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# Multinuclear NMR investigation of the composition-dependent structural role of Pb(II) in lead borogallate and boroaluminate glasses

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## Abstract

Knowledge about network connectivity in lead aluminoborate glasses remains poor despite diverse applications ranging from optical materials to nuclear waste immobilization. Several investigations on lead-bearing glass systems have shown that Pb(II) can function as a network former or modifier or both, depending on its concentration, however the mechanism governing these roles is unclear. In this work, Pb-207, B-11, Al-27 and Ga-71 nuclear magnetic resonance (NMR) spectroscopy are used to examine the short-range structure of parallel series of lead boroaluminate and borogallate glasses. The chemical similarity of Al and Ga provides a sensitive measure of the role of cation field-strength in driving structural arrangements. High-field Ga-71 magic-angle spinning NMR indicates that Ga is present in three different coordination environments, similar to the polyhedral distribution of Al, confirming that the isostructural nature of Al and Ga in borates is consistent with previous observations in silicate and phosphate glass systems. Spectroscopic analysis of these glasses implies a hierarchy in the charge compensation of network-forming units following the order: (AlO<sub>4</sub>)<sup>-</sup> > (BO<sub>4</sub>)<sup>-</sup> > (GaO<sub>4</sub>)<sup>-</sup>. Pb-207 CPMG NMR spectra consist of signals spanning large spectral breadths resulting from overlapping peaks associated with different Pb coordination numbers and large chemical shift anisotropies. The relative fractions of Pb(II) in low- and high-coordinate environments estimated by peak-fitting suggest the presence of low-coordinate "network-forming" Pb(II) even at low PbO contents. This behaviour can be rationalized by considering the respective cation field-strengths of the constituents.

**Keywords:** NMR, lead, borate, gallate, bond, valence

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