

On the Properties of the Zirconium and Hafnium Dichalcogenides

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The dichalcogenide phases of zirconium and hafnium have been studied by means of X-ray diffraction and diffuse reflectance measurements. The results show that these phases have the general formula $T_{1+t}X_2$, where T and X denote the metal and chalcogen components, respectively, and $t \geq 0$. The $Zr_{1+t}Se_2$, $Zr_{1+t}Te_2$, $Hf_{1+t}Se_2$, and $Hf_{1+t}Te_2$ phases exhibit appreciable ranges of homogeneity, whereas $Zr_{1+t}S_2$ and $Hf_{1+t}S_2$ exist only for $t \approx 0.00$. Single crystals of all phases have been prepared by chemical transport reactions. The $Zr_{1+t}S_2$, $Zr_{1+t}Se_2$, $Hf_{1+t}S_2$, and $Hf_{1+t}Se_2$ phases are intrinsic semiconductors, whereas no conclusion could be drawn as to the type of electrical conduction of $Zr_{1+t}Te_2$ and $Hf_{1+t}Te_2$ from their diffuse reflectance spectra.

Three features emerge on considering the occurrence of the $Cd(OH)_2$ type structure among transition metal compounds (*cf.*, *e.g.*, Refs. 1-3):

(i) This structure type occurs exclusively with a chalcogen (S, Se, or Te) as the non-metal component.

(ii) The metal component of these phases belongs to the beginning and end of the transition periods.

(iii) The $Cd(OH)_2$ phases in which the metal comes from an earlier group of the transition series generally exhibit broad ranges of homogeneity in contrast with those (except for the $NiTe_2$ phase) in which the metal belongs to a later group.

Reasons for these trends are not clearly understood as yet and more extensive investigations are necessary in order to clarify the situation.

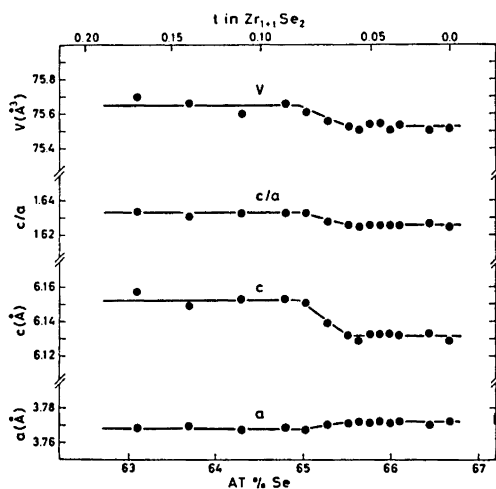
The present paper concerns the dichalcogenides of zirconium and hafnium, which, despite several previous studies,⁴⁻²⁸ have not hitherto been fully explored.

EXPERIMENTAL

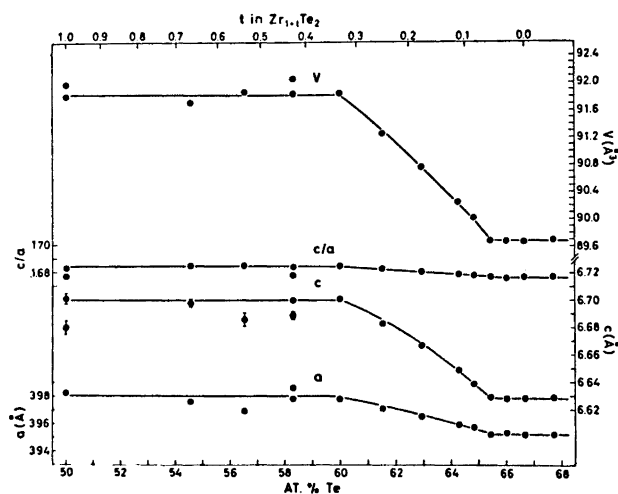
The experimental details concerning the purity of the elements, sample preparation (see also the results section), X-ray diffraction, and diffuse reflectance measurements have been presented in a previous communication.²⁹

RESULTS AND DISCUSSION

(i) *Polycrystalline samples.* Polycrystalline samples of $Zr_{1+t}S_2$, $Zr_{1+t}Se_2$, $Zr_{1+t}Te_2$, $Hf_{1+t}S_2$, $Hf_{1+t}Se_2$, and $Hf_{1+t}Te_2$ are easily synthesized by direct reactions between the elements at 800°C. Guinier data show, in addition to confirming the identity with earlier investigations, that the di-phases are isostructural with $Cd(OH)_2$. When $t > 0$, i.e. with an excess of metal,^{12,18} the structure is modified to an intermediate between the $Cd(OH)_2$ and NiAs types.¹ The largest deviations from the $Cd(OH)_2$ type structure are found for the $Zr_{1+t}Te_2$ and $Hf_{1+t}Te_2$ phases, in which cases the maximum values of t are 0.33 and 0.43, respectively.



(a)



(b)

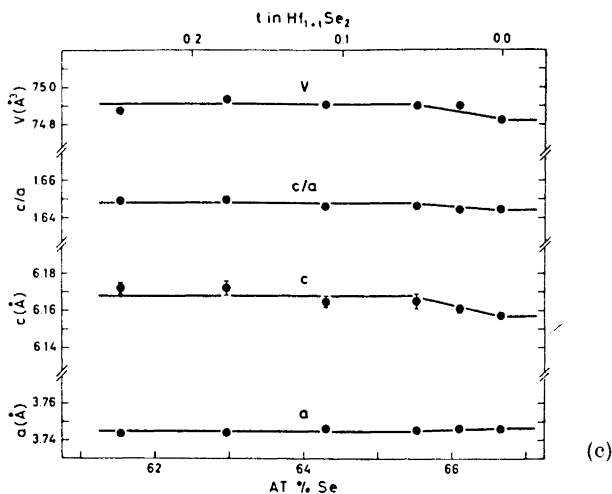


Fig. 1. Unit cell dimensions versus composition for the (a) $Zr_{1+t}Se_2$, (b) $Zr_{1+t}Te_2$, and (c) $Hf_{1+t}Se_2$ phases. Vertical bars show calculated error limits (twice the standard deviations) where these exceed the size of the symbols.

The Guinier photographs of the $Zr_{1+t}Te_2$ phase show additional reflections for samples with $t > 0.3$ which cannot be indexed on the basis of the $Cd(OH)_2/NiAs$ type unit cell. These reflections could, on the other hand, be indexed by doubling the c axis in accordance with the findings of Gleizes and Jeannin.²⁷ A determination of this structure is not attempted since only powder data are at hand, but it is assumed that the $Cd(OH)_2/NiAs$ type structure is modified by the spiral dislocations which are induced during the crystal growth, the problem being apparently analogous to that encountered for CdI_2 (cf. Ref. 31).

The variation of the unit cell dimensions with composition (Fig. 1) shows that there is an appreciable region of homogeneity for the $Zr_{1+t}Se_2$, $Zr_{1+t}Te_2$, and $Hf_{1+t}Se_2$ phases. The corresponding data for the $Hf_{1+t}Te_2$ phase are given in a previous communication.³⁰ The present data show that the homogeneity range of $Zr_{1+t}Se_2$ extends from 65.5 ± 0.2 to 64.9 ± 0.1 atomic % Se ($0.05 \pm 0.01 \leq t \leq 0.08 \pm 0.01$); for $Zr_{1+t}Te_2$ from 65.5 ± 0.1 to 60.0 ± 0.5 atomic % Te ($0.05 \pm 0.01 \leq t \leq 0.33 \pm 0.03$); and for $Hf_{1+t}Se_2$ from 66.6 ± 0.1 to 65.5 ± 0.5 atomic % Se ($0.00 \pm 0.01 \leq t \leq 0.05 \pm 0.02$). The $Zr_{1+t}S_2$ and $Hf_{1+t}S_2$ phases exhibit no variations beyond the standard deviations in the unit cell dimensions ($a = 3.6617(6)$ Å, $c = 5.8275(11)$ Å for $Zr_{1+t}S_2$ and $a = 3.6318(8)$ Å, $c = 5.8517(12)$ Å for $Hf_{1+t}S_2$), and it is assumed that their homogeneity ranges are extremely narrow.

In some cases, contaminations from the phases TOS ^{32,33} and/or $T'SiX$ ³⁴⁻³⁷ were noted in the samples. The oxide impurity TOS was only detected for the sulphides. As a matter of fact, $HfOS$ ($a = 5.6659(14)$ Å) has only briefly been mentioned in a recent, independent report³³ on hafnium sulphides. As a

consequence of the disturbing presence of these impurities it proved in some cases difficult to establish the correct sample composition. However, the results obtained on samples with appreciable amounts of impurities are not included in this paper.

In connection with the above phase-analytical data we also report a continuous range of solid solubility between hafnium disulphide and hafnium diselenide. In terms of the formula $\text{HfS}_{2-x}\text{Se}_x$ this implies that possible values of x cover the entire range $0.00 \leq x \leq 2.00$. The unit cell dimension a of $\text{HfS}_{2-x}\text{Se}_x$ exhibits (Fig. 2) a linear dependence with x , the c axis, however, does not show such a linear behaviour.

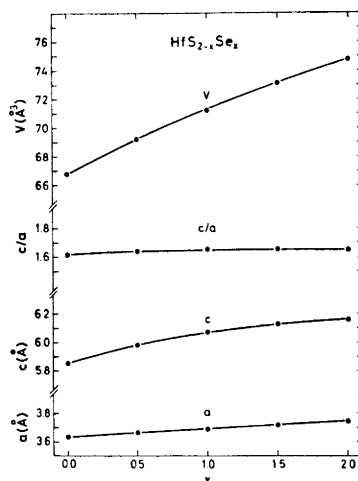


Fig. 2. Unit cell dimensions of the $\text{HfS}_{2-x}\text{Se}_x$ phase as a function of composition. The calculated error limits do not exceed the size of the symbols.

(ii) *Single crystals.* A systematic search for the suitable thermal conditions necessary for large single crystal growth employing chemical transport reactions was performed. Table 1 shows the optimum thermal conditions required for the binary phases. The transport and/or growth rates of the crystals vary considerably from one phase to the other, ranging from ~ 10 h for the production of large amounts of $\text{Zr}_{1+t}\text{S}_2$ crystals to ~ 100 h in the case of $\text{Hf}_{1+t}\text{Se}_2$.

Table 1. Suitable thermal conditions for chemical transport reactions.

Phase	t_1 (°C)	t_2 (°C)	$\Delta t/l$ (°C/mm)
$\text{Zr}_{1+t}\text{S}_2$	900	770	0.9
$\text{Zr}_{1+t}\text{Se}_2$	900	780	0.8
$\text{Zr}_{1+t}\text{Te}_2$	1100	850	1.7
$\text{Hf}_{1+t}\text{S}_2$	900	810	0.6
$\text{Hf}_{1+t}\text{Se}_2$	900	775	0.8
$\text{Hf}_{1+t}\text{Te}_2$	1025	850	1.2

The transport conditions for the individual phases are, on the other hand, somewhat insensitive to the choice of hot and cold zone temperatures t_1 and t_2 , respectively, of the reaction vessel. A homogeneous sample of $Zr_{1+t}Te_2$ is required in order to obtain this phase by means of transport reaction, otherwise crystals of $ZrTe_3$ are invariably obtained.

Flaky single crystals of up to 2 mm thickness and 100 mm² cross section were obtained in accordance with the typical layer structure of the phases. Although the colours of the various crystals are thickness dependent, in general, the sulphides are red, the selenides range from green to black, and the tellurides possess a bronze-like appearance. These observations agree with earlier findings.^{12,16-20,26}

The unit cell dimensions, obtained from Guinier data of the crushed crystals (Table 2), gave constant values for each phase, showing the crystals to be of constant composition. A comparison of the values listed in Table 2

Table 2. Estimated compositions and unit cell dimensions for zirconium and hafnium dichalcogenides prepared by chemical transport reactions.

Phase	Estimated composition		Unit cell dimensions		
	Atomic % X	<i>t</i>	<i>a</i> (Å)	<i>c</i> (Å)	<i>c/a</i>
$Zr_{1+t}S_2$	66.7	0.00	3.6617(6)	5.8275(11)	1.5915(5)
$Zr_{1+t}Se_2$	65.5	0.05	3.7706(12)	6.133(3)	1.627(2)
$Zr_{1+t}Te_2$	65.5	0.05	3.9524(9)	6.625(2)	1.676(1)
$Hf_{1+t}S_2$	66.7	0.00	3.6320(9)	5.8500(14)	1.6107(8)
$Hf_{1+t}Se_2$	66.7	0.00	3.7440(7)	6.155(2)	1.644(1)
$Hf_{1+t}Te_2$	61.5	0.25	3.9509(9)	6.651(3)	1.683(2)

with the corresponding data for the polycrystalline samples provided a means of estimating crystal composition. These estimated compositions show, as expected, that the crystals belong to the non-metal rich phase-limit in all cases. Further confirmation as to the average compositions was provided by electron microprobe analyses on single crystals. However, in addition the latter analyses suggested concentration gradients of ≤ 2 atomic % X. Such a result conflicts with the Guinier data and the most probable explanation is that the electron microprobe results are reflecting local inhomogeneities at or near the crystal surfaces. The electron microprobe technique did, however, indicate the absence of detectable amounts of iodine.

The most suitable transport conditions according to the present study (Table 1) differ to some extent from the data already recorded in the literature.^{19,20,26} There are in particular considerable differences between the values for t_1 and t_2 listed in Table 1 and the corresponding data recently published by Rimmington *et al.*²⁶ The less favourable transport conditions used by the latter authors are clearly reflected in the longer reaction periods employed in their study.

(iii) *Diffuse reflectance.* Fig. 3 shows the diffuse reflectance spectra of $HfS_{2-x}Se_x$ for different x , which are also representative for $Zr_{1+t}S_2$ and

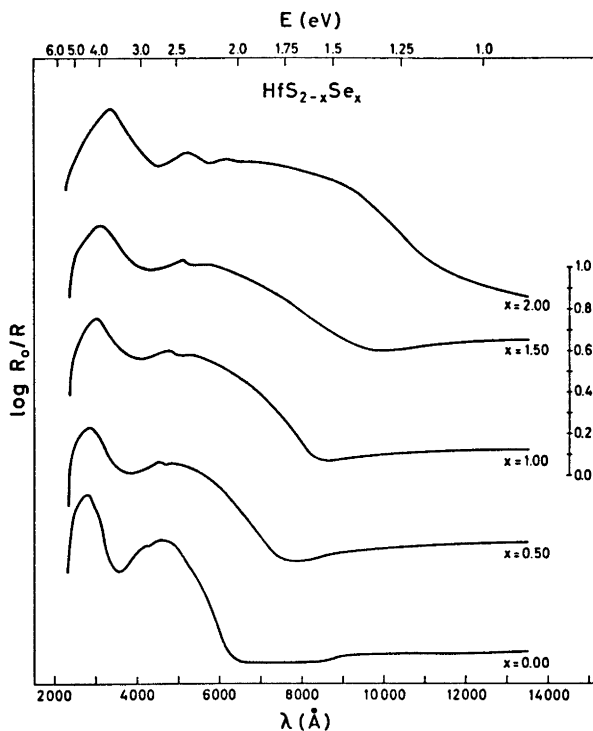


Fig. 3. Diffuse reflectance spectra of various samples of the $\text{HfS}_{2-x}\text{Se}_x$ phase.

$\text{Zr}_{1+t}\text{Se}_2$. In the corresponding spectra of $\text{Zr}_{1+t}\text{Te}_2$ and $\text{Hf}_{1+t}\text{Te}_2$ there is a characterless, rather uniform increase in $\log R_0/R$ between 2000 and 19 000 Å. Repeated measurements on different samples show that the results are well reproducible.

The evaluation of the band gap (ΔE) from diffuse reflectance spectra depends on the determination of the location of the absorption edge. By employing the extrapolation method³⁸ for determining the band gap, ΔE values of 1.72 ± 0.02 and 1.97 ± 0.03 eV were obtained for ZrS_2 and HfS_2 , respectively. The band gaps for the corresponding selenides increase with t for both $\text{Zr}_{1+t}\text{Se}_2$ and $\text{Hf}_{1+t}\text{Se}_2$. The compositional dependence of the band gap is more substantial for the case of $\text{Zr}_{1+t}\text{Se}_2$ (0.87 ± 0.02 eV at $t=0.05$; 1.61 ± 0.02 eV at $t=0.08$) than for $\text{Hf}_{1+t}\text{Se}_2$ (1.08 ± 0.02 eV for $t=0.00$; 1.14 ± 0.02 eV for $t=0.05$). The present values for the sulphides are reasonably consistent with those previously reported.^{19,20,22,25} For the selenides, on the other hand, the agreement is less satisfactory. The reported $\Delta E=1.13$ eV for $\text{Hf}_{1+t}\text{Se}_2$ ($t=0$) by Greenaway and Nitsche¹⁹ is in close agreement with the present finding whereas the value 1.31 eV given by Murray *et al.*²⁵ is incompatible. On taking into account the variation of ΔE with t , the values

reported by Lee *et al.*²² and Murray *et al.*²⁵ for the $Zr_{1+t}Se_2$ phase become consistent. The inconsistency apparently arises in the latter case because of the assumption of stoichiometric $ZrSe_2$.

Murray *et al.*²⁵ have presented semiempiric, tight binding calculated band structures for $Zr_{1+t}S_2$, $Zr_{1+t}Se_2$, $Hf_{1+t}S_2$, and $Hf_{1+t}Se_2$ ($t=0$). The calculated band gaps are in good agreement with the experimental values reported here for ZrS_2 and HfS_2 , whereas the discrepancy increases in the order $HfSe_2$ and $ZrSe_2$, and becomes quite large for the latter compound. These calculations, however, are based on an idealized model and on slightly incorrect experimental parameters. In this connection it is relevant to note that there is a substantial difference between the calculated reduction parameters for $ZrSe_2$ and those for ZrS_2 , HfS_2 , and $HfSe_2$.

Since ΔE decreases with x in an approximately linear manner (Fig. 4), it is assumed that a similar relationship holds for the ΔE values for $Zr_{1+t}S_2$

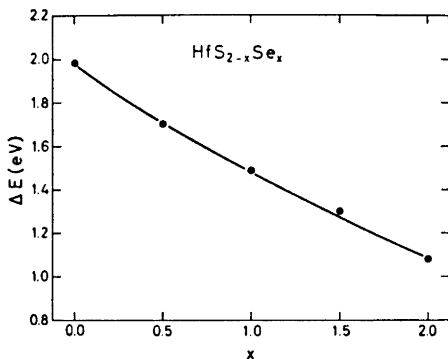


Fig. 4. Band gap (ΔE) versus x in $HfS_{2-x}Se_x$.

and $Zr_{1+t}Se_2$; $Hf_{1+t}S_2$ and $Hf_{1+t}Se_2$ to $Zr_{1+t}Te_2$ and $Hf_{1+t}Te_2$, respectively. This procedure yields $\Delta E \approx 0.2$ eV for both cases.

For all permitted values of t the $Zr_{1+t}Se_2$ and $Hf_{1+t}Se_2$ phases exhibit semiconductivity, which is tentatively explained in terms of the generalized (8-N) rule (*cf.*, *e.g.*, Ref. 39). The correct mathematical formulation of the rule is in this case $n + P - Q = 8a$, where, per formula unit, n is the total number of electrons involved in bonding, P and Q are the number of electrons in $X-X$ and $T-T$ bonds, respectively, and a is the number of X atoms. In accordance with previous experience and the observed diamagnetism for the compounds, each T atom is assumed to contribute 4 electrons, and each X atom 6 electrons to n ($= 16$), *i.e.* the valence states of the constituent atoms correspond to their group number of the Periodic Table. For $t=0$, the crystal structure unequivocally requires that $P=Q=0$. The semiconducting nature of the dichalcogenides are consistent with this result. For $t \neq 0$ the interpretation of Q from the structure becomes less certain. The shortest metal-metal distance along [001] for $t \neq 0$ corresponds to $c/2$ which amounts to:

- 3.077–3.065 Å for $Zr_{1+t}Se_2$,
 3.350–3.314 Å for $Zr_{1+t}Te_2$,
 2.929–2.925 Å for $Hf_{1+t}S_2$,
 3.085–3.078 Å for $Hf_{1+t}Se_2$, and
 3.325–3.316 Å for $Hf_{1+t}Te_2$.

Although these distances appear to be somewhat longer than those expected for Zr–Zr or Hf–Hf single bonds (~ 3.0 Å) they may possibly be interpreted as such. Thus, assuming that each additional T atom incorporated in the lattice for $t > 0$ is bonded to two neighbouring T atoms and that two electrons are involved in these bonds, $Q = 4t$. The total number of valence electrons $n = 4(1+t) + 2 \times 6 = 16 + 4t$ when a metal valence of 4 is maintained. With $n = 16 + 4t$, $P = 0$, $Q = 4t$, and $a = 2$ the generalized (8–N) rule is satisfied for all values of t . This appears to provide an explanation for the observed semi-conducting properties of $Zr_{1+t}Se_2$ and $Hf_{1+t}Se_2$ for $t > 0$.

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