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Detection of “free” oxide ions in low-silica Ca/Mg silicate glasses: Results from $^{17}O \rightarrow ^{29}Si$ HETCOR NMR

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ABSTRACT

Silicon and oxygen are the two most abundant elements in most technological and geological glasses and glass-forming liquids, and extensive studies of the structures of these materials have been made using ^{29}Si and ^{17}O high-resolution solid-state NMR. Double resonance NMR experiments hold great potential for revealing new details about the network structures of such important materials but have not yet been done for this particular pair of spins because of several technical challenges. Using a crystalline model compound, Ca_3SiO_5 (calcium trisilicate or the ‘alite’ phase of Portland cement), which contains oxide ion sites bonded either to one Si^{4+} or only to Ca^{2+}, we demonstrate that the $^{17}O \rightarrow ^{29}Si$ Cross-Polarization Heteronuclear Correlation (CP-HETCOR) experiment can clearly distinguish between these two types of oxygen sites. The latter species, so-called ‘free’ oxide ions that are bonded to no network cations such as Si^{4+}, play an important role in models of glass and melt structure but have been difficult to directly detect in many systems. In two Ca/Mg silicate glasses near to the orthosilicate composition ($O/Si \geq 4$), the HETCOR experiment clearly shows the presence of such ‘free’ oxide ions, whose 1D ^{17}O NMR signals are actually completely hidden under those for the predominant non-bridging oxygens. Their observed chemical shifts suggest coordination by predominantly Mg^{2+} cations, an ordering that may be expected from the smaller size and stronger bonding interactions of this cation relative to those of Ca^{2+}. The estimated abundances of ‘free’ oxide ions in these glasses are consistent with previous, indirect estimates based on analyses of 1D ^{29}Si NMR spectra.

1. Introduction

High-resolution solid-state NMR has become a method of choice for quantifying many aspects of the short- to intermediate-range structures of oxide and silicate glasses. One-dimensional (1D) and two-dimensional (2D) experiments of single nuclides, for example ^{11}B, ^{17}O, ^{23}Na, ^{27}Al, ^{29}Si, and ^{31}P, show strong correlations between chemical shifts and parameters such as coordination number, identity and numbers of cation and anion neighbors, bond distance and bond length [1–5]. Double resonance NMR experiments, in which the signal from an observed nuclear spin system is perturbed by or coupled to a second nuclear spin system, have revealed important and unique information on connectivities among various network cations, and have been used to enhance and make more accurate structural assignments in spectra that can be severely overlapped. Most commonly, these have involved pairs of abundant nuclides with relatively high gyromagnetic ratios γ (e.g. ^{1}H, ^{11}B, ^{19}F, ^{27}Al, ^{31}P) that give rise to strong inter-nuclear dipolar couplings and thus better encode distance information [6,7]. Some double resonance experiments that can be especially revealing about correlations among structural groups for two different nuclides, notably Cross-Polarization Heteronuclear Correlation (CP-HETCOR and related experiments), can be difficult when one or both nuclides have spin $I > 1/2$, but have been developed and tested in both crystalline and glassy oxide materials [8–15].

With careful experimental setup, testing, and calibration of experimental conditions, unique and useful results have been obtained in glasses, for example for the ^{11}B-^{27}Al pair in aluminoborates [16]; ^{11}B-^{29}Si in borosilicates [17], ^{27}Al-^{1}H in hydrous, high pressure aluminosilicates [18] and ^{19}F-^{27}Al in fluorides [19]. In a few cases, new information on glass structure has been revealed through dipolar coupling (and ‘recoupling’) experiments involving ^{17}O as the observe nuclide and the couplings to relatively high γ nuclides such as ^{27}Al [14,20], ^{11}B [21] and ^{31}P [22]. Such experiments are challenging, because of the relatively low γ of ^{17}O, leading to relatively weak dipolar coupling, and the common requirement of isotopic enrichment far above its natural abundance of 0.035%.

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In spite of this progress, double resonance NMR experiments involving the two most common components of both naturally occurring and technologically important oxide glasses, (oxygen and silicon), have not yet been reported. ^{29}Si-^{17}O double resonance experiments are challenging in several aspects. ^{29}Si also has a low natural abundance of 4.7%, and the gyromagnetic ratios of both nuclides are relatively low compared to other commonly studied spin pairs such as ^{31}P-^{27}Al. ^{29}Si has spin $I = ½$, which contributes to its often very slow spin-lattice relaxation, making signal averaging time consuming. In addition to its very low natural abundance, ^{17}O ($I = 5/2$) has a quadrupolar moment, which causes line broadening and complicates experiments. Nonetheless, there are important and unresolved questions of silicate glass structure that would benefit greatly from the detailed information on cation-anion proximities that could come from the appropriate ^{29}Si-^{17}O double resonance experiment.

The example that we choose to test this approach is one that has been the subject of considerable controversy recently in the glass science and geoscience literature, namely the abundance and significance of so-called 'free' oxide ions, which denotes O^{2-} ions not bonded to any of the typical 'network-forming' cations Si^{4+}, B^{3+}, Al^{3+}, Ge^{4+}, or P^{5+} that make up the strongly bonded network of common oxide glasses. The usual starting point for this question is the reaction of 'bridging' oxygens (BO, 2 network cation neighbors) with an added metal oxide (FO, 'free' oxide ion) to form 'non-bridging' oxygens (NBO, exactly 1 network cation neighbor) that takes place upon the addition of the oxide of a low-charged metal cation to silica. For example, in a simple binary silicate:

$$\begin{aligned}&\mathrm{Si{-}O{-}Si} + \mathrm{O}^{2-} \Leftrightarrow 2\mathrm{Si{-}O}^{-}\\ &\text{or,}\\ &\mathrm{BO} + \mathrm{FO} \Leftrightarrow 2\mathrm{NBO}.\end{aligned} \tag{1}$$

Here, the 'network-modifying' cation is not shown explicitly, but serves to balance negative charges wherever they occur. In compositions with O/Si > 4, 'free' oxide ions must be present simply by stoichiometry, if, as is usually the case at low pressures, all Si^{4+} is four-coordinated. Liquids of such compositions are generally very difficult to quench to glasses because of high melting points and low viscosities, but in some cases such 'sub-orthosilicate' compositions can be made, as described previously for Ca/Mg silicate glasses [23] and studied here. In contrast, non-glass forming liquids of such low silica contents do have enormous technological importance as metallurgical slags, leading to a long history of experimental and theoretical studies of such reactions [24–26].

In higher silica compositions (O/Si < 4), 'free' oxide ion need not be present, and in common first approximations, Reaction (1) may be described as 'going to completion.' In simple thermodynamic terms, the extent of reaction can be described by an "apparent equilibrium constant" K_{app}, defined in terms of relative concentrations of oxygen species (square brackets) and thus ignoring activity coefficients:

$$K_{app} = [\mathrm{NBO}]^2/([\mathrm{BO}] \times [\mathrm{FO}]). \tag{2}$$

Going to completion' thus implies the approximation that $K_{app} \approx \infty$, which of course cannot be strictly correct. Recent indirect estimations of 'free' oxide concentrations in alkali silicate glasses, based on XPS data, have suggested values of K_{app} in the range of 12–14 or lower, but such results have been controversial and unconfirmed by direct ^{17}O NMR measurements [27–31]. There is better agreement that analyses of ^{29}Si NMR spectra of low-silica Ca/Mg and Mg silicate glasses may yield estimates of K_{app} of about 500 to 100 [23,32–35], probably decreasing considerably at temperatures well above the glass transition [33,36]. 'Free' oxide ions in large excess over the $K_{app} \approx \infty$ approximation have been unequivocally and directly detected by ^{17}O MAS NMR in PbO-SiO_2 melt-quenched glasses [37], and in Hf/ZrO_2-SiO_2 sputtered, glassy thin films [38].

The 'free' oxide ion in a silicate glass is an ideal example of a structural species to be investigated by double resonance NMR methods. In simple models ($K_{app} \approx \infty$) for glasses at or above the 'orthosilicate' composition (O/Si ≤ 4), all ^{17}O oxygen ions could be bonded to one or two Si cations (all BO and NBO, no FO) and would thus provide significant dipolar coupling to ^{29}Si. Conversely, the 'free' oxide itself, having no Si neighbors, would have little or no such coupling. We have thus used the question of 'free' oxide speciation to develop and test a novel application of the ^{17}O → ^{29}Si HETCOR experiment. We are able to confirm the presence of 'free' oxide ions and characterize their coordination environment in low-silica Ca/Mg silicate glasses with O/Si ≥ 4 as described recently in the literature [23], but conclude that the previous interpretation of their ^{17}O MAS NMR spectra needs to be re-assessed.

2. Experimental

2.1. Sample syntheses

Glass samples CMS33.3 and CMS28 were selected from those described in a previous study [23], which were made by melting mixtures of CaO, MgO, and 100% ^{17}O-enriched SiO_2, using an aerodynamic levitation system and CO_2 laser heating to rapidly quench melts of these extremely low silica contents. Compositions, as reported there from electron microprobe analyses, have mole % CaO, MgO, SiO_2 as 32.9, 33.5, 33.6 (CMS33.3) and 35.7, 36.5, 28.6 (CMS28) respectively.

Crystalline Ca_3SiO_5 (tricalcium silicate, the most common phase in Portland cement, also known as 'alite' and the rare naturally occurring mineral hatrurite) is an ideal test compound for the ^{17}O → ^{29}Si HETCOR NMR experiment because it contains abundant 'free' oxide ions as well as more common non-bridging oxygens [39]. An ^{17}O-enriched sample of Ca_3SiO_5 was therefore synthesized from CaO and 40% ^{17}O-enriched SiO_2 with methods similar to those described previously [40], except that approximately 0.2 wt.% CoO was added to enhance spin-lattice relaxation rates. After three cycles of heating at 1400 °C for 8 h in an Ar atmosphere and grinding, ^{29}Si and ^{17}O MAS NMR showed that minor proportions of incompletely reacted CaO and Ca_2SiO_4 remained, which do not affect the results described here.

2.2. NMR methods

For the glasses, one-dimensional MAS NMR spectra for ^{29}Si and ^{17}O, as well as 3QMAS ^{17}O NMR, collected at 11.7 T external magnetic field, and analyses of the data, were previously described in detail [23]. For the new sample of crystalline Ca_3SiO_5, preliminary ^{17}O and ^{29}Si MAS NMR spectra were collected with a Varian Inova 600 spectrometer (14.1 T field), with a 3.2 mm diameter "Pencil" zirconia rotor, spinning speed of 20 kHz, radiofrequency power of about 100 kHz, and 'solids' *rf* tip angle of about 30°. Relaxation behavior was characterized by collection of spectra with a wide range of pulse delays. These spectra, as well as those described below, are referenced to external tetramethylsilane (TMS, ^{29}Si) and 20% ^{17}O H_2O (^{17}O), both set to $\delta_{iso} = 0$ ppm (*Note of caution*: indirect ^{29}Si referencing by multiplying the ^{17}O frequency of H_2O with the frequency ratios of the corresponding reference compounds set out in the 2001 IUPAC recommendations [41], i.e., $\delta_{iso}(^{29}\mathrm{Si, TMS, Hz}) = \delta_{iso}(^{17}\mathrm{O, H_2O, Hz}) \times 19.867187 / 13.556457$ leads to a shift error of −3.8 ppm).

NMR experiments at 18.8 T were performed at the National High Magnetic Field Laboratory (NHMFL) using a Bruker Avance III HD 800 spectrometer and a 3.2 mm triple-resonance Low-*E* MAS probe built at NHMFL, operating at 159.0 and 108.5 MHz for ^{29}Si and ^{17}O, respectively. Low-*E* probes use separate orthogonal coils for high- and low-frequency irradiation [42,43]. They can outperform conventional NMR probes at higher magnetic fields such as 18.8 T because their low-frequency detection coil is not subject to limitations imposed by high-frequency tuning and also because separated RF circuits eliminate ^{1}H isolation traps and the low-frequency losses associated with such