



Network Structure and Connectivity in SnO-P₂O₅ Glasses: Results from 2D ³¹P and ¹¹⁹Sn NMR

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Introduction

Interest in tin phosphate (SnO-P₂O₅) glasses is driven primarily by their high refractive index, zero stress-optic response and low glass transition temperature T_g , which make them suitable for applications in optics as well as in low-temperature glass-to-metal sealing. The structure of these glasses were investigated extensively in recent years using a variety of characterization techniques including infrared and Raman spectroscopy as well as ³¹P and ¹¹⁹Sn NMR spectroscopy. However, due to the strongly overlapping ³¹P resonances and broadening of the static ¹¹⁹Sn NMR spectra by chemical shift dispersion and anisotropy, deconvolution of these 1-D NMR spectra and their structural assignment remained equivocal. In the present study we report 2D ³¹P and ¹¹⁹Sn isotropic-anisotropic correlation NMR spectra of (SnO)_x(P₂O₅)_{100-x} glasses with 35 ≤ x ≤ 55 to build a model of the compositional evolution of the structure of these glasses.

Experimental

The Sn-phosphate glasses were prepared in 10 g batches from Sn₂P₂O₇ and P₂O₅ in a silica ampoule and held at 200° C for 1 hour under vacuum to remove any water. All ³¹P and ¹¹⁹Sn NMR spectra were collected using a Bruker DRX spectrometer, equipped with a 31 mm bore magnet operating at 19.6 T at NHMFL. Samples were spun at 10 or 15 kHz in ZrO₂ rotors with a 3.2 mm HX MAS probe designed and built at the NHMFL. Each ³¹P MAS spectrum is the Fourier transform of 32 free induction decays acquired with a Hahn-echo pulse sequence using $\pi/2$ - and π -pulses of 2.5 and 5 μ s, respectively, and a recycle delay of 300 s. ¹¹⁹Sn projection Magic-Angle Turning/CPMG (*pj*MAT/CPMG) NMR spectroscopy was employed to separate the CSA from the isotropic chemical shift in order to study the coordination environment of Sn in the tin phosphate glasses. The *pj*MAT/CPMG NMR uses magic-angle turning and projection pulses to sample a large chemical shift range, making it an ideal sequence for ¹¹⁹Sn NMR in glasses. Each ¹¹⁹Sn 2D *pj*MAT/CPMG spectrum was obtained using an indirect dimension spectrum window of 320 kHz, 10 hypercomplex t_1 data points with 648 transients per point, 83 CPMG echoes per transient, and a recycle delay of 25 s. A 2.5 μ s duration was used for all pulses in the pulse sequence.

Results and Discussion

A self-consistent structural model results from the consideration of the full chemical shift tensor for the ³¹P and the ¹¹⁹Sn nuclides [1]. The Q-speciation is found to follow the binary model. With increasing SnO, the phosphate network dominated by the Q³ and the Q² species is gradually replaced by a more closely packed structure consisting of phosphate chains and dimers i.e. the Q² and the Q¹ species. ¹¹⁹Sn 2D *pj*MAT/CPMG NMR results demonstrate that Sn atoms are present in both 3 and 4 -fold coordination with the NBO atoms in all glasses, and the relative fraction of the latter decreases with increasing SnO. The low coordination number of Sn in combination with its preference for bonding to NBOs that are on the same Q² chain or Q¹ dimer leads to an unusually low network connectivity that is manifested in rather low and nearly composition-independent T_g values characteristic of SnO-P₂O₅ glasses.

Conclusions

The network modification in these Sn-phosphate glasses can be described in terms of a binary Q-speciation model. On the other hand, the ¹¹⁹Sn NMR spectra suggest that the Sn-O coordination environment in these glasses is composition dependent. Sn is present in both 3-fold (trigonal pyramid) and 4-fold (trigonal bipyramid) coordination with oxygen in these glasses. The relative fraction of the trigonal pyramidal environment increases with increasing SnO content. The unusually low glass transition temperature T_g of these glasses (241-266° C) is argued to be related to the low coordination number of Sn, leading to a relatively sparsely connected structural network.

Acknowledgements

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References:

[1] Xia, Y., *et al.*, Journal of Physical Chemistry B, **122**(29), 7416-7425 (2018).

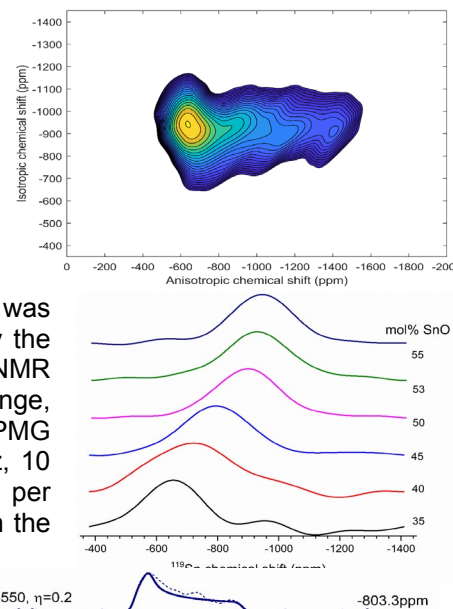


Fig.1 Representative ¹¹⁹Sn 2D *pj*MAT NMR spectrum of 53SnO-47P₂O₅ glass (top) Isotropic projections of ¹¹⁹Sn *pj*MAT NMR spectra of all Sn-phosphate glasses (middle) Experimental (dashed line) and simulated (solid line) anisotropic line shapes at different isotropic shifts for 53SnO-47P₂O₅ glass (bottom) with corresponding CSA parameters listed on the left.