Thermodynamics of the vitreous state: a tool for establishing structure-property relationships

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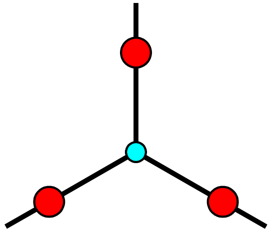
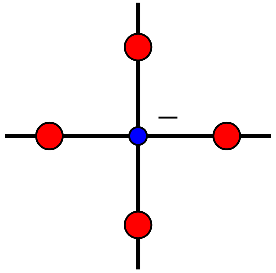
It is generally known that that the structure of glass determines its properties. In the case of borate glasses, the first attempt to establish the structure-property relationship was based on the experimental fact that boron-oxygen triangles are converted into tetrahedra when a modifying oxide is added to B_2O_3.

Basic structural units

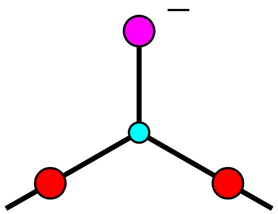
Borate



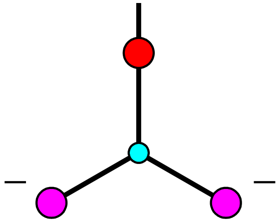
$BØ_3$



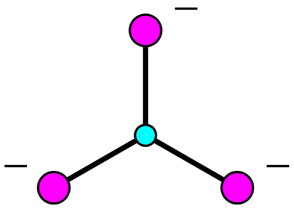
$[BØ_4]^-$



$BØ_2O^-$

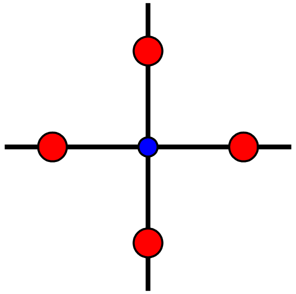


$BØO_2^{2-}$

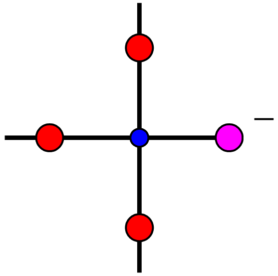


BO_3^{3-}

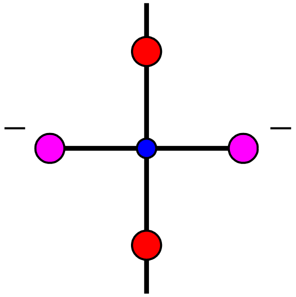
Silicate



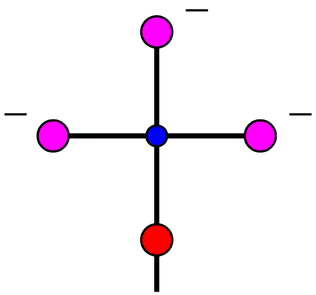
Q^4



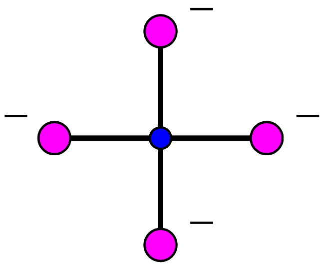
Q^3



Q^2

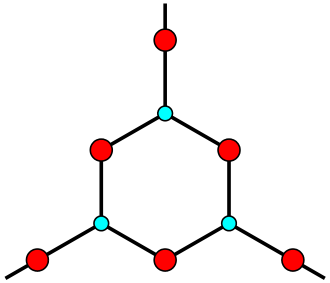


Q^1

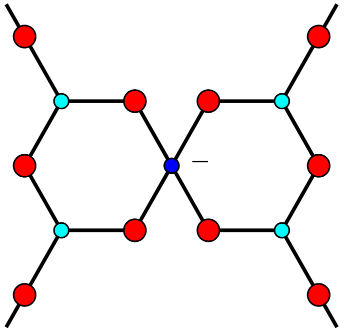


Q^0

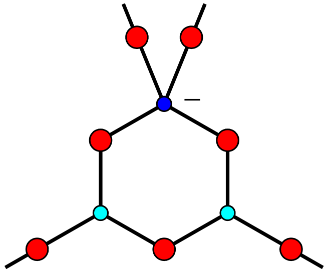
Supertructural units



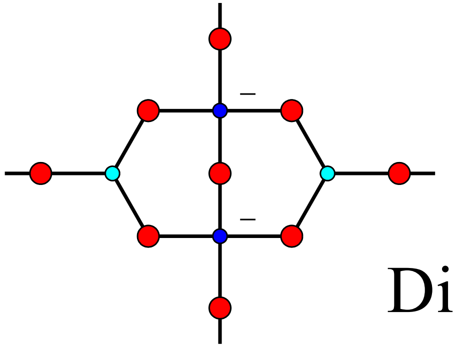
Boroxol ring



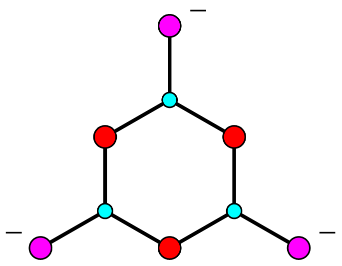
Pentaborate



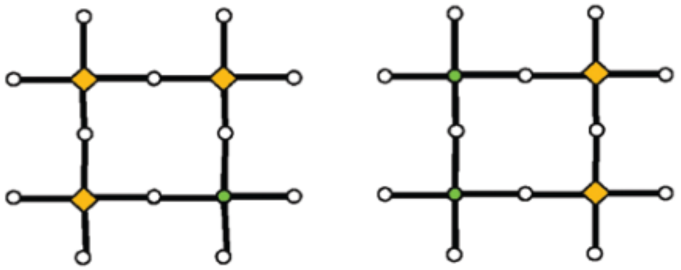
Triborate



Diborate



Cyclic metaborate anion

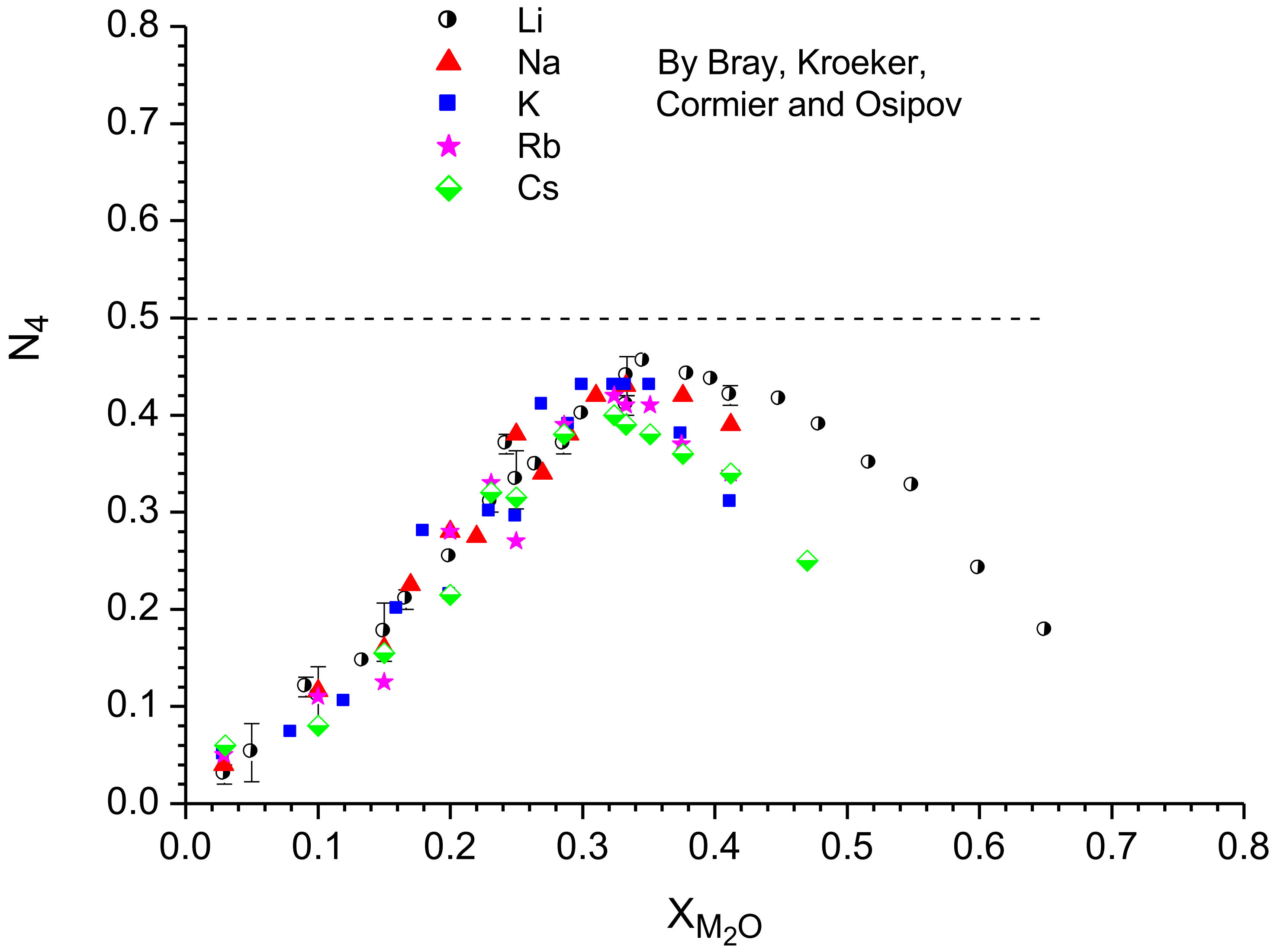


(a) (b)

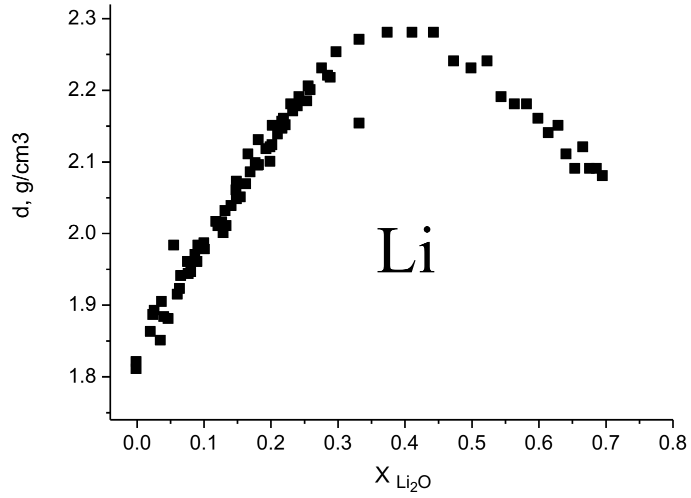
Borosilicate rings

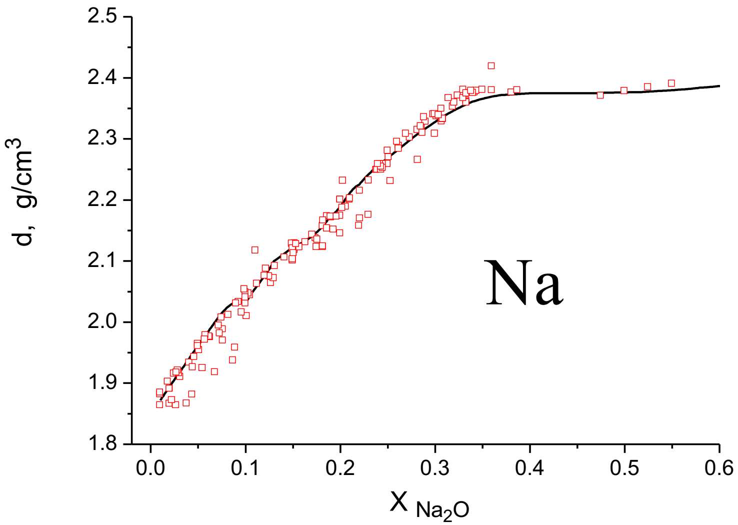
(a) Reedmergnerite
(b) Danburite

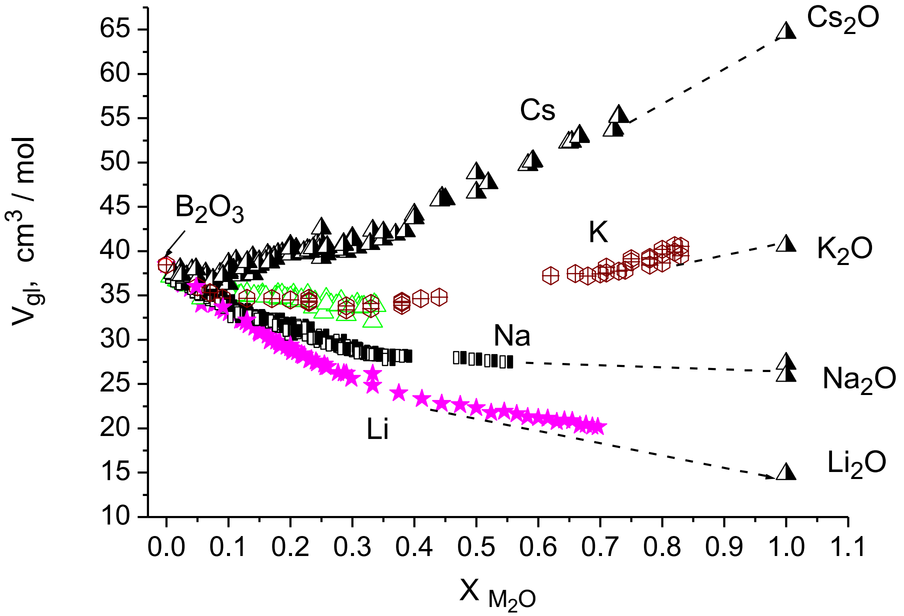
The fraction of 4-fold co-ordinated boron in alkali borate glasses



The densities of alkali borate glasses (SciGlass data)



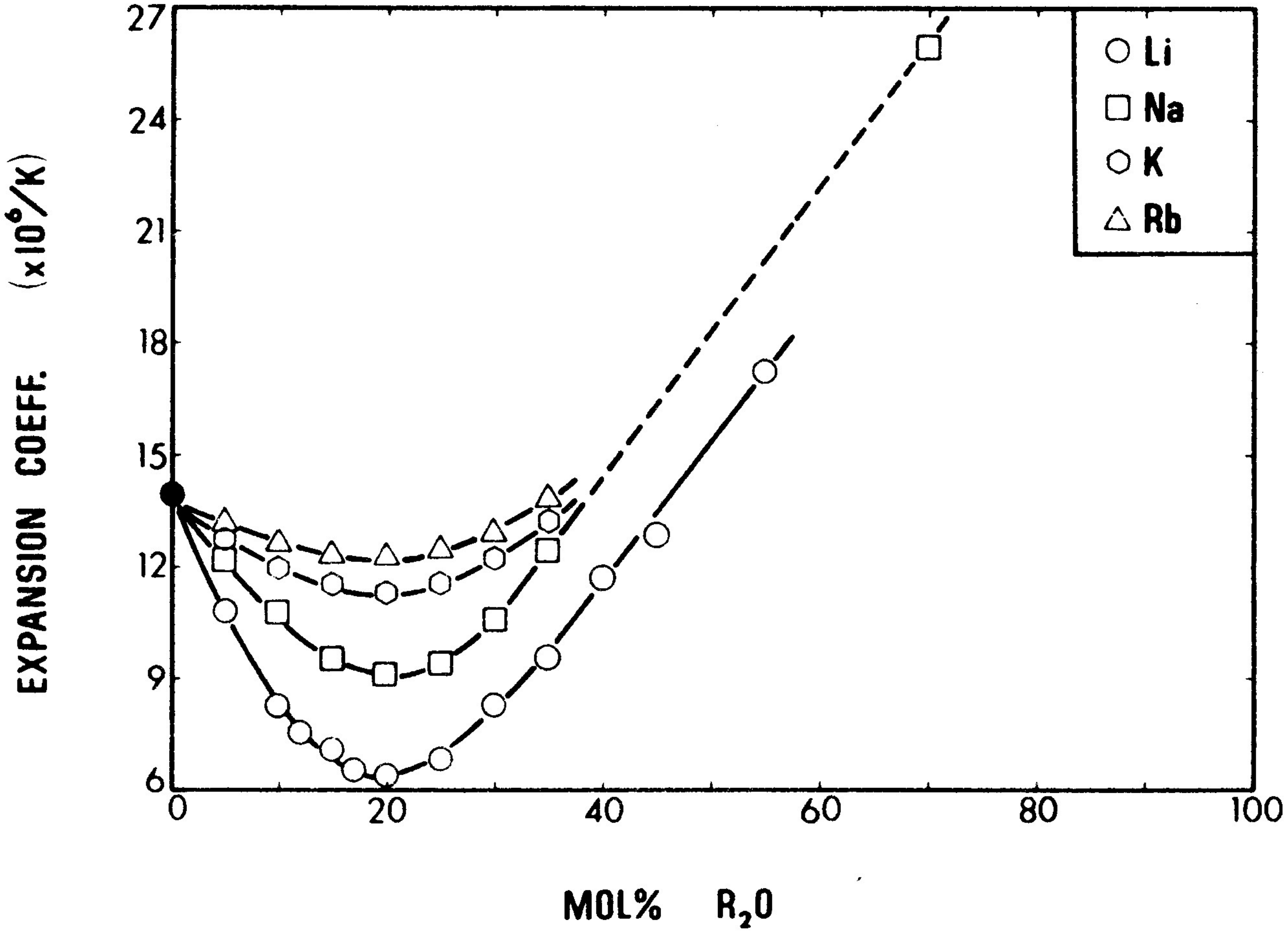




The molar volumes of alkali borate glasses

The coefficient of thermal expansion of alkali borate glasses

Symbols – SciGlass data



The majority of structural models described in the literature are based on incomplete information about the glass (melt) structure, which concerns ***only the atoms forming the network*** of a given system (*e.g*. boron-oxygen units or silicon-oxygen units, solely), whilst the presence of metal-oxygen polyhedra, which are also basic structural units, is neglected.

Thus, such models do not observe the requirements of the mass and charge balance and that of the minimal Gibbs energy of a given system. To compensate this inadequacy, the models use adjustable parameters. They do not have a predictive ability.

CHEMICAL APPROACH

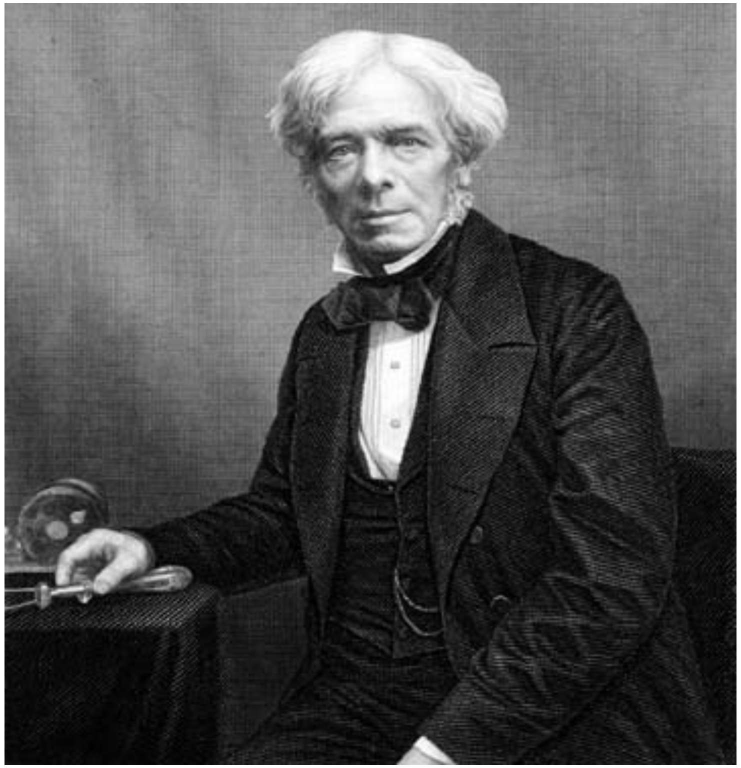
Glasses are products of chemical interactions between the substances forming the batch rather than the result of direct melting . This idea was first put forward as long ago as in the 19th century.

Mikhail Vasilievich Lomonosov

(1711-1765)

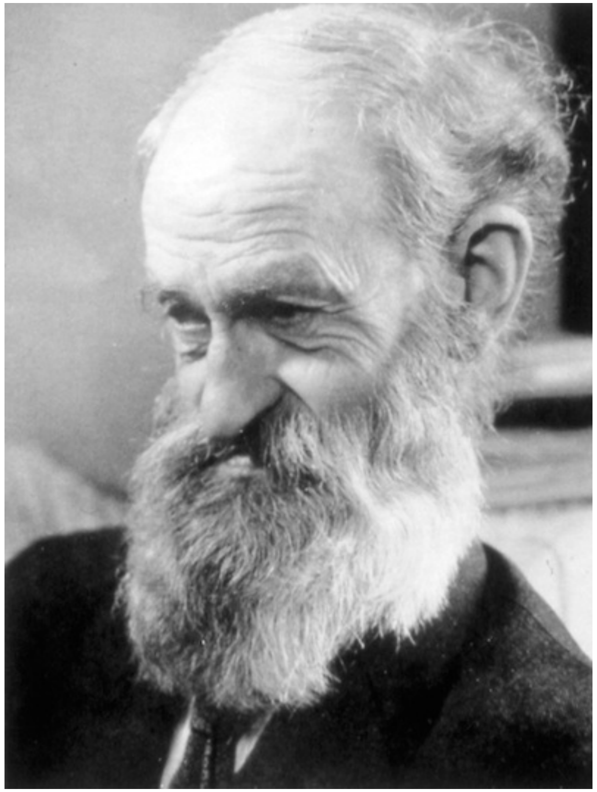
Wrong are all those,
Dear friend Shouvalov,
Who value glass below minerals

Letter Concerning the Usefulness of Glass,
M.V. Lomonosov, 1752



Michael FARADAY,
(1830-50s)

Dmitry I. MENDELEEV,
(1860s)



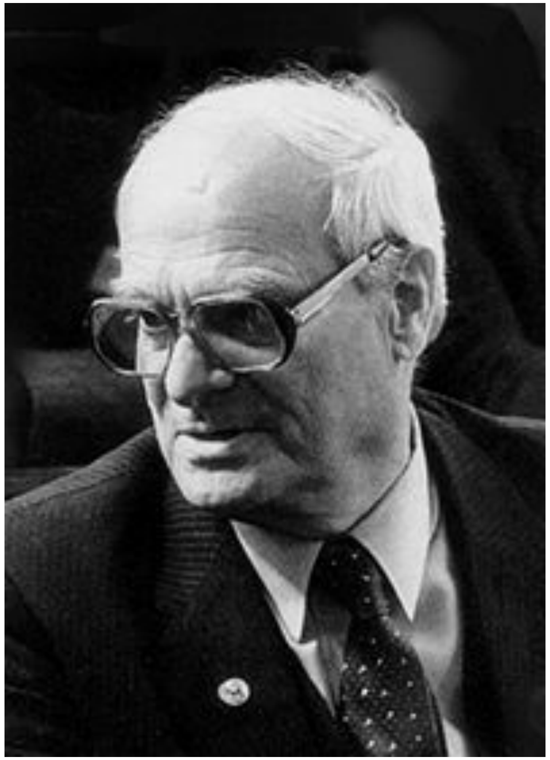
William E.S. TURNER,
(1920s)

Evgeny A. PORAI-KOSHITS,
(1930s)

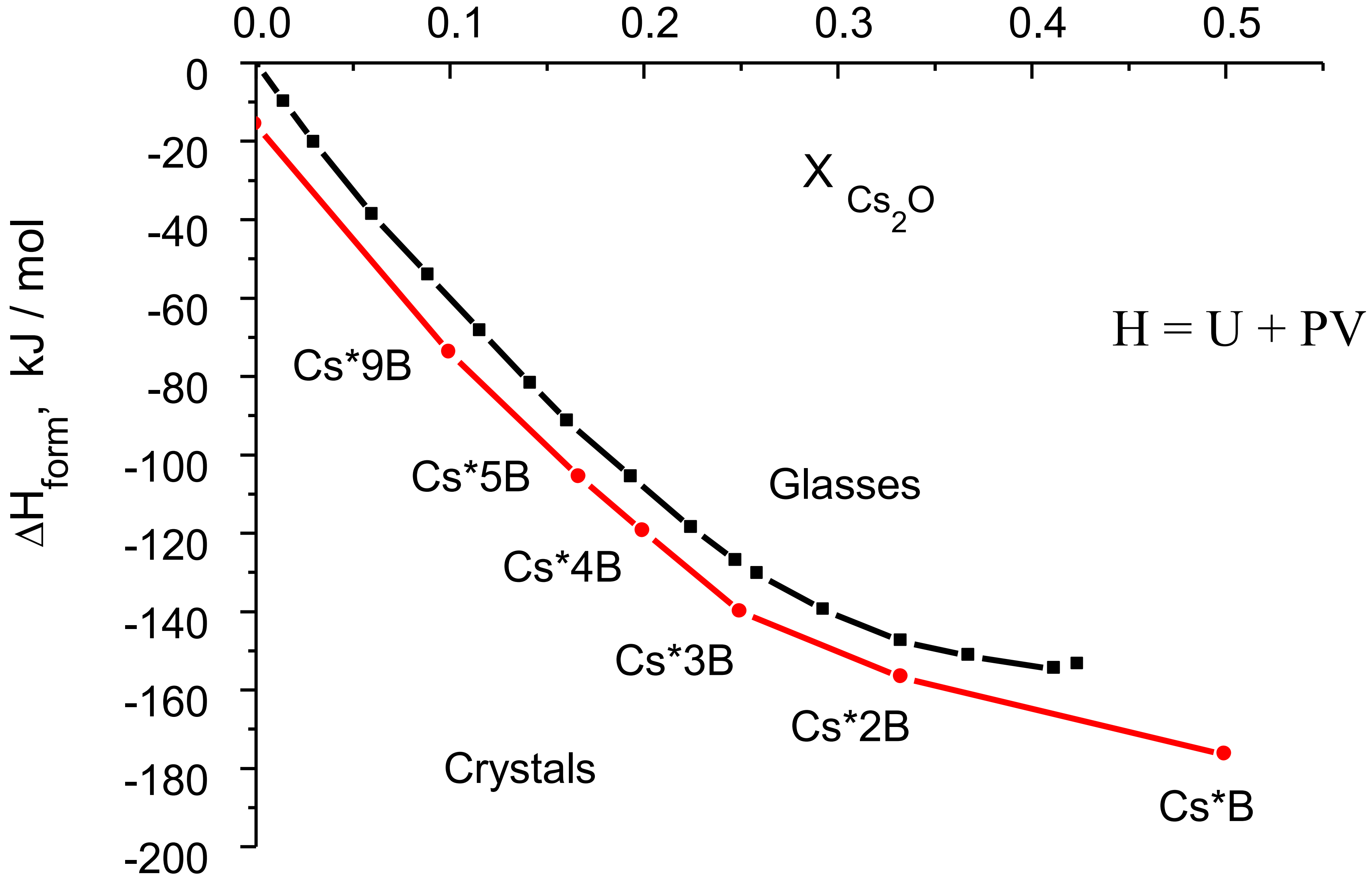
1996: At the 2nd International Conference on Borate Glasses, Crystals and Melts in Abingdon (UK): P.J. Bray with E.A. Porai-Koshits and S.K. Filatov

Jan KROGH-MOE
(1960s)

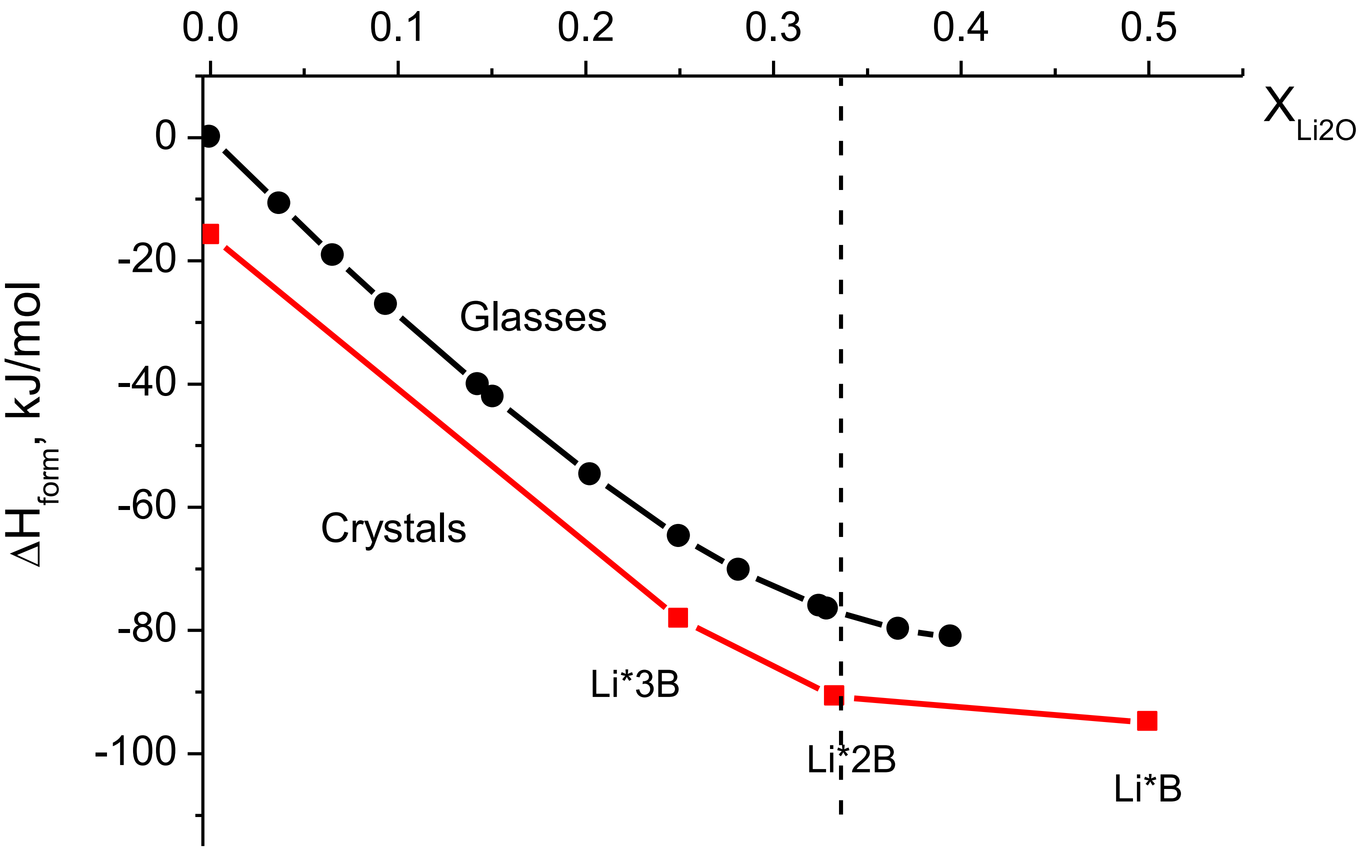
Mikhail M. SHULTZ
(1960-70s)



Enthalpies of formation of caesium borate glasses and crystals from oxides referred to mole of the type $xCs_2O\cdot(1-x)B_2O_3$.



Enthalpies of formation of lithium borate glasses and crystals from oxides referred to mole of the type $x\mathrm{Li_2O}\cdot(1\text{-}x)\mathrm{B_2O_3}$.



$\Delta H_{\mathrm{Li\cdot 2B,\ cryst}} = -90.6$ kJ/mol

$\Delta H_{\mathrm{crystallisation}} = -13.2$ kJ/mol

$\Delta H_{\mathrm{Li\cdot 2B,\ glass}} = -77.4$ kJ/mol

Glass: the non-equilibrium state or … ?

Roman Empire, I-III AD

Boris SHAKHMATKIN

Concept of the chemical structure of glasses and melts (1980s)

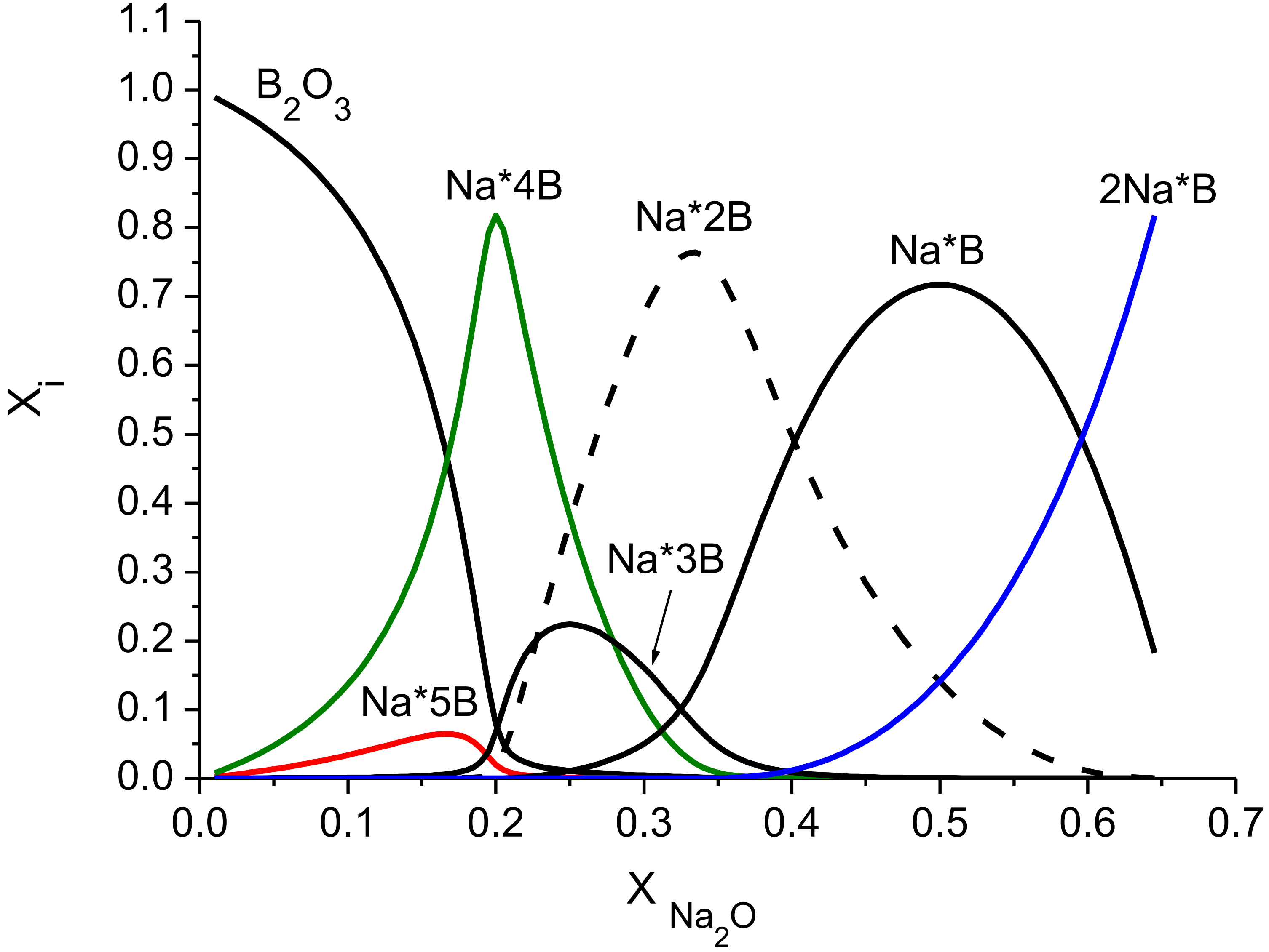
Glasses & melts are considered as solutions formed from nano-scale chemical groupings, which are products of interaction between oxide components. It is assumed that the stoichiometry and structure of groupings are closely related to those of the crystalline compounds existing in a given system.

This concept is based on the rigorous thermodynamic model of associated solutions applied by Shakhmatkin to glass-forming systems. The mathematical formalism of this approach consists of solving the set of equations for the law of mass action for all of the reactions between oxides proceeding in a given system,

$$mM_2O + nB_2O_3 = mM_2O \cdot nB_2O_3$$

and the equations of the law of mass balance of the components. A solution of this set of equations allows the equilibrium concentrations of all groupings to be calculated.

The chemical structure of glasses in the system Na_2O-B_2O_3



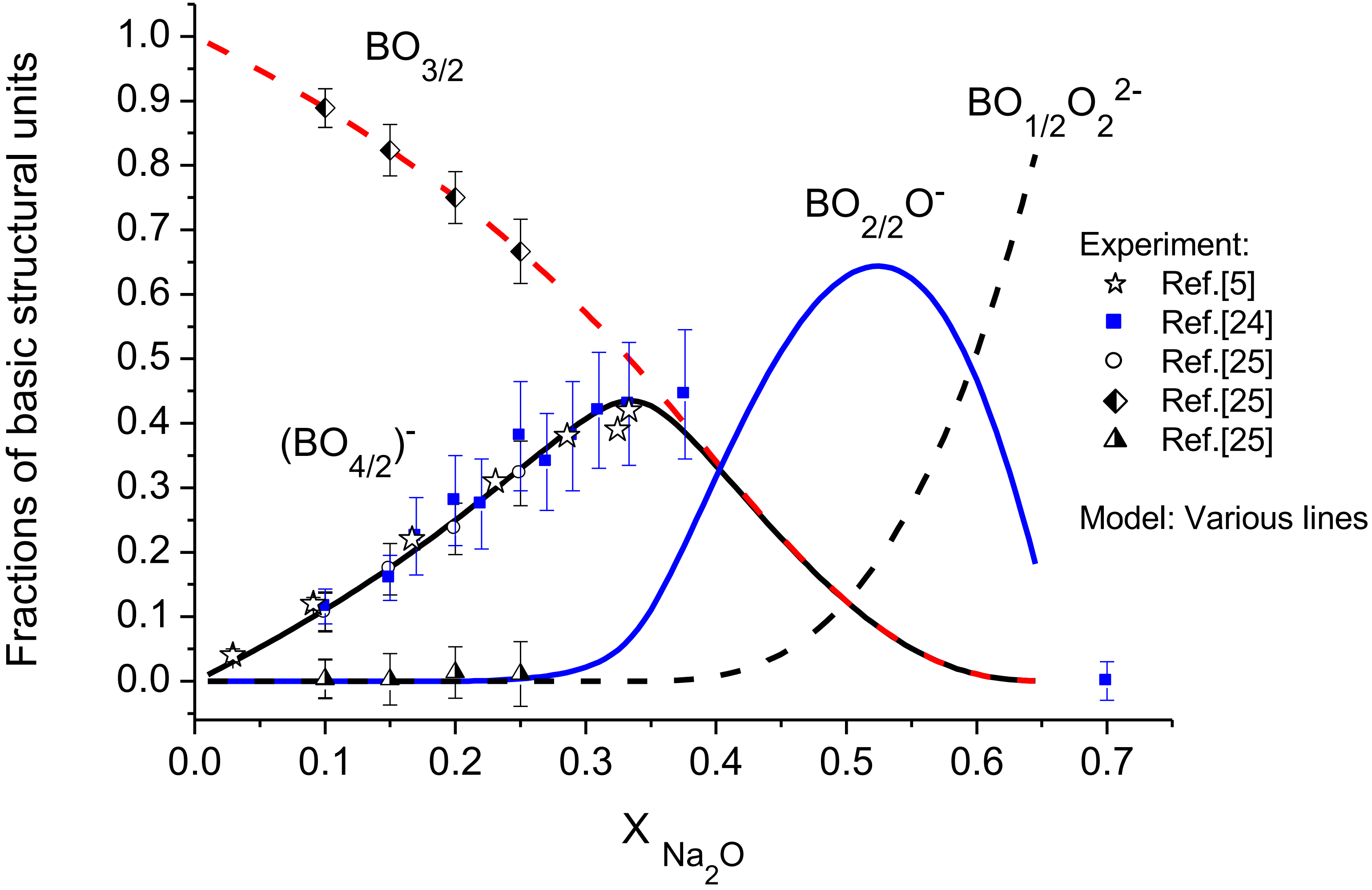
The borate and borosilicate chemical groupings present in sodium borosilicate glasses, and their relation to the short-range and intermediate-range order

Chemical groupings	Types and numbers of the basic structural units and superstructural units introduced into the glasses by 1 mole of each chemical grouping	
	Basic structural units	Superstructural units
B_2O_3	2BØ_3	Boroxol ring (½), BØ_3 (½)
$Na_2O\cdot 5B_2O_3$	$2[\text{BØ}_4]^-$, 8BØ_3	Pentaborate rings (2)
$Na_2O\cdot 4B_2O_3$	$2[\text{BØ}_4]^-$, 6BØ_3	Pentaborate ring (1), Triborate ring (1)
$Na_2O\cdot 3B_2O_3$	$2[\text{BØ}_4]^-$, 4BØ_3	Triborate rings (2)
$Na_2O\cdot 2B_2O_3$	$2[\text{BØ}_4]^-$, 2BØ_3	Diborate ring (1)
$Na_2O\cdot B_2O_3$	$2\ \text{BØ}_2\text{O}^-$	Cyclic metaborate ring (⅔)
$Na_2O\cdot B_2O_3\cdot 2SiO_2$	$2[\text{BØ}_4]^-$, $2Q^4$	Danburite ring (1)
$Na_2O\cdot B_2O_3\cdot 6SiO_2$	$2[\text{BØ}_4]^-$, $6Q^4$	Reedmergnerite rings (2)

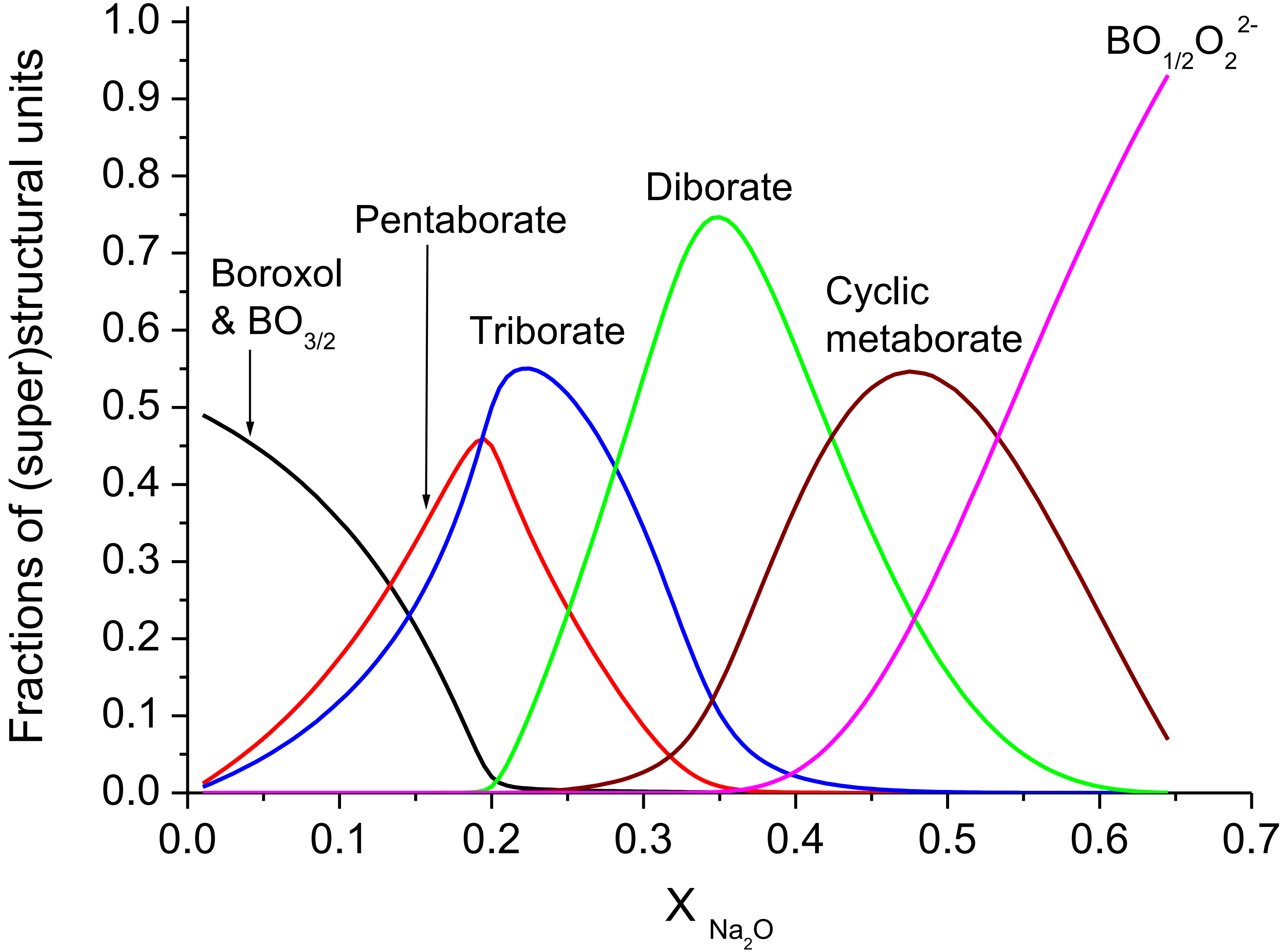
The silicate chemical groupings present in sodium silicate glasses, and their relation to the short-range order in the glass structure

Chemical groupings	Types and numbers of the basic structural units and superstructural units introduced into the glasses by 1 mole of each chemical grouping	
	Basic structural units	Superstructural units
SiO_2	Q^4	None
$3Na_2O\cdot8SiO_2$	$2Q^4$, $6Q^3$	
$Na_2O\cdot2SiO_2$	$2Q^3$	
$Na_2O\cdot SiO_2$	Q^2	

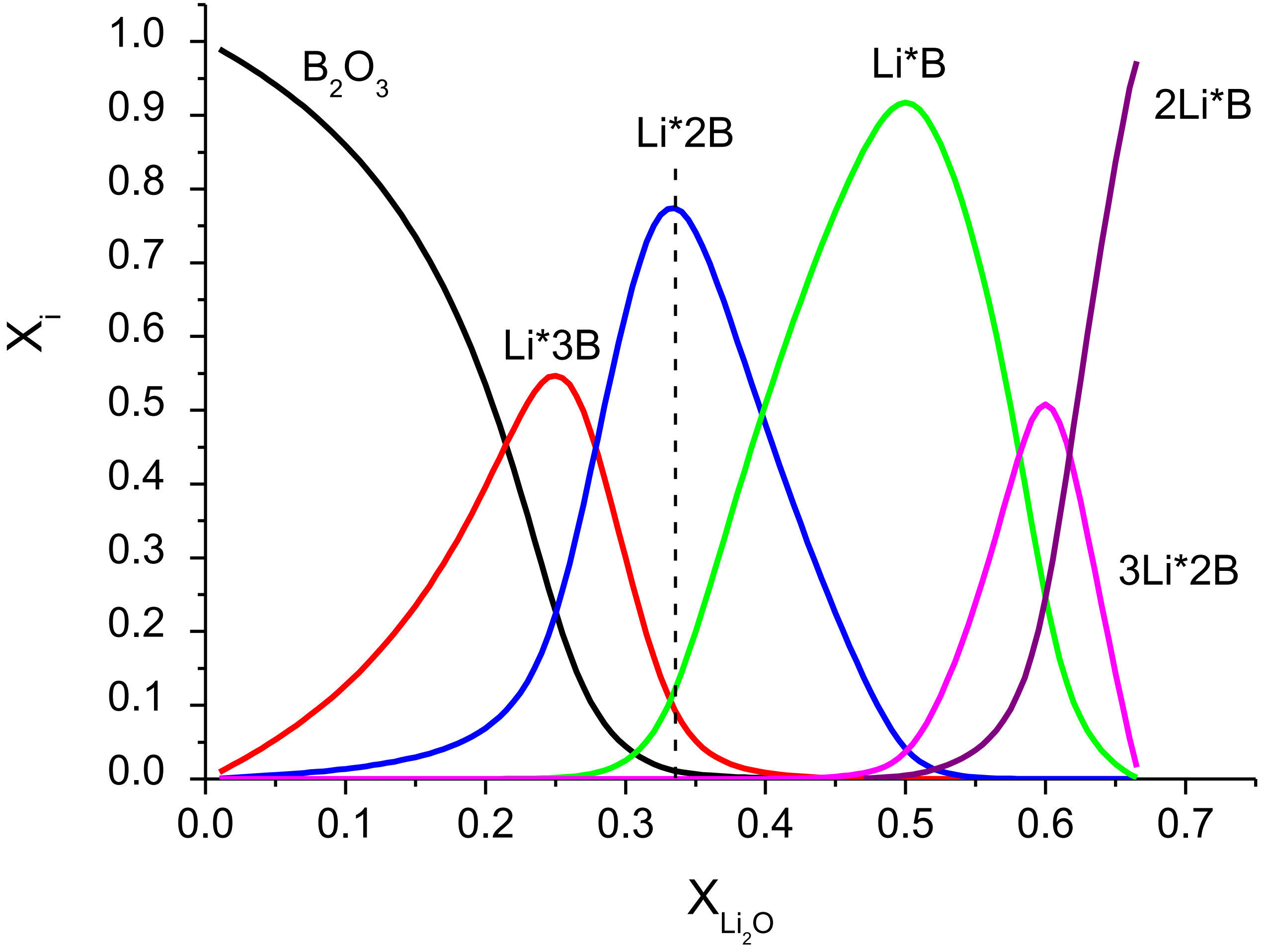
Basic structurtal units (the short-range order) in glasses of the system Na_2O-B_2O_3



Superstructural units in sodium borate glasses



The chemical structure of lithium borate glasses

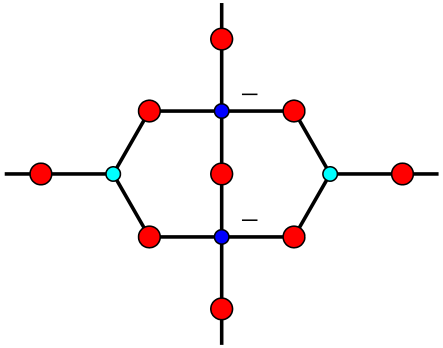


Glass of the diborate composition, $0.33Li_2O{\cdot}0.67B_2O_3$:

77.4% $Li_2O{\cdot}2B_2O_3$, 12.0% $Li_2O{\cdot}B_2O_3$, 9.4% $Li_2O{\cdot}3B_2O_3$, 1.1% B_2O_3

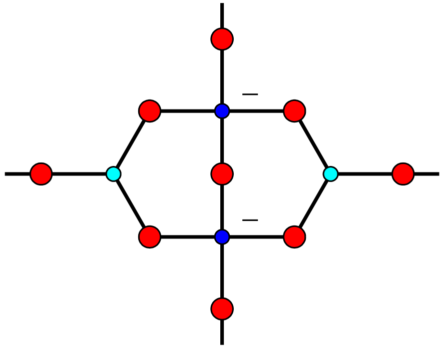
$Li_2O*2B_2O_3$

Crystal d = 2.44 g/cm^3

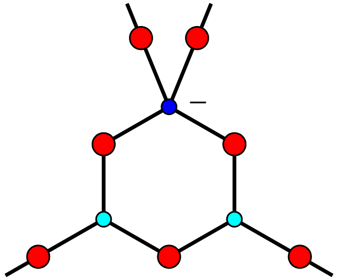


Diborate, 100%

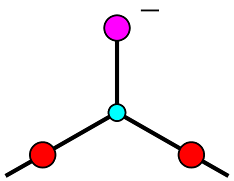
Glass d = 2.27 g/cm^3



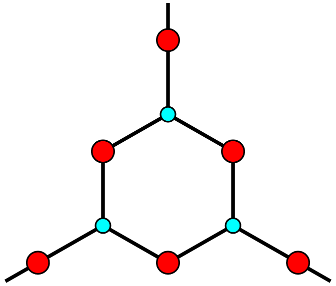
Diborate, 74.8%%



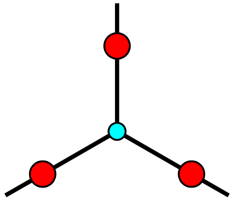
Triborate, 14.7%



$\text{BØ}_2\text{O}^-$, 10.1%



Boroxol, 0.2%



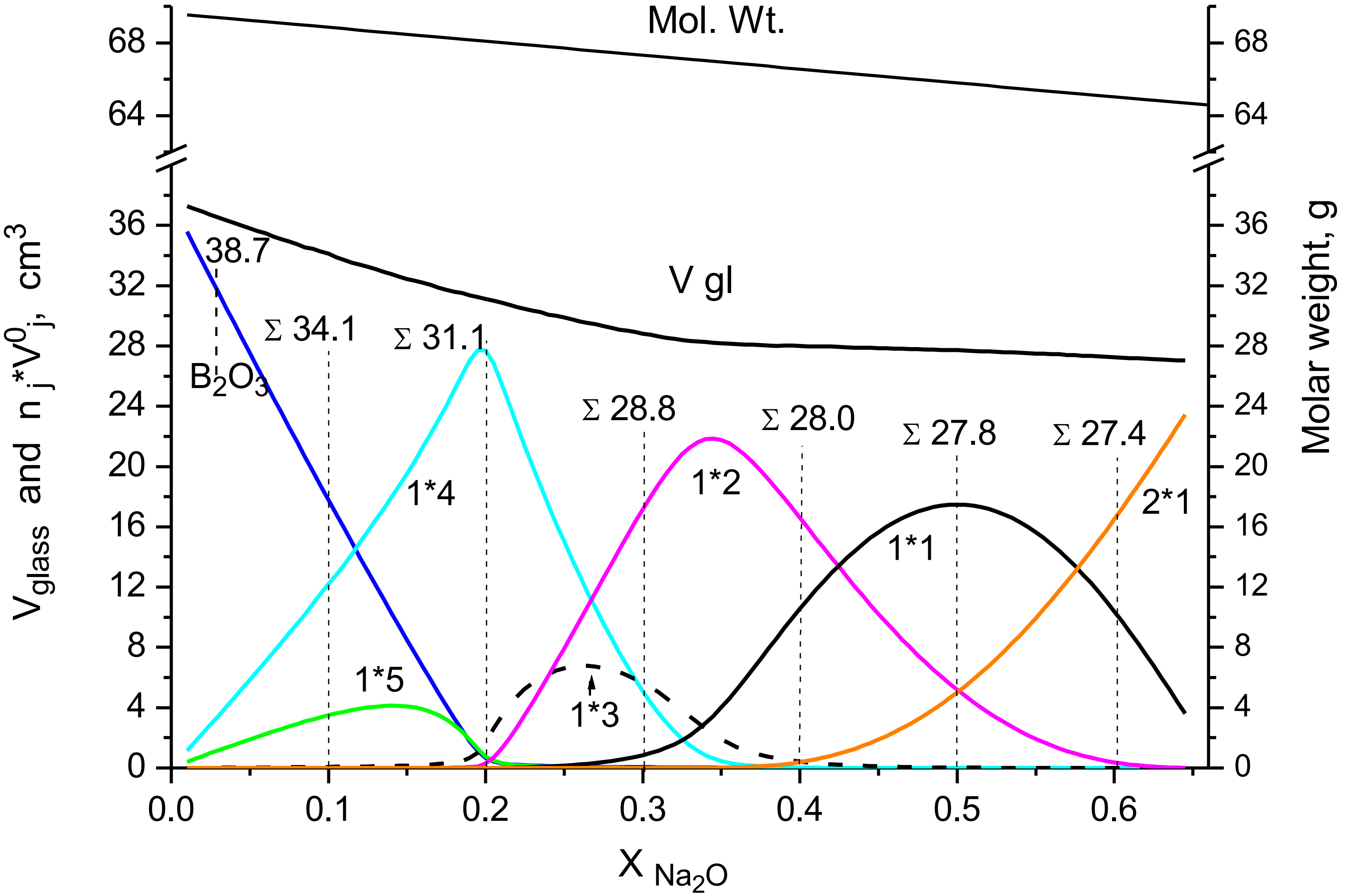
BØ_3, 0.2%

The structure-property relationship

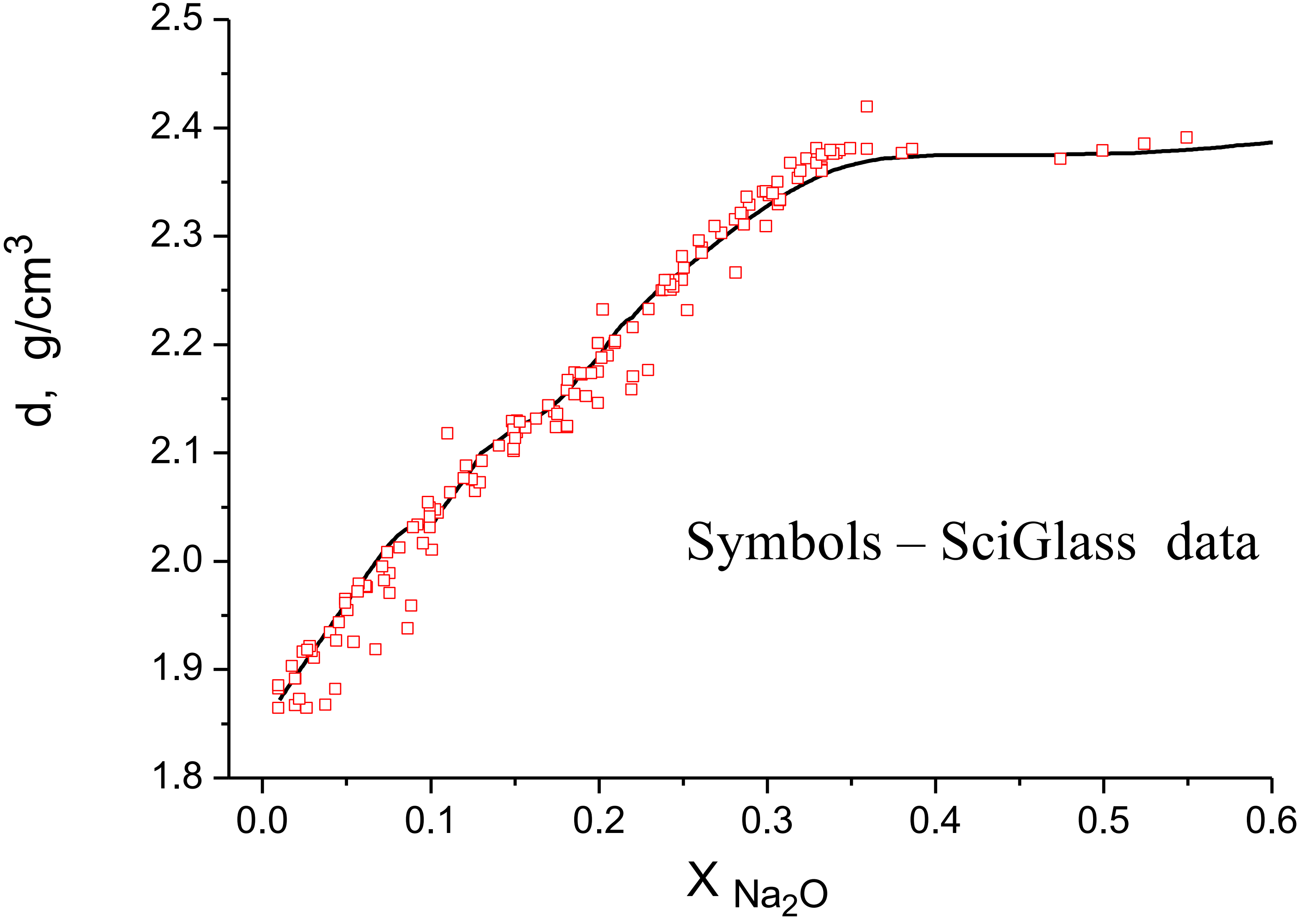
The concept of the chemical structure allows a wide range of glass properties to be calculated, without use of adjustable parameters, as an additive function of the relevant property of the crystalline compounds that form in a given system:

$$V_{glass} = \Sigma n_j \cdot V^0_j$$

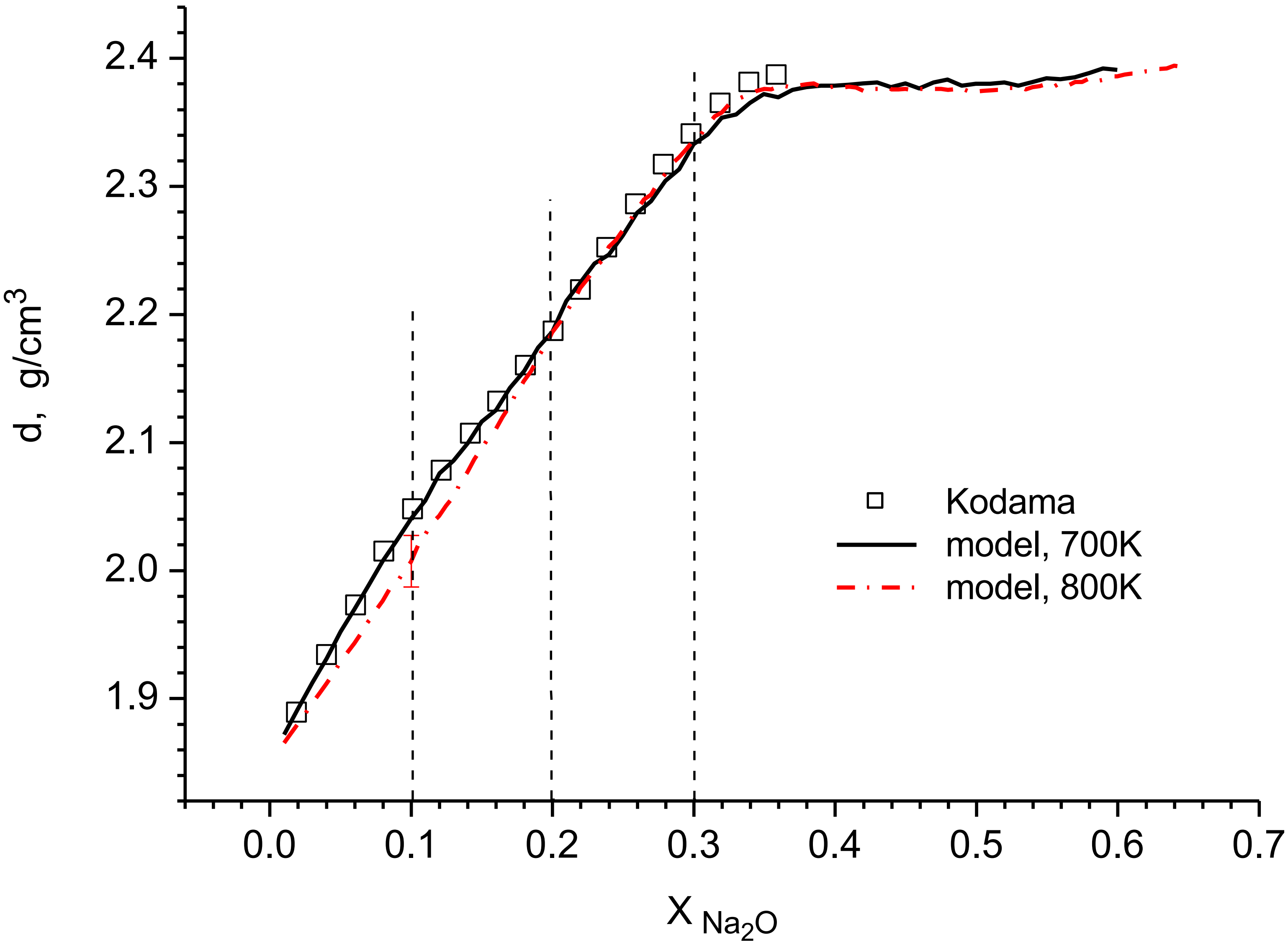
The contribution from various chemical groupings to the molar volume of sodium borate glass at 800K



The density of sodium borate glasses



Na_2O-B_2O_3 : a comparison of the calculated densities at 700 and 800K with the experimental values



Chemical origin of phase separation

1968: Shaw & Uhlmann reported immiscibility regions were found over extended composition regions in glasses of five alkali borate systems (Electron microscopy).

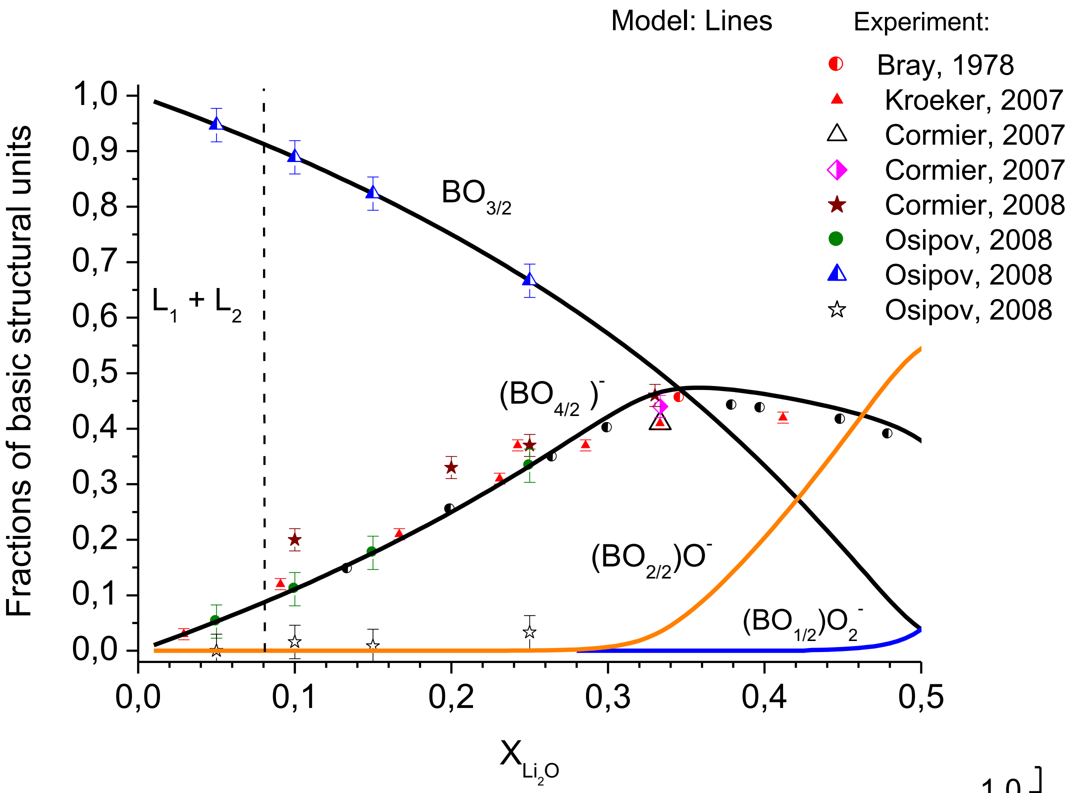
R.R. Shaw, D.R. Uhlmann, *J. Amer. Ceram. Soc.* 1968, **51**, p. 377.

1977: Golubkov & Porai-Koshits convincingly demonstrated that it is only lithium borate glasses that tend to phase separate and this occurs over a much narrower region than that reported by Shaw & Uhlmann (SAXS)

V.V. Golubkov, A.P. Titov, T.N. Vasilevskaya & E.A. Porai-Koshits, *Sov. J. Glass Phys. Chem.*, 1977, **3**, p. 289.

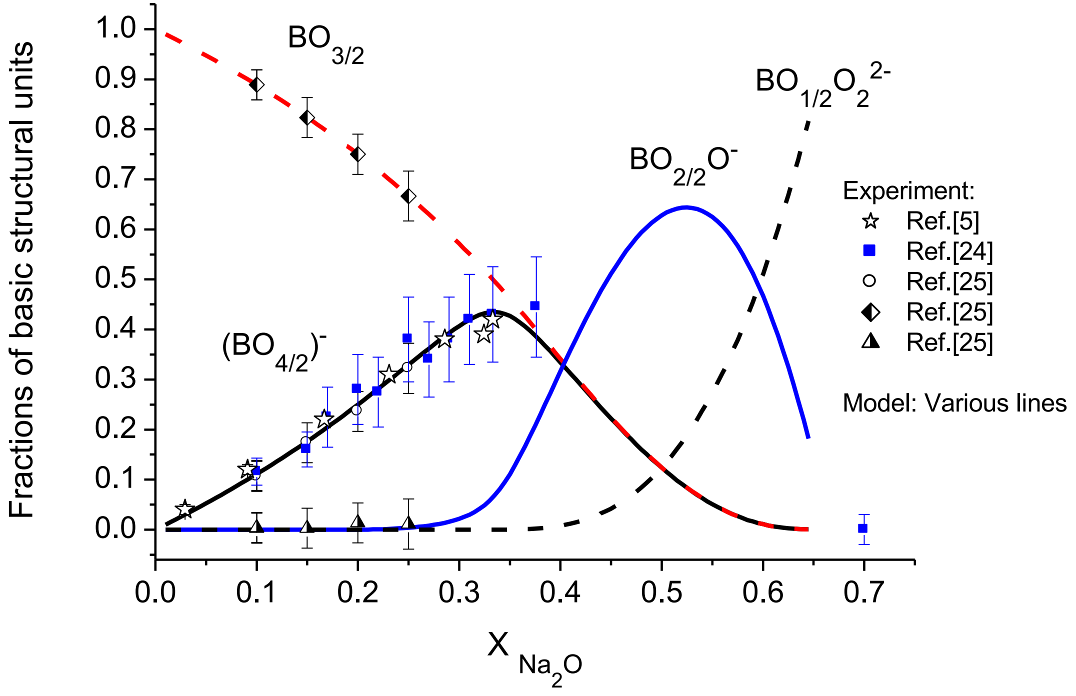
XI International Congress on Glass, Prague, 1977

The short-range order in alkali borate glasses



Li_2O-B_2O_3

Na_2O-B_2O_3



Phase separation regions and crystalline compounds in binary systems

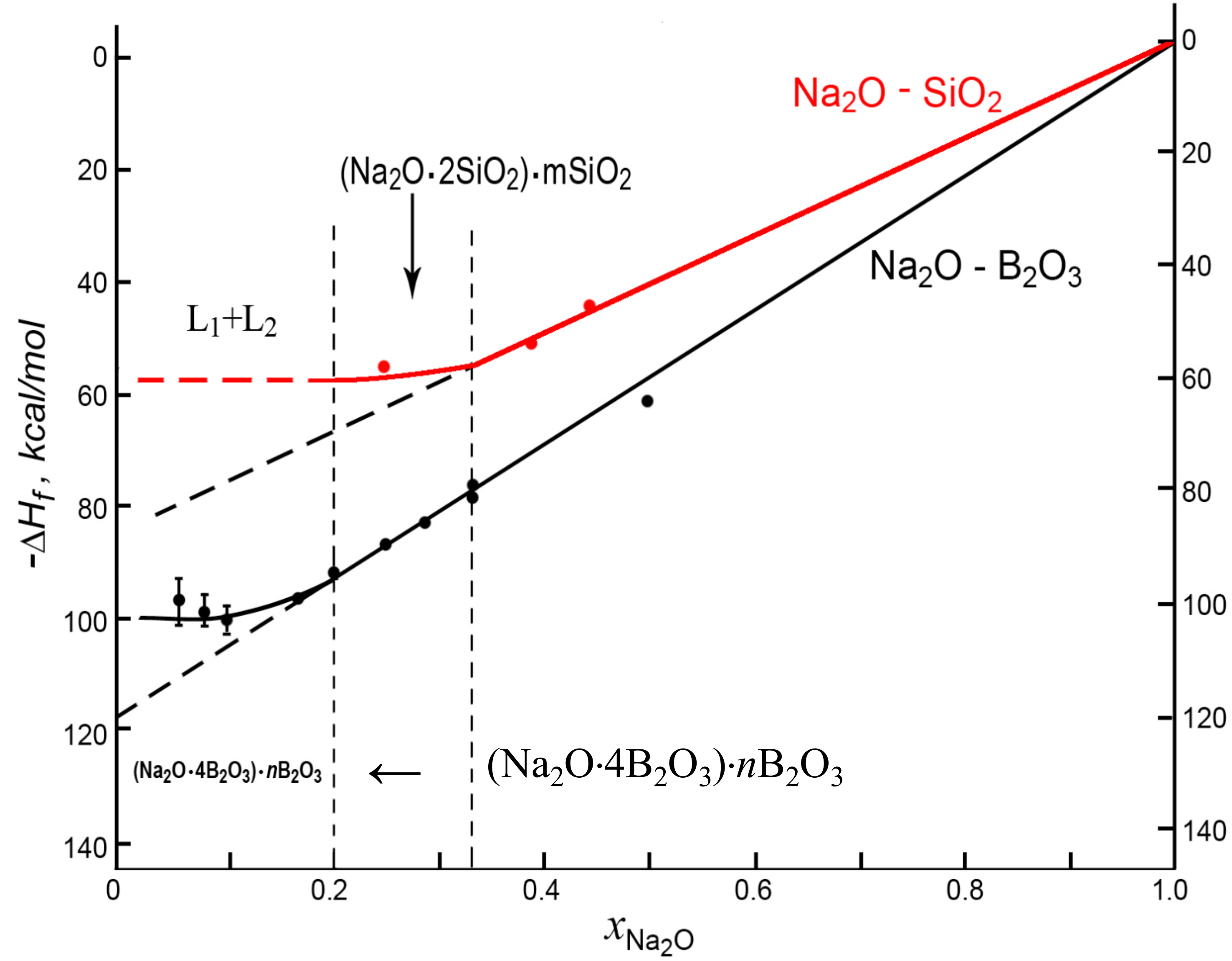
Systems	mol. % $M_2O(MO)$	Crystalline compounds
$MgO-B_2O_3$	0 – 40	Mg·B, 2Mg·B, 3Mg·B
$CaO-B_2O_3$	0 – 33	Ca·2B, Ca·B, 2Ca·B, 3Ca·B
$BaO-B_2O_3$	0 – 18	Ba·4B, Ba·2B, Ba·B, 2Ba·B
Li_2O-SiO_2	0 - 33	Li·2Si, Li·Si, 2Li·Si
Na_2O-SiO_2	0 – 20	3Na·8Si, Na·2Si, Na·Si, 3Na·2Si, 2Na·Si
$CaO-SiO_2$	0 – 35	Ca·Si, 3Ca·2Si, 2Ca·Si, 3Ca·Si
$Li_2O-B_2O_3$	0 – 8	Li·3B, Li·2B, Li·B, 2Li·B
$Na_2O-B_2O_3$	No phase separation	Na·9B, Na·5B, Na·4B, Na·3B, Na·2B, Na·B, 2Na·B
$K_2O-B_2O_3$		K·5B, 5K·19B, K·3B, K·2B, K·B
$Rb_2O-B_2O_3$		Rb·5B, 5Rb·19B, Rb·3B, Rb·2B, Rb·B
$Cs_2O-B_2O_3$		Cs·9B, Cs·5B, 3Cs·13B, Cs·3B, Cs·2B, Cs·B

The nature of phase separation in glasses can be understood if chemical interactions that proceed in course of glass formation are considered together with the enthalpies of these reactions:

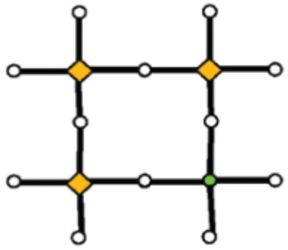
$M_2O + nB_2O_3 \leftrightarrow M_2O{\cdot}nB_2O_3$ in borate systems,

$M_2O + mSiO_2 \leftrightarrow M_2O{\cdot}mSiO_2$ in silicate systems.

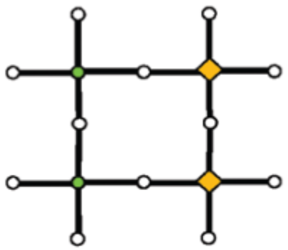
Experimental enthalpies of formation of glasses from oxides referred to moles of the type $Na_2O{\cdot}nB_2O_3$ and $Na_2O{\cdot}mSiO_2$



System $Na_2O \cdot B_2O_3 \cdot 2SiO_2$: phase separation and the content of borosilicate rings



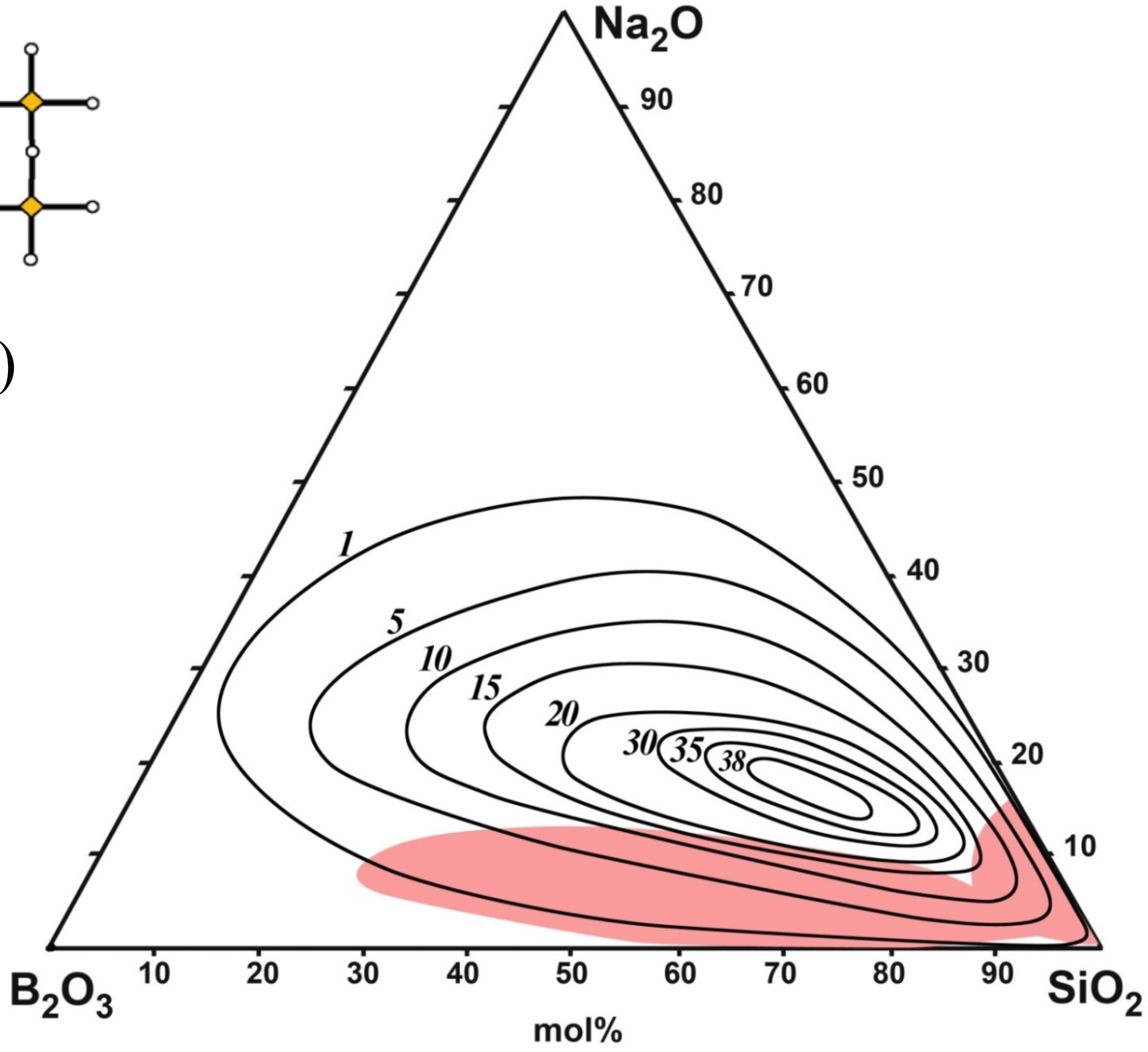
(a)



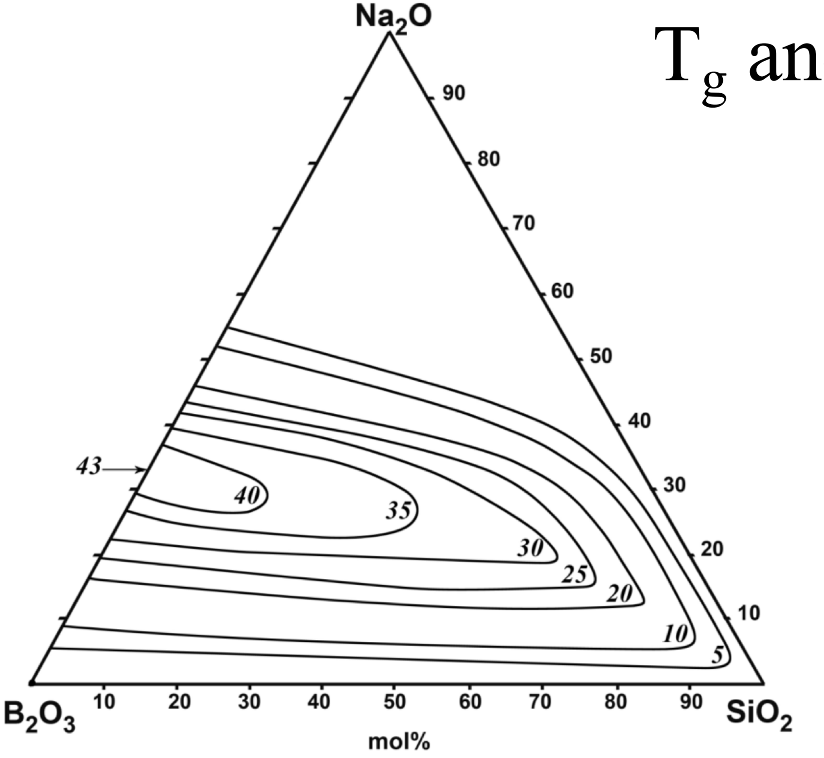
(b)

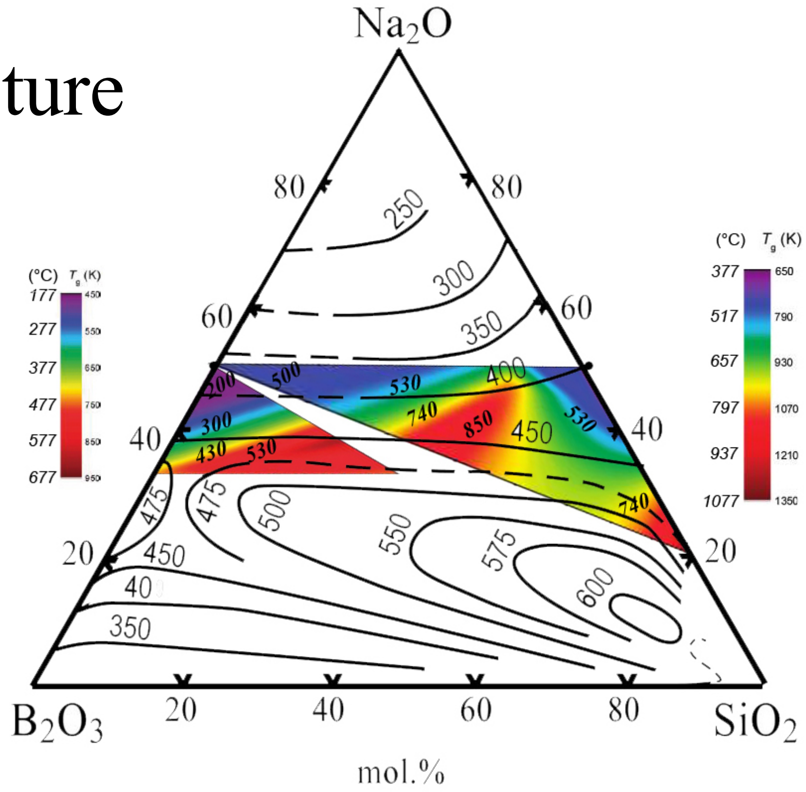
(a) $[B\text{Ø}_4]^{-} : 3Q^4$

(b) $2[B\text{Ø}_4]^{-} : 2Q^4$



T_g and the structure





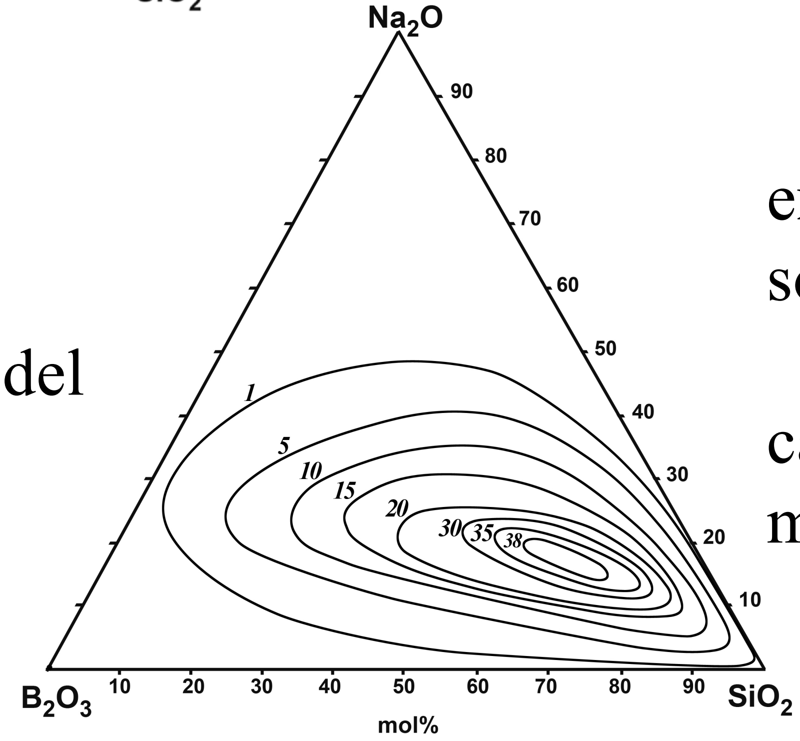
$[BO_{4/2}]^-$

↑

Thermodynamic model

↓

Reedmergnerite
+ Danburite



T_g,
experimental [SciGlass,
solid and dashed lines]
and
calculated (topological
model, triangles)

Conclusions

A small difference between the enthalpies of formation of borate glasses and crystals points to their structural similarity.

The concept of the chemical structure enables a variety of properties of glasses and their structure to be calculated on the unified basis. Due to this, the structure-property relationship and the relationship between the short-range and intermediate-range order in the structure are established quantitatively.

It is shown that the presence of 4-fold co-ordinated boron atoms in glasses cannot explain experimentally observed changes in their properties. Hence, the notion of boron anomaly, which exists since the 1960s, had lost its significance.

It is revealed that binary glasses tend to phase separate only in the systems where no low-alkali/alkaline-earth crystalline compounds form (< 20 mol. % M_2O or MO).