

Titanium phosphate glasses: Beyond tetrahedral network structures

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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) and Raman 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. A detailed ^{31}P magic angle spinning (MAS) NMR lineshape analysis, aided by the results obtained from double-quantum coherence spectroscopy, indicate the presence of P-O-P connected network forming units at a level decreasing from 23 to 11% with increasing x . 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 both two-coordinated oxygen atoms, O(II), and three-coordinated oxygen atoms, O(III). The Ti-centered polyhedral units contribute towards a network in which the phosphate groups form P-O(II)-Ti and P-O(III)-2Ti connections, with signatures that are evident in the ^{31}P MAS 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 with coexisting O(II) and O(III) species.