Soret coefficient of a sodium borate melt: Experiment with a vertical furnace and thermodynamic theory

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The Soret effect or thermodiffusion is temperature-gradient-driven diffusion in a multicomponent system. A physical model to accurately predict the Soret coefficient of oxide melts has not yet been proposed. Here, for the first time, we report a quantitative comparison between experiment and theory concerning the Soret coefficient in binary glass-forming oxide melts. We measured the Soret coefficient of 11Na₂O–89B₂O₃ (mol %) after 90- and 180-h heat treatment under a temperature gradient near 1200 K and estimated the Soret coefficient for the steady state. We used a vertical furnace to reduce the effect of natural convection on the Soret effect by heating the sample from the top side. The Soret coefficient estimated for the steady state near 1200 K was 5.12 x 10⁻³ K⁻¹, whereas that obtained by the adjusted Kempers model, in which we adjusted the original Kempers thermodynamic model for binary oxide melts, was 6.09 x 10⁻³ K⁻¹. The sign and order of magnitude were consistent, which suggests that the adjusted Kempers model is a promising model to explain the Soret effect and that the equilibrium thermodynamic parameters of partial molar volume, partial molar enthalpy, and chemical potential are important factors in the phenomenon.

Key-words : Glass, Glass melts, Borate, Soret effect, Temperature gradient, Diffusion

1. Introduction

1.1 Soret effect and Soret coefficient

The Soret effect, or thermodiffusion, is temperature-gradient-driven diffusion in a multicomponent system. It was discovered by Ludwig¹ in the 19th century. The Soret coefficient is a value that expresses whether the components diffuse toward the hot or cold region and presents the degree of separation of the components in the hot and cold regions. Chapman formulated an equation to predict the Soret coefficient for molecular gases.³ The mechanism of the Soret effect in liquids is controversial, however, because of the strong, complicated interaction between the diffusion species.⁴ The mass flux under a one-dimensional temperature gradient in a binary non-electrolyte system can be written as follows:⁵

\[ J_{1,x} = -\rho \left[ D_M \left( \frac{\partial n_1}{\partial x} \right) + n_1(1 - n_1) D_T \left( \frac{\partial T}{\partial x} \right) \right], \]

where \( x \) is the position, \( n_1 \) is the mole fraction of species 1, \( \rho \) is the mass density, \( T \) is the temperature, and \( D_M \) and \( D_T \) are the mutual and thermal diffusion coefficients, respectively. We neglected the effect of convection here. In a steady state, the flux \( J_{1,x} = 0 \) and the Soret coefficient can be written as follows:

\[ \sigma_{\text{soret,1}} = \frac{D_T}{D_M} = -\frac{1}{n_1(1 - n_1)} \frac{\partial n_1}{\partial T}. \]  (2)

A positive Soret coefficient indicates that the diffusion species concentrate in the cold region, whereas a negative value indicates that they concentrate in the hot region. The relation \( \sigma_{\text{soret,1}} = -\sigma_{\text{soret,2}} \) should be valid in a binary system.

1.2 Soret effect in silicate melts

There have been many reports on the Soret effect in silicate melts in the field of Earth science, where researchers used multicomponent silicate melts containing more than two oxides⁶⁻¹⁰ to describe the characteristics of magma under a temperature gradient. There are only two experimental clues to silicate melts; the silica component migrates to the hot side⁶⁻⁷ heavier isotopes concentrate in the cold side more easily than lighter isotopes.⁸⁻¹⁰ In 2012, Lacks et al. suggested that the mass effect of isotopes can be explained by the classical collision effect.¹⁰ Chemical factors affecting the Soret effect in silicate melts have not been clarified.
1.3 Soret effect in glass melts

In industrial glass-melting tanks\cite{11} and glass-melting crucibles, temperature gradients would cause the Soret effect, which could lead to spatial inhomogeneity of the glass melts. This inhomogeneity would affect not only the crystallization behavior of the glass melts but also the optical properties and thermal stability of the produced glass. In laser welding\cite{12} and cutting\cite{13} processes applied to glasses, a sharp temperature gradient may also cause the Soret effect. However, the factors affecting the Soret effect in glass-forming oxide melts remain unclear.

The migration directions of oxide components in binary-component glass melts were investigated by use of a femtosecond laser to create a steep temperature gradient inside the glass. In 50CaO–50SiO\textsubscript{2} (mol%), the concentration of CaO was higher on the colder side,\cite{14} which was reproduced by molecular dynamics simulation.\cite{15} The concentration of Na\textsubscript{2}O was higher on the colder side in 30Na\textsubscript{2}O–70SiO\textsubscript{2},\cite{16} 15Na\textsubscript{2}O–85B\textsubscript{2}O\textsubscript{3},\cite{17} and in 15Na\textsubscript{2}O–85GeO\textsubscript{2}.\cite{18}

The laser local-heating method does not provide temperature distribution, however, because the heated region is too small (<100 μm). Recently, to demonstrate a method of obtaining the Soret coefficients of binary oxide melts, we have reported an experiment on alkali borate melts using a transverse furnace,\cite{19} where we can measure the temperature distribution with a thermocouple. The migration directions were the hot side, cold side, and cold side for Li\textsubscript{2}O, Na\textsubscript{2}O, and K\textsubscript{2}O in 15Li\textsubscript{2}O–85B\textsubscript{2}O\textsubscript{3} (mol%), 15Na\textsubscript{2}O–85B\textsubscript{2}O\textsubscript{3}, and 15K\textsubscript{2}O–85B\textsubscript{2}O\textsubscript{3}, respectively, and the absolute values of the Soret coefficients were on the order of 10\textsuperscript{-4}–10\textsuperscript{-5} K\textsuperscript{-1}.

1.4 Scope of this study

To discuss the factors affecting the Soret effect, we should compare the experimentally obtained Soret coefficient with that obtained by a theoretical model. There are two key points for obtaining an accurate steady-state Soret coefficient experimentally. First, we should reduce the convection in the system, because convection disturbs the mole-fraction distribution formed by the Soret effect.\cite{20} A convection-less system for reduction of natural convection in which the sample is heated from the top side has been proposed.\cite{20} This system has not been applied in the case of binary oxide melts. Second, it generally takes a long time for the system to reach steady state in the case of binary oxide melts. It is necessary to trace the time evolution of the Soret coefficient.\cite{7} Here, taking into account these points, we introduce an experimental method with a vertical furnace, and an analysis method designed to obtain the steady-state Soret coefficient. We employed 10Na\textsubscript{2}O–90B\textsubscript{2}O\textsubscript{3} (mol%) as the starting composition in this experiment because the viscosity of the melt at 1173 K (11 dPas) is less than that of 15.7Na\textsubscript{2}O–84.3B\textsubscript{2}O\textsubscript{3} (14 dPas) and is the minimum in the range of 0 Na\textsubscript{2}O to 20 Na\textsubscript{2}O.\cite{21} We discuss the dominant factors of the Soret effect of a sodium borate glass melt, moreover, by comparing the steady-state Soret coefficient obtained by the experiment and that by an adjusted Kempers model. Kempers proposed a thermodynamic model to predict the Soret coefficient in molecular gas systems.\cite{22,23} We adjusted the original Kempers model\cite{22,23} to apply to oxide melts. In this adjusted Kempers model, the mixing thermodynamic parameters are assumed to be important for the Soret effect.

2. Experiment

2.1 Preparation of glass and platinum capsule

Sodium borate glasses, 10Na\textsubscript{2}O–90B\textsubscript{2}O\textsubscript{3} (mol%), were prepared by the conventional melt-quenching method using a platinum crucible to melt a Na\textsubscript{2}CO\textsubscript{3} and H\textsubscript{3}BO\textsubscript{3} powder mixture, with a melting temperature and time of 1423 K and 30 min, respectively. The glasses were sealed in platinum capsules because the oxide components are easily volatilized. Figure 1(a) shows the sizes of the platinum capsules and the glasses. The procedure used to make the capsules is described below. One end of each platinum pipe was welded. A glass sample was ground into powder. A part of the glass powder was entered into the pipe and melted at 1423 K for 10 min. After cooling, it was noted that the end of the glass lifted up approximately 5 mm along the inner surface of the platinum tube. The glass-filling process was conducted 2–4 times until the length from one end of the glass to the bottom of the non-flat surface at the other end reached approximately 21 mm, at which time the other end of the pipe was welded.

2.2 Thermal treatment

The platinum capsules containing the glasses were set in a tube furnace with an inner diameter of 60 mm to measure the Soret coefficient, as shown in Fig. 1(b). The temperature was highest in the center of the furnace, and the top of the glass has the highest temperature inside the glass. We measured the temperature distribution around the platinum capsules by Method A with a moveable R-type thermocouple with a diameter of 0.5 mm in every run. The part of the thermocouple except for the measuring junction was covered with an alumina protective tube. To obtain a temperature close to that inside the glass, we used correction factors obtained by a more direct temperature-measurement method (Method B). Figure 1(c) shows the setup for the temperature measurement test to obtain the correction factor for this temperature gradient and temperature. The measuring junctions of naked R-type thermocouples with diameters of 0.5 mm were fixed on the platinum capsules using a ceramic adhesive.

Figure 1(d) shows the results of the temperature measurement test. The temperature-gradient correction factor, \(\alpha\), was determined to be 1.04, which is defined as the ratio of the temperature gradients obtained with Method B to that with Method A. The \(\alpha\) is used to determine the Soret coefficient in the latter part of this paper. The temperature correction factor, \(\Delta \beta\), was -10 K, which was calculated by subtracting the average temperature obtained with Method B from that with Method A. The \(\Delta \beta\) is used to...
determine the actual average temperature in the experiment. Although the ideal temperature-gradient correction factor and ideal temperature correction factor may change with every experiment, we use the same correction factors determined by the test for all of the experiments. This may cause some uncertainty for sample temperatures and the Soret coefficient. In this paper, we neglect the uncertainty. To avoid crystallization, the heat treatment temperature for obtaining the Soret coefficient was above the liquidus temperature (974 K) of 10Na₂O-90B₂O₃.²⁴) Since it is difficult to seal glass melts in platinum capsules at high temperatures (e.g. 1500 K), we conducted the experiment in the temperature range of 1100–1350 K. This is why we did not use silicate melts, which have high viscosity in this temperature range, extending the time for the system to reach the steady state under the temperature gradient. By calculating with vapor pressure,²⁵) we confirmed that the effect of volatilization of the glass component into the air on the concentration distribution is negligible. After heat treatment for 90 or 180 h, the platinum capsules were quickly removed from the furnace tube and quenched in water.

2.3 Determination of mole-fraction distribution

The platinum capsules were cut at intervals of several millimeters and polished. A rotating diamond wheel with a thickness of 0.3 mm was used to cut the platinum capsules after heat treatment. The polishing loss was a thickness of within 0.1 mm.

The mole fraction of the heat-treated glass of each slice was measured by confocal Raman spectroscopy (LabRAM HR Evolution, Horiba).¹⁹) To determine the mole-fraction, we used the ratio of the area of peaks at around 776 and 806 cm⁻¹, which was assigned to the symmetric breathing vibration of six-membered rings with one BO₄ tetrahedron and the symmetric breathing vibration of boroxol rings, respectively.²⁶) The standard glass samples were made by the conventional melt-quenching method. The melting temperature and time were 1423 K and 30 min. It was assumed that the standard glasses have compositions corresponding to the charged amount of the Na₂CO₃ and H₃BO₃ powder. The ratio of the peak area increases with the Na₂O mol %, as shown in Fig. 2, and the fitting curve is expressed as follows:

\[ R = a + b \exp(cn_1), \]  

where \( R \) is the ratio of the area of peaks around 776 and 806 cm⁻¹, \( n_1 \) is the mole fraction of Na₂O, and \( a, b, \) and \( c \) are fitting parameters. \( a, b, \) and \( c \) are determined to be 0.11844 ± 0.007, 0.00711 ± 0.0008, and 32.211 ± 0.7, respectively. The uncertainties(±) show the standard uncertainties of the fitting parameters. To determine the mole fraction of Na₂O and its uncertainty for each slice, we measured the peak area ratio at 10 random positions on the surface. The weighted average and weighted standard deviation for the 10 data of Na₂O content were calculated, where the weight was the inverse square of the combined standard uncertainty of Na₂O content at each position. In
in this paper, we assume that water dissolved in glass and that the fictive temperature will not affect the ratio of the peak area.

2.4 Experiment with a transverse furnace

For comparison, we conducted a 90-h heat treatment in a transverse furnace with an inner diameter of 42 mm. The experimental setup and results of the temperature measurement test are shown in Figs. 1(e)–1(g) and Fig. 1(h), respectively. We used the same thermocouples as in the case of the vertical furnace. The transverse system used in this study was similar to one reported previously but had a small difference: the alumina plate to hold the platinum capsule was set only under the edge of the platinum capsule in this study in order to minimize the effect on temperature distribution inside the platinum capsule.

3. Results

All data for temperature versus mole fraction of Na₂O after heat treatment under the temperature gradient are shown in Fig. 3. We conducted two trials of the same experiment for each condition to check reproducibility. The vertical error bar indicates the weighted standard deviation for the mole fraction of Na₂O for each slice. The horizontal error bar indicates the uncertainty of the temperature of each slice. To calculate the temperature uncertainty, we estimated the displacement and the combined uncertainty, of the sample position stemming from cutting loss, positioning error of the diamond wheel, and polishing loss, as follows:

\[ \Delta x_{\text{total}} = \Delta x_{\text{cut}} + \Delta x_{\text{cut position}} + \Delta x_{\text{polish}} \]
\[ = (0.15 \pm 0.0) \text{ mm} + (0.0 \pm 0.2) \text{ mm} + (0.05 \pm 0.05) \text{ mm} \]
\[ = (0.2 \pm 0.25) \text{ mm} \]  

where \( \Delta x_{\text{cut}} \) corresponds to half the thickness of the diamond wheel. In Fig. 3, deviations of the average mole fraction from 10Na₂O–90B₂O₃ (mol %) may be attributed to the 1423 K heat treatment in the process of inserting the glass into the capsule, which was the only difference between the heating processes applied to the glass inside platinum capsule and the standard glass samples. The filling process, the melting duration of which is 10 min, was conducted 2–4 times.

We calculated the Soret coefficient of Na₂O after heat treatment time \( t \) by the following equation and plotted it in Fig. 4:

\[
\sigma_{\text{Soret,1}}(t) = -\frac{1}{\alpha n_1(t) [1 - n_1(t)]} \frac{\partial n_1(t)}{\partial T},
\]  

where \( \alpha \) is the temperature-gradient correction factor, and the bar above \( n \) indicates the average of \( n \). In this study, we set Na₂O and B₂O₃ to components 1 and 2, respectively. The error bar indicates combined uncertainty stemming from uncertainties concerning the mole fraction and temperature. The conditions and results are summarized in Table 1. The reason for the gap between the Soret coefficients in the two identical trials is not clear.

4. Discussions

4.1 Vertical furnace vs transverse furnace

In Fig. 3, the value for heating in the vertical furnace for 90 h is several times larger than that for the transverse furnace. This appears to be due to the reduction in natural convection in the case of the vertical furnace. However, Marangoni convection may still exist even in a vertical furnace. The absolute value \( \sim 10^{-4} \text{K}^{-1} \) of the Soret coefficient when using the transverse furnace is about one order of magnitude larger than that in the previous reports \( \sim 10^{-5} \text{K}^{-1} \). This appears to be due to the different compositions of the 19 mol % Na₂O in this study and the 15 mol % Na₂O in previous studies and the size differences of the alumina plates holding the platinum capsules, as mentioned in 2.4, and of the glass regions inside the platinum capsules.

4.2 Estimation of the steady-state Soret coefficient

The time evolution of the Soret coefficient was discussed by de Groot and Tyrell; Lesher used the following equation to trace the time evolution of the Soret coefficient of the silica component in silicate melts:

\[ \sigma_{\text{Soret,1}}(t) = \sigma_{\text{Soret,1}}^{\text{steady state}} \left( 1 - e^{-t/\theta} \right), \]

where \( t \) is the heat treatment time, and \( \theta \) is the characteristic time for the Soret coefficient to reach 63% of the steady state. By fitting the data plots for the vertical furnace in Fig. 4, we determined the \( \sigma_{\text{Soret,1}}^{\text{steady state}} \) and \( \theta \) to be 5.12 \times 10^{-3} \text{K}^{-1} and 272 h, respectively. It must be noted that the standard uncertainties of the \( \sigma_{\text{Soret,1}}^{\text{steady state}} \) and \( \theta \) are 5.2 \times 10^{-3} \text{K}^{-1} and 360 h, which are larger than the above values.

4.3 Adjusted Kempers model

Next, we pursued a theoretical consideration. Kempers derived a thermodynamic equation for the Soret coefficient.
Fig. 3. Mole fraction versus temperature. (a), (b) 90-h heat treatment with a vertical furnace. (c), (d) 180-h heat treatment with a vertical furnace. (e), (f) 90-h heat treatment with a transverse furnace. The plots are the average value of the mole fraction of Na$_2$O for each piece of the sample after cutting. The vertical error bar indicates the weighted standard deviation of the mole fraction of Na$_2$O. The horizontal error bar indicates the temperature uncertainty of each slice. The solid line indicates the fitting line. The temperature was measured by Method A.
based on the idea that the partition function in the system reaches a maximum at steady state under a temperature gradient. The thermodynamic portion of the Kempers model is expressed as follows:22),23)  

\[
\sigma_{\text{Kempers,}1} = \frac{v_1 v_2}{v_1 x_1 + v_2 x_2} \frac{h_2 - h_1}{u_2} - \frac{h_1 - h_1}{u_1}, \tag{7}
\]

where \(v\), \(h\), and \(\mu\) are the partial molar volume, partial molar enthalpy, and chemical potential, respectively. Kempers said that the reference state \(^{(1)}\) is normally considered the ideal gas state of the pure component.22) It should be noted that \(\mu_1\) includes the chemical potential \(\mu_1^{(1)}\) of the reference state.22) When we calculate the Soret coefficient of oxide melts by Eq. (7), there are two problems: the value of \(\sigma_{\text{Kempers,}1}\) apparently depends on setting of the reference state of \(h_2\) and \(h_1\); and we cannot obtain the value of \(\mu_1\) because the chemical potential is generally measured as the difference from a reference state. In this study, we assumed that only mixing thermodynamic parameters of the two oxides of the liquid state contributes to the Soret coefficient and, therefore, took the pure liquid state as the reference state. We adjusted the Kempers model as follows:

\[
\sigma_{\text{Adjusted Kempers,}1} = \frac{v_1 v_2}{v_1 x_1 + v_2 x_2} \frac{h_2 - h_2^{\text{PL}}}{u_2} - \frac{h_1 - h_1^{\text{PL}}}{u_1} - \frac{T_n}{\frac{\partial (\mu_1 - \mu_1^{(1)})}{\partial n_1}}, \tag{8}
\]

where the superscript, \(\text{PL}\), indicates the pure liquid state, which is the reference state in this model. The \(h_2 - h_2^{\text{PL}}\), \(h_1 - h_1^{\text{PL}}\), and \(\mu_1 - \mu_1^{(1)}\) are mixing thermodynamic parameters and can be obtained from the literature.

The parameters for the calculation are summarized in Table 2. The calculated Soret coefficient of \(\text{Na}_2\text{O}\) at 1180 K, which is the average of the experimental temperature \(T_{\text{ex}}\) in Table 1) of the four runs, is \(6.09 \times 10^{-3}\) K\(^{-1}\) for 11\(\text{Na}_2\text{O}–89\text{B}_2\text{O}_3\) (mol%).
4.4 Experiment vs theory

We summarize all the data for the Soret coefficient in Fig. 5, which includes the value estimated for the steady state with a vertical furnace and the theoretical value from the adjusted Kempers model. The sign and order of magnitude of the steady-state Soret coefficient in the experiment are consistent with those in the adjusted Kempers model. This suggests that the adjusted Kempers model is a promising model for the Soret effect in this system and that the equilibrium thermodynamic factors of partial molar volume, partial molar enthalpy, and chemical potential are the dominant factors. Judged from Eq. (8), the concentrated region (cold region or hot region) of the Na2O component is determined by $v_2(h_1 - h_1^{PL})$ and $v_1(h_2 - h_2^{PL})$, and the Na2O component should concentrate in the cold region because Na2O has a large negative partial molar enthalpy in the glass melt. The difference between the experimental steady-state value and the theoretical value is 19%, which may be attributed to the Marangoni convection, kinetic factors such as the classical collision effect between ions, or measurement uncertainty.

4.5 Prediction of composition dependence

It is worth while calculating the composition dependence of the theoretical value for future study. As shown in Fig. 6 and Table 2, the Soret coefficient of Na2O at 1180 K decreases with increase in the Na2O content. The calculation was conducted from 0.11 mol% Na2O to 0.30 mol% Na2O because the experimental thermodynamic data can be obtained only in the composition range. In Ref. 30, the magnification correlation of the mixing partial molar enthalpy of $h_1 - h_1^{PL}$ and $h_2 - h_2^{PL}$ is reversed at around 75 mol% Na2O, which indicates that there is a possibility that, with increasing Na2O content, the Na2O-concentrated region under the temperature gradient will be flipped from the cold to the hot region around the composition.

5. Conclusion

For the first time, we reported a quantitative comparison between the experimental and theoretical the Soret coefficients in binary glass-forming oxide melts. In the 11Na2O–89B2O3 (mol%) glass melts, the sign and order of magnitude of the steady-state Soret coefficient in the experiments are consistent with those in the adjusted Kempers model. This suggests that the adjusted Kempers model is a promising model for explaining the Soret effect and that the equilibrium thermodynamic parameters of the partial molar volume, partial molar enthalpy, and chemical potential...
potential are important in the phenomenon. Furthermore, we demonstrate the effectiveness of a vertical furnace in determining the Soret coefficient. As future work, the adjusted Kempers model and this experimental method should be applied to other binary oxide melts.

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References
1) C. Ludwig, *Sitz. Math. Naturwiss. Classe Kaiserichen. Akad. Wiss.*, 20, 539 (1856).
2) C. Soret, *Arch. Sci. Phys. Nat.*, 2, 48–61 (1879).
3) S. Chapman and T. G. Cowling, *The mathematical theory of non-uniform gases* (Third edition), Chapter 9, 149–166, Cambridge University Press (1970).
4) M. Eslamian and M. Z. Saghir, *J. Non-Equil. Thermodyn.*, 34, 97–131 (2009).
5) P. A. Artola and B. Rousseau, *J. Chem. Phys.*, 143, 174503 (2015).
6) D. Walker and S. E. Delong, *Contrib. Mineral. Petr.*, 79, 231–240 (1982).
7) C. E. Lesher and D. Walker, *Geochim. Cosmochim. Ac.*, 50, 1397–1405 (1986).
8) F. Huang, P. Chakraborty, C. C. Lundstrom, C. Holmden, J. J. G. Glessner, S. W. Kieffer and C. E. Lesher, *Nature*, 464, 396–400 (2010).
9) G. Dominguez, G. Wilkins and M. H. Thiemens, *Nature*, 473, 70–73 (2011).
10) D. J. Lacks, G. Goel, C. J. Bopp, J. A. V. Orman, C. E. Lesher and C. C. Lundstrom, *Phys. Rev. Lett.*, 108, 065901 (2012).
11) H. Mase and K. Oda, *J. Non-Cryst. Solids*, 388-39, 807–812 (1980).
12) I. Miyamoto, K. Cvecek and M. Schmidt, *Opt. Express*, 21, 14291–14302 (2013).
13) K. Kim, J. Kim, D. Farson, H. W. Choi and K. Kim, *Jpn. J. Appl. Phys.*, 47, 6978–6981 (2008).
14) M. Shimizu, M. Sakakura, S. Kanehira, M. Nishi, Y. Shimotsuma, K. Hirao and K. Miura, *Opt. Lett.*, 36, 2161–2163 (2010).
15) M. Shimizu, H. Kato, M. Nishi, D. Hanakawa, K. Nagashima, H. Visbal, H. Itasaka, M. Sakakura, Y. Shimotsuma, K. Miura and K. Hirao, *J. Ceram. Soc. Jpn.*, 125, 180–184 (2017).
16) M. Shimizu, K. Miura, M. Sakakura, M. Nishi, Y. Shimotsuma, S. Kanehira, T. Nakaya and K. Hirao, *Appl. Phys. A-Mater.*, 100, 1001–1005 (2010).
17) Y. Liu, B. Zhu, L. Wang, J. Qiu, Y. Dai and H. Ma, *Appl. Phys. Lett.*, 92, 121113 (2008).
18) X. Wang, M. Sakakura, Y. Liu, J. Qiu, Y. Shimotsuma, K. Hirao and K. Miura, *Chem. Phys. Lett.*, 511, 266–269 (2011).
19) M. Shimizu, D. Hanakawa, M. Nishi, K. Nagashima, H. Visbal, M. Sakakura, Y. Shimotsuma, K. Miura and K. Hirao, *J. Ceram. Soc. Jpn.*, 124, 774–776 (2016).
20) J. K. Platten, *J. Appl. Mech.*, 73, 5–15 (2006).
21) O. V. Mazurin, M. V. Streltsina and T. P. Shvaiko-Shvaikovskaya, “Handbook of glass data, Part B”, Elsevier (1985) pp. 119–120.
22) L. J. T. M. Kempers, *J. Chem. Phys.*, 90, 6541–6548 (1989).
23) L. J. T. M. Kempers, *J. Chem. Phys.*, 115, 6330–6341 (2001).
24) E. M. Levin, C. R. Robbins and H. F. McMurdie, “Phase Diagrams for Ceramists”, The American Ceramic Society, Columbus (1964) pp. 87–93.
25) S. S. Cole and N. W. Taylor, *J. Am. Ceram. Soc.*, 159, 82–85 (1935).
26) B. N. Meera and J. Ramakrishna, *J. Non-Cryst. Solids*, 159, 1–21 (1993).
27) S. R. De Groot, *Physica*, 9, 699–708 (1942).
28) H. J. V. Tyrrell, *Diffusion and heat flow in liquids*. Third edition, Chapter 8, 183–229, Butterworths (1961).
29) E. F. Riebling, *J. Am. Ceram. Soc.*, 50, 46–53 (1967).
30) M. Fan, Ph.D. Thesis, RTWH, Aachen, Germany (1991).
31) M. Itoh, S. Sato and T. Yokokawa, *J. Chem. Thermodyn.*, 8, 339–352 (1976).