Observation of a Continuous Random Network Structure in Ge_xSe_{100-x} Glasses: Results from High-Resolution ^{77}Se MATPASS/CPMG NMR Spectroscopy

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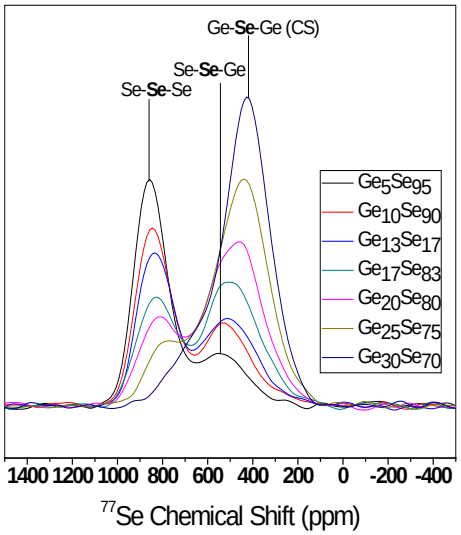
Introduction

The short and intermediate range structure of the Ge_xSe_{1-x} chalcogenide glass system has recently been the subject of much debate. Due to large chemical shift anisotropy (CSA) induced line broadening exhibited in the ^{77}Se MAS NMR spectra, only two peaks are readily observed by. Bureau et al. [1] assigned these peaks to Se-**Se**-Se and Ge-**Se**-Ge environments, implying the clustering of Se chain and $GeSe_4$ tetrahedral domains in the glass structure. Edwards et al. [2] have proposed the existence of a third Se site (Se-**Se**-Ge) in the glass structure implying a more random distribution of structural units. The identification and quantification of these Se sites is crucial for the development of structure-property relationships in these glasses. In this study, we have employed the recently developed 2D Magic Angle Turning Phase Adjusted Spinning Sideband (MATPASS) NMR technique coupled with Car Purcell Meiboom Gill (CPMG) sequence [3] to investigate the Se environments in a suite of Ge_xSe_{100-x} glasses. The ^{77}Se MATPASS/CPMG NMR spectra allow for correlation between isotropic and anisotropic chemical shifts and unprecedented resolution in the isotropic dimension.



Experimental

Experiments were performed on a 19.6 T magnet equipped with a Bruker DRX console and a 4 mm MAS probe. Samples were spun at 10 kHz. For each 2D experiment, 16 hypercomplex t_1 points were acquired with 96 transients per point and 64 CPMG echoes per transient, in ~51 hours. Each transient was obtained using the MAT sequence of five π pulses with inter-pulse delays that were incremented according to the MAT inter-pulse delay timings [3]. The MAT sequence is followed by the CPMG pulses for the echo train acquisition. The π/2 and π pulse lengths were 2.0 and 4.0 μs, respectively, and a 60 s recycle delay was used. The details of the pulse sequence can be found elsewhere [3].

Results and Discussion

Figure 1 shows the pure isotropic ^{77}Se NMR spectrum for each of the Ge_xSe_{100-x} ($5 \leq x \leq 30$) glasses. These spectra provide superior resolution compared to regular MAS spectra. Both the chemical shift anisotropy and the isotropic distribution in these glasses are much larger than the 10 kHz MAS frequency resulting overlapping spinning sidebands. The 2D MATPASS experiment separates the sidebands such that an isotropic projection can be obtained as if the spinning is infinite fast [3].The isotropic chemical shift of each distinct Se site is denoted by the solid vertical lines in Figure 1. From the 2D MATPASS/CPMG spectra the Ge-**Se**-Ge, Se-**Se**-Se and Se-**Se**-Ge sites can be distinguished by their unique combination of CSA values and isotropic chemical shifts. The chemical shift tensor parameters for these sites offer important insights into their local site symmetries and nearest and next-nearest neighbor coordination environments. The compositional variation of the relative fraction of the Se sites is consistent with the model of a stochastic random network structure that is formed by random interconnection between $GeSe_4$ tetrahedra and Se-Se chain fragments.

Conclusions

The 2D MATPASS/CPMG technique allows for the identification and quantification of the different Se sites present in Ge_xSe_{100-x} glasses. The results provide direct evidence in favor of the existence of a randomly connected network of $GeSe_4$ tetrahedra and Se-Se chain fragments in these glasses.

Acknowledgements

This work was supported by the NSF grant DMR GOALI-1104869. NHMFL is supported through the NSF Cooperative Agreement (DMR-0084173) and by the State of Florida.

References

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