Solid Electrolytes: Extremely Fast Charge Carriers in Garnet-Type $Li_6La_3ZrTaO_{12}$ Single Crystals

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The development of all-solid-state electrochemical energy storage systems, such as lithium-ion batteries with solid electrolytes, requires stable, electronically insulating compounds with exceptionally high ionic conductivities. Considering oxides, garnet-type $Li_7La_3Zr_2O_{12}$ and derivatives, see Zr-exchanged $Li_6La_3ZrTaO_{12}$ (LLZTO), have attracted great attention because of its high Li^+ ionic conductivity of up to 1 $mS \cdot cm^{-1}$. Despite numerous studies focusing on conductivities of powder samples, only a few use time-domain NMR methods to probe Li ion diffusion parameters in single crystals. Here we report, for the first time, on temperature-variable ^{7}Li NMR relaxometry measurements using both laboratory and spin-lock techniques to probe Li jump rates in monocrystalline Li-bearing garnets. Time-domain NMR offers the possibility to study Li ion dynamics on both the short-range and long-range length scale. The techniques applied yield a fully consistent picture of correlated Li ion jump diffusion in LLZTO; the data perfectly mirror a modified BPP-type relaxation response being based on a Lorentzian-shaped relaxation function. The rates measured could be parameterized with a single set of diffusion parameters. Dynamic information about the elementary jump processes, such as jump rates and activation energies, were extracted from complete diffusion-induced rate peaks that are obtained when the relaxation rate is plotted vs inverse temperature. Results from NMR are completely in line with ion transport parameters derived from 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.