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STRUCTURE AND PROPERTIES OF QUATERNARY CHALCOGENIDES; THE STRUCTURE AND INTERCALATION BEHAVIOUR OF TiZrTe<sub>h</sub>

Z. Cybulski, A. Feltz and M. Andratschke

Department of Chemistry of the Friedrich Schiller University, GDR

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#### ABSTRACT

Titanium(IV)-Zirkonium(IV)-telluride TiZrTe<sub>4</sub> has been prepared in order to prove the intercalation behavior for purposes of battery applications. The Ti and Zr atoms are not randomly distributed at the sites of a CdI<sub>2</sub> like structure. An ordered structure with the space group P2/m is found evaluated from powder diffraction measurements. Contrary to expectation the ability for intercalating Li is lowered in comparison with TiTe<sub>2</sub> and ZrTe<sub>2</sub>.

MATERIALS INDEX: tellurides, zirconium, titanium

#### INTRODUCTION

In comparison with the binary ditellurides the intercalation behaviour of ternary ditellurides of transition metals seems to be less investigated. Keeping TiTe, in contact with a solution of  $\text{LiC}_4\text{H}_9$  in hexane  $\text{Li}_x\text{TiTe}_2$  is formed in a compositional range 0 < x < 1 (1). TiTe, crystallizes in the space group P3m1 with a = 376.8+0.3 pm and c = 652.4+0.6 pm (2,3). The analogous data for ZrTe, are a = 395 pm and c = 663 pm (4). Obviously, materials of the type of mixed crystals as Ti<sub>x</sub>Zr<sub>1-x</sub>Te<sub>2</sub> did not be studied. On the other hand, TiZrTe<sub>4</sub> (x = 0.5) has been found to form an own ordered structure (5).

# PREPARATION AND PROPERTIES OF TiZrTe

Preparation of TiZrTe, starts from the elements whose mixture is heated up to 900  $^{6}$ C in a closed silica tube for 10 days. After grinding in a dry argon atmosphere and repeating the procedure for about 5 days a bright black crystalline powder is obtained.

The compound is unstable in the air yielding the oxide hydrates of Ti and Zr as a result of hydrolysis. Amorphous Te is formed because of the oxidation of  $H_2$ Te.

 $TiZrTe_4 + nH_2O + 2O_2 \longrightarrow TiZrO_{4-n} (OH)_{2n} + 4Te (1)$ 

Fig. 1 shows the water and oxygen contamination in dependence on time. The behavior of  $\text{TiZrTe}_4$  is more similar to  $\text{ZrTe}_2$  which appears to be significantly less stable at room temperature in the air than  $\text{TiTe}_2$ . Therefore in order to pre-



vent decomposition during the measuring time of the X-ray diffraction pattern the powder samples were prepared using an epoxide polymer for imbedding.

Fig. 1: Action of humidity and  $0_2$  from the air on TiZrTe<sub>4</sub> at 22 °C and on TiTe<sub>2</sub> and 2rTe<sub>2</sub> for comparison according to equation (1) (mole  $H_20$  per MTe<sub>2</sub>)

#### X-RAY DIFFRACTION AND STRUCTURE

X-ray diffraction data observed are collected in table 1 together with the calculated spacings and intensities. Obviously because of the relatively small number of diffraction lines two distinct possibilities for indexing are found. Taking into account a (I) = 386.0 pm for the hexagonal cell I which is in accordance with the average value of a for TiTe, and ZrTe, (a = 385.9 pm) an eight-layer structure with c (I) = 2606 pm has to be taken into consideration:  $z = 2.9 \exp = 6.04$ ,  $9_{x-ray} = 6.38 \text{ g} \cdot \text{cm}^{-3}$ . The structure is shown in part schematically in fill in the fill. shown in part schematically in fig. 1a. The sequencies coch and hhhc are the two kinds of package of the Te layers which are compatibel with 8 layers in the unit. In the latter case the structure appears to be closer to the parent compounds. The Ti and Zr atoms are expected to be either randomly distributed on the octahedral sites between pairs of dense packed Te layers or the Ti and Zr atoms occupy alternatively these inter-layers of octahedral vacancies yielding an ordered pattern. For both possibilities the reason for the formation of one c-configuration per three h-packed layers seems to remain as an open question. The average deviation between calculated and observed d-values has been found to be about  $\pm 0.4$  %. Nevertheless a second hexagonal cell appears to be

Nevertheless a second hexagonal cell appears to be more favoured because of the structure of  $\operatorname{AgTiZrTe}_{4}$  which is formed by silver intercalation at relatively low temperatures (6). The unit cell laterally enlarged to a (II) = 1339 pm  $\simeq 2$  a (I)/3 is in accord with a two-layer structure with a lattice constant c (II) = 651.6 pm which is very close to TiTe<sub>2</sub>. The unit cell follows imperatively when the octahedral sites between the two layers are alternatively occupied by Ti and Zr atoms yielding rows perpendicular to the (110) direction Which is shown in fig. 1b:  $9 \times reay = 6.39 \text{ g} \cdot \text{cm}^{-3}$  based on z = 6 TiZrTe<sub>4</sub> in the repeating voit. Indexing succeeded with an average error of 0.2 %.

As shown in fig. 1c such a pattern should involve a smaller orthorhombic cell containing only once the unit TiZrTe<sub>4</sub>. Indeed, indexing has been successfully carried out based on this smaller orthorhombic cell. However the space group P2/m is monoclinic. LAZY PULVERIX calculations and refinement yield spacings and intensities of the third column of table 1 with following lattice parameters:

								2	-
a	≕	653.3 <u>+</u> 1.3 pm	9	=	6.04g.cm <sup>-3</sup>	Ti	0	0	0
b	=	385.5 <u>+</u> 0.1 pm	8 X-ray	=	6.43g·cm <sup>-3</sup>	Zr	0	1/2	1/2
ັ	=	665.5 <u>+</u> 3.8 pm	Z	=	1	Te(1)	1/4	1/2	1/6
ß	=	90.06 <u>+</u> 0.04 °	space	g	roup: P2/m	Te(2)	1/4	0	2/3

High intensity reflexes calculated have been completely found in the observed diagram. Random orientation of the powder particles has scarcely to be expected because of their anisotropic habitus which explains relatively large deviations between the calculated and observed intensities.

dexp	Iexp	Hexa	g.I:	dcalc	Hexag.II:	d calc	Monocl	dcalc	Icalc	
pm	e e	hk	1	pm	hk1	pm	hkl	pm	20	
644.9	30	00	4	651.5	001	651.5	001	665.5	10.8	
	-						100	653.3	}	
	-	-		-	-	-	011	333.6	1 4 1	
						_	002	332.8	) **'	
325.5	74	00	8	325.8	002	325.8	200	326.7	13.6	
							111	297.2	}	
295.5	100	10	4	297.8	221	297.8	111	297.0	100	
~			•	~//	~~.	~///*	102	296.6		
							102	296.4	,	
246.0	23	10	7	249.0	321	246.0	210	249.2	0.2	
							211	233.5	}	
232.8	47	10	8	233.5	222	233.5	211	233.3	\$ 37.4	
	•						202	233.2		
0.47	4 174	00	4.0	045 0	000	047 0	202	233.0	, , ,	
217.0	17	00	12	217.2	003	217.2	300	217.0	, 0.7	
192.3	13	11	1	192.8	600	193.3	020	192.0	28.0	
							120	192.5	}	
							1120	184.9	1 2 3	
-			•		-	-	112	18/1	2.5	
							211	182 L	) >	
182 2	34	10	10	182 0	223	182 2	302	182 3	1 22 0	
ر میں ا			12	102.0	225	102.2	302	182.1	( ~). )	
					1		220	166.0	, 1	
165.9	6	02	2	166.1	602	166.2	213	165.8	\$ 11.0	
	Ŭ		~				213	165.6	}	
I	l	ł			1					

Table 1

Spacings and intensities of the powder diffraction pattern of  $\text{TiZrTe}_{h}$  (CuK  $\alpha$ :  $\lambda$  = 154.056 pm)

160			z. c	YBULSKI,	et al.		Vol. 24,	No. 2
d	I	Hexag.I:	d	Hexag.I	I: d	Monocl	d	I
	<u>exp</u>	hk 1	pm	hkl		hkl	pm	<u> </u>
162 5	27	00.16	162 0	004	162 0	400	162 3	
	~1	00 10	102.9	004	102.9	112	161.6)	ر •ر
161 1	10	00 //	162.2	500	161 0	122	161.6	16 1
101.5	10	02 4	160.8	544	101.3	104	161.3	10.1
						104	161.2/	:
				1.1.0	11.0 0	222	148.6	
148.7	6	02 8	148.9	442 540	140.9	222	140.5	8.8
ĺ				540	140.5	204	148.2	
						214	138.4	
137.6	6	00 19	137.2	613	137.1	214	138.3	0.13
			-			412	137.1	_
				l		322	132.5	_
132.6	3	02 12	132.6	443	132.6	322	132.4	8.2
				[		304	132.3	
124 6	10	11 16	125 2	604	124 5	420	124.0	12 2
124.0	10	11 10	123.2	004	127.5	413	124.4	<b>،</b> ،ر۱
1						131	123.91	
						131	123.9	
				Į		510	123.8	
						124	123.7	13.2
						124	123.7	
						115	123.0	
						231	117 71	
						231	117.7	
_	_	_	-	-	-	224	117.6	8.2
						224	117.5	
				l		215	117.4	
						215	117.4 J	
110 7	20	02 2	110 7	822	110 7	033	111.2	1, 9
110.7	20		110.7	2ر0	110.7	330	110.7	4.0
1				1		331	109.18	١
						331	109.16	
-	-	-	-	-	-	324	109.06	9.3
ļ						315	108.99	
1						315	108.89	,
1			1			225	103.87	}
				1101	104.1	617	103.53	
103.94	20	30 9	104.2	842	103.9	602	103.52	13.0
			i			611	103.49	1
						602	103.45	1
I	لما		**************************************	L				



- Fig. 2: TiZrTe<sub>4</sub> structure showing close packing of the Te atoms with Ti and Zr in the octahedral sites
  a) First 2 of 8 layers of the hexagonal cell I
  - b) Hexagonal cell II showing the alternating occupation of the octahedral sites by Ti and Zr atoms
  - c) pseudo-rhombic cell for TiZrTe<sub>4</sub> P2/m deduced from b)

### INTERCALATION STUDIES

TiZrTe<sub>4</sub> contaminates Ag powder at 300 °C within a few hours under formation of AgTiZrTe<sub>4</sub> (6). The interpretation of the X-ray diffraction diagram has been successfully carried out utilizing the hexagonal cell II of TiZrTe<sub>4</sub> which is compatible with the smaller monoclinic (pseudo-orthorhombic) cell yielding the lattice constants a = 1307.040.3 and c = 822.040.1 pm. Of course, because of the intercalation of the Ag<sup>+</sup>ions the c parameter becomes enlarged and at the same time a small lateral compression takes place. When the TiZrTe<sub>4</sub> powder is submitted to the action of LiC<sub>4</sub>H<sub>0</sub> in hexane Li<sub>2</sub>TiZrTe<sub>4</sub> is slowly formed during a reaction time of several hundred hours. There is a variation of the kinetic runs because of the heterogeneous kind of this reaction. However, TiTe<sub>2</sub> interacts with a solution of LiC<sub>4</sub>H<sub>0</sub> at room temperature already within the time of 50 h completely yielding LiTiTe<sub>2</sub>. ZrTe<sub>2</sub> shows a comparable high reactivity with LiC<sub>4</sub>H<sub>0</sub> in hexane forming LiZrTe<sub>2</sub>.

ding LiTiTe. Zrre, such a contract of the mole volume of TiO.5 Te2 has a value of V=50.58 cm<sup>3</sup>/mole which is about 1 % cm<sup>3</sup>/mole which is about 1 % cm<sup>3</sup>/mole) and ZrTe2 (V = 53.96 cm<sup>3</sup>/mole). Therefore, the entering of Li into the van der Waals layers should be a little more inhibited because of the smaller space. Primarily the kinetics is expected to be

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influenced. The intercalation capacity should be maintained. Obviously, differences of the properties between the Li intercalated binary tellurides LiTeTe, and LiZrTe, on the one side and of the ternary telluride Li2Tre4 on the other side become widely equilibrated because of the quasi metallic bond state in these materials.

# CONCLUSIONS

TiZrTe<sub>4</sub> prepared from the elements consists in a layerlike structure of the CdI, type whose cationic sites are alternatively occupied by Ti and Zr atoms yielding rows perpendicular to the (110) direction. Obviously, because of local distortions the intercalation behavior is kinetically diminished in comparison with TiTe, and ZrTe, which is in accordance with 1 % shrinkage of the mole volume for Ti<sub>0.5</sub>Zr<sub>0.5</sub>Te<sub>2</sub>

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