diffusion-fundamentals.org

The Open-Access Journal for the Basic Principles of Diffusion Theory, Experiment and Application

^{7}Li ion diffusion in isotope-diluted glassy $Li_2Si_3O_7$ — The generation of pure spin-3/2 spin-alignment NMR echoes

Dominik Wohlmuth[1,2*], Viktor Epp[1,2], Ute Bauer[1,3], Anna-Maria Welsch[1,3], Harald Behrens[1,3], Martin Wilkening[1,2]

[1]DFG-Forschergruppe 1277 "Mobility of lithium ions in solids"
[2]Christian Doppler Laboratory for Lithium Batteries, Institute for Chemistry and Technology of Materials, Graz University of Technology, Graz, Austria
[3]Leibniz University Hannover, Institute of Mineralogy, Hannover, Germany
*dominik.wohlmuth@tugraz.at

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, 2]. However, ^{7}Li 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 [3].

Here, glassy $Li_2Si_3O_7$ served as a suitable model system to study the positive influence of isotope dilution on ^{7}Li 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% ^{7}Li and the other one with 5% ^{7}Li (95% ^{7}Li), were investigated by ^{7}Li NMR line-shape analysis, spin-lattice relaxation NMR as well as mixing-time and preparation-time dependent ^{7}Li 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 ^{7}Li was greatly reduced by substitution with ^{6}Li. The so-obtained diffusion parameters are compared with results deduced from broadband conductivity spectroscopy.

References

[1] V. Epp, C. Brüning, M. Binnewies, P. Heitjans, M. Wilkening: *Studying Li dynamics in a gas-phase synthesized amorphous oxide by NMR and impedance spectroscopy*. Z. Phys. Chem. **226**, 513–524 (2012); M. Wilkening, A. Kuhn, P. Heitjans: *Atomic-scale measurement of ultraslow Li motions in glassy $LiAlSi_2O_6$ by two-time ^{6}Li spin-alignment echo NMR correlation spectroscopy*. Phys. Rev. B **78**, 054303 (2008)

[2] M. Wilkening, P. Heitjans: *From micro to macro: Access to long-range Li^+ diffusion parameters in solids via microscopic ^{6,7}Li spin-alignment echo NMR spectroscopy*. Chem. Phys. Chem. **13**, 53–65 (2012)

[3] X.-P. Tang, Y. Wu: *Alignment echo of spin-3/2 ^{9}Be nuclei: Detection of ultraslow motion*. J. Magn. Res. **133**, 155–165 (1998)