Crystal Structure of 3R-LiTiS₂ and its Stability Compared to Other Polymorphs

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Dedicated to Professor Wolfgang Bensch on the Occasion of His 60th Birthday

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Abstract. The crystal structure of 3R-LiTiS₂ was studied with combined experimental and theoretical approaches. The 3R polymorph of lithium titanium disulfide crystallizes rhombohedrally in the well-known NaCrS₂ type with lattice parameters a = 352.98(1) pm, c = 1807.51(3) pm. The relative stability of 3R-LiTiS₂ with respect to

Introduction

Titanium disulfide is known to be a highly suitable host material for species such as Li⁺ or Na⁺,^[1,2] ammonia, and many other guests. Lithium ions can be easily inserted into the van der Waals gap between the TiS₂ layers electrochemically or chemically by treatment with *n*-butyllithium.^[2] Titanium disulfide has been a promising new intercalation electrode material when it was developed by the *Whittingham's* group at Exxon Laboratories in 1976.^[3] The discovery of the TiS₂ intercalation chemistry was followed by the development of new Li-ion batteries and higher voltage electrode materials like LiCoO₂.^[4]

Two polymorphs of titanium disulfide (1T- and c-TiS₂) are known. 1T-TiS₂ exhibits the well-known cadmium iodide CdI₂-type structure (space group $P\bar{3}m1$). It can be described as layered structure consisting of S–Ti–S "sandwiches" stacked upon each other and held together by relatively weak van der Waals forces. In addition, a cubic spinel-type polymorph exists.^[5,6] prepared by removing copper out of the thiospinel CuTi₂S₄. As mentioned above, lithium can be intercalated electrochemically or chemically (using solution of *n*-butyllithium in hexane) at room temperature, forming compounds Li_xTiS₂ with *x* up to 1.0.

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other known and hypothetical polymorphs was evaluated theoretically at DFT level employing the hybrid method B3LYP. 3R-LiTiS₂ is less stable than the most common 1T phase (by 4 kJ·mol⁻¹), and is more stable (by 5 kJ·mol⁻¹) than the known phase c-LiTiS₂ thus confirming the importance of this phase for further investigations.

In 1T-LiTiS₂ lithium occupies the octahedral voids between the S-Ti-S layers, in the spinel-type phase it is found on the 16c position, also octahedrally coordinated by sulfur.^[7] It should be mentioned that in both binary sulfides all titanium ions are octahedrally coordinated. In 1989, Colbow et al.[8] reported the synthesis of a 3R-polymorph of LiTiS₂ by reacting Li₂CO₃ with 1T-TiS₂ in graphite capsules. Unfortunately, no refined structural parameters are given. Compared to the 1Ttype, the 3R-type shows a different stacking sequence of the sulfide layers (for details see Figure 1). Electrochemical delithiation of 3R-LiTiS₂ did not result in the formation of 3R-TiS₂. At $x \approx 0.4$ a non-reversible transformation to the 1Tphase is observed. Taking into consideration the enormous interest in Li, TiS₂ as electrode material for electrochemical applications it is surprising that 3R-LiTiS₂, which exhibits a higher average voltage against lithium compared to 1T-LiTiS₂,^[8] has attracted no real attention in the following years. The authors show a charge curve down to the transformation to the 1T phase but, unfortunately, carried out no cycling experiments within the 0.4-1.0 range.^[8]

Apart from 1T-LiTiS₂, 3R-LiTiS₂, and c-LiTiS₂, two additional polymorphs (not known yet for LiTiS₂) can be considered: the 2H-phase exhibiting a different stacking sequence for sulfur, which is reported for LiNbS₂ (space group $P6_3/mmc^{[9]}$). Another hypothetical rhombohedral polymorph has AgCrSe₂-type structure^[10] (space group R3m). All these five crystal structures are illustrated in Figure 1.

In this contribution we report a joint experimental and theoretical investigation on 3R-LiTiS₂. The crystal structure was refined by means of X-ray powder diffraction. Quantum-chemical calculations based on the DFT/Hartree-Fock hybrid method B3LYP were performed on different polymorphs of

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Figure 1. Comparison of the crystal structures of 1T-LiTiS₂ (top left), c-LiTiS₂ (top right), 3R-LiTiS₂ (bottom left), 2H-LiNbS₂ (bottom middle), and AgCrSe₂ (bottom right). Unit cells are shown as solid lines.

LiTiS₂ such as 1T, 3R, c, 2H, and AgCrSe₂-type. Their relative stability was evaluated on the basis of fully relaxed structures.

Experimental Section

Preparation and Chemical Characterization: 3R-LiTiS₂ samples were prepared via two different routes: (1) titanium powder, sulfur, and lithium sulfide Li2S (ABCR, 99.9%) were dried under vacuum at 100 °C for 24 h. A stoichiometric mixture was heated at 800 °C for two weeks in a sealed evacuated silica glass tube and then rapidly quenched to ambient temperature. The reaction products always contain ca. 10% spinel-type $Li_{1+r}Ti_{2-r}O_4$ and TiO_2 (rutile), respectively, as also reported by Colbow et al.^[8] Therefore the samples were reheated in a flowing H₂S gas stream in an alumina crucible at 750 °C for 4 h (phase purity ≈90%, see next section). Excess sulfur was removed at 150 °C in vacuo. (2) In a first step, 1T-TiS₂ was prepared by mixing titanium and sulfur powders (ratio 1:2.1) followed by a thermal treatment at 500 °C for two weeks. This was reacted with lithium sulfide Li₂S (alumina crucible) in a flowing H₂S gas stream at 700 °C for 4 h to give 3R-LiTiS₂ (phase purity 95%, TiS₃ as second phase). Whereas the powder from the first route contains larger amounts of side phases it was chosen for structural characterization. The second route always led to samples exhibiting severe texture effects. It should be mentioned that Colbow et al.^[8] prepared Li_xTiS₂ phases with x =0.4–1.0. The reported cell volume of their x = 1 sample is in good agreement with that of the material reported herein. This may be interpreted as an indication that x is ca. 1.0 in our sample.

The powders were chemically characterized with a Leco EF-TC 300 N_2/O_2 analyzer (hot gas extraction) for oxygen content determination. The absence of silicon and aluminum was checked by means of X-ray fluorescence analysis (PANalytical Axios PW4400/24 X-ray fluorescence spectrometer with an Rh-tube and a wavelength dispersive detector).

Crystal Structure Determination: A PANalytical X'Pert PRO MPD diffractometer [Cu- K_{α} radiation, Bragg-Brentano (θ - θ) geometry] with a PIXcel detector was used for the powder XRD measurements. Structural refinements were carried out with the program package FULL PROF 2006.^[11] The reflection profiles were fitted with a pseudoVoigt function.

Computational Methods: A full optimization of all non-symmetry determined atomic coordinates and lattice parameters was performed for five different polymorphs of LiTiS2 with periodic quantum-chemical calculations at DFT level. The well-known B3LYP hybrid method^[12,13] was used as implemented in the plane wave program VASP.^[14-16] The projector-augmented wave (PAW) method^[17,18] was used for the core electron representation. We used a converged value of the plane-wave cutoff energy $E_{cut} = 364 \text{ eV}$, derived from preliminary test calculations. The integration in reciprocal space was performed with a Monkhorst-Pack grid^[19] using $8 \times 8 \times 4$, $6 \times 6 \times 6$, $15 \times 15 \times 3$, $12 \times 12 \times 3$, and $14 \times 14 \times 2$ k points for 1T, c, 3R, 2H, and AgCrSe₂-type LiTiS₂ polymorphs, respectively. With these settings the **k** point density in the irreducible Brillouin zone is comparable in all systems. The SCF energy convergence was set to 10⁻⁴ eV per cell. In all cases, the magnetic ground state was assumed to be ferromagnetic in order to reduce the computational effort and all the calculations were performed with the spin-polarized method (unrestricted Kohn-Sham, UKS). The effect of functional on the calculated structural parameters was further checked by using a pure DFT method based on the Perdew-Burke-Ernzerhof (PBE) functional.^[20,21] In order to consider the effect of dispersion forces due to the presence of van der Waals gaps between the sulfur layers, we used recently proposed DFT-D method (PBE-D) based on D3^[22] empirical correction scheme.

Results and Discussion

Crystal Structure Refinement

3R-LiTiS₂ was prepared as described in the Experimental Section. The crystal structure was refined using conventional X-ray powder techniques, structural parameters are presented in Figure 2, Table 1, and Table 2. 3R-LiTiS₂ crystallizes rhombohedrally in the NaCrS₂ type;^[23] the unit cell contains three formula units. As side phases, $Li_{1+x}Ti_{2-x}O_4$ (ca. 2%) and TiO_2 (rutile, ca. 9%) are observed. The crystal structure is derived from a cubic closest-packing of the anions with titanium occupying one half of the octahedral voids. Along the c axis there is an alternate sequence of fully occupied and empty layers. As a consequence, TiS2 "sandwiches" are formed. Lithium occupies the remaining octahedral voids between these sandwiches. No indication for titanium on lithium positions (or oxygen on sulfur positions) was found in the Rietveld refinement. Figure 3 depicts a detailed representation of the crystal structure of 3R-LiTiS₂. All cations are perfectly coordinated by six anions forming octahedra.



Figure 2. X-ray powder diagram of 3R-LiTiS₂ with the results of the Rietveld refinement. Markers: upper row: LiTiS₂, middle: Li_{1+x}Ti_{2-x}O₄, lower row: TiO₂ (rutile).

Table 1. Refined structural parameters for 3R-LiTiS₂.

Structure type	NaCrS ₂
Space group	R3m
Crystal system	rhombohedral
Lattice parameter /pm	a = 352.98(1)
	c = 1807.51(3)
Unit cell volume /10 ⁶ pm ³	V = 195.03(1)
Density /g·cm ⁻³	3.04
Formula units	Z = 3
Diffractometer	PANalytical X'Pert PRO MPD
2θ range /°	10–120
R _{wp}	0.037
R _{Bragg}	0.040
R _{exp}	0.019
S	1.95

The average bond lengths between titanium, lithium and the surrounding anions (shown in Figure 4) are the following: d(Ti-S) = 247.8 pm, d(Li-S) = 259.2 pm. These values are similar to the bond lengths known from 1T-LiTiS₂: $d(\text{Ti}-\text{S}) = 248.1 \text{ pm}, d(\text{Li}-\text{S}) = 257.2 \text{ pm}.^{[24]}$ The density of the 3R polymorph (3.04 g·cm⁻³) is slightly lower than that of the well-known thermodynamically stable 1T modification (3.08 g·cm⁻³, calculated from reference^[24]). Interestingly, up to 800 °C no transformation to 1T-LiTiS₂ is observed.

Relative Stability of Various Polymorphs

After optimization of the cell parameters of the above-mentioned LiTiS_2 polymorphs, the energies per formula unit were compared among each other as shown in Figure 5. It can be



Figure 3. Unit cell of NaCrS₂-type 3R-LiTiS₂, outlined by black lines, together with the TiS₆- and LiS₆-polyhedra.



Figure 4. TiS_{6} - and LiS_{6} -polyhedra in 3R-Li TiS_{2} with the determined bond lengths.

seen that the most stable structure is 1T-LiTiS₂, followed by 3R-LiTiS₂ with an energy difference of $4 \text{ kJ} \cdot \text{mol}^{-1}$.

Table 2. Experimental and calculated atomic coordinates and refined Debye-Waller factors for 3R-LiTiS₂.

Atom	Wyck. site	x	у	z		$B_{\rm iso}$ /Å ²	-
		Exp.	Exp.	Exp.	Calc.		
Ti	3 <i>a</i>	0	0	0	0	1.82(5)	
Li	3 <i>b</i>	0	0	1/2	1/2	1.15	
S	6 <i>c</i>	0	0	0.2555(5)	0.255	1.50(4)	





Figure 5. Relative stability of all known polymorphs and plausible crystal structures of $LiTiS_2$ obtained with B3LYP.

It is important to note that the 3R phase is more stable than another known polymorph (c-LiTiS₂) by 5 kJ·mol⁻¹. This finding emphasizes the importance of the 3R-LiTiS₂ phase as an interesting material concerning electrochemical applications. According to the B3LYP results the 2H polymorph is less stable than 3R-LiTiS₂ and the AgCrSe₂-type phase is the least stable among all. This is reasonable as 2H- and AgCrSe₂-type structures are not even known yet for LiTiS₂.

Our calculated fractional coordinates for 3R-LiTiS₂ are compared with the experimental values in Table 2, which are in well accord with one another. In Table 3, the calculated structural parameters such as lattice parameters *a* and *c*, and bond lengths, Ti–S and Li–S (pm), are compiled.

Table 3. Calculated lattice parameters and bond lengths /pm for 3R-LiTiS $_2$.

		B3LYP	PBE	PBE-D	
Lattice parameters /p	m			1	
	а	359.9	350.7	349.4	
	С	1846.5	1834.0	1792.3	
Bond lengths /pm					
0 1	Ti–S	260.5	248.6	245.5	
	Li–S	253.4	259.0	257.4	

It is observed that the calculated lattice parameters with B3LYP approach are overestimated by up to 3% compared to the experimental values. The Ti-S bond length is larger (by 7%) compared to our experimental value. This is associated with the extension of the *c* lattice parameter ($\Delta c = 39$ pm). On the contrary, the Li–S bond length is slightly smaller (-2%)than the experimental value. The pure DFT approach PBE underestimates the experimental value of $a (\Delta a = -2.3 \text{ pm})$ and overestimates c ($\Delta c = +26.5$ pm). Therefore, d(Ti–S) is slightly overestimated (by 0.3%) and d(Li-S) is close to the experimental distance. The application of dispersion corrected DFT approach (PBE-D) leads to an improved c parameter compared to the other considered methods ($\Delta c = -15$ pm), whereas the *a* parameter remains almost unchanged. Both d(Ti-S) and d(Li-S) are close to the experimental bond length (within 2 pm). These findings are in line with our previous investigation on 1T-LiTiS₂.^[25] The remaining differences between calculated and measured structural parameters could be due to slightly smaller lithium contents in the experiment compared to x = 1.0 in the calculations.

Conclusions

Based on quantum-chemical calculations at DFT level we find that 3R-LiTiS₂ is only 4 kJ·mol⁻¹ less stable than the well-known and deeply investigated 1T polymorph. Keeping in mind the promising electrochemical properties of the 3R phase^[8] the severe problems in preparing large amounts of phase-pure material must be considered as one of the main reasons for the missing interest of the battery community in this material.

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