

Germanium-73 NMR of germanate glasses

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Germanium oxide materials play key roles in a variety of advanced technologies. The detailed structure of amorphous germanates, however, remains poorly understood. The use of NMR in this capacity has been hampered by the unfavourable NMR properties of ^{73}Ge . High field makes a decisive difference, enabling structurally informative ^{73}Ge NMR spectra to be acquired and interpreted. We have applied these methods to a series of crystalline germanates to determine the dependence of measurable NMR parameters on structure. Figure 1 illustrates the ^{73}Ge NMR spectrum of Ca_2GeO_4 and its associated fit, to yield parameters characteristic of four-coordinate germanium. Along with high-level theoretical calculations, we have found that the quadrupolar coupling constant can be measured with high accuracy, and is related to the local structural environment. While this relationship is not simple, it appears to be sufficiently robust to provide a means to detect tell-tale features in alkali germanate glasses, and thereby adjudicate amongst conflicting models of glass structure. More specifically, ^{73}Ge NMR spectra of alkali glasses show evidence of a substantial fraction of five- and/or six-coordinate germanium in addition to the expected four-coordinate germanium (Figure 2), supporting the traditional explanation for composition-dependent density and refractive index changes. Preliminary results have been published in *Chemical Communications* [1].

[1] V.K. Michaelis, P.M. Aguiar, V.V. Terskikh and Scott Kroeker, "Germanium-73 NMR of Amorphous and Crystalline GeO_2 ," *Chemical Communications* (2009) 4660-4662. (Cover Article)

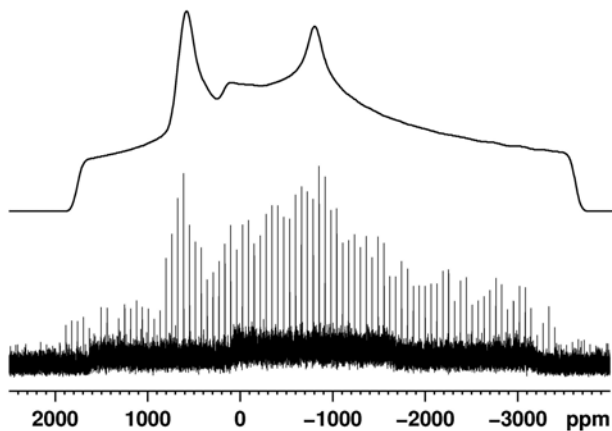
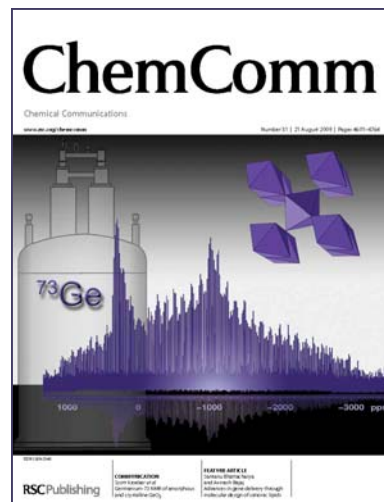


Figure 1: ^{73}Ge QCPMG NMR spectrum of Ca_2GeO_4 , along with spectral simulation.



This research was featured on the cover of *Chemical Communications*

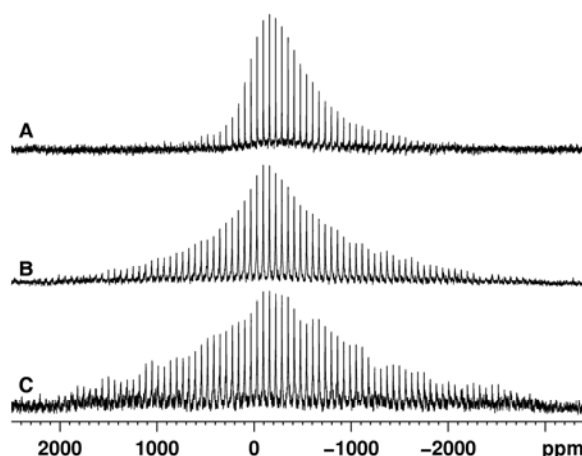


Figure 2: ^{73}Ge QCPMG NMR spectra of germanate glasses: (A) GeO_2 , (B) 9 mol% Li_2O , (C) 14 mol% Na_2O .