Structure of Gallium-Phospho-Oxyfluoride Glasses by NMR Spectroscopy

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Phospho-oxyfluoride glasses are interesting as optical materials as they combine various key properties such as low refractive index, radiation resistance, wide transmission range and favorable emission characteristics for rare-earth dopants with good glass forming ability, ensuring the material to be drawable into fibers. As the development of optimized glass compositions by traditional trial-and-error methods is laborious, time consuming, and expensive, it is important to develop glass compositions based on a fundamental understanding of the glass structure and establish structure-property relation models. To this end we have used NMR spectroscopy to study the structure of gallium-based phospho-oxyfluoride glasses with composition xGa$(PO_3)_3$–(40-x)GaF_3–20BaF_2–20ZnF_2–20Sr$F_2$for x= 5, 10, 15, 20 25 mol%, i.e., as a function of GaF_3/Ga$(PO_3)_3$ratio. Since the glasses are prone to F volatilization, first a ^{19}F NMR technique was designed for quantifying these losses and measuring the exact F contents of these glasses. ^{71}Ga NMR results show that Ga is mainly six-coordinated with a mixed fluoride/phosphate coordination. Quantitative estimates of this ligand distribution around gallium were obtained by combined ^{71}Ga{^{19}F} and ^{71}Ga{^{31}P} rotational echo double resonance (REDOR) measurements. ^{19}F NMR results indicate that the local environment of F is dominated by $Ga^{3+}$and the divalent cations, and the absence of P-F bonding. The latter is also confirmed by while ^{31}P{^{19}F} REDOR results; furthermore, ^{31}P INADEQUATE and Raman results give no evidence of P-O-P linkages. Thus, the glass network is largely sustained by bridging oxygen atoms via P-O-Ga linkages, as intended by the compositional design of this glass system.

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