Investigation of Free Oxide Ions in Glass by ^{17}O-^{29}Si CP/HETCOR NMR

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Introduction

Silicate glasses are of wide-ranging technological importance. Silica (SiO_2) is the archetypal glass former made up of a fully connected network of corner-sharing SiO_4 tetrahedra. Therefore, the oxygen atoms are two-coordinated in Si-O-Si linkages, designated as bridging oxygen (BO). Addition of network-modifying M (alkali or alkaline-earth) cations results in the depolymerization of the network with the formation of non-bridging oxygen (NBO), bonded to only one Si atom, forming Si-O-M linkages. A very different situation arises in silicate glasses with O/Si > 4 where "free" oxide ions (O^{2-} ions not bonded to any network-forming cations such as Si) are required by stoichiometry. This is the situation for "sub-orthosilicate" compositions with less than 33.3% SiO_2 in MO-SiO_2 or M_2O-SiO_2 binaries. Although glass formation in these systems becomes increasing difficult with decreasing SiO_2 concentration, it was demonstrated in a recent study that sub-orthosilicate glasses in the CaO-MgO-SiO_2 system can be synthesized using laser melting under container-less levitation and rapid melt quenching.[1] However, direct spectroscopic observation of the free oxide ion in these glasses has remained elusive. Here we report application of $^{29}Si/^{17}O$ CP/HETCOR NMR spectroscopy that may allow for observation of free oxide ions in silicate glasses.

Experimental

Two glasses with nominal compositions (1-***x***)(Ca,Mg)O-***x***SiO_2 with ***x*** = 0.33 and 0.28 were melted using CO_2 laser, under aerodynamic levitation and quenched by shutting down the laser.[1] NMR measurements were carried out at the NHMFL on a Bruker Avance III HD console equipped with a 18.8 T medium bore (63 mm) magnet. The CP/HETCOR NMR experiments were carried out using the multiple-pulse CP method[2] for polarization transfer.

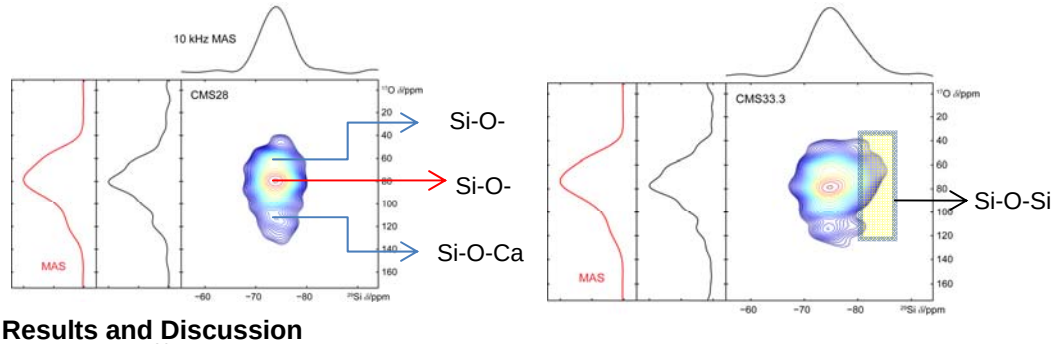

Fig.1. $^{29}Si/^{17}O$ CP/HETCOR NMR spectra of CMS28 (left) and CMS33.3 (right) glasses with projections along the ^{29}Si (horizontal) and ^{17}O (vertical) dimensions. ^{17}O MAS spectra (red lines) are shown for comparison. See text for details.

Results and Discussion

The ^{17}O-^{29}Si CP/HETCOR NMR spectra of the two CMS glasses are shown in Fig. 1 and compared with the regular MAS spectra for both nuclides. Both spectra clearly show good agreement between regular MAS and HETCOR for ^{17}O and the main signal corresponds to NBO atoms with equal number of Mg and Ca nearest neighbors at ^{17}O shift of ~ 80 ppm, with weaker signals corresponding to NBO bonded primarily to Mg (60 ppm) and to Ca (110 ppm) atoms. This result indicates a random distribution of Mg and Ca atoms in the glass structure. More interestingly, for the CMS33.3 glass, substantial signal in the shaded region (Fig. 1) corresponds to the presence of BO in the glass structure. For an orthosilicate glass this result, by itself, implies disproportionation according to $2Q^0 = 2Q^1 + O^{2-}$ and the formation of free oxide ion.[1] The ^{17}O NMR signal for the free oxide ion, being not bonded to any Si, should be absent from the HETCOR spectra while present in the regular MAS line shape. This hypothesis is currently being tested by performing this experiment on Ca_3SiO_5 crystal which is known to contain a significant fraction of free oxide ion with well-resolved ^{17}O chemical shift near 270 ppm.[3] Once this hypothesis is confirmed, careful subtraction of the ^{17}O HETCOR spectra from the regular ^{17}O MAS spectra will be carried out to quantitatively analyze the presence and relative fraction of free oxide ion in the CMS glasses.

Conclusions

The feasibility of the ^{17}O-^{29}Si CP/HETCOR NMR spectroscopy on ^{17}O-enrcihed silicate glasses with natural abundance ^{29}Si is demonstrated. Detailed quantitative characterization of the free oxide ion is currently underway.

Acknowledgements

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References

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