Structural role of aluminum cation in alkaline-earth aluminosilicate glasses

Sohei Sukenaga*†[1], Koji Kanehashi[2], Kyung-Ho Kim[1], Hiroki Yamada[3], Toru Wakihara[3], Koji Ohara[4], Koji Inoue[5], Yasuyoshi Nagai[5], and Hiroyuki Shibata[1]

[1]Institute of Multidisciplinary Research for Advanced Materials (IMRAM), Tohoku University [Sendai] – 2-1-1 Katahira, Aoba-ku, Sendai, 980-8577 Japan, Japan

[2]Nippon Steel and Sumitomo Metal Corporation (NSSMC) – 20-1 Shintomi, Futtsu, 293-8511, Japan, Japan

[3]Department of Chemical System Engineering, The University of Tokyo – 7 Chome-3-1 Hongo, Bunkyo, Tokyo 113-8654, Japon, Japan

[4]Research and Utilization Division, Japan Synchrotron Radiation Research Institute (JASRI, SPring-8) – 1-1-1 Kouto, Sayo-cho, Sayo-gun, Hyogo 679-5198, Japan

[5]Institute for Materials Research (IMR), Tohoku University – 2145-2, Narita-cho, Oarai-machi, Higashiibaraki-gun, Ibaraki, Japan

Abstract

One of the most important goal of physical chemistry for molten materials (and their glasses) are to deeply understand how each components are mixed together in their non-crystalline structure, impacting on physical and chemical properties of the disordered materials. Alumina is a common component of silicate melts and glasses, which are important system for earth-science and high-temperature-industries (e.g. metallurgy, glass making). Therefore, the detailed chemical state, i.e. short-range structure, in the neighborhood of aluminum cations in silicate glasses has been studied for a long time. It is well known that the coordination number of aluminum cations varies from 4 to 6 in the melts and glasses where the structural role of 5- and 6-coordinated aluminum cations are still not sufficiently understood while the 4-coordinated aluminum cations acts as a network former. In the present study, the kinds of non-framework cations in aluminosilicate glasses are changed from calcium (Ca) to magnesium (Mg), giving a variation in coordination number of aluminum cations; aluminum-27 magic angle spinning nuclear magnetic resonance (MAS NMR) spectra shows that 5-coordinated aluminum cations ([5]Al) increase with replacing Ca by Mg cations in (30-x)CaO-xMgO-15Al2O3-55SiO2 glasses (x = 0, 7.5, 15, 22.5 or 30 mol%). Silicon-29 MAS NMR spectra of these glasses shows that the amount of non-bridging oxygens decreased with increasing the Mg/Ca ratio, indicating non-framework cations are consumed in-part to compensate the negative charge of oxygen between 4-coordinated silicon ([4]Si) and [5]Al cations ([4]Si-O-[5]Al), which has a larger negative charge than that of [4]Si-O-[4]Al. These phenomena indicated that [5]Al cations should behave as a network former. It is also found that the atomic packing density, which is derived from the density of the glasses, increases with increasing the amount of [5]Al cations. These structural change by increasing [5]Al will impact the thermal conductivity of these glasses.

*Speaker

†Corresponding author: sohei.sukenaga.d3@tohoku.ac.jp

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