Viscosity, configurational entropy and Raman spectroscopy of sodium borosilicate glasses and melts

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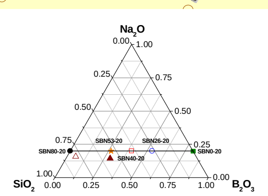
INTRODUCTION

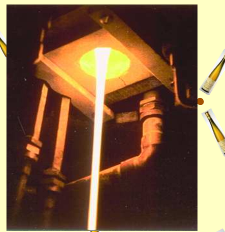
Though the low natural abundance of boron classifies it as a trace element, its unique chemistry allows it to occur in occasional massive deposits of minerals such as borax. This concentration gave boron a visibility and technological importance early in human history. During the antiquity, boron was used in the preparation of glass and enamel. Actually, borosilicate glasses have long found a wide range of industrial applications in particular for nuclear waste storage and special glass. Because the viscosity of these glasses is an important parameter governing mass transfer in industrial and natural processes, it is useful to study its variations with composition and temperature. To better understand the structure and properties variation of borosilicate glasses and melts, we have investigated five compositions with constant Na_2O content. Measurements of the viscosities and heat capacities of these glasses have been performed in order to determine the configurational entropy S^{conf} of the liquid using Adam and Gibbs theory. The configurational entropy gives us an idea of the structure of the glasses and melts. This structural observation is completed by Raman spectroscopy investigations.

Chemical composition



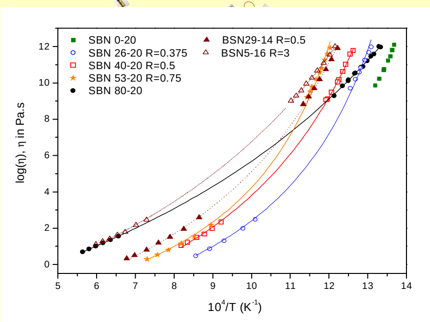
	SiO_2		B_2O_3		Na_2O	
%mol	*nominal*	*analysed*	*nominal*	*analysed*	*nominal*	*analysed*
SBN0-20	0	-	80	-	20	-
SBN26-20	26.66	-	53.34	-	20	-
SBN40-20	40	40.75	40	38.78	20	20.47
SBN53-20	53.34	53.86	26.66	26.01	20	20.13
SBN80-20	80	79.99	0	0	20	20.01

Compositions of five borosilicate glasses synthesized at constant alkaline content (20%mol Na_2O) and analysed by electron microprobe. Two compositions elaborated by Y. Linard [1] are added on the diagram : BSN5-16 (△ ; %mol : 78.66SiO_2-5.34B_2O_3-16Na_2O) and BSN29-14 (▲ ; en %mol : 56.71SiO_2-28.86B_2O_3-14.43Na_2O).

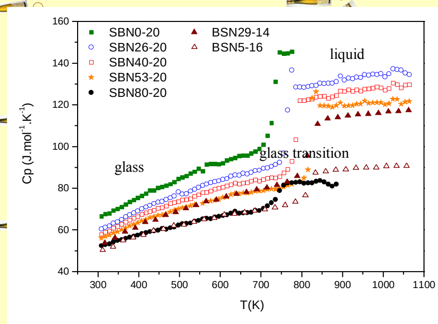


Examples of glass pouring (CEA Valrhô-Marcoule, France)

The SiO_2-B_2O_3-Na_2O vitreous system : rheologic properties and structure



Viscosity of molten borosilicate as a function of 1/T. At low viscosity, measurements were made at CEA Marcoule for SBN40-20 and SBN26-20 and at IPGP for other melts. △ and ▲ are data from Y.Linard [1].



Heat capacities of the borosilicate melts. Measurements were made at IPGP between 300 and 1073K with a differential scanning calorimeter (DSC). △ and ▲ correspond to data from Y.Linard [1] .

• ***Heat capacity (C_p), viscosity (η) and configurational entropy (S^{conf}) markedly depend on glass composition:***

→ from Cp and η measurements we have obtained S^{conf} (using the relation $\log\eta = A_e + B_e / TS^{conf}$ where A_e and B_e are two constants (Adam and Gibbs theory) [2, 3])

→ borosilicate glasses seem to have the same behaviour as borate glasses up to a high content of SiO_2 and it concerns viscosity as well as configurational entropy. Here, BSN5-16 is the only one which has a behaviour close to the silicate one.

This could mean that the glass former of the ternary system which has the lower η and the higher S^{conf} (here B) mainly controls the rheologic properties. This is due to the many distinct coordination environments of boron.

→ at high temperatures, the viscosity of borosilicate melts decreases faster than the viscosity of the silicate melt, whereas their entropy increases faster.

• ***Structural observations :***

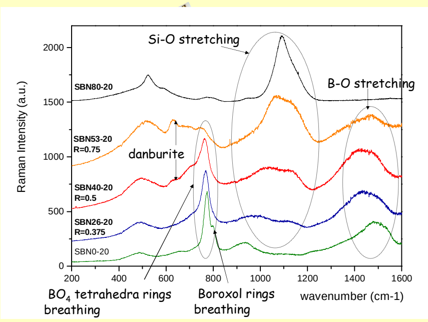
According to previous literature studies [4, 5], alkaline ions convert boron from BO_3 to BO_4 depending on the ratio $[Na_2O]/[B_2O_3]$. In our case (at constant Na_2O content) Raman spectroscopy shows:

→ an increase of BO_4 units in the borate network of borosilicate glasses by substituting Si by B (spectral region between 1400 and 1600 cm^{-1})

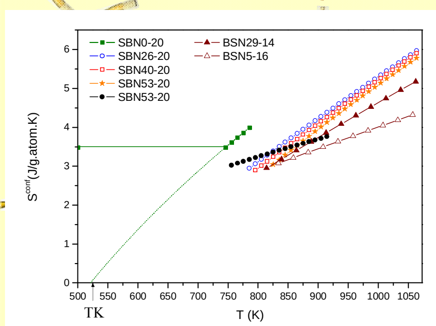
→ a depolymerization of the silicate network by substituting Si by B with a decrease of Q^3 and Q^4 units and an increase of Q^2 units (spectral region between 900 and 1200 cm^{-1}).

Then, in borosilicate glasses, from SBN53-20 to SBN26-20, the substitution of Si by B increases the number of possible configurational units (coordination environments of boron and mixture between SiO_4 and BO_4 tetrahedrons [6]) which involves an increase of S^{conf} .

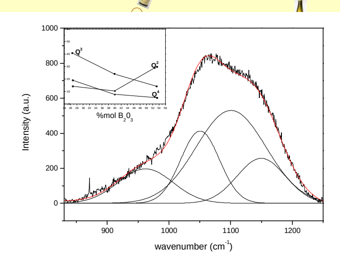
→ according to the literature [7, 8], increasing the temperature implies in the borate network an increase of the number of possible units including boron. Nevertheless, that result has to be completed by Raman spectroscopy measurements at high temperature.



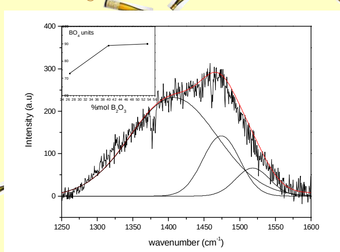
Comparison of Raman spectra of the five borosilicate glasses with constant Na_2O content. The spectra have been measured at IPGP (Jussieu) at room temperature and λ=488nm.



Configurational entropy of borosilicate melts against temperature. △ and ▲ correspond to data from Y.Linard [1].



Curve fitted Raman spectra SBN53-20 of the spectral region between 800-1200 cm^{-1}. Q^n denotes a tetrahedral site SiO_4 where n is the number of bridging oxygen per tetrahedron.



Curve fitted Raman spectra of the borosilicate glass SBN53-20 of the spectral region between 1200-1600 cm^{-1}.

CONCLUSION

• A substitution of Si by B induces an increase of BO_4 units and a decrease of Q^3 and Q^4 units which leads to an increase of the entropy.

• Boron has an important role in borosilicate glasses mainly controlling their viscosity and their configurational entropy

• A similar study will be performed on barium borosilicate glasses to search the importance of boron. A comparison with sodium borosilicate glasses will be made to see the influence of the modifier ion.

Références : [1]Y. Linard, thèse de doctorat de l'Université Paris VII (2000) [2] G.Adam, J.H.Gibbs, *J.Chem.Phys*, 43 (1965) 139 [3] Richet P. and Bottinga Y., Rev. Geophysics 24 (1986) 1 [4] Y.H.Yun, P.J.Bray, *J.Non-Cryst.Solids*, 27 (1978) 363 [5] W.J.Dell *et al.*, *J.Non-Cryst.Solids*, 58 (1983) 1 [6] P.Richet *et al.*, *J.Non-Cryst.Solids*, 211 (1997) 271-280 [7] J.F.Stebbins and S.E.Ellsworth, *J.Am.Ceram.Society*, 79,9 (1996) 2247-2256 [8] T.Yano *et al.*, *J.Non-Cryst.Solids,* 321 (2003) 147-156