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Structural studies of the hydrated lithium intercalates of TiX_2 (X = S,Se)

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Lithium intercalated titanium disulphide and diselenide form a number of hydrated complexes. Two types of hydrate are found, one containing a monolayer and the other a bilayer of water molecules between the layers TiX_2 (X = S, Se). By powder X-ray diffraction the crystal structures have been determined of $Li(H_2O)Ti(S,Se)_2$, $Li(H_2O)_2Ti(S,Se)_2$ and refined parameters are given for the sulphur and selenium positions. The compounds $Li_{0.4}(H_2O)Ti(S,Se)_2$ and $Li_{0.4}(H_2O)_2Ti(S,Se)_2$ are isostructural with these materials, with statistical occupation of the lithium sites.

1. Introduction

Titanium disulphide and titanium diselenide are isomorphous members of a group of transition metal dichalcogenides which crystallize in space group $P\bar{3}ml$ with the characteristic cadmium iodide layer structure. Their structures consist of stacked composite layers, each comprising two sheets of hexagonally close-packed dichalcogenide atoms sandwiching a sheet of metal atoms in such a way that half of the octahedral interstices are filled. The atomic stacking sequence is $A\gamma B$: $A\gamma B$: where A and B are the chalcogenide atoms and γ is the metal atom. Since primary valency is satisfied within the sandwich :$A\gamma B$: adjacent layers are held together by relatively weak van der Waal's forces. The resulting structure is markedly anisotropic, with pronounced cleavage perpendicular to the *c*-axis of the trigonal crystals.

The van der Waal's gap between the layers is sufficiently large for the material to be able to intercalate a range of metals (particularly the alkali metals) and other electron donors. A number of alkali metal intercalation compounds have been reported [1–7]. Gamble *et al.* [8] report that aqueous solutions of the alkali metals react with TaS_2, a like material, considerably expanding the crystal lattice and resulting in an increase of the superconducting transition temperature. Intercalation compounds of TiS_2, formed with ammonium ions, are reported by Schollhorn and Weiss [9] and by Chianelli *et al.* [10]. More recently, Whittingham [11] has made a study of the hydrated lithium intercalation complexes of TiS_2 and gives X-ray powder data and derived structures for two hydrated forms of $Li_{0.4}TiS_2$. These structures are confirmed in the present work and the study is extended to hydrated forms of $Li_{1.0}TiS_2$ and $Li_{1.0}TiSe_2$.

2. Experimental details

Single crystals of TiS_2 and $TiSe_2$ were prepared by iodine vapour transport in a two-zone furnace, using a technique based on that of Rimmington and Balchin [12]. Stoichiometric amounts of titanium (99.5% purity; Koch-Light Laboratories Ltd) and sulphur or selenium (99.999% purity) were placed in a fused quartz ampoule 20 cm long × 1.7 cm internal diameter. Iodine in the form of 99.998% purity flakes was inserted into the ampoule by use of an evacuated transfer tube, also of fused silica. The iodine concentration used was between 4.0 and 5.0 mg cm^{-3} of ampoule volume.

The evacuated, sealed ampoule was heated in a linear temperature gradient for 500 h, with the charged end maintained at the high reaction temperature of 800° C and the empty growth end at a cooler temperature of 720° C, during which time single crystals of TiS_2 of size 10 mm × 10 mm × 0.1 mm accumulated at the cooler end. A similar

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TABLE I Stoichiometry of lithium intercalates, Li_xTiX_2, indicated by different methods of analysis

Nominal composition	Acid-Base titration x	UV spectroscopy x	Flame photometry x
$Li_{0.4}TiS_2$	0.391 ± 0.007	0.398 ± 0.003	0.402 ± 0.002
$Li_{0.4}TiSe_2$	0.399 ± 0.005	0.390 ± 0.009	0.403 ± 0.003
$Li_{1.0}TiS_2$	0.980 ± 0.004	0.978 ± 0.004	1.001 ± 0.003
$Li_{1.0}TiSe_2$	0.978 ± 0.004	0.980 ± 0.005	1.001 ± 0.002

method was used to grow $TiSe_2$ crystals over a growth period of 400 h at a reaction temperature of 780° C and a growth temperature of 740° C.

Single crystals of TiS_2 and $TiSe_2$ were powdered to pass through a 350 mesh sieve. 4.4 m mol of material were placed in a dried, evacuated reaction tube and reacted with 4.65 m mol of 1.55 M n-butyllithium in hexane. To exclude ambient water vapour, all manipulations were done in a dry box. The reacting mixture quickly became hot enough to boil the hexane, and the reaction could be followed by colour changes in the solid material. (TiS_2 golden yellow to dark brown, $TiSe_2$ purple to black.) The reaction was allowed to go to completion (TiS_2 24 h, $TiSe_2$ 36 h) and the product was filtered and washed with hexane.

To determine the lithium content of the material, the filtrate containing excess unchanged lithium was titrated with n-butyl-alcohol in xylene, using 1,10-phenanthroline indicator. The lithium stoichiometry of the solid material was checked by ultraviolet (UV) spectroscopy and by flame photometry. The resulting analyses are given in Table I.

A similar method was used for the preparation of $Li_{0.4}TiX_2$ (X = S,Se). 0.775 M butyllithium was used to monitor the very slow reaction.

To obtain the hydrates, a sample of $Li_{1.0}TiX_2$ (X = S,Se) was placed in a Perspex dry box at a relative humidity of 30% for several days. The water take-up was monitored by weighing before and after exposure to the moist atmosphere. The measured water content is indicated in Table II. The hydrates were characterized by X-ray powder photographs of sealed specimens, using Cu*Kα* radiation and a Philips Straumanis powder camera. All X-ray photographs could be indexed on the basis of hexagonal unit cells. Lattice parameters are given in Table II. Measured powder data for the hydrated materials are listed in Tables III to VI.

3. Structure calculations

The powder data for the compounds $Li_{0.4}(H_2O)TiS_2$ and $Li_{0.4}(H_2O)_2TiS_2$ are markedly similar to those tabulated by Whittingham [11]. On the basis of his proposed structures for these compounds, trial structures were available for the monolayer and the bilayer hydrates $Li(H_2O)TiX_2$ and $Li(H_2O)_2TiX_2$ (X = S,Se). The trial structures gave good agreement between I_{obs} and I_{calc} for the powder data (Tables III to VI) and were refined to minimize the differences ($I_{obs} - I_{calc}$) by adjusting the z-coordinates of the atomic sites.

TABLE II Water content and X-ray lattice parameters of hydrated intercalates $Li_x(H_2O)_yTiX_2$ (X = S, Se)

Measured water content, y	Indicated stoichiometry	Lattice parameters	
		a (nm)	c (nm)
	$LiTiS_2$	0.3458 ± 0.0002	0.6182 ± 0.0004
1.029 ± 0.009	$Li(H_2O)TiS_2$	0.3425 ± 0.0005	2.5410 ± 0.0085
1.997 ± 0.008	$Li(H_2O)_2TiS_2$	0.3412 ± 0.0014	1.1215 ± 0.0055
	$Li_{0.4}TiS_2$	0.3426 ± 0.0006	0.6078 ± 0.0008
0.991 ± 0.007	$Li_{0.4}(H_2O)TiS_2$	0.3423 ± 0.0005	2.5574 ± 0.0006
2.002 ± 0.004	$Li_{0.4}(H_2O)_2TiS_2$	0.3420 ± 0.0003	1.1279 ± 0.0074
	$LiTiSe_2$	0.3633 ± 0.0003	0.6474 ± 0.0007
1.015 ± 0.006	$Li(H_2O)TiSe_2$	0.3581 ± 0.0010	2.6297 ± 0.0082
2.008 ± 0.009	$Li(H_2O)_2TiSe_2$	0.3604 ± 0.0010	1.1675 ± 0.0089
	$Li_{0.4}TiSe_2$	0.3590 ± 0.0006	0.6314 ± 0.0003
0.998 ± 0.004	$Li_{0.4}(H_2O)TiSe_2$	0.3593 ± 0.0009	2.5500 ± 0.0138
2.015 ± 0.009	$Li_{0.4}(H_2O)_2TiSe_2$	0.3605 ± 0.0004	1.1181 ± 0.0002

TABLE III X-ray powder diffraction data for $Li(H_2O)TiS_2$ and $Li(H_2O)TiSe_2$ $CuK\alpha$ radiation

hkl	$Li(H_2O)TiS_2$			$Li(H_2O)TiSe_2$		
	d_{obs} (nm)	I_{obs}	I_{calc}	d_{obs} (nm)	I_{obs}	I_{calc}
003	0.8468	vvs	100	0.8749	vvs	90
006	0.4222	vw	2			
102	0.2890	s	26	0.3025	s	37
105	0.2554	vs	60	0.2634	vvs	100
107	0.2293	ms	31	0.2388	s	48
108	0.2166	mw	4	0.2251	vw	6
10(10)	0.1926	m	11			
110	0.1712	s	20	0.1760	s	36
113	0.1680	vvw	3			
105	0.1626	vw	2			
10(13)	0.1474	vvw	3			
205	0.1426	m	8	0.1480	w	16
209				0.1369	w	7
10(17)	0.1346	m	9			
20(10)	0.1279	vw	3			
20(13)				0.1220	w	4
21(10)				0.1079	w	3
300				0.1030	w	14
20(20)				0.1000	w	3

TABLE IV X-ray powder diffraction data for $Li(H_2O)_2TiS_2$ and $Li(H_2O)_2TiSe_2$ $CuK\alpha$ radiation

hkl	$Li(H_2O)_2TiS_2$			$Li(H_2O)_2TiSe_2$		
	d_{obs} (nm)	I_{obs}	I_{calc}	d_{obs} (nm)	I_{obs}	I_{calc}
001	1.1218	vs	100	1.1783	vs	100
002	0.5597	vvw	2	0.5811	m	10
003				0.3868	m	12
101				0.3074	ms	20
100	0.2965	m	15			
004				0.2927	vvw	2
005				0.2324	ms	20
006				0.1953	vw	4
110	0.1716	w	9			
111	0.1685	vvw	1	0.1775	vvw	2
202				0.1518	vw	5
107				0.1473	vw	5
207				0.1137	vvw	2
00(10)	0.1123	vvw	2			
211	0.1109	vvw	2			
212	0.1099	vvw	2			
10(10)	0.1058	vvw	1			
00(11)	0.1024	vvw	1			
215	0.0993	vw	3			
300	0.0987	vw	3			
302	0.0970	vvw	1	0.1025	vvw	2
222				0.0889	vvw	2
00(13)	0.0860	vw	2			
220	0.0854	vvw	1			
307	0.0836	vvw	1			
311	0.0816	vw	2			
313	0.0799	vw	3			
314	0.0784	vw	2			

TABLE V X-ray powder diffraction data for $Li_{0.4}(H_2O)TiS_2$ and $Li_{0.4}(H_2O)TiSe_2$ $CuK\alpha$ radiation

hkl	$Li_{0.4}(H_2O)TiS_2$			$Li_{0.4}(H_2O)TiSe_2$		
	d_{obs} (nm)	I_{obs}	I_{calc}	d_{obs} (nm)	I_{obs}	I_{calc}
003	0.8529	vvs	100	0.8749	vvs	90
006	0.4254	vw	1			
102	0.2881	m	23	0.3025	s	37
105	0.2560	s	50	0.2634	vvs	100
107	0.2301	m	26	0.2388	s	48
108	0.2168	vw	2	0.2251	vw	6
109	0.2044	vw	2			
10(10)	0.1933	w	10			
110	0.1705	w	16	0.1760	s	36
113	0.1674	vw	1			
202	0.1473	vw	3			
205	0.1424	w	6	0.1480	w	16
209				0.1369	w	7
20(13)				0.1220	w	4
215	0.1093	vw	3			
21(10)				0.1079	w	3
300	0.0983	vw	6	0.1030	w	14
20(20)				0.1000	w	3
220	0.0856	vw	3			
315	0.0811	vw	4			

The small atomic number of lithium makes the calculated structure factors relatively insensitive to variations in the positions of these atoms. In placing the lithium atoms in these structures it was considered desirable to retain the lithium coordination of the $LiTi(S,Se)_2$ compounds, thus retaining the same chemical bond pattern around lithium in the hydrated materials also. By this means lithium atoms could be located to ± 0.007 in the z-coordinate. In the bilayer materials they lie, in any case, at special positions of the space group $P\bar{3}ml$. X-ray powder data alone is insufficient to determine the lithium positions in these compounds.

Atomic coordinates for the proposed structures of $Li(H_2O)TiS_2$ and $Li(H_2O)TiSe_2$ are listed in Table VII. The unit cell is shown diagrammatically in $(11\bar{2}0)$ section in Fig. 1. Hydrogen atoms are indicated on the water molecules to suggest a possible scheme for hydrogen bonding. Also shown in Fig. 1 is the unit cell for $Li(H_2O)_2TiS_2$. Atomic coordinates for this structure, and for that of $Li(H_2O)_2TiSe_2$ are listed in Table VIII.

4. Discussion

The stages of hydration of fully lithium intercalated TiS_2 are shown in Fig. 1, indicating how the structure changes from $LiTiS_2$ to $Li(H_2O)TiS_2$ and then to $Li(H_2O)_2TiS_2$ may occur. On reaction

TABLE VI X-ray powder diffraction data for $Li_{0.4}(H_2O)_2$ TiS_2 and $Li_{0.4}(H_2O)_2$ $TiSe_2$ Cu$K\alpha$ radiation

hkl	$Li_{0.4}(H_2O)_2TiS_2$			$Li_{0.4}(H_2O)_2TiSe_2$		
	d_{obs} (nm)	I_{obs}	I_{calc}	d_{obs} (nm)	I_{obs}	I_{calc}
001	1.1384	vvs	100	1.1180	vvs	100
002	0.5671	s	40	0.5781	w	8
003				0.3760	w	7
100	0.2950	vvw	2			
101	0.2858	m	20	0.3061	w	9
004	0.2818	vw	10	0.2715	m	14
102	0.2618	vs	70			
103	0.2323	m	18			
005				0.2230	w	8
104	0.2037	m	13			
105	0.1795	vw	11			
108				0.2140	w	7
109				0.2072	w	8
110	0.1709	s	23			
111	0.1687	m	16	0.1780	m	12
112	0.1637	vw	1			
113				0.1670	w	6
007	0.1609	vw	1			
118				0.1522	w	8
106	0.1583	vw	1			
201	0.1473	vw	1			
202	0.1432	w	1	0.1480	w	6
008	0.1410	vw	1			
203	0.1376	vw	1			
204	0.1311	vw	1			
214	0.1040	vw	1			
215	0.1000	vw	1			
300	0.0985	vw	1			
20 (14)				0.1139	w	4
20 (18)				0.1021	w	5
30 (12)				0.0885	w	4
21 (20)				0.0843	w	3

TABLE VII Refined atomic coordinates in the structures of $Li(H_2O)TiS_2$ and $Li(H_2O)TiSe_2$

Atom	x	y	z	
			X = S ± 0.007	X = Se ± 0.004
Li (1)	0.000	0.000	0.164	0.167
Li (2)	0.333	0.667	0.836	0.833
Li (3)	0.667	0.333	0.500	0.500
Ti (1)	0.000	0.000	0.000	0.000
Ti (2)	0.333	0.667	0.667	0.667
Ti (3)	0.667	0.333	0.333	0.333
X (1)	0.000	0.000	0.406	0.380
X (2)	0.000	0.000	0.594	0.620
X (3)	0.333	0.667	0.082	0.081
X (4)	0.667	0.333	0.918	0.919
X (5)	0.333	0.667	0.255	0.265
X (6)	0.667	0.333	0.745	0.735
H_2O (1)	0.000	0.000	0.834	0.834
H_2O (2)	0.333	0.667	0.500	0.500
H_2O (3)	0.667	0.333	0.166	0.166

TABLE VIII Refined atomic coordinates in the structures of $Li(H_2O)_2TiS_2$ and $Li(H_2O)_2TiSe_2$

Atom	x	y	z	
			X = S ± 0.008	X = Se ± 0.005
Li	0.000	0.000	0.500	0.500
Ti	0.000	0.000	0.000	0.000
X (1)	0.333	0.667	0.195	0.198
X (2)	0.667	0.333	0.805	0.792
H_2O (1)	0.333	0.667	0.602	0.606
H_2O (2)	0.667	0.333	0.398	0.394

with water $LiTiS_2$ gives two phases, of c-lattice spacing 3 x 0.8470 nm and 1 x 1.1215 nm, respectively. These represent structures containing a monolayer and a bilayer of water molecules between the TiS_2 layers. Water molecules can be readily removed from the monolayered material by heating under vacuum, but this reverse reaction occurs with more difficulty in the bilayered material, consistent with the salt-like character of the alkali-metal complexes.

The structures of $Li(H_2O)TiS_2$ and $Li(H_2O)TiSe_2$ are isostructural with the compound $Li_{0.4}(H_2O)$ TiS_2 described by Whittingham [11]. Similarly $Li(H_2O)_2TiS_2$ and $Li(H_2O)_2TiSe_2$ are isostructural with Whittingham's $Li_{0.4}(H_2O)_2TiS_2$.

In all the hydrates described, the minimal layers of TiX_2 remain integral and planar, and lithium and water are intercalated between the layers. The bonding between the titanium and the chalcogen atoms remains predominantly covalent. However, variations are found in the bond lengths Ti–X. Thus in the monohydrate sulphide the distance Ti–S is typically 0.287 nm (cf. 0.243 nm in TiS_2, 0.250 nm in $LiTiS_2$) whereas in the dihydrate it is 0.294 nm. Similarly in the monohydrate selenide, Ti–Se is 0.298 nm whereas in the dihydrate Ti–Se is typically 0.311 nm (cf. 0.254 nm in $TiSe_2$ and 0.262 nm in $LiTiSe_2$). Even within adjacent layers of a single compound the Ti–X distances are not constant. For instance, in the monohydrate selenide (see Table VII) the distances Ti–Se vary from Ti (1)–Se (3) = 0.298 nm to Ti (2)–Se (6) = Ti (3)–Se (5) = 0.273 nm. These differences fall within the experimental accuracy of the z-coordinate, but are thought to be significant, and may be caused by the strong polarizing influence of the neighbouring lithium cations and hydrogen-bonded water molecules, which produce slightly different environments around each chalcogen atom.

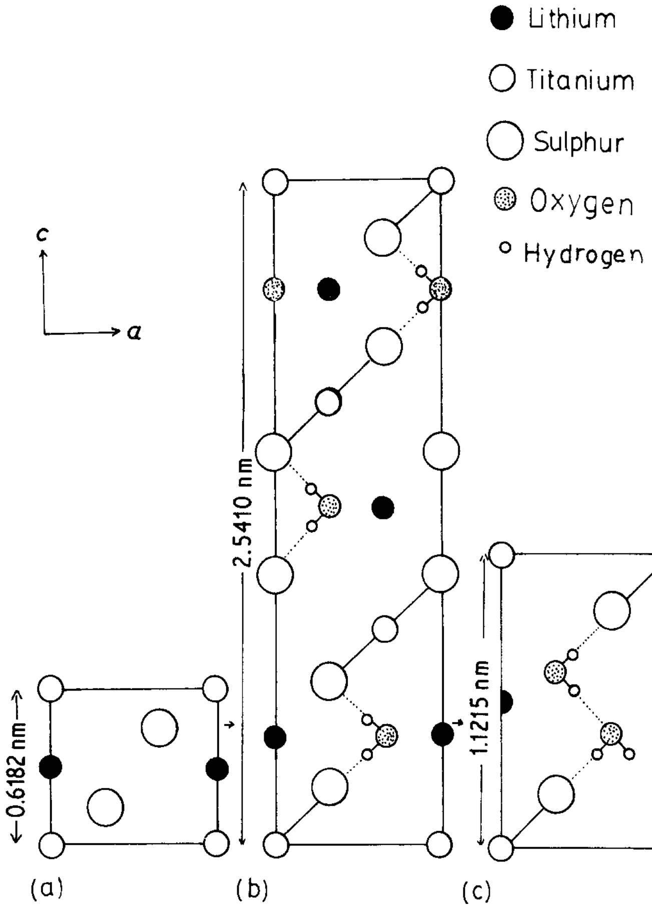

Figure 1 Stages of hydration of $LiTiS_2$-Sections on $(11\bar{2}0)$. (a) $LiTiS_2$, (b) $Li(H_2O)TiS_2$, (c) $Li(H_2O)_2TiS_2$. Possible hydrogen configuration shown dotted.

In the hydrated materials sulphur and selenium atoms are separated in their respective structures by rings of water molecules. A conjectural bonding scheme for the water molecules is suggested in Fig. 1.

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