Paramagnetic Metal Ion Dopants for Endogenous Dynamic Nuclear Polarization in the Bulk of Inorganic Solids

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In recent years magic angle spinning - dynamic nuclear polarization (MAS-DNP) developed as an excellent approach for boosting the sensitivity of solid state NMR (ssNMR) spectroscopy, thereby enabling the characterization of challenging systems in biology and chemistry. Most commonly, MAS-DNP is based on the use of nitroxide biradicals as polarizing agents. In materials science, since the use of nitroxides often limits the signal enhancement to the materials' surface and subsurface layers, there is need for hyperpolarization approaches which will provide sensitivity in the bulk of micron sized particles. Recently, an alternative in the form of paramagnetic metal ions has emerged.
Here I will present the remarkable efficacy of Mn(II) dopants, used as endogenous polarization agents for MAS-DNP, in enabling the detection of ^{17}O at a natural abundance of only 0.038% in oxides. Furthermore, I will discuss the enhancements obtained for $^{6,7}Li$ with various metal ion dopants in MAS-DNP experiments on battery materials.

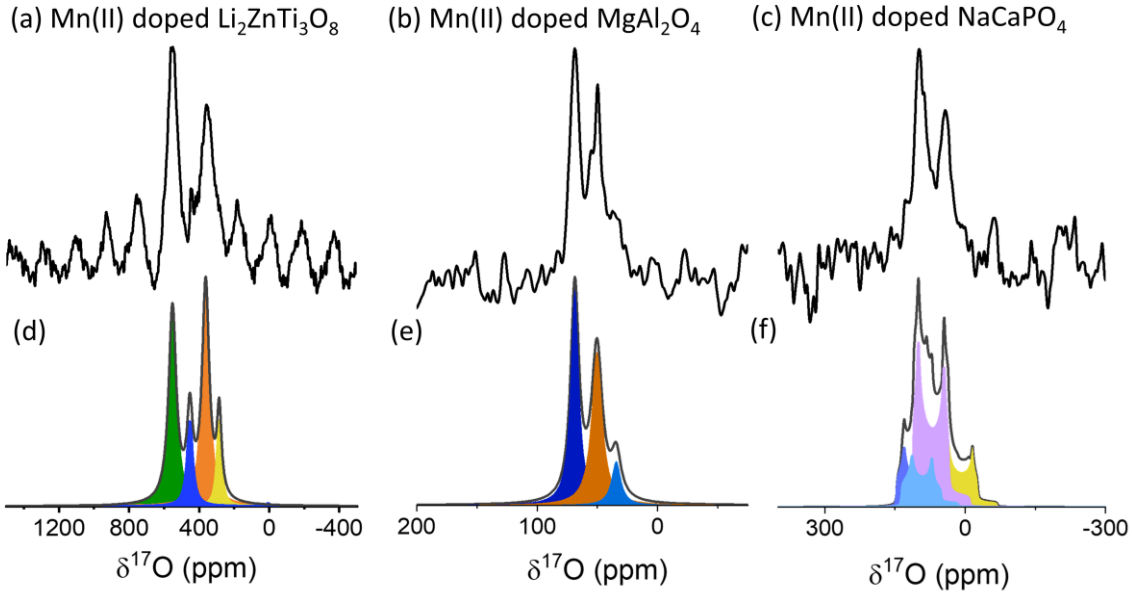

Figure 1 (a-c) ^{17}O MAS-DNP spectra acquired at natural abundance with single pulse excitation following a polarization build up time of 60 seconds. The dopant content per stoichiometric formula was (a) 0.005, (b) 0.001 and (c) 0.002. Spectra were acquired at approximately 100K with MAS of 10kHz with (a) 992, (b)3258 and (c) 2514 scans.
(d-f) Spectral deconvolution were performed for the isotropic resonances, guided by density functional theory calculations of the ^{17}O NMR parameters of the oxides.