

Chemical approach to the glass structure and properties

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Abstract

This paper continues the series of works by the present authors on the modelling of glass structure and properties. Calculations are performed using the concept of the chemical structure based on the rigorous thermodynamic model of associated solutions. The aim of the present contribution is to demonstrate the applicability of the concept to a wider range of systems than that considered before. For this reason, glasses in the systems with different chemical natures determined by the acidity and basicity of the constituent oxides are considered. The glass structure is calculated at the level of the short-range order in the systems BaO–SiO₂ and M₂O(MO)–P₂O₅ (M = Li, Na and Zn) and the intermediate-range order in the systems Rb₂O–B₂O₃ and Cs₂O–B₂O₃. The structure-property relationship is quantitatively established by example of the molar volume of BaO–SiO₂ glasses. All calculations are performed without use of adjustable parameters and the results obtained are compared with the experimental data available in the literature.

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1. Introduction

Theoretical approaches to a description of the vitreous state can be considered as a useful tool for an efficient planning of experiments and an interpretation of the results obtained. Models, which can be considered as reliable, are characterized by a number of specific features. A reliable model must be able to describe glasses with any number of components and over extended compositional regions, to use the minimum number of well-reasoned assumptions and avoid employing adjustable parameters or, if needed, they must have a clear physical meaning. It ultimately should allow the glass structure and properties to be calculated on a unified basis from which a relationship between them is established quantitatively and without the need of additional experimental data as it should have a predictive ability.

The model used in this paper was developed in the late 1970s by Boris Shakhmatkin at the Institute of Silicate Chemistry (St. Petersburg, Russia). Glasses are considered as a product of chemical interactions between oxide components of a given system rather than as a result of the batch melting. The approach is based on a rigorous thermodynamic model of associated solutions, which led to a development of the concept of chemical structure of glasses. This concept, considered further in more detail, meets all of the above requirements that characterize a reliable model. It became internationally known in 1994 [1] and has been successfully used for calculations of a large variety of glass properties in different binary and ternary systems. Among them are the integral and partial thermodynamic potentials, heat capacity, density, refractive index, transport properties (diffusion coefficient and electrical conductivity), red-ox equilibria and the solubility of gases in glasses and melts. In all cases, the calculation error is comparable to the error of reliable experimental measurements. The concept also enables the tendency of glasses

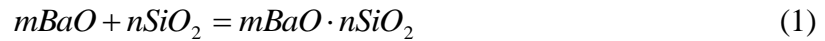
towards crystallization and their chemical durability of glasses to be estimated as well as their tendency towards phase separation to be analyzed on the basis of information about the phase diagram of the system in question [1-6].

This approach was successfully used for a description of the short-range order in the structure of borate, silicate and borosilicate glasses, and the intermediate-range order in borate and borosilicate glasses. The error of these calculations does not noticeably exceed that of experimental studies of glasses by NMR and Raman spectroscopies. The approach also allows the relationship between two levels (the short- and intermediate-range order) in the glass structure to be established quantitatively. The same refers to the structure-property relationship in glasses. Most examples of calculations can be notably found in various papers by Vedishcheva in co-authorship with Wright & Shakhmatkin and more recently by Liska and coworkers in phosphate glasses [7-9]. In the present paper, the concept of chemical structure is reviewed for a description of structure and properties of glasses in silicate, borate and phosphate systems that were not considered before. They have been chosen due to the fact that they are characterized by different acidity and basicity of their oxide components. The acid-base nature of any system is quantitatively determined by a difference between the electronegativity (χ) of the elements forming the acidic and basic oxides, which in the present case are Si and Ba, B and Rb, Cs, and P and Zn, Li, Na. From the χ values reported for these elements by Pauling [10], it follows that the difference increases in the series $(\chi_{\text{P}}-\chi_{\text{Zn}}) < (\chi_{\text{Si}}-\chi_{\text{Ba}}) < (\chi_{\text{B}}-\chi_{\text{Rb}}) \approx (\chi_{\text{P}}-\chi_{\text{Li}}) < (\chi_{\text{B}}-\chi_{\text{Cs}}) \approx (\chi_{\text{P}}-\chi_{\text{Na}})$, and hence the acid-base interactions become more pronounced in the same direction.

2. Thermodynamic approach and the concept of chemical structure

This approach considers glasses formed from components with different chemical natures as solutions, whose constituents are the unreacted oxides and the products of their interaction. It is assumed that (i) these products form chemical groupings similar in stoichiometry to those of the crystalline compounds existing in the phase diagram of the system in question; (ii) a structural similarity between the groupings and crystals also exists, at least in terms of the ratio of the basic structural units; and (iii) the groupings and the unreacted oxides form an ideal solution. All of these assumptions are well-founded as is shown in Ref. [11].

The mathematical formalism of this consists in solving the set of equations for the law of mass action for reactions of formation of chemical groupings from oxides that proceed in a given system, and the equations of the law of mass balance of the components. It is necessary to take into account the formation of all chemical groupings whose crystalline analogues can be found in the equilibrium phase diagram of the system considered. In the case of the system BaO–SiO₂ [12], these are the compounds BaO·2SiO₂, 2BaO·3SiO₂, BaO·SiO₂, 2BaO·SiO₂. The groupings with these stoichiometries form from oxides, according to the reaction



where m is equal to 1 and 2, and n is equal to 1, 2 and 3. The set of equations to be solved comprises the following relationships:

$$K_i = \frac{X_{mBaO \cdot nSiO_2}}{X_{BaO}^m \cdot X_{SiO_2}^n} \quad (2)$$

$$X_{BaO}^* = n_{BaO} + n_{BaO \cdot 2SiO_2} + 2n_{2BaO \cdot 3SiO_2} + n_{BaO \cdot SiO_2} + 2n_{2BaO \cdot SiO_2} \quad (3)$$

$$X_{SiO_2}^* = n_{SiO_2} + 2n_{BaO \cdot 2SiO_2} + 3n_{2BaO \cdot 3SiO_2} + n_{BaO \cdot SiO_2} + n_{2BaO \cdot SiO_2} \quad (4)$$

$$K = \exp \left(-\frac{\Delta G_f^0}{RT} \right) \quad (5)$$

$$X_i = \frac{n_i}{\Sigma n} \quad (6)$$

Equation (2) is the law of mass action written, in an ideal form, for reaction (1). The symbol K_i represents the equilibrium constant of reaction (1), $X_{mBaO \cdot nSiO_2}^m$, X_{BaO}^m and $X_{SiO_2}^n$ are the equilibrium concentrations of the above chemical groupings and the unreacted oxides. The relationships (3) and (4) are the equations of the law of mass balance, where the symbols $n_{mBaO \cdot nSiO_2}$, n_{BaO} and n_{SiO_2} depict, respectively, the numbers of moles of the chemical groupings and the unreacted oxides in a given glass (melt), and X_{BaO}^* and $X_{SiO_2}^*$ represent its analytical composition in mole fractions. Equation (5) is used for calculating the equilibrium constants, K_i , on the basis of the standard Gibbs free energies of formation from oxides, ΔG_f^0 , of the compounds existing in the system. These potentials are obtained using the data from reference books, hence avoiding the use of adjustable parameters. Equation (6) describes the relationship between a mole fraction, X_i , and the numbers of moles, n_i , of the species i in a given glass or melt. The index i refers both to the chemical groupings and the unreacted oxides. The symbol Σn denotes the total number of their moles. The solution of the set of equations (2)-(5) yields information on the numbers of moles of the chemical groupings and the unreacted oxides, which enables the chemical structure of glasses (melts) to be determined. Note that at constant temperature, pressure and numbers of moles of the initial substances, the above set of nonlinear equations has the only solution.

The notion of chemical structure of glasses formed from components with different chemical natures implies the content of various chemical groupings that are the products of the chemical interaction between the constituent oxides, together with the unreacted oxides themselves. The content of all of the groupings can be presented as absolute values, *i.e.* in terms of the numbers of moles, n_i , or as relative values, the molar fractions, X_i . Note that the chemical groupings are formed from the basic structural units, the ratio of these units being similar to that in the crystalline compounds with the same stoichiometry. The observance of the principle of the minimum Gibbs free energy of a system in the vitreous state requires that the basic structural units in the groupings are combined together in the same manner as those in the relevant crystalline compounds. In other words, it can be expected that the chemical groupings present in glasses comprise associates similar to the superstructural units present in the crystals that form in the system under consideration. Hence, the concept of the chemical structure enables both the short-range order and the intermediate-range order in the glass structure to be described, at the levels of the basic structural units and superstructural units, respectively.

The concept of the chemical structure explains the difference between the structures of glasses and crystals in terms of the model of associated solutions. The model considers glasses as a superposition of various chemical groupings, whose stoichiometries correspond to those of the crystalline compounds forming in the given system. All of these groupings are present in any glass of the system but in different quantities that depend on the glass composition. As a result, in glasses of stoichiometric compositions, the characteristic grouping is always present together with other species.

3. Results and discussion

BaO-SiO₂ glasses

The chemical structure of glasses in the system BaO–SiO₂, which is determined by the groupings BaO·2SiO₂, 2BaO·3SiO₂, BaO·SiO₂, 2BaO·SiO₂ and the unreacted oxides SiO₂ and BaO, is shown in Fig. 1 in terms of the molar fractions of the groupings, X_i . These values were calculated with the accuracy of ± 0.05 .

It is seen that the unreacted SiO₂ dominated the chemical structure up to the BaO content equal to ~ 23 -25 mol. % BaO. At a higher modifier content, the equilibrium concentration of SiO₂ decreases due to the simultaneous formation of the groupings BaO·2SiO₂, 2BaO·3SiO₂ and BaO·SiO₂, with the domination of the latter over the composition region 42-60 mol. % BaO. The grouping 2BaO·SiO₂ determines the chemical structure in glasses where the BaO content exceeds 60 mol. %.

The groupings introduce into glasses the following basic structural units, which are silicon-oxygen tetrahedra with different numbers of bridging oxygen atoms indicated in brackets: Si^[4] (SiO₂), Si^[3] (BaO·2SiO₂ and 2BaO·3SiO₂), Si^[2] (BaO·SiO₂ and 2BaO·3SiO₂) and Si^[0] (2BaO·SiO₂). Knowledge of the numbers of structural units in each grouping (which is equal to those in the corresponding crystals) and the equilibrium concentration of the groupings is used for calculating the distribution of Si^[n] units in the barium silicate glasses, which presents the short-range order in their structure (Fig. 2). The calculations were performed with the error not exceeding ± 0.05 , using the following equations:

$$\text{Si}^{[4]} = \frac{X_{\text{SiO}_2}}{\Sigma Q^n} \quad (7) \quad \text{Si}^{[3]} = \frac{2(X_{\text{BaO} \cdot 2\text{SiO}_2} + X_{2\text{BaO} \cdot 3\text{SiO}_2})}{\Sigma Q^n} \quad (8)$$

$$\text{Si}^{[2]} = \frac{X_{\text{BaO} \cdot \text{SiO}_2} + X_{2\text{BaO} \cdot 3\text{SiO}_2}}{\Sigma Q^n} \quad (9) \quad \text{Si}^{[0]} = \frac{X_{2\text{BaO} \cdot \text{SiO}_2}}{\Sigma Q^n} \quad (10)$$

$$\Sigma \text{Si}^{[n]} = X_{\text{SiO}_2} + 2X_{\text{BaO} \cdot 2\text{SiO}_2} + 3X_{2\text{BaO} \cdot 3\text{SiO}_2} + X_{\text{BaO} \cdot \text{SiO}_2} + X_{2\text{BaO} \cdot \text{SiO}_2} \quad (11)$$

Here the symbol X_i denotes the molar fractions of the chemical groupings present in barium silicate glasses. The calculated distribution of $\text{Si}^{[n]}$ units in glasses and the available experimental values from Ref. [13] are shown in Fig. 2, which reveals a good agreement between them.

The knowledge of the chemical structure of glasses, expressed in terms of the numbers of moles of the chemical groupings and of the unreacted constituent oxides, allows the calculation of a wide range of glass properties without use of adjustable parameters, as an additive function of the relevant property of the crystalline compounds that form in a given system. The molar volume of glass, V_{glass} , is one of such properties and is calculated as the additive function of the molar volume of the relevant crystalline compounds (V_j^0):

$$V_{glass} = \sum n_j \cdot V_j^0 \quad (12)$$

where V_j^0 represents the molar volume of the crystalline compounds (with the exception of the unreacted glass-forming oxides whose molar volume should refer to their vitreous state), and n_j represents the number of moles of the species j present in the glass. The index j refers both to the chemical groupings and to the unreacted oxides. On average, the inaccuracy of these calculations, estimated in terms of the density, does not exceed $\pm 0.02 \text{ g.cm}^{-3}$, which is comparable to the uncertainty of reliable experimental measurements. This is confirmed by the good agreement between the calculated and experimental densities of barium silicate glasses shown in Fig. 3.

It is seen that there are two divergent sets of the experimental data. Due to the fact that the model dependence is calculated with the observance of the principle of the minimal Gibbs free energy of the system, it undoubtedly points to the experimental values, which are reliable.

Establishing structure-property relationships is one of the important problems of material science in general and glass science in particular. However, the majority of structural models described in the literature cannot be used for establishing quantitatively this relationship in glasses. This is due to the fact that these models are based on incomplete information about the glass structure, which concerns *only the atoms forming the network* of a given system (e.g. boron-oxygen units, solely, in borate glasses or silicon-oxygen units in silicate glasses), whilst the presence of metal-oxygen polyhedra, which are also basic structural units, is not considered. It should be stressed that, in terms of the energy gain, structural changes that take place in the boron-oxygen or silicon-oxygen networks are of no significance whatsoever, since they are endothermic. These changes can proceed only due to the energy gain that results from an increase in the coordination number of a modifying atom with respect to oxygen, since new metal-oxygen bonds are strongly exothermic [11]. Thus, in the structural models, the requirements of the mass and charge balance and that of the minimal Gibbs free energy of a given system are not observed. However, the violation of these laws remains unnoticed because this inadequacy is compensated for by use in the models of adjustable parameters, either explicit or implicit, and not always having a physical meaning. Therefore, the structural models cannot be used for establishing rigorous structure-property relationships in glasses. It is the concept of the chemical structure that can be employed, since it uses the notion of chemical groupings that comprise not only structural units forming the vitreous network but metal-oxygen polyhedra, as well.

Figure 4 demonstrates the quantitative relationship between the molar volume of barium silicate glasses calculated using Eq. (12) and partial contributions to it from different chemical groupings. It is seen that the unreacted SiO_2 is present in glasses

over the extended composition region, practically up to 40 mol. % BaO, but as a dominating species it is observed only up to 20 mol. % BaO. The grouping $\text{BaO}\cdot 2\text{SiO}_2$ dominates in the chemical structure over the region 20-35 mol. % BaO, the grouping $2\text{BaO}\cdot 3\text{SiO}_2$ – from 35 to 44 mol. % BaO, the grouping $\text{BaO}\cdot \text{SiO}_2$ – from 44 to 58 mol.% BaO, and the grouping $2\text{BaO}\cdot \text{SiO}_2$ is a dominating species when the BaO content is larger than 58 mol.%. Over the entire region considered, the dominating groupings are present in glasses together with other species, the most complex picture being observed over the region 30-50 mol. % BaO. The dashed vertical lines in Fig. 4 show that the sums of contribution from various groupings are equal to the molar volume of glasses that contain from 10 to 60 mol. % BaO. In this analysis, the laws of mass and charge balance are not violated.

Rb₂O-B₂O₃ and Cs₂O-B₂O₃ glasses

It is known that the structure of borate glasses can be considered at the levels of the short-range and intermediate-range order. The first level is characterized by the distribution in glasses of the basic structural units (boron-oxygen tetrahedra and triangles with and without non-bridging oxygen atoms). Figure 5 (a,b) shows the modelled and experimental [14-16] short-range order in the structure of rubidium borate and cesium borate glasses. According to the phase diagrams of both systems as given in Ref. [17], the following crystalline compounds form in them: $\text{Rb}_2\text{O}\cdot 5\text{B}_2\text{O}_3$, $5\text{Rb}_2\text{O}\cdot 19\text{B}_2\text{O}_3$, $\text{Rb}_2\text{O}\cdot 3\text{B}_2\text{O}_3$, $\text{Rb}_2\text{O}\cdot 2\text{B}_2\text{O}_3$, $\text{Rb}_2\text{O}\cdot \text{B}_2\text{O}_3$, and $\text{Cs}_2\text{O}\cdot 9\text{B}_2\text{O}_3$, $\text{Cs}_2\text{O}\cdot 5\text{B}_2\text{O}_3$, $3\text{Cs}_2\text{O}\cdot 13\text{B}_2\text{O}_3$, $\text{Cs}_2\text{O}\cdot 3\text{B}_2\text{O}_3$, $\text{Cs}_2\text{O}\cdot 2\text{B}_2\text{O}_3$, $\text{Cs}_2\text{O}\cdot \text{B}_2\text{O}_3$. The relationship between the chemical groupings present in glasses and the basic structural units brought by them is given in Table 1. The fractions of boron-oxygen tetrahedra, $[\text{B}\emptyset_4]^-$, where \emptyset is bridging oxygen atom, and those of triangles with and without

non-bridging oxygens, respectively, $B\emptyset_2O^-$ and $B\emptyset_3$, are calculated using Eqs. (13)-(16) written here for cesium borate glasses. They present the ratios between the numbers of boron-oxygen polyhedra of each type (the numerators of Eqs. 13-15) and the total number of all borate units, tetrahedra and triangles with and without non-bridging oxygen atoms present in a given glass (Eq.16).

$$[B\emptyset_4]^- = \frac{2(X_{Cs_2O \cdot 9B_2O_3} + X_{Cs_2O \cdot 5B_2O_3} + 3X_{3Cs_2O \cdot 13B_2O_3} + X_{Cs_2O \cdot 3B_2O_3} + X_{Na_2O \cdot 2B_2O_3})}{\Sigma B_n} \quad (13)$$

$$[B\emptyset_3] = \frac{2(X_{B_2O_3} + 8X_{Cs_2O \cdot 9B_2O_3} + 4X_{Cs_2O \cdot 5B_2O_3} + 10X_{3Cs_2O \cdot 13B_2O_3} + 2X_{Cs_2O \cdot 3B_2O_3} + X_{Cs_2O \cdot 2B_2O_3})}{\Sigma B_n} \quad (14)$$

$$[B\emptyset_2O^-] = \frac{2X_{Cs_2O \cdot B_2O_3}}{\Sigma B_n} \quad (15)$$

$$\Sigma B_n = 2X_{B_2O_3} + 18X_{Cs_2O \cdot 9B_2O_3} + 10X_{Cs_2O \cdot 5B_2O_3} + 39X_{3Cs_2O \cdot 13B_2O_3} + 6X_{Cs_2O \cdot 3B_2O_3} + 4X_{Cs_2O \cdot 2B_2O_3} + 2X_{Na_2O \cdot B_2O_3} \quad (16)$$

As is seen from Fig. 5(a,b), this level in the structure of alkali borate glasses does not depend on the chemical nature of the modifying oxides, since up to 30 mol. % M_2O the fraction of 4-fold coordinated boron atoms is determined by the same ratio $[B\emptyset_4]^- = X_M / (1 - X_M)$, where X_M is the fraction of M_2O . Hence, the short-range order does not reflect all the complexity of the structure of B_2O_3 -containing glasses.

A more detailed picture is given by consideration of the glass structure in terms of the superstructural units, *i.e.* beyond the first co-ordination sphere of boron atoms. These units (rings) are formed from basic structural units, and their various types are depicted in Ref. [17]. Table 1 lists the superstructural units present in rubidium and cesium borate glasses, together with the chemical groupings that brought them into glasses.

A knowledge of the equilibrium concentrations of the chemical groupings together with information on the types and numbers of superstructural units that they bring into glasses enable the structure of the intermediate-range order to be quantitatively described, as shown in Fig. 6 (a,b) for Rb₂O and Cs₂O borate systems. The calculation of the fractions of all (super)structural species are performed using the equations given below. They have been derived using the knowledge about the chemical structure of rubidium and cesium borate glasses, together with information on the types and numbers of the superstructural units introduced into glasses by various chemical groupings (Table 1). These equations present the ratios between the numbers of (super)structural units of each type (the numerators of Eqs. 17-23) and the total number of all superstructural units, denoted SSU, and independent triangles and tetrahedra, denoted B_n, present in a given glass (Eq. 24).

$$[\text{B}\emptyset_3] = \frac{0.5X_{\text{B}_2\text{O}_3}}{\Sigma(\text{SSU} + \text{B}_n)} \quad (17) \quad [\text{B}\emptyset_4]^- = \frac{4X_{3\text{Cs}_2\text{O}\cdot 13\text{B}_2\text{O}_3}}{\Sigma(\text{SSU} + \text{B}_n)} \quad (18)$$

$$[\text{Boroxol}] = \frac{0.5X_{\text{B}_2\text{O}_3} + X_{\text{Cs}_2\text{O}\cdot 9\text{B}_2\text{O}_3}}{\Sigma(\text{SSU} + \text{B}_n)} \quad (19)$$

$$[\text{Pentaborate}] = \frac{2X_{\text{Cs}_2\text{O}\cdot 5\text{B}_2\text{O}_3} + 2X_{3\text{Cs}_2\text{O}\cdot 13\text{B}_2\text{O}_3}}{\Sigma(\text{SSU} + \text{B}_n)} \quad (20)$$

$$[\text{Triborate}] = \frac{2X_{\text{Cs}_2\text{O}\cdot 3\text{B}_2\text{O}_3} + 4X_{3\text{Cs}_2\text{O}\cdot 13\text{B}_2\text{O}_3}}{\Sigma(\text{SSU} + \text{B}_n)} \quad (21)$$

$$[\text{Diborate}] = \frac{X_{\text{Cs}_2\text{O}\cdot 2\text{B}_2\text{O}_3}}{\Sigma(\text{SSU} + \text{B}_n)} \quad (22)$$

$$[\text{Cyclic metaborate}] = \frac{0.667X_{\text{Cs}_2\text{O}\cdot \text{B}_2\text{O}_3}}{\Sigma(\text{SSU} + \text{B}_n)} \quad (23)$$

$$\Sigma(\text{SSU} + \text{B}_n) = X_{\text{B}_2\text{O}_3} + 4X_{\text{Cs}_2\text{O}\cdot 9\text{B}_2\text{O}_3} + 2X_{\text{Cs}_2\text{O}\cdot 5\text{B}_2\text{O}_3} + 10X_{3\text{Cs}_2\text{O}\cdot 13\text{B}_2\text{O}_3} + 2X_{\text{Cs}_2\text{O}\cdot 3\text{B}_2\text{O}_3} + X_{\text{Cs}_2\text{O}\cdot 2\text{B}_2\text{O}_3} + 0.667X_{\text{Cs}_2\text{O}\cdot \text{B}_2\text{O}_3} \quad (24)$$

Vertical dashed lines in Fig. 6 (a,b) show the compositions of glasses whose structures are either very similar to those of the corresponding crystals or differ from them. Thus, the structures of glasses with 16.7 mol. % Rb_2O and 25 mol.% Cs_2O are practically identical to those of their crystalline analogs, which is a very rare case for glasses containing less than 50 mol. % M_2O . It is seen that, in both systems, the content of the characteristic superstructural units is very large (95 % pentaborate unit in rubidium glass and 97 % triborate unit in cesium glass), whilst the total content of other units present is equal to just a few percent. The glasses with 25 mol. % Rb_2O and 16.7 mol.% Cs_2O , on the contrary, are not structurally similar to the corresponding crystals as the content of the characteristic superstructural units is, respectively, 78 % (triborate rings in rubidium glasses) and 68 % (pentaborate rings in cesium glasses). These results are confirmed by thermodynamic studies of glasses and crystals in both systems [18].

As is seen from Fig. 6 (a,b), the level of the intermediate-range order indeed reflects specific features in the glass structure. For example, this is a very complex shape of the curve depicting the distribution of triborate superstructural units in cesium glasses. This curve has two maxima, at 10 and 25 mol. % Cs_2O , which is due to the fact that these units are mainly brought into glasses by two chemical groupings, $\text{Cs}_2\text{O}\cdot 9\text{B}_2\text{O}_3$ (10 mol. % Cs_2O) and $\text{Cs}_2\text{O}\cdot 3\text{B}_2\text{O}_3$ (25 mol. % Cs_2O). An insignificant contribution is also made by the grouping $3\text{Cs}_2\text{O}\cdot 13\text{B}_2\text{O}_3$ (18.75 mol. % Cs_2O) whose content in the chemical structure is small because of its complex stoichiometry. (The probability of formation in a melt of triborate groupings is much higher because only 4 particles should interact, while the formation of the grouping $3\text{Cs}_2\text{O}\cdot 13\text{B}_2\text{O}_3$ requires an interaction of 16 particles). Another difference in the structure of rubidium and cesium glasses is the fact that the content of boroxol rings and boron-oxygen triangles

is depicted by the same dependence in rubidium glasses and by different curves in cesium glasses. In the latter system, boroxol rings are brought into glasses by two groupings, B_2O_3 and $Cs_2O \cdot 9B_2O_3$, whilst boron-oxygen triangles are brought only by the unreacted B_2O_3 . The dependences shown in Fig. 5 and 6 can thus be considered as unique, since there is no quantitative experimental data on the intermediate-range order in the structure of rubidium and cesium borate glasses.

$Na_2O-P_2O_5$, $Li_2O-P_2O_5$ and $ZnO-P_2O_5$ glasses

The structure of phosphate glasses has been remarkably reviewed in the past in two well-known works by Martin [19] and Brow [20]. Phosphorous atoms are known to be in four-fold coordination in all composition ranges and so they early adopted the Q^n (n = the number of bridging oxygens) nomenclature as established before by Lippmaa in silicates [21]. On the other hand, the pentavalency of phosphorous requires of double bonded oxygens in P_2O_5 based networks which, in the end, may become indistinguishable from the non-bridging oxygens bonded to modifier cations. Therefore, phosphate tetrahedra appear in phosphate glasses in the form of Q^3 , Q^2 and Q^1 , from ultraphosphate to polyphosphate compositions, and less likely as Q^0 , close to the orthophosphate line. If one adds an alkali oxide, for instance, to the P_2O_5 network, this is depolymerized and Q^2 tetrahedra form, where the two non-bridging oxygens are equally bonded to the modifying cation. Therefore, Q^3 and Q^2 simultaneously coexist up to the metaphosphate composition, where Q^2 will ideally represent 100 % of all phosphorous and where the structure is composed of long metaphosphate chains. In practice, having a pure metaphosphate composition is quite difficult to reach and small amounts of Q^1 groups may appear, either by a phosphorous defect or by hydration. From metaphosphate to polyphosphate compositions, the structure is

then dominated by Q^2 and Q^1 basic structural units over the rest of the glass-forming region, that in phosphate glasses extends till about 60 mol. % of the modifying oxide, though in the case of PbO and ZnO systems may reach more than 65 %. In his review, Brow described the very simple rules that in phosphate glasses can be used to calculate the relative contents of Q^n tetrahedra from the molar fraction of the modifying oxide. In this respect, the use of ^{31}P MAS NMR experiments has been very useful in determining the proportions of Q^n groups and a comparison of the experimentally determined and the calculated Q^n was illustrated in [22] for the ultraphosphate region in binary phosphate glasses of Na, Zn, Ca, Sr and Ba. Overall, the calculated plots agree well with the experimental results, although the presence of water issue was analyzed in detail because in such a region, with high P_2O_5 contents, the glasses may retain high contents of water if not adequately obtained. Unfortunately, there were no data in the polyphosphate regions of these systems, but Kirkpatrick *et al.* had shown previously the fraction of Q^n groups for the whole range of compositions in ZnO- P_2O_5 glasses [22].

In a recent work on the thermodynamic approach to the Li_2O - P_2O_5 glasses [23], the authors obtained the calculated structures of glasses for Li_2O contents between 44 and 58 mol. %, covering all regions, from ultra- to polyphosphate compositions. According to the equilibrium phase diagram of the system [24], Li_2O , P_2O_5 , $\text{Li}_2\text{O}\cdot\text{P}_2\text{O}_5$, $2\text{Li}_2\text{O}\cdot\text{P}_2\text{O}_5$, and $3\text{Li}_2\text{O}\cdot\text{P}_2\text{O}_5$ are the compounds to consider and from which distribution of Q^n structural units is calculated. In the case of Na_2O - P_2O_5 system, the triphosphate compound, $5\text{Na}_2\text{O}\cdot 3\text{P}_2\text{O}_5$, should additionally be considered for the calculations. Figure 7 shows the calculated chemical structure of glasses in the Na_2O - P_2O_5 system from the Gibbs free energy of formation from elements of the

compounds $\text{Na}_2\text{O}\cdot\text{P}_2\text{O}_5$ (NP), $5\text{Na}_2\text{O}\cdot 3\text{P}_2\text{O}_5$ (N5P3), $2\text{Na}_2\text{O}\cdot\text{P}_2\text{O}_5$ (N2P), $3\text{Na}_2\text{O}\cdot\text{P}_2\text{O}_5$ (N3P) and the constituent oxides Na_2O and P_2O_5 .

Above the metaphosphate composition (> 0.5 mol. % Na_2O), N5P3 appears together with metaphosphate and pyrophosphate chemical groupings before reaching a null content just before Na_2O equals 0.67 mol. %, where pyrophosphate groupings would be the sole species. At first sight, these results would suggest substantial differences when compared with those obtained in $\text{Li}_2\text{O}\text{-P}_2\text{O}_5$ glasses, where only lithium metaphosphate and pyrophosphate compounds coexist.

The previously calculated Q^n relative contents from the chemical composition in the $\text{Li}_2\text{O}\text{-P}_2\text{O}_5$ glasses are in agreement with those obtained by simulation of the ^{31}P MAS NMR spectra as well as with those calculated by the thermodynamic approach. This means that both ways of calculating the Q^n distributions in lithium phosphate glasses are consistent with experimental results within the compositional range studied up to 58 mol. % Li_2O . However, if one looks at the pyrophosphate composition (67 mol.%), their results showed some disproportionation of Q^1 groups into Q^2 and Q^0 , whose proportions at that Li_2O content are not null [23]. As stated by Kirkpatrick & Brow [22], the depolymerization model cannot predict disproportionation reactions of the type $2Q^1 \leftrightarrow Q^0 + Q^2$ that, on the other hand, were assumed possible by Van Wazer [25]. Chain length measurements coupled to NMR quantification of phosphate groups allowed establishing a correlation between constants for equilibriums of disproportionation and the ionic field strength of the modifier, from which it was deduced that higher values of modifier strength result in higher constant of disproportionation [26]. The use of the concept of chemical structure, herein explained, in a compositional range where disproportionation reactions need to be considered, would be of utmost importance in order to validate its applicability,

where other models cannot. Glass formation in lithium and sodium binary systems is limited to about 60 mol. % alkali oxide because of spontaneous crystallization above that content; however, Tatsumisago was able to prepare lithium phosphate glasses by roller-quenching with contents of Li_2O up to 70 mol. %, and the relative contents of meta-, pyro- and ortho-phosphate groupings were determined by Raman [27]. Therein, it was shown that at the pyrophosphate composition, Q^2 and Q^0 tetrahedra did also appear together with Q^1 groups, thus confirming the disproportionation that we have seen in this system through the thermodynamic model of associated solutions [23]. Furthermore, in another work Brow *et al.* studied the system $\text{ZnO-P}_2\text{O}_5$ that shows very good glass-forming ability up to contents of ZnO of nearly 70 mol. % [28]. They published the ^{31}P NMR spectrum of a $67\text{ZnO-33P}_2\text{O}_5$ glass sample, where it was demonstrated that Q^0 and Q^2 groups also appeared with Q^1 , with relative contents of 12, 12 and 66 %, respectively, demonstrating that disproportionation reactions are possible and that rate constants may also be dependent on the nature of the modifier cations.

From the results of molar fractions in $\text{Na}_2\text{O-P}_2\text{O}_5$ system (Fig. 7) and the same calculation that we have performed in the $\text{ZnO-P}_2\text{O}_5$ glasses, the Q^n groups in lithium, sodium and zinc systems have been gathered in Fig. 8 between 50 and 75 mol. % modifying oxide, where lines represent calculated values and data points are experimentally determined Q^n values for the $\text{ZnO-P}_2\text{O}_5$ system from reference [28].

When comparing the two alkali phosphate systems, it could be thought that the same behavior obtained in $\text{Li}_2\text{O-P}_2\text{O}_5$ does not work for the $\text{Na}_2\text{O-P}_2\text{O}_5$ system as sodium triphosphate (N5P3) chemical groupings add to meta- and pyro-phosphate ones. However, it can be seen that up to contents of modifier ca. 60 mol. % both systems reach practically equal values of Q^2 and Q^1 , the same happening in the $\text{ZnO-P}_2\text{O}_5$ one.

Then, between 60 and 67 %, Q^1 groups in $Li_2O-P_2O_5$ glasses, but most particularly in $ZnO-P_2O_5$, start to deviate from the Q^1 line in $Na_2O-P_2O_5$ ones where disproportionation is not observed. At the pyrophosphate composition, Q^1 in the Na system represent nearly 100 % while in lithium glasses its content is reduced down to above 90 %, in parallel with the presence of some Q^0 and Q^2 groups (with 6 and 3 %, respectively), and about 80 % in $ZnO-P_2O_5$ glasses, taking values very close to those observed in [28].

The observed sequence $Q^1(Zn) < Q^1(Li) < Q^1(Na)$ could be explained through the different chemical nature of the modifying oxides in terms of the electronegativity (χ) of the alkalis and phosphorus since it quantitatively characterizes the acid-base properties of their oxides. A larger different ($\chi_P - \chi_M$) (M=modifier) the more intensively the oxides interact to form the reactions products, such as the alkali or zinc pyrophosphate. From the values reported in [10] by Pauling, it follows that the differences in electronegativity increases in the order $(\chi_P - \chi_{Zn}) < (\chi_P - \chi_{Li}) < (\chi_P - \chi_{Na})$, which would agree with the dependences shown on Fig. 8.

Conclusions

Herein, several key issues were tackled and illustrated through the following systems with different chemical natures characterized by acid-base interactions between their oxide components: $BaO-SiO_2$, $Rb_2O-B_2O_3$, $Cs_2O-B_2O_3$, $ZnO-P_2O_5$, $Li_2O-P_2O_5$ and $Na_2O-P_2O_5$. The reliability of the calculated density and structure of the short- and intermediate-range order in the above glasses is confirmed by good agreement between model and experimental values available in the literature. Results of modelling are reliable due to the fact that all calculations are performed with the observance of the principle of the minimum Gibbs energy of the systems considered.

The structure-property relationship established quantitatively in barium silicate glasses is based on a consideration of the role of chemical groupings. Opposite to traditional structural models, this approach considers the fact that structural changes in the vitreous network can proceed only in the presence of the modifying oxide. Due to this, neither the law of mass balance nor the law of charge balance is violated.

On the other hand, the intermediate-range order, *i.e.* the distribution of the super-structural units, has been modelled in rubidium borate and cesium borate glasses over their glass-forming regions. The results obtained enable the compositions of glasses with the maximum structural resemblance to crystals to be determined: $\text{Rb}_2\text{O}\cdot 5\text{B}_2\text{O}_3$ (16.7 mol. % Rb_2O) and $\text{Cs}_2\text{O}\cdot 3\text{B}_2\text{O}_3$ (25 mol. % Cs_2O).

Finally, the influence of the chemical nature of modifying oxides, Li_2O , Na_2O and ZnO , on the structure of phosphate glasses has been established quantitatively. The application of the concept of chemical structure of glasses is consistent with available experimental data in phosphate glasses and reliable in predicting a behavior that ultimately depends on the chemical nature of a given system, without the need of introducing equilibrium constants of disproportionation equilibria *ad-hoc*.

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Figure captions

Figure 1. The chemical structure of glasses in the system BaO–SiO₂ at 800 K.

Figure 2. The short-range order in the structure of barium silicate glasses: model (lines) and experiment (squares from ref. [13]).

Figure 3. The density of barium silicate glasses: model (line) and experiment (squares [14] and triangles [15]).

Figure 4. The molar volume of sodium borate glasses (solid line) calculated as a sum of partial contributions from different chemical groupings.

Figure 5 (a,b). The distribution of basic structural units in rubidium borate and cesium borate glasses. Model – lines, experimental data – symbols (Squares – Bray, 1963; circle – Bray, 1989; triangles – Kroeker *et al.*, 2006)

Figure 6 (a,b). The distribution of superstructural units in barium borate and cesium borate glasses.

Figure 7. Chemical structure of the Na₂O–P₂O₅ system between 0 and 100 mol. % Na₂O.

Figure 8. Relative proportions of Qⁿ groups in Li, Na and Zn binary phosphate glass systems calculated at 1000 K (Li and Na) and 1275 K (Zn). Data points in the graph have been plotted from experimentally determined Qⁿ values for the ZnO–P₂O₅ system from reference [28]. The error bars represent standard deviations from average of data points at given compositions.

Table captions

Table 1. The chemical groupings present in glasses of the systems Rb₂O–B₂O₃ and Cs₂O–B₂O₃, and their relation to the short-range and intermediate-range order in the glass structure.

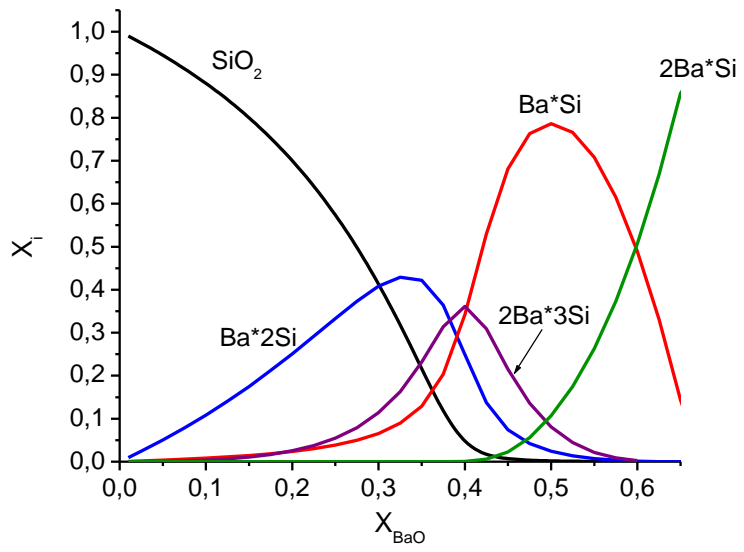


Figure 1

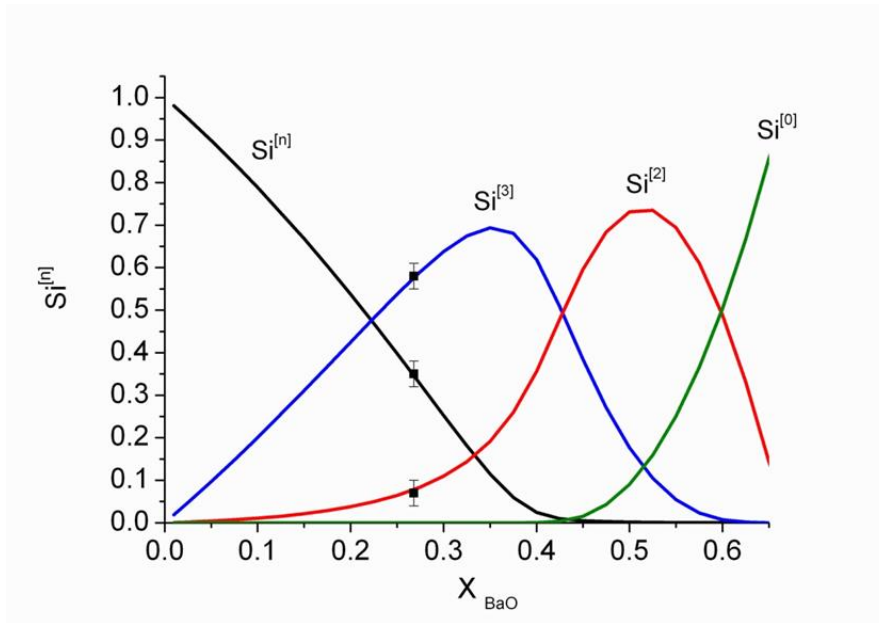


Figure 2

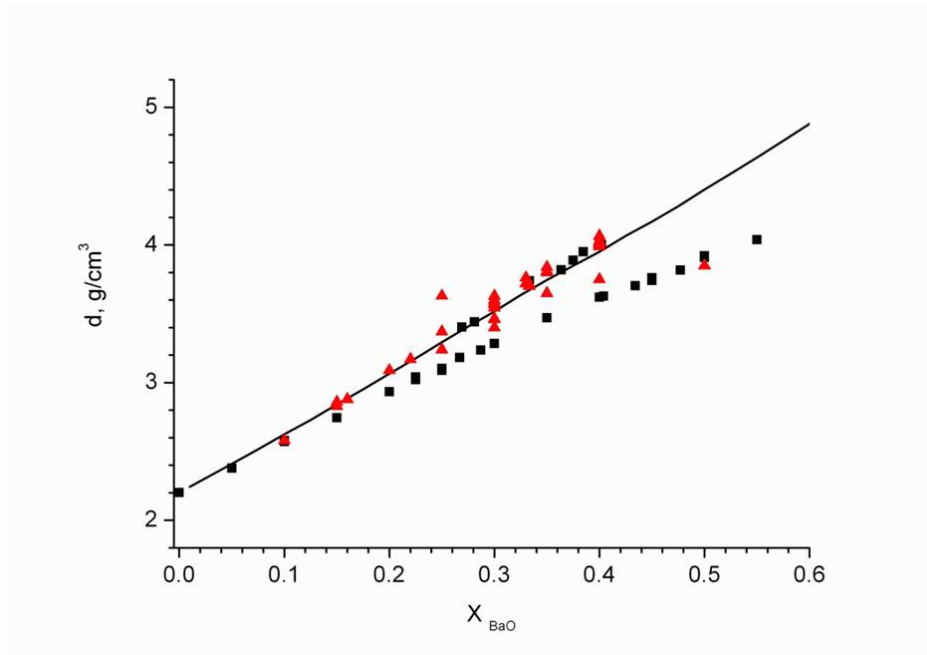


Figure 3

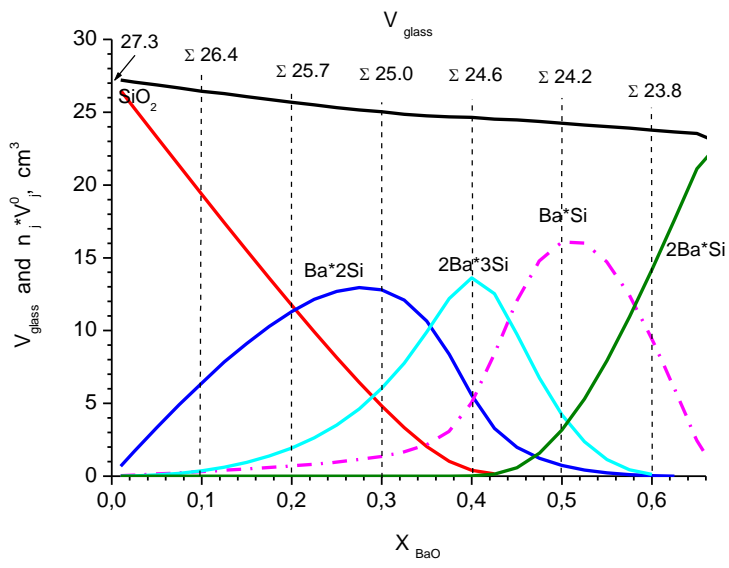
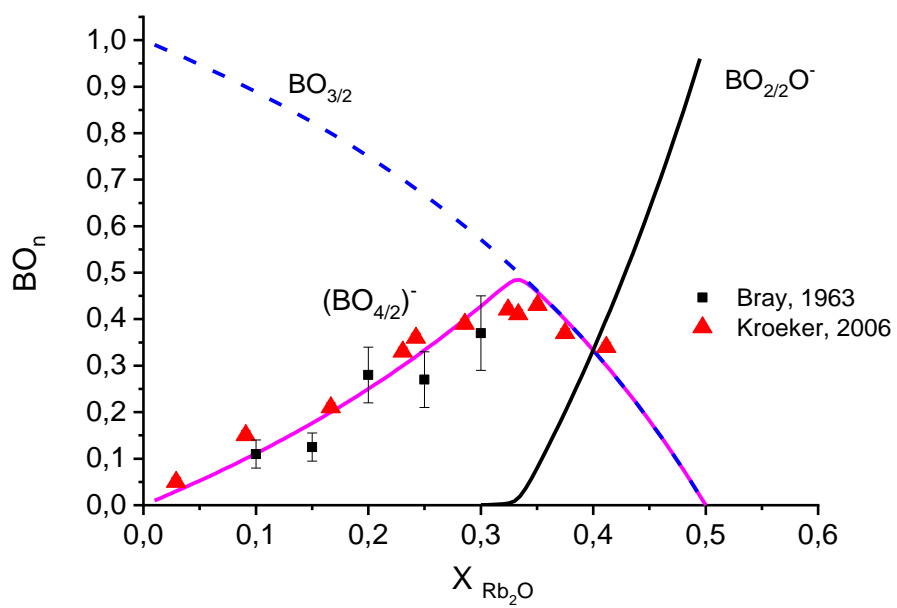


Figure 4

(a)



(b)

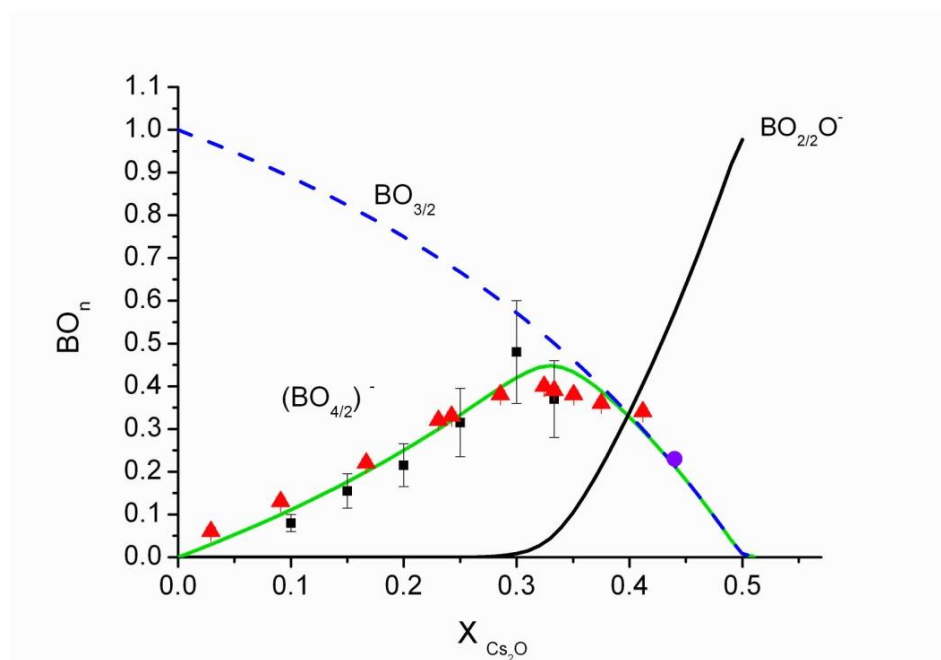


Figure 5

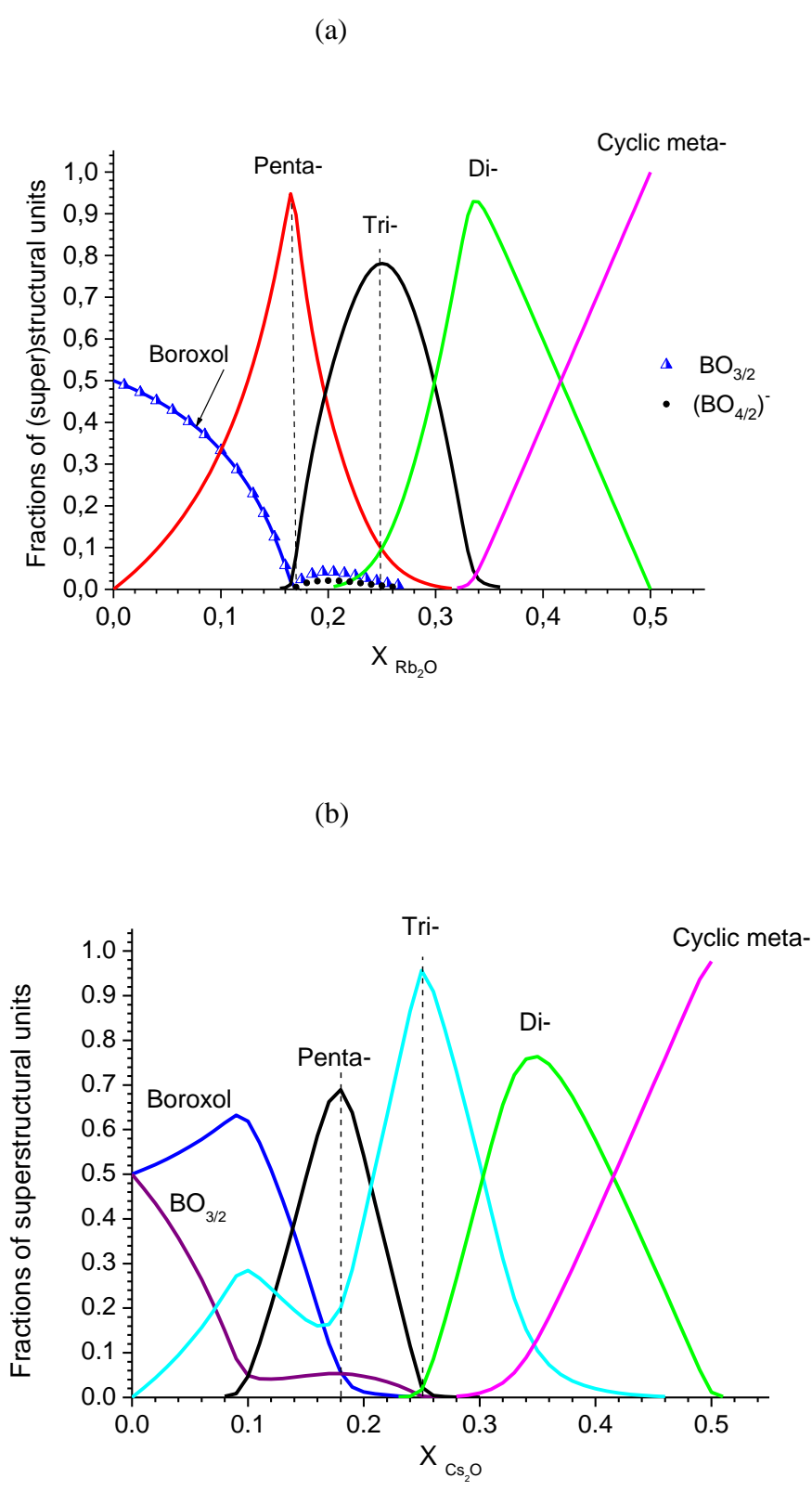


Figure 6

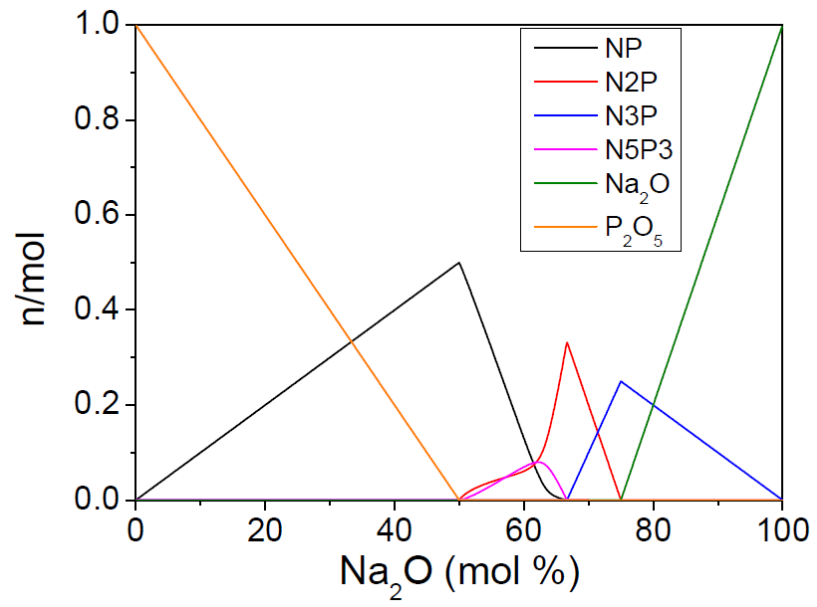


Figure 7

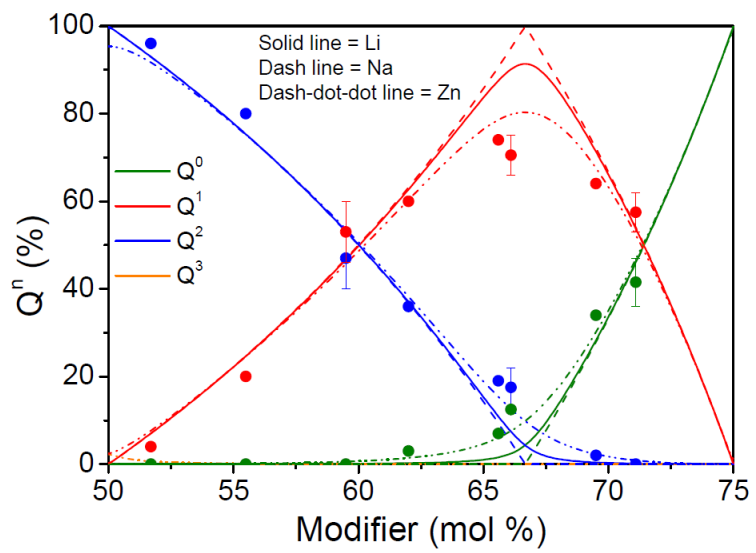


Figure 8

Table 1

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	$2B\emptyset_3$	Boroxol ring ($1/2$), $B\emptyset_3$ ($1/2$)
$Cs_2O \cdot 9B_2O_3$	$2[B\emptyset_4]^-$, $16B\emptyset_3$	Boroxol rings (4), Triborate rings (2)
$Rb_2O \cdot 5B_2O_3$ & $Cs_2O \cdot 5B_2O_3$	$2[B\emptyset_4]^-$, $8B\emptyset_3$	Pentaborate rings (2)
$5Rb_2O \cdot 19B_2O_3$	$10[B\emptyset_4]^-$, $28B\emptyset_3$	Pentaborate rings (4), Triborate rings (4), $2[B\emptyset_4]^-$, $4B\emptyset_3$
$3Cs_2O \cdot 13B_2O_3$	$6[B\emptyset_4]^-$, $20B\emptyset_3$	Pentaborate rings (2), Triborate rings (4), $4[B\emptyset_4]^-$
$Rb_2O \cdot 3B_2O_3$ & $Cs_2O \cdot 3B_2O_3$	$2[B\emptyset_4]^-$, $4B\emptyset_3$	Triborate rings (2)
$Rb_2O \cdot 2B_2O_3$ & $Cs_2O \cdot 2B_2O_3$	$2[B\emptyset_4]^-$, $2B\emptyset_3$	Diborate ring (1)
$Rb_2O \cdot B_2O_3$ & $Cs_2O \cdot B_2O_3$	$2B\emptyset_2O^-$	Cyclic metaborate ring ($2/3$)