

Titanium phosphate glasses: Beyond tetrahedral network structures

Esther Girón Lange,^{1,2} Randall E. Youngman,³ Bruce G. Aitken,³ Anita Zeidler,¹
Kyle T. Hufziger,³ Sung Hoon Lee,⁴ Gabriel J. Cuello,² Gavin B. M. Vaughan,⁵ &
Philip S. Salmon¹

¹*Department of Physics, University of Bath, Bath, BA2 7AY, UK*

²*Institut Laue Langevin, 71 Avenue des Martyrs, 38042 Grenoble Cedex 9, France*

³*Science and Technology Division, Corning Incorporated, Corning, NY 14831, USA*

⁴*Corning Technology Center Korea, Corning Precision Materials Company Ltd.,
212 Tangjeong-ro, Asan, Chungcheongnam-do 31454, Republic of Korea*

⁵*ESRF–The European Synchrotron, 71 Avenue des Martyrs, 38000 Grenoble, France*

Corresponding Author e-mail: p.s.salmon@bath.ac.uk

The structure of titanium phosphate glasses $(\text{TiO}_2)_x(\text{P}_2\text{O}_5)_{1-x}$ with $0.70 \leq x \leq 0.75$ was investigated by combining neutron and high-energy x-ray diffraction with solid-state ^{31}P nuclear magnetic resonance (NMR), Raman and electron paramagnetic resonance spectroscopy. The results were interpreted with the aid of an analytical model that delivers the composition dependence of the structural motifs. The structure of these materials was also simulated using *ab initio* molecular dynamics. ^{31}P static NMR spectra show that orthophosphate groups predominate and the diffraction results find a Ti-O coordination number of 5.32(7) at $x = 0.715$ that increases to 5.49(7) at $x = 0.750$. The findings show the prevalence of five- and six-coordinated titanium atoms and the coexistence of two-coordinated O(II) and three-coordinated O(III) oxygen atoms. The Ti-centred polyhedra contribute towards a network in which the orthophosphate groups form P-O(II)-Ti and P-O(III)-2Ti connections, with signatures that are evident in the ^{31}P magic angle spinning NMR spectra. The results suggest that structural variability is a key factor in promoting the vitrification of this atypical glass-forming system. The findings will provide a benchmark for investigating the structure of other glass-forming materials based on networks of higher-coordinated polyhedral units.