for the Roy and Navrotsky data. The correlations suggest that the magnitude of ΔH_{stab} is controlled by the ability of the nonframework cation to perturb the bridging oxygen, thereby weakening the T–O–T bonds.[2,7]

This conclusion is supported by the results of ab initio molecular orbital studies on T–O–T groups,[6] which show that the coordination of a monovalent or divalent cation with the bridging oxygen results in an increase in length and consequent weakening of the T–O bonds. The degree to which these bond lengths are increased correlates with the tendency of the M^{n+} cation to form a strong covalent bond with the oxygen. Navrotsky *et al.*[1,7] used the results of the molecular orbital studies to show that ΔH_{stab} is indeed a smooth function of the change in T–O bond lengths induced by M^{n+} cations.

In the present study, the variation is in the framework cation rather than in the network modifier. ΔH_{stab} does not vary smoothly with z/r (or r/z) of the framework cation or the bond length (see Table III and Fig. 2). Indeed, although the Ga–O and Fe–O distances are longer than that of Al–O (and the bonds accordingly weaker), the tetrahedral B–O bond is substantially shorter and stronger than that of either Al–O or Si–O. Yet the magnitude of ΔH_{stab} is smallest in the B-bearing system, largest in the Al-bearing system, and intermediate in the Fe- and Ga-bearing systems. Moreover, if the perturbation of the tetrahedral framework were the controlling energetic factor, one might hypothesize that Na can perturb T–O bonds more as they become weaker, i.e., in the series B,

Table II. Enthalpies of Solution in Molten $2PbO \cdot B_2O_3$ of Glasses in the Systems xNaT^{3+}O$_2$–(1 − x)SiO$_2$

x	ΔH_{sol} (kJ·mol^{-1})*	$-\Delta H_{stab}$ (kJ·mol^{-1})
	T = Fe	
0.000	−11.31 ± 0.04 (6)	
0.125	−6.24 ± 0.13 (6)	40.5
0.250	0.01 ± 0.23 (7)	46.5
0.333†	2.32 ± 0.73 (8)	40.9
	T = Ga	
0.100	−5.78 ± 0.05 (6)	55.3
0.250	1.30 ± 0.13 (6)	46.9
0.400	9.61 ± 0.13 (6)	52.3
0.500†	13.95 ± 0.13 (6)	50.5

*Error is standard deviation of mean; number of experiments performed is in parentheses. †Combination of transposed-temperature-drop and drop solution calorimetric experiments, eight of each.

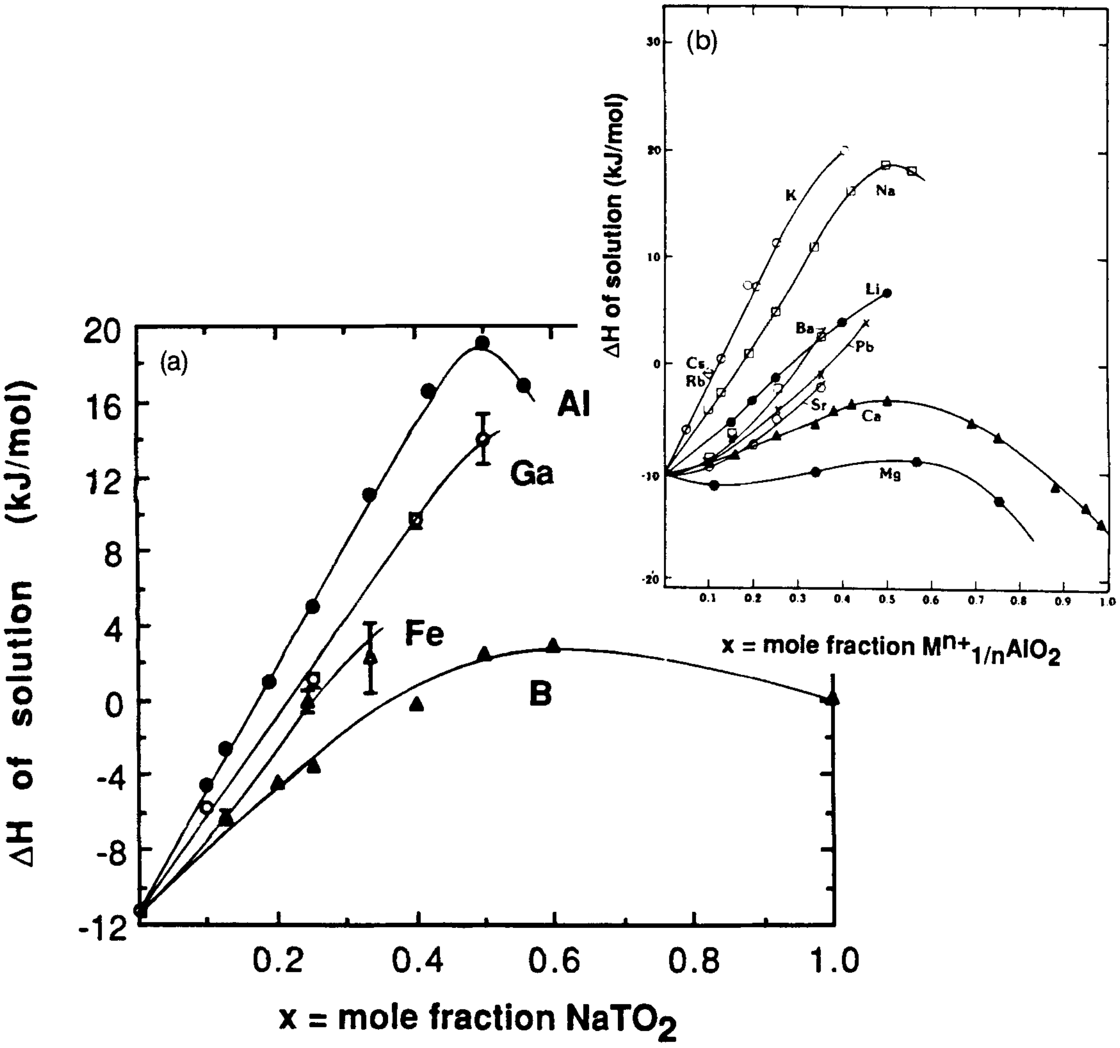

Fig. 1. (a) Enthalpies of solution of glasses in the system $x\mathrm{NaT^{3+}O_2}$–$(1-x)\mathrm{SiO_2}$ in molten $2\mathrm{PbO}\cdot\mathrm{B_2O_3}$ near 973 K (kJ per 2 mol of oxygen). Data for T = Al from Refs. 4 and 5; data for T = B from Ref. 3. Error bars for T = Ga, Fe are plus or minus one standard deviation. (b) Insert shows data for $x\mathrm{M}^{n+}_{1/n}\mathrm{AlO_2}$–$(1-x)\mathrm{SiO_2}$ (Ref. 2).

Si, Al, Ga, Fe and that ΔH_{stab} should decrease in magnitude in the order B, Al, Ga, Fe. This is clearly not the case, with the $\mathrm{NaBO_2}$ substitution showing, instead, the least stabilization. Therefore, one needs to consider other factors, particularly changes in network geometry due to the T cation itself rather than effects due to the weak perturbation of the tetrahedral framework by Na.

In the system $x\mathrm{M}^{n+}_{1/n}\mathrm{AlO_2}$–$(1-x)\mathrm{SiO_2}$, it is generally agreed that Al substitutes tetrahedrally for Si, maintaining a fully polymerized framework.[12–16] Consequently, it is possible to examine the effects of varying M without addressing changes in the polymerization of the framework brought about by this substitution. To compare the calorimetric data for the various glasses in the system $x\mathrm{NaT^{3+}O_2}$–$(1-x)\mathrm{SiO_2}$ (T = Al, Ga, Fe, B), it is necessary to address the degree to which the substitution of the other trivalent cations for Si depolymerizes the framework.

Spectroscopic studies on the Ga- and Fe-bearing systems show that, like Al, these two cations substitute tetrahedrally for Si, leaving the framework fully polymerized (for a review, see Ref. 8). In contrast, studies on the B-bearing system have identified both tetrahedrally and trigonally coordinated $\mathrm{B^{3+}}$. Using ^{11}B NMR (nuclear magnetic resonance) spectroscopy on $x\mathrm{NaBO_2}$–$(1-x)\mathrm{SiO_2}$ glasses, Yun and Bray[17] concluded that $\mathrm{B^{3+}}$ is tetrahedrally coordinated in the framework for $x < 0.2$ but that, beyond $x = 0.2$, an increasing fraction of $\mathrm{B^{3+}}$ cations form tetrahedrally or trigonally coordinated groups isolated from the silicate framework. Geisinger *et al.*[18] found that 29% of the $\mathrm{B^{3+}}$ in $\mathrm{Na_{0.25}B_{0.25}Si_{0.75}O_2}$ was in trigonal coordination and that some was in trigonal coordination throughout the

Table III. Parameters for Substitution $\mathrm{Si^{4+}} = \mathrm{Na^+} + \mathrm{T^{3+}}$

	Si	Al	Ga	Fe	B
$-\Delta H_{stab}$ (kJ·mol^{-1})		56	51	43	30
Radius of $\mathrm{T^{3+}}$ (nm)	0.026	0.039	0.047	0.049	0.002
T–O bond length (nm)	0.160	0.175	0.180	0.170	0.137
Predominant ring size in glass	6	6	6, 4, 3	6, 4, 3	6, 3
Optimum or average T–O–Si angle (deg)	144–150	145	?	140	125–130
Reference	7, 20, 11	2, 7, 11	22–24	21, 24, 11	3, 7, 25, 11

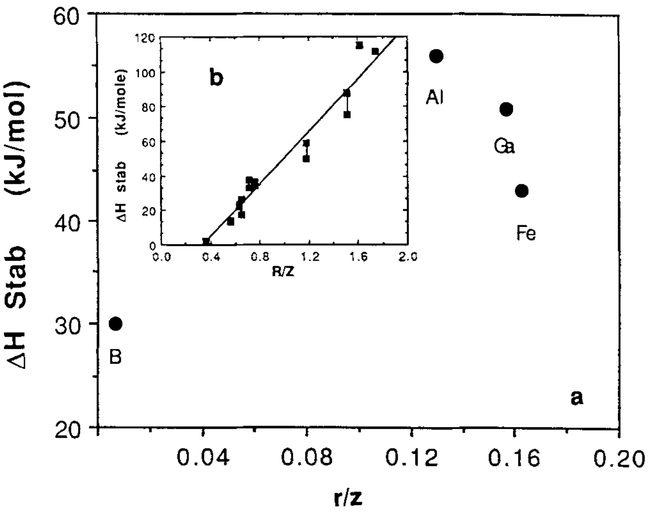

Fig. 2. (a) Enthalpy of stabilization from Table II versus r/z for glasses in the system $NaTO_2-SiO_2$, where r is the Shannon and Prewitt ionic radius[11] of T and z is the formal charge. (b) Insert shows the same comparison for the system $M^{n+}_{1/n}AlO_2-SiO_2$.[1,2]

$NaAlSi_3O_8-NaBSi_3O_8$ glass system. That join showed positive heats of mixing.[18] A tendency toward clustering into borate-rich and silicate-rich regions occurs frequently in borosilicate glasses and may be destabilizing along the SiO_2-NaBO_2 join.

Using molecular orbital techniques, Geisinger *et al.*[6] calculated curves of potential energy as a function of T–O–T angle for a number of cation clusters, including (Si–O–Si), (Si–O–Al), and (Si–O–B). For (Si–O–Si) and (Si–O–Al) the potential energy curves have broad, shallow minima, whereas that of (Si–O–B) is much deeper and narrower. These results are in agreement with observed T–O–T angle distributions in solids. In amorphous SiO_2 the Si–O–Si angle takes on values ranging from 130° to 180° (Ref. 19), and the total range of Si–O–Si angles observed in crystalline framework silicates in various solids is 60°.[6] In contrast, the total range of Si–O–B angles observed in solids is only about 22°. In the calculations of Geisinger *et al.*,[6] the decreased range of energetically favorable angles observed in Si–O–B (and Si–O–Be) is correlated with a decrease in the optimum T–O–T angle determined from both potential energy curves and from the average angle observed in solids. Thus, the optimum bonding geometries for silicate and borosilicate frameworks are significantly different.

These observations provide a basis for understanding the calorimetric data (see Table III). In the system $NaT^{3+}O_2-SiO_2$ the substitution of Fe, Ga, or B (and, to a minor extent, Al) results in a decrease in the optimum T–O–T angle and a narrowing of the range of energetically favorable T–O–T angles. Such a decrease of angle has been observed directly by X-ray techniques for Fe by Henderson *et al.*[20] and for Ga by Iwamoto *et al.*[21] A similar narrowing has been suggested for B, both through molecular orbital calculations and observed distributions of Si–O–B and B–O–B angles in solids as described above. The Raman spectral data of Henderson *et al.*[22] and Virgo *et al.*[23] provide further evidence of this effect for Al, Fe, and Ga. Henderson *et al.*[22] observed changes in intensity and shifts to lower frequency in the T–O–T stretching bands of $NaAlO_2-SiO_2$ and $NaGaO_2-SiO_2$ glasses. These were attributed to the preferential bonding of Ga and Al into three-membered rings. Virgo *et al.*[22] obtained similar data on the systems $NaTO_2-SiO_2$ (T = Al, Ga, Fe). They found that the magnitude of the effects increased in the order Al < Ga < Fe.

In three-membered rings, the optimum T–O–T angle, either as calculated by molecular orbital techniques or as observed in solids, is 10° to 20° less than that of the four- or six-membered rings[24] which are the most common in silicates. The molecular orbital calculations[24,25] predict that the three-membered rings are less stable than the four- or six-membered rings, but, as pointed out by Henderson *et al.*,[22] the correlation between increasing T–O bond length and decreasing T–O–T angle, both calculated and observed,[24] implies that the substitution of the larger ions (Al^{3+}, Ga^{3+}, or Fe^{3+}) for Si^{4+} would tend to stabilize the smaller rings with their reduced T–O–T angles. The substitution of B for Si also stabilizes three-membered rings because B–O–Si and B–O–B have much narrower optimum angles which alleviate the ring strain.[24] In fact, the optimum Si–O–B angle of 125° calculated by Geisinger *et al.*[6] and the average Si–O–B angle of 129° observed in solids[6] are both very close to the optimum Si–O–Si angle of 130° calculated by Chakoumakos *et al.*[24] for three-membered rings. Based on these observations, we propose that ΔH_{stab} in the $NaTO_2-SiO_2$ series is controlled by the flexibility of the T–O–T angle as measured by the width of the minimum in the potential energy. This is in turn reflected in the magnitude of the shift in the position of the average T–O–T angle toward lower angles. Thus, the stabilization energy decreases as the optimum bond angle requirements for Si–O–Si linkages and for Si–O–T (T = Al, Ga, Fe, B) groupings become more different and, by inference, less mutually compatible. This may lead to a tendency toward clustering and phase separation. In addition, the disorder inherent in glass formation may be favored by a wide range of energetically allowable intertetrahedral angles, as well as by similar values for Si–O–Si and Si–O–T angles. The steeper minima seen in potential energy curves for Si–O–B than those for Si–O–Si or Si–O–Al may further destabilize the glasses by making angular variation inherent in a glass energetically more costly. Thus, a decreased magnitude of ΔH_{stab} and an increased tendency toward clustering and phase separation may occur together in the SiO_2-NaTO_2 systems as has already been seen in the $SiO_2-M^{n+}_{1/n}AlO_2$ systems studied earlier.[1-7]

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