Structure and Chemical Order in S-Se Binary Glasses: Results from 2D ^{77}Se NMR

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Introduction

Chalcogenide glasses consist of one or more of the chalcogen elements S, Se and Te and constitute an important class of optical materials that has received great attention for wide range of applications in photonics, non-volatile memories and remote sensing. The elemental chalcogens, i.e., S, Se and Te are also glass-formers by themselves and their structure-property relations have been extensively investigated. However, to the best of our knowledge, no systematic structural study of glasses in the binary S-Se system has been reported in the literature to date. In the present study, we report the results of a structural investigation of binary S_xSe_{100-x} glasses with $0 \leq x \leq 90$, using high-resolution 2D magic-angle-turning phase adjusted spinning sideband (MATPASS) ^{77}Se NMR spectroscopy. The compositional evolution of the chain and molecular topological elements and chemical order thus obtained is used to build a structural model of these glasses that is shown to be consistent with their thermophysical properties.

Experimental

Binary S_xSe_{100-x} glasses ($0 \leq x \leq 90$) were synthesized by a standard melt-quench method in fused quartz ampoules. The 2D ^{77}Se MATPASS NMR spectra of these samples were acquired at NHMFL using a a 63-mm bore magnet (18.8 T) operating at a ^{77}Se Larmor frequency of 152.7 MHz. The crushed samples were packed into 3.2 mm ZrO_2 rotor and were spun at 10 kHz. The details of the pulse sequence and timings can be found in [1]. The sample temperature was maintained at 263K throughout the duration of these NMR experiments to avoid any heating of these glass samples above their glass transition temperatures from spinning.

Results and Discussion

The results indicate that the structure of S-Se glasses consist of two types of topological elements (Fig. 1), namely polymeric $[Se,S]_n$ chains and eight-membered Se_yS_{8-y} rings ($0 \leq y \leq 8$). The relative concentration of Se atoms monotonically decreases in the chain elements and concomitantly increases in the ring elements with increasing S concentration. Moreover, the Se speciation results are consistent with an average heterocyclic ring composition of Se_1S_7 at low S content (≤ 40 at.% S), while the composition shifts to $Se_{1.5}S_{6.5}$ at higher S content (≥ 60 at.% S), indicating increasing incorporation of multiple Se atoms in each ring element. As in their elemental forms, the S and Se atoms retain their preference of forming rings and chains in binary S_xSe_{100-x} glasses, which predicts a linear compositional variation in the relative fractions of these topological elements. This structural evolution is consistent with the corresponding linear decrease in the T_g and molar volume with increasing S concentration.

Fig.1 ^{77}Se 2D MATPASS NMR spectrum of $S_{75}Se_{25}$ glass with total isotropic projection showing the chain and ring Se sites in the glass structure. Arrows connect the resonances to the corresponding sites in the structural cartoon (S and Se atoms are shown in yellow and red, respectively).
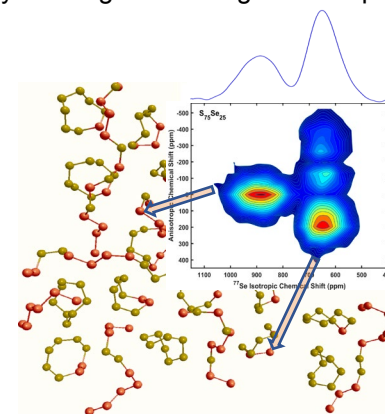
Conclusions

When taken together, these results unequivocally demonstrate that Se and S atoms show strong preference to form the chain and the ring elements, respectively, which prevents a random or homogeneous mixing between these two elements. It is, however, not the peculiar chemical order between S and Se but the total chain vs. ring content in the structure that controls both the packing and the mobility of the constituent structural units. As the total chain content increases with increasing Se concentration in these glasses, the stronger interaction between the chain elements compared to rings, results in less efficient atomic packing and lower mobility, which are manifested in the decreasing molar volume and increasing T_g, respectively.

Acknowledgements

References

[1] Yuan, B., *et al*., Journal of Physical Chemistry B, **122(50)**, 12219-12226 (2018).