

^7Li Ion Diffusion in Isotope-diluted Glassy $\text{Li}_2\text{Si}_3\text{O}_7$ – The Generation of pure Spin-3/2 Spin-alignment NMR Echoes

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Solid-state diffusion plays one of the most important roles in materials science. In particular, the precise measurement of ion dynamics in materials with structural disorder is of great interest. Spin-alignment echo (SAE) nuclear magnetic resonance (NMR), being comparable to exchange spectroscopy, turned out to be a powerful method to probe (ultra-)slow Li dynamics even in amorphous materials [1–3]. However, ^7Li Jeener-Broekaert echoes can be influenced by the simultaneous generation of dipolar with quadrupolar order. In many cases, the first can be suppressed by choosing proper evolution times t_p of less than 20 μs [4, 5].

Here, glassy $\text{Li}_2\text{Si}_3\text{O}_7$ served as a suitable model system to study the positive influence of isotope dilution on ^7Li SAE NMR, *i.e.*, the reduction of homonuclear dipole-dipole interactions through spatial separation of the spin-3/2 probe nuclei. Two samples, one with 100% ^7Li and the other one with 5% ^7Li (95% ^6Li), were investigated by ^7Li NMR line-shape analysis, spin-lattice relaxation NMR as well as mixing-time and preparation-time dependent ^7Li SAE NMR using a 32-fold phase cycle. Jeener-Broekaert echoes and their Fourier transforms show that at sufficiently short t_p the interfering dipolar interactions can be completely suppressed in that sample for which the proportion of ^7Li was greatly reduced by substitution with ^6Li . The so-obtained diffusion parameters are compared with results deduced from broadband conductivity spectroscopy.

Acknowledgement. We thank our colleagues at the University of Hannover and the TU Graz for valuable discussions. Financial support by the Deutsche Forschungsgemeinschaft (WI3600/2-2 and 4-1) as well as by the Austrian Federal Ministry of Science, Research and Economy, and the Austrian National Foundation for Research, Technology and Development is greatly appreciated.

- [1] Studying Li Dynamics in a Gas-Phase Synthesized Amorphous Oxide by NMR and Impedance Spectroscopy, V. Epp, C. Brüning, M. Binnewies, P. Heitjans, M. Wilkening, *Z. Phys. Chem.* 226 (2012) 513.
- [2] Atomic-scale Measurement of Ultraslow Li Motions in Glassy $\text{LiAlSi}_2\text{O}_6$ by two-time ^6Li Spin-alignment Echo NMR Correlation Spectroscopy, M. Wilkening, A. Kuhn, P. Heitjans, *Phys. Rev. B* 78 (2008) 054303.
- [3] From Micro to Macro: Access to Long-Range Li^+ Diffusion Parameters in Solids via Microscopic $^{6,7}\text{Li}$ Spin-Alignment Echo NMR Spectroscopy, M. Wilkening, P. Heitjans, *Chem. Phys. Chem.* 13 (2012) 53.
- [4] Alignment Echo of Spin-3/2 ^9Be Nuclei: Detection of Ultraslow Motion, X.-P. Tang and Y. Wu, *J. Magn. Res.* 133 (1998) 155.
- [5] Ion Dynamics in Solid Electrolytes: NMR Reveals the Elementary Steps of Li^+ Hopping in the Garnet $\text{Li}_{6.5}\text{La}_3\text{Zr}_{1.75}\text{Mo}_{0.25}\text{O}_{12}$, P. Bottke, D. Rettenwander, W. Schmidt, G. Amthauer, M. Wilkening, *Chem. Mater.* 27 (2015) 6571.

