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LOW-TEMPERATURE OXIDATIVE DEGRADATION OF LOW-DIMENSIONAL ZIRCONIUM AND HAFNIUM TELLURIDES

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The penta-, tri- and ditellurides of zirconium and hafnium easily take up oxygen and become partly oxidized at and below room temperature. Complete oxidation of these phases to (amorphous) ZrO_2 or HfO_2 and (crystalline) Te is attained at some 320 to 500 K (depending on compound, sample characteristics and experimental conditions) provided sufficient amounts of oxygen are available. Explanations for the different anomalies in $ZrTe_5$ and $HfTe_5$ are advanced as adsorbed/absorbed oxygen in the voids of the structure, partial oxidation, partial destruction of the Te_{III}–Te_{III} zig-zag chains in the structure and decomposition to the corresponding tritelluride and Te.

1. INTRODUCTION

CONSIDERABLE ATTENTION HAS recently been paid to the properties of the low-dimensional pentatellurides $ZrTe_5$ and $HfTe_5$ [1–28]. The original interest was inspired by the observation of giant resistivity anomalies [3–5] at ~ 150 and ~ 80 K for $ZrTe_5$ and $HfTe_5$, respectively. These anomalous behaviours are also manifested in other electronic transport properties [7, 10, 11, 15, 17], magnetic susceptibility [6, 7, 11, 14] and (less convincing) in heat capacity [23]. However, the anomalies could not be confirmed by Raman spectroscopy [12, 18–21], powder X-ray and neutron diffraction [26], nor by experimental [14, 16] or theoretical [9, 13] studies of the electronic band structure. Hence, the peculiar low-temperature properties of $ZrTe_5$ and $HfTe_5$ are still mysterious.

Other strange features of these pentatellurides are the recently reported anomalies occurring above room temperature [25, 27, 28]. However, no indications of these anomalies could be established by the powder X-ray diffraction technique [26] for temperatures up to 830 K.

$ZrTe_5$ and $HfTe_5$ are unquestionably metastable with respect to the oxides ZrO_2 and HfO_2 at ambient conditions in an atmosphere which contains oxygen. Partial surface oxidation of $ZrTe_5$ and $HfTe_5$ has in fact already been advanced as an explanation for the observation of elementary Te in the Raman spectra of the compounds [12, 21]. It was consequently decided to test whether the influence of oxygen, which may cause partial or complete oxidation at elevated temperature, can account for, or be correlated with, the recently discovered high-temperature anomalies. This brief report includes also a few findings for the related low-dimensional phases $Zr_{1+t}Te_2$, $Hf_{1+t}Te_2$, $ZrTe_3$ and $HfTe_3$ [29–32].

2. EXPERIMENTAL

Polycrystalline samples of $Zr_{1+t}Te_2$, $Hf_{1+t}Te_2$, $ZrTe_3$, $HfTe_3$, $ZrTe_5$ and $HfTe_5$ were synthesized by the sealed silica-glass capsule technique as described in [1, 2, 29–31]. Characterization of the samples and reaction products was performed by powder X-ray diffraction at room-temperature (Guinier technique, $CuK\alpha_1$ radiation, Si as internal standard). High-temperature powder diffraction data were collected between 300 and 1100 K in a Guinier–Simon camera ($CuK\alpha_1$ radiation). Unit cell dimensions were deduced through least-squares refinements of the positions of some 20 reflections. Thermal analysis was performed by DSC measurements between 100 and 850 K by a Mettler TA 3000 system using closed or open sample holders (with N_2 or dried air as atmosphere). Thermogravimetric data for the oxidative degradation of the compounds were obtained using a Stanton Redcroft 785 thermoanalyzer. The pure and reacted samples were investigated by metallographic methods and in a scanning electron microscope connected with equipment for X-ray fluorescence analysis.

3. RESULTS AND DISCUSSION

Clear indications for the instability of $ZrTe_5$ and $HfTe_5$ in air are already at hand from the Raman studies [12, 21], which show that increasing amounts of elementary Te develop with time at room temperature on initially clean single-crystal surfaces. It is however not known if or how this oxidation process

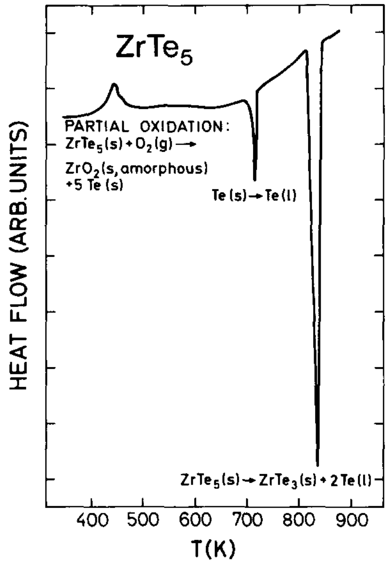

Fig. 1. DSC run for ZrTe$_5$ from 350 to 870 K. Interpretation of peaks is indicated.

ultimately affects the bulk physical properties of ZrTe$_5$ and HfTe$_5$. Certainly, any such effect will increase in importance on turning from single crystals to powder samples.

A typical DSC curve for a powdered ZrTe$_5$ sample (which prior to the experiment showed no free Te as probed by X-ray diffraction) placed in a closed silica-glass ampoule is shown in Fig. 1. The endothermic effects at 720 and 830 K are due to melting of Te and decomposition of ZrTe$_5$ into ZrTe$_3$ (ascertained from powder X-ray diffraction data), respectively. The less marked, broader exothermic feature at ~440 K is ascribed to a partial oxidation of the sample during which process elementary Te is released. Similar DSC data were recorded for HfTe$_5$. (The location of the exothermic peak, which is found at roughly the same temperature for ZrTe$_5$ and HfTe$_5$, appears to be sensitive to distinctions in the preparation procedure, in particular the crushing of the sample.) Repeated DSC measurements (100–800 K) on ZrTe$_5$ and HfTe$_5$ samples which had not been exposed to air in the meantime did not show the exothermic peak. Powder samles of ZrTe$_5$ and HfTe$_5$ with considerably enlarged particle size, were now synthesized by chemical transport reactions using I$_2$ as the transport agent. DSC runs for such freshly prepared samples (notably without being subjected to crushing or exposed to air over any extended period of time) showed no peaks at ~440 and ~720 K. These discoveries, which are consistent with the Raman-spectroscopic findings (*vide supra*), provoke a more general study of the oxidative degradation of zirconium and hafnium tellurides.

The recent explorations of the high-temperature properties of ZrTe$_5$ and HfTe$_5$, by means of electric resistivity [25] and ^{181}Ta time dependent perturbed angular correlation (TDPAC) [27, 28] measurements, revealed several anomalies. For ZrTe$_5$ (HfTe$_5$) a resistivity anomaly is detected at 450 K (500 K), while for HfTe$_5$ the TDPAC data give evidences for anomalies at 470, 743 and 816 K. It is immediately clear that these temperatures are all rather close to those where chemical reactions, melting and degradation take place according to Fig. 1.

As an example of the oxidation process, the behaviour of a ZrTe$_5$ sample studied in air at 432 K by thermogravimetric methods is shown in Fig. 2. The initial part of the relative weight gain ($\Delta w/w(0)$), vs time (t) curve varies almost linearly with time, up to $t \approx 3$ h whereupon the reaction rate is gradually reduced and becomes quite low for $t > \sim 10$ h. An estimate of the potential maximum weight gain was obtained by extrapolating a $\Delta w/w(0)$ vs $1/t$ plot to $1/t = 0$. The thus derived value $\Delta w/w(0) = 0.0445$ corresponds very well to that calculated assuming complete conversion of all ZrTe$_5$ to ZrO$_2$ and Te ($\Delta w/w(0) = 0.0439$). The corresponding observed (extrapolated) and calculated $\Delta w/w(0)$-values for HfTe$_5$ are 0.0385 and 0.0392, respectively.

Experiments were also carried out at fixed temperature (400–900 K) with ZrTe$_5$ and HfTe$_5$ filled in open crucibles and placed in a furnace with ordinary air atmosphere. After a short heat treatment at high temperatures (say 5 h at 900 K) or after prolonged time at lower temperatures (e.g. 30 h at 600 K) complete oxidation of all Te into TeO$_2$ was found in addition to conversion of Zr (Hf) into ZrO$_2$ (HfO$_2$). At temperatures below some 470 K the Te, which is released during the oxidation of Zr (Hf), is left unreacted, *viz.* occurs as elementary Te. However, in all cases attempts to detect Bragg reflections from ZrO$_2$ (HfO$_2$) in the powder X-ray diffraction patterns of the oxidized samples failed. For e.g. a ZrTe$_5$ sample oxidized

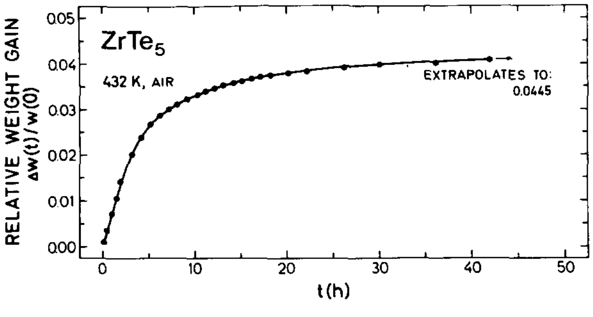

Fig. 2. Relative weight gain vs time for oxidation of ZrTe$_5$ in air at 432 K. Experimental points (extracted from continuous recordings) in relation to calculated curve (see text).

in air at 450 K for 60 h, only reflections from $ZrTe_5$ and Te could be identified. Visual inspection of the reaction products for $T < \sim 470$ K, nevertheless showed the existence of a white substance (together with $ZrTe_5$ ($HfTe_5$) and needles of Te) which consequently must be X-ray amorphous. It was not possible to obtain crystallization of the amorphous products under the present conditions (heating in air for $t < 100$ h at $T < 900$ K). The latter observation can well be rationalized on the assumption that the X-ray-amorphous product is ZrO_2 (HfO_2), for which crystallization (e.g. for samples initially made by precipitation from aqueous solution) only occurs at elevated temperatures, $T > \sim 1300$ K.

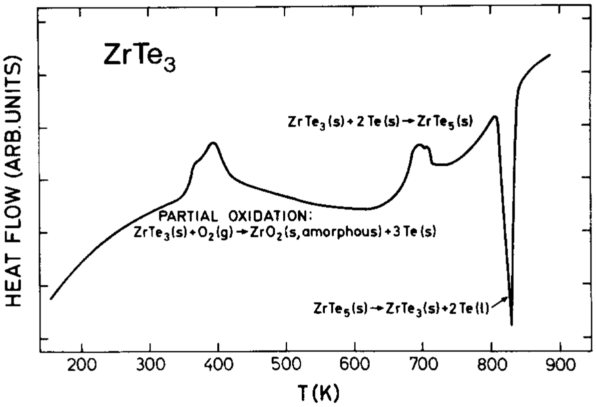

Fig. 3. DSC run for $ZrTe_3$ between 150 and 870 K. Interpretation of peaks is indicated.

On returning to Fig. 2 it is reasonable to ascribe the weight gain to the progressing reaction $ZrTe_5(s) + O_2(g) \rightarrow ZrO_2(s,\text{amorphous}) + 5Te(s)$. The $\Delta w/w(0)$ vs t curve is neither linear nor parabolic over the entire period of this experiment. In order to develop a model description for the time dependence of $\Delta w/w(0)$ it is useful to recall the low-dimensional nature of the $HfTe_5$ type crystal structure [2, 26]. To a very good approximation $ZrTe_5$ ($HfTe_5$) is built up of two-dimensional layers separated by Te–Te van der Waals distances [2, 9, 13, 21, 26]. It seems possible that oxygen can penetrate into (tunnel within) the cavities between these layers. Hence one is led to assume that the oxidation rate (weight gain per unit of time, dw/dt) is proportional to the available amounts of unreacted $ZrTe_5$ ($HfTe_5$) and adsorbed/absorbed O_2 in the sample. The oxygen content is in turn also proportional to the amount of unreacted $ZrTe_5$ ($HfTe_5$). Since the number of moles of $ZrTe_5$ ($HfTe_5$) is proportional to the weight difference $[w(\infty) - w(t)]$ it then follows that:

$$dw/dt = C[w(\infty) - w]^2.$$

Integration of this simple differential equation gives, after introduction of the boundary condition $w(t) = w(0)$ at $t = 0$ and rearrangement:

$$w(t) = w(\infty) - \frac{w(\infty) - w(0)}{[w(\infty) - w(0)]Ct + 1},$$

and then

$$\frac{\Delta w(t)}{w(0)} = \frac{\Delta w(\infty)}{w(0)} \cdot \frac{At}{At + 1},$$

where $\Delta w(t) = w(t) - w(0)$ and $A = [w(\infty) - w(0)]C = \Delta w(\infty)C$. As seen from Fig. 2 there is a remarkably good fit between the calculated curve for $\Delta w(\infty)/w(0) = 0.0440$ (*viz.* virtually the extrapolated value for complete conversion of $ZrTe_5$ to ZrO_2 and Te) and $A = 0.3167\,h^{-1}$ in the above expression, and the experimental data. A slightly enhanced deviation between observed and calculated data for low values of t can be overcome by introducing a time correction term ($\Delta t \approx 0.3$ h) which allows for the fact that the present $ZrTe_5$ sample was a little oxidized in advance, an initiation period of the reaction, etc. Similar deductions were made for the $HfTe_5$ data. The conclusion is accordingly that the oxidative degradation of $ZrTe_5$ and $HfTe_5$ at a given temperature is largely controlled by the amount of oxygen which the sample is exposed to.

Samples of $ZrTe_3$, $HfTe_3$, $Zr_{1+t}Te_2$ and $Hf_{1+t}Te_2$ were also preliminary studied by DSC measurements and the results for $ZrTe_3$ are shown as an example in Fig. 3. The closely corresponding exothermic effects in the di-, tri- and pentatellurides are all believed to signalize oxidation reactions in the temperature range 320–500 K. The variation in temperature is, at least partly, likely to reflect sample characteristics (particle size, mechanical treatment etc.), and/or experimental conditions (e.g. filling of sample holder and/or differences in the reaction atmosphere).

A second exothermic peak is located near 700 K in the DSC curve for $ZrTe_3$ (Fig. 3). On the basis of the high-temperature powder X-ray diffraction data for a matching $ZrTe_3$ sample under corresponding conditions, all three DSC peaks in Fig. 3 can be accounted for. At ~ 700 K, the bulk, non-oxidized $ZrTe_3$ reacts with the Te which is liberated during the oxidation process (probably fairly uniformly distributed as tiny particles throughout the sample) to form $ZrTe_5$. At 830 K $ZrTe_5$ decomposes as discussed above. (The reaction mechanism for converting $ZrTe_3$ plus Te to $ZrTe_5$ as well as the reverse decomposition, is in principle very simple from a structural point of view [2].)

The present experiments have shown that the low-dimensional zirconium and hafnium tellurides are much more unstable in air than first anticipated. Probably, rather large amounts of oxygen are easily and rapidly adsorbed/absorbed on the external and internal surfaces of the crystallites. This amount of oxygen is sufficient to bring about a partial oxidation of either of the $ZrTe_5$, $HfTe_5$, $ZrTe_3$, $HfTe_3$, $Zr_{1+t}Te_2$ and $Hf_{1+t}Te_2$ phases to amorphous ZrO_2 (HfO_2) and Te upon heating. This calls for great care when various types of physical or chemical measurements on these compounds are to be undertaken. However, the sensitivity of the zirconium and hafnium tellurides towards oxygen is just a part of a more universal problem concerning oxidative degradation of transition metal compounds in general. The authors will return to this aspect in forthcoming papers.

Returning finally to the zirconium and hafnium pentatellurides the authors seriously believe that most, if not all, of the anomalies reported for these compounds have chemical rather than physical origins. It is convenient to use the $HfTe_5$ case to briefly comment on the different anomalies.

Below ~80 K the oxygen, which is incorporated in the voids of the structure, may undergo a process parallel to condensation (*viz.* experience limitations in the freedom to move). The origin of the anomaly in the electronic transport properties at ~80 K could then be associated with entirely different movement patterns of these oxygen defects below and above this temperature. In fact all available information on the low-temperature anomaly can apparently be qualitatively rationalized on this simple oxygen hypothesis.

At some 450 to 500 K (depending on the particle size of the sample and other experimental factors) partial oxidation to ZrO_2 and Te takes place. It is almost imperative that this event manifests itself in electrical resistivity and TDPAC spectra. The few experimental facts which are available on this high temperature anomaly are fully consistent with an explanation based on partial oxidation.

The hysteresis accompanied anomaly at ~750 K established by the TDPAC technique cannot be directly associated with the melting of elementary Te (*vide supra*) since only the metal sites are probed in these experiments. However, the $HfTe_5$ type structure comprises a building block (*viz.* the infinite Te_{III}–Te_{III} zig-zag chains) recovered from elementary Te. It is therefore tempting to suggest that the onset of the destruction of the structural unit starts at a comparable temperature to the melting of elementary Te — some 100 K below the decomposition of $HfTe_5$ to $HfTe_3$ and Te. (Decomposition of $HfTe_5$ to $HfTe_3$ just implies the complete removal of the Te_{III}–Te_{III} zig-zag chains from the structural arrangement.)

The anomaly at ~820 K recorded by the TDPAC technique can unambiguously be attributed to the decomposition of $HfTe_5$ to $HfTe_3$ and Te.

The authors are fully aware of the fact that some, perhaps, most, of these explanations of the anomalies in $HfTe_5$ (and $ZrTe_5$) must be subject to future careful experimental checking before they are raised to truths. However, the present rather messy situation concerning the anomalies in $ZrTe_5$ and $HfTe_5$ invites for new tracks in the search for the ultimate scientific truth.

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