New Solid State NMR and EPR Strategies for the Structural Characterization of Photonic Glasses and Glass-Ceramics

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Rare-earth ion (RE) doped glasses and glass-ceramics are luminescent photonic materials with promise for laser applications. To optimize the luminescent properties of these materials, detailed structural information regarding the local environment of the rare-earth species is essential. While solid state nuclear magnetic resonance (NMR) is in general a useful tool for such purposes; unfortunately, the rare-earth ions themselves cannot be studied by NMR due to their paramagnetism. To overcome this difficulty, a three-fold examination strategy has been developed including (1) NMR studies of diamagnetic mimics, (2) NMR studies of framework nuclei affected by paramagnetic interactions, and (3) pulsed-EPR studies sensitive to the magnetic dipolar interactions of the unpaired electrons with nearby nuclear spins, using electron spin echo envelope modulation (ESEEM) and hyperfine sublevel correlation (HYSCORE) spectroscopy. These approaches are complementary in terms of the relevant length scale of the interactions studied and their combination has turned out very successful in eludicating the short- and medium-range order details of the rare-earth ion local environments, allowing a rationalization of the luminescent properties of these glasses on a structural basis. Recent applications of this experimental strategy to fluoride phosphate laser glasses will be discussed.