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Ultraslow Lithium Diffusion in Li_3NbO_4 Probed by ^{7}Li Stimulated Echo NMR Spectroscopy

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While huge research activities are being directed towards fast lithium ion conductors as potential electrolytes in batteries, it should be noted that also materials with low lithium diffusivity have many applications in modern technology. They are used, *e.g.*, in semiconductor fabrication as non-doping substrate or are considered as tritium breeding blankets in fusion reactors offering both a slow lithium release and a fast release of tritium after neutron irridiation. Many of the materials investigated and discussed for the latter applications are lithium metal oxides. A well known example is single or microcrystalline lithium niobate, $LiNbO_3$, which is not only interesting due to its ferroelectricity, but also due to its very slow lithium diffusion [1,2]. Here, we report on ultraslow lithium diffusion in lithium orthoniobate, Li_3NbO_4, a cubic (space group *I*-43m, see [3]) lithium rich phase in the lithium niobium oxide system. The correlation time of the hopping lithium ions was accessed *via* one-particle two-times correlation functions recorded using the ^{7}Li spin alignment echo nuclear magnetic resonance (SAE NMR) technique [4-6].

Microcrystalline Li_3NbO_4 was prepared in a solid state reaction of equimolar amounts of $LiNbO_3$ (99.9%, Cerac/Pure Inc.) and Li_2CO_3 (99.95%, Alfa). After heat treatment in a tube furnace (20 h at 973 K followed by 48 h at 1123 K) the crystallinity and phase purity of the product was verified by x-ray diffraction (XRD) using a Philips PW 1800 powder diffractometer operating at 40 kV. For the NMR measurements the sample material was dried under vacuum (373 K) and sealed into quartz tubes.

^{7}Li NMR spectroscopic measurements were carried out by means of a Bruker MSL 400 NMR spectrometer operating at $\omega_0/2\pi = 155$ MHz and a commercial probe (Bruker). ^{7}Li NMR spin–lattice relaxation rates were obtained using a saturation recovery pulse sequence and by subsequent fitting of the data with a stretched exponential function. In order to study ultraslow hopping processes of Li^+, mixing time (t_m) dependent ^{7}Li stimulated NMR echoes were recorded. Therefore, the pulse sequence $(\pi/2)_{\varphi 1} - t_p - (\pi/4)_{\varphi 2} - t_m - (\pi/4)_{\varphi 3} - t$ introduced by Jeener and Broekaert was applied [7]. The first two pulses generate an alignment state and are separated by the preparation time t_p. After the third pulse a stimulated spin echo is formed whose intensity depends on the correlation between the quadrupolar frequencies $\omega_Q(t_p)$ and $\omega_Q(t_m)$ before and after the mixing time t_m. In the ideal case, the t_m-dependent damping of the echo $S_2(t_p, t_m, t)$ occurs when ω_Q changes due to successful hopping processes between crystallographic sites with different electrical field gradients. In that case the damping rate of S_2 corresponds to the probe's hopping rate. The mixing time dependent echo amplitude $S_2(t_p, t_m, t = t_p)$ was read out at $t = t_p$ and recorded for a fixed preparation time $t_p = 10$ µs.

Below 400 K the ^{7}Li NMR spin alignment echo decay rates $1/\tau$ show only a weak temperature dependence and are not thermally activated. In this regime $1/\tau$ is dominated by background effects such as relaxation and spin diffusion. The background rate is almost four times larger than the spin–lattice relaxation rate $1/T_1$ in this temperature regime, which is also dominated by background relaxation. In theoretical calculations the ratio of the quadrupolar spin–lattice relaxation rate $1/T_{1Q}$ and the spin-lattice relaxation rate $1/T_1$ was predicted to be 25/8 [8], which points to the $1/\tau$ background observed here being mainly caused by quadrupolar spin–lattice relaxation of the spin alignment state generated. With increasing temperature the SAE decay rates $1/\tau = 1/\tau_c + 1/T_{1Q}$ are more and more dominated by the correlation rate $1/\tau_c$ of the hopping Li nuclei, showing Arrhenius behavior $1/\tau_c = 1/\tau_0 \cdot \exp(-E_a/k_BT)$ where k_B denotes Boltzmann's constant, E_a the activation energy of lithium hopping processes and the prefactor $1/\tau_0$ the lithium hopping rate for $T \rightarrow \infty$. Correction for the relaxation background $1/T_{1Q}$ gives access to correlation rates $1/\tau_c$ even from the $1/\tau$ data below 400 K. An Arrhenius fit yields $E_a = 0.7$eV and a prefactor $1/\tau_0 = 4 \times 10^{11}$ 1/s.

The activation energy found in the SAE NMR experiments is similar to the value of 0.80 eV obtained in preliminary dc conductivity measurements. Hence, this confirms that long-range diffusion is probed by the SAE NMR technique being sensitive to ionic motion on a long timescale [9]. Thus, the small hopping rates of $1/\tau_c = 3 \times 10^{-1}$ ... 8×10^3 1/s between 353 K and 553 K accessed in the measurements presented here give proof of very slow diffusion in Li_3NbO_4. In terms of diffusion coefficients these rates correspond to $D \approx 4 \times 10^{-21} \ldots 1 \times 10^{-16}$ m^2/s.

Currently, we are investigating crystalline Li_3NbO_4 samples prepared from a melt showing a weaker NMR background relaxation. Thus, in the future even smaller lithium diffusion coefficients in Li_3NbO_4 will be accessible by NMR spectroscopy.

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