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 ^7Li 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.

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