A ^{73}Ge MAS NMR STUDY OF THE GE ANOMALY IN OXIDE GLASSES: PRELIMINARY RESULTS

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Introduction

Germanium is an important network-forming cation in oxide glasses, however, its structural role is poorly understood even in relatively simple binary alkali germanate glasses. The "germanate anomaly" in alkali germanate glasses is a maximum or minimum in physical properties as a function of alkali content. Density measurements show an non-linear trend with increasing alkali content which is attributed to the conversion of 4-fold to 6-fold Ge up to the anomaly maximum. Beyond the maximum, the density behavior follows a decreasing trend which is attributed to the reconversion of 6-fold Ge back to 4-fold Ge. However, numerous spectroscopic techniques have failed to provide sufficient evidence of such a structural change and the structural nature of this anomaly remains highly controversial to date. ^{73}Ge NMR spectroscopy would be an ideal tool to address this structural issue. We have recently attempted to perform systematic ^{73}Ge MAS NMR spectroscopy for the very first time on germanate crystals and glasses at the NHMFL.

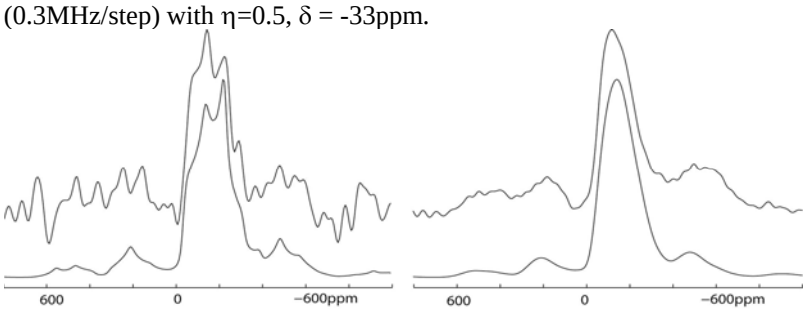
Experimental

All germanate crystals and glasses were prepared according to the previously published procedures in the literature [1].
The ^{73}Ge MAS NMR experiments were performed using the 830 MHz magnet (Larmor frequency for ^{73}Ge: 29 MHz) with a quad echo pulse sequence and a solids MAS probe.

Results and Discussion

Our preliminary results indicate that chemical shifts and quadrupolar parameters can be successfully obtained for the pure quartz-GeO_2 crystal and glass where all Ge atoms are 4-coordinated to oxygen forming corner-shared GeO_4 tetrahedra (Fig. 1) at a relatively moderate spinning speed of 10 kHz. However, sufficient spectral resolution couldn't be obtained for crystalline phases where Ge is 6-coordinated to oxygen (rutile-GeO_2 and $K_2Ge_8O_{17}$) as well as for the sodium germanate glasses. Strongly overlapping spinning sidebands persist in these spectra even when the spinning speed was increased to 33 kHz. These results indicate a large chemical shift anisotropy associated with the 6-coodinated (octahedral) Ge sites, at least in the crystal phases whereas a distribution of quadrupolar coupling constants may also contribute in the case of sodium germanate glasses. We plan to carry out QPASS experiments next on these samples to suppress spinning sidebands and to obtain the chemical shift scale for ^{73}Ge as well as quadrupolar parameters for octahedrally coordinated Ge in oxides.

Fig. 1. Experimental (top) and simulated (bottom) ^{73}Ge MAS NMR spectra of the quartz-GeO_2 crystal (left) and GeO_2 glass with Ge in tetrahedral sites. The CSA was set to zero for these simulations. Simulations include spinning sidebands. The NMR parameters for the crystal: Cq=9.3MHz, η=0.5, δ = -13ppm and for the glass: spectra were added with Cq=6.9 to 10.2MHz (0.3MHz/step) with η=0.5, δ = -33ppm.



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References

[1] Wang, H.M., *et al*., Chemical Geology, **213**, 17-30 (2004).