Conductivity of Mechanosynthesized Phase-Pure Cubic and Tetragonal $BaSnF_4$

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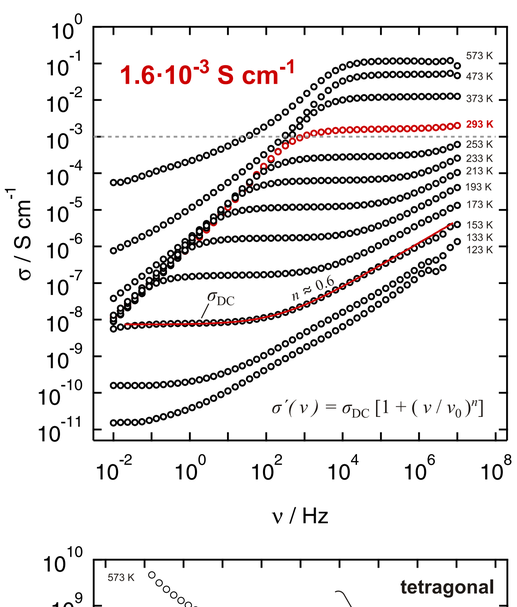
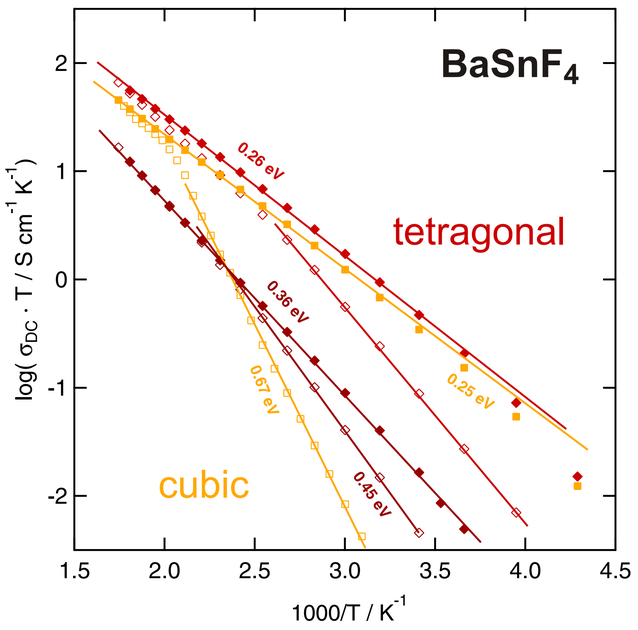
Introduction & Motivation

$BaSnF_4$ was investigated due to its promising properties to be used as a solid **fluorine-ion conductor** in, e.g., fluorine-ion batteries, which were recently reported by Reddy et al [1]. Here, **mechanosynthesized $BaSnF_4$** was investigated by means of broadband impedance spectroscopy over a large temperature range. The ternary fluoride exists in a metastable cubic form and a **highly conductive tetragonal modification** [2]. The preparation of the phase pure cubic modification has been achieved by fine tuning of the ball-milling conditions. The transport parameters of tetragonal, layered $BaSnF_4$ strongly depend on the annealing conditions chosen. A sample with an extraordinary high ion conductivity, reaching the values of $PbSnF_4$, was prepared by shortening the annealing time to inhibit grain growth of the polycrystalline powder.

Results & Discussion

■ **conductivity isotherms**





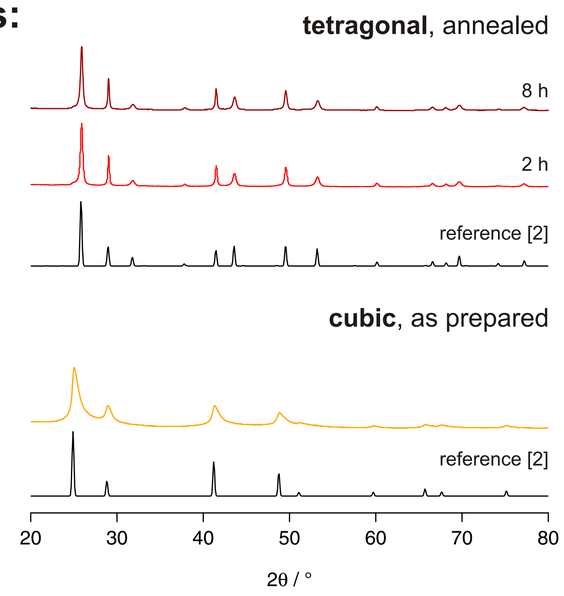
□ **preparation & measurements:**

■ **X-ray diffraction (XRD)**

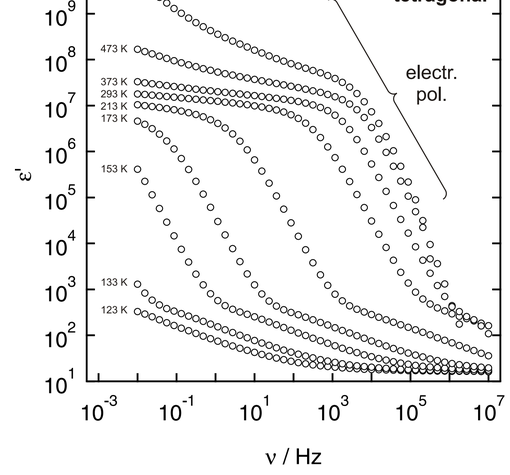
- ball-milled, 180 balls / 4 g powder, 600 rpm,10 h (40 cycles), argon atmosphere
- annealed, 2 h, 573 K, N_2 atmosphere
- annealed, 8 h, 573 K, N_2 atmosphere

■ **impedance measurements**

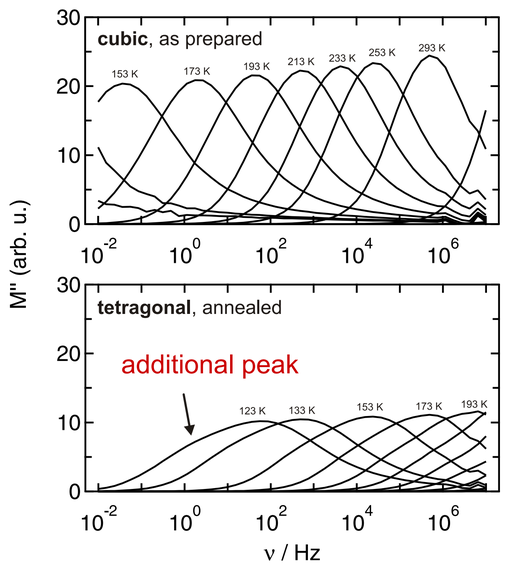
- as prepared
- annealed
- linear fit
- heating
- cooling



■ **permittivity spectra**



■ **modulus representation**



□ **electric modulus:**

- cubic → tetragonal: modulus peaks shift towards higher frequencies
- tetragonal: evolution of additional peak upon heating which decreases with increasing annealing time

□ **transport properties of polycrystalline $BaSnF_4$:**

- increase of ion conductivity by three orders of magnitude (293 K) upon phase transition
- very high ion conductivity of **$1.6 \cdot 10^{-3}$ S·cm^{-1}** at **room temperature** compared to other polycrystalline materials reported in the literature:
  - $PbSnF_4$: $\sigma_{DC} \approx 1 \cdot 10^{-3}$ S·cm^{-1} [3]
  - $La_{0.9}Ba_{0.1}F_{2.9}$: $\sigma_{DC} \approx 1 \cdot 10^{-6}$ S·cm^{-1} [1]
  - $Ba_{0.5}Ca_{0.5}F_2$: $\sigma_{DC} \approx 3 \cdot 10^{-8}$ S·cm^{-1} [4]
- low activation energy for long-range ion transport (0.25 eV)

- XRD patterns confirm phase purity of the as prepared and annealed samples
- control of phase purity by variation of ball-milling conditions
- peak narrowing reflects crystallite growth after annealing

Outlook

- characterization of the electrochemical stability window employing **solid-state cyclic voltammetry**
- **polarization experiments** to evaluate contribution of electronic conductivity
- **transmission electron microscopy** to study crystallite structure and morphology
- structural investigation by means of **^{19}F MAS (magic angle spinning) NMR spectroscopy**, studying diffusion parameters
- further increase of conductivity via mono- and trivalent **doping** by, e.g., LaF_3

References & Acknowledgment

[1] Reddy, M. A.; Fichtner, M. *J Mater Chem*, **2011,** *21*, 17059.
[2] Ahmad, M. M.; Yamane, Y.; Yamada, K. *J Appl Phys*, **2009,** *106*, 074106-1.
[3] Dénès, G.; Birchall, T. *Solid State Ionics*, **1984**, *13*, 213.
[4] Düvel, A.; Ruprecht, B.; Heitjans, P.; Wilkening, M. *J Phys Chem*, **2011**, *115*, 23784.

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