25Mg Solid State NMR Studies of Mg-doped Lanthanum Gallate Anionic Conductors

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Introduction

New materials with improved ionic conductivity at moderate temperatures, and hence materials with higher numbers of mobile oxygen-ion vacancies (the charge carriers), are required in order to lower the operating temperature of a solid oxide fuel cell (SOFC). Dopant ions M\textsuperscript{n+} are substituted for higher valent ions, M\textsuperscript{(n+1)+} or M\textsuperscript{(n+2)+} in order to create these vacancies. In the particular case studied here, vacancies in lanthanum gallate perovskite LaGaO\textsubscript{3} are created by accommodation of Sr\textsuperscript{2+} and Mg\textsuperscript{2+} into the A = La and B = Ga sites, respectively.\textsuperscript{1} Unfortunately, vacancies cannot be observed directly but should be associated with metal at lower coordination numbers. We have thus tried in the following work to observe the NMR signals of metal ions directly and correlate it to the coordination number of the dopant.\textsuperscript{2} We thus focused here on 25Mg NMR at very high field in an attempt to determine the coordination number of the Mg site in Sr and Mg-doped LaGaO\textsubscript{3}.

Experimental

Solid state NMR experiments were performed at 830 MHz in the NHMFL facility at Tallahassee, FL using a single-channel 4 mm MAS probe at a spinning frequency of 10 kHz. An rf field of around 90 kHz was used for 25Mg. Spectra were referenced to MgCl\textsubscript{2} in H\textsubscript{2}O. Samples were prepared by the solid state route as described previously\textsuperscript{1} using 98% enriched 25MgO.

Results and Discussion

Figure 1 shows the 1D 25Mg single pulse and shifted echo SPAM MQMAS\textsuperscript{3} spectra of 20 % Mg doped LaGaO\textsubscript{3}. The spectra show 2 resonances at isotropic chemical shifts of 26 (sharp peak) and 22 (broad peak) ppm. While the former is easily assigned to 25MgO (residual starting material), the later corresponds to Mg dopant incorporated in LaGaO\textsubscript{3}. Firstly, this 22 ppm isotropic chemical shift is in the range of the shift region expected for 6 coordinate Mg\textsuperscript{2+} which would indicate that the vacancy in 20 % Mg doped LaGaO\textsubscript{3} is not near the Mg site for which a 5 coordinate Mg is expected (isotropic shift in the range of 45 – 30 ppm).\textsuperscript{3} Secondly, the lineshape of the 2D MQMAS spectra shows that there is for the signal at 22 ppm a distribution of quadrupolar coupling constants which speak for a large variety of Mg sites in the lattice.

Conclusions

Very high field 25Mg NMR spectroscopy on doped 20 % Mg LaGaO\textsubscript{3} reveals that the vacancy is not near the Mg site.

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References