Structural investigation of Mg local environments in silicate glasses by ultra-high field $^{25}$Mg 3QMAS NMR spectroscopy

KEIJI SHIMODA,1,* YASUHIRO TOBU,1 MORIAKI HATAKEYAMA,1 TAKAHIRO NEMOTO,2 AND KOJI SAITO1

1Advanced Technology Research Laboratories, Nippon Steel Corporation, 20-1 Shintomi, Futtsu, Chiba 293-8511, Japan
2JEOL Ltd., 3-1-2 Musashino, Akishima, Tokyo 196-8558, Japan

ABSTRACT

Structural information on divalent cations such as Mg$^{2+}$ should have important implications for magmatic liquids because of their abundance in the Earth’s interior; nevertheless, little is confirmed about their coordination environments. We here apply a $^{25}$Mg triple-quantum magic-angle spinning (3QMAS) NMR technique at an ultra-high magnetic field (21.8 T) and successfully show the occurrence of multiple Mg sites in MgSiO$_3$ glass. We find that these sites are distinguished by the degree of polyhedral distortion, not by the coordination number. The present study concludes that the highly distorted MgO$_6$ species occur in MgSiO$_3$ glass, in strong contrast with a recent radial distribution study.

Keywords: Mg local environment, MgSiO$_3$ glass, $^{25}$Mg 3QMAS NMR, ultra-high magnetic field

INTRODUCTION

Alkali and alkaline earth cations act as network modifiers in silicate melts and glasses. Most studies on their structures have focused on SiO$_4$ and AlO$_4$ tetrahedral networks, whereas the lack of local information about the monovalent or divalent cations has been a long-standing problem in understanding the complete picture of amorphous structures. Some researchers have examined the local environments of the Mg$^{2+}$ ion in MgSiO$_3$ and CaMgSi$_2$O$_6$ glasses, which are still controversial issues. The coordination number, one of the most important factors affecting dynamic properties, of Mg in such glasses was concluded as fourfold coordination in some studies (Tabira 1996; Wilding et al. 2004) and fivefold (Ildefonse et al. 1995; Li et al. 1999) or sixfold in others (Kroeker and Stebbins 2000).

NMR spectroscopy is a robust tool for collecting structural information focused on a specific element in multi-component systems. Unfortunately, $^{25}$Mg NMR has been difficult to apply because of its low resonance frequency (18.4 MHz at 7.0 T) and relatively low natural abundance (10.1%). Using a high magnetic field and $^{25}$Mg isotopic enrichment drastically alleviates these shortcomings. Nevertheless, $^{25}$Mg MAS NMR further suffers from the large second-order quadrupolar broadening. To overcome this, we here applied the $^{25}$Mg 3QMAS technique to Mg-containing silicate glasses and clarified the detailed environments surrounding the Mg$^{2+}$ ions in these glasses.

EXPERIMENTAL PROCEDURE

A series of $^{25}$Mg-enriched glass samples (MgSiO$_3$, CaMgSi$_2$O$_6$, Ca$_2$MgSi$_2$O$_7$, Mg$_3$Al$_2$Si$_3$O$_12$, Na$_2$MgSi$_2$O$_6$, and K$_2$MgSi$_2$O$_6$ glasses) and diopside (CaMgSi$_2$O$_6$) and åkermanite (Ca$_2$Mg$_5$Si$_7$O$_{24}$) crystals were prepared from appropriate mixtures of 99%-enriched $^{25}$MgO, Ca(OH)$_2$, K$_2$CO$_3$, Al$_2$O$_3$, and SiO$_2$ reagents. The MgSiO$_3$, CaMgSi$_2$O$_6$, Ca$_2$MgSi$_2$O$_7$, and Mg$_3$Al$_2$Si$_3$O$_12$ glasses were obtained by melting the powder mixtures at 1500–1700 °C and quenching in air or water, but Na$_2$MgSi$_2$O$_6$ and K$_2$MgSi$_2$O$_6$ glass was melted at 1300 °C. XRD indicated that they were amorphous. Diopside and åkermanite were prepared by melting at 1500 °C and subsequent annealing at 1000 °C for 6 hours.

The $^{25}$Mg NMR measurements were conducted on a JNM-ECA930 spectrometer (21.8 T) at the National Institute for Materials Science. The working frequency was 56.9 MHz. The 90° pulse lengths were optimized to 1.6–1.8 μs for the glasses. Spin-lattice relation times $T_1$ were estimated to be less than 0.5 s by the saturation recovery method. All the MAS spectra were acquired with a spin-echo sequence (a pulse length of 1.8 and 3.6 μs) to avoid acoustic ringing, and a recycle delay of 0.5 s. Longer delays did not influence the peak shape.

The $^{25}$Mg 3QMAS spectra were acquired with a z-filter sequence and a delay of 0.5 s. Triple-quantum excitation and subsequent conversion pulses were optimized to 6.0 and 2.5 μs, respectively. Samples set in 4 mm MAS rotors were rotated at a spinning rate of 18 kHz. Chemical shifts were externally referenced to MgSO$_4$ solution at 0.0 ppm.

RESULTS AND DISCUSSION

Figure 1 shows the MAS spectra for Mg-containing silicate glasses. There are apparent differences between MgSiO$_3$, CaMgSi$_2$O$_6$, Ca$_2$MgSi$_2$O$_7$, Mg$_3$Al$_2$Si$_3$O$_12$ glasses (Figs. 1a–1d) and akermanite (Ca$_2$Mg$_5$Si$_7$O$_{24}$) crystals. The isotropic chemical shift (δ), asymmetry parameter (η), and quadrupolar product $P_Q$ were derived from the sheared two-dimensional spectra with the following equations (Amoureux et al. 2002):

\[
\delta = \frac{17}{27} \delta_1 - \frac{10}{27} \delta_2
\]

\[
P_Q = \frac{\sqrt{70 \{4(25-1)^2 \}}}{\sqrt{67 \{4(25-1)^2 \}}}(\delta_1 - \delta_2) \cdot \nu_s \cdot 10^{-3},
\]

where $\delta_1$ and $\delta_2$ are the chemical shifts in F1 and F2 dimensions, $\nu_s$ is the Zeeman frequency, and S is the spin number. The $P_Q$ is also related to the quadrupolar coupling constant $C_Q$, with the equation of $P_Q = C_Q \sqrt{1 + \eta^2}/3$, where $\eta$ is the asymmetry parameter ($\eta = 0$ to 1).

A series of FID signals in the 3QMAS measurements were Fourier-transformed and sheared to obtain the separate isotropic (F1) and anisotropic (F2) dimensions.