

Chemistry and Physical Properties of the Phosphide Telluride Zr_2PTe_2

Kristina Tschulik,^[a] Michael Ruck,^[a] Michael Binnewies,^[b] Edgar Milke,^[b]
Stefan Hoffmann,^[c] Walter Schnelle,^[c] Boniface P. T. Fokwa,^[d] Michael Gilleßen,^[d] and
Peer Schmidt*^[a]

Dedicated to Prof. Dr. Martin Jansen on the occasion of his 65th birthday

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The synthesis of the phosphide telluride Zr_2PTe_2 by solid-state reaction from the elements at 850 °C or by thermite-type reaction of Zr and $\text{Te}_8\text{O}_{10}(\text{PO}_4)_4$ was accomplished. Crystals were grown by chemical vapour transport by using iodine from 800 °C in the direction of higher temperatures up to 900 °C. The chemical bonding in Zr_2PTe_2 was investigated by the linear muffin-tin orbital (LMTO) method. The non-

vanishing DOS of zirconium and tellurium states at the Fermi level (E_F) complies with the metallic conductivity ($\rho \approx 40 \mu\Omega\text{cm}$ at 300 K) and temperature-independent Pauli paramagnetism.

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Introduction

Quite a large number of zirconium pnictide chalcogenides have been described so far as nitride sulfides,^[1] arsenide selenides,^[2] arsenide tellurides,^[2,3] antimonide selenides^[4] and antimonide tellurides.^[5] In contrast, ternary phosphide tellurides seem to be extraordinary compounds, because only a small number of those are known by now. Two of them consist of isolated phosphide and telluride anions: the uranium phosphide telluride $\text{UPTe}^{[6,7]}$ and the recently found compound Ti_2PTe_2 .^[8] Four other phosphorus- and tellurium-containing compounds are known: the three telluro-phosphides IrPTe ,^[9] $\text{OsPTe}^{[10]}$ and $\text{RuPTe}^{[10]}$ consisting of M^{3+} cations besides $[\text{P}-\text{Te}]^{3-}$ dumbbells, and the compound BaP_4Te_2 ^[11] built from Ba^{2+} cations and $^{1/2}[\text{P}_4\text{Te}_2]^{2-}$ anions.

Remarkably, no binary phosphorus and tellurium compounds are known, which additionally reflects the low affinity of the two elements as well as kinetic restraints. Therefore, syntheses of compounds containing phosphorus and tellurium are quite challenging and detailed studies of their thermal properties are indispensable in order to under-

stand the complex mechanisms of phase formation. We succeeded in synthesising the new metal phosphide telluride Zr_2PTe_2 through several pathways and investigated its thermal properties by using experimental methods and thermodynamic modelling. On the basis of these results single-crystals became available for the determination of the crystal structure and the physical properties. Results of measurements of electrical resistivity and magnetic susceptibility are discussed together with band-structure calculations. In this way it is possible to give a comprehensive view on the chemistry and the physical properties of Zr_2PTe_2 .

Results and Discussion

Methods of Synthesis

We achieved the synthesis of Zr_2PTe_2 in three different ways. Single-phase products can be obtained performing common solid-state reactions. Besides the possibility of using the elements as starting materials [Equation (1)], which require strictly controlled thermal conditions, the binaries ZrP and ZrTe_2 can be used as reagents under easily controllable conditions [Equation (2)].



Sublimation of phosphorus and tellurium is not negligible at temperatures above 500 °C. Yet, below this temperature an adjustment of the ternary equilibrium is not ac-

[a] Inorganic Chemistry, Dresden University of Technology, Helmholtzstraße 10, 01069 Dresden, Germany
Fax: +49-351-463-37287
E-mail: peer.schmidt@chemie.tu-dresden.de
<http://www.peer-schmidt.de>

[b] Inorganic Chemistry, Leibniz University Hannover, Callinstr. 9, 30167 Hannover, Germany

[c] Max Planck Institute for Chemical Physics of Solids, Nöthnitzer Str. 40, 01187 Dresden, Germany

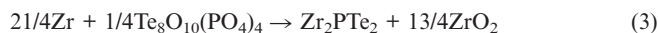
[d] Inorganic Chemistry, RWTH Aachen, Landoltweg 1, 52074 Aachen, Germany

completable in reasonable reaction times. Actually, control of the composition of a solid under evaporation conditions of its components is a general problem of synthesis of phosphorus- and tellurium-containing compounds. Hence, it is extremely difficult to ensure a complete incorporation of tellurium and phosphorus – which sublime readily – into the ternary compound at the reaction temperature of 800 °C, according to Equation (1).

However, starting with ZrP and ZrTe_2 [Equation (2)] diminishes this problem, as only the latter compound decomposes remarkably at the reaction temperature. Consequently, the equilibrium state is easier to access. Nonetheless, slow cooling of the reaction mixture is required to ensure complete incorporation of tellurium and phosphorus into the solid to form Zr_2PTe_2 . Although no explicit kinetic studies were carried out, no single-phase product was observed at higher cooling rates.

A long reaction time is also necessary to obtain a well-crystallised product. Reduction of reaction time by increasing the reaction temperature above 850 °C results in side products due to reactions with the silica wall of the reaction tube.

The third method of synthesis is a thermite-type reaction of elementary zirconium and the tellurium oxide phosphate $\text{Te}_8\text{O}_{10}(\text{PO}_4)_4$ leading to the products ZrO_2 and Zr_2PTe_2 [Equation (3)].



This way, the kinetic restraints of the other methods of synthesis can be avoided. The use of $\text{Te}_8\text{O}_{10}(\text{PO}_4)_4$, which remains solid at temperatures below 800 °C,^[8] is preferred over TeO_2 and P_4O_{10} , which would sublime at lower temperatures.

The possibility to form Zr_2PTe_2 besides ZrO_2 through a redox reaction with elementary zirconium originates from differences in the oxygen partial pressures between tellurium and phosphorus oxides and elemental zirconium, respectively. These differences represent a potential gradient in the sense of an electromotive series of solids.^[12] The equalisation of this gradient results in a thermodynamic equilibrium, represented by zirconium oxide besides elemental phosphorus and tellurium (Figure 1).

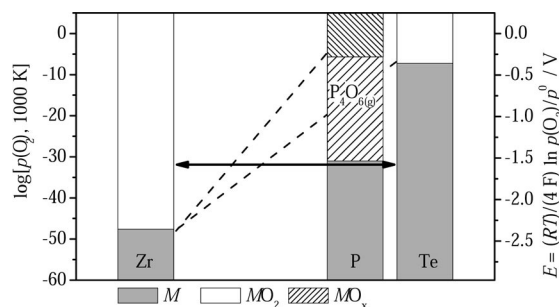


Figure 1. Oxygen partial pressure and electrochemical potential above the oxides of zirconium, phosphorus and tellurium calculated for $T = 1000 \text{ K}$ {calculation of $\log[p(\text{O}_2)/\text{bar}]$ and E based on data in ref.^[31] see ref.^[12]}, the arrow marks the level of equalisation of $p(\text{O}_2)$.

Because the crystallisation of zirconium phosphide telluride through this reaction path is even worse than in those paths mentioned before, chemical vapour transport reactions were performed to gain (single) crystals.

Thermal Properties

Thermogravimetric Measurements

The thermal decomposition of Zr_2PTe_2 does not start below 1000 °C; its degradation temperature is higher than for ZrTe_2 , whereas ZrP is stable under the given experimental conditions. The ternary compound decomposes in one single step that is not finished at 1500 °C when applying a heating rate of 10 K h^{-1} . Thus, another decomposition process can be observed along the cooling curve (— —, Figure 2) of the TG measurement down to 1300 °C.

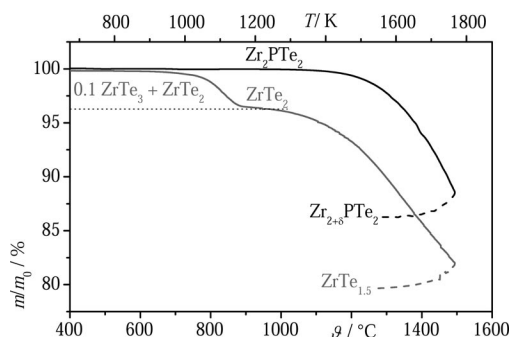
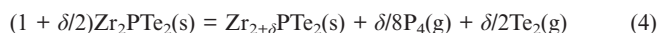


Figure 2. Thermal decomposition of Zr_2PTe_2 applying a heating rate of 10 K min^{-1} in comparison with the degradation of the binary compound ZrTe_2 .

In contrast to the thermal decomposition of Ti_2PTe_2 ,^[8] which decomposes in several steps at much lower temperatures to form Ti_2P (s) with release of gaseous tellurium species only, decomposition of Zr_2PTe_2 occurs with release of gaseous species of phosphorus and tellurium. The residue is a ternary phase with increased Zr content [Equation (4)].



Unfortunately, total pressure measurements with the use of a silica zero-point membrane manometer,^[13] as performed for Ti_2PTe_2 ,^[8] are not useful in the case of Zr_2PTe_2 , as sufficient partial pressures are not reached.

Thermodynamic Modelling of the System Zr/P/Te

In order to gain a better understanding of the complex mechanism of the formation and the thermal behaviour of Zr_2PTe_2 and to optimise the synthesis, a detailed thermodynamic modelling and description of the ternary system Zr/P/Te was established by using the computer program Tragmin.^[14] This was hampered by lacking thermodynamic data for the binary systems Zr/P and Zr/Te . Nevertheless, we succeeded by considering those condensed species for which thermodynamic data are known [$\text{Zr}_5\text{Te}_4(\text{s})$, $\text{ZrTe}_2(\text{s})$, $\text{Zr}(\text{s})$, $\text{P}(\text{s,red})$, $\text{Te}(\text{s})$] and adding $\text{ZrP}(\text{s})$ and $\text{Zr}_2\text{PTe}_2(\text{s})$ as essential species, whose thermodynamic data had to be estimated.

All gaseous species that have been found by mass spectrometric analysis of the gas-phase during the decomposition of Zr_2PTe_2 were taken into account: $\text{P}_4(\text{g})$, $\text{P}_2(\text{g})$, $\text{P}(\text{g})$, $\text{Te}_2(\text{g})$ and $\text{Te}(\text{g})$.

The results of the modelling of the thermal decomposition of Zr_2PTe_2 over a temperature range of 700–1000 °C are visualised in Figure 3. In agreement with Equation (4) $\text{P}_4(\text{g})$ and $\text{Te}_2(\text{g})$ represent the dominating gaseous species besides $\text{P}_2(\text{g})$ and $\text{Te}(\text{g})$, whereas the calculated partial pressure of $\text{Zr}(\text{g})$ is negligible $\{p[\text{Zr}(\text{g})] \approx 10^{-28} \text{ bar}\}$. Consequently the calculations confirm the assumption that the mechanism of the thermal decomposition of Zr_2PTe_2 differs fundamentally from the decomposition mechanism of Ti_2PTe_2 as a result of the formation of a homogeneity range $\text{Zr}_{2+\delta}\text{PTe}_2(\text{s})$.

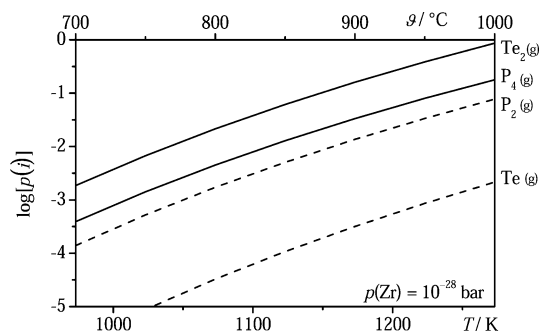


Figure 3. Temperature dependence of the gas-phase equilibrium of Zr_2PTe_2 .

Chemical Vapour Transport

Because single crystals, needed for investigation of the crystal structure of the new compound, were not accessible by the methods of synthesis introduced before, and isolation of Zr_2PTe_2 from the product mixture of the thermite-type reaction was required, chemical vapour transport of the zirconium phosphide telluride was aspired.

An attempt of chemical vapour transport of Zr_2PTe_2 into the direction of lower temperatures by adding TeCl_4 – by using the parameters for chemical vapour transport of Ti_2PTe_2 – failed. Detailed investigations of the appropriate transport agents and transport directions/temperature gradients became necessary.

Knudsen Cell Mass Spectrometry

As shown in Figure 4, the results of Knudsen cell mass spectrometric analysis of gas phase Zr_2PTe_2 containing iodine reflect the fact that iodine is able to dissolve Zr_2PTe_2 by reactions forming gaseous species at temperatures much lower than 1000 °C. Obviously, binary compounds of zirconium and iodine, like ZrI_4 are the gaseous species of zirconium with the highest partial pressure, yet neither binary species of phosphorus nor tellurium can be found. The latter two elements are detectable as P_4^+ , P_2^+ and P^+ as well as Te_2^+ and Te^+ , respectively, whereas Te^+ is the second most frequently detected species, surpassed only by I^+ .

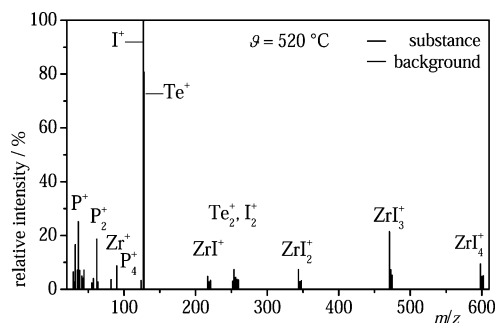


Figure 4. Results of the mass spectrometric analysis of a precipitate of Zr_2PTe_2 heated to $\vartheta = 520$ °C in the presence of iodine.

Because all components of Zr_2PTe_2 form sufficient amounts of gaseous species in the quaternary system $\text{Zr}/\text{P}/\text{Te}/\text{I}$, chemical vapour transport could be possible, if the solubility of all these components can be lowered significantly by applying a reasonable temperature gradient. For this reason, mass spectrometric analysis of the gas phase over Zr_2PTe_2 containing iodine was performed at different temperatures. Actually, the relative intensities of gaseous species of zirconium (ZrI_3^+), phosphorus (P_4^+ , P_2^+) and tellurium (Te^+ , Te_2^+) decrease with increasing temperature, as it becomes obvious by comparison of Figures 4 ($\vartheta = 520$ °C) and 5 ($\vartheta = 600$ °C). We assume that the chemical vapour transport of Zr_2PTe_2 proceeds in the quaternary system $\text{Zr}/\text{P}/\text{Te}/\text{I}$ in the direction of increasing temperatures from source to sink.

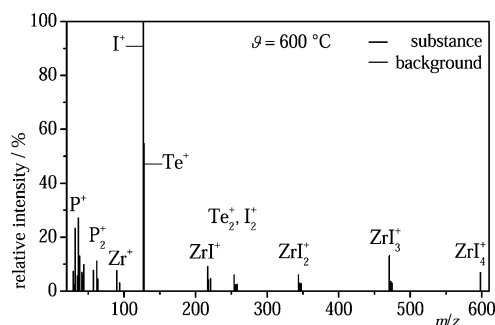


Figure 5. Results of the mass spectrometric analysis of a precipitate of Zr_2PTe_2 heated to $\vartheta = 600$ °C in the presence of iodine.

Chemical Vapour Transport Experiments of Zr_2PTe_2

For all attempts of chemical vapour transport, 300 mg of Zr_2PTe_2 powder and 15 mg of iodine were stacked in a large ampoule ($l = 12 \text{ cm}$, $A = 1.2 \text{ cm}^2$). By using a horizontal two-zone furnace, the residual was heated to $\vartheta = 800$ °C (source), and the top of the ampoule was heated to $\vartheta = 900$ °C (sink) for five days. Near the top of the ampoule shiny black hexagonal platelets of Zr_2PTe_2 resulted. Unfortunately, these platelets were intergrown crystals and hence not suitable for crystal investigations.

In order to optimise the conditions for growth of single crystals, chemical vapour transport was performed at various source temperatures and temperature gradients. All

other parameters were kept constant and equal to those mentioned above. These experiments were carried out by using a transport balance^[15] that permits in situ measurements of the mass flow by time. Figure 6 shows the transported mass for three different temperature gradients:

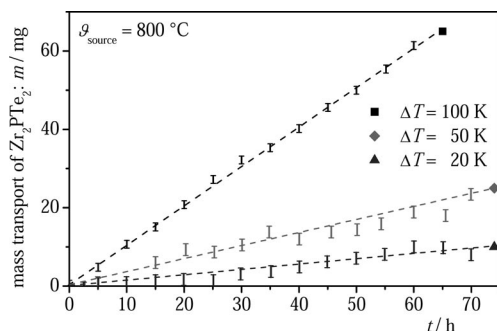


Figure 6. Rate of mass transport by vapour transport experiments of Zr_2PTe_2 , starting temperature $\vartheta_{\text{source}} = 800\text{ }^\circ\text{C}$, precipitation temperature $\vartheta_{\text{sink}} = \vartheta_{\text{source}} + \Delta T$.

Basically, transports are feasible from the source at $\vartheta = 800\text{ }^\circ\text{C}$ in a wide range of sink temperature $\vartheta_{\text{sink}} = \vartheta_{\text{source}} + \Delta T$ with $\Delta T = 20\text{--}100\text{ K}$. Large gradients result in a large amount of deposited polycrystalline material and are thus suitable for purification and separation. A small gradient leads to formation of a diminutive number of crystals. Some of them were convenient for single-crystal investigations. The rates of mass transport displayed in Table 1 were determined as the slopes of linear fits of the different m - t -transients.

Table 1. Rate of mass transport by vapour transport experiments of Zr_2PTe_2 , starting temperature $\vartheta_{\text{source}} = 800\text{ }^\circ\text{C}$, precipitation temperature $\vartheta_{\text{sink}} = \vartheta_{\text{source}} + \Delta T$.

$\vartheta_{\text{source}} / \text{ }^\circ\text{C}$	$\Delta T / \text{K}$	Rate of mass transport / mg h^{-1}
800	20	0.1
800	50	0.3
800	100	1.0

Thermodynamic Modelling of the Chemical Vapour Transport of Zr_2PTe_2

In order to verify the predicted conditions of chemical vapour transport of Zr_2PTe_2 as well as to reveal its mechanism, thermodynamic modelling of the quaternary system Zr/P/Te/I was performed by using the program Tragmin.^[14] In addition to the species considered in the modelling of the ternary system Zr/P/Te the iodine containing species $\text{ZrI}_4(\text{s})$, $\text{ZrI}_2(\text{s})$, $\text{TeI}_4(\text{s})$, $\text{I}_2(\text{s})$, $\text{ZrI}_4(\text{g})$, $\text{ZrI}_3(\text{g})$, $\text{ZrI}_2(\text{g})$, $\text{ZrI}(\text{g})$, $\text{PI}_3(\text{g})$, $\text{TeI}_4(\text{g})$ and $\text{TeI}_2(\text{g})$ were taken into account (Table 3). $\text{Zr}(\text{g})$ was not taken into account, as isothermal calculations proved its influence on the chemical vapour transport to be negligible $\{p[\text{Zr}(\text{g})] \approx 10^{-28}\text{ bar}\}$.

The composition of gas phase (Figure 7) displays only species with partial pressures exceeding $p(i) = 10^{-5}\text{ bar}$, as this region of partial pressures is said to be relevant for chemical vapour transport reactions. Obviously all elements can be found in the gas phase, as already known from mass spectrometric analysis. Yet the calculation shows that

$\text{Te}_2(\text{g})$, $\text{P}_4(\text{g})$ and $\text{ZrI}_4(\text{g})$ are the dominating gaseous species, which was not directly visible by the results of mass spectrometric analysis due to fragmentation and unequal tendency of ionisation of the different gaseous species.

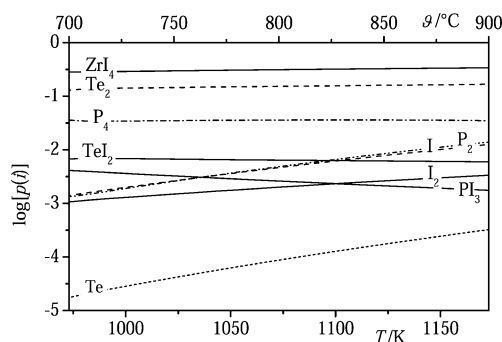
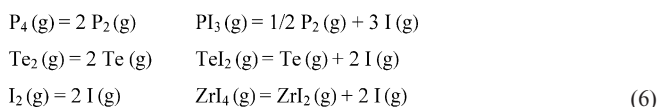


Figure 7. Temperature dependence of the gas-phase equilibria and composition of gas phase for reaction of $\text{Zr}_2\text{PTe}_2(\text{s})$ with iodine; $[p(i) < 10^{-5}\text{ bar for } i = \text{ZrI}, \text{ZrI}_3, \text{P}, \text{TeI}_4 \text{ not shown}]$.

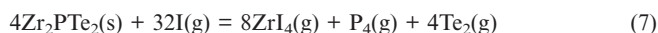
Furthermore, the calculated transport efficiencies of all gaseous species for a chemical vapour transport from $800\text{ }^\circ\text{C}$ (source) to $900\text{ }^\circ\text{C}$ (sink) enables a clarification of the transport mechanism and specification of the transport reaction. The transport efficiency is defined as the difference of the partial pressure of a compound in the source and its partial pressure in the sink normalised to the partial pressure of a solvent L at both temperatures [here inert nitrogen gas, see [Equation (5)]}. This is attributed to the fact that transport effective species exhibit positive and transport agents negative transport efficiencies, respectively, whereas transport efficiencies are zero for species that are not involved in the transport reaction.^[16]

$$\Delta = \left(\frac{p_i}{p^*_L} \right)_{T,\text{source}} - \left(\frac{p_i}{p^*_L} \right)_{T,\text{sink}} \quad (5)$$

Admittedly, as a result of the temperature difference between source and sink, secondary gas phase equilibria [Equation (6)] are included in the calculated transport efficiencies as well, which have to be deducted.



The effective transport efficiencies received this way are visualised in Figure 8. Hence Zr_2PTe_2 is transported, according to the transport reaction [Equation (7)].



Additional calculations indicate that an enrichment of zirconium by chemical vapour reaction is possible by adjustment of different parameters: high temperature of the source, major temperature gradient, zirconium-rich precipitate in the source and a small amount of iodine.

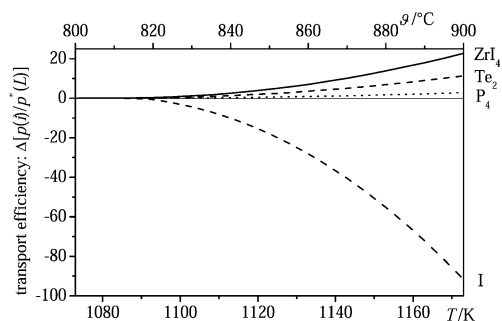


Figure 8. Effective transport efficiencies of gaseous species above a precipitate of Zr_2PTe_2 .

Crystal Structure of Zr_2PTe_2

Zr_2PTe_2 crystallises in the Bi_2STe_2 structure type.^[17] For better recognition of structural motives the hexagonal setting will be described in the following (Figure 9, prepared with DIAMOND^[18]). Phosphide as well as telluride anions are arranged in hexagonal layers, which are stacked along the hexagonal c axis in a sequence with two layers of telluride ions followed by one layer of phosphide ions. All octahedral vacancies between phosphide and telluride layers are filled by zirconium cations. Because the voids between neighbouring telluride layers remain completely empty, sandwich layers [Te–Zr–P–Zr–Te] result. Thereby, the anions form an ordered close sphere packing with stacking order [ABABCBCAC], which is known from samarium metal.^[19] The zirconium cations fill two thirds of the octahedral vacancies of this packing. The zirconium positions as well as the phosphorus and tellurium positions were found to be fully occupied.

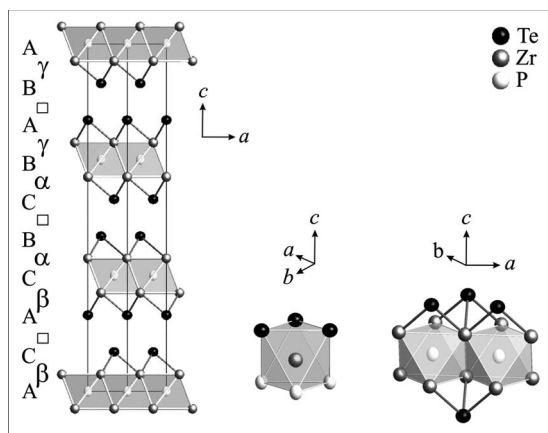


Figure 9. From left to right: crystal structure of Zr_2PTe_2 [projection along the b axis (unit cell outlined)] with $[\text{PZr}_6]$ octahedra (grey drawn polyhedra) and stacking sequence of the hexagonal layers of anions (Latin letters) and cations (Greek letters); trigonal-antiprismatic coordination of Zr (light grey) by three Te (black) and three P (white) ions; μ^3 -bridging of $[\text{PZr}_6]$ octahedra by Te ions. Plotted ellipsoids represent 99.99% probability at 293(2) K.

The same structural principle was reported for Ti_2PTe_2 .^[20] Furthermore, the zirconium arsenide tellurides $\text{Zr}_{0.29}\text{Zr}_{1.71}\text{AsTe}_2$ and $\text{NaZr}_2\text{AsTe}_2$ exhibit the same stacking

sequence, but in these compounds octahedral voids between the sandwich layers are partially or completely filled.^[3]

In Zr_2PTe_2 the interatomic distance Zr–Te is 288.98(2) pm, which is slightly larger than the one in the layered binary compound ZrTe_2 (282 pm; CdI_2 structure type^[21]). This might be due to the fact that in Zr_2PTe_2 the zirconium cations are coordinated by three (smaller) phosphide and three (larger) telluride anions and therefore slightly move out of the centre of the octahedra in the direction of the phosphide anions, so that a trigonal-antiprismatic coordination results. On the contrary, zirconium ions occupy the central position of the octahedral voids in ZrTe_2 , as they are coordinated by six equivalent telluride ions. The interatomic distances Zr–P in Zr_2PTe_2 [262.98(2) pm] and ZrP (263 pm; NaCl structure type^[22]) are about equal. Telluride ions in adjacent layers are separated by 380.52(2) pm from each other in Zr_2PTe_2 , which is slightly shorter than that in the similar compound Ti_2PTe_2 .^[20] This can be explained by the fact that – as zirconium cations [$r_{\text{6j}}(\text{Zr}^{4+}) = 72$ pm^[23]] are larger than titanium cations [$r_{\text{6j}}(\text{Ti}^{4+}) = 61$ pm^[23]] – they expand the layers in the hexagonal plane and hence the distance between tellurium atoms in one layer. In consequence, telluride anions in adjacent layers lie closer to each other.

Obviously the compound Zr_2PTe_2 can be described with two different ionic boundary formulae: $[(\text{Zr}^{4+})(\text{Zr}^{3+})(\text{P}^{3-})(\text{Te}^{2-})_2]$ or $[(\text{Zr}^{4+})_2(\text{P}^{3-})(\text{Te}^{2-})_2\text{e}^-]$. Here the crystal structure might be indicative of the latter to be preferred, as only one zirconium position was found and not several positions as might be expected for different oxidation states of zirconium. In order to verify this assumption physical properties of Zr_2PTe_2 were determined, as the compound should be metallic according to the second formula.

Physical Properties of Zr_2PTe_2

Measurements of Electrical Resistivity

Figure 10 shows the results of electrical resistivity measurements in a temperature range of 4 K to 320 K. Zr_2PTe_2 exhibits a resistivity of 40 $\mu\Omega\text{cm}$ at 300 K and a linear increase in resistivity with temperature. This typical metallic behaviour corresponds to the ionic formula

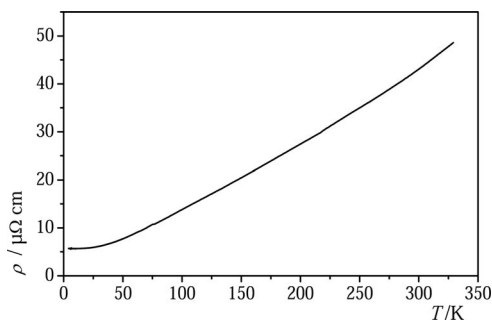


Figure 10. Temperature dependence of the electrical resistivity of Zr_2PTe_2 .

$[(\text{Zr}^{4+})_2(\text{P}^{3-})(\text{Te}^{2-})_2\text{e}^-]$, that is, delocalised electrons. The low residual resistivity indicates the absence of large grain boundary resistances.

Measurements of Magnetic Susceptibility

Measurements of magnetic properties of Zr_2PTe_2 were performed for various magnetic fields between 20 Oe and 70 kOe in the temperature range 1.8–400 K. Neither phase transitions nor superconductivity were detected within these ranges.

Figure 11 exemplifies the temperature dependence of corrected magnetic susceptibility. The visible decrease in magnetic susceptibility is due to a paramagnetic contamination of the analysed powder specimen, whereas its main component Zr_2PTe_2 is characterised by temperature-independent Pauli paramagnetism. The value of magnetic susceptibility at 0 K was extrapolated to $\chi_{\text{mol},0} \approx -54 \times 10^{-6} \text{ emu mol}^{-1}$. Subtraction of the diamagnetic increments of the included ions ($\Sigma\chi_{\text{dia}} \approx -164 \times 10^{-6} \text{ emu mol}^{-1}$ ^[24]) reveals the Pauli paramagnetic term $\chi_{\text{p}} \approx 110 \times 10^{-6} \text{ emu mol}^{-1}$. As this equals a density of states of about $3.4 \text{ states eV}^{-1}$ at the Fermi level Zr_2PTe_2 could be proved to be a metallic compound by means of its magnetic properties.

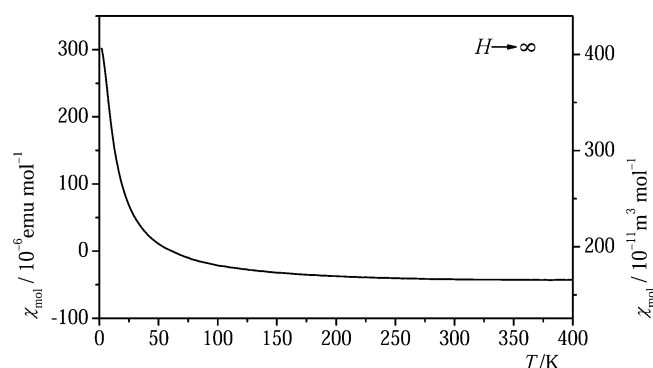


Figure 11. Temperature dependence of the corrected magnetic susceptibility of a powder sample of Zr_2PTe_2 .

These results are consistent with those reported by Philipp et al.^[20] for the related compound Ti_2PTe_2 .

Quantum Chemical Calculations

The chemical bonding in Zr_2PTe_2 was investigated by the linear muffin-tin orbital (LMTO) method. Figure 12 illustrates the total DOS curve calculated for Zr_2PTe_2 and its decomposition into contributions from the ionic constituents. The non-vanishing DOS matches at the Fermi level (E_{F}) indicate metallic character, and thus confirm measured electrical resistivity and Pauli paramagnetism. The Fermi level lies ca. 0.5 eV below a small pseudogap in the DOS. Bands located between -6 and -3 eV arise from valence orbitals of all three constituents. Bands beginning at ca. -3 eV and extending to the vicinity of the Fermi level involve significant combinations of Zr and Te valence orbitals: Throughout this region of the total DOS curve, Te valence orbitals dominate. At the Fermi level Zr and Te valence

orbitals have the greatest contributions and are therefore mainly responsible for the metallic behaviour of the compound. Above the Fermi level, Zr valence orbitals show a greater contribution to the DOS.

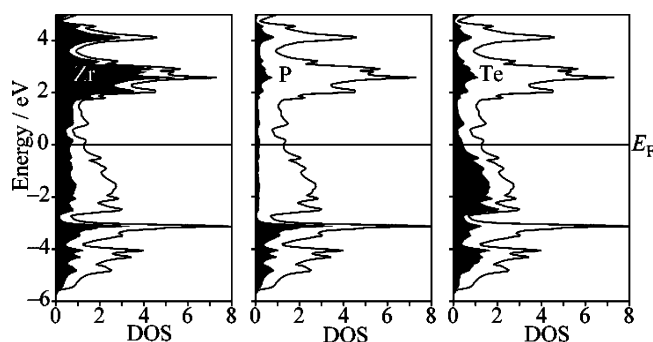


Figure 12. Total and partial DOS curves for Zr_2PTe_2 obtained from spin-polarised calculations. The Fermi level has been set to zero.

A chemical bonding analysis is possible on the basis of the shapes and integrated values of COHP curves (ICOHP = integrated value of COHP) for various interatomic interactions in the solid. The COHP curve in Figure 13a indicates that Zr–P orbital interactions are optimised in Zr_2PTe_2 : bonding orbitals are filled, antibonding orbitals are empty. However, the Zr–Te orbital interactions are not fully optimised, as some antibonding orbitals are present at the Fermi level (Figure 13b), which surely weaken the bonding compared to Zr–P. Both P–P and Te–Te interactions (not shown) reveal antibonding character around the Fermi level. The Zr–Zr orbital interactions show virtual bonding levels in the conduction band (Figure 13c) indicating that this unit could host even more electron density, in agreement with the slightly lowered DOS (pseudogap) just above the Fermi level. This COHP analysis suggests that the heteroatomic Zr–P and Zr–Te bonds are responsible of the structural stability of Zr_2PTe_2 , as expected. In agreement with this assessment, the largest ICOHP values are found for the Zr–P ($-0.82 \text{ eV bond}^{-1}$) and Zr–Te ($-0.59 \text{ eV bond}^{-1}$) contacts. This is reflected by the fact that both bond lengths, 262.98(2) and 288.98(2) pm for Zr–P and Zr–Te, lie close to the sum of their covalent radii (255 and 282 pm^[25,26]). Also, as already mentioned above, Zr–P [262.98(2) pm] in Zr_2PTe_2 almost equals the distance found in ZrP (263 pm; NaCl structure type^[22]), and Zr–Te [288.98(2) pm] in Zr_2PTe_2 is just slightly larger than the one observed in the similarly layered binary compound ZrTe_2 (282 pm; CdI₂ structure type^[21]). The average ICOHP value for Zr–Zr contacts amounts to $-0.041 \text{ eV bond}^{-1}$ suggesting weak interactions, and this result is in line with the long average Zr–Zr distance of 374.92(5) pm, which is 0.72 Å longer than the sum of the metallic radius of Zr for CN 12 (303 pm^[25,26]). In fact, these weak Zr–Zr interactions can be easily understood because most of the electron density on Zr is engaged in the heteroatomic Zr–X ($X = \text{P, Te}$) bonds. No significant interactions based on ICOHP values were found for P–P and Te–Te contacts in the structure.

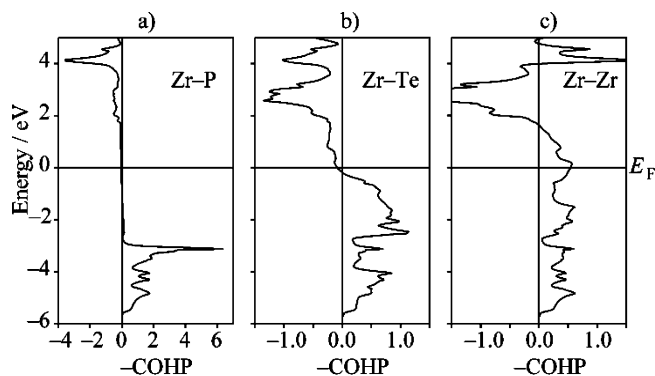


Figure 13. COHP curves for (a) Zr–P, (b) Zr–Te and (c) Zr–Zr contacts in Zr_2PTe_2 obtained from spin-polarised calculations. The Fermi level has been set to zero.

Conclusions

The new phosphide telluride Zr_2PTe_2 was prepared by different methods of synthesis. Its thermochemical properties were investigated and chemical vapour transport was performed. On the basis of experimental data, thermodynamic modelling of thermal decomposition and chemical vapour transport of Zr_2PTe_2 , estimation of its thermodynamic data was possible. Furthermore, it has been ascertained that Zr_2PTe_2 crystallises in a layered structure and exhibits delocalised electrons according to the boundary formula $[(\text{Zr}^{4+})_2(\text{P}^{3-})(\text{Te}^{2-})_2\text{e}^-]$, which has been validated by resistivity and magnetic measurements as well as quantum mechanical calculations.

Experimental Section

General: Starting materials used were red amorphous phosphorus (Fluka, 99%, washed with NaOH according to ref.^[27]), tellurium (Acros, 99.8%), zirconium powder (freshly filed from a rod, Chem-Pur, 99.8%), iodine (Merck, doubly sublimated over BaO_2), tellurium oxide phosphate (synthesised according to ref.^[28]), ZrP (prepared by heating of an equimolar mixture of Zr and P at 800 °C for 7 d) and ZrTe_2 (synthesised according to ref.^[29]). As some of

the starting materials as well as Zr_2PTe_2 are sensitive to air and moisture, all reagents were handled in an argon-filled glove box [$c(\text{O}_2, \text{H}_2\text{O}) < 0.1$ ppm, M. Braun LAB 130].

Syntheses were performed in evacuated closed silica tubes of small volume ($V \approx 1$ mL) to diminish sublimation of phosphorus and tellurium and the thereby resulting changes in the composition of the reaction mixture during the syntheses. Stoichiometric amounts of the well-mixed starting materials were filled into ampoules that had been freed from adherent moisture by heating under dynamic vacuum prior to use. Using the elements as starting materials the reaction requires heating of the elements from room temperature up to 700 °C within 90 h, further heating to 800 °C within the next 48 h and keeping this temperature for 120 h. In the following 150 h the reaction mixture must be cooled down to a temperature of 400 °C and quenched afterwards. In contrast to this quite complex regime of temperatures the synthesis of Zr_2PTe_2 by reaction of ZrP and ZrTe_2 allows fast heating of the starting materials up to 850 °C, holding the reagents at this temperature for 120 h and cooling them down to 400 °C with a cooling rate of 5 K h^{−1} before quenching. A third method of synthesis is a thermite-type reaction of elementary zirconium and the tellurium oxide phosphate $\text{Te}_8\text{O}_{10}(\text{PO}_4)_4$ leading to the products ZrO_2 and Zr_2PTe_2 . The temperature regime is identically to the one used for reaction of the binary starting materials.

Thermogravimetric Measurements: Performed under argon atmosphere with the use of a Netzsch STA 449 C apparatus situated in an argon-filled glove box; the heating rate applied was 10 K min^{−1} in a temperature range of 25–1500 °C, same cooling rate downwards.

Investigations of the composition of the gas phase in the quaternary system Zr/P/Te/I were performed by using the mass spectrometer Varian MAT 212 coupled to a Knudsen effusion cell.^[30] The sample was heated isothermally to 460, 520, 600, 700 and 800 °C. Evaporated species were ionised by electron impact ionisation with an energy of 70 eV and detected by a quadrupole mass spectrometer with $m/z \leq 600$.

Thermodynamic Modelling: The phase equilibria of the ternary system Zr/P/Te as well as of the quaternary system Zr/P/Te/I were studied by using Calphad methods based on the Eriksson–Gibbs energy minimiser implemented in the computer program Tragmin.^[14] The solid state/gas phase equilibria in the ternary and quaternary systems Zr/P/Te/(I) were calculated for different composi-

Table 2. Thermodynamic data of condensed species used for modelling of the system Zr/P/Te/I.

Species	ΔH_{298}^0 / kJ mol ^{−1}	ΔS_{298}^0 / J mol ^{−1} K ^{−1}	C_p / J mol ^{−1} K ^{−1} [a]			Ref.
			a	b	c	
Zr(s)	0	38.996	22.856	8.968	−0.712	[31]
P(s,red)	−17.488	22.801	16.735	14.897	0	[31]
Te(s)	0	49.706	19.121	22.094	0	[31]
Te(l)	12.545	55.578	37.660	0	0	[31]
ZrO ₂ (s)	−1051.496	132.869	70.120	7.021	−1.423	[31]
TeO ₂ (s)	−272.220	160.840	65.178	14.560	−0.502	[31]
ZrP(s)	−293.076	58.615	39.590	23.865	−0.712	this work
ZrTe ₂ (s)	−294.102	124.239	69.693	15.060	0.134	[33]
Zr ₅ Te ₄ (s)	−828.999	329.999	212.091	44.409	3.161	[34]
Zr ₂ PTe ₂ (s)	−607.086	180.032	109.275	38.937	−0.586	this work
ZrI ₄ (s)	−488.692	250.203	124.097	15.106	−3.098	[31]
ZrI ₂ (s)	−277.815	150.206	102.137	−6.586	−5.359	[31]
TeI ₄ (s)	−49.999	226.087	79.369	185.354	0	[31]
I ₂ (s)	0	116.133	30.124	81.630	0	[31]

[a] $C_p = a + b(10^{-3})T + c(10^6)T^{-2}$.

Table 3. Thermodynamic data of gaseous species used for modelling of the system Zr/P/Te/I.

Species	ΔH_{298}^0 / kJ mol ⁻¹	ΔS_{298}^0 / J mol ⁻¹ K ⁻¹	<i>a</i>	<i>C_p</i> / J mol ⁻¹ K ⁻¹ [a] <i>b</i>	<i>c</i>	Ref.
Zr(g)	601.241	181.339	22.994	3.052	3.638	[31]
Te ₂ (g)	160.371	262.152	34.646	6.615	-0.251	[31]
Te(g)	211.710	182.699	19.414	1.842	0.754	[31]
P ₄ O ₆ (g)	-2214.290	345.745	216.355	8.665	-6.795	[31]
P ₄ O ₁₀ (g)	-2902.076	406.697	292.830	19.192	-10.715	[31]
P ₄ (g)	59.118	279.980	81.839	0.678	-13.440	[31]
P ₂ (g)	144.302	218.128	36.295	0.800	-4.145	[31]
P(g)	333.885	163.201	20.670	0.172	0	[31]
I ₂ (g)	62.191	260.159	37.254	0.779	-0.498	[31]
I(g)	106.776	180.782	20.394	0.402	-0.289	[31]
ZrI ₄ (g)	-355.246	446.556	107.969	0.075	-3.010	[31]
ZrI ₃ (g)	-128.866	397.788	83.104	0.025	-2.052	[31]
ZrI ₂ (g)	-85.277	344.787	58.176	0.017	-0.842	[31]
ZrI(g)	402.921	275.810	37.384	0.929	-0.670	[31]
TeI ₄ (g)	61.953	443.716	90.0	0	0	[32]
TeI ₂ (g)	81.627	333.206	54.962	0	0	[32]
PI ₃ (g)	-17.991	374.372	82.843	0	-0.385	[31]
N ₂ (g)	0	191.609	30.417	2.546	-2.378	[31]

[a] $C_p = a + b(10^{-3})T + c(10^6)T^{-2}$.

tions isothermally in the temperature range 800–1300 K with $\Delta T = 100$ K. The thermodynamic data of condensed phases used are displayed in Table 2. The data sets of all gaseous species containing the components Zr, P, Te and I were adopted from ref.^[31,32] (Table 3).

Estimation and Optimisation of Standard Data: First, the standard enthalpy of formation of ZrP had to be estimated, which was done by using the particular value of the analogous compound TiP $\{\Delta H_{298}^0[\text{TiP(s)}] \approx -250 \text{ kJ mol}^{-1}\}$ as a starting point. Optimisation of this value was accomplished by varying the standard enthalpy of formation of ZrP until modelled coexistences of condensed phases were consistent with the experimental determined ones and reveals $\Delta H_{298}^0[\text{ZrP(s)}] \approx -290 \text{ kJ mol}^{-1}$. As for all unknown standard entropies of formation and functions of heat capacity presented in this work, approximations of S_{298}^0 (ZrP) and $C_p(T)$ (ZrP) were performed according to the Neumann–Kopp rule as the stoichiometric sum of the particular values of the elements.

The standard enthalpy of formation of zirconium phosphide telluride could be estimated on the basis of the results of the thermogravimetric measurements that indicate the decomposition pressure of Zr₂PTe₂ equals 1 bar at a temperature of about 1100 °C and optimised according to experimental determined coexistences of condensed species. The obtained value is $\Delta H_{298}^0(\text{Zr}_2\text{PTe}_2) = -607 \text{ kJ mol}^{-1}$. A comparison of the optimised standard enthalpy of formation of Zr₂PTe₂ with the particular value of the analogous titanium compound ($\Delta H_{298}^0 = -450 \text{ kJ mol}^{-1}$) shows the latter one to be smaller, what is consistent with the lower thermal stability of Ti₂PTe₂ that already decomposes at temperatures above 700 °C. Anyway, all thermodynamic data used for modelling of the ternary system Zr/P/Te taken from the literature as well as estimated data are presented in Table 2.

Single crystals of Zr₂PTe₂ suitable for structural investigations were selected on the basis of precession photographs. Intensity data were collected with an imaging plate diffractometer (Stoe IPDS-II) by using graphite-monochromated Mo-K α . ($\lambda = 71.073 \text{ pm}$) radiation. The microscopic crystal description was optimised by using sets of symmetry equivalent reflections^[35] and used afterwards in numerical absorption corrections.^[36] The crystal structure was solved in

space group $R\bar{3}m$ (no. 166) by direct methods^[19] and refined by full-matrix least-squares on F_o^2 (SHELX-97^[37]). Details of data collection and structure solution are gathered in Tables 4 and 5.

Table 4. Crystallographic data and details of structure determination for Zr₂PTe₂.

Formula	Zr ₂ PTe ₂
Crystal system	rhombohedral
Space group	$R\bar{3}m$ (no. 166), hexagonal setting
Formula units per cell	3
Temperature / K	293(2)
<i>a</i> / pm	381.17(3)
<i>c</i> / pm	2918.9(3)
Cell volume / pm ³	367.27(2)10 ⁶
Calculated density / g cm ⁻³	6.356
Crystal size / mm ³	0.2 × 0.15 × 0.01
Measurement modii	0–180° ($\omega = 0^\circ$) and 0–90° ($\omega = 30^\circ$); $\Delta\phi = 1^\circ$
Measurement limits μ / mm ⁻¹	$2\theta \leq 59.90^\circ$; $-5 \leq h, k \leq 5$; $-40 \leq l \leq 40$ 16.1 (Mo-K α)
Extinction correction	isotropic, empirical
Extinction parameter	0.0093(6)
Independent reflections	176
Measured reflections	4776
<i>R</i> _{int} ; <i>R</i> _{σ}	0.092; 0.042
Parameters; restrictions	10; 0
Residual e^- density / $e^- \text{ pm}^{-3}$	1.99×10^{-6} to -1.32×10^{-6}
<i>R</i> ₁ (for all F_o)	0.027
<i>wR</i> ₂ (for all F_o^2)	0.058
GooF	1.88

Table 5. Wyckoff positions (W.p.), coordinates, and coefficients U_{ij}/pm^2 of the anisotropic displacement parameters according to $\exp[-2\pi^2(h^2a^{*2}U_{11} + \dots + 2hka^*b^*U_{12} + \dots)]$ for Zr₂PTe₂; $U_{13} = U_{23} = 0$.

Atom	W.p.	<i>x</i>	<i>y</i>	<i>z</i>	$U_{11} = U_{22}$	U_{33}	U_{12}
P	3 <i>a</i>	0	0	0	60(20)	80(30)	29(8)
Te	6 <i>c</i>	2/3	1/3	0.11376(2)	90(6)	75(7)	45(3)
Zr	6 <i>c</i>	1/3	2/3	0.04943(3)	78(6)	80(9)	39(4)

All sample handling for physical properties measurements was done under Ar or He atmospheres. The electrical resistance of a microcrystalline sample, which was cold compressed in a cylindrical sapphire cell, was measured in the temperature range 4–320 K by a DC method (van der Pauw). As a result of the nature of the sample the estimated inaccuracy of the absolute resistivity is $\pm 20\%$.

Magnetisation measurements were performed between 1.8 and 400 K for selected magnetic field strengths with a SQUID magnetometer (MPMS XL-7, Quantum Design). About 100 mg of a microcrystalline sample were contained in a precalibrated quartz tube. Because the sample contained a small amount of ferromagnetic impurities the susceptibility data were corrected by the Honda–Owen method [extrapolation of high-field $\chi(H)$ data for $1/H \rightarrow 0$ for all temperatures].

The quantum-mechanical calculations were carried out by using the linear muffin-tin orbital (LMTO) method^[38–40] in its tight-binding representation^[41] through the LMTO-ASA 4.7 program.^[42] The chemical bonding was investigated by using the Crystal Orbital Hamilton Population (COHP) concept,^[43] which is an energy-resolved partitioning technique of the band-structure energy (sum of the Kohn–Sham eigenvalues) in terms of atomic and bonding contributions.^[44] For convenience, the COHP plots are set up such that bonding contributions are given to the right and antibonding contributions are given to the left. The figures were generated with the program wxDragon.^[45]

Further details of the crystal-structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository number CSD-420650.

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