

Re-examination of the Crystal Structure of $ZrTe_3$

Sigrud Furuseth* and Helmer Fjellvåg

Department of Chemistry, University of Oslo, N-0315 Oslo 3, Norway

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Re-examination of the crystal structure of $ZrTe_3$ by single-crystal methods shows that $ZrTe_3$, contrary to earlier reports, takes the type A structure for MX_3 compounds. Repeated syntheses of a large number of crystals, using various conditions in the transport reactions, gave only type A crystals. The powder X-ray and neutron diffraction patterns are only compatible with a type A bulk material. Two other representatives of the type B class of MX_3 compounds were studied, but in less detail. However, the present results clearly show that their structures are also of type A. No indication for a type B material was found for any of these compounds. It is recommended that property measurements of low-dimensional MX_3 compounds are accompanied by structural characterization in order to ascertain the type of the studied material. A list of Bragg reflections (powder X-ray diffraction data), particularly suited for differentiating between type A and type B materials, is provided.

Considerable interest has recently been devoted to low-dimensional transition-metal trichalcogenides MX_3 ($M = Ti, Zr, Hf$ and $X = S, Se, Te$). Their strongly anisotropic electrical properties, including a superconducting state for $ZrTe_3$, as well as their optical properties, have been studied and related to electronic band structure calculations.¹⁻⁷

The majority of these MX_3 compounds are semiconductors, whereas as an exception $ZrTe_3$ appears to be a semi-metal with low, approximately isotropic, resistivity within the layered *ab*-plane but with high resistivity across the layers.

The crystal structure is built up by trigonal-prismatic MX_3 chains which are connected to form layers of composition MX_3 .^{8,9} The structure is relatively simple and is built from only one kind of trigonal prism, and thus provides a good model system for theoretical calculations.

The MX_3 compounds are reported to crystallize in two closely related modifications,⁹ termed type A and type B. $ZrSe_3$ and HfS_3 are reported to take the type A structure, TiS_3 , ZrS_3 , $ZrTe_3$ and $HfTe_3$ type B, whereas ZrS_3 and $HfSe_3$ are known to have both types of structure. The two types are structurally closely related, and experimental data suggest that the relationship between their respective positional parameters (x_A, y_A, z_A and x_B, y_B, z_B for M as well as X atoms) is $x_A = 1 - x_B, y_A = y_B$ and $z_A = z_B$.

No detailed study has so far explained the strange occurrence of the two closely related structures, which are almost mirror images of each other. Recently, calculations of the electronic band structure of $ZrTe_3$ showed that the type B structure is crucial to its semimetallic nature.⁷

A consideration of the details of the trigonal-prismatic

coordination around M shows that type A has almost equal M–X bond lengths, whereas a much larger scatter in the M–X distances is found for type B. In fact the spread in the latter distances is unusually large, and this may call for a re-examination of the crystal structure of such MX_3 compounds. However, a more obvious reason for performing a new single-crystal diffraction study is the observation that a powder diffraction diagram for type B compounds, e.g. $ZrTe_3$, calculated on the basis of reported structural parameters does not fit the observed powder diffraction pattern. The present report concerns in particular $ZrTe_3$. Results from single-crystal studies are presented, and comparisons are made with TiS_3 and $HfSe_3$, mainly on the basis of powder diffraction data.

Experimental

Single crystals of $ZrTe_3$ were prepared by chemical transport reactions. Powder samples of $ZrTe_3$ were synthesized by heating weighed mixtures of 99.9 % Zr and 99.999 % Te (both Koch-Light Laboratories) in sealed, evacuated silica-glass tubes for two periods at 700 °C for 7 days with intermediate crushing. The $ZrTe_3$ powder was thereafter placed in a horizontal two-zone furnace. Crystals were grown at different growth conditions, the temperature of the cold (growth) zone varying from 500 to 700 °C and the temperature gradient from 10 to 100 °C. Crystals were prepared with and without iodine as transport agent, and with and without a surplus of tellurium. Single crystals of TiS_3 (99.97 % Ti, Johnson Matthey; 99.9999 % S, Koch-Light Laboratories) were prepared similarly at 500 °C in the growth zone, and powder samples of $HfSe_3$ (99.9 % Hf, Koch-Light Laboratories; 99.998 % Se, Boliden) were prepared as described above for $ZrTe_3$.

* To whom correspondence should be addressed.

Table 1. Position parameters and temperature factors for ZrTe₃.^a

Atom	x	y	z	U _{eq}	U ₁₁	U ₂₂	U ₃₃	U ₁₃
Zr	0.28825(19)	0.25	0.66571(11)	0.011	0.0122(5)	0.0098(5)	0.0108(4)	0.0011(4)
Te1	0.76355(13)	0.25	0.55515(7)	0.011	0.0120(3)	0.0115(4)	0.0093(3)	0.0012(2)
Te2	0.43267(13)	0.25	0.16749(8)	0.014	0.0119(3)	0.0140(4)	0.0149(3)	-0.0001(3)
Te3	0.90477(14)	0.25	0.16096(8)	0.015	0.0143(3)	0.0141(4)	0.0159(3)	0.0047(3)

^aSpace group $P2_1/m$; $R = 0.051$, $R_w = 0.059$; 1136 independent reflections. Calculated standard deviations in parentheses. Thermal parameters in 10^4 pm^2 .

Powder X-ray diffraction (PXD) data were obtained with a Guinier camera (using $\text{CuK}\alpha_1$ radiation and Si as internal standard) at room temperature. Unit cell dimensions were obtained by least-squares refinements using the CELLKANT¹⁰ program. Integrated intensities were extracted from the Guinier films using a Nicolet L18 microdensitometer and the SCANPI^{11,12} program system. The calculation of powder diffraction intensities based on structural data was accomplished with the LAZY PULVERIX¹³ program. Powder neutron diffraction (PND) data were collected with the OPUS III two-axis diffractometer at the JEEP II reactor, Kjeller, using neutrons of wavelength 187.7 pm. The scattering lengths, $b_{\text{Zr}} = 7.16$ and $b_{\text{Te}} = 5.43$ fm, were used in the Rietveld refinements.¹⁴

Intensity data were recorded for two single crystals of ZrTe₃ (a smaller one $0.10 \times 0.10 \times 0.05 \text{ mm}^3$ and a larger one $0.40 \times 0.55 \times 0.15 \text{ mm}^3$ grown at 540 and 650 °C, respectively) with a Nicolet P3/F diffractometer using the $\omega/2\theta$ scan technique and $\text{MoK}\alpha$ radiation ($\lambda = 71.069 \text{ pm}$) at room temperature. Data were collected up to $2\theta = 70^\circ$ at a scan speed of 3° min^{-1} . Only reflections with $I > 3\sigma(I)$ were considered as observed during the subsequent refinements. Corrections were made for Lorentz and polarization effects and for absorption and isotropic extinction. Full-matrix least-squares refinements were performed according to the program in Ref. 15. The adopted weighting of intensities was $w = 1/\sigma^2(F_{\text{obs}})$.

Results and discussion

Any possible twinning of the MX_3 crystals may seriously hamper the present single-crystal study. In fact, there are well known examples of studies of compounds where the

Table 2. Interatomic distances (in pm) for ZrTe₃ at room temperature, with calculated standard deviations in parentheses.

Zr–Te1 (2×)	295.6(1)	Te2–Te3	279.3(2)
Zr–Te1	315.6(2)	Te2–Te3	310.3(2)
Zr–Te1	314.0(2)		
Zr–Te2 (2×)	293.9(2)		
Zr–Te3 (2×)	296.1(2)		
(Zr–Te) _{av. trig pr.}	295.2		
(Zr–Te) _{av. all}	300.1		

powder diffraction pattern calculated on the basis of position parameters refined from single-crystal data does not fit the observed powder pattern. The latter situation also seems to exist for the MX_3 compounds (ZrTe₃, TiS₃ and HfSe₃) of type B. This problem was attacked during the present single-crystal study of ZrTe₃ by selecting and comparing a large number of crystals obtained from different crystal growth experiments, undertaken at various conditions.

The results from one single crystal study of ZrTe₃ are given in Table 1. The derived position parameters for the other crystal (see Experimental section) are identical within one calculated standard deviation. The unit cell dimensions $a = 589.48(8)$, $b = 392.64(6)$ and $c = 1010.4(2)$ pm and $\beta = 97.93(2)^\circ$ were deduced from PXD data. Relevant interatomic distances calculated on the basis of these results are given in Table 2. The results clearly prove that ZrTe₃ takes the type A structure.

All studied single crystals (some 20) of ZrTe₃ (grown with and without transport agent) gave Weissenberg photographs fully compatible with the four-circle diffraction studies. This implies that all the crystals studied are of type A, and notably not of type B as previously reported for ZrTe₃.

The observed PXD and PND diagrams were compared with powder diffraction patterns calculated on the basis of data in Table 1. A comparison of integrated PXD intensities as read from Guinier films is provided in Table 3. As is clearly seen, the observations fit the calculations only under the assumption that the powder sample (at least the major part) is of type A (although deviations are expected owing to preferred orientation effects of the needle-shaped crystallites). Also, the profile refinements of the PND data unambiguously showed the sole existence of type A material in the large-scale (ca. 20 g) sample. A refinement allowing the coexistence of two phases, type A and type B ZrTe₃, respectively (for the relationship between the positional parameters, see Introduction), in the sample, showed that the fraction of type A material is $93 \pm 3\%$. Since the R -factors are not significantly improved on going from the single-phase model to the two-phase model, it is concluded that the entire PND sample is of type A.

The present results contradict earlier reports on ZrTe₃. A natural consequence is hence to check the relevance of the present findings for other MX_3 compounds of type B. TiS₃ and HfSe₃ were thus studied.

A large number of TiS_3 single crystals (needle-shaped) were studied by the Weissenberg technique. The intensities of all well defined reflections were in agreement with a type A atomic arrangement. However, for reflections of the types $h0l$ and $h1l$ with $h = 2n + 1$ streaks occurred indicating order-disorder features in the crystals. No crystals were found that did not give such streaks. On the other hand, the PXD pattern for TiS_3 is fully compatible with a type A structure, and again notably not compatible with the type B structure reported earlier. For HfSe_3 only PXD data were considered. The observed pattern is again only compatible with the calculated diffraction diagram for a type A structure.

High-temperature powder diffraction studies were performed for ZrTe_3 and HfSe_3 using a Guinier Simon camera. Normal thermal expansion behaviour was observed. No drastic intensity changes were observed for any reflections, and thus no transformation from type A to type B occurs in the temperature range prior to thermal decomposition of MX_3 into MX_2 .

The present single-crystal and powder diffraction studies of ZrTe_3 , TiS_3 and HfSe_3 clearly show that these compounds take the type A structure for MX_3 compounds. This

Table 3. Observed and calculated PXD intensities for ZrTe_3 for $d > 175$ pm (type A and type B; intensities normalized to 100 for strongest reflection).

d_{hkl}/pm	h	k	l	I_{obs}	$I_{\text{calc,A}}$	$I_{\text{calc,B}}$
1001.0	0	0	1	3	8	8
537.7	1	0	-1	1	4	4
499.8	0	0	2	2	5	6
365.2	0	1	1	13	9	9
333.4	0	0	3	7	20	20
317.1	1	1	-1	1	2	3
308.9	0	1	2	86	100	100
291.5	2	0	0	5	2	2
	2	0	-1		2	37
283.0	1	1	-2	2	8	13
269.8	2	0	1	79	31	2
	2	0	-2		29	3
263.9	1	1	2	2	11	6
254.2	0	1	3	3	4	4
250.2	0	0	4	2	5	5
242.5	1	1	-3	2	10	6
	1	0	-4		6	7
238.3	2	0	2	1	2	21
234.2	2	1	0	100	24	24
	2	1	-1		27	8
222.6	2	1	1	20	7	24
	2	1	-2		6	1
211.0	0	1	4	3	7	7
202.5 ^a	2	1	-3	0	1	17
196.7	0	2	0	46	22	22
182.4	2	1	3	7	13	1
181.8	1	0	5	10	5	4
	2	1	-4		14	0
178.3	0	1	5	6	11	10
	2	0	4		4	2

^aNot observed.

Table 4. List of selected reflections useful for distinguishing type A and type B materials of ZrTe_3 , TiS_3 and HfSe_3 ; d_{hkl} and relative intensities, normalized to $I = 1000$ for (012), as calculated for Guinier type camera and $\text{CuK}\alpha_1$ radiation, are given.

Compound	d_{hkl}/pm	h	k	l	$I_{\text{calc,A}}$	$I_{\text{calc,B}}$
ZrTe_3	202.6	2	1	-3	9	178
	182.5	2	1	3	133	7
	181.3	2	1	-4	136	1
	162.8	2	2	-1	9	100
	162.3	2	1	4	1	100
	158.9	2	2	1	141	9
	158.5	2	2	-2	136	16
TiS_3	229.1	2	0	1	193	51
	227.9	1	1	2	102	15
	226.8	2	0	-2	173	17
	203.3	2	0	2	12	123
	188.7	2	1	-2	102	1
HfSe_3	377.8	1	0	-2	108	20
	330.1	1	0	2	15	78
	246.9	1	1	2	134	28
	246.6	2	0	-2	135	50
	205.6	2	1	-2	150	8

study thereby addresses the questions as to whether structures of type B exist at all for pure MX_3 compounds, and whether the earlier studies were hampered by twinning effects, impurities or by other unforeseen factors. In spite of great efforts, it was found impossible throughout a large number of crystal growth experiments to reproduce the synthesis of type B crystals. The present new structural evidence for ZrTe_3 , TiS_3 and HfSe_3 must be considered when measurements of physical properties of MX_3 compounds are performed, and until the situation is totally clear, property studies should be accompanied by structural characterization. It should, however, be mentioned that the present structural data do not comply with the electronic band structure calculations,⁷ which concluded that the type B structure is essential for the observed semi-metallic nature of ZrTe_3 .

In order to facilitate a fast and easy characterization of powder samples by PXD, a list of reflections with corresponding intensities that are particularly useful in differentiating between type A and type B materials is provided for ZrTe_3 , TiS_3 and HfSe_3 in Table 4. When collecting experimental PXD data, measures should be taken to reduce the preferred orientation of the normally needle-shaped crystallites.

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