Nanostructured solid electrolytres: Increasing the Li diffusivity of poorly conducting $Li_2B_4O_7$ by mechanical treatment

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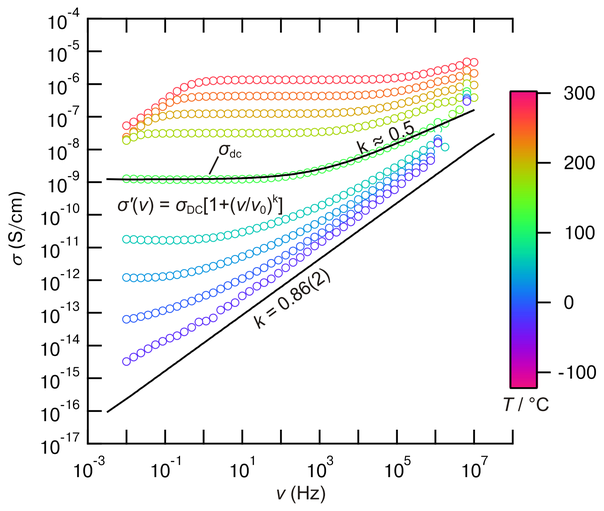
Introduction & motivation

In many cases fast solid ion conductors are characterized by a large number fraction of different kinds of defects that enable the ions to move over long distances.[1] High-energy ball milling is an easily applicable top-down approach to prepare nm-sized crystallites and to introduce structural disorder.[2,3]

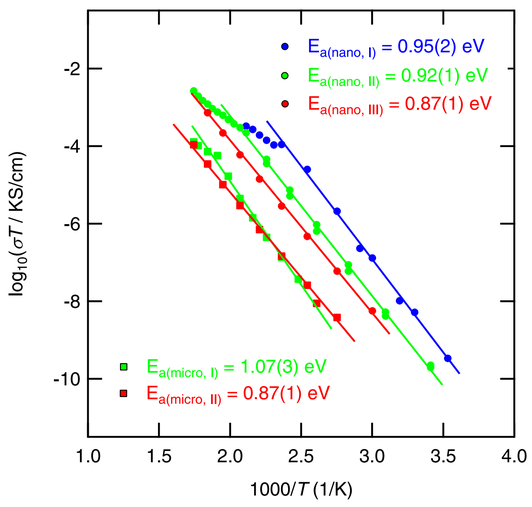
Lithium tetraborate, $Li_2B_4O_7$ (LBO), with an average particle size in the µm range is known as a very poor Li ion conductor. The conductivity of Li^+ can be increased by several orders of magnitude when the oxide is mechanically treated in a high-energy planetary ball mill.

The effect of different milling times on the ion dynamics in $Li_2B_4O_7$ was complementarily studied by both impedance spectroscopy and Li nuclear magnetic resonance (NMR) spectroscopy.

Impedance spectroscopy



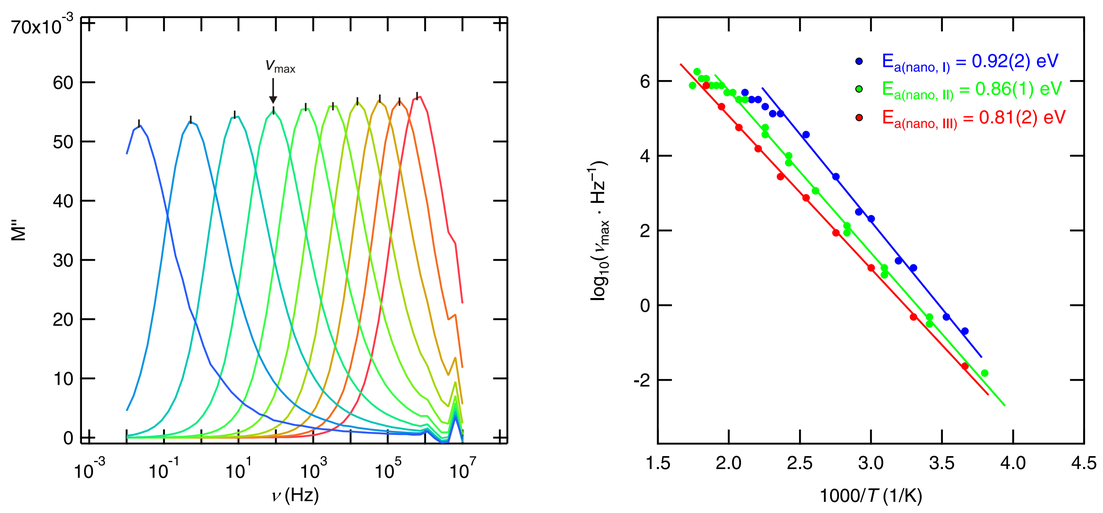
- **conductivity spectra** of nanocrystalline LBO at temperatures *T* ranging from 243 and 543 K
- 303 to 543 K: dc plateau and dispersive region at higher frequencies
- low-frequencies, high temperatures: electrode polarization effects



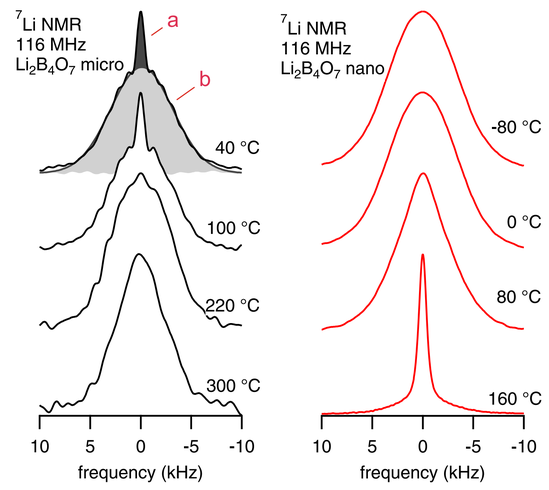
- **Arrhenius plot** of $\sigma_{dc}T$ vs inverse temperature $1/T$
- I, II and III denote subsequent annealing steps
- Li conductivity in nano-LBO is about three orders of magnitude higher than that of micro-LBO

MODULUS REPRESENTATION

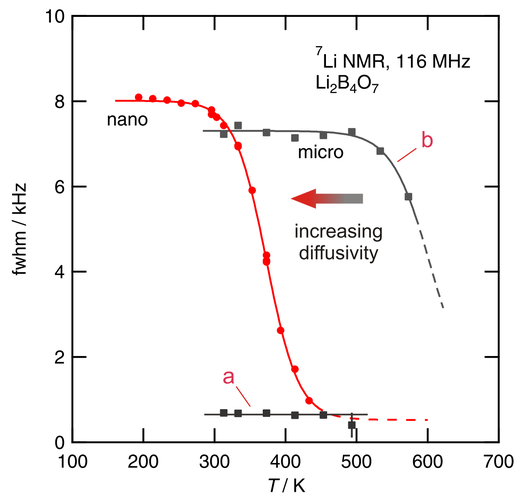
- maxima of modulus peaks yield thermally activated relaxation rates: $2\pi \times \nu_{max} = 1/\tau$
- shape of modulus spectra remains unchanged with increasing *T* (see also conductivity spectra, *i.e.*, fullfilling master curve scaling)
- activation energies E_a are very similar to those obtained from σ_{dc}



^{7}Li NMR spectroscopy



- microcrystalline sample reveals two spectral components; major signal (b) reflects slow ions while sharp line (a) represents a small fraction of fast Li ions
- pronounced motion-induced NMR line narrowing compared to microcrystalline LBO

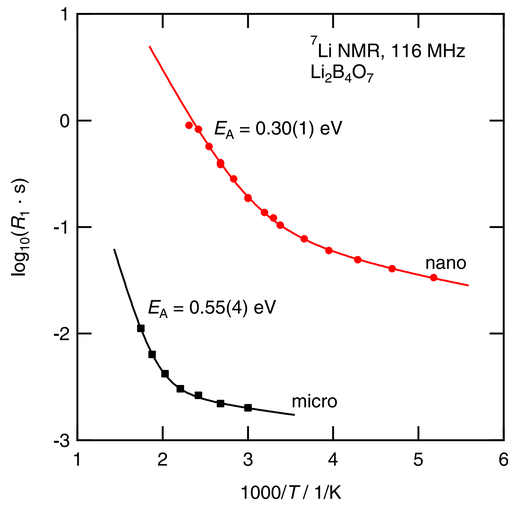


MOTIONAL NARROWING (MN)

- ^{7}Li NMR line width (fwhm) as a function of temperature
- onset of MN shifted towards lower *T* for the milled sample (from about 500 K to 300 K)
- sharp line (a) of micro LBO shows almost no further MN

SPIN-LATTICE RELAXATION RATES

- NMR rates ($1/T_1$) plotted vs $1/T$
- activation energy (E_a) of micro-LBO is much larger (0.55(4) eV) compared to nano (0.30(1) eV)
- increase of „background rates" in nano LBO ➡ localized jumps, non-diffusive contributions, ...



Conclusions & outlook

- **high-energy ball milling** represents a powerful tool to prepare nanocrystalline materials characterized by a large degree of structural disorder
- here, ion **dc conductivity** of ball-milled LBO is **increased by three orders of magnitude**
- the effect is **corroborated by NMR** line shape and spin-lattice relaxation measurements (NMR: $E_{a(nano)} < E_{a(micro)}$)

OUTLOOK

- preparation of two-phase composites consisting of ion conductor (LBO) and insulator such as B_2O_3, Al_2O_3
- investigation of Li transport in LBO glass

References

[1] M. Winter, J. O. Besenhard, M. E. Spahr, P. Novák, *Adv. Mater.*, **10** (1998) 725.
[2] J. Maier, *Solid State Ion.*, **131** (2000) 13.
[3] M. Wilkening, V. Epp, A. Feldhoff, P. Heitjans, *J. Phys. Chem. C.*, **112** (2008) 9291.

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