Japan Geoscience Union Meeting 2014
(28 April - 02 May 2014 at Pacifico YOKOHAMA, Kanagawa, Japan)

SMP47-22 Room:422 Time:May 1 16:30-16:45

Temperature-dependent thermal expansivities of aluminum-free silicate melts and borosilicate melts

SUGAWARA, Toru[1*] ; KATSUKI, Junki[2] ; YOSHIDA, Satoshi[2] ; MATSUOKA, Jun[2] ; MINAMI, Kazuhiro[3] ; OCHI, Eiji[3]

[1]Akita University, [2]The University of Shiga Prefecture, [3]Japan Nuclear Fuel Limited

Thermal expansivities (dV/dT) of silicate melts are essential in a thermodynamic calculation of phase equilibira in magmatic system as a function of pressure and temperature and in a numerical simulation of flow and thermal structures in glass melting furnace. Previous studies have been suggested that the dV/dT of alumino-silicate melts (Lange, 1996; Potuzak et al., 2006) and magmatic silicate melts (Lange, 1997; Ghiorso and Kress, 2004) is a function of composition, but independent of temperature. On the other hand, it has been reported that the dV/dT of SiO_2-TiO_2-Na_2O melt (Liu and Lange, 2001) and 50SiO_2-25CaO-25MgO melt (Gottsmann and Dingwell, 2000) decrease with increasing temperature. Recently, we found that simulated-radioactive waste glass melt which has sodium-borosilicate composition also shows negative temperature-dependent dV/dT (Sugawara et al., 2013). We carried out density measurements for sodium-silicate melts ((100-x)SiO2-xNa2O, x=23 or 32.3 mol%), commercial soda-lime silicate melt (71SiO_2-6MgO-9CaO-14Na_2O, mol%) and borosilicate melts (66.6SiO_2-yB_2O_3-(33.33-y)Na_2O where y=8.3, 16.6, 25; 66.6SiO_2-(12.5+z)B_2O_3-(4.2-z)Al_2O_3-zCaO-(16.7-z)Na_2O where z=0 or 4.2 mol%). The temperature and compositional dependences of the dV/dT are discussed based on the new density data and the literature data.

The high-temperature density (dHT) measurement has been made by double-bob Archimedean method between 1173K and 1665K. The glass samples were annealed around glass transition temperature (Tg) for 6-396 hours and quenched. Then the density of annealed glasses at 298K (d298) and linear thermal expansivity (dL/L) were determined by Archimedean method and TMA. respectively. The densities of supercooled melt around Tg (dTg) were calculated from the d298 and the dL/L of glasses. Then, molar volume as a function of temperature and the dV/dT of melts were obtained by combining the dTg and the dHT.

The dV/dT values of all samples examined in this study show negative temperature dependence. In the sodium silicate melts, the temperature dependence of the dV/dT is remarkable when the SiO2 content increases from 50 to 67 mol%, while the dV/dT becomes close to zero as further increase in the SiO2 content. The negative temperature-dependent dV/dT observed in the 71SiO_2-6MgO-9CaO-14Na_2O melt can be reproduced by an additive sum of the dV/dT of 67.8SiO_2-32.2Na_2O, diopside (Gottsmann and Dingwell, 2000) and wollastonite (Potuzak et al., 2006) melts. High-temperature Raman spectroscopy for the SiO_2-Na_2O and SiO_2-Na_2O-MgO melts has been indicated that amount of Q4 species increases with increasing temperature and SiO_2 and MgO contents (Maehara et al., 2004, 2005). Therefore, the temperature dependent dV/dT for the sodium-silicate, commercial soda-lime silicate and diopside melts can be rationalized by an increase of rigid Q4 species at high temperature. The temperature dependence of the dV/dT is most remarkable in the 66.6SiO_2-8.3B_2O_3-25Na_2O melt among the borosilicate melts. The dV/dT decreases with replacement of Na_2O by B_2O_3 or CaO and of B_2O_3 by Al_2O_3, suggesting that partial molar dV/dT of B_2O_3 depends on temperature-induced coordination change of boron and their composition dependence (Wu and Stebbins, 2010).

Acknowledgements: This work was a part of the research supported by Japan Nuclear Fuel Limited with Grant-in-Aid by the Ministry of Economy, Trade and Industry.

Keywords: silicate melt, thermal expansivity, densitometry