Soret coefficients of alkali oxides in alkali borate glass melts

Masahiro SHIMIZU, Daisuke HANAKAWA, Masayuki NISHI, Kohji NAGASHIMA, Vishal HEIDY, Masaaki SAKAKURA, Yasuhiko SHIMOTSUMA, Kiyotaka MIURA and Kazuyuki HIRAO

Department of Material Chemistry, Graduate School of Engineering, Kyoto University, Kyoto 615-8510, Japan

We measured the Soret coefficients of alkali oxides in binary alkali borate glass melts. The alkali borate glasses, 15(mol %)Li2O–85B2O3, 15Na2O–85B2O3, and 15K2O–85B2O3, were encapsulated in platinum capsules and heat-treated at 1000°C with a temperature gradient in a tube furnace. After the heat treatment, the compositional distribution of the glass sample was measured by Raman spectroscopy. The Soret coefficients of the alkali oxides Li2O, Na2O, and K2O increased with the atomic numbers of the alkali metal ions. This indicates that alkali oxides more easily have high concentration in cold regions as the atomic numbers of the alkali metal ions in the alkali oxides increase. This result provides new information about the diffusion properties in glass melts.

Key-words : Soret effect, Glass melts, Borate glass

1. Introduction

In 1879, Soret observed that the concentration of salts in a salt solution increases at the cold end of a temperature gradient.1) Generally, temperature gradient-driven diffusion in liquid is called the Soret effect. The mechanism of the Soret effect is still controversial and it is an area of interest in non-equilibrium thermodynamics.2) In the last three decades, the Soret effect in silicate melts has also been investigated in the field of earth science3) using multicomponent silicate melts that contain more than two oxides. It was revealed that the heavier isotopes migrated more easily to the cold end of the gradient than the lighter isotopes.4–7)

Reuther et al. investigated the Soret effect in glass below the glass transition temperature.8,9) Studies have also been conducted in glass melts. The migration directions of glass components in binary-component glass melts were investigated by using a femtosecond laser to create a steep temperature gradient inside the glass. In CaO–SiO2 glass, the concentration of CaO was higher on the colder side;10) in Na2O–SiO2 glass, the concentration of Na2O was higher on the colder side;11) in Na2O–B2O3 glass, the concentration of Na2O was higher on the colder side;12) and in Na2O–GeO2 glass, the concentration of Na2O was higher on the colder side.13) However, this method does not provide the temperature distribution because the heated region is too small (<100 μm). To calculate the Soret coefficient, the temperature and concentration distributions are required. Therefore, although the migration direction (to the hot or cold side) can be determined by the laser irradiation method, we cannot calculate the Soret coefficient and compare the migration behavior and mechanism of glasses quantitatively. To our knowledge, the Soret coefficients in binary glass melts have not been measured.

The Soret effect in glass melts is important for the glass industry because homogeneous glasses are crucial for optical devices and thermally stable glass. In industrial glass-melting tanks14) and laboratory glass-melting crucible, temperature gradients would induce the Soret effect. Furthermore, laser irradiation during laser welding15) and cutting16) of glasses would also induce the Soret effect because the small focal spot produces a steep temperature gradient. Measuring Soret coefficients will enable us to discuss and predict damage, such as stress and inhomogeneity, caused by laser irradiation.

In this paper, we measure the Soret coefficients of alkali oxides in alkali borate glass and discuss the main parameters that contribute to the Soret coefficient of alkali oxides.

2. Experiment

Alkali borate glasses, 15(mol %)Li2O–85B2O3, 15Na2O–85B2O3, and 15K2O–85B2O3, were prepared by the conventional melt quenching method. The glasses were sealed in platinum capsules because the alkali oxides are easily volatilized. Figure 1(a) shows sizes of the platinum capsule and the glass inside the capsule. The procedure to make the capsule is described below. One end of a platinum pipe was welded. The glass sample was ground into powder. This powder was put into the pipe, and melted at 1300°C. The other end of the pipe was welded.

The platinum capsule containing the glass was put in a tube furnace. Figure 1(b) shows a schematic of the inside of the furnace. The temperature is highest in the center of the furnace. We measured the temperature distribution by Method A with a movable thermocouple. Figure 1(c) shows the typical temperature distribution measured in the furnace tube. In Method A, we measured the temperature of the air around the platinum capsule. Otherwise, the temperature on the edges of the platinum capsule was measured by Method B. The temperature measured at the cold end of the platinum capsule by Method B was higher than that measured by Method A owing to the high thermal conductivity of platinum.17) We define the temperature-gradient correlation factor, $\alpha = 0.48$, as the ratio of the temperature gradients obtained with Methods A and B. As shown in Table 1, the platinum capsule was heat-treated for 90 or 135 h in the various temperature ranges. The heat treatment temperature was above the liquidus temperature for this composition and components.18) By calculating with vapor pressure,19) we confirmed that the effect of volatilization of the glass component to the air on concentration...
distribution is negligible. After the heat treatment, the platinum capsule was quickly removed from the furnace tube and quenched in air.

The platinum capsule was cut at 5 mm intervals and polished, and the concentration of the heat-treated glass was measured at each position by confocal Raman spectroscopy (LabRAM HR Evolution, Horiba). Figure 1(d) shows the measured data and fitted curve. The peak around 776 cm\(^{-1}\) was assigned to the symmetric breathing vibration of six-membered rings with one BO\(_4\) tetrahedron.\(^{20}\) The peak around 806 cm\(^{-1}\) was assigned to the symmetric breathing vibration of boroxol rings.\(^{20}\) The peak area ratio of the two peaks depended on the mole ratio of the alkali oxide in the alkali borate glasses and was determined by fitting with pseudo-Voigt functions and a line. As shown in inset of Fig. 1(d), we prepared the standard curve by measuring glass samples with known compositions, and we determined the composition at each position in the heat-treated glass samples with the standard curve. In this paper, we assume that water dissolved in glass and fictive temperature will not affect the ratio of the peak area.

3. Results and discussion

After heat treatment, the glasses were transparent. Figure 2 shows an example of the mole fraction measured after the heat treatment plotted against heat treatment temperature. We assumed that the ions did not migrate during sample cooling. Li\(_2\)O had higher concentration in the hot region, while Na\(_2\)O and K\(_2\)O had higher concentration in the cold region after the heat treatment. The composition gradient of K\(_2\)O is steeper compared with that of Na\(_2\)O. To quantify this behavior, we calculated the Soret coefficient, \(\sigma_{\text{soret}}\), with\(^{21}\)

\[
\sigma_{\text{soret}} = -\frac{1}{\alpha n(1 - n)} \frac{dn}{dT},
\]

where \(n\) is the mole fraction of component \(M_2O\) (\(M = \text{Li, Na, or K}\)), \(T\) is the temperature, and \(\alpha\) is the temperature correlation factor described in the experimental session. This is the modified version of the equation for a binary non-electrolyte system.\(^{21}\) The difference between our equation and that in Ref. 21 is that our equation includes the temperature correlation factor, \(\alpha\). The value of \(dn/dT\) in the Eq. (1) should be affected by many factors, such as weight, size, and bond strength, of the diffusing species. The Soret coefficients of 15Li\(_2\)O–85B\(_2\)O\(_3\), 15Na\(_2\)O–85B\(_2\)O\(_3\), and 15K\(_2\)O–85B\(_2\)O\(_3\) in Fig. 2 were \(-6.28 \times 10^{-5}\), \(4.47 \times 10^{-5}\), and \(18.3 \times 10^{-5}\) K\(^{-1}\), respectively. The positive value of the Soret coefficient indicates that the alkali oxides have higher concentration in the cold region compared that in the hot region. The Soret coefficients and experimental conditions in this study are summarized in Table 1. The Soret coefficients obtained after 90 h heat treatment sample had the same order of magnitude as those...
The experimental results in this paper also can be explained from this point of view since the single bond strengths between alkali metal ions and oxide ion in Li2O, Na2O, and K2O are 151, 84, and 54 kJ/mol, respectively. Further research should be done to elucidate factors controlling the Soret effect in glass melts.

4. Conclusion

We conclude that the Soret coefficients of alkali oxides Li2O, Na2O, and K2O in alkali borate glasses increase with the atomic numbers of alkali metal ions. The higher concentration of Na2O in the cold region in sodium borate glass melts is consistent with previous femtosecond laser results. These findings will contribute to elucidating the Soret effect in glass melts.

Acknowledgment

This work was financially supported by the Nippon Sheet Glass Foundation for Materials Science and Engineering, and the Shimadzu Science Foundation. We thank K. Tanaka in Kyoto University for valuable suggestions.

References

1) C. Soret, *Arch. Phys. Nat.*, 2, 48–61 (1879).
2) M. Eslamian and M. Z. Saghir, *J. Non-Equilib. Thermodyn.*, 34, 97–131 (2009).
3) D. Walker and S. E. DeLong, *Contrib. Mineral. Petrol.*, 79, 231–240 (1982).
4) C. E. Lesher and D. Walker, *Geochim. Cosmochim. Acta*, 50, 1397–1411 (1986).
5) 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).
6) G. Dominguez, G. Wilkins and M. H. Thiennens, *Nature*, 473, 70–73 (2011).
7) D. J. Laacks, G. Goel, J. C. Bopp, J. A. V. Orman, C. E. Lesher and C. C. Lundstrom, *Phys. Rev. Lett.*, 108, 065901 (2012).
8) H. Reuther and W. Hinz, *Phys. Stat. Sol.*, 59, K87–K89 (1980).
9) H. Reuther and W. Hinz, *Phys. Stat. Sol.*, 83, 173–178 (1984).
10) M. Shimizu, M. Sakakura, S. Kanchira, M. Nishi, Y. Shimotsuma, K. Hirao and K. Miura, *Opt. Lett.*, 36, 2161–2163 (2010).
11) M. Shimizu, K. Miura, M. Sakakura, M. Nishi, Y. Shimotsuma, S. Kanchira, T. Nakaya and K. Hirao, *Appl. Phys. A Mater. Sci. Process.*, 100, 1001–1005 (2010).
12) Y. Liu, B. Zhu, L. Wang, J. Qiu, Y. Dai and H. Ma, *Appl. Phys. Lett.*, 92, 121113 (2008).
13) X. Wang, M. Sakakura, Y. Liu, J. Qiu, Y. Shimotsuma, K. Hirao and K. Miura, *Chem. Phys. Lett.*, 511, 266–269 (2011).
14) H. Mase and K. Oda, *J. Non-Cryst. Sol.*, 388, 807–812 (1980).
15) I. Miyamoto, K. Cvecek and M. Schmidt, *Opt. Express*, 21, 14291–14302 (2013).
16) K. Kim, J. Kim, D. Farson, H. W. Choi and K. Kim, *Jpn. J. Appl. Phys.*, 47, 6978–6981 (2008).
17) R. W. Powell and R. P. Tye, *Br. J. Appl. Phys.*, 14, 662–666 (1963).
18) E. M. Levin, C. R. Robbins and H. F. McMurdie, “Phase Diagrams for Ceramists”, The American Ceramic Society, Columbus (1964) pp. 87–93.
19) S. S. Cole and N. W. Taylor, *J. Am. Ceram. Soc.*, 59, 82–85 (1935).
20) B. N. Meera and J. Ramakrishna, *J. Non-Cryst. Solids*, 159, 1–21 (1993).
21) P. Artola and B. Rousseau, *J. Chem. Phys.*, 143, 174503 (2015).
22) K. H. Sun, *J. Am. Ceram. Soc.*, 30, 277–281 (1947).