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Electrical conductivity and viscosity of borosilicate glasses and melts

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Simple sodium borosilicate and silicate glasses were melted on a very large scale (35 l Pt crucible) to prepare model glasses of optical quality in order to investigate various properties depending on their structure. The composition of the glass samples varied in a wide range: 3 to 33·3 mol% Na_2O, 0 to 62·5 mol% B_2O_3, and 25 to 85 mol% SiO_2. The glass samples were characterised by different methods. Refractive indices, density and thermal expansion were measured. Phase separation effects were investigated by electron microscopy. The electrical conductivity of glasses and melts were determined by impedance measurements in a wide temperature range (250 to 1450°C). The activation energies were calculated by Arrhenius plots in various temperature regions: below the glass transition temperature, T_g, *above the melting point,* T_l, *and between* T_g *and* T_l. *Viscosity measurements were carried out with different methods from* T_g *to the melt. The measured data were fitted and the activation energies calculated. Simple exponential behaviour was found only in very narrow temperature ranges. The effect of* B_2O_3 *in sodium borosilicate glasses and melts is discussed in comparison with sodium silicate glasses and melts.*

Introduction

Electrical conductivities and viscosities of solid glasses and melts are of great importance for a better understanding of the temperature dependence of the structure and also for industrial melting processes.

Borosilicate glasses based on the Na_2O–B_2O_3–SiO_2 system are of interest for various applications, ranging from chemically and thermal resistant technical glass to optical, sealing and nuclear waste glasses. The properties and structure are strongly dependent on the composition, mainly on the Na_2O/B_2O_3 ratio and the SiO_2 content. Many investigations exist and are published.(1–7) The glass former B_2O_3 affects the properties in a particular way, due to the possibility of forming $BØ_3$ triangles and $BØ_4^-$ tetrahedra with only bridging oxygen, and also borate groups with nonbridging oxygen. The study of the structure has been greatly influenced by the so-called borate anomaly: for example, the thermal expansion coefficient of binary sodium borate glasses decreases with increasing Na_2O content up to about 16 mol% Na_2O, after which it begins to increase again. The present work concentrates on investigations of electrical conductivity and viscosity of four sodium borosilicate model glasses and melts in comparison with two sodium silicate glasses and melts over a wide temperature range up to 1500°C. Phase separation effects were investigated by electron microscopy.

Experimental

The batch compositions and properties of the model glasses are shown in the tables and figures. High purity grade raw materials, Na_2CO_3, H_3BO_3 and SiO_2 were mixed and melted in an industrial scale, 35 l Pt crucible to prepare glasses to optical quality, with glass compositions which are specified as model glasses by Technical Committee TC03 of the International Commission on Glass. The melting temperature varied between 1300 and 1580°C. Glasses were obtained by pouring the melts into a mould. After annealing from T_g+50 K to room temperature at 3 K/min, the glasses were cut, ground and polished to produce samples for different measurements. The refractive indices in the visible range were measured with a refractometer from transparent homogenous samples which were obtained by remelting 200 g of glass in a Pt crucible, pouring in a mould and annealing at 5 K/min. The error was $\Delta n \pm 2\times10^{-5}$. The density was determined using Archimedes' principle with an error ±0·002. DTA (10 K/min) and dilatometry measurements (5 K/min) were carried out to obtain values for the thermal properties, T_g and thermal expansion coefficient (TEC). The viscosities as a function of temperature were determined with a rotating cylinder method in the η range, $10^{1·5}$–10^5 dPa s, and with the beam bending method in the range 10^9–10^{11} dPa s. The electrical conductivity of the glasses and melts was determined by impedance measurements over a wide temperature range. Solid samples were measured to a temperature where the viscosity was about 10^4 dPa s. Cylindrical glass samples with a diameter 10 mm and thickness ~5 mm were used. Low viscosity melts were measured with a high accuracy coaxial Pt crucible/Pt cylinder technique. The electrical resistance was measured depending on dipping depth of the cylinder in the melt and variation of the temperature. Impedance spectra were recorded with a Zahner IM5d electrochemical workstation, with an ac voltage of 20 or 50 mV, and frequencies in the range of

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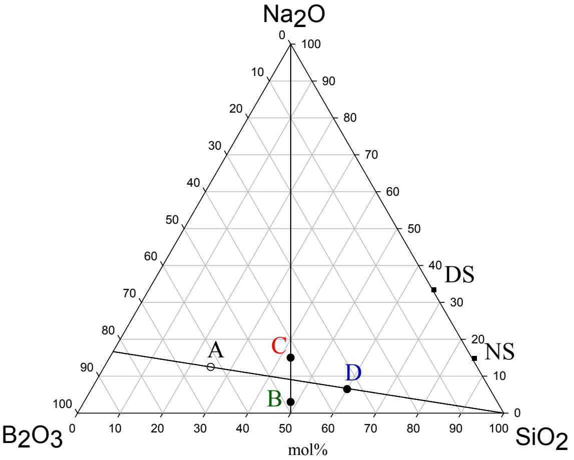

Figure 1. Binary sodium silicate NS, DS, and ternary sodium borosilicate NBS-A,-B,-C,-D model glasses in the ternary diagram: NBS-A and -D are on the borate anomaly line

0·1 Hz to 1 MHz, normally in steps of 20–50 K. The dc potentials were always 0 mV. The error of the resistance values was <5%. More details are given in Refs 8 to 11.

Results

This paper concentrates on investigations of the electrical conductivity and viscosity of four sodium borosilicate (NBS) model glasses and melts, in comparison with two sodium silicate glasses and melts, over a wide temperature range up to 1500°C. Phase separation effects were investigated by electron microscopy.

The composition of the NBS model glasses was varied in a wide range: 3 to 15 mol% Na_2O, 33·5 to 62·5 mol% B_2O_3, and 25 to 60 mol% SiO_2. Figure 1 shows the positions of the glasses in the ternary phase diagram: NBS-A and -D, with the molar ratio Na_2O/B_2O_3=0·2, and different SiO_2 content, 25 and 60 mol%, lie on the borate anomaly line; NBS-B and -C have a constant ratio B_2O_3/SiO_2=1 and different Na_2O content, 3 and 15 mol%. The two binary sodium silicate model glasses are NS with 15 mol% Na_2O and DS with 33 mol% Na_2O.

Table 1 gives an overview of the four NBS glasses in comparison with the two binary sodium silicate compositions, NS and DS, which were already used as model glasses in previous papers.(10,12,13) Figure 2 illustrates the different viscosity–temperature behaviours of the melts. Figures 3 to 6 summarise how the electrical conductivities depend on temperature from solid glasses to liquid melts, as Arrhenius plots with calculated activation energies E_σ for different regions. Tables 2 to 6 give an overview of selected measured data and calculated values for electrical and viscosity properties. Figures 7(a)–(c) represent the comparison of measured (thick lines) and fitted (thin lines) viscosity data of NBS A–D samples in different temperature ranges. Figure 8 shows a graphical comparison of measured electrical conductivity and viscosity data of the sodium borosilicate melts NBS-A, -B, -C, -D, and the sodium silicate melts NS and DS, for constant temperatures in the range 1000–1500°C. Solid lines are guides for the eye. The errors of all experimental data in the figures are within the point symbols.

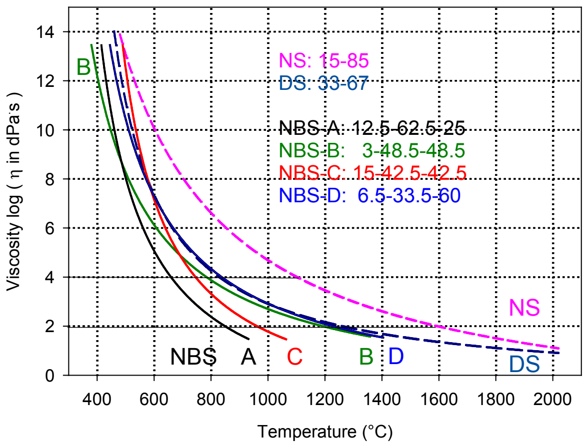

Figure 2. Viscosity curves of the four sodium borosilicate and two sodium silicate samples as global VFT-fits

Discussion

Composition and characteristic properties

All four NBS glasses and also the NS glass can undergo sub-liquid phase separation by slow cooling of large melts or annealing below the binodal temperature.(1–3) It is well known and often investigated that NBS glasses form a nearly pure SiO_2 and a sodium borosilicate phase with various SiO_2 contents depending on composition, temperature and time. After slow cooling of these large melts the glass samples NBS-A and -C were translucent; NBS-B and -D, and NS white opaque. Electron microscopy investigations have shown the following results: NBS-A and -C are separated into small SiO_2 droplets, size ~100 nm, in a sodium borate rich matrix; NBS-B and -D consist of connected phases

Table 1. Composition and properties of glass sample

Glass (mol%)	*NBS-A*	*NBS-B*	*NBS-C*	*NBS-D*	*NS*	*DS*
Na_2O	12·5	3·0	15·0	6·5	15·0	33·3
B_2O_3	62·5	48·5	42·5	33·5	-	-
SiO_2	25·0	48·5	42·5	60·0	85·0	66·7
T_g (°C) ±5	415	380	490	445	485	460
TEC (ppm/K) ±0·3 100–300°C	8·5	6·4	8·7	5·3	7·5	16·0
Density (g/cm^3) ±0·01	2·18	2·04	2·31	2·15	2·34	2·49
Refractive index* n_e±0·00002	1·49621	1·47151	1·50626	1·47595	1·48331	1·50832
Dispersion coeff.* ν_e±0·3	62·5	62·4	64·2	64·2	61·0	55·0

* The values of refractive indices and dispersion coefficients were measured with homogeneous samples.

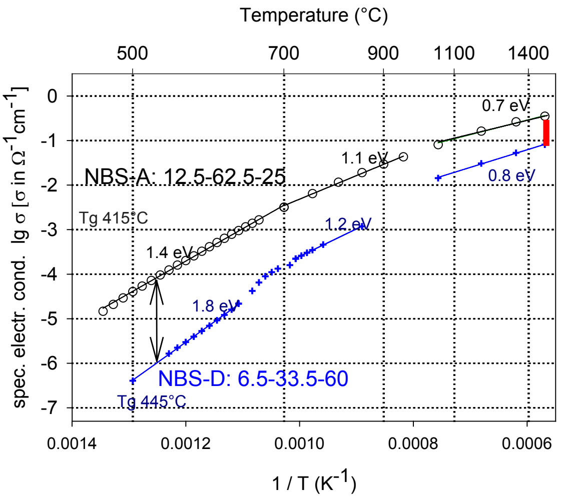

Figure 3. Temperature dependence of electrical conductivity of NBS-A and NBS-D from solid to liquid state: Solid lines represent Arrhenius linear fits with calculated activation energies

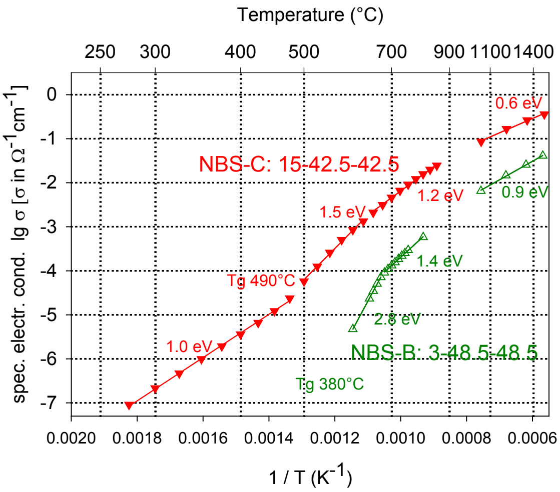

Figure 4. Temperature dependence of electrical conductivity of NBS-B and NBS-C from solid to liquid state: Solid lines represent Arrhenius linear fits with calculated activation energies

of μm size. The NS sample was separated into SiO_2 rich droplets and a sodium silicate matrix. It was possible to obtain homogenous glass samples by remelting of phase separated glass samples on a small scale with a faster cooling rate of the melts.

The temperatures for a viscosity log*η*=4 vary between 650°C for NBS A and 1100°C for NS; and for log*η*=2 between 850°C for NBS A and 1600°C for NS (Figure 2). These are very large differences, mainly affected by introducing B_2O_3. In contrast, the values for

Table 2. Measured data

Temperature T (*°C*)	*Viscosity* *log*η (η *in dPa s*)	*Specific electrical conductivity* *ln*σ (σ *in* $Ω^{-1}m^{-1}$)	*log*σ	*log*σ ($Ω^{-1}cm^{-1}$)	σ	*Specific electrical resistance* ϱ (*Ω cm*)	*log*ϱ (ϱ *in Ω cm*)
NBS-A: $12·5Na_2O.62·5B_2O_3.25SiO_2$ T_g: 415°C T_{k100}: 290°C							
1500	−0·33	3·56	1·54	−0·45	0·35	2·84	0·45
1350	−0·03	3·27	1·42	−0·58	0·26	3·80	0·58
1200	0·36	2·79	1·21	−0·79	0·16	6·14	0·79
1050	0·88	2·09	0·91	−1·09	0·08	12·37	1·09
900	1·65	1·08	0·47	−1·53	0·03	33·88	1·53
800	2·39	0·15	0·06	−1·94	0·01	86·50	1·94
700	3·44	−1·14	−0·50	−2·50	$3×10^{-3}$	314·0	2·50
600	5·05	−2·97	−1·29	−3·29	$5×10^{-4}$	$20×10^2$	3·29
500	7· 85	−5·50	−2·39	−4·39	$4×10^{-5}$	$24·5×10^3$	4·39
NBS-B: $3Na_2O.48·5B_2O_3.48·5SiO_2$ T_g: 380°C T_{k100}: 480°C							
1500	1·29	1·41	0·61	−1·39	0·04	24·42	1·39
1350	1·59	0·94	0·41	−1·59	0·02	39·07	1·59
1200	1·97	0·38	0·16	−1·84	0·01	68·39	1·84
1050	2·49	−0·43	−0·19	−2·19	$6×10^{-3}$	153·71	2·19
800	3·87	−2·85	−1·24	−3·24	$5×10^{-4}$	$17·2×10^2$	3·34
700	4·78	−4·33	−7·88	−3·88	$1×10^{-5}$	$75·5×10^2$	3·88
600	7·66	−7·66	−3·33	−5·33	$5×10^{-6}$	$21·2×10^4$	5·33
NBS-C: $15Na_2O.42·5B_2O_3.42·5SiO_2$ T_g: 490°C T_{k100}: 220°C							
1500	0·17	3·58	1·55	−0·44	0·36	2·79	0·45
1350	0·49	3·27	1·42	−0·58	0·26	3·02	0·58
1200	0·92	2·82	1·22	−0·78	0·17	5·96	0·78
1050	1·52	2·15	0·93	−1·07	0·09	11·65	1·07
800	3·33	0·45	0·20	−1·80	0·02	63·55	1·80
700	4·70	−0·77	−0·34	−2·34	$5×10^{-3}$	217·6	2·34
600	7·02	−2·46	−1·07	−3·07	$8×10^{-4}$	$11·8×10^2$	3·07
500	11·76	−5·16	−2·24	−4·24	$6×10^{-5}$	$17·4×10^3$	4·24
400		−7·93	−3·44	−5·44	$3×10^{-6}$	$27·7×10^4$	5·44
300		−10·74	−4·67	−6·67	$2×10^{-7}$	$46·4×10^5$	6·67
NBS-D: $6·5Na_2O.33·5B_2O_3.60SiO_2$ T_g: 445°C T_{k100}: 410°C							
1500	1·33	2·09	0·91	−1·09	0·08	12·37	1·09
1350	1·66	1·67	0·72	−1·28	0·05	18·83	1·28
1200	2·09	1·12	0·49	−1·51	0·03	32·63	1·51
1050	2·68	0·36	0·16	−1·84	0·01	69·77	1·84
800	4·33	−2·71	−1·18	−3·18	$6·6×10^{-4}$	$15·1×10^2$	3·18
700	5·47	−4·41	−1·92	−3·92	$1·2×10^{-4}$	$82·2×10^2$	3·92
600	7·20	−6·99	−3·04	−5·04	$9·2×10^{-6}$	$10·8×10^4$	5·04
500	10·15	−10·11	−4·39	−6·39	$4·1×10^{-7}$	$24·6×10^5$	6·39

T_g are more similar. NBS-B with the lowest Na_2O content, 3 mol%, has the lowest T_g of 380°C due to the high content of $BØ_3$ and only a small content of $BØ_4^-$ units. NBS-C has the highest T_g of 490°C and should have a higher content of $BØ_4^-$ units. This T_g value is nearly the same as the T_g value 485°C for NS glass with the same Na_2O content, 15 mol%. The lowest TEC value, 5·3 ppm/K, is for NBS-D which lies on the anomaly line and has the highest SiO_2 content. NBS-B has the lowest density, 2·04 g/cm^3, and the lowest refractive index, n_e=1·47151 (at the e-line of Hg, λ_e=546·07 nm) caused by the lowest Na_2O and high B_2O_3 content.

Electrical properties

Electrical conductivity is the property of the greatest practical importance among the electrical properties. The strong change over large temperature ranges is of great interest.(8–11,14–17) As a global rule, the temperature dependence of a kinetic process may be described by a Boltzmann relation, and electrical conductivity σ and temperature are related by

$$\log\sigma=A-(E_\sigma/T) \tag{1}$$

The activation energies E_σ are nearly constant up to the glass transition temperature, T_g, in all cases measured (Figures 3–6); for NBS glasses E_σ~1·0 eV, for NS E_σ~0·8 eV, and for DS E_σ is only 0·6 eV.

The electrical conduction in these glasses is based on the transport of Na^+ ions through the glassy network. Thus, it should be dependent on the concentration of mobile Na^+ ions and their bond strength to the network. In silicate glasses, Na^+ ions are bonded to nonbridging oxygen. In borosilicate glasses, Na^+ ions prefer bonds to $BØ_4^-$ groups with one bridging oxygen which are stronger. This decreases the mobility of Na^+, thus the electrical conductivity, and increases the activation energy of the solid NBS glass samples. The electrical conductivity of the borosilicate glass NBS-C is about three orders lower than that of the silicate glass NS with the same Na_2O content, 15 mol% (Figure 5). With increasing temperature the conductivity of NBS-C approaches that of NS, and at ~1000°C the values are nearly the same.

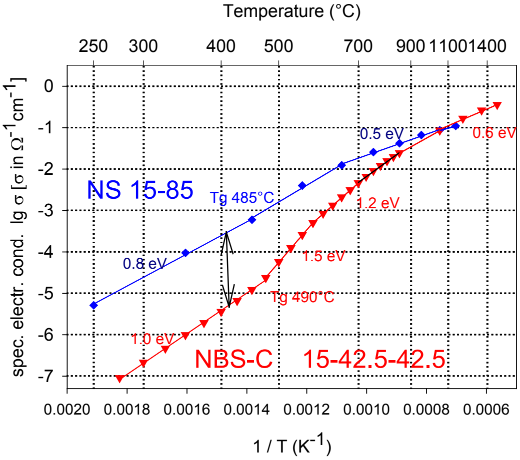

Figure 5. Temperature dependence of electrical conductivity of NBS-C in comparison with NS from solid to liquid state: Solid lines represent Arrhenius linear fits with calculated activation energies

There is a remarkably strong increase of the activation energy and electrical conductivity in the temperature range above T_g in the softening region of the glass network (Figures 3–6(a)). This increase is much stronger in NBS than in NS glasses (Figure 5). The highest activation energy, ~2·8 eV was measured for the NBS-B sample which has the lowest Na_2O content and a high B_2O_3 content (Figure 4). The E_σ values decrease with increasing Na_2O content and increasing

Table 3. Measured data

Temperature	*Viscosity*	*Specific electrical conductivity*				*Specific electrical resistance*	
T (°C)	logη (η in dPa s)	lnσ (σ in $\Omega^{-1}m^{-1}$)	logσ	logσ ($\Omega^{-1}cm^{-1}$)	σ	ϱ (Ω cm)	logϱ (ϱ in Ω cm)
NS: $15Na_2O.85SiO_2$ T_g: 485°C T_{k100}: 120°C							
1500	2·11						
1350	2·78						
1200	3·61						
1050	4·65	2·16	0·94	−1·06	0·09	11·56	1·06
900	6·01	1·58	0·69	−1·31	0·05	20·51	1·31
800	7·16	1·10	0·48	−1·52	0·03	33·19	1·52
700	8·61	0·52	0·23	−1·77	0·02	59·16	1·77
600	10·47	−0·17	−0·08	−2·08	8×10^{-3}	$1·2\times10^{2}$	2·07
500	12·95	−1·61	−0·70	−2·70	2×10^{-3}	$5·0\times10^{2}$	2·70
400		−3·90	−1·69	−3·69	2×10^{-4}	$4·9\times10^{3}$	3·69
300		−6·80	−2·95	−4·95	1×10^{-5}	$9·0\times10^{4}$	4·95
200		−10·9	−4·73	−6·73	2×10^{-7}	$5·4\times10^{6}$	6·73
DS: $33Na_2O.67SiO_2$ T_g: 460°C T_{k100}: 25°C							
1400	1·68	4·52	1·96	−0·04	0·92	1·09	0·04
1200	2·16	4·39	1·91	−0·09	0·81	1·24	0·09
1000	2·91	4·15	1·80	−0·20	0·63	1·58	0·20
900	3·47	3·64	1·58	−0·42	0·38	2·62	0·42
800	4·26	3·35	1·45	−0·54	0·28	3·51	0·54
700	5·43	cryst.					
600	7·36	cryst.					
500	11·19	cryst.					
400		−0·81	−0·35	−2·35	4×10^{-3}	$2·25\times10^{2}$	2·35
300		−2·71	−1·18	−3·18	7×10^{-4}	$1·50\times10^{3}$	3·18

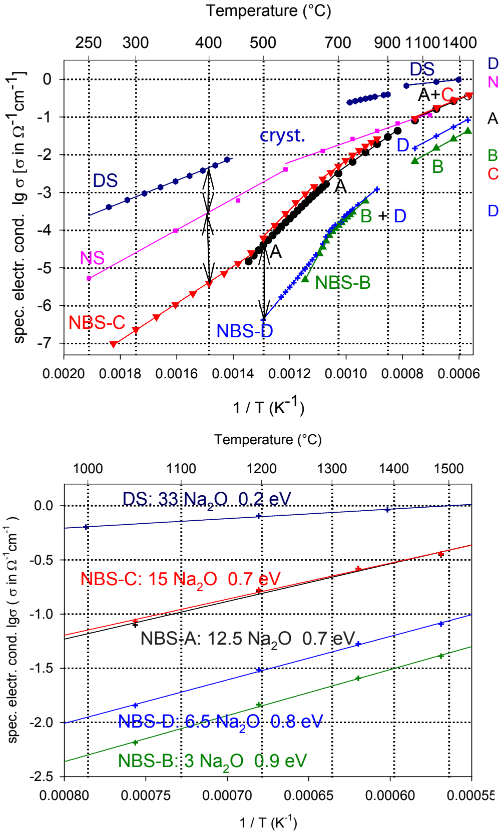

Figure 6. Overview of the electrical conductivities and activation energies (solid lines represent Arrhenius linear fits with calculated activation energies): (a) Glasses and melts, (b) Melts in more detail

temperature (Figure 6(a)). A superposition of different processes occurs: transport of mobile Na^+ ions and breaking the network which leads to viscous flow.

The electrical conductivities of the liquid melts in the temperature range 1000–1500°C correlate well with Arrhenius behaviour (Figure 6(b)). The conductivity increases and the activation energy decreases with increasing Na_2O content. Significant differences between silicate and borosilicate melts could not be recognised. Vogel–Fulcher–Tammann (VFT)-constants, A, B and T_0, for the conductivity and resistivity, according to

$$\log\sigma=A-B/(T-T_0) \qquad (2)$$

and

$$\log\rho=A-B/(T-T_0) \qquad (3)$$

were calculated for the NBS melts in the temperature range 1000–1500°C (Table 4). The electrical insulation of technical glasses is often defined by the temperature for electrical resistivity 10^8 Ω cm, denoted

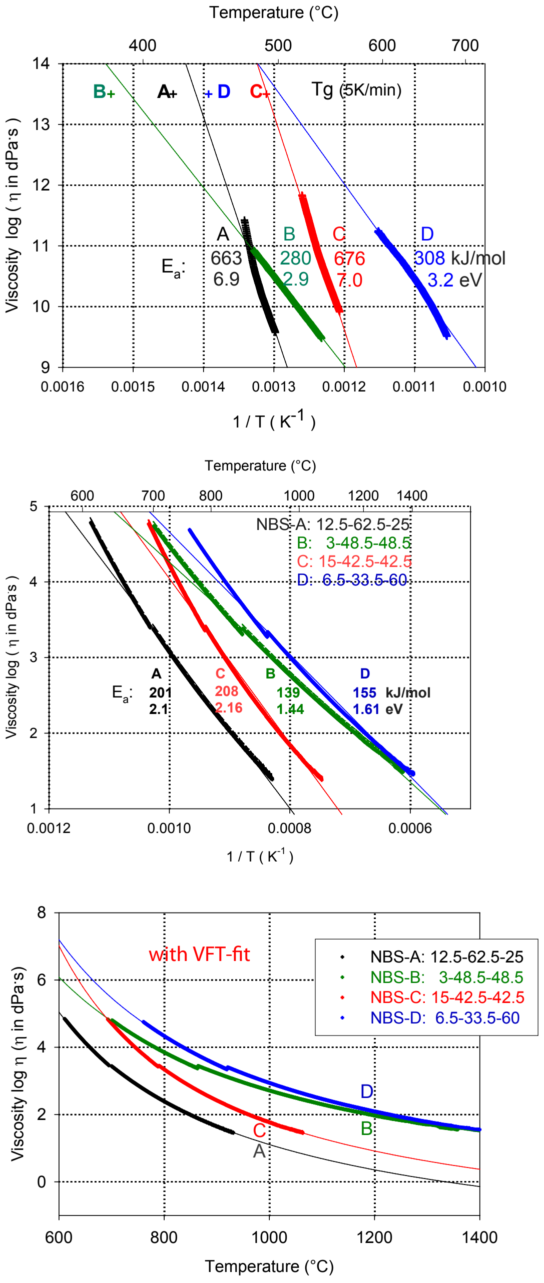

Figure 7. Comparison of measured (thick lines) and fitted (thin lines) viscosity data of NBS samples:(a) High viscosity region in comparison with T values at T_g determined by dilatometer; (b) Low viscosity region; (c) Measured data and VFT-fit in the temperature range 600 to 1400°C

Table 4. Calculated VFT-constants (VFT –fit only for the region 1000–1500°C)

	Viscosity VFT constants			*Spec. electr. conductivity VFT constants*			*Spec. electr. resistance VFT constants*		
	A	B	T_0	A	B	T_0	A	B	T_0
NBS-A	−2·5	2820·1	228·7	0·3	−793·6	493·7	−0·3	737·7	521·7
NBS-B	−1·1	3251·7	148·4	0·002	−1713·1	267·3	−0·08	1884·9	217·9
NBS-C	−2·0	2642·1	308·6	0·4	−874·9	447·0	−0·36	834·7	465·5
NBS-D	−1·2	3220·1	215·8	0·2	−1663·9	252·1	−0·25	1675·9	248·4
DS	−0·5	2391·3	295·0	0·16	−172·8	514·9	fit not possible		
NS	−4·4	10363·6	−98·4	1100°C					

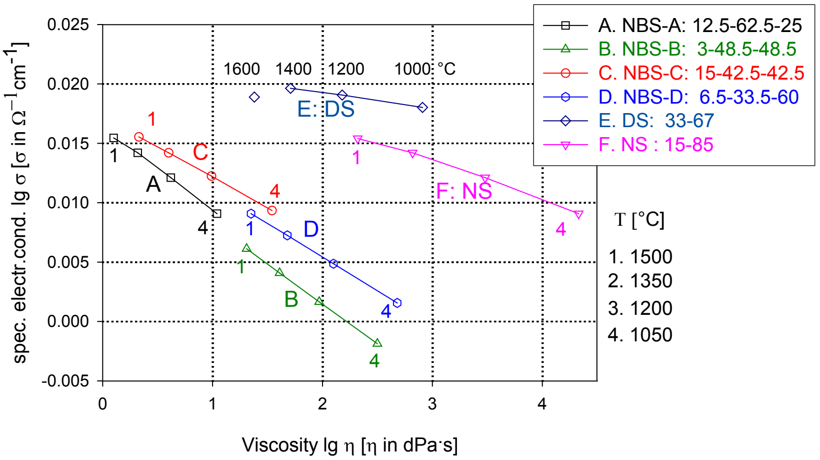

Figure 8. Electrical conductivity and viscosity of NBS, NS and DS samples for different temperatures: 1. 1500°C; 2. 1350°C; 3. 1200°C; 4. 1050°C (Solid lines are guides for the eye)

as T_{k100},(2) and in Tables 2 and 3, values of T_{k100} are also given. The lowest value, T_{k100}~25°C, was found for DS glass, and the highest, T_{k100}~480°C, for NBS-B. The NBS glasses have generally higher T_{k100} values than silicate glasses with the same Na_2O content.

Temperature dependence of viscosity

Structural changes of borate and borosilicate glasses have been intensively studies by different methods with regard to the borate anomaly.(1–4,6–7) It has been shown in previous papers(18–20) that melting and annealing conditions of two borosilicate model glasses and melts, NBS1 ($16Na_2O.10B_2O_3.74\ SiO_2$) and NBS2 ($4.3Na_2O.20.7B_2O_3.1Al_2O_3.74SiO_2$) affect their structure in a different way. The measured viscosity (η) temperature data were fitted by the VFT equation

$$\log\eta = A - B/(T - T_0) \qquad (4)$$

The VFT fit for the NBS1 sample was in good agreement with the experimental data and the effect of the melting and annealing conditions on the glass structure was very low. In contrast the NBS2 sample could not be fitted with the VFT equation. A strong deviation in the temperature range T_g+(150–200)°C was found due to the effect of $BØ_3$ groups. It can be shown by NMR, IR and Raman studies that in annealed glasses were more of $BØ_3$ groups are linked in boroxol rings, but in quenched glasses more $BØ_3$ groups are connected with SiO_4 tetrahedra.(19–20) Differences in the thermal history of NBS2 samples result in glass structures with the same short range order (SRO) structural units while the medium range order (MRO) structure of the borosilicate network was found to be sensitive to changes in melt and cooling temperature.(20) Figure 7(a) shows the high viscosity region as Arrhenius plots with calculated activation energies, E_η, in comparison with a value, $\eta=10^{13\cdot5}$ dPa s at T_g, determined by dilatometer measurements with a heating rate 5 K/min. Simple exponential behaviour was found in only very narrow ranges. NBS-C with the highest Na_2O content, 15 mol%, offers the best agreement with the value at T_g. The activation energy, E_η=7·0 eV, is very high; much higher than for the silicate sample NS, E_η=3·0 eV, with the same Na_2O content (Table 6). NBS-A, which has the highest B_2O_3 content, has a similar high value, E_η=6·9 eV. But NBS-A has a large deviation from the viscosity at T_g. Such large deviation near T_g was also detected for the samples NBS-B and -D. The activation energies for NBS-B and NBS-D, 2·9 eV and 3·2 eV, respectively, are much lower. The effect of phase separation on the viscosity data is relatively low.

Figure 7(b) shows the measured (thick lines) and calculated data for the low viscosity region.

Simple exponential behaviour was again found

Table 5. Activation energies of the electrical conductivity for various temperature ranges (calculated by Arrhenius plots)

Sample		$T<T_g$ E_σ *1*		$T\sim T_g$ *region* E_σ *2*		$T>T_g$ E_σ *3*		$T>$*1000°C* E_σ *4*	
		kJ/mol	*eV*	*kJ/mol*	*eV*	*kJ/mol*	*eV*	*kJ/mol*	*eV*
NBS-A	E_A			135	1·4	100	1·05	65	0·7
	T (°C)			470–700		700–950		1050–1500	
NBS-B	E_A			265	2·75	130	1·35	80	0·85
	T (°C)			600–670		680–800		1050–1500	
NBS-C	E_A	95	1·0	145	1·5	110	1·15	60	0·65
	T (°C)	275–475		500–625		650–850		1050–1500	
NBS-D	E_A			175	1·8	120	1·25	80	0·8
	T (°C)			500–630		720–850		1050–1500	
NS 15-85	E_A	80	0·85			50	0·5		
	T (°C)	250–550				650–1150			
DS 33-67	E_A	60	0·6			30	0·3	15	0·15
	T (°C)	250–440				730–900		1000–1400	

Table 6. Activation energies of the viscosity for various temperature ranges (calculated by Arrhenius plots)

Sample	T_g (°C)	ΔT (°C)	E_η *1* (kJ/mol)	(eV)	ΔT (°C)	E_η *2* (kJ/mol)	(eV)
NBS-A	415	450–500	663	6·9	620–900	201	2·1
NBS-B	380	450–550	280 (279)	2·9 (2·9)	750–1400	139	1·4
NBS-C	490	490–580	676 (720)	7·0 (7·5)	700–1100	208	2·2
NBS-D	445	580–650	308 (377)	3·2 (3·9)	800–1400	155	1·6
NS 15-85	485	500–600 (520–630)	284 (350)	3·0 (3·6)	1200–1500	205	2·1
DS 33-67	460	480–520	551	5·7	850–1500	146	1·5

The values in the brackets are for phase separated samples

only in very narrow ranges. The calculated activation energies from Arrhenius plots are in the following order: NBS-C>-A>-D>-B.

Figure 7(c) shows the measured data and VFT-fits in the temperature range 600–1400°C. The experimental viscosity data are in good agreement with the VFT-fit in this temperature range. The calculated VFT constants are given in Table 4.

Electrical conductivity and viscosity of NBS, NS and DS melts for different temperatures

It is interesting to look for a correlation between data for the electrical conductivity and viscosity of the melts. It is clear that the mechanisms are different.

Figure 8 shows a graphical comparison of the measured electrical conductivity and viscosity data of the sodium borosilicate melts NBS-A, -B, -C, -D, and the sodium silicate melts NS and DS, for constant temperatures in the range 1000–1500°C. Solid lines are merely guides for the eye. It could be assumed that a nearly linear correlation exists between electrical conductivity, logσ, and viscosity, logη, dependent on composition and structure of the melts.

Conclusions

Four simple sodium borosilicate and two silicate model glasses were melted to investigate various properties of glasses and melts which depend on the structure. The composition of the samples varied over a wide range: 3 to 33·3 mol% Na_2O, 0 to 62·5 mol% B_2O_3, and 25 to 85 mol% SiO_2. The glass samples were characterized by several different methods.

The electrical conductivity of glasses and melts were determined by impedance measurements over a wide temperature range (250 to 1450°C). The activation energies were calculated by Arrhenius plots in various regions: below T_g, above the melting point, T_l, and between T_g and T_l.

Viscosity measurements were carried out with different methods from T_g to the melt. The measured data were fitted and the activation energies were calculated. Simple exponential behaviour was found only in very narrow temperature ranges.

The electrical conductivity is strongly dependent on the content of Na^+ ions and their mobility through the glassy network. Sodium borosilicate glasses ($T \le T_g$) have much lower electrical conductivity than sodium silicate glasses due to the special borate units. The Na^+ ions are more strongly bonded to BØ_4^- tetrahedra with bridging oxygen than to $\text{SiØ}_3\text{O}^-$ tetrahedra with nonbridging oxygen.

Above T_g, in the softening region, the electrical conductivity of sodium borosilicate glasses increases strongly and approaches the values of sodium silicate samples near 1000°C. It is assumed that BØ_4^- units with bridging oxygen are transformed into $\text{BØ}_2\text{O}^-$ units with nonbridging oxygen which increases the electrical conductivity drastically. Different mechanisms are superimposed.

The viscosity of sodium borosilicate melts is strongly dependent on the Na_2O/B_2O_3 ratio, the SiO_2 content and the temperature. A strong deviation from Arrhenius behaviour and a VFT-fit was found for $Na_2O/B_2O_3 \le 0{\cdot}2$ at $T \ge T_g$ depending on linking of BØ_3 units in medium range order (MRO). The introduction of B_2O_3 in sodium silicate glasses strongly decreases the viscosity of the melts. It is found that a nearly linear correlation between the logs of electrical conductivity and viscosity exists for the melts.

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