

THE 3R PHASE OF Li_xTiS_2

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Summary

When Li_xTiS_2 ($0 \leq x \leq 1$) is synthesized at elevated temperature ($500^\circ\text{C} \leq T \leq 900^\circ\text{C}$), a new polytype, 3R- Li_xTiS_2 , is found for some values of x . Here we discuss the structure of the new phase and present a preliminary phase diagram which shows the regions of stability of the 3R polytype and the well known 1T polytype. Lithium can be intercalated or de-intercalated from both polytypes at room temperature. Ambient temperature Li/3R- Li_xTiS_2 cells have higher average voltages than Li/1T- Li_xTiS_2 cells.

Introduction

Previous studies [1, 2] have shown that of the group IV transition metal dichalcogenides, only ZrS_2 and HfS_2 undergo a structural transition to the 3R phase when intercalated with lithium. No such transition has been reported to occur for TiS_2 . However, when Li_xTiS_2 ($0 \leq x \leq 1$) is synthesized at elevated temperature ($500^\circ\text{C} \leq T \leq 900^\circ\text{C}$), a new polytype, 3R- Li_xTiS_2 , is found for some values of x . Here we discuss the new phase and show the variation of the lattice parameters with x as determined by X-ray diffraction on Li/3R- Li_xTiS_2 cells at ambient temperature.

Experimental

With the goal of making pure 3R- Li_xTiS_2 ($0 \leq x \leq 1$) stoichiometric quantities of either Li_2S (99%), Ti (99.9%), and TiS_2 ; Li_2S , Ti, and TiS_2 ; or Li_2CO_3 (99.5%) and TiS_2 were allowed to react in a graphite ampoule under an argon atmosphere at temperatures ranging between 500°C and 900°C for 20 h. For reactions of Li_2CO_3 and TiS_2 , the stoichiometry was

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such that the Li-Ti-S ratios were controlled, but the carbon and oxygen from the carbonate group is thought to be expelled as CO_2 . However, as we discuss later, there is evidence for the presence of some oxygen-containing compounds. The lithiated compounds are handled in an inert-atmosphere glove-box since they react rapidly in air. Both the TiS_2 and TiS_3 were prepared by reacting stoichiometric ratios of Ti (99.9%) and S (99.9%) powders in sealed glass ampoules at 550°C for approximately four days.

Results and discussion

Figure 1 shows, schematically, the results of these preparations. It is evident from the Figure that when Li_2S was used as a starting material the product was predominantly the 3R phase for values of $x > 0.7$ and a temperature range of $500 - 700^\circ\text{C}$. As x decreases, the 3R polytype no longer forms and the 1T polytype is prevalent. At very high temperatures ($800 - 900^\circ\text{C}$), the 1T polytype is the more stable phase. This would suggest that the 1T polytype is the thermodynamically stable phase. In an effort to determine the stability of the 3R polytype at lower temperatures, a sample of LiTiS_2 was synthesized at 900°C , and instead of quenching it to room temperature quickly, the sample was slowly cooled over a period of two days. The result was a pure 1T phase, implying that the 3R polytype may be a metastable phase.

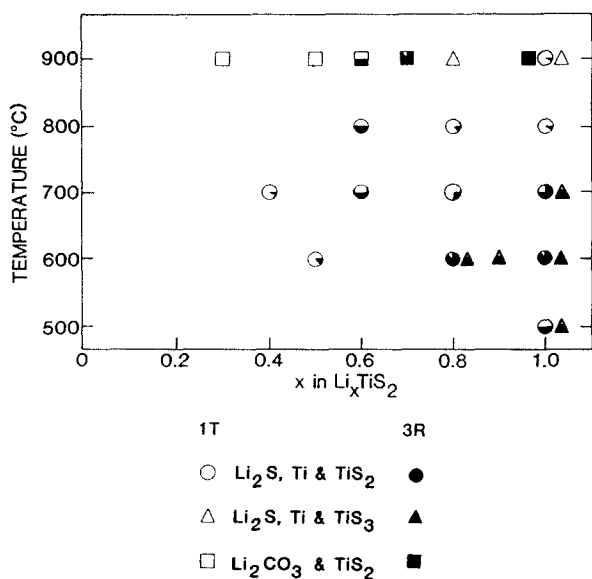


Fig. 1. Diagram showing the 3R:1T ratio for various starting materials. Shaded area represents the portion of the 3R phase and unshaded that of the 1T phase.

The most apparent exception was the formation of the 3R phase at 900 °C for $x > 0.6$ when Li_2CO_3 was used as a starting material. Samples prepared with Li_2CO_3 showed the presence of two impurity compounds, namely, TiO_2 , and an $\text{Li}_{1+x}\text{Ti}_{2-x}\text{O}_4$ ($0 \leq x \leq 1/3$) compound, that were not evident in the other preparations. Li_2CO_3 is the obvious source of the oxygen allowing these oxides to form. The presence of oxygen may stabilize the 3R phase.

Figure 2 shows projections of the structures of 1T- TiS_2 and 3R- Li_xTiS_2 in the (110) plane. In the 1T polytype, the metal atoms are positioned above each other in each TiS_2 repeat layer. The two structures are related by simply displacing adjacent pairs of TiS_2 layers in opposite directions, leaving every third TiS_2 layer fixed, thus obtaining the 3R phase. The unit cell for 3R- Li_xTiS_2 now becomes 3 layers thick as compared with just a single layer unit cell for the 1T structure. The dashed lines in the Figure indicate the unit cells of the structures. The 3R polytype only begins to appear once lithium atoms have been inserted into the van der Waals gap. Possibly, in the 3R polytype, coulomb repulsion between the metal atoms and inserted lithiums is reduced by staggering their positions in the subsequent layers. Table 1 compares the X-ray patterns for the two polytypes of LiTiS_2 .

Figure 3 shows the a and c lattice parameters *versus* x in 1T- Li_xTiS_2 for both the high temperature and the room temperature material. The room temperature data were collected by Dahn *et al.* [3] using the *in situ* X-ray diffraction technique. It appears that the lattice parameters of the high temperature material change in the same fashion as the electrochemically intercalated material.

Figure 4 shows the variation of the a and $c/3$ lattice parameters *versus* x in 3R- Li_xTiS_2 as determined by *in situ* X-ray diffraction. Most of the transition metal dichalcogenides undergo an increase in the c lattice

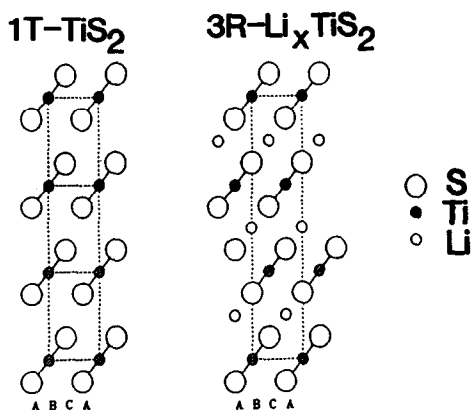


Fig. 2. 110 projections of the structures of 1T- TiS_2 and 3R- Li_xTiS_2 . The dashed lines indicate the unit cells of the structures, and the letters ABCA indicate the equivalent x and y coordinate positions within the hexagonal unit cell. [e.g., A($x = 0.67$, $y = 0.33$) B($x = 0$, $y = 0$) C($x = 0.33$, $y = 0.67$)].

TABLE 1

Comparison of the X-ray patterns of 1T-LiTiS₂ and 3R-LiTiS₂

1T polytype $a = 3.461 \text{ \AA}$, $c = 6.182 \text{ \AA}$				3R Polytype $a = 3.521 \text{ \AA}$, $c = 18.152 \text{ \AA}$			
(h k l)	$2\theta_{\text{obs}}$	$2\theta_{\text{calc}}$	Rel. Int.	(h k l)	$2\theta_{\text{obs}}$	$2\theta_{\text{calc}}$	Rel. Int.
0 0 1	14.339	14.327	vs	0 0 3	14.618	14.639	m
0 0 2	28.893	28.883	w	1 0 1	29.706	29.706	m
1 0 0	29.814	29.808	w	1 0 2	30.927	30.934	w
1 0 1	33.225	33.217	vs	1 0 4	35.491	35.464	vs
1 0 2	41.960	41.986	vs	1 0 5	38.574	38.555	w
0 0 3	—	43.936	vw	0 0 9	—	44.942	vw
1 1 0	52.887	52.908	s	1 0 7	45.931	45.938	w
1 0 3	53.938	53.998	m	1 0 8	50.106	50.109	s
1 1 1	55.119	55.110	m	1 1 0	51.908	51.934	s
0 0 4	59.873	59.840	m	1 1 3	54.301	54.260	m
2 0 1	62.937	63.915	m	1 1 6	—	60.875	vw
2 0 2	69.742	69.733	m	2 0 1	—	60.978	vw
				2 0 4	64.444	64.466	m

v = very, s = strong, m = medium and w = weak.

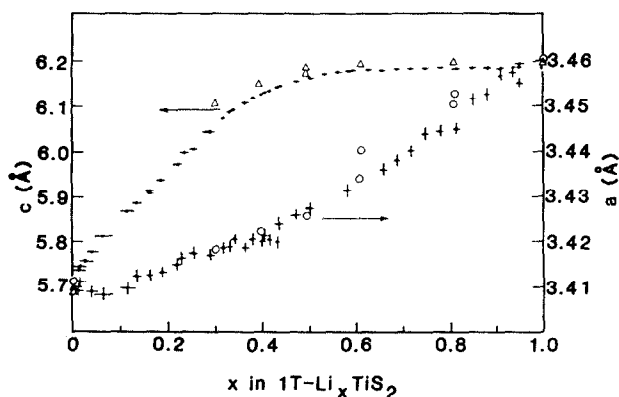


Fig. 3. Variation of lattice parameters of (·) room temperature and (○, △) high temperature 1T-Li_xTiS₂ with x . (Room temperature data after Dahn *et al.* [3]).

parameter when intercalated with lithium. However, $c/3$ is relatively unchanged through the full range of x for 3R-Li_xTiS₂. By contrast, the a lattice parameter of the 3R polytype shows the same variation as the 1T polytype, namely a 1.5% decrease with decreasing x .

Figure 5 shows $V(x)$ for the first cycle of an Li/3R-Li_xTiS₂ cell cycled at ambient temperature at a rate of 30 h for $\Delta x = 1$. The cathode material was initially 3R-LiTiS₂ prepared at $T = 900^\circ\text{C}$ using Li₂CO₃ and TiS₂ as the starting materials. The 3R cells have higher average voltages than 1T cells. On charge, 3R cells exhibit a step in the voltage curve. This step is only

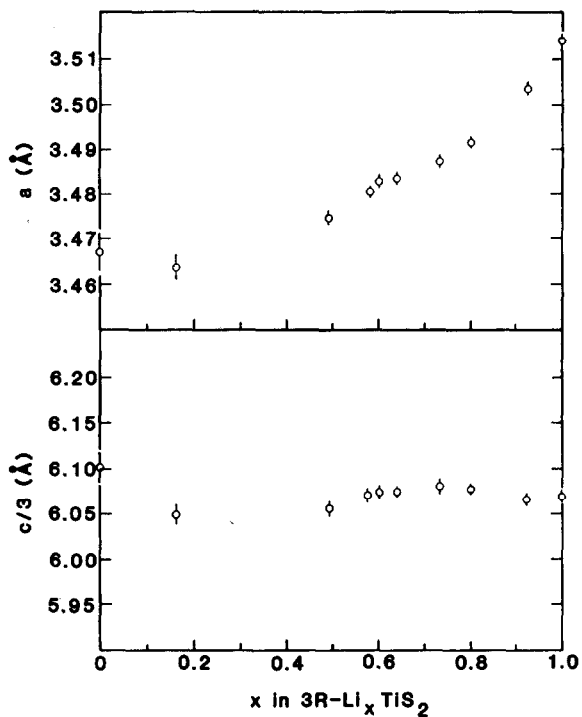


Fig. 4. Variation of lattice parameters of $3R\text{-Li}_x\text{TiS}_2$ with x .

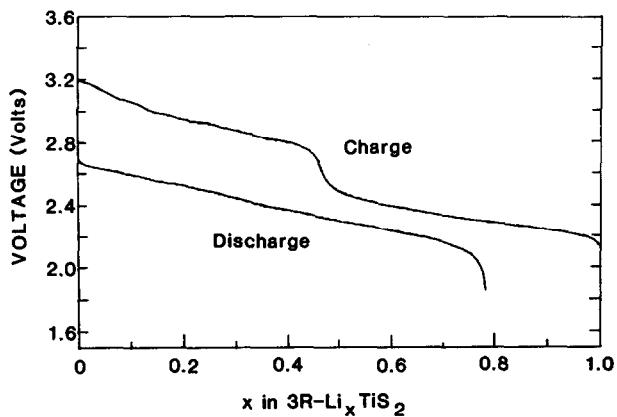


Fig. 5. $V(x)$ for the first cycle of an $\text{Li}/3R\text{-Li}_x\text{TiS}_2$ cell at 21°C and a discharge rate of 30 h for $\Delta x = 1$. The cathode material was initially $3R\text{-LiTiS}_2$ synthesized at high temperature.

resolved at relatively slow discharge rates, typically 30 - 50 h for $\Delta x = 1$. Even at these slow rates this feature becomes less pronounced as one cycles these cells.

The $V(x)$ behaviour of these cells is similar to that of other MX_2 intercalation compounds. The voltage varies with lithium composition and, on discharge, as the available sites for lithium become filled, a uniform drop in voltage is observed. However, upon charging $Li/3R-Li_xTiS_2$ cells, a step in the voltage curve is observed. It is not clear why we observe such a step only on charge and see no evidence of it on discharge. The origin of this step probably requires consideration of both thermodynamic and kinetic aspects. Furthermore, it might be associated with the formation of the 1T phase.

Figure 6 shows portions of X-ray diffraction profiles taken during the first charge and subsequent discharge of a $Li/3R-Li_xTiS_2$ cell (an *in situ* diffraction cell) at room temperature. The Miller indices of peaks of the 1T and 3R phases are indicated. The high-angle peak is due to the Li anode. The values of x corresponding to these scans are also shown. The scans were taken in chronological sequence from front to back. The 1T phase first appears in the fourth scan. Apparently, $3R-Li_xTiS_2$ is unstable to the formation of $1T-Li_xTiS_2$ at room temperature when x is decreased on the initial charge of the cell. The transition from the 3R phase to the 1T phase begins at $x \leq 0.4$. Upon the subsequent discharge, when lithium is reinserted, the 1T phase does not re-form the 3R phase. Instead, co-intercalation of the PC solvent into the TiS_2 cathode material is thought to occur. This causes the disappearance of the 1T phase from the X-ray pattern shown in Fig. 6. PC co-intercalation in TiS_2 is known to occur in 1 M $LiAsF_6/PC$ electrolyte [4]. Since co-intercalation of PC into TiS_2 renders that portion of the cathode inactive for further cycling, one observes a decreased value of Δx

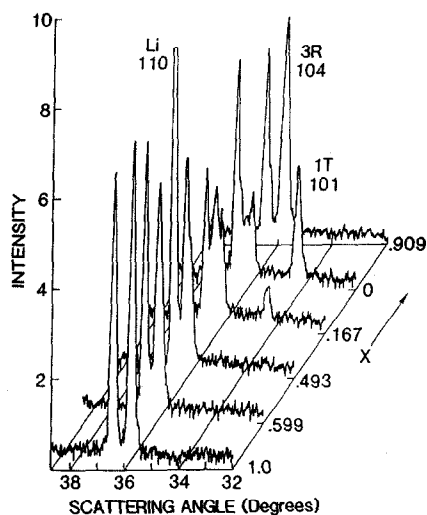


Fig. 6. *in situ* X-ray diffraction profiles taken during the first charge of an $Li/3R-Li_xTiS_2$ cell. The values of x are indicated. The final scan is after discharge at $x = 0.909$.

for the discharge of the cell (Fig. 5). Further evidence of PC co-intercalation is the decrease in the 3R peak intensity after one cycle.

The shift of the 3R peak to a slightly higher angle as x decreases leaves behind the inactive 3R component of the cathode. From the peak intensities, this un-utilized portion of the cathode is estimated to be approximately 35%.

Conclusions

We have determined the existence of a new polytype, $3R\text{-Li}_x\text{TiS}_2$, synthesized by solid state reaction at high temperature. Cells employing $3R\text{-Li}_x\text{TiS}_2$ as the cathode material have higher average voltages than $1T\text{-Li}_x\text{TiS}_2$ cells. The 3R phase is metastable and converts to the more stable 1T phase when the lithium content is lowered by de-intercalation. Phase conversion begins for $x \leq 0.4$ in Li_xTiS_2 .

Acknowledgements

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