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1

Nanostructured tungsten sulfides: insights into precursor decomposition and the microstructure using X-ray scattering methods

Sebastian Mangelsen, Bikshandarkoil R. Srinivasan, Ulrich Schürmann, Lorenz Kienle, Christian Näther and Wolfgang Bensch

The entire path from a thiotungstate precursor via its decomposition intermediate to nanosized WS₂ with heavy stacking disorder is traced using various X-ray scattering methods.

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PAPER

Nanostructured tungsten sulfides: insights into precursor decomposition and the microstructure using X-ray scattering methods†

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Sebastian Mangelsen,^a Bikshandarkoil R. Srinivasan,^b Ulrich Schürmann,^c Lorenz Kienle,^c Christian Näther ^a and Wolfgang Bensch ^a

Herein we present an in-depth study of precursor derived tungsten sulfides, with a focus on their micro- and local structures. We prepared a new tetrathiotungstate based precursor $(\text{N}_2\text{H}_5)_2\text{WS}_4$ and unveiled the details of its unique decomposition mechanism by a combination of *in situ* and *ex situ* analytical techniques. Upon heating the precursor, a new compound with composition $(\text{NH}_4)(\text{N}_2\text{H}_5)\text{WS}_4$ is formed by the decomposition of one hydrazinium molecule. Above $\sim 190^\circ\text{C}$, $(\text{NH}_4)_2\text{WS}_4$ crystallized as the second crystalline intermediate followed by successive decomposition to WS_2 via amorphous WS_3 upon increasing the temperature. Using X-ray diffraction, total scattering data and pair distribution function (PDF) analyses we are able to develop a detailed picture of the microstructure of nanosized WS_2 samples obtained by the thermal decomposition of the precursor. The microstructure is described by global optimization of the stacking pattern of WS_2 slabs in a supercell containing a large number of layers. The results clearly demonstrate that both stacking faults and random shifts of the WS_2 layers contribute to the disorder in the material. This is significantly distinct to bulk materials, where solely stacking faults with no turbostratic disorder components were found.

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Introduction

Since the discovery of the outstanding properties of graphene¹ many layered materials became the focus of research.^{2–6} One of these layered materials is tungsten disulfide, WS_2 , which is extensively studied due to a variety of possible applications including the following: as a photocatalyst in the hydrogen evolution reaction (HER),^{7–10} as a gas sensor,^{11,12} for water purification,¹³ as an electrochemical supercapacitor¹⁴ or in photovoltaics.¹⁵ WS_2 can be prepared by different synthetic protocols and the most convenient way is a high temperature synthesis using the elements as starting materials. The use of this synthetic approach leads to the formation of highly crystalline products with a (nearly) perfect stoichiometry. Another synthetic methodology is the thermal decomposition of suitable precursors such as $(\text{NH}_4)_2\text{WS}_4$.^{16,17} The decomposition

proceeds in two steps with intermediate formation of amorphous WS_3 at about 280°C and poorly crystalline, defect-rich WS_2 is obtained at about 340°C .^{18–20} Other potentially suitable precursors are compounds with the general composition $(\text{R}_4\text{N})_2\text{WS}_4$ (R = alkyl chain).^{21–23} But such starting materials require much higher decomposition temperatures until nearly C, N and H free WS_2 is obtained. In the search for a precursor allowing the preparation of phase pure WS_2 by thermal decomposition at relatively low temperatures we prepared the new compound $(\text{N}_2\text{H}_5)_2\text{WS}_4$, determined its crystal structure and investigated its optical and thermal properties. Nanostructured materials are well known to be prone to defects as they represent a metastable state of matter, and layered materials are especially prone to dislocations, stacking faults and turbostratic disorder. For MoS_2 , WS_2 and *e.g.* intercalated NbS_2 , many efforts were made for modelling faults in the layered structures and the resulting ill-shaped reflections in the experimental X-ray diffraction patterns.^{24–31} Refinement of turbostratic disorder in exfoliated and restacked MoS_2 intercalated with organic cations has recently been demonstrated.^{32–34} Total scattering – also known as pair distribution function (PDF) – has only scarcely been applied to such layered compounds, *e.g.* to lithiated MoS_2 ,³⁵ restacked WS_2 ,³⁶ Ag_xMoS_2 ³⁷ or a molybdenum polysulfide chalcogenel.³⁸ Recently, it has been demonstrated that Rietveld refinement compatible

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global optimisation approaches to model stacking faults in layered materials using a supercell approach is a powerful tool to tackle defective layered materials.^{39–42} To the best of our knowledge this method has yet not been applied to nano-structured WS₂, especially not in an approach that involves simultaneous refinement of XRD and PDF data. Here, we demonstrate that characterization using IR and Raman spectroscopy, chemical analyses, thermoanalysis, HRTEM, nitrogen sorption and simultaneous XRD and PDF refinement yields a comprehensive picture of the microstructure of highly defective WS₂.

Experimental section

Preparation of [N₂H₅]₂WS₄ (HTT)

Ammonium tetrasulfidotungstate (ATT),⁴³ [NH₄]₂WS₄ (20.0 g, 57.4 mmol), was dissolved in distilled water (360 mL) and stirred to complete dissolution under purging with nitrogen. 99% hydrazine hydrate (39 mL, 779 mmol) was added and the solution was purged with nitrogen for 24 h, a methodology adapted from the literature.⁴⁴ After the addition of methanol (300 mL) the mixture was cooled to −18 °C. After one week, yellow crystals of HTT (9.9 g, 26.2 mmol, 46% yield) were obtained by filtering and washing with isopropanol (~50 mL) and diethylether (~100 mL). The product was stored in a refrigerator. Special care must be taken when handling hydrazine due to its hazardous nature.

IR data (in cm^{−1}): 3275, 3216, 3030, 1592, 1496, 1491, 1218, 1094, 1070, 953, 948 (ν_{N–N}), 481, 450 (ν₃), 188 (ν₄).

Raman data: 479 (ν₁), 448 (ν₃), ~200 (ν₂) and 188 (ν₄) cm^{−1}.

Anal. found (calcd): H 2.54 (2.59), N 14.69 (14.88), S 33.39 (34.6)%.

Single crystal X-ray diffraction

Intensity data for HTT were collected on a STOE IPDS-1 diffractometer at room temperature using graphite monochromated Mo-Kα radiation (λ = 0.7107 Å). The crystal showed dimensions of 0.2 × 0.15 × 0.14 mm³. A numerical absorption correction was performed. The structure was solved with direct methods using SHELXS-97⁴⁵ and refinement was carried out against F² using SHELXL-97.⁴⁶ All non-hydrogen atoms were refined using anisotropic displacement parameters. The hydrogen atoms were positioned with idealized geometry and refined using the riding model with fixed isotropic displacement parameters. The technical details of data acquisition and some selected refinement results are summarized in Table S1.†

Thermoanalytic measurements

Simultaneous differential thermal analyses, thermogravimetry and mass spectrometry were performed in Al₂O₃ crucibles using the Netzsch STA 409 CD apparatus equipped with skimmer coupling to a quadrupole mass spectrometer QMA 400 (max. 512 amu) from Balzers under a helium flow of 50 mL min^{−1} at a heating rate of 4 K min^{−1}. A second empty

crucible was used as a reference and corrections for buoyancy and currents effects were applied.

Ex situ samples for crystal structure determination: 150 mg of HTT were loaded in silica ampoules (inner diameter: 8 mm, length ~ 15 cm), evacuated and sealed. The ampoules were heated over one hour to 160 °C in a tube furnace. Ampoule one (A1) was removed after 20 minutes, and ampoule two (A2) after 60 minutes.

IR and Raman spectroscopy

A Genesis FTIR spectrometer from ATI Mattson was used for collecting IR spectra in the range from 400 to 4000 cm^{−1}.

Raman spectra were recorded with a Bruker IFS 66 Fourier transform Raman spectrometer (wavelength: 541.5 nm) in the region from 100 to 3500 cm^{−1}.

Preparation of bulk WS₂

Stoichiometric amounts of the elements (W: 99.9995%, abcr, S: 99.9995%, Alfa Aesar) were loaded in a fused silica ampoule which was sealed at $p \sim 1 \times 10^{-4}$ mbar. After slow heating to 450 °C for one day the temperature was raised to 900 °C for another 5 days and finally the furnace was allowed to cool to room temperature naturally during ~8 h. The ampoule was opened in air, and the free floating powder was stored in air.

Powder X-ray diffraction

In situ X-ray powder diffraction (XRPD) was carried out on a STOE STADI-P diffractometer with Cu-Kα₁ radiation (λ = 1.540598 Å), a Ge(111) monochromator, a DECTRIS® MYTHEN 1 K detector and a STOE capillary furnace. Samples were prepared in 0.5 mm quartz capillaries, and the material (8 mg) was diluted with amorphous carbon (2 mg) to minimize absorption effects. During the measurement the capillaries were kept under flowing Ar. *Ex situ* powder patterns were collected on a Panalytical Empyrean diffractometer equipped with Cu-Kα radiation, a focusing mirror and a PIXEL 1D detector.

Synchrotron XRD and PDF were collected at PETRA III, beamline P02.1 (DESY, Hamburg), using photons of 60 keV (λ = 0.2072 Å).⁴⁷ Samples were measured in 0.5 mm glass capillaries and for PDF analysis an empty glass capillary was measured to account for its background. Instrumental contributions to line broadening (XRPD) and dampening (PDF) were corrected by measurements of the standard material LaB₆ (NIST SRM 660c) and described using a Thompson–Cox–Hastings pseudo-Voigt function and dampening⁴⁸ with radius r respectively. The program suite Topas-Academic^{49,50} was used for structure solution and refinements.

N₂ sorption experiments

The sorption measurements were carried out with a BeISorpMax system. The samples were degassed at $T = 100$ °C. The nitrogen purity was 5.0.

Results and discussion

Crystal structure of HTT

HTT crystallizes in the space group $P2_12_12_1$ with four formula units in the unit cell. There are two unique $N_2H_5^+$ cations and one independent WS_4^{2-} anion with all atoms located at general positions. The $[WS_4]^{2-}$ moiety deviates from an ideal tetrahedron both by W–S bond lengths (ranging from 2.182(11) to 2.200(12) Å) and by S–W–S angles (108.10(5) to 110.34(5)°). The distortion is likely the result of S...H hydrogen bonding interactions and was also observed previously in several tetrathiotungstate compounds.^{23,51–56} The $[WS_4]^{2-}$ anion is surrounded by two crystallographically distinct hydrazinium ions. The hydrazinium cations (N3 and N4) make up an infinite chain connected by N...H bonds along the *b*-axis (Fig. 1, right) and the protonated N atom N3 is linked to the hydrazinium cation (N1 and N2) by N...H hydrogen bonds. This side chain is linked by S...H–N bonds to the sulfur atoms S3 and S4, while S2 is linked to the backbone of the hydrogen network *via* N3. Data and description of the infrared- and Raman spectra of HTT can be found in Fig. S1.†

The Hirshfeld surface analysis is a powerful tool for gaining a detailed picture of close intermolecular contacts.^{57–63} The Hirshfeld surface reflects the distance from the surface, d_e , and the distance from the surface to the nearest atom within the molecule, d_i . Then a normalized contact distance d_{norm} is calculated on the basis of d_i and d_e taking into account the van der Waals (vdW) radii: $d_{\text{norm}} = ((d_i - r_{\text{vdWi}})/r_{\text{vdWi}} + (d_e - r_{\text{vdWe}})/r_{\text{vdWe}})$, (r_{vdWi} and r_{vdWe} : van der Waals radii of the atoms). Red areas on the Hirshfeld surface indicate interatomic distances which are shorter than the sum of the vdW radii, while white to blue colors are used for distances longer than the sum of the vdW radii. The two-dimensional representation of the three-dimensional

Hirshfeld surface is called fingerprint plot displaying the d_e , d_i pairs. In Fig. 2, the Hirshfeld surface of the anion and the fingerprint plots of the anion and cations are shown. The flat bright red regions on the Hirshfeld surface of the anion (Fig. 2, top left) are caused by S...H interactions making 92.6% of the intermolecular interactions, and which are seen in the fingerprint plot as spikes (Fig. 2, top right). The next important contribution stems from non-covalent S...S interactions (6%) located in the fingerprint plot at d_i – $d_e \approx 1.8$ Å.

The fingerprint plots of the two independent hydrazinium cations (Fig. 2, bottom left and right) exhibit remarkable differences. For N1 and N2, only one clear spike occurs for H...S bonds (d_e – d_i : 1.58–0.9 Å, 68.5%), a broad distribution of H...H interactions (22.9%), and N...H contacts (d_e – d_i : 1.3–0.9 Å, 7.3%), but no N...H bonds are observed. In contrast, the fingerprint plot for N3 and N4 shows three spikes which are caused by intermolecular S...H contacts (spike at d_e – d_i : 1.5–0.85 Å, 51.7%), H...H interactions (26.1%), N...H bonds (spike at d_e – d_i : 1.2–0.8 Å, 7.4%) and H...N contacts (spike at d_e – d_i : 0.8–1.2 Å, 14.8%). Obviously, the different intermolecular interactions between the two unique $N_2H_5^+$ cations are caused by the different arrangements in the unit cell.

Thermal analyses

ATT is known to decompose in two steps according to:^{18,19}

The temperatures indicated were reported for decomposition under a nitrogen atmosphere.¹⁹ The TG curve for HTT (Fig. 3) displays two mass steps in the range up to 600 °C; however the DTA trace indicates a more complex decomposition mechanism. The first mass loss (24%) is accompanied

Q6 Fig. 1 View of the arrangement of the cations and anions in the structure of the title compound; dashed lines indicate S...H interactions up to 2.7 Å (left) and the intermolecular H bonding between the two independent hydrazinium cations (right).

Fig. 2 The Hirshfeld surface of the WS_4^{2-} anion (top, left) and the corresponding fingerprint plot (top, right). Bottom, left: the fingerprint plot of N_1 and N_2 containing N_2H_5^+ cations and bottom, right: the fingerprint plot of N_3 and N_4 containing cations. d_e and d_i correspond to the distances from the surface to the nearest atom outside the surface and to the nearest atom of the molecule, respectively.

by an exothermic event at a peak temperature (T_p) of 187 °C that seems to involve multiple thermal reactions. At around 210 °C, an endothermic signal is observed ($T_p = 239$ °C) upon further heating. The DTG curve reveals that the mass step is actually comprised of two sequential steps. The second mass step is accompanied by an exothermic event and a mass loss of 9.2% ($T_p = 347$ °C). This exothermal event is caused by a crystallization process and sulfur removal, as also reported for $(\text{NH}_4)_2\text{WS}_4$ ($T_p = 339$ °C).¹⁹ The simultaneously recorded mass spectrum shows emission of the masses $m/z = 16$ and 17 (NH_2 and NH_3) starting at about 160 °C. The intensity of these signals decreases at about 200 °C and increases with further increase of the temperature. Two new signals ($m/z = 32, 34$; probably H_2S and S) appear at $T > 200$ °C and all mass signals

disappear at $T > 260$ °C. We note that all mass signals occur at the onsets of the exothermic and endothermic events. On increasing the temperature, another signal with $m/z = 32$ is detected which can be assigned to the emission of sulfur.

In situ X-ray diffraction experiments

As the results of the **thermoanalytic** investigation indicated a more complex thermal decomposition reaction, temperature dependent XRPD experiments were performed. Surprisingly, HTT does not directly decompose to WS_3 (Fig. 4, bottom) as in the case of ATT (Fig. 4, top); instead a structural phase transition occurs at a temperature where the first mass step was observed in the TG curve. The first reflections of an intermediate crystalline compound appear at $T = 130$ °C (Fig. 4, bottom),

Fig. 3 TG, DTG, DTA and MS curves of the thermal decomposition of HTT. Mass losses are given for the two decomposition steps and masses m/z are indicated in parentheses with assigned ions for the different MS traces.

Fig. 4 Evolution of the *in situ* XRPD patterns with increasing temperature for ATT (top) and HTT (bottom). Dashed horizontal lines indicate phase transitions from HTT (a), to HTT + intermediate (b), intermediate (c), ATT (d) and finally to the amorphous material (e).

which coexists with the starting material HTT for only about 20 °C. Upon further heating, a second crystalline phase occurs starting at about 190 °C, and the reflections of this phase can be assigned to the structure of ATT crystalliz-

ing in the orthorhombic space group $Pnma$ (HS-ATT). Above 230 °C all reflections disappear, presumably because the sample is decomposed into an amorphous material. We note that the different temperatures obtained with DTA-TG and *in situ* XRPD are likely due to the different thermal treatments, as the DTA-TG data were acquired under continuously increasing temperature, while the diffraction data were acquired at fixed temperatures with acquisition times of about 0.5 h per powder pattern. Additionally, the differing gas atmospheres may play a role because a gas flow was used for DTA-TG experiments while for X-ray powder diffraction investigations a static atmosphere was present. Under the former conditions, gaseous reaction products are constantly removed which is not the case for the latter experiments.

In order to further elucidate the structural nature of the intermediate phases, we synthesized larger amounts of the phases that occur upon decomposition of HTT up to 230 °C. Sample A1 shows the powder pattern observed *in situ* in the temperature range 130–190 °C (Fig. 5), that of A2 (Fig. 6) corresponds to the phase observed above 190 °C. Elemental analysis of A1 yielded a S/W ratio of 4 and a N/W ratio of 3. The IR spectrum displays bands assignable to both ammonium and hydrazinium cations (Fig. 7). The Raman spectrum (Fig. S3†) clearly shows a splitting of the deformation vibrations located at 170 cm^{-1} , likely caused by the different cations. All results indicate the sum formula $(\text{NH}_4)(\text{N}_2\text{H}_5)\text{WS}_4$ (AHTT) for the intermediate crystalline phase A1.

The X-ray powder pattern of sample A1 could be indexed using singular value decomposition⁶⁴ in an orthorhombic cell, and the extinction conditions are in agreement with the space groups $Pnma$ (point group mmm) and $Pna2_1$ (point group $mm2$). The centrosymmetric space group is more likely and, therefore, $Pnma$ was chosen for structure solution. The crystal structure was solved *ab initio* using global optimisation⁶⁵ from XRPD data. The structure was refined using rigid bodies in the z -matrix notation for all three ions with fixed interatomic distances and angles for the cations and a flexible WS_4 tetrahedron. The background was modeled using a one on x function combined with an artificial phase, which models the halo caused by the amorphous content (diluent and capillary). The sum formula combined with space group symmetry requires the ions to be located on the mirror planes, which was accounted for by fixing the location to $b = 0.25$ and allowing rotation only around β . The experimental XRPD pattern is in good agreement with that calculated with the crystallographic data obtained by the Rietveld refinement⁶⁶ (Fig. 5). We note that an ordered arrangement of the cations was used, although one can expect a certain degree of disorder on their positions. However, a disordered arrangement did not improve the fit significantly. AHTT is isopunctual to ATT with an ammonium ion replaced by hydrazinium (a comparison is shown in Fig. S4† and structural data are provided in Table S2†).

The second *ex situ* sample A2 is identical to ATT in terms of the crystal structure, vibrational spectra and elemental compo-

Fig. 5 Observed (black) and calculated patterns (red) and the difference (green) for the intermediate phase AHTT (sample A1); black bars indicate Bragg reflection positions for AHTT. An inclined view of the structure is shown in the inset.

Fig. 6 Experimental (black) and calculated (red) pattern for sample A2 that is identified as ATT; the difference is shown in green; black bars indicate the Bragg reflection positions. The inset shows an inclined view on the structure.

sition with only a small impurity of AHTT. When comparing the structures of ATT and AHTT the positions of the cations are very similar with only minor shifts that are likely caused by the hydrogen bonding network that is formed when the hydrazinium cation is involved. These interactions may be responsible for the shorter *a*-axis and the larger *c*-axis upon the isopunctual phase transition. On the basis of the results dis-

cussed above the thermal decomposition of HTT should occur *via* the following steps, with hydrazine being known to decompose according to different reaction pathways:^{44,67}

Fig. 7 Infrared spectra of ATT, HTT and the *ex situ* samples A1 and A2. Note that for A1 the cation bands of both N_2H_5^+ and NH_4^+ are present while A2 shows only the cation band for NH_4^+ .

or in an intermediate way:

Because the emission of N_2 is accompanied by the release of NH_3 we assume that eqn (4) and (5) are most adequate to describe the process, and a further distinction is not possible. Based on eqn (4) one can formulate:

Both reactions (3) and (4) are exothermic⁶⁷ in agreement with the heat flow observed in the DTA measurement (eqn (6)), and together with the crystallisation of the second phase the 'buckled' shape of the DTA curve can be well explained. The two-step decomposition of HTT *via* AHTT to ATT is formally described by steps (6) and (7), and the reactions according to steps (8) and (9) are in agreement with the literature.^{18,19,68} The reactions (6)–(8) sum up to an expected mass loss of 26%, while the observed mass loss of 24% is slightly lower. This discrepancy can be explained by the residual contents of N and H in WS_3 , in agreement with our observations from combustion analysis (*vide infra*). The expected mass loss according to (9) is larger (11.4%) compared to the observed mass loss of 9.2%, which is most likely due to the kinetically slow removal of sulfur. An important question is why only half of the hydrazinium ions are decomposed in the first thermal reaction step. In the literature only a few reports are available for the thermal stability of hydrazinium salts. For $\text{Mn}(\text{N}_2\text{H}_5)_2 \cdot (\text{SO}_4)_2 \cdot \text{H}_2\text{O}$, first H_2O is removed and the water-free compound is decomposed to $\text{Mn}(\text{N}_2\text{H}_4)_{0.5}(\text{HSO}_4)(\text{SO}_4)_{0.5}$ at $T_p = 295^\circ\text{C}$. A slightly lower decomposition temperature of $T_p = 275^\circ\text{C}$ was observed for

$\text{Co}(\text{N}_2\text{H}_5)(\text{SO}_4)_2$ yielding $\text{Co}(\text{N}_2\text{H}_4)_{0.5}(\text{HSO}_4)(\text{SO}_4)_{0.5}$.⁶⁹ But in these two compounds the hydrazinium cation is coordinated to the metal center while in HTT only H bonds to the anions are observed. For $(\text{N}_2\text{H}_5)_3\text{Ge}_7\text{O}_{15}(\text{OH}) \cdot 2.5\text{H}_2\text{O}$, it has been reported that the decomposition of the N_2H_5^+ cations is completed at 235°C and NH_3 is emitted during thermal decomposition.⁷⁰ The formation of $(\text{NH}_4)(\text{N}_2\text{H}_5)\text{WS}_4$ seems to be rather unusual and eventually the exothermic formation of a denser and more stable structure is a likely explanation. One may argue that hydrogen bonds are also involved in the distinction of the hydrazinium cations. In HTT, the N1N2 cation is linked to three neighboring WS_4^{2-} moieties within a distance of $2.7 \text{ \AA}$, while the N3N4 cations forming the backbone of the hydrogen bond network are only bonded to one of the anions. With the assumed orientation of the hydrogen atoms in AHTT again three $\text{S} \cdots \text{H}$ bonds can be identified linking N_2H_5^+ to three WS_4^{2-} units.

Characterization of the decomposition products

Thermal decomposition products of ATT and HTT obtained at different temperatures were prepared in order to gain insight into the influence of the decomposition process on the properties of the resulting WS_2 samples. Results from combustion analysis (see Fig. 8) reveal that the elemental compositions are independent of the precursor. Samples obtained at decomposition temperatures of 205 and 240°C can be described as WS_3 with some remaining nitrogen and hydrogen, whereas materials obtained at $T = 340$ and 450°C are very close to stoichiometric WS_2 .

X-ray powder diffraction (XRPD)

For WS_3 , only one broad reflection and a very extended halo can be observed in the XRPD patterns, while for the WS_2 materials more reflections are seen (Fig. 9).

Fig. 8 Results from the chemical analysis of the samples obtained at different decomposition temperatures.

Fig. 9 XRPD patterns of the materials obtained from the decomposition of ATT (left) and HTT (right) at different temperatures as indicated.

All XRPD patterns of the WS_2 materials (Fig. 9) are very similar in terms of reflection positions and reflection shapes, indicating comparable microstructures. The higher decomposition temperature (450 vs. 340 °C) does not lead to significantly sharper reflections or to a change of the shape of the reflections. Hence, higher temperatures are needed to induce a reasonable diffusion of the atoms to allow for the growth of larger coherently scattering domains. The powder patterns are characterised by very broad reflections typical of a low average size of coherently scattering domains and the shapes indicate the presence of different types of defects. Specifically, the broad 002 reflection clearly indicates a low number of stacked WS_2 layers, while the broad 100 and 110 reflections are caused by low lateral layer dimensions. The shapes of the cross reflections $h0l$ and $0kl$ indicate the presence of stacking faults and turbostratic disorder, *i.e.* additional small shifts of the layers in addition to the 2H- and 3R-type stacking sequences. This is further underscored by the asymmetric peak shape of *e.g.* the 100 reflection with a long tail to a higher diffraction angle. This is identified as the so-called Warren-type peak shape that is known to appear in layered materials with stacking faults.⁷¹

Another feature is the high intensity scattering (Debye scattering, DS) at low diffraction angles that is ascribed to so-called uncorrelated single layers.^{25,27} Although, to a smaller extent, this can also be observed for the WS_3 samples, it is much less pronounced for the material derived from HTT (see Fig. 9). A simple Rietveld refinement⁶⁶ of the patterns of the WS_2 materials with the 2H- WS_2 structure and a model for anisotropic broadening⁷² for size and strain effects yields no satisfactory fit (see Fig. 10). Hence, a supercell approach was applied to model stacking faults and turbostratic disorder, and details of this model will be presented in the following section.

The DS at low angles is generally found to result from the so-called uncorrelated single layers. In the literature, a strategy to extract the number of single layers was given;^{25,73} a corresponding scheme for this is shown in Fig. 11. First the contribution from the sample holder (acetate film and glue) is subtracted from the experimental data, and then the relative fractions of DS and stacked layers (represented by the integral of the 002 reflection) are evaluated. The corrected powder patterns for the four nanostructured samples are presented in

Fig. 10 Rietveld refinement of the XRPD pattern of HTT340.

Fig. 11 Left: Difference (main panel) of the observed pattern and the scaled background (inset). From the difference plot the relative proportion of Debye scattering and stacked layers is obtained by integration. In the right panel the corrected data for all four samples are shown with the percentage value of the Debye scattering.

Fig. 11 along with the extracted fraction of the DS. To allow for an easy comparison among the datasets the intensities of the 002 reflection were normalized. Indeed the ATT derived samples show a higher fraction of DS (73%) compared to the samples synthesized from HTT (69 and 68%). However, there is no exact model to show how to describe the intensity of the DS quantitatively; thus the values presented here should not be seen as a quantitative measure. Moreover, simulations performed with stacks containing only a few layers also lead to high scattering at low backgrounds but to a smaller extent.^{24,26} In addition, the relative intensity of DS is also affected by the starting angle of the X-ray powder pattern. Nevertheless, the evaluation of the background using DS yields valuable insights for samples measured under identical conditions, as is the case here.

Pair distribution function analysis and supercell approach

PDF is a powerful method for understanding the local structures of nanoscale and heavily disordered systems.⁷⁴ The intensity of a signal in the PDF depends both on the multiplicity of the interatomic distance and the scattering factors of the contributing scattering partners. Thus a W...W distance shows a much stronger signal compared to a S...S distance of the same multiplicity. The four samples show virtually identical PDF data (Fig. S5†), and therefore we present the detailed analysis of the data set collected on HTT340 as an example. An approach to model stacking faults is the so-called super cell approach, and a scheme for this method is shown in Fig. 12. In the case of WS₂, the 2H- and 3R-types of layer stacking are known with space groups *P*_{6₃}/*mmc* and *R*3*m*, respectively. The individual layers are identical, but the stacking pattern differs. In the 2H-type, a rotation of the layers by 180° occurs, while the layers are translated by a vector (2/3,1/3) within the *a*-*b*-plane for the 3R-type. The introduction of stacking faults breaks the symmetry elements, as *e.g.* the screw axis present in *P*_{6₃}/*mmc* is not compatible with a 3R stacking. Thus, the symmetry needs to be lowered to *P*1 to allow for arbitrary stacking

patterns and thus stacking faults. The cell metrics were kept as in the hexagonal system, and the only requirement was to expand the *c*-axis according to the number of layers in the supercell. Moreover, this modelling step allows us to take turbostratic disorder into account, that is, additional small shifts in the plane (maximum 0.1667 of an *a* or *b* vector) or small rotations around the *c*-axis (not shown in the scheme). In the present evaluation of the data a supercell with 12 layers to model the pattern was used. This number allows modelling both ideal 2H- and 3R-type stacking sequences and a high number of possible stacking fault patterns, *e.g.* longer sequences of one type, interrupted by only a few layers of the other kind.

Because a large number of possible stacking sequences is possible (11 layers stacked on the first one, 2 possible kinds of stacking each, 2¹¹ = 2048 sequences) a global optimization using simulated annealing⁶⁵ as implemented in TOPAS⁴⁹ was applied. After the generation of a stacking sequence, the lattice parameters, turbostratic components, zero errors, Debye-Waller factors, S...W distances and the parameters of an anisotropic size model⁷² are refined in a Rietveld-like⁶⁶ minimization. After convergence, another stacking sequence is generated and so on. At least 15 000 cycles were performed to ensure that a reasonable global minimum was found.

In Fig. 13, the observed data are shown together with calculated PDFs for pure 2H- and 3R-type stacking and an optimized random sequence of stacking with and without turbostratic components of up to 0.1667·*a* or *b*. Moreover, calculations including an additional random shifting of the layers along the *c*-axis and with an unrefined position of sulfur in the layer are shown. In the range up to 5.6 Å all models are nearly identical, because in this region the short range order mainly within one layer dominates, *i.e.* W⁴⁺ in the trigonal prismatic coordination sphere of six S²⁻ ions and the next neighbours. The first distances are observed at 2.4 (W...S) and 3.15 Å (W...W, S...S). An interlayer S...S distance expected at 3.5 Å is not visible in the calculated data due to its low multiplicity

Fig. 12 This scheme explains the supercell model. Starting with the ideal stacking types 2H and 3R shown on the left, the introduction of stacking faults (red box) breaks the symmetry elements and requires the space group *P1*. In the middle a supercell with the six layers shown on the left with one stacking fault is shown. Additionally, small random shifts are allowed along all axes, indicated by the small red arrows on the right side.

Fig. 13 Observed PDF for HTT340 along with various calculated PDFs using a 12 layer supercell. Dotted and dashed vertical lines correspond to intra- and inter-layer W...W distances, respectively; the R_{wp} values in % are given in brackets.

and the low scattering power of S. The signals located at 2.8 and 3.5 Å are caused by ripples occurring due to the finite scattering momentum q_{max} applied in the Fourier transformation.

In the long range region, significant differences between the models are observed which can be explained by different

neighbors within each layer and neighbors in the next layers. Discrepancies are clearly visible when comparing the experimental data with that calculated for 2H, 3R and random stacking. Some of the distances with a high amplitude for $G(r)$ from the calculated PDFs have no or only a very low experimentally

observed amplitude. By including turbostratic disorder components these differences can be resolved and the fit is improved enormously as can be seen from the sharp drop in the R_{wp} (66.7% to 36.1%). The need for a refinement of the position of the sulfur atoms along the c -axis is demonstrated by the somewhat higher R_{wp} of 37.6% when the unrefined position from bulk WS_2 is assumed; notably the calculated and observed $W\cdots S$ distances deviate in this case. Another significant improvement is achieved when additional slight shifts of the layers along the c -axis are allowed ($R_{wp} = 22.3\%$). The R_{wp} values are high in comparison with Rietveld refinements which is not uncommon for fits of PDF data.^{35,36,75} For a deeper understanding the observed and calculated distances are discussed in more detail. To simplify the discussion we mainly focus on the $W\cdots W$ distances because these have typically much higher amplitudes compared to the $W\cdots S$ and $S\cdots S$ distances due to the much higher atomic form factor of W. All intralayer $W\cdots W$ distances (dotted vertical lines) are clearly visible in the experimental pattern, and therefore the model of edge sharing WS_6 trigonal prisms explains well the intralayer structure. In contrast, interlayer $W\cdots W$ distances calculated for 2H, 3R and random stacking have only low amplitudes in the experimental PDF. The signal at 5.9 Å corresponds to the shortest interlayer $W\cdots S$ distance (and the interlayer $S\cdots S$ distance), which is weakened for random stacking and totally suppressed if turbostratic disorder is invoked. The distances discussed here span solely the range from the first to the second layer; thus, from the results presented here it is clear that there is no ordered stacking even between adjacent layers.

Another major difference between the calculated and observed PDFs are the signals around 6.5 Å, which can be explained by the intralayer $W\cdots S$ (6.7 Å) and $S\cdots S$ (6.7 Å) distances of adjacent layers as well as intralayer $W\cdots W$ (6.3 Å) and interlayer $W\cdots W$ (6.7 Å) distances. The signal is well modelled if an additional slight shift of the layers along the c -axis is included. Possibly this reflects the microstrain caused by the bending of the layers and in a simplified way it is modelled by layers that shift closer or further away from each other. The microstrain along the c -axis shortens the intralayer $W\cdots S$ distances on the concave side of the bent layer and elongates these distances on the convex side. Moreover, this bending modulates the interlayer $S\cdots S$ distances due to compressive and tensile stress and strain acting on the sulfur atoms. Another factor is the possible expansion of the interlayer distance depending on the number of stacked layers, blurring out the interlayer $W\cdots W$ distance while the intralayer distance remains well defined.

After developing this structure model we performed a global optimization using the PDF and XRD data from the sample HTT340, a weighting scheme was applied such that the GOF parameters for both data sets were about equal. The Rietveld method⁶⁶ was applied to minimize the difference between the observed and calculated patterns. For each Rietveld refinement an arbitrary stacking pattern was generated with the turbostratic components set to zero. These were allowed to be refined together with the lattice parameters, zero point errors, the position of S in the layer and the Debye Waller factors. For modelling the XRD data, anisotropic line broadening due to size effects was taken into account,⁷² and the PDF was modeled using a simple spherical model of uniform radius for the size effect. The ripples caused by a finite q_{max} were modeled using an approach described in the literature.⁷⁶ The resulting structural data are presented in Table 1 and the corresponding plots are shown in Fig. 14.

Both XRD and PDF data are well fitted applying the above discussed model and several global optimizations were conducted with similar results. The average size of the crystallites from the PDF data is a sphere of 22 Å, corresponding to particles of 4.4 nm diameter, a reasonable number compared to the results from TEM (*vide infra*). The anisotropic size model applied to the XRD data yields in-plane dimensions from the 110 reflection of ~4.5 nm and a stacking height of ~2.5 nm, corresponding to 4 stacked layers on average. Compared to the value of bulk WS_2 the interlayer distance is significantly expanded by 0.336 Å (see Fig. S6† for a direct comparison), while the a -axis remains virtually unaffected. The apparent intralayer contraction (see Fig. S6,† position of the 100 reflection) is expected for nanostructured layered materials with pronounced stacking disorder, but not related to actual structural changes.⁷¹ The $W\cdots S$ bond length is virtually unaffected when taking the error values into account (2.405(6) Å vs. 2.414(4) Å in the bulk material). The stacking is random with a higher contribution of 3R-components, and because each layer contributes ~8% to the stacking probability the result can be interpreted as a 50/50 mixture of 2H and 3R stacking. Anyway due to the strong contribution of the turbostratic components the underlying base stacking in terms of 2H and 3R type stacking should not be overinterpreted. The high values for the Debye Waller factors are clearly indicative of the disorder and correlations with parameters modelling disorder (*i.e.* random stacking sequences, turbostratic components, c -shifts, and size model for the XRPD data) cannot be ruled out. Instructive here is a comparison with the refined values for the more ordered

Table 1 Global and atomic parameters for the 12 layer supercell approximating HTT340

HTT340 (supercell 12 layers)	$a = b$ (Å)	Interlayer distance (Å)	Average turbostratic component $\times a/b$	Average c -shift (Å)	Percentage 2H-stacking (%)
	3.1568(6)	6.515(2)	0.106	0.038	42
Atom	x	y	z	Occupancy	B_{iso} (Å ²)
W1	1/3	2/3	0.5	1	0.68(2)
S1	2/3	1/3	0.2566(8)	1	1.67(5)
S2	2/3	1/3	0.7434(8)	1	1.67(5)

Fig. 14 Observed and calculated PDF (main panel) and XRD (inset) data for the 12 layer supercell fitted to the data for HTT340.

bulk WS_2 sample (*vide infra*) where these values are roughly halved. Regarding the parameter correlations we note that the simultaneous refinement of XRPD and PDF significantly stabilizes the refinement. For example the S...W distance can directly be read from the PDF data and the turbostratic components are also stabilized from this data, whereas the stacking pattern is more contained in the XRPD data. Small shifts of the layers along the c -axis are clearly needed for an optimal fit and cannot be compensated by increased turbostratic components. Thus, the key result is clear: turbostratic vectors are

needed to explain the observed XRD and PDF data for the nanostructured WS_2 presented here.

In order to check the capabilities of the model we applied it to bulk WS_2 that was prepared by solid state synthesis, but a different strategy for global optimization was used. The XRD pattern of this material also indicates a reasonable number of stacking faults as can be concluded from the broadened cross reflections indicated in the inset of Fig. 15, while the very sharp $00l$, $h00$, $0k0$ and $hk0$ reflections suggest the presence of a high number of stacked layers with only minimal broadening

Fig. 15 Observed, calculated and difference plots for the PDF and XRD (inset) data for the bulk WS_2 subjected to global optimization using a 24-layer supercell.

Table 2 Global and atomic parameters for the 24 layer supercell approximating bulk WS₂

WS ₂ bulk (supercell 24 layers)	$a = b$ (Å)	Interlayer distance (Å)	Average turbostratic component $\times a/b$	Average c -shift (Å)	Percentage 2H-stacking (%)
Atom	x	y	z	Occupancy	B_{iso} (Å ²)
W1	1/3	2/3	0.5	1	0.336(2)
S1	2/3	1/3	0.246(1)	1	0.67(1)
S2	2/3	1/3	0.754(1)	1	0.67(1)

due to size effects. The broadening of cross reflections is due to both size and strain contributions. Due to the large domain size of the crystallites and lower density of stacking faults compared to the nanostructured samples a supercell with 24 layers was set up to give a reasonable approximation. The results of the global optimization are presented in Fig. 15 and Table 2. An extended plot for the PDF data up to 100 Å can be found in Fig. S7,[†] demonstrating the larger domain size compared to HTT340 in real space. The dominating stacking type is 2H with ~20% of 3R-type stacking, but no turbostratic components or c -shifts had to be invoked for a satisfactory fit. The Debye–Waller (atomic displacement) factors for both S and W are lower by a factor of ~2 compared to the nanostructured WS₂, which is reasonable as disorder increases the apparent atomic displacement. The PDF data are modeled very well, and the distances in the short and long range regions are well matched. For the XRD data the broadening of the cross reflections and particularly the different degrees of broadening of the 101, 102 and 103 reflections are treated with an average domain size of 20 nm; however the fit is not perfect. The approach of one single supercell is limited as it cannot account for the real structure containing domains with varying densities of faults that sum up to the observed pattern. This distribution function typically leads to a particular Lorentzian peak shape⁷⁷ which is also observed here. Moreover, strain was not taken into account because an anisotropic model for triclinic symmetry requires many parameters making the fit less reliable due to the correlation of parameters. Nevertheless, we want to emphasize that the model is capable of identifying the different degrees of stacking disorder in the samples presented here. While the nanostructured sample contains small crystallites with random stacking and additional turbostratic disorder components, the bulk sample is characterized by well defined stacking vectors and no turbostratic disorder.

PDF of WS₃

Possible structural motifs contained in WS₃ have been discussed in the literature based on the analysis of PDF and extended X-ray absorption fine structure (EXAFS) data. Both a chain like structure similar to those of the other crystalline transition metal trichalcogenides (*e.g.* the sulfide, selenides and tellurides of Ti, Zr and Hf) and interconnected molecular structures were proposed.^{20,78–80} For the related compound MoS₃ a modelling study clearly favored a chain-like structure.⁸¹ The PDF of HTT240 identified as WS₃ is shown in Fig. 16. From the raw data one can see only very few and broad reflec-

Fig. 16 PDF for HTT240 (WS₃); the most prominent distances are indicated. The inset shows the first part of the raw data with only very few and broad reflections.

tions that indicate reduced long range order and small coherently scattering domains in the material, but still it is not totally amorphous. From the PDF one can extract few but well defined interatomic distances, which are in agreement with the published PDF.⁷⁸ The first two and very intense signals at 2.37 and 2.77 Å are well resolved due to the much higher resolution arising from the use of a much shorter wavelength compared to the previous report. Their virtually identical intensity is different compared to the data for WS₂ (Fig. 14 and 15), which is necessary due to a higher count of W...S distances as a consequence of the larger sulfur content. The proposed chain like structure where WS₆-prisms are stacked on top of each other seems reasonable in view of the related transition metal trichalcogenides. However, the assumed alternating short and long intra-chain W...W distances cannot be supported from our data, as this would require a splitting of the signal at 2.77 Å, which is very sharp and symmetric. Rather the signal at 2.37 Å seems to show a tail to the lower distance side, a possible support for the discussed disulfides.⁷⁸ The signal at 3.14 Å is sharp indicating a well defined interatomic distance. The low intensity points to only S...S distances being its origin. The signals following at 3.81, 4.97 and 5.81 Å seem to be broadened while around 8 Å there is only a very broad hump visible, most likely due to pronounced disorder. Thus, the order in the material is limited to distances below 8 Å corresponding to only a few bond lengths. The low number of

Fig. 17 Representative TEM images of the sample HTT340.

observed distances and the very broad reflections in the powder pattern make it virtually impossible to give a decent and unambiguous structure model or to define a unit cell.

Transmission electron microscopy (TEM)

In order to cross check the results from the PDF and XRPD data analysis high resolution transmission electron microscopy (HRTEM) was applied. In Fig. 17, representative images of the sample HTT340 are presented (additional images: ESI Fig. S8†). The main features are lattice fringes from stacks oriented such that the (00 l) planes are under diffraction conditions. Thus, the number of stacked layers and their lengths can be seen. The individual stacks are randomly oriented within the agglomerates; their height varies from mostly less than six layers down to single layers and a length of less than 10 nm. Moreover some bent stacks can be seen

and typically within each stack the layer length is not uniform. Unfortunately no direct imaging of the stacking type and turbostratic disorder was feasible due to the limited resolution and beam sensitivity of the sample. TEM probes only a very small area/amount of the sample while XRD and PDF average over a large sample volume. However, the supercell approach is not capable of modelling bent layers or layers of different lengths within one single stack. Therefore, TEM investigation is a complementary method and the results are in agreement with the PDF/XRD results, but deliver additional insights into the microstructure of the material.

Infrared spectroscopy

The MIR spectra (Fig. 18) display broad bands in the region around 450 cm^{-1} for the WS_3 materials, which is similar to the position of the characteristic $[\text{WS}_4]^{2-}$ stretching- and defor-

Fig. 18 MIR-spectra of the decomposition products using ATT (left) and HTT (right).

mation bands but there are clearly multiple broad bands. From this observation no conclusion can be drawn whether residues of $[\text{WS}_4]$ -moieties are present or whether WS_3 is actu-

ally comprised of condensed $[\text{WS}_4]$ units. In addition, several bands in the range of $1200\text{--}1600\text{ cm}^{-1}$ point to different NH_x species, in agreement with the results of combustion ana-

Fig. 19 Representative SEM images of the decomposition products of HTT (top row) and ATT (bottom row).

Fig. 20 N_2 sorption isotherms for the materials obtained by thermal decomposition of ATT and HTT.

lysis. This is further supported by the observations made for a Mo-S-N-H-composite material⁸² and the bands observed for ammonia adsorbed on MoS₂.⁸³ For the WS₂ materials all these bands vanished and no clear absorption could be observed.

Scanning electron microscopy (SEM) images

The morphology of the decomposition products was studied with SEM. All materials display a broad distribution of particle sizes from a few to hundreds of microns and arbitrary shapes (Fig. 19). A closer inspection of the surface morphology reveals that the ATT based materials show a rather smooth surface texture while the HTT derived materials display repeatedly sponge like features also with different pore sizes on the scale of several μm . No significant differences depending on the decomposition temperature were observed.

Nitrogen sorption

Sorption measurements with N₂ were used to assess the specific surface area and porosity of the materials. In general for all materials similar shapes of the isotherms (type IVa according to the IUPAC classification⁸⁴) were observed (Fig. 20) with a pronounced hysteresis for $p/p_0 < \sim 0.4$, which can be associated with a textural porosity. The BET surface areas are significantly larger for all materials obtained from ATT, which is likely related to the different decomposition mechanisms. In addition, the BET surface areas of ATT derived decomposition products are almost constant, while those for samples obtained from HTT show a slight increase of surface areas with the decomposition temperature (Fig. 21). It is likely that the one step decomposition of ATT is the driving force for the higher BET surface, as the gas released during the decomposition is emitted in one step, within a short time and a small temperature interval.

Fig. 21 Summary of the BET surfaces evaluated from the N₂ sorption isotherms.

Conclusions

We presented an in-depth study of the thermal decomposition of the new precursor HTT and of nanostructured tungsten sulfides that can be prepared by this synthetic route. The results were compared to those of materials derived from the well known ATT. The thermal decomposition of HTT is rather unusual due to the formation of the stable mixed cation intermediate AHTT, whose structure and composition were accessed by combined *in situ* and *ex situ* methods. Comparing the materials (*i.e.* WS₃ and WS₂) derived from the precursors we found that differences arise especially on the macroscale, *i.e.* the BET surface and the materials morphology, likely linked to the different decomposition pathways involving one or multiple steps. The microstructure is not dependent on the type of precursor.

Applying the supercell approach we were able to model the stacking disorder in nanostructured WS₂ by simultaneous fitting of XRPD and PDF data, yielding significant progress compared to previous reports and modelling studies. From the PDF data turbostratic disorder, *i.e.* random shifts and small rotations of the layers, was identified as a necessary ingredient besides random stacking to fully describe the observed data. Moreover small domain sizes of only a few nanometers were obtained from the refinement. The highly disordered and nanoscaled nature of the materials was confirmed by TEM; moreover additional features like bent layers and a wide distribution of layer sizes and stacking heights could be observed. This underscores the necessity to combine methods probing a large sample volume like XRPD/PDF and the validation of the results with a high resolution local probe like TEM. In comparison with the nanostructured WS₂ a bulk sample containing stacking faults was studied, where solely stacking faults and no turbostratic disorder were identified. These results are a significant progress towards the modelling of TMDCs and other layered materials microstructures as this knowledge can be used in future studies to link structural parameters like stacking faults and disorder to physical and catalytic properties.

Conflicts of interest

There are no conflicts to declare.

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