The structural role of fluorine in ionic glasses via fluorine-19 MAS NMR

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Abstract

Ionic glasses, defined as compositions with more modifying ions than network formers, are of interest since their properties are dominated by ionic interactions, allowing an opportunity to understand the role of these interactions in structure-property relationships. Recent publications have demonstrated the stability of fluoro-phospho-sulfate (FPS) glasses over large compositional ranges. The addition of F- *via* AlF3 has been found to greatly increase the stability of the glass-forming region of the FPS family, leading us to question the exact role of the fluorine in the glass structure. Furthermore, FPS glasses have been found to possess high ionic conductivity, indicating that F- may be mobile in these structures at elevated temperatures. The fluorine peaks resolved in fluorine-19 MAS NMR are highly sensitive to the identity of neighbours; for example, F-Na-O, F-Al-O and M-F-M-O (where M = metal) units are discernible. This allows for the quantification of terminal and cross-linking fluorine atoms in FPS glasses, which will then be related to the mechanical and thermal properties, and the ionic conductivity of these glasses. Terminal fluorine atoms are interesting as they essentially remove cations from the glass network leading to a paucity of charge-compensators in the phospho-sulfate region which coincides with an increase in Al coordination (AlOxFy). It is expected that at low fluorine content, more terminal fluorines are present compared with at higher fluorine content, where non-bridging oxygens are replaced by cross-linking fluorines (M-F-M).

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