Tellurium Speciation in As_xTe_{100-x} Glasses: Results From 2D ^{125}Te NMR Spectroscopy

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Introduction

Tellurium containing chalcogenide glasses in the Ge-As-Sb-Te system are technologically important materials that have found widespread applications in the areas of phase change memory and infrared photonics. However, an atomistic understanding of the structure-property relationships remains elusive, even in simple binary telluride glasses due to controversies surrounding even the short-range structure of these materials, preventing the development of a robust structural model. In the present study, we employ ^{125}Te projection-Magic-Angle-Turning/CPMG (*pj*MAT/CPMG) NMR to study the structure of As_xTe_{100-x} glasses. A structural model is proposed on the basis of these ^{125}Te NMR results and its implications on the structure-property relationships are discussed.

Experimental

^{125}Te (252.5 MHz) NMR was carried out at the NHMFL on a Bruker Avance III HD console equipped with a 18.8 T medium bore (63 mm) magnet and a home-built 4 mm probe spinning at 10 kHz MAS.

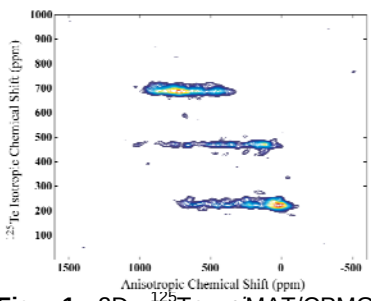

Fig. 1 2D ^{125}Te *pj*MAT/CPMG spectrum of monoclinic As_2Te_3 crystal showing the three Te sites in the As_2Te_3 crystal structure.

Results and Discussion

The ^{125}Te *pj*MAT/CPMG spectrum of the As_2Te_3 crystal is shown in Fig. 1. The broad range of chemical shifts and large CSAs characteristic of ^{125}Te have prevented previous studies from accurate line shape analysis and structural interpretation of the ^{125}Te MAS NMR data for both glassy and crystalline tellurides.[1] It is clear from Fig. 1 that the application of *pj*MAT/CPMG drastically enhances the spectral resolution by separating the CSA patterns into a separate dimension, by their isotropic shifts (Fig. 1). Three structurally inequivalent Te sites observed at δ_{iso} = 224, 471, and 689 ppm, characteristic of monoclinic As_2Te_3. The CSA and asymmetry parameter η of the anisotropic line shapes allow their structural assignments to 3, 1 and 2–fold coordinated Te sites in the As_2Te_3 crystal structure, respectively. The isotropic projections of the ^{125}Te *pj*MAT/CPMG spectra of the As_xTe_{100-x} glasses indicate the presence of three different Te environments: Te-**Te**-Te, Te-**Te**-As and As-**Te**-As at δ_{iso} = 995, 830 and 655 ppm, respectively, and distinct CSA tensors (Fig. 2). The Te speciation as obtained from simulation of these NMR spectra indicate that the structure of these glasses is dictated by the dissociation $As_2Te_3 \rightarrow 2As + 3Te^{II}$ in the melt, resulting in considerable chemical disorder for all compositions. This structural model is consistent with the energetics of interatomic bonding and with the monotonic compositional variation of a variety of physical properties in this glass-forming system.

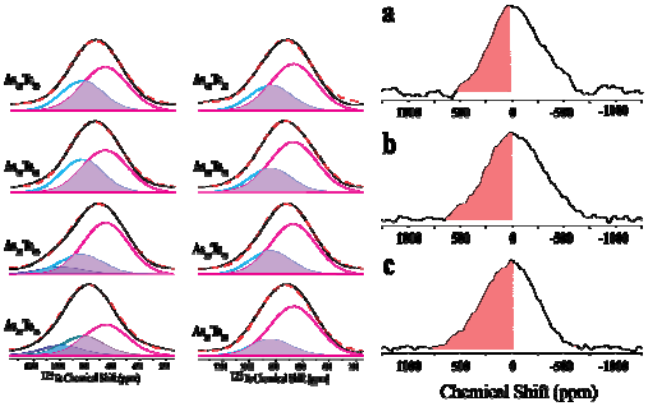

Fig. 2 The isotropic projections of ^{125}Te *pj*MAT/CPMG spectra of the As_xTe_{100-x} glasses with simulations (left) and the CSA line shapes (right) at δ_{iso} = 995, 830 and 655 ppm for the Te environments (a) Te-**Te**-Te (b) Te-**Te**-As and (c) As-**Te**-As, respectively.

Conclusions

The ^{125}Te *pj*MAT NMR results indicate that the coordination of Te atoms obey the 8-N coordination rule in As-Te glasses. However, significant violation of chemical order is observed over the entire composition range in the form of homopolar As-As (Te-Te) bonds, even in severely As (Te) -deficient glasses. These structural characteristics can be attributed to the high metallicity of Te and the strong energetic similarity between the Te-Te, Te-As and As-As bonds and they are consistent with the monotonic and often nearly linear variation of physical properties observed in telluride glasses as a function of the Te content.

Acknowledgements

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References [1] Edwards, T.G., *et al*., Journal of Non-Crystalline Solids, ***357***, 3036-3041 (2011).