Li Diffusion in Garnet-type $Li_{6.5}La_{2.5}Ba_{0.5}ZrTaO_{12}$ Crystallizing with Cubic Symmetry

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Introduction and Motivation

Today, lithium-ion batteries see an ever increasing use in various portable electronic devices. Furthermore, together with the demand for (hybrid) electric vehicles the development of clean energy storage systems is expected to be of overriding importance in the near future.

This application area is in need of lithium-ion cells which meet the following requirements: (i) a high energy density, (ii) environmental compatibility, and (iii) chemical compatibility of electrolyte and cathode.

Recently, garnet-type oxides with the nominal chemical compositions $Li_5La_3M_2O_{12}$ (M = Nb, Ta, Sb), $Li_6La_2AM_2O_{12}$ (A = alkaline earth) and $Li_7La_3Zr_2O_{12}$ have been developed and studied for this purpose [1].

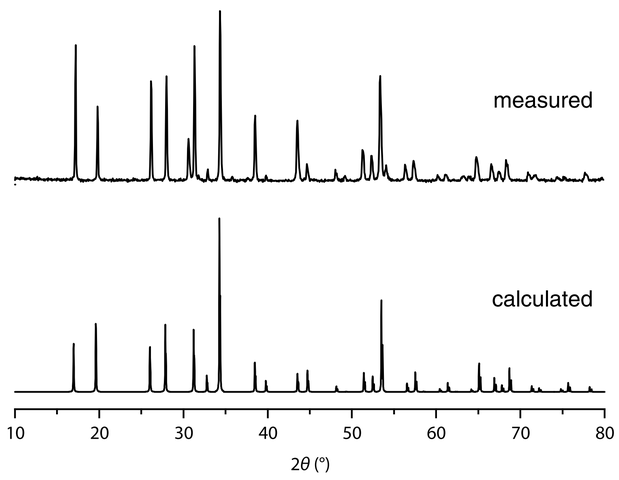
In this study we examine Li diffusion parameters of cubic $Li_{6.5}La_{2.5}Ba_{0.5}ZrTaO_{12}$ by means of ^{7}Li NMR spectroscopy.

Synthesis

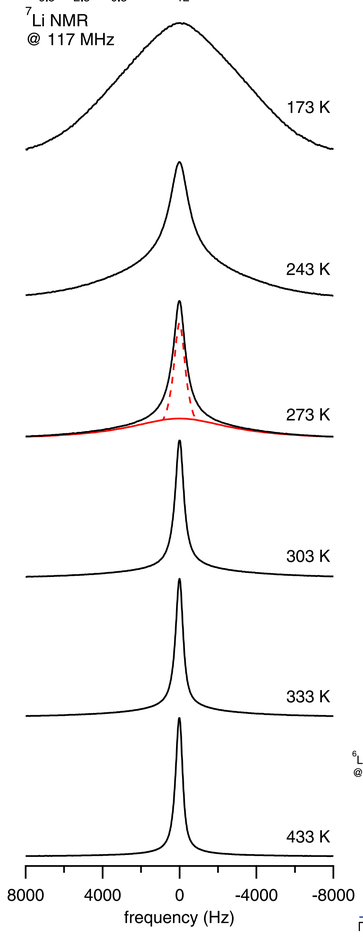
- cubic $Li_{6.5}La_{2.5}Ba_{0.5}ZrTaO_{12}$ was prepared by conventional solid state synthesis (ceramic method)
- precursors: $LiNO_3$, La_2O_3, $Ba(NO_3)_2$, ZrO_2, and Nb_2O_5
- stoichiometric amounts of precursors were milled in planetary ball mill (12 h at 200 rpm, in 2-propanol)
- mixture was heated for 6 h at 973 K
- resultant powder was ball-milled again to ensure homogeneous mixing and then pressed into pellets (isostatic pressure: 300 kN)
- pellets were sintered for 6 h at 1373 K

Structural Characterization

- XRPD peaks can be indexed according to **cubic** garnet-like parent $Li_5La_3Nb_2O_{12}$
- space group: *Ia*–3*d*, cell constant: a = 12.775(4) Å
- BSEM & WDS indicate uniform distribution of heavy elements in $Li_{6.5}La_{2.5}B_{0.5}ZrTaO_{12}$

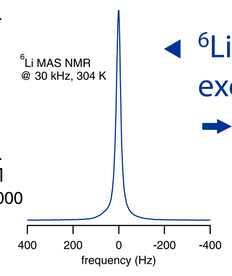


^{6,7}Li NMR Measurements



^{6,7}Li NMR Spectra

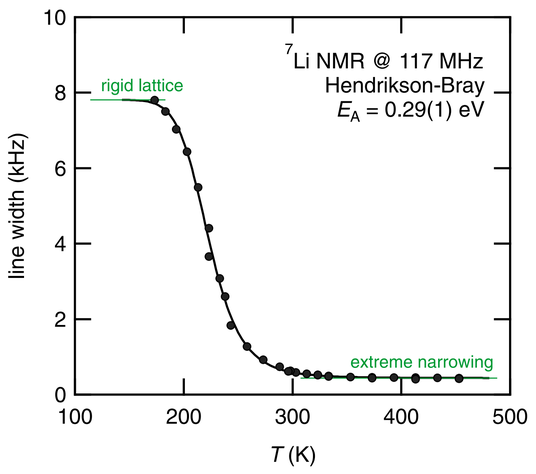
- spectra recorded at temperatures between 173 K and 433 K
- at low T: dipolarly broadened lines (Li-Li interactions)
- with increasing T: homonuclear dipole-dipole interactions averaged due to onset of fast local Li jumps ($1/\tau \approx 10^3\ s^{-1}$)
- at intermediate T: spectra composed of two contributions
  ➡ broad Gaussian and motionally narrowed Lorentzian line shape (*cf.*, [2])
- heterogeneous line narrowing points to distribution of jump rates, reflecting slow and fast Li ions in the garnet [3]



◀ ^{6}Li MAS NMR spectra indicate rapid Li exchange process
➡ single, extremely narrow line (fwhm ≈ 20 Hz at RT and 30 kHz spinning rate)

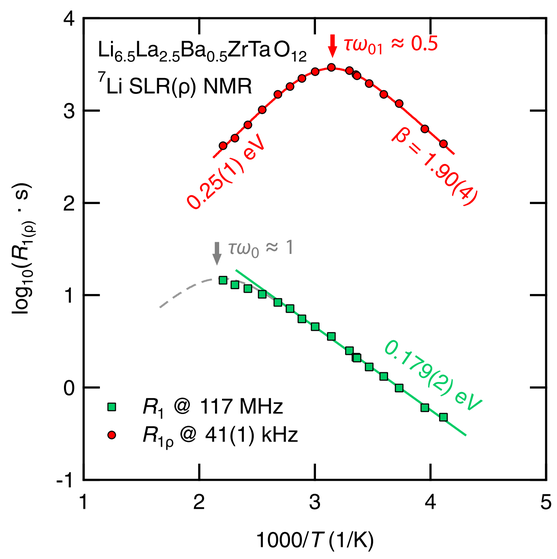
Motional Narrowing (MN)

- almost full MN curve obtained
- curve offers rough estimation of **short length-scale** Li diffusion parameters
- onset of significant MN **at 200 K**
  ➡ $1/\tau \approx 10^3\ s^{-1}$, $D_{sd} \approx 7 \times 10^{-14}\ cm^2 s^{-1}$
- inflection point of MN curve **at 230 K**
  ➡ $1/\tau \approx 5 \times 10^4\ s^{-1}$, $D_{sd} \approx 3.5 \times 10^{-12}\ cm^2 s^{-1}$
- expressions introduced by Waugh and Fedin [4] and Hendrickson and Bray [5] yield activation energies of $E_{a,MN} \approx 0.3$ eV and $E_{a,MN} \approx 0.29$ eV, respectively



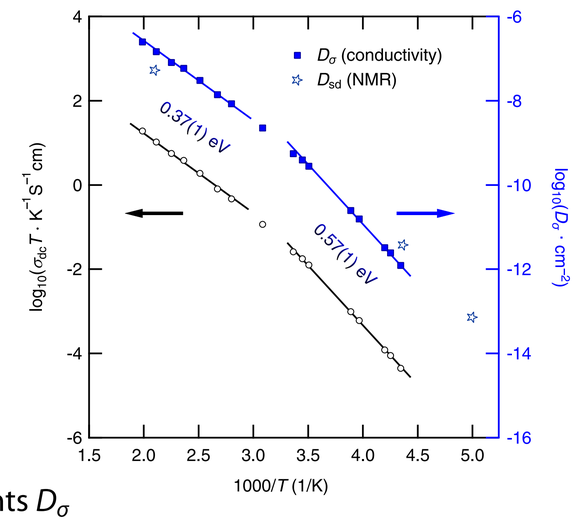
^{7}Li NMR Spin-Lattice Relaxation (SLR)

- ^{7}Li NMR SLR rates measured in laboratory (R_1) and rotating ($R_{1\rho}$) frame of reference
- diffusion-induced rate maximum **at 320 K**
  ➡ $1/\tau_{R_{1\rho}} \approx 5 \times 10^5\ s^{-1}$ ($\tau\omega_{01} \approx 0.5$, $\omega_{01}/2\pi$ = 41 kHz)
  ➡ much smaller than expected from σ_{dc} and MN
- $E_{a,R_{1\rho}} = 0.25\ eV > E_{a,R_1}$ (low-T flank)
- β indicates deviation from BPP-type behaviour [6]
  ➡ $\beta = 2$: uncorrelated motion
  $1 < \beta < 2$: correlated motion
- R_1-values: maximum expected at **T > 460 K**
  ➡ $1/\tau_{R_1} \approx 7 \times 10^8\ s^{-1}$ ($\tau\omega_0 \approx 1$, $\omega_0/2\pi$ = 117 MHz)



Impedance Spectroscopy

- dc-conductivity σ_{dc} probed follows Arrhenius behaviour
- above 330 K activation energy $E_a \approx 0.37$ eV is obtained
- below 300 K E_a increases (0.57 eV)
  ➡ indication for change in conduction mechanism
- activation energies and absolute conductivity values comparable with those of other garnet-type Li ion conductors
- from σ_{dc} macroscopic diffusion coefficients D_σ can be calculated using Nernst-Einstein relation
- self-diffusion coefficients D_{sd} estimated from ^{7}Li NMR measurements are in good agreement with D_σ



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