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The thermochemical behaviour of $\text{Te}_8\text{O}_{10}(\text{PO}_4)_4$ and its use for phosphide telluride synthesis

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<p>Note: The following files were submitted by the author for peer review, but cannot be converted to PDF. You must view these files (e.g. movies) online.</p> <p>fig_1_Spannung.emf fig_2_TG.emf fig_3_Cp.emf fig_4_GasTe8.emf fig_5_DeltaH.emf fig_6_GasTiPTe-O.emf fig_7_GasTiPTe.emf</p>	



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The thermochemical behaviour of $\text{Te}_8\text{O}_{10}(\text{PO}_4)_4$ and its use for phosphide telluride synthesis

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Dedicated to Prof. Dr. Dr. h. c. Heinrich Oppermann with our highest esteem on the occasion of his 75th birthday

Keywords: tellurium oxide phosphate; telluride phosphides; thermochemical behaviour; thermodynamic modelling

The tellurium oxide phosphate $\text{Te}_8\text{O}_{10}(\text{PO}_4)_4$ has been synthesised by thermal decomposition of $\text{Te}_2\text{O}_3\text{HPO}_4$ at temperatures above 400 °C. $\text{Te}_8\text{O}_{10}(\text{PO}_4)_4$ melts at 570 °C and evaporates at 820 °C. The thermodynamic standard data have been determined by solution calorimetry and differential scanning calorimetry and have been optimised by thermodynamic modelling of the binary system $\text{TeO}_2/\text{P}_2\text{O}_5$:

$$\Delta H_{298}^0(\text{Te}_8\text{O}_{10}(\text{PO}_4)_4) = -5844(2) \text{ kJ}\cdot\text{mol}^{-1};$$

$$S_{298}^0(\text{Te}_8\text{O}_{10}(\text{PO}_4)_4) = 823.3 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}.$$

The phase relations in quaternary systems $M/\text{P}/\text{Te}/\text{O}$ ($M = \text{Ti}, \text{Zr}, \text{Ce}$) have been calculated and optimised synthesis parameters for phosphide tellurides have been derived.

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Introduction

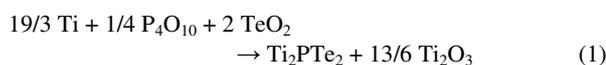
A quite large number of metal pnictide chalcogenides have so far been described as antimonides selenides [1-5], antimonide tellurides [4-19], arsenides selenides [4, 18-31], arsenides tellurides [18, 30-37] and even phosphide sulfides [6, 18, 29, 38-42] and phosphide selenides [4, 18, 23, 40-42]. On the other hand ternary phosphide tellurides seem to be extraordinary compounds, as only a small number of those are known by now. Few consist of isolated phosphide and telluride anions: the uranium phosphide telluride UPTe [43] and the recently found compounds Ti_2PTe_2 [44, 45], Zr_2PTe_2 [46] and $\text{Ce}_3\text{Te}_{4-x}\text{P}_x$ [47]. Beside these other phosphorus and tellurium containing compounds are described: The tellurophosphides IrPTe [48], OsPTe [49] and RuPTe [49], consisting of M^{3+} cations besides $[\text{P}-\text{Te}]^3$ -dumbbells, and the compound BaP_4Te_2 [50] build from Ba^{2+} cations and $^{1-}_\infty[\text{P}_4\text{Te}_2]^{2-}$ -anions. On the other hand, in the cationic clathrate $\text{Si}_{46-2x}\text{P}_{2x}\text{Te}_x$ [51, 52] the framework is built from 4-bonded silicon and phosphorus atoms, the cages are filled with tellurium atoms. As the smaller cages in the type I clathrate structure are often only filled partially with tellurium, the compound exhibits a phase width.

Remarkably, no binary phosphorus-tellurium compounds are known, which additionally reflects the low affinity of the two elements to each other. Therefore, synthesis of compounds containing phosphorus and tellurium is quite challenging and detailed studies of the thermochemical behaviour of the reactants and products are indispensable in order to understand the complex mechanisms of phase formation.

Common solid state reactions in which ternary phosphide tellurides are formed from the elements face a general problem:

sublimation of phosphorus and tellurium is not negligible for temperatures exceeding 500 °C. Below this temperature the ternary equilibrium is not attained in reasonable reaction times. Actually, the control of the composition of a solid with volatile components is the central problem of synthesis of phosphorus and tellurium containing compounds. Hence, it is extremely difficult to ensure a complete incorporation of tellurium and phosphorus into the ternary compound at reaction temperatures above 800 °C.

Avoiding these problems we succeeded in synthesising new metal phosphide tellurides via thermite type reactions deoxidising tellurium oxide and phosphorus oxide by an ignoble metal. The reduction of P_4O_{10} and TeO_2 by titanium to form the target compound Ti_2PTe_2 besides Ti_2O_3 [44] can be considered as an example of this reaction type. The formation of the titaniumsesquioxide from elemental titanium lowers significantly the free gibbs energy of the reaction (1) and can be assumed as the driving force for the synthesis of Ti_2PTe_2 . The resulting free gibbs energy is $\Delta_R G_{(1000\text{K})}^0 = -2295 \text{ kJ}\cdot\text{mol}^{-1}$ compared to $\Delta_R G_{(1000\text{K})}^0 = -405 \text{ kJ}\cdot\text{mol}^{-1}$ for reaction of the elements [44]. Otherwise the reaction path (1) is obvious favoured kinetically at low temperatures.



This kind of redox-reaction is enabled by the difference in oxygen partial pressure between the titanium oxides and the tellurium respectively phosphorus oxide. As only one distinct partial pressure can exist above the reaction mixture, an equalisation is reached by the reaction. These equilibria can principally be illustrated utilizing phase barograms or Ellingham- and Richardson-Jeffes-Diagrams. However, a global classification of the existence ranges ($p(\text{O}_2)$, T) and thus the redox potential of a large number of oxidic solids is problematic. A systematic overview illustrated with an extent of information equal to the earlier mentioned diagrams is given by the electromotive series of solids [53].

In the sense of the electromotive series of solids there is a potential gradient between titanium and the tellurium and phosphorus oxides, which will be compensated by reaction (1).

If also the gaseous species $P_4O_{6(g)}$ is taken into account, it can be seen, that the level of this equalisation lies at Ti_2O_3 besides elemental tellurium and phosphorus (figure 1). In the same way the formation of the zirconium phosphide telluride $Zr_{2+8}PTe_2$ [46] and the cerium phosphide tellurides $Ce_3Te_{4-x}P_x$ and $CeTe_{2-x}P_x$ [47] can be understood. Remarkably the equilibrium state for the thermite reaction is distinct for each system - Ti_2O_3 , ZrO_2 (2) and Ce_2O_2Te (3), (4). This is defined by the oxygen potential of metal oxide compounds beside phosphorus and tellurium (figure 1).

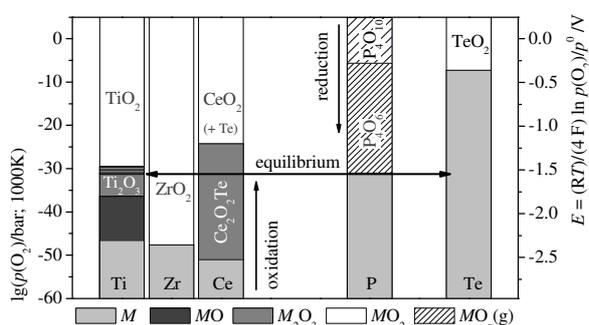
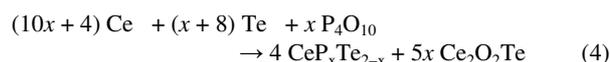
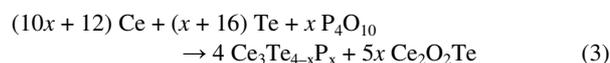
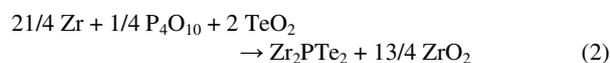


Figure 1. Oxygen partial pressure and electrochemical potential above the oxides of titanium, zirconium and cerium, respectively phosphorus and tellurium calculated for $T = 1000$ K (calculation of $\lg(p(O_2)/bar)$ and E based on data in ref. [54], see [53]), the arrow marks the level of equalization of $p(O_2)$.

A further problem of synthesis is the loss of TeO_2 and even more P_2O_5 due to their sublimation already at temperatures below 600 °C. Here the use of the tellurium oxide phosphates as an oxidic precursor instead of TeO_2 and P_4O_{10} is advantageous. The compound $Te_8O_{10}(PO_4)_4$ particularly should be preferred for the synthesis of Ti_2PTe_2 and Zr_2PTe_2 , as it contains phosphorus and tellurium in the appropriate ratio.

In order to determine the benefit of $Te_8O_{10}(PO_4)_4$ for thermite type reactions in phosphide telluride synthesis we investigated the thermochemical behaviour of this compound by thermal analyses and calorimetry. Based on ascertained standard data thermodynamic modelling of solid-gas equilibria has been performed and, finally, synthesis parameters for thermite type reactions have been derived.

Results and Discussion

1 Synthesis and thermal properties

The synthesis of single crystals of tellurium oxide phosphate $Te_8O_{10}(PO_4)_4$ has been described as a chemical transport reaction of TeO_2 and P_2O_5 at 550 °C [55]. Otherwise $Te_8O_{10}(PO_4)_4$ can be obtained by thermal degradation of the ditellurium trioxide hydrogenphosphate $Te_2O_3(HPO_4)$ [56] at 500 °C [57]. As the authors suggest, the further decomposition proceeds from 600 °C under release of TeO_2 by formation of $Te_3O_3(PO_4)_2$ which is described to melt incongruently at 640 °C.

In our investigations, several methods of synthesis resulted in different products. Attempts to form the known tellurium phosphates $Te_8O_{10}(PO_4)_4$ [55], $Te_3O_3(PO_4)_2$ [57], $Te_2P_2O_9$ and TeP_2O_7 [58] by solid state reactions at 550 °C led to inhomogenous, multiphase mixtures. Even after repeated homogenisation and long reaction time no single phase samples have been obtained. Higher temperatures of synthesis cannot be used because of incongruent melting reactions of the diverse tellurium phosphate phases. Additionally the melting of the phases resulted in tellurium phosphate glasses without recrystallisation at lower temperatures.

In order to characterise the synthesis of $Te_8O_{10}(PO_4)_4$ by thermal decomposition of the ditellurium trioxide hydrogenphosphate thermogravimetric measurements have been carried out. The TG-curve proves that the thermal decomposition of $Te_2O_3(HPO_4)$ occurs from $\vartheta_{onset} = 398(1)$ °C ($\vartheta_{peak} = 415(1)$ °C) under release of water. The observed mass loss ($\Delta m/m = -2.1(1)$ %) covers the theoretical one ($\Delta m/m_{theor} = -2.2$ %) and confirms the composition of the obtained sample in agreement with reaction (5), figure 2. XRD measurements affirm the formation of a crystalline, single phase sample of $Te_8O_{10}(PO_4)_4$.

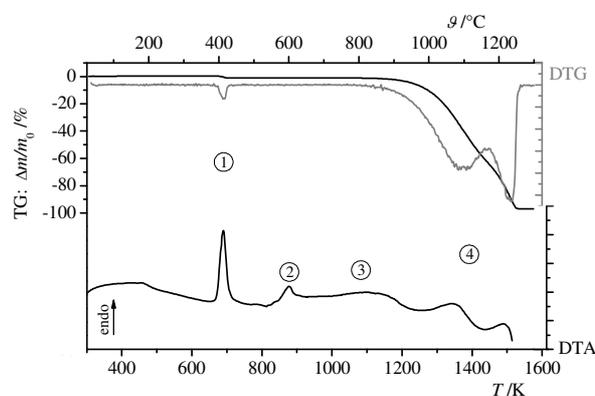
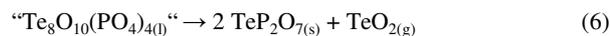


Figure 2. Thermal analysis (DTA/TG) of the precursor $Te_2O_3(HPO_4)$: ① formation of $Te_8O_{10}(PO_4)_4$ by loss of water; ② incongruent melting point; ③ progress of the liquidus line, ④ evaporation by release of $TeO_{2(g)}$ and $P_4O_{10(g)}$.

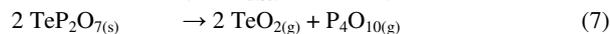
The TG experiment shows that the product is stable up to 800 °C, as no further mass loss could be detected. The described formation of $Te_3O_3(PO_4)_2$ at $\vartheta > 600$ °C under release of $TeO_{2(g)}$ [57] is not validated. In fact the incongruent melting of $Te_8O_{10}(PO_4)_4$ occurs at $\vartheta_{onset} = 570(2)$ °C ($\vartheta_{peak} = 602(2)$ °C) under formation of P_2O_5 -richer phases (probably $Te_3O_3(PO_4)_2$) and melt, poorer in P_2O_5 , as shown in the DTA curve, figure 2 (②). Afterwards more incongruent decomposition stages take place while following the liquidus line, figure 2 (③). Nevertheless, the observed thermal effects (③) are contiguous and it is impossible to distinguish between the formation of particular compounds. Basically, these effects coincide with the description of the thermal effects in the pseudo binary phase diagram TeO_2/P_2O_5 [58].

Further thermal decomposition reactions occur as solid-gas equilibria. They can be observed at temperatures above 800 °C ($\vartheta_{onset} = 820(10)$ °C). Up to 1250 °C the mass declines to zero (mass loss = -100 %) – that means, the sample is evaporated completely. Analysing the DTG curve two high-temperature decomposition steps can be distinguished: the first step at $\vartheta_{onset} = 820(10)$ °C ($\vartheta_{peak} = 1100(10)$ °C) with a mass loss of $\Delta m/m = -60(1)$ % and the second step at $\vartheta_{onset} = 1160(10)$ °C ($\vartheta_{peak} =$

1230(10) °C) with a mass loss of $\Delta m/m = -38(1) \%$. This behaviour can be described with the evaporation of $\text{TeO}_{2(\text{g})}$ in equilibrium (6) and the terminal simultaneous volatilisation of $\text{TeO}_{2(\text{g})}$ and $\text{P}_4\text{O}_{10(\text{g})}$ (7):



$$(\Delta m/m)_{\text{theor}} = -60.0 \%$$



$$(\Delta m/m)_{\text{theor}} = -37.8 \%$$

Thus, $\text{Te}_8\text{O}_{10}(\text{PO}_4)_4$ can be easily obtained as a precursor for thermite type reactions by thermal degradation of $\text{Te}_2\text{O}_3(\text{HPO}_4)$ at $\beta > 400$ °C. Although the phase melts at 570 °C, the composition keeps constant up to 800 °C, so that it looks promising to perform experiments at temperatures of about 650 °C.

In order to describe the complex phase equilibria in systems M/P/Te/O more precisely, detailed investigations concerning the thermodynamic properties of $\text{Te}_8\text{O}_{10}(\text{PO}_4)_4$ were carried out.

2 Calorimetry

The enthalpy of formation of $\text{Te}_8\text{O}_{10}(\text{PO}_4)_4$ could be derived from the enthalpies of solution of the ternary compound, P_2O_5 , TeO_2 and TeCl_4 , measured in a solution calorimeter with 4n HCl at 298 K. Based on the dissolution equilibria for TeO_2 (8), P_2O_5 (9) and $\text{Te}_8\text{O}_{10}(\text{PO}_4)_4$ (10) a formation reaction (11) can be formulated without detailed knowledge of thermodynamic behaviour of species in the aqueous solution. The combination of schemes of dissolution results in the formation reaction (11), which leads to the enthalpy $\Delta H_{298}^0(\text{Te}_8\text{O}_{10}(\text{PO}_4)_4)$ according to the rule of Hess: ($\Delta H_{298}^0 = -5845(2) \text{ kJ}\cdot\text{mol}^{-1}$).

Table 1. Average values of enthalpies of solution of compounds in 4n HCl at 298 K.

compound	$\text{TeO}_{2(\text{s})}$	$\text{P}_2\text{O}_{5(\text{s})}$	$\text{Te}_8\text{O}_{10}(\text{PO}_4)_{4(\text{s})}$	$\text{TeCl}_{4(\text{s})}$
equilibrium	(8)	(9)	(10)	(12)
$\Delta_{\text{sol}}\bar{H}_{298}^0 / \text{kJ}\cdot\text{mol}^{-1}$	+10.53(5)	-161.71(5)	+1.99(1)	-51.42(2)

Table 2. Enthalpies of formation of compounds used for calculation of the enthalpy of formation of $\text{Te}_8\text{O}_{10}(\text{PO}_4)_4$.

compound	$\text{TeO}_{2(\text{s})}$	$\text{TeCl}_{4(\text{s})}$	$\text{P}_2\text{O}_{5(\text{s})}$	$\text{HCl}_{(\text{sol})}$	$\text{H}_2\text{O}_{(\text{l})}$
$\Delta H_{298}^0 / \text{kJ}\cdot\text{mol}^{-1}$	-323.4	-323.8	-1505.0	-158.4	-285.8

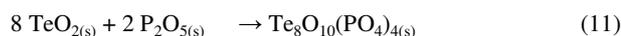
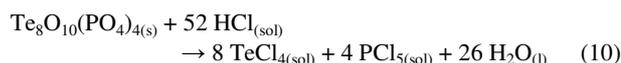
Since the dissolution of $\text{TeO}_{2(\text{s})}$ proceeds slowly, the evaluation of the caloric effect is more difficult. In order to avoid this problem and to check the above mentioned result, a scheme of dissolution including $\text{TeCl}_{4(\text{s})}$, $\text{H}_2\text{O}_{(\text{l})}$ and $\text{HCl}_{(\text{sol})}$ has been set up (13). The dissolution of $\text{TeCl}_{4(\text{s})}$ proceeds rapid and shows a strong exothermic effect. This way the enthalpy of formation for $\text{Te}_8\text{O}_{10}(\text{PO}_4)_4$ is calculated with nearly the same value ($\Delta H_{298}^0 = -5843(2) \text{ kJ}\cdot\text{mol}^{-1}$) as obtained including $\text{TeO}_{2(\text{s})}$. That means, the enthalpy of formation of $\text{Te}_8\text{O}_{10}(\text{PO}_4)_4$ has been obtained on different schemes with high accordance; for further calculations the average value $\Delta H_{298}^0(\text{Te}_8\text{O}_{10}(\text{PO}_4)_4) = -5844(2) \text{ kJ}\cdot\text{mol}^{-1}$ has to be recommended.

The obtained enthalpy agrees well with the feasible estimation:

$$\Delta H_{298}^0(\text{Te}_8\text{O}_{10}(\text{PO}_4)_{4(\text{s})}) < (8 \Delta H_{298}^0(\text{TeO}_{2(\text{s})}) + 2 \Delta H_{298}^0(\text{P}_2\text{O}_{5(\text{s})})) \approx -5600 \text{ kJ}\cdot\text{mol}^{-1}$$

The resulting enthalpy of reaction of about $-250 \text{ kJ}\cdot\text{mol}^{-1}$ is relatively small in relation to the mole mass of $\text{Te}_8\text{O}_{10}(\text{PO}_4)_{4(\text{s})}$. But that is intelligible since both binaries are acid oxides with only weak interactions in the formation of common ternary compounds. The enthalpies of solution of other tellurium phosphates were not accessible using the method of solution calorimetry, as no single phase samples could be obtained by solid state syntheses. Nevertheless, their enthalpies of formation could be derived based on the enthalpy of $\text{Te}_8\text{O}_{10}(\text{PO}_4)_{4(\text{s})}$.

Scheme of dissolution:

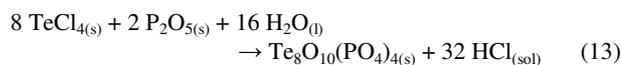
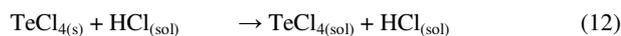


$$\Delta_{\text{R}} H_{298}^0(11) = 8 \cdot \Delta_{\text{sol}} H_{298}^0(8) + 2 \cdot \Delta_{\text{sol}} H_{298}^0(9) - \Delta_{\text{sol}} H_{298}^0(10)$$

$$\Delta_{\text{R}} H_{298}^0(11) = -247.5(10) \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H_{298}^0(\text{Te}_8\text{O}_{10}(\text{PO}_4)_4) = \Delta_{\text{R}} H_{298}^0(11) + 8 \cdot \Delta H_{298}^0(\text{TeO}_2) + 2 \cdot \Delta H_{298}^0(\text{P}_2\text{O}_5)$$

$$\Delta H_{298}^0(\text{Te}_8\text{O}_{10}(\text{PO}_4)_4) = -5845(2) \text{ kJ}\cdot\text{mol}^{-1}$$



$$\Delta_{\text{R}} H_{298}^0(13) = 8 \cdot \Delta_{\text{sol}} H_{298}^0(12) + 2 \cdot \Delta_{\text{sol}} H_{298}^0(9) - \Delta_{\text{sol}} H_{298}^0(10)$$

$$\Delta_{\text{R}} H_{298}^0(13) = -736.8(10) \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H_{298}^0(\text{Te}_8\text{O}_{10}(\text{PO}_4)_4) = \Delta_{\text{R}} H_{298}^0(13) - 32 \cdot \Delta H_{298}^0(\text{HCl}_{(\text{sol})}) + 8 \cdot \Delta H_{298}^0(\text{TeCl}_4) + 2 \cdot \Delta H_{298}^0(\text{P}_2\text{O}_5) + 16 \cdot \Delta H_{298}^0(\text{H}_2\text{O})$$

$$\Delta H_{298}^0(\text{Te}_8\text{O}_{10}(\text{PO}_4)_4) = -5843(2) \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H_{298}^0(\text{Te}_8\text{O}_{10}(\text{PO}_4)_4) = -5844(3) \text{ kJ}\cdot\text{mol}^{-1}$$

3 C_p -measurement

In order to obtain the temperature dependence of thermodynamic standard data of $\text{Te}_8\text{O}_{10}(\text{PO}_4)_4$, measurements of the heat capacity were carried out using a *heat flow*-differential scanning calorimeter. The measurement shows a characteristic curve of the molar heat capacity with a nonlinear increase. Fitting this curve one obtains the standard polynomial dependent on T which is used for further calculations.

$$C_p(T)_{\text{meas}} = (798.9 + 299.04 \cdot 10^{-3} \cdot T - 13.600 \cdot 10^6 \cdot T^{-2}) \text{ J}\cdot\text{mol}^{-1} \cdot \text{K}^{-1}$$

The experimental progress of the molar heat capacity can be proven by estimation of the pertinent function using the rule of *Neumann and Kopp*. This rule implies that no change in heat capacity occurs by reaction of two solids since the level of order is almost unchanged, see [59].

$$C_p(T)_{\text{est}} = 8 \cdot C_p(\text{TeO}_2) + 2 \cdot C_p(\text{P}_2\text{O}_5)$$

$$C_p(T)_{\text{est}} = 8 \cdot (65.2 + 14.56 \cdot 10^{-3} \cdot T - 0.502 \cdot 10^6 \cdot T^{-2})$$

$$+ 2 \cdot (74.9 + 162.34 \cdot 10^{-3} \cdot T - 1.561 \cdot 10^6 \cdot T^{-2}) \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

$$C_p(T)_{\text{est}} = (671.4 + 441.16 \cdot 10^{-3} \cdot T - 7.138 \cdot 10^6 \cdot T^{-2}) \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

The measurement is in good agreement with the estimation yet slightly higher. The heat capacities of other tellurium phosphates have been derived using the rule of *Neumann and Kopp* based on the C_p -functions of $\text{Te}_8\text{O}_{10}(\text{PO}_4)_4(\text{s})$ and $\text{P}_2\text{O}_5(\text{s})$.

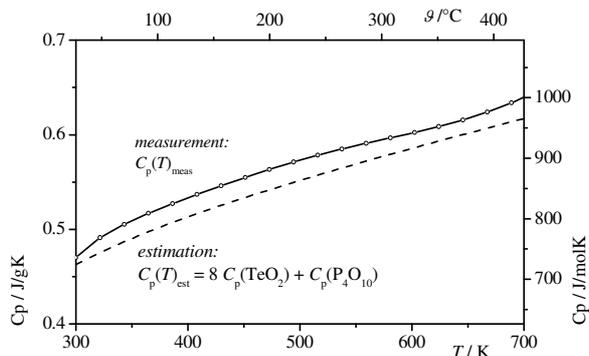


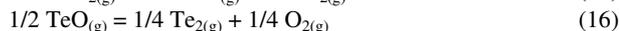
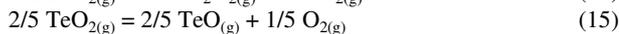
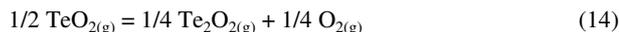
Figure 3. Measurement of the molar heat capacity C_p of $\text{Te}_8\text{O}_{10}(\text{PO}_4)_4$ with a heat flow-differential scanning calorimeter in comparison with the estimation of the C_p -function using the rule of *Neumann-Kopp* based on data of $\text{TeO}_2(\text{g})$ and $\text{P}_4\text{O}_{10}(\text{g})$.

4 Thermodynamic modelling

In order to describe the thermal behaviour of $\text{Te}_8\text{O}_{10}(\text{PO}_4)_4(\text{s})$ in more detail, the ternary system $\text{Te}/\text{P}/\text{O}$ has been investigated by thermodynamic modelling using the program *Tragmin* [60]. We started by considering the phases with known thermodynamic standard data $\text{TeO}_2(\text{s})$, $\text{Te}_8\text{O}_{10}(\text{PO}_4)_4(\text{s})$ and $\text{P}_2\text{O}_5(\text{s})$. Thermodynamic data of $\text{Te}_3\text{O}_3(\text{PO}_4)_2$, $\text{Te}_2\text{P}_2\text{O}_9$ and TeP_2O_7 have been estimated and optimised according to the thermal behaviour observed in thermogravimetric experiments. Even if the crystal structures of $\text{Te}_2\text{P}_2\text{O}_9$ and TeP_2O_7 are yet unknown and their compositions has been stated only from powder analysis, these compounds has been assumed to be thermodynamic stable. The gaseous species $\text{TeO}_2(\text{g})$, $\text{TeO}(\text{g})$, $\text{Te}_2\text{O}_2(\text{g})$, $\text{P}_4\text{O}_{10}(\text{g})$, $\text{P}_4\text{O}_6(\text{g})$, $\text{Te}_2(\text{g})$, $\text{Te}(\text{g})$, $\text{P}_4(\text{g})$, $\text{P}_2(\text{g})$, $\text{P}(\text{g})$, $\text{O}_2(\text{g})$ and $\text{O}(\text{g})$ have been taken into account, data see [54]. Different enthalpy data have been reported for $\text{P}_4\text{O}_6(\text{g})$ ($\Delta H_{298}^0 = -2214.3 \text{ kJ} \cdot \text{mol}^{-1}$ [54] ... $-1606.0 \text{ kJ} \cdot \text{mol}^{-1}$ [61]). Based on transport experiments of a number of phosphates the value $\Delta H_{298}^0 = -1883.7 \text{ kJ} \cdot \text{mol}^{-1}$ [62] has been deduced. In this work the currently accepted and reported value [63] $\Delta H_{298}^0 = -2214.3 \text{ kJ} \cdot \text{mol}^{-1}$ has been used for calculations. Using all the described data we succeeded in modelling of the solid-gas equilibria of the system $\text{TeO}_2/\text{P}_2\text{O}_5$ in full agreement with experimental results. The result of the modelling of the thermal decomposition of $\text{Te}_8\text{O}_{10}(\text{PO}_4)_4(\text{s})$ in the temperature range of 400 – 1000 °C is visualized in Figure 4. In agreement with equation (6) $\text{TeO}_2(\text{g})$ represents the dominating gaseous species, whereas the calculated partial pressure of $\text{P}_4\text{O}_{10}(\text{g})$ is lower by one order of magnitude. This way, $\text{Te}_8\text{O}_{10}(\text{PO}_4)_4(\text{s})$ decomposes by loss of $\text{TeO}_2(\text{g})$. The observed decomposition temperature (820 °C) corresponds to a total pressure of 10^{-3} bar.

The calculated oxygen partial pressure $p(\text{O}_2)$ results predominantly from the decomposition of gaseous species of tellurium (14 – 16), while the decomposition of $\text{P}_4\text{O}_{10}(\text{g})$ to $\text{P}_4\text{O}_6(\text{g})$ does not play an important role. This observation is in full

agreement with our expectation according to the electromotive series of oxides [53].



Consequently partial pressures of molecular species of phosphorus are negligible ($p(\text{P}_4(\text{g}); \text{P}_2(\text{g})) \ll 10^{-10}$ bar), Figure 4.

The thermal behaviour of the other tellurium phosphates $\text{Te}_3\text{O}_3(\text{PO}_4)_2$, $\text{Te}_2\text{P}_2\text{O}_9$ and TeP_2O_7 origin from the activity of P_2O_5 , which increases with the content of P_2O_5 . Thus the partial pressure of $\text{P}_4\text{O}_{10}(\text{g})$ rises and, finally, TeP_2O_7 decomposes by simultaneous volatilisation of $\text{TeO}_2(\text{g})$ and $\text{P}_4\text{O}_{10}(\text{g})$ (7).

The optimisation of thermodynamic standard data of tellurium phosphates generates a consistent data set for the system $\text{TeO}_2/\text{P}_2\text{O}_5$. According to the rule of *Neumann and Kopp*, the entropies follow an almost straight line. On the other hand the enthalpies of formation proceed along a continuous curve including the exothermic enthalpy of reaction for the formation from the binaries TeO_2 and P_2O_5 , figure 5. Thereby the average enthalpy of reaction per mole reactant is about $-30 \text{ kJ} \cdot \text{mol}^{-1}$.

The establishment of a consistent data set of tellurium phosphates was the basis for further calculations of more complex systems $M/\text{P}/\text{Te}/\text{O}$. Here the equilibrium states for different compositions of elements M constituting the redox system with $\text{Te}_8\text{O}_{10}(\text{PO}_4)_4(\text{s})$ were of highest interest.

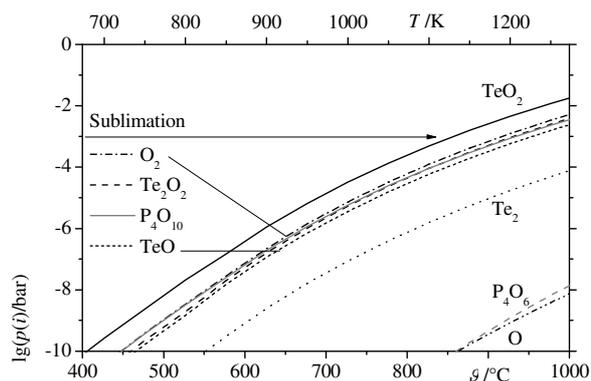


Figure 4. Temperature dependence of the gas phase equilibria and composition of gas phase above $\text{Te}_8\text{O}_{10}(\text{PO}_4)_4(\text{s})$, calculated using the program *TRAGMIN* [60].

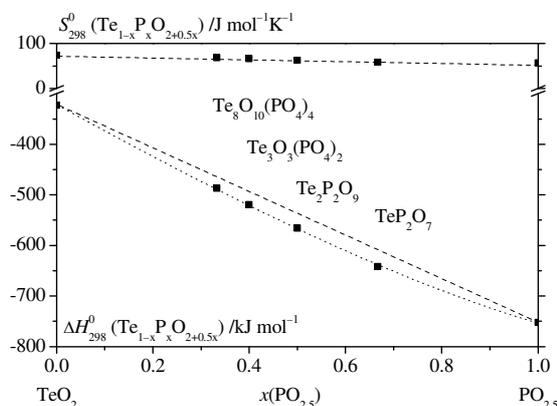


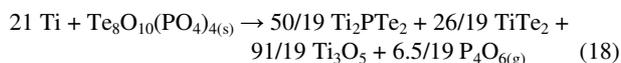
Figure 5. Progress of optimised thermodynamic standard data ΔH_{298}^0 and S_{298}^0 of tellurium phosphates, presentation of normalised data for $\text{Te}_{1-x}\text{P}_x\text{O}_{2+0.5x}$ (e.g. $1/12 \text{Te}_8\text{O}_{10}(\text{PO}_4)_4 = \text{Te}_{0.667}\text{P}_{0.333}\text{O}_{2.167}$; $1/3 \text{TeP}_2\text{O}_7 = \text{Te}_{0.333}\text{P}_{0.667}\text{O}_{2.333}$).

Conclusions

The use of the tellurium oxide phosphates as an oxidic precursor instead of TeO_2 and P_2O_5 is advantageous due to its thermal stability in the range up to 800 °C. For this reason, the desired thermite type reactions can be carried out at temperatures of about 700 °C without deficit of one of the reactants by evaporation. $\text{Te}_8\text{O}_{10}(\text{PO}_4)_4$ particularly is preferred for the synthesis of Ti_2PTe_2 and Zr_2PTe_2 , as it contains phosphorus and tellurium in the appropriate ratio.

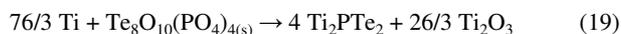
Since the synthesis of the pertinent compounds from the elements requires temperatures above 800 °C, the reaction path via $\text{Te}_8\text{O}_{10}(\text{PO}_4)_4$ is obviously kinetically favoured at lower temperatures. The possibility of thermite type reactions results from the oxygen partial pressure behaviour of $\text{Te}_8\text{O}_{10}(\text{PO}_4)_4$, see figure 4. Since only the redox potential of tellurium is influenced by stabilisation of the ternary compound $\text{Te}_8\text{O}_{10}(\text{PO}_4)_4$ compared with TeO_2 , the scheme of the electromotive series (Figure 1) does not change significantly. Hence again the redox potential of $\text{P}_4\text{O}_{6(\text{g})}$ is crucial for the equilibrium state of thermite reaction.

The resulting complex solid-gas equilibria have been calculated for different initial compositions in the systems $M/\text{P}/\text{Te}/\text{O}$ ($M = \text{Ti}, \text{Zr}, \text{Ce}$). They will be represented here using the example of the formation of Ti_2PTe_2 . The formation of Ti_2PTe_2 can be assumed as a thermite reaction with titanium forming titanium oxides. The calculation of the composition of the gas phase for the initial composition $21 \text{ Ti} + \text{Te}_8\text{O}_{10}(\text{PO}_4)_{4(\text{s})}$ evidences that not only TiO_2 is formed according to (17) but also phosphorus remains partially oxidised. Thus substantial amounts of $\text{P}_4\text{O}_{6(\text{g})}$ remain in the gas phase, figure 6, and mainly Ti_3O_5 is formed as a product of oxidation of titanium (18). This result proves completely the statement of figure 1, where the existence of P_4O_6 is illustrated.



Depending on temperature and volume of the reaction ampoule the presence of P_4O_6 in the gas phase leads to significant changes of the composition in the solid state. Notably TiTe_2 has been obtained besides Ti_2PTe_2 and Ti_3O_5 (18). The former hinders the subsequent separation of Ti_2PTe_2 from the thermite mixture by chemical vapour transport, since TiTe_2 is transported under similar conditions.

In order to reduce P_4O_6 completely, higher amounts of titanium are necessary. The equilibrium oxygen partial pressure is reached in coexistence with Ti_2O_3 , according to reaction (19).



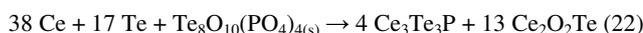
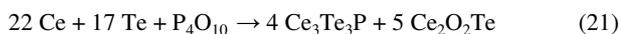
The gas phase above the mixture of reaction (19) only shows $\text{Te}_{2(\text{g})}$ as dominating species of thermal decomposition of Ti_2PTe_2 , figure 7. Oxygen containing species do not have an influence on the equilibrium state. That means, the tellurium phosphate $\text{Te}_8\text{O}_{10}(\text{PO}_4)_{4(\text{s})}$ has been reacted completely to form Ti_2PTe_2 and Ti_2O_3 .

Since $\text{Te}_8\text{O}_{10}(\text{PO}_4)_{4(\text{s})}$ is stable up to 800 °C and the thermal decomposition of Ti_2PTe_2 starts at temperatures above 700 °C (see figure 7), the best synthesis conditions for the thermite type reaction can be concluded: the reaction has to be carried out at temperatures up to 700 °C with an initial mixture according to equation (19).

The conditions for the formation of Zr_2PTe_2 are somewhat different. Here the formation of ZrO_2 reduce the oxygen partial pressure sufficiently to avoid the formation of $\text{P}_4\text{O}_{6(\text{g})}$ (20). The temperature is restricted by the decomposition temperature of $\text{Te}_8\text{O}_{10}(\text{PO}_4)_{4(\text{s})}$ while Zr_2PTe_2 is stable up to 1100 °C [45].



The synthesis of cerium phosphide telluride $\text{Ce}_3\text{Te}_3\text{P}$ is accompanied by the formation of cerium oxide telluride $\text{Ce}_2\text{O}_2\text{Te}$ requiring an excess of tellurium, equation (21). The addition of $\text{Te}_8\text{O}_{10}(\text{PO}_4)_{4(\text{s})}$ (22) instead of P_4O_{10} is thus not practical.



It becomes obvious, that the results of a specific system can't be passed on directly to the synthesis of other ternary phosphide tellurides $M_x\text{PTe}_y$, as the distinct conditions have to be regarded individually for each system. But generally the synthesis from the oxides is applicable for every metal that can form an oxide, whose oxygen partial pressure is below the one of $\text{P}_4\text{O}_{6(\text{g})}$. In this respect the *electromotive series of solid oxides* [53] can be taken as an easy, far-reaching tool for a systematic design of inorganic synthesis. As only compounds with shared ranges of electrochemical or oxygen potential can interact, a combinational solution of synthesis result.

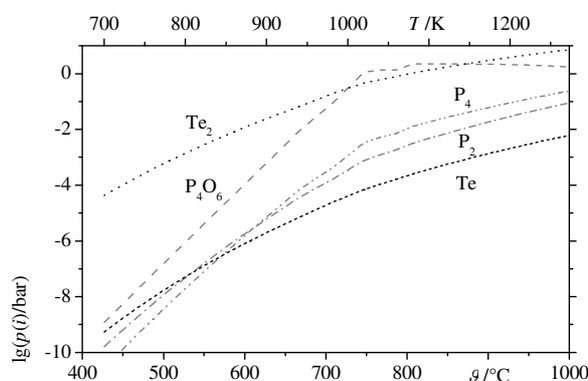


Figure 6. Temperature dependence of the gas phase equilibria and composition of gas phase for the equilibrium (18), calculated using the program TRAGMIN [60].

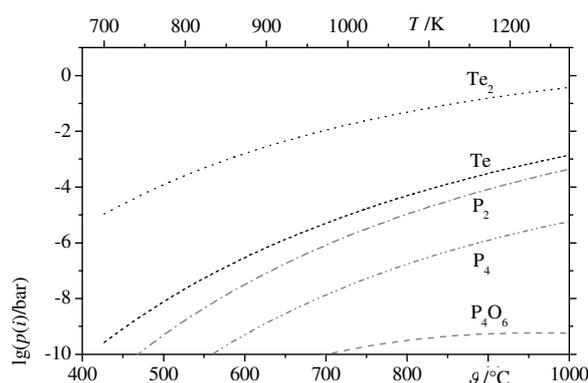


Figure 7. Temperature dependence of the gas phase equilibria and composition of gas phase for the equilibrium (19), calculated using the program TRAGMIN [60].

Experimental Section

Starting materials used to produce tellurium phosphates were phosphoric acid (*Baker*, p.a.), tellurium oxide (*Alfa Aesar*, 99.99 %) and phosphorus oxide (*Riedel deHaen*, 98.5 %, sublimed).

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Synthesis of ditellurium trioxide hydrogenphosphate $\text{Te}_2\text{O}_3(\text{HPO}_4)$ has been performed by reaction of 6.4 ml H_3PO_4 with 5 g TeO_2 under hydrothermal conditions in an iron autoclave with silica tube inlay (15 ml), similar to [57]. The mixture has been heated for 24 h up to 190 °C and quenched rapidly by water. Autoclave temperatures above 200 °C led to partial decomposition of the product. The white precipitation has been exhausted and washed with water and acetone. Drying the product at 100 – 150 °C a single phase powder sample, identifiable by powder XRD, has been obtained.

Synthesis of $\text{Te}_8\text{O}_{10}(\text{PO}_4)_4$ succeeded by thermal decomposition of ditellurium trioxide hydrogenphosphate $\text{Te}_2\text{O}_3(\text{HPO}_4)$ at 450 °C in air.

Solid state syntheses of tellurium phosphates have been performed in evacuated closed silica tubes of small volume ($V \approx 1$ ml) to diminish sublimation of phosphorus oxide and tellurium oxide and the thereby resulting changes of the composition of the reaction mixture during the syntheses. As P_2O_5 is sensitive to air and moisture, all reagents were handled in an argon filled glove box ($V(\text{O}_2, \text{H}_2\text{O})/V_0 < 0.1$ ppm, *M. Braun* LAB 130). Stoichiometric amounts of the well-mixed educts were filled in those ampoules that had been freed from adherent moisture by heating under dynamic vacuum prior to use. Solid state reactions required heating from room temperature up to 300 °C within 24 hours, further heating to 550 °C within the next 24 hours and keeping this temperature for 500 hours. Despite the long reaction time we found mixtures of several phases in the product. Although the purposed compounds $\text{Te}_8\text{O}_{10}(\text{PO}_4)_4$, $\text{Te}_3\text{O}_3(\text{PO}_4)_2$, $\text{Te}_2\text{P}_2\text{O}_9$ and TeP_2O_7 could be detected as the main product at a time, always the educts TeO_2 and P_2O_5 were contained. In addition $\text{Te}_3\text{O}_3(\text{PO}_4)_2$ has been identified as a by-product of all solid state syntheses.

Thermite-type reactions of elementary titanium or zirconium and the tellurium oxide phosphate $\text{Te}_8\text{O}_{10}(\text{PO}_4)_4$ led to the products $\text{Ti}_2\text{O}_3 + \text{Ti}_2\text{PTe}_2$ and $\text{ZrO}_2 + \text{Zr}_2\text{PTe}_2$, respectively. Stoichiometric amounts of the well-mixed educts were filled in silica ampoules, which were evacuated and sealed. The synthesis by thermite reaction allows fast heating of the educts up to 800 °C, holding the reagents at this temperature for 120 hours and cooling them down to 400 °C with a cooling rate of $5 \text{ K}\cdot\text{h}^{-1}$ before quenching [44, 46].

Phase identification of products has been realised by powder XRD. Patterns of synthesised compounds and mixtures were collected with a *SIEMENS* D5000 diffractometer using $\text{CuK}\alpha$ -radiation (reflexion mode) with an acceleration voltage of 40 kV and a filament current of 25 mA. The diffractometric scans were obtained between 5 and $110^\circ 2\theta$ at a scan speed of $0.875 \text{ deg}\cdot\text{min}^{-1}$.

Thermogravimetric measurements (TG) and difference thermal analysis (DTA) were carried out in a simultaneous thermal analyser (*NETZSCH* STA 409 Luxx). Measurements were carried out in the temperature range from $\vartheta = 25$ to 1300 °C with a heating rate of $10 \text{ K}\cdot\text{min}^{-1}$ in air. The particular decomposition temperature, derived from the first decomposition step, was determined at the onset of the corresponding thermal effect.

The enthalpy of formation of $\text{Te}_8\text{O}_{10}(\text{PO}_4)_4$ could be derived from the enthalpies of solution of the ternary compound, P_2O_5 , TeO_2 and TeCl_4 , measured in a solution calorimeter SCS 2225 (*THERMOMETRIC*) with 4n HCl at 298 K, see [64]. In order to prove the reproducibility and accuracy of measurement the solution enthalpy of KCl has been determined; the measured value $\Delta_{\text{sol}}H_{298}^0(\text{KCl}_{(\text{s})}) = 17.5 \pm 0.1 \text{ kJ}\cdot\text{mol}^{-1}$ were in good agreement with the reference [65]. Single phase samples have been filled in glass ampoules ($V_{\text{amp}} = 1$ ml) and placed in the isothermic calorimeter cell ($V_{\text{cal}} = 100$ ml). Measurement and evaluation followed the *Regnault-Phaundler* method. At least five individual measurements for each sample have been realised and the average value has been determined for further calculations (Table 1).

Measurements of the heat capacity of $\text{Te}_8\text{O}_{10}(\text{PO}_4)_4$ were carried out with a heat flow-differential scanning calorimeter DSC 404 (*NETZSCH*). Data have been collected in a stepwise mode from $\vartheta = 25$ up to 445 °C with an increment of $\Delta T = 20$ K. Sensitivity of the heat flow detector has been determined by the measurement of a sapphire plate as a standard.

In order to determine the oxygen partial pressure $p(\text{O}_2)$ measurements have been performed in a potentiometric solid electrolyte device “*Oxylyr*”, see [66]. The adjustment of the desired oxygen partial pressure in the gas flow was realised by electrolytic pumping of oxygen to or from a carrier gas flow of argon, which contained H_2O and H_2 of various concentrations. Unfortunately, the partial pressure of $\text{Te}_8\text{O}_{10}(\text{PO}_4)_4$ were not measurable within the existence range of the solid phase. At higher temperatures, the reduction process led to elemental tellurium, which sublimed out of the reaction zone. Thus no equilibrium conditions could be reached.

Thermodynamic modelling of phase equilibria were accomplished using Calphad-methods based on the *Eriksson Gibbs* energy minimizer implemented in the program *Tragmin* [60]. The solid state–gas phase equilibria in the ternary system Te/P/O have been calculated for different compositions isothermally in the temperature range 600 – 1300 K with $\Delta T = 20$ K. The optimised thermodynamic data of condensed phases used are displayed in Table 3. The data sets of all gaseous species containing the components P, Te and O were adopted from [54]. Further calculations of phase equilibria in the quaternary systems *M/P/Te/O* ($M = \text{Ti, Zr, Ce}$) became feasible by addition of the data sets of the constitutive ternary systems. The concerning data of the systems *M/P/Te* has been optimised previously [44, 46, 47].

Estimation of standard data: The standard enthalpy of formation of $\text{Te}_8\text{O}_{10}(\text{PO}_4)_4$ has been estimated to be more negative as the sum of the enthalpies of binary phases ($\Delta H_{298}^0(\text{Te}_8\text{O}_{10}(\text{PO}_4)_{4(\text{s})}) < (8 \Delta H_{298}^0(\text{TeO}_{2(\text{s})}) + 2 \Delta H_{298}^0(\text{P}_2\text{O}_{5(\text{s})}) \approx -5600 \text{ kJ}\cdot\text{mol}^{-1}$) as a starting point. Optimization of this value was accomplished by solution calorimetry and thermodynamic modelling of solid-gas equilibria, as determined in TG experiments. The enthalpies of formation for the other tellurium phosphates have been estimated based on this value and optimised confirming the TG results.

As for all unknown standard entropies and functions of heat capacity presented in this work, approximations of S_{298}^0 and $C_p(T)$ have been performed according to the *Neumann-Kopp* rule as the stoichiometric sum of the particular values of $\text{TeO}_{2(\text{s})}$ and $\text{P}_2\text{O}_{5(\text{s})}$ or alternatively $\text{Te}_8\text{O}_{10}(\text{PO}_4)_{4(\text{s})}$ and $\text{P}_2\text{O}_{5(\text{s})}$.

Table 3: Thermodynamic data of condensed species used for modelling of the systems Te/P/O and Ti/P/Te/O.

Species	$\Delta H_{298}^0 /$ kJ·mol ⁻¹	$S_{298}^0 /$ J·mol ⁻¹ ·K ⁻¹	$C_p / \text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ [a]			Reference
			a	b	c	
TeO _{2(s)}	-323.4	74.3	65.178	14.560	-0.502	[54]
TeO _{2(l)}	-324.0	50.3	112.633	2.176		[54]
Te ₈ O ₁₀ (PO ₄) _{4(s)}	-5844.0	823.3	798.921	299.04	-1.360	this work
Te ₃ O ₃ (PO ₄) _{2(s)}	-2594.4	329.3	318.301	152.701	-5.490	this work
Te ₂ P ₂ O _{9(s)}	-2264.4	249.1	237.199	155.900	-4.180	this work
TeP ₂ O _{7(s)}	-1925.9	174.0	156.000	159.098	-2.870	this work
P ₂ O _{5(s)}	-1505.0	114.4	74.893	162.339	-1.560	[54]
Ti ₂ O _{3(s)}	-1520.9	77.3	53.070	163.444		[54]
Ti ₃ O _{5(s)}	-2459.1	129.4	158.992	50.208		[54]
TiO _{2(rutile,s)}	-944.7	50.6	73.346	3.054	-1.703	[54]
Ti ₃ P _(s)	-331.8	114.4	86.280	32.600		[44]
Ti ₂ P _(s)	-321.6	83.7	64.140	22.300		[44]
Ti ₇ P _{4(s)}	-1265.0	303.3	234.400	78.900		[44]
Ti ₅ P _{3(s)}	-941.7	220.4	170.280	56.600		[44]
Ti ₄ P _{3(s)}	-852.3	189.7	148.140	46.300		[44]
TiP _(s)	-248.0	51.7	42.000	12.000		[44]
Ti ₅ Te _{4(s)}	-621.2	351.0	187.700	139.400	0.040	[44]
Ti ₃ Te _{4(s)}	-582.6	287.5	142.900	119.300		[44]
Ti ₂ Te _{3(s)}	-397.1	208.2	101.600	87.000		[44]
TiTe _{2(s)}	-196.6	136.4	60.400	54.300		[44]
Ti ₂ PTe _{2(s)}	-447.9	183.8	99.474	79.491	-0.016	[44]

$$[a] C_p = (a + b \cdot 10^{-3} K^{-1} \cdot T + c \cdot 10^6 K^{-2} \cdot T^2) \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$$

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