Experimental report

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Proposal:	**5-21-1106**	**Council:**	10/2016
Title:	Pathways of Sodium-Ion Diffusion in NaxTiS2 (x = 0.5, 0.9)		
Research area:	Chemistry		

This proposal is a new proposal

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Samples: Na0.5TiS2
Na0.9TiS2

Instrument	Requested days	Allocated days	From	To
D2B	3	2	06/03/2017	08/03/2017

Abstract:

We intend to determine the pathways of thermally induced diffusion in the layered polytypic materials Na0.5TiS2-3R1 and Na0.9TiS2-3R2, ultimately aiming at the detection of weak cation interactions in the co-intercalates LixNayTiS2 (x + y <= 1). To this end, powder neutron diffractometry at high temperature followed by careful analysis of the Debye-Waller factors including anharmonic contributions is necessary. Reconstruction of the scattering-length density using the maximum-entropy method (MEM) and derivation of probability-density functions (PDFs) allows mapping of the actual ion pathways. The associated effective one-particle potentials (OPPs) give access to the energy barriers for migration. Comparing these results to high-temperature NMR investigations (Prof. Wilkening, Graz) and quantum-chemical computations (Prof. Bredow, Bonn), we hope to acquire a fundamental understanding of mobility in sodium-ion conductors and lay a foundation for further experiments with mixed alkali-cation sets.

Experimental Report

Pathways of Sodium-Ion Diffusion in Na_xTiS_2 *(x = 0.5, 0.9)*

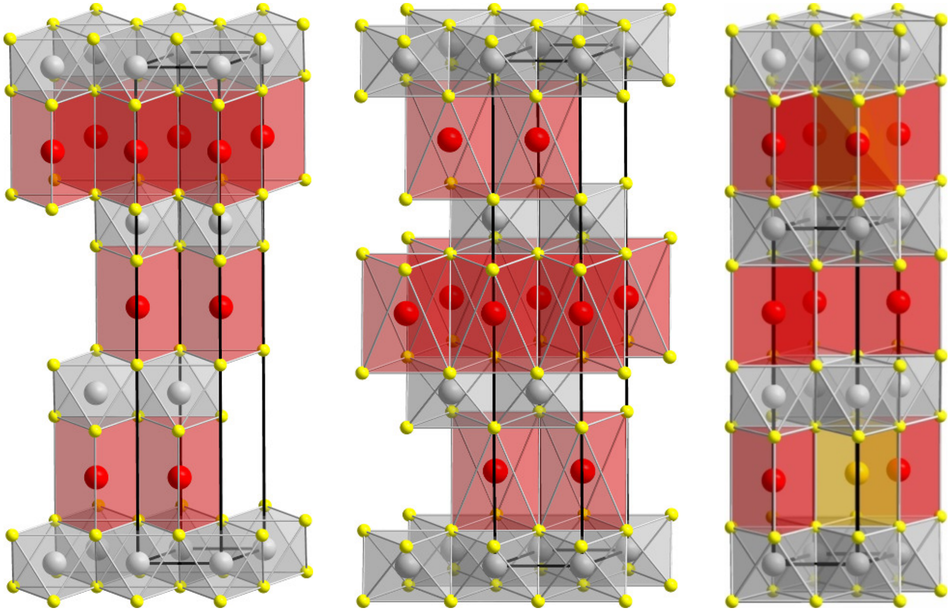

Fig. 1. Structures of Na_xTiS_2-3R_1 (left), -3R_2 (center), and -2H (right) at r.t. (red/orange: Na^+/□, gray: Ti^{3+}/Ti^{4+}, yellow: S^{2-}; arbitrary radii, unit cell in black).

Layered lithium-ion conductors are a hugely successful substance class for energy storage, whereas high-voltage low-cost sodium analogues do not play a commercial role yet. Using high-temperature neutron diffraction, we aim to investigate the possible interplay of the two types of mobile alkali cations in the layered materials $Li_xNa_yTiS_2$ ($x + y \leq 1$). To start this endeavor, we want to map diffusion pathways and determine activation barriers in powders of Na_xTiS_2 as one endpoint of the series. Studies on Li_xTiS_2, the other one, are already finished.[1,2] Careful evaluation of Debye–Waller factors (DWFs) including anharmonic contributions should allow for the modelling of probability-density functions (PDFs) and one-particle potentials (OPPs)—if data quality permits.

Diffractograms of powders with the tentative compositions $Na_{0.5}TiS_2$ and $Na_{0.9}TiS_2$ in a vanadium container were acquired at room temperature (r.t.), 300, 600, and 700 °C. Rietveld refinements of initial models were performed with Jana2006 using a pseudo-Voigt profile following the Thompson–Cox–Hastings approach.[3] Besides standard corrections (background model with ten Legendre polynomials interpolating manually defined points, zero-shift correction, and two-term Bérar–Baldinozzi asymmetry correction), a slight preferred orientation in the (001) plane was modelled for $Na_{0.9}TiS_2$ according to March and Dollase. A minor by-phase—probably steel in the beam path—was treated as austenite.

Models could be refined to indicators $R_p \leq 0.028$, $wR_p \leq 0.037$, $S \leq 2.1$, $R_F \leq 0.041$, and $R_B \leq 0.065$ (Na_xTiS_2 phase, all reflections). Although the diffractograms are of ample quality, fits were significantly better for high temperatures; difference plots show some inexplicable features (small additional reflections, broadening of the {003} reflection at $2\theta \approx 13°$). During some refinements, a few displacement parameters behaved rather unruly and showed strong correlations. Thus, displacement had to be restricted to be isotropic or at least harmonic in many cases.

For $Na_{0.5}TiS_2$, we found the expected 3R_1 polytype. We were, however, surprised to detect $Na_{0.9}TiS_2$ in its 2H instead of the 3R_2 structure (see Fig. 1). The main difference between the latter two is the trigonal prismatic coordination of the sodium ions and the existence of two partly occupied, independent sodium positions, but only one sulfide position in Na_xTiS_2-2H. Refinements indicate a sodium content of significantly less than 0.9.

Nevertheless, it was obvious that the sodium ions exhibit—presumably static—disorder manifesting in enlarged displacement parameters already at r.t. In comparison to those of the titanium and sulfide ions, they increase disproportionately with temperature (*cf.* Fig. 2) and show anharmonicity from 300 °C upwards. This is caused by the onset of thermally activated sodium-ion diffusion. The oblate shape of the displacement ellipsoids suggests that the migration pathways extend in the (001) plane.

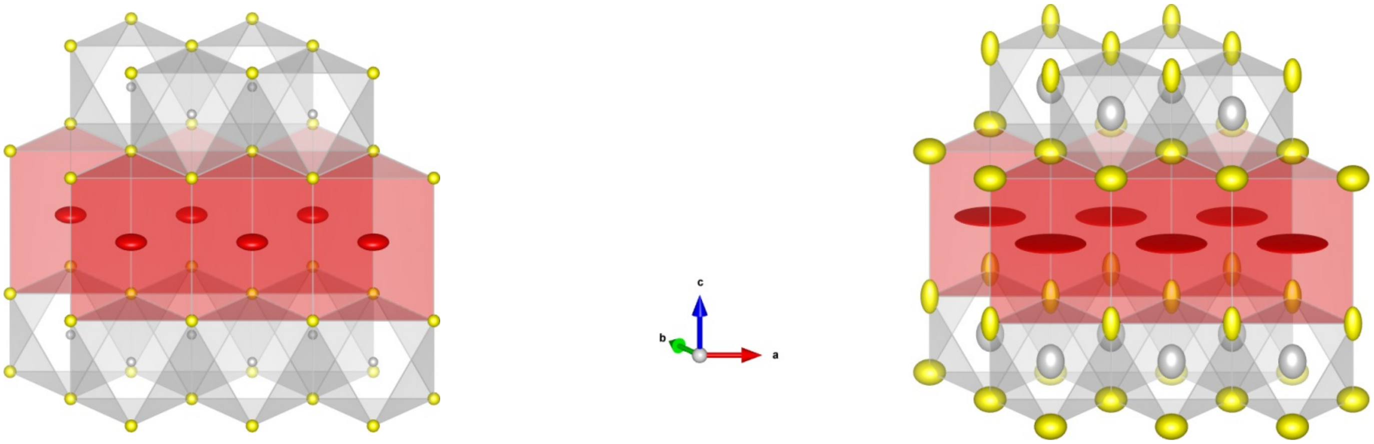

Fig. 2. Structure of $Na_{0.5}TiS_2$-3R_1 at r.t. (left) and 600 °C (right). Ellipsoids/spheres for 90% probability (red: Na^+/□, gray: Ti^{3+}/Ti^{4+}, yellow: S^{2-}; unit cell in black).

Models of the sodium PDFs at high temperatures shows that this is indeed the case (see Fig. 3): diffusion pathways in the *ab* plane, which are slightly curved for $Na_{0.5}TiS_2$-3R_1 and straight for $Na_{0.9}TiS_2$-2H, connect neighboring sodium positions. Using the OPP formalism, preliminary activation barriers for migration are estimated to be roughly 0.5 eV and 0.2 eV for $Na_{0.5}TiS_2$-3R_1 and $Na_{0.9}TiS_2$-2H, respectively. These values will be compared to those measured for $Li_{0.7}TiS_2$-3R and $Li_{0.9}TiS_2$-3R (*ca.* 0.5 eV and *ca.* 1.5 eV, respectively).[2]

Fig. 3. Detail of the structure of $Na_{0.5}TiS_2$-3R_1 (left) and $Na_{0.9}TiS_2$-2H (right) at 600 °C with isosurface plot of sodium PDF for $F = 0.003$ Å^{-3} (red: Na^+, yellow: S^{2-}; ions with arbitrary radius).

[1] D. Wiedemann, M. M. Islam, S. Nakhal, A. Senyshyn, T. Bredow, M. Lerch, *J. Phys. Chem. C* **2015**, *119*, 11370–11381.

[2] D. Wiedemann, S. Nakhal, A. Senyshyn, T. Bredow, M. Lerch, *Z. Phys. Chem.* **2015**, *229*, 1275–1288.

[3] V. Petříček, M. Dušek, L. Palatinus, *Z. Kristallogr. – Cryst. Mater.* **2014**, *229*, 345–352.