High Field ^{75}As NMR Study of Local Bonding Symmetry in Ternary Chalcogenide Glasses

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Introduction

Quadrupole coupling constant, ν_Q and asymmetry parameter of an electric field gradient (EFG) at nuclear site, η are unique parameters providing direct information on nearest-neighbor bonding of a quadrupolar nucleus. For ^{75}As nucleus (with spin I = 3/2 and 100 % abundance) a combination of NQR and NMR measurements can provide an accurate and unique way for obtaining both ν_Q and η. We report here a high field ^{75}As NMR study of arsenic bonding symmetry in $Ge_xAs_ySe_{1-x-y}$ glasses as a function of average coordination number, <r>.

Experimental

High field ^{75}As NMR measurements were performed in field-sweep regime using 30 T highly homogeneous core bore magnet at the NHMFL. The pulsed NMR spectrometer was operated at 137 MHz which corresponds to a Zeeman field (B_0) of 18.78 T for ^{75}As nucleus.

Results and Discussion

Figure 1 represents high field NMR spectra for $Ge_{0.18}As_{0.18}Se_{0.64}$, $Ge_{0.22}As_{0.22}Se_{0.56}$, and $Ge_{0.33}As_{0.12}Se_{0.55}$ glasses with average coordination numbers of 2.54, 2.67, and 2.78, respectively. Specific divergences at central transition have been observed for $Ge_{0.18}As_{0.18}Se_{0.64}$, a composition representing chemical threshold in the system. NMR powder pattern has been simulated using NQR data [1] to fit the line shape (Fig. 2). The simulation reveals asymmetry parameter of 0.2 ± 0.01, which represents nearly axially symmetric As sites in the glass. Thus in $Ge_{0.18}As_{0.18}Se_{0.64}$ 64 arsenic atoms are bonded in regular pyramidal structural units. In the compositions with higher <r>, however, there is no resolved structure on the NMR lineshapes. These spectra can not be fitted with single asymmetry parameter and the distribution of η is needed commensurate with NQR lineshapes. The simulations suggest that a broad distribution of the asymmetry parameter should be taken to fit the data. In these glasses a significant contribution to the line shapes comes from highly distorted arsenic sites. This indicates that As atoms in the glasses are bonded in complex structural units or molecular nodules containing homopolar As-As bonds.

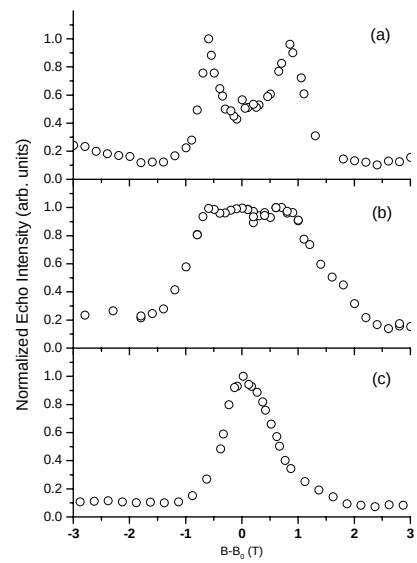

Figure 1. ^{75}As NMR spectra of the central transition for (a) $Ge_{0.18}As_{0.18}Se_{0.64}$, (b) $Ge_{0.22}As_{0.22}Se_{0.56}$, and (c) $Ge_{0.33}As_{0.12}Se_{0.55}$ glasses.

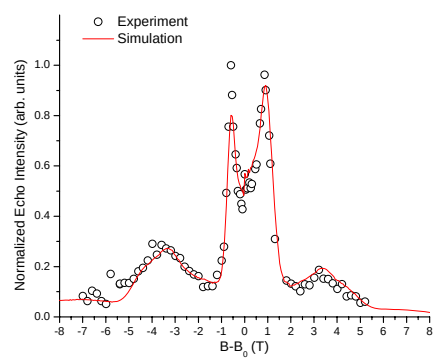

Figure 2. NMR spectrum and simulation for $Ge_{0.18}As_{0.18}Se_{0.64}$.

Conclusions

The local structure in $Ge_xAs_ySe_{1-x-y}$ glasses becomes more disordered as the average coordination number increases. The results of high field ^{75}As NMR experiments combined with NQR data provide a detailed description of the local bonding structure in this ternary system.

Acknowledgments

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References

[1] E. Mammadov *et al*., J. Non-Cryst. Solids **354** 2732-2735 (2008).