Thermodynamic properties and vaporization processes of the ionic silicate melts

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Abstract: Advantages of high temperature mass spectrometric method to study thermodynamic properties and vaporization processes of the ionic silicate melts up to the temperature 2500 K are illustrated. Information on the vaporization processes and thermodynamic properties of binary and multicomponent silicate systems containing Na_2O, Cs_2O, Rb_2O, MgO, CaO, SrO, BaO, PbO, ZnO, B_2O_3, Al_2O_3 and TiO_2, obtained by high temperature mass spectrometric method is discussed. Various types of vapour species were found over these silicate melts studied such as the associated, dissociated and polymerized products of vaporization. It was shown that the content of vapour over multicomponent silicate systems was in agreement with the composition of the gaseous phase over the corresponding binary systems. The regularities of the vaporization of corresponding binary and multicomponent silicate systems according to the position of oxide modifier in the Periodic table of atoms were also illustrated and discussed from the point of view of the acid-base concept. Results on determination of thermodynamic functions in the ionic silicate systems mentioned were considered taking into account the main requirements for the confirmation of their reliability. Thermodynamic functions of these systems showed various signs of the deviations from the ideal behaviour. For modeling of these thermodynamic properties of the ionic silicate melts studied the ideal associated solution model and the general lattice theory of associated solutions were used. Using these approaches the different levels of deviation from the ideality in the silicate melts studied were clarified.

Keywords: Silicate melts, vaporization, thermodynamics, high temperature mass spectrometry

1. Introduction

The understanding of high temperature behaviour of the ionic silicate melts have the great importance for the development of the modern material science as well as for various technologies such as for the incorporation of nuclear wastes, for obtaining metals from slags in metallurgy and for preparation the special glasses. High temperature mass spectrometry is one of the most informative methods of high-temperature chemistry along with calorimetry and electromotive force measurements. The method enables one not only to determine thermodynamic properties of components in both condensed and gaseous phases but also to identify the composition of the vapour. Advantages of the Knudsen effusion mass spectrometric method for the investigations of thermodynamic properties and vaporization processes at high temperatures in various classes of oxide systems and materials were considered in details in [1]. Wide potential abilities of high temperature mass spectrometry to study the vaporization processes and thermodynamic properties of the ionic silicate melts in the following high temperature processes should be mentioned

- preparation and exploiting of glasses, ceramics, films, coatings;
- preparation of refractory materials and materials for microelectronics;
- consideration of the materials stability in the various gaseous atmospheres;
- the chemical processes in the energetic plants, including the nuclear power plants;

- optimization of processes of utilization of wastes;
- processes of preventing of pollution of the environment;
- geo- and astrochemical processes;
- metallurgical processes and some others.

It should be underlined also that the high temperature mass spectrometric method allows obtaining the unique thermodynamic information at high temperatures that is crucial for prediction and modeling of physicochemical properties of oxide materials based on statistical thermodynamic and semi-empirical approaches. That is why the purpose of the present paper is the consideration of the main information on the vaporization processes and thermodynamic properties obtained by high temperature mass spectrometry as well as one of the statistical thermodynamic approaches used for modeling of the ionic silicate melts.

The previous results of the mass spectrometric studies of the vaporization processes and thermodynamic properties of oxide systems and materials were summarized in monograph [1] and reviews [2-9].

As to such objects of investigations as binary and multicomponent ionic silicate systems and the unique information on their vaporization processes and thermodynamic properties at high temperatures is summarized in the present paper obtained mainly last ten years. The systems under consideration are of great importance in various fields of high temperature material chemistry and technologies such as glass, ceramics, coatings production, metallurgy, geochemistry, nuclear and space technologies and some others. Results on the vaporization processes and thermodynamic properties of the ternary ionic silicate systems $Na_2O-B_2O_3-SiO_2$, $Cs_2O-B_2O_3-SiO_2$, $Rb_2O-B_2O_3-SiO_2$, $MgO-B_2O_3-SiO_2$, $CaO-B_2O_3-SiO_2$, $SrO-B_2O_3-SiO_2$, $BaO-B_2O_3-SiO_2$, $PbO-B_2O_3-SiO_2$, $ZnO-B_2O_3-SiO_2$, $MgO-Al_2O_3-SiO_2$, $CaO-Al_2O_3-SiO_2$, $CaO-TiO_2-SiO_2$ and $BaO-TiO_2-SiO_2$ together with the earlier obtained data [1-9] are discussed.

2. Experimental

2.1 Vaporization features of oxide systems

The variety of the vapour species with different volatilities, identified over oxide systems, is one of the reasons that restrict their use at high temperatures, especially in the processes involving interaction with other materials.

The method of high temperature mass spectrometry [1] allows to identify gas phase compositions, to determine partial pressures and enthalpies of vaporization of components, and also such thermodynamic functions of systems, as activities and chemical potentials of components, Gibbs energies and the relevant excess quantities.

Using high temperature mass spectrometric method it was demonstrated that in the vapour over oxide systems various types of species could be identified such as associates, polymers and the products of dissociation processes [1].

In addition to the processes of polymerization and dissociation, vaporization of multicomponent ionic silicate melts is accompanied by association of vapour molecular forms, which leads to generation of new compounds in the gas phase. The formation of such compounds is due to various factors, including interaction of oxides in the condensed or gaseous phase.

The vapour composition over the binary phosphate, borate and silicate systems identified by high temperature mass spectrometric method was summarized and grouped according to the number of outer valence electrons of an oxide modifier [4, 10]. This analysis pertained to high temperatures, when the partial pressures of the vapour species were in the range 10^{-9}-10^{-4} bar. More complex associated vapour species over oxide systems were observed as a result of increasing atomic mass numbers of oxide-modifiers in lower rows of the Periodic Table. This fact may be connected with the participation of d- and f- electrons in the chemical bonds and the penetration of 6s-electrons under the cover of 3d-, 4d-, 4f- and 5d- electrons. The following parameters were taken into account to understand the vaporization behaviour of the binary oxide systems from the point of view of the acid-base concept [10, 11]:

- values of the differences of electron potentials, forming oxides;
- enthalpies of formation of oxide modifier;
- the lattice energy of oxide modifier per mole of O^{-2} at 298 K;
- the energies of the M-O-X bond (X= B, Si).

These values for the binary borate systems (as a part of ternary ionic silicate melts) as a function of atomic mass of the elements of the first row of the Periodic Table are given in Fig. 1.
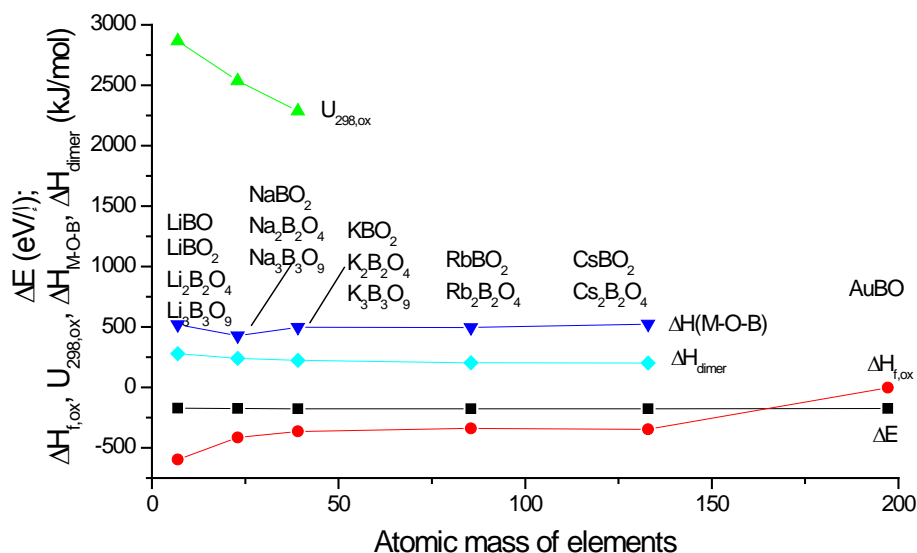

Figure 1. Changes of values of the differences of electron potentials, forming oxides (Δ E); (Δ $H_{f,ox}$) enthalpy of formation of oxide modifier; ($U_{298,ox}$) the lattice energy of oxide-modifier per mole of O^{-2} at 298 K; (Δ H (M-O-B)) the energies of M-O-B bond; (Δ H_{dimer}) the dissociation energy of dimer borate molecules as a function of atomic mass of elements of the first raw of the Periodic Table.

Analysis of the curves presented in Fig. 1 allows to conclude that one of the main reasons of decreasing of the polymerization level from 3 to 2 observed in the alkali borates as the increasing the atomic mass of elements [12] is the decreasing of the lattice energy of oxide-modifier per mole of O^{-2} at 298 K and the increasing of the enthalpy of formation of oxide modifier. Based on the experimental results available it can be shown that the associated gaseous molecules that were found over binary borate and silicate systems with the same relative volatility of the individual oxides and the difference of the electron potential, forming oxides in the binary systems, about 200-100 eV/Å [1, p. 331]. (It should be mentioned that as a measure of the electronegativity of an oxide, the ratio of the first ionization

energy of the element forming oxide to the radius of the ion of this element in the corresponding oxidation degree had been chosen. This value is used in the text as the electron potential of the oxide.) This idea is confirmed by the mass spectrometric identification of a lot of gaseous borates found over oxide systems and summarized in [12] and also in the CaO-B_2O_3 system [11], in the SrO-B_2O_3, BaO-B_2O_3 systems [13] as well as in the MgO-B_2O_3 system [14]. As to the gaseous silicates formed over binary ionic silicates systems they also were identified in the gaseous phase according to the same rule in the BaO-SiO_2 [15, 16], SrO-SiO_2 [17] and CaO-SiO_2 [18] systems. But the significant difference in the relative volatility of oxide modifier and silica did not allow identification in vapour the associated species, for example, in the MgO-SiO_2 system [19, 20] as well as in the PbO-SiO_2 and ZnO-SiO_2 systems studied recently.

The correlation of the values of the maximum differences of electron potentials of the elements forming oxides in binary systems, from which multicomponent melts can be composed, with the information on the occurrence of gaseous monomers of borates and their dimers in the vapour over them, makes it possible to predict, to the first approximation, the tendency to association and polymerization of oxides in the vapour over multicomponent systems. The suggested criterion, however, requires additional discussion.

From the point of view of the acid-base concept [1, 3] the following major factors should be taken into consideration when comparing the volatility of oxide systems:

    (a) the relationship of the partial pressures of molecular forms in the vapour over individual oxides (volatility of oxides) forming a system under isothermal conditions;

    (b) the relative content (concentration) of oxides in the condensed phase of a multicomponent system;

    (c) the tendency to association of molecular forms of the gaseous phase of oxide pairs forming a multicomponent system, one of the criteria determining this being the differences of electron potentials of the elements forming the oxides;

    (d) the values of oxygen partial pressures characterizing the acid-base properties of oxide melts which are determined by their relative volatilities, allowing the most probable processes of the vaporization of components to be estimated.

The availability of the data obtained by the high temperature mass spectrometric technique concerning the thermodynamic properties of glass forming oxide melts in conjunction with the values of electron potentials of elements forming the oxides, made it possible to reveal the principal regularities of vaporization of oxide systems.

The main factors for the prediction of the relative volatility of the binary and multicomponent glass forming systems were considered on the basis of the data on the composition of vapour and thermodynamic properties obtained by the high temperature mass spectrometric method. They were as follows:

    1. if oxide modifier was the same one could observe the increase of volatility of components in the order from silicate and to borate melts, as a consequence of the increase of acidity of the melts in the order indicated;

    2. predominant species in the vapour over silicate glass forming melts were the forms characteristic of dissociative vaporization of the oxides forming the systems;

    3. in the vapour over borate melts containing oxides of alkali metals and of beryllium, lead, bismuth or barium, the

formation of gaseous borates was most probable, their polymerization was also possible;

4. in multicomponent alkali metal boro-silicate melts with a higher content of boron oxide than of oxides of alkali metals and silica, alkali borates were the main vapour species.

This approach devised for evaluation of the vapour composition over multicomponent oxide ionic silicate melts was successfully confirmed by the prediction of the vaporization processes in the systems presented in [8, 21] , for example, and used for comparison of the relative volatilities of various multicomponent silicate glasses [22]. In agreement with the regularities of the vaporization of oxide systems mentioned above was the composition of vapour over the following ionic silicate melts in the Na_2O-B_2O_3-SiO_2 [23, 24], Cs_2O-B_2O_3-SiO_2 [8, 25], Rb_2O-B_2O_3-SiO_2 [26], MgO-B_2O_3-SiO_2 [9, 27], CaO-B_2O_3-SiO_2 [28, 29], SrO-B_2O_3-SiO_2 [9, 29, 30], BaO-B_2O_3-SiO_2 [9, 29, 31], PbO-B_2O_3-SiO_2 [32], ZnO-B_2O_3-SiO_2 [32], MgO-Al_2O_3-SiO_2 [8, 33], CaO-Al_2O_3-SiO_2 [7, 34-36], CaO-TiO_2-SiO_2 [7, 36-38] and BaO-TiO_2-SiO_2 [7, 36, 39] systems specified in Table 1.

Table 1. Composition of vapour over ternary ionic silicate systems studied [7-9, 23-39].

System	T, K	Composition of vapour over systems studied	References
Na_2O-B_2O_3-SiO_2	1200	$NaBO_2$, $(NaBO_2)_2$, B_2O_3	[23, 24]
Cs_2O-B_2O_3-SiO_2	1020	$CsBO_2$, $(CsBO_2)_2$, B_2O_3	[8, 25]
Rb_2O-B_2O_3-SiO_2	900	$RbBO_2$, $(RbBO_2)_2$, B_2O_3	[26]
MgO-B_2O_3-SiO_2	1550-1800	$MgBO_2$, MgB_2O_4, B_2O_3, SiO, O_2	[9, 27]
CaO-B_2O_3-SiO_2	1800	$CaBO_2$, CaB_2O_4, B_2O_3, SiO, O_2	[28, 29]
SrO-B_2O_3-SiO_2	1720	$SrBO_2$, SrB_2O_4, B_2O_3, SiO, O_2	[9, 29, 30]
BaO-B_2O_3-SiO_2	1650	$BaBO_2$, BaB_2O_4, B_2O_3, SiO, O_2	[9, 29, 31]
PbO-B_2O_3-SiO_2	1100	PbO, Pb, O_2	[32]
ZnO-B_2O_3-SiO_2	1100	Zn, O_2	[32]
MgO-Al_2O_3-SiO_2	1770-1940	Mg, SiO, O_2	[8, 33]
CaO-Al_2O_3-SiO_2	1800-2000	Ca, CaO, $CaSiO_3$, $AlSiO$, Al, AlO, SiO, O_2	[7, 34-36]
CaO-TiO_2-SiO_2	1800-2000	Ca, CaO, TiO_2, TiO, SiO, O_2	[7, 36-38]
BaO-TiO_2-SiO_2	1800-2000	Ba, BaO, TiO_2, TiO, SiO, O_2	[7, 36, 39]

Using traditional high temperature mass spectrometric approach it was shown that in the temperature range 1600-2000 K the vaporization processes over the samples of the PbO-B_2O_3-SiO_2, ZnO-B_2O_3-SiO_2, MgO-Al_2O_3-SiO_2, CaO-Al_2O_3-SiO_2, CaO-TiO_2-SiO_2 and BaO-TiO_2-SiO_2 systems are similar to the transition to the gaseous phase of the corresponding individual oxides. As to the ionic silicate melts of the Na_2O-B_2O_3-SiO_2, Cs_2O-B_2O_3-SiO_2, Rb_2O-B_2O_3-SiO_2, MgO-B_2O_3-SiO_2, CaO-B_2O_3-SiO_2, SrO-B_2O_3-SiO_2, BaO-B_2O_3-SiO_2 systems in addition to the vaporization of individual oxides the corresponding monomers and dimers of borates, as well as gaseous silicates (in some concentration and temperature ranges), were identified in the vapour.

Thus various types of vapour species were found over ternary ionic silicate melts such as the associated, dissociated and polymerized products of vaporization. It was shown also that the content of vapour over these systems was in agreement with the composition of the gaseous phase over the corresponding binary systems.

2.2 Thermodynamic data of the ionic silicate melts studied by high temperature mass spectrometric method

Thermodynamic properties of the binary and multicomponent ionic silicate melts such as activities and chemical potentials of components, the Gibbs energies and the partial and integral enthalpies of mixing obtained by high temperature mass spectrometric method were discussed in detail in [1-3].

In all experimental studies mentioned [1-39] a lot of attention was given to the accuracy and the reliability of thermodynamic data obtained by high temperature mass spectrometric method in the binary and multicomponent oxide systems under investigations.

For this reason all thermodynamic functions obtained in oxide systems by the method mentioned were traditionally considered

- from the point of view of the required stability conditions as regards the continuous nature its change of state;
- making verification of the consistency of the data using the Gibbs-Duhem equation;
- zexamining mutual agreement of the results obtained using various experimental methods of high temperature chemistry (EMF, the exchange equilibriums in slags, the sulphide capacity method, the high temperature solution calorimetry, the ion-molecular equilibrium method) as well as the procedures of high temperature mass spectrometry (the dimer-monomer method, the Belton-Fruehan and Wagner methods, the ion current comparison method [1, p. 48]);
- establishing their correlation with the information on phase diagrams of the system studied.

The variety of results of such approach for obtaining the reliable experimental thermodynamic data by high temperature mass spectrometry in oxide systems may be found in [1-3]. Thermodynamic regularities and reliability of high temperature mass spectrometric data for the ionic glass-forming oxide melts were considered also in [40]. The advantages of application of the Belton-Fruehan method to studies of the thermodynamic functions of oxide systems were illustrated in details in [41].

As an example of the mutual agreement of the results obtained using various experimental methods of high temperature mass spectrometry with the data traditionally used for studies thermodynamic properties of the ionic silicate melts such as the EMF and exchange equilibria in slags results obtained for SiO_2 activities in the $CaO-SiO_2$ melts in the temperature range 1873-1933 K presented in Fig. 2 [42].
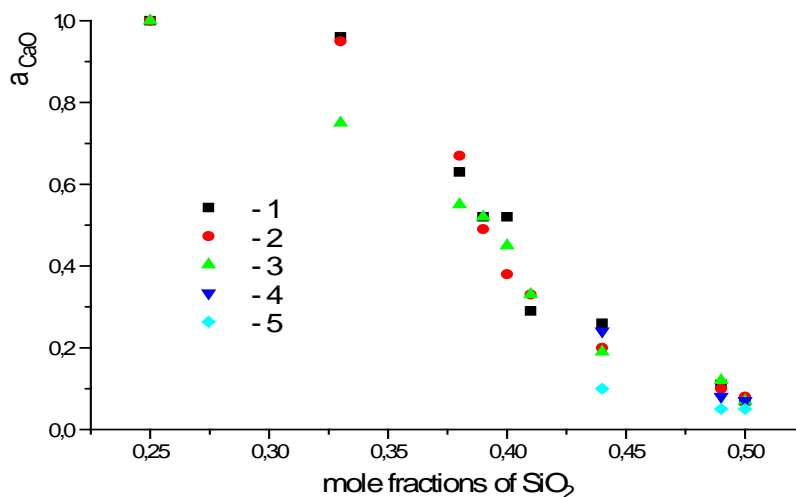

Fig. 2. The CaO activities as a function of the concentration in the CaO-SiO2 system, obtained in the temperature range 1873-1933 K by : 1- mass spectrometric method of comparing of the ion currents; 2- calculated using the Gibbs-Duhem equation from the SiO_2 activities; 3- the Belton-Fruehan mass spectrometric method [42]; 4- the EMF method [43]; 5- measuring of exchange equilibria in slags [44].

The correlation of thermodynamic properties obtained by high temperature mass spectrometry with the information on phase diagrams of the system studied was shown for example in the following systems CaO-SiO$_2$ [42], MgO-SiO$_2$ [20] and MgO-Al$_2$O$_3$-SiO$_2$ [33]. Isothermal cross-sections of the MgO-Al$_2$O$_3$-SiO$_2$ phase diagram at the temperatures 1770 K, 1820 K and 1890 K were calculated based on high temperature mass spectrometric data obtained in this system [33]. Using this information about phase diagram and Gay-Kapoor-Frohberg approach the MgO and SiO$_2$ activities in this system were calculated and compared with the high temperature mass spectrometric results. The good agreement of this comparison was illustrated in [33].

As the examples of the thermodynamic data obtained Figs. 3-6 illustrate the thermodynamic information found first for the melts in the MgO-B$_2$O$_3$-SiO$_2$ and PbO-B$_2$O$_3$-SiO$_2$ systems. It should be mentioned that according to the data obtained [9] there is no immiscibility region found in the MgO-B$_2$O$_3$-SiO$_2$ system compared with the previous data [45].

3. Discussion

Thermodynamic functions of the ionic silicate melts under investigation such as activities and chemical potentials of components as well as the Gibbs energies showed mainly negative sign of the deviations from the ideal behaviour. The features of thermodynamic description of the melts in the systems studied recently may be found also as mentioned above for the Na$_2$O-B$_2$O$_3$-SiO$_2$ [23, 24], Cs$_2$O-B$_2$O$_3$-SiO$_2$ [8, 25], Rb$_2$O-B$_2$O$_3$-SiO$_2$ [26], MgO-B$_2$O$_3$-SiO$_2$ [9,27], CaO-B$_2$O$_3$-SiO$_2$ [28, 29], SrO-B$_2$O$_3$-SiO$_2$ [9, 29, 30], BaO-B$_2$O$_3$-SiO$_2$ [9, 29, 31], PbO-B$_2$O$_3$-SiO$_2$ [32], ZnO-B$_2$O$_3$-SiO$_2$ [32], MgO-Al$_2$O$_3$-SiO$_2$ [8, 33], CaO-Al$_2$O$_3$-SiO$_2$ [7, 34-36], CaO-TiO$_2$-SiO$_2$ [7, 36-38], BaO-TiO$_2$-SiO$_2$ [7, 36-39] systems. The negative deviations from the ideal behaviour were observed in the melts of all these systems except CaO-TiO$_2$-SiO$_2$ and BaO-TiO$_2$-SiO$_2$ where the existence of wide immiscibility regions may be expected as in the TiO$_2$-SiO$_2$ system according to [45].

The values of thermodynamic functions in the ionic silicate melts found by the high temperature mass spectrometric method that were discussed above were used for modeling based on one of the statistical thermodynamics methods such as the general lattice theory of associated solutions (GLTAS) [1, 36]. This approach on the one hand allowed to illustrate the possibility of prediction of thermodynamic properties of the ionic silicate melts with the purpose of obtaining new materials with the properties required and on the other hand allowed to find the correlation between thermodynamic properties of melts and the features of their structural description. While with the theory of ideal associated solutions one can obtain information on the quantity of associates of the given type formed in a certain concentration range in the melt, the generalized lattice theory of associated solutions makes it possible to calculate the relative numbers of bonds formed in the melts and to reveal the relationship between the values of thermodynamic functions and the structure of melt. Development of this theory for the calculation of thermodynamic properties was carried out for the ternary ionic silicate melts with one oxide-modifier and one glass-forming oxide such as the CaO-Al$_2$O$_3$-SiO$_2$, CaO-TiO$_2$-SiO$_2$ and BaO-TiO$_2$-SiO$_2$ systems [7, 36] and with one oxide-modifier and two glass-forming oxides such as the Na$_2$O-B$_2$O$_3$-SiO$_2$ [24, 46] and Cs$_2$O-B$_2$O$_3$-SiO$_2$ [8, 47, 48] systems. The relative numbers of various types of bonds formed in these melts when the second coordination spheres were taken into consideration were calculated based on

GLTAS as a function of composition. The values of the Gibbs energies in the melts of the CaO-B_2O_3-SiO_2, SrO-B_2O_3-SiO_2 and BaO-B_2O_3-SiO_2 systems in the temperature range 1650-1800 K calculated as described [29] using GLTAS at the mole fraction of SiO_2= 0.50 were presented as a function of the melt concentration. Variation of the relative numbers of bonds of different types B-O[B], Si-O[Si], B-O[Si], B-O[M], Si-O[M], M-O[B], M-O[Si], Si-O[B], Si-O[B], M-O[M], where M = Ca, Sr, Ba, in the melts of the CaO-B_2O_3-SiO_2, SrO-B_2O_3-SiO_2 and BaO-B_2O_3-SiO_2 systems in the temperature range 1650-1800 K was calculated according to GLTAS at the mole fraction of SiO_2= 0.50 as a function of the melt concentration.
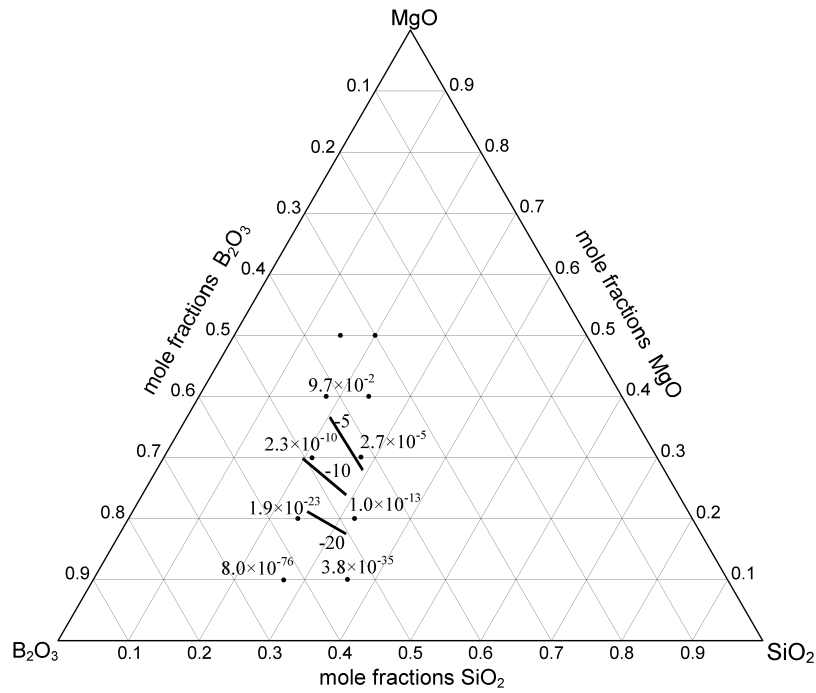

Fig. 3. Iso-activity lines of MgO in the MgO-B_2O_3-SiO_2 system at the temperature 1623 K.
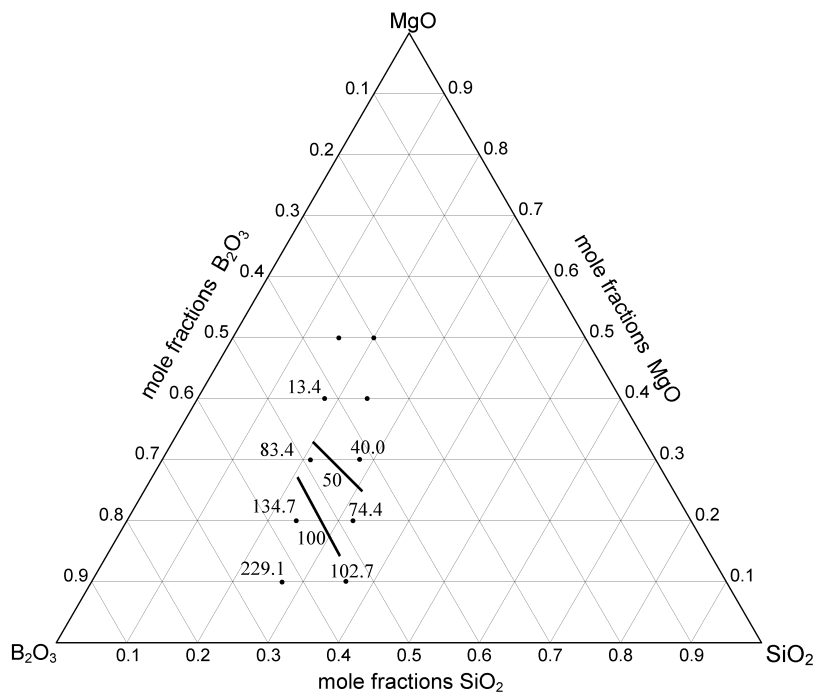
Fig.4. Excess Gibbs energy (kJ/mole) in the MgO-B_2O_3-SiO_2 system at the temperature 1623 K.
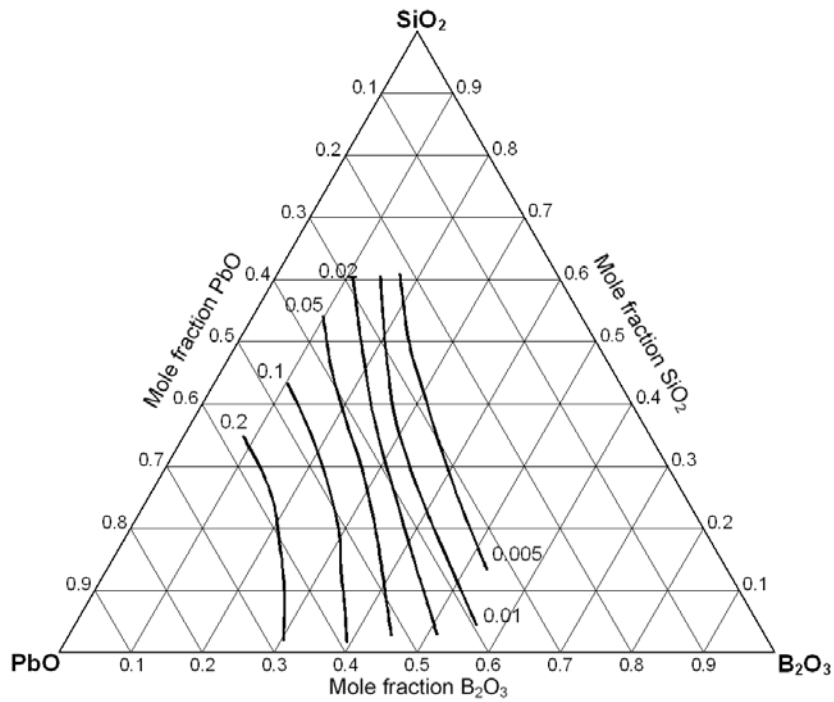

Fig. 5. Iso-activity lines of PbO in the melts of the PbO-B_2O_3-SiO_2 system at the temperature 1100 K.
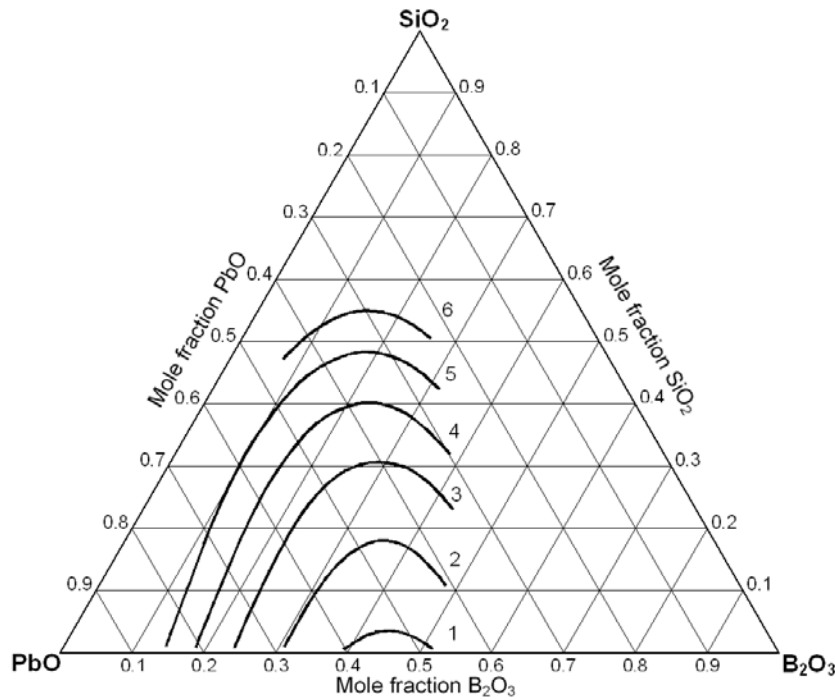
Fig. 6. Excess Gibbs energy in the melts of the PbO-B_2O_3-SiO_2 system at the temperature 1100 K: kJ/mole: 1 – 20, 2 – 18, 3 – 16, 4 – 14, 5 – 12, 6 – 10.

As follows from the comparison of the values of the Gibbs energies in the melts of the CaO-B_2O_3-SiO_2, SrO-B_2O_3-SiO_2 and BaO-B_2O_3-SiO_2 systems in the temperature range 1650-1800 K calculated according to GLTAS at the mole fraction of $SiO_2 = 0.50$ as a function of the melt concentration with the corresponding variations of the relative numbers of bonds of different types in these melts, the structural features of these melts were very close to each other and illustrated the fact that their glass-forming networks were strongly destroyed by oxide-modifier and contained substantial fractions of ionic bonds. The accuracy of such structural interpretation of the melts behaviour in the SrO-B_2O_3-SiO_2 system using GLTAS was recently confirmed also by the result of the direct experimental studies of glasses in this system by the X-ray scattering method [49]. Thus, this example is one more demonstration of the potential abilities of GLTAS for modeling thermodynamic properties of oxide glass-forming melts and for the consideration the correlations between them and their structure.

The general approaches discussed above to study vaporization processes and thermodynamic properties of the ionic silicate melts by high temperature mass spectrometric method as well as corresponding predictions of these processes using acid-base concept and calculations of these properties based on statistical thermodynamics models had a wide spectrum of the practical applications [1]. The following important results may be mentioned in this connection as the study of vaporization processes and thermodynamic properties of slags containing heavy metals (Cr, V, Pb, Zn) for optimization of metallurgical processes and for establishing of safe environmental conditions in industry [32, 50, 51].

4. Conclusions

Further application of high temperature mass spectrometry for the solution of the task "High temperature materials science and processing of the ionic silicate melts" may include consideration of the following important questions:

- to find the regularities of vaporization processes of oxide systems and materials at high temperatures;

- to predict relative volatilities of oxide materials involved in different kind of high temperature technologies;

- to predict thermodynamic properties of oxide materials using statistical thermodynamic approaches including the consideration of the correlation between the thermodynamic properties studied and the structure of these materials;

- to create data bases of thermodynamic properties of oxide systems and models for prediction:

   a) the partial pressures of vapour species over oxide materials,

   b) thermodynamic properties of oxide materials,

   c) phase diagrams of the complex oxide systems;

- to improve the experimental approaches for the purposes indicated.

Acknowledgement

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