Structural Evolution of Li Environments in Mixed-Cation Silicate Glasses under Crystallization by Solid-State NMR Spectroscopy

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Lithium is among the critical elements with strong applications in the energy-storing materials industry where a crucial demand for an enhanced and efficient transport of Li in non-crystalline oxides has recently been proposed. In particular, exploring the distribution and mobility of Li in silicate glasses is fundamental to elucidating crystallization kinetics and thermodynamic properties in Li-bearing silicate materials. Solid-state nuclear magnetic resonance (NMR) spectroscopy provides quantitative and bulk-sensitive insights into the local atomic environments around specific nuclei in amorphous materials. Previous studies have revealed the exceptional mobility of Li in silicate glasses under various compositional and pressure conditions by solid-state NMR spectroscopy[1,2)]. Nevertheless, systematic investigations into the composition-dependent mobility of Li and the structural evolution of Li environments during crystallization remain limited.

In this study, we explored the local environments of Li in silicate glasses and crystallized glasses using ^{6}Li MAS NMR spectroscopy. Li-bearing silicate samples were prepared by quenching from ternary Li-alkali or alkaline-earth mixed silicate melts, with variations in cation compositions. The significantly longer spin-lattice relaxation times of crystalline phases, compared to amorphous phases, enabled the resolution of phases[3)] and quantification of crystallinity based on signal ratios. Crystalline fractions were modeled as a simple function for describing crystallization kinetics[4)]. The ^{6}Li MAS NMR results also revealed that both the peak position and line shape of the Li signals varied depending on the glass composition, particularly the type of network modifiers. Glasses containing smaller ionic radius differences relative to Li exhibited enhanced random cation mixing in glass structure, leading to an increase in cation mobility, consistent with previous studies on nature of cation mixing and ordering. These findings highlight the significant impact of compositional tuning on Li mobility and local structure in silicate glasses, contributing to the structural behavior of Li-bearing amorphous materials and their advanced functionality[5)].

1) S.Y. Park and S. K. Lee, *J. Am. Ceram. Soc.* **99**, 3948 (2016).
2) E. J. Kim, Y. H. Kim, and S. K. Lee, *J. Phys. Chem. C.* **123**, 26608 (2019)
3) S. K. Lee et al., *Nat. Geosci.* **10**, 436 (2017)
4) S. B. Ryu and S. K. Lee, *J. Phys. Chem. Lett.* **9**, 150 (2018)
5) See https://g2mat.snu.ac.kr/ for further details.