

Vaporization and thermodynamics of glasses and glass-forming melts in ternary oxide systems

Valentina L. Stolyarova

Saint Petersburg State University,

Universitetskaya nab. 7/9, Saint Petersburg, 199034, Russian Federation

E-mail: v.stolyarova@inbox.ru

Innovation development of the approaches for preparation and application of advanced materials requires the knowledge on vaporization processes and thermodynamic properties of glass-forming oxide systems. These data obtained by high temperature mass spectrometric method in the PbO-B₂O₃-SiO₂, ZnO-B₂O₃-SiO₂, CdO-B₂O₃-SiO₂, Bi₂O₃-B₂O₃-SiO₂, Bi₂O₃-GeO₂-SiO₂ glass-forming systems are discussed. Thermodynamic functions of glass-forming melts in these systems such as activities and chemical potentials of components as well as the Gibbs energies showed various signs of the deviations from the ideal behavior. For modeling of thermodynamic properties of glasses and melts studied the theory of the generalized lattice theory of associated solutions was used. Based on this model the different levels of deviations from the ideality in the glass-forming oxide melts under consideration were clarified.

Keywords: Glass-forming oxide melts, Thermodynamics, Vaporization

Introduction

As well known design of the advanced glass materials requires the reliable information on vaporization processes and thermodynamic properties of glass-forming melts. This paper is the continuation of the systematic studies of ternary silicate glass-forming melts obtained by Knudsen effusion mass spectrometric method that are summarized in the following reviews [1-7]. It was shown that the main regularities of the vaporization of oxide systems were in agreement with the acid-based concept of interactions in the oxide melts. It was also repeatedly illustrated that the data on determination of thermodynamic functions in oxide systems were satisfied the main requirements for the confirmation of their reliability in comparison with the results obtained by the electromotive force method and the high temperature solution calorimetric method. In the current study the high-temperature behavior of the following ternary glass-forming melts will be considered based on the PbO-B₂O₃-SiO₂, CdO-B₂O₃-SiO₂, ZnO-B₂O₃-SiO₂, Bi₂O₃-B₂O₃-SiO₂ and Bi₂O₃-GeO₂-SiO₂ systems. The subjects of this consideration have the wide range of practical applications in the production of glasses, enamels, glazers and ceramics as well as in the various high temperature technologies such as obtaining of optical fibers and others. Since 1959 when Knudsen effusion mass spectrometric method was suggested to study the vaporization processes and thermodynamic properties of inorganic compounds [8] till nowadays this approach still one of the powerful tool of high temperature chemistry of inorganic materials including multicomponent glass-forming

melts [6]. It should be noted that the recent advances and improvements of this experimental technique may be found in [9].

Experimental

High-temperature Knudsen effusion mass spectrometry was used to study vaporization processes and to determine the partial pressures of vapor species as well as the component activities of the PbO-B₂O₃-SiO₂, CdO-B₂O₃-SiO₂, ZnO-B₂O₃-SiO₂, Bi₂O₃-B₂O₃-SiO₂ and Bi₂O₃-GeO₂-SiO₂ melts [7, 10-14]. Measurements were performed with MS-1301 mass spectrometer developed by the Institute of Analytical Instrumentation of the Russian Academy of Sciences, Saint Petersburg, Russia. Vaporization was carried out using two effusion cells containing the sample under study and pure oxide (reference substance). The main part of experiments were done from molybdenum effusion cells except the PbO-B₂O₃-SiO₂ system when vaporization was carried out from quartz effusion cells [10-12] as well as except the Bi₂O₃-B₂O₃-SiO₂ and Bi₂O₃-GeO₂-SiO₂ systems when the iridium-plated molybdenum effusion cells were used [7, 13, 14]. Ions were produced by electron ionization at the energy of 25 eV. To facilitate interpretation of mass spectra of vapor over glass-forming melts under consideration the appearance energies of ions were also measured. The installation was calibrated using the vapor pressure of gold, recommended by IUPAC as the standard.

Results and discussion

Various types of vapor species were found over the glass-forming melts of the PbO-B₂O₃-SiO₂,

Table 1

Composition of vapor over ternary glass-forming oxide melts studied at the temperature indicated

System under study	Temperature, K	Composition of vapor	References
PbO-B ₂ O ₃ -SiO ₂	1100	PbO, Pb, O ₂	[10-12]
ZnO-B ₂ O ₃ -SiO ₂	1250	Zn, O ₂	[11-13]
CdO-B ₂ O ₃ -SiO ₂	1023	Cd, O ₂	[12,13]
Bi ₂ O ₃ -B ₂ O ₃ -SiO ₂	1000	Bi, O ₂	[7,13]
Bi ₂ O ₃ -GeO ₂ -SiO ₂	1200	Bi, O ₂	[7, 14]

CdO-B₂O₃-SiO₂, ZnO-B₂O₃-SiO₂, Bi₂O₃-B₂O₃-SiO₂ and Bi₂O₃-GeO₂-SiO₂ systems studied [7, 10-14] such as dissociated products of vaporization of oxide-modifier, Table 1.

It should be mentioned that the composition of vapor found over these melts was in agreement with the content of gaseous phase during vaporization of corresponding binary systems [1]. The main feature of thermodynamic description of glass-forming melts under consideration was the negative deviations from the ideal behavior. As examples Figures 1-2 illustrate some of the experimental thermodynamic data obtained in the melts of the PbO-B₂O₃-SiO₂, ZnO-B₂O₃-SiO₂, CdO-B₂O₃-SiO₂ and Bi₂O₃-GeO₂-SiO₂ systems [7, 10-14]. Figure 1 illustrates the comparison of the concentration dependencies of chemical potentials of oxide-modifiers in the melts of the PbO-B₂O₃-SiO₂, ZnO-B₂O₃-SiO₂, CdO-B₂O₃-SiO₂ systems obtained by Knudsen effusion mass spectrometric method in Refs. [10-13].

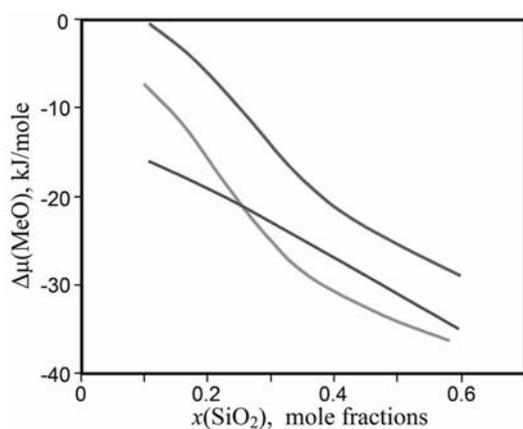


Fig. 1. The comparison of chemical potentials of oxide-modifiers in the melts of the PbO-B₂O₃-SiO₂ (blue), ZnO-B₂O₃-SiO₂ (red) CdO-B₂O₃-SiO₂ (green) systems along the $x(\text{MeO})/(x(\text{MeO})+x(\text{B}_2\text{O}_3)) = 0.667$ section at the temperature range 1023-1250 K as a function of SiO₂ concentration obtained by Knudsen effusion mass spectrometric method in Refs. [10-13]

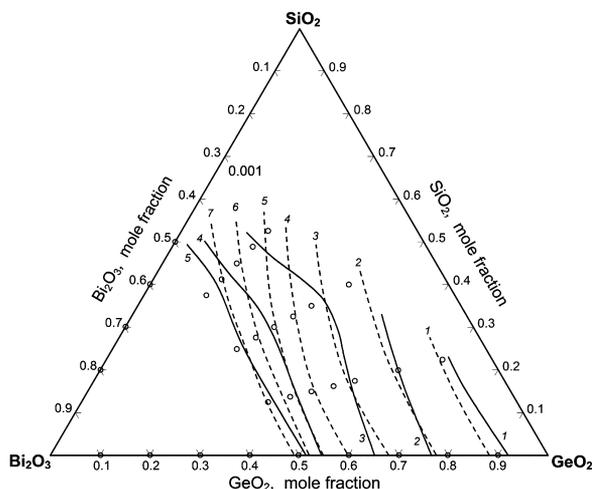


Fig. 2. The values of Bi₂O₃ activities in the melts of the Bi₂O₃-GeO₂-SiO₂ system calculated using GLTAS at the temperature 1200 K (dashed lines). The isoactivity curves of Bi₂O₃ correspond to the values equal to: 1 – 0.00003, 2 – 0.0001, 3 – 0.0003, 4 – 0.001, 5 – 0.003, 6 – 0.01, 7 – 0.03. Solid lines are the interpolation of the experimental results obtained by high temperature mass spectrometric method [14]

It is very important to mention that the level of the deviations of thermodynamic properties from the ideal behavior in the glass-forming melts considered was in agreement with the acid-base concept of interactions in oxide melts [1] and depended on the basicity of the melts. The concentration dependencies of the Bi₂O₃ isoactivity curves in Bi₂O₃-GeO₂-SiO₂ melts at the temperature 1200 K [14] are presented on Figure 2 found by high temperature mass spectrometric method also.

Modeling of thermodynamic properties of glass-forming melts in the PbO-B₂O₃-SiO₂, CdO-B₂O₃-SiO₂, ZnO-B₂O₃-SiO₂, Bi₂O₃-B₂O₃-SiO₂ and Bi₂O₃-GeO₂-SiO₂ systems was done using the generalized lattice theory of associated solutions (GLTAS) described in details for the application for glass-form-

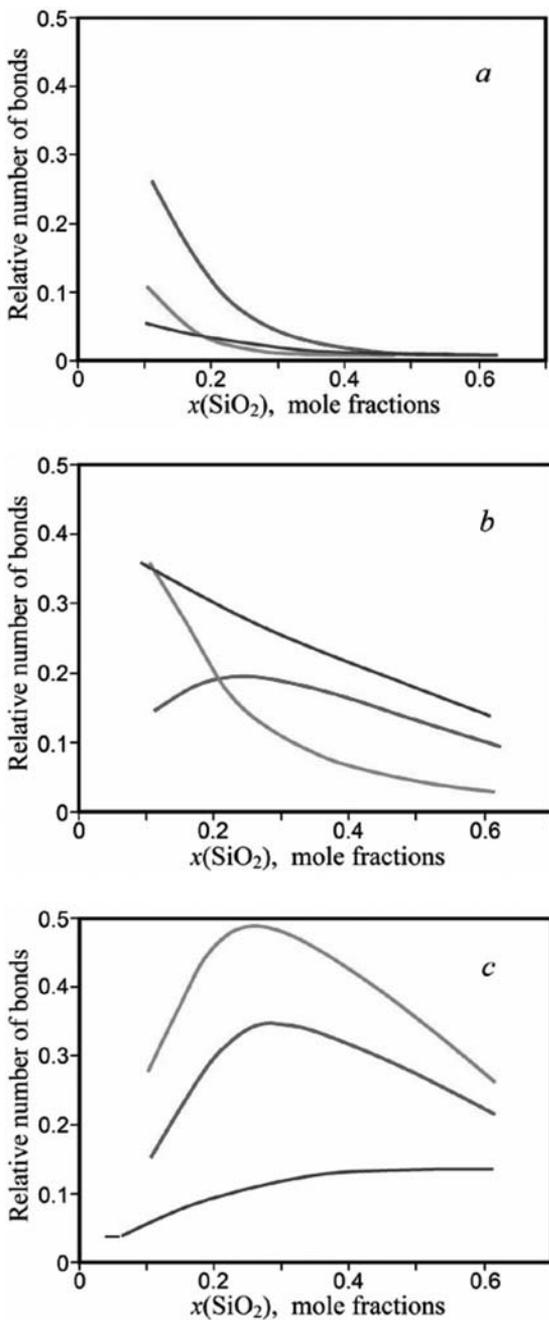


Fig. 3. The relative number of bonds of different types in $\text{MeO-B}_2\text{O}_3\text{-SiO}_2$ melts: *a* – Me-O[Me] , *b* – Me-O[B] , *c* – Me-O[Si] bonds, where Me is Zn, Cd and Pb, calculated using GLTAS [10-13]. Symbols are $\text{ZnO-B}_2\text{O}_3\text{-SiO}_2$ system (red); $\text{CdO-B}_2\text{O}_3\text{-SiO}_2$ system (green); $\text{PbO-B}_2\text{O}_3\text{-SiO}_2$ system (blue)

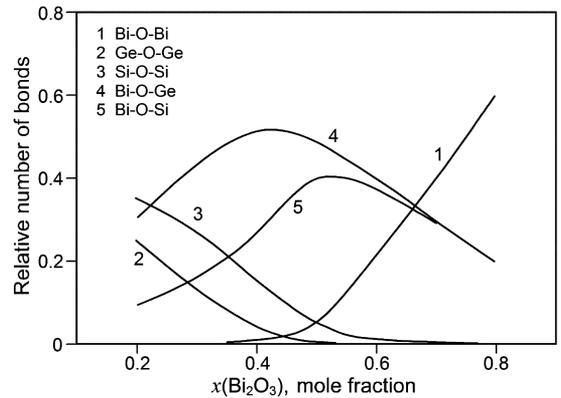


Fig. 4. Relative number of bonds of different types in the melts of the $\text{Bi}_2\text{O}_3\text{-GeO}_2\text{-SiO}_2$ system calculated using GLTAS at the temperature 1200 K: mole fractions of GeO_2 and SiO_2 in the melts are equal

ing melts earlier in [1]. This approach is suggested by Barker [15] for modeling of organic mixtures and may be represented by the Guggenheim model of the strongly regular solutions in the systems where molecules differs on the sizes and their interaction energy depends on mutual orientation of the molecules. Peculiarities of description of this model to glass-forming melts under consideration may be found in [16, 17] including the features of introduction of Bi_2O_3 in the structure of melt as in [14]. The mutual agreement of thermodynamic properties of glass-forming oxide melts containing one oxide modifier and two glass-forming oxides (as in case of the melts under consideration at the present study) was repeatedly shown as the result of comparison of such modeling and experimental data obtained by high temperature mass spectrometric method. As one additional example of this fact Figure 2 shows the mutual correlation between experimental values of the Bi_2O_3 activities obtained in $\text{Bi}_2\text{O}_3\text{-GeO}_2\text{-SiO}_2$ melts and results of modeling based on GLTAS at the temperature 1200 K [14].

One of the advantages of GLTAS model is the opportunity to find the correspondence between the changes of thermodynamic properties of glass-forming melt and its structure such as the relative number of bonds of different types formed in the melt when the second coordination sphere is taken into consideration. As the results of modeling using GLTAS information on the relative numbers of bonds of different types in these melts may be also found [1, 15-17]. Figure 3 (a,b,c) illustrates the relative number of

bonds of different types in $\text{MeO-B}_2\text{O}_3\text{-SiO}_2$ melts: a – Me-O[Me] , b – Me-O[B] , c – Me-O[Si] bonds, where Me is Zn, Cd and Pb, calculated using GLTAS [10-13]. As follows in particular from Figure 4 the data calculated in Ref. [14] allow concluding that the Bi-O-Si bonds have the predominant role in the formation of the $\text{Bi}_2\text{O}_3\text{-GeO}_2\text{-SiO}_2$ melts with the negative deviations from the ideality. As the molar ratio of $\text{GeO}_2\text{:SiO}_2$ decreases the influence of Bi-O-Ge and Bi-O-Si bonds on the negative deviations from the ideality of these melts is more valid. The features of structural description of glass-forming melts under study obtained as the result of modeling were successfully confirmed using X-ray scattering method [18, 19].

Conclusions

Using high temperature Knudsen effusion mass spectrometric method it is shown that the composition of vapor over the $\text{PbO-B}_2\text{O}_3\text{-SiO}_2$, $\text{CdO-B}_2\text{O}_3\text{-SiO}_2$, $\text{ZnO-B}_2\text{O}_3\text{-SiO}_2$, $\text{Bi}_2\text{O}_3\text{-B}_2\text{O}_3\text{-SiO}_2$ and $\text{Bi}_2\text{O}_3\text{-GeO}_2\text{-SiO}_2$ melts is in agreement with the content of gaseous phase over corresponding binary systems. In the ternary glass-forming melts studied the negative deviations from the ideal behavior were found that were in accordance with the main statements of the acid-base concept. Reliability of application of the generalized lattice theory of associated solutions for modeling of thermodynamic properties and structural features of ternary glass-forming melts with one oxide modifier was illustrated.

Acknowledgements

Financial support for this work from the Russian Fund for Basic Research according to the Projects N 10-03-00705 and N 13-03-00718 is gratefully acknowledged.

References

1. Valentina Stolyarova, and German Semenov, *Mass Spectrometric Study of the Vaporization of Oxide Systems*. Second revised edition with addenda (Chichester: John Wiley & Sons Ltd., 1994), 434.
2. V.L. Stolyarova, "A Mass Spectrometric Study of the Thermodynamic Properties of Oxide Melts," *Glass Physics and Chemistry*, 27 (2001), 3-15.
3. V.L. Stolyarova, "High Temperature Mass Spectrometric Study of Thermodynamic Properties and Vaporization Processes of Oxide Systems: Experiment and Modeling," *The Open Thermodynamics Journal*, 7 (2013), 57-70.
4. V.L. Stolyarova, "Vaporization Processes and Thermodynamic Properties of Oxide Systems

Studied by High Temperature Mass Spectrometry," *ECS Transactions*, 46 (2013), 55-68.

5. V.L. Stolyarova, "Thermodynamic Properties and Structure of Ternary Silicate Glass-forming Melts: Experimental Studies and Modeling," *J. Non-Crystalline Solids*, 354 (2008), 1373-1377.
6. V.L. Stolyarova, "Vaporization and Thermodynamics of Glass-Forming Oxide Melts: Mass Spectrometric Study and Modeling," *J. Materials Science and Chemical Engineering*, 3 (2015), 81-86.
7. V.L. Stolyarova, "Mass spectrometric thermodynamic studies of oxide systems and materials," *Russian Chemical Review*, 86 (2016), 60-80.
8. M.G. Inghram, and J. Drowart, "Mass Spectrometry Applied to High Temperature Chemistry," *Proceedings of International symposium on high temperature technology* (Asilomar, California, New York: McGraw-Hill, 1959), 219-240.
9. J. Drowart, C. Chatillon, J. Hastie, and D. Bonnell, "High-temperature Mass Spectrometry: Instrumental Techniques, Ionization Cross-sections, Pressure Measurements, and Thermodynamic Data," *Pure Appl. Chem.*, 77 (2005), 683-737.
10. V.L. Stolyarova, S.I. Lopatin, A.L. Shilov, and S.M. Shugurov, "High-temperature Mass spectrometric Study of the Vaporization Processes and Thermodynamic Properties of Melts in the $\text{PbO-B}_2\text{O}_3\text{-SiO}_2$ System," *Rapid Commun. Mass Spectrom.*, 27 (2013), 1559-1566.
11. V.L. Stolyarova, S.I. Lopatin, A.L. Shilov, and S.M. Shugurov, "Thermodynamic Properties of Melts in the $\text{PbO-B}_2\text{O}_3\text{-SiO}_2$ and $\text{ZnO-B}_2\text{O}_3\text{-SiO}_2$ Systems: Experimental Study and Modeling" (Paper presented at the 25th European Symposium on Applied Thermodynamics. ESAT 2011, Saint Petersburg, Russia, 24 June 2011), 296.
12. V.L. Stolyarova, S.I. Lopatin, A.L. Shilov, and S.M. Shugurov, "Thermodynamic Properties of Borosilicate Glasses and Melts Containing Oxides of Heavy Metals (Cd, Zn, Pb)" (Paper presented at XIX International Conference on Chemical Thermodynamics in Russia, Moscow, Russia, 24-28 June 2013), 318.
13. V.L. Stolyarova, S.I. Lopatin, A.L. Shilov, and S.M. Shugurov, "Application of Knudsen Effusion Mass Spectrometric Method for Environmental Science: Vaporization of Heavy Metals from Borosilicate Melts" (Paper presented at The Innovation in Mass Spectrometry Instrumentation Conference, Saint Petersburg, Russia, 18 July 2013), 54-55.

14. V.L. Stolyarova, S.I. Lopatin, S.M. Shugurov and A.L. Shilov, "Thermodynamic Properties of Glasses in the $\text{Bi}_2\text{O}_3\text{-GeO}_2\text{-SiO}_2$ system," Proceedings of XIV Russian Conference (with International Participation) on Thermo Physical Properties of Substances (RCTP-14) (Kazany, Russia: Otechestvo, 2014), 2, 251-253.
15. J.A. Barker, "Cooperative orientation effects in solutions," J. Chem. Phys., 20 (1952) 1526-1532.
16. V.L. Stolyarova and A.L. Shilov, "Modeling of Thermodynamic Properties and Structure of Borosilicate Melts Using High Temperature Mass Spectrometric Data," Proceedings of the 6th International Conference on Mathematical Modeling and Computer Simulation of Materials Technologies MMT-2010. (Ariel, Israel: The Israel Materials & Processes Society, 2010), 1-56-1-64.
17. V.L. Stolyarova and A.L. Shilov, "Application of the Barker Lattice Theory to Modeling of Thermodynamic Properties of $\text{PbO-B}_2\text{O}_3\text{-SiO}_2$ Melts," J. Non-Crystalline Solids, 366 (2013), 6-12.
18. V.V. Golubkov, P.A. Onushchenko and V.L. Stolyarova, "On the Structure of Glass of the $\text{PbO-B}_2\text{O}_3\text{-SiO}_2$ and $\text{CdO-B}_2\text{O}_3\text{-SiO}_2$ Systems," Glass Physics and Chemistry, 39 (2013), 624-633.
19. V.V. Golubkov, P.A. Onushchenko and V.L. Stolyarova, "Studies of Glass Structure in the System $\text{Bi}_2\text{O}_3\text{-B}_2\text{O}_3\text{-SiO}_2$," Glass Physics and Chemistry, 41 (2015), 247-253.