Lithium Diffusion Studies of Gas-Phase Synthesized Amorphous Oxides – An NMR Investigation

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The search for new Li ion conductors continues to be of great importance as these materials show promise for use as components in, *e.g.*, chemical sensors, smart windows or as solid electrolytes in energy storage systems. Currently, there are two strategies to find novel materials for such applications. One is synthesizing new bulk materials with improved transport properties, the other is modifying the microstructure of known materials. It is often observed that disordered materials are characterized by a higher diffusivity than their crystalline counterparts [1-3]. Recently, we have shown that mechanical treatment of $LiTaO_3$ in a high-energy ball mill leads to an increase of the dc-conductivity by five orders of magnitude compared to that of the source material [3]. This can be attributed to the formation of a highly-defective microstructure which was probed by ^{7}Li NMR solid echo spectra.

In the present study metastable, highly non-stoichiometric oxides containing Li, Al and Si were synthesized via a gas-phase reaction of aluminum chloride, lithium chloride and silicon tetrachloride using a three-zone tube-furnace. The procedure is described in detail in Ref. [4]. It allows an easy adjustment of the sample stoichiometry, thus enabling the synthesis of samples with a wide range of different compositions simply by varying the preparation conditions such as the gas flow rate or the reaction temperature.

As an example, we report on the Li diffusion parameters of a sample with an Al : Li : Si ratio of approximately 1 : 2.3 : 2.1, which was determined by ICP-AES analysis. The white powder was found to be X-ray amorphous. SEM images show micrometer-sized agglomerates of spherical particles with diameters ranging from 200 to 750 nm.

Li diffusion parameters were probed by recording temperature dependent ^{7}Li solid-echo NMR spectra as well as ^{7}Li NMR spin-lattice relaxation (SLR) rates in both the laboratory (T_1^{-1}) and rotating frame of reference ($T_{1\rho}^{-1}$) using the saturation recovery pulse sequence and the spin-lock technique, respectively [5]. Furthermore, ^{7}Li NMR spin alignment echoes (SAE) were recorded in the same temperature range by employing the Jeener-Broekaert pulse sequence [6]. All measurements were carried out with a modified Bruker MSL-100 spectrometer at a resonance frequency of 77.7 MHz. The lock-
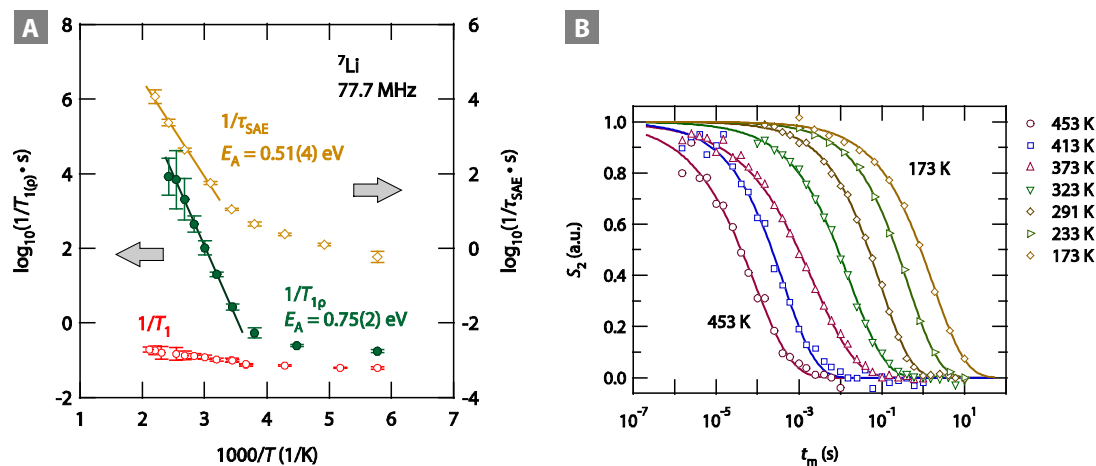
Fig. 1 A: Temperature dependence of the relaxation rates $1/T_1$ (open circles), $1/T_{1\rho}$ (closed circles) and $1/\tau_{SAE}$ (open diamonds). B: ^{7}Li SAE two-time correlation functions $S_2(t_m,t_p,t)$ as a function of mixing time at temperatures ranging from 173 to 453 K.

ing frequency used was 11(1) kHz. Impedance spectroscopy (IS) measurements were performed in the frequency range from 5 Hz to 1 MHz. A home-built impedance cell connected to an HP 4192A RF impedance analyzer was used to record impedance spectra composed of a well-defined dc-plateau and a dispersive regime showing up at higher frequencies.

In Fig. 1 A the relaxation rates T_1^{-1}, $T_{1\rho}^{-1}$ and the decay rates τ_{SAE}^{-1} are shown as functions of inverse temperature. Below 500 K the T_1^{-1} rates probed in the laboratory frame are controlled by non-diffusive background effects, only. This is in contrast to the $T_{1\rho}^{-1}$ and SAE NMR results. Already above 300 K both the ^{7}Li NMR spin-lattice relaxation in the rotating frame of reference as well as the decay of ^{7}Li NMR spin-alignment echoes are clearly induced by Li diffusion. The SAE decay rates τ_{SAE}^{-1} were derived from ^{7}Li SAE NMR two-time correlation functions $S_2(t_m,t_p,t)$ shown in Fig. 1 B. The S_2 decay curves were measured as a function of mixing time t_m but at constant preparation time t_p of 10 µs. In both cases the rates follow Arrhenius behavior revealing two different activation energies of $E_A^{SLR} = 0.75(2)\,eV$ and $E_A^{SAE} = 0.51(4)\,eV$, respectively. IS measurements yield an activation energy of $E_A^{dc} = 0.81(1)\,eV$ which is in good agreement with that deduced from $T_{1\rho}^{-1}$ measurements. The differences in the activation energies point to a highly heterogeneous Li dynamics in the investigated oxide which is corroborated by the fact that the S_2 curves do not follow single-exponential time behavior. Instead, they can be best described by stretched exponentials.

The NMR results clearly reveal that the Li diffusivity in the investigated oxide is rather slow. This is confirmed by an analysis of the ^{7}Li NMR line width as a function of temperature. Significant motional narrowing of the central line is observed at 355 K pointing to a Li jump rate τ^{-1} of the order of $10^3\,s^{-1}$. This value is in reasonable agreement with the rate probed by SAE NMR at this temperature. For comparison, at 400 K the dc-conductivity is only 4×10^{-9} S/cm, which is by two orders of magnitude smaller than that of the above mentioned $LiTaO_3$ sample [3].

However, preliminary NMR studies on other samples, which were prepared from the corresponding bromides instead of the chlorides (see above), indicate a Li diffusivity comparable to that of the nanostructured $LiTaO_3$ sample of Ref. [3]. Presumably, further improvements of the transport properties of materials prepared by gas-phase synthesis can be achieved.

References

[1] P. Heitjans, S. Indris, J. Phys.: Condens. Matter 15 (2003) R1257.
[2] P. Heitjans, M. Masoud, A. Feldhoff, M. Wilkening, Faraday Discuss. 134 (2007) 67.
[3] M. Wilkening, V. Epp, A. Feldhoff, P. Heitjans, J. Phys. Chem. C 112 (2008) 9291.
[4] T. Giesenberg, S. Hein, M. Binnewies, G. Kickelbick, Angew. Chem. Int. Ed. 43 (2004) 5697.
[5] E. Fukushima, S. B. W. Roeder, Experimental Pulse NMR: A Nuts and Bolts Approach, Addison-Wesley, Reading, 1981.
[6] J. Jeener, P. Broekaert, Phys. Rev. 157 (1967) 232.