Tungsten

Newsletter – June 2013

The Beautiful Colours of Tungsten Oxides

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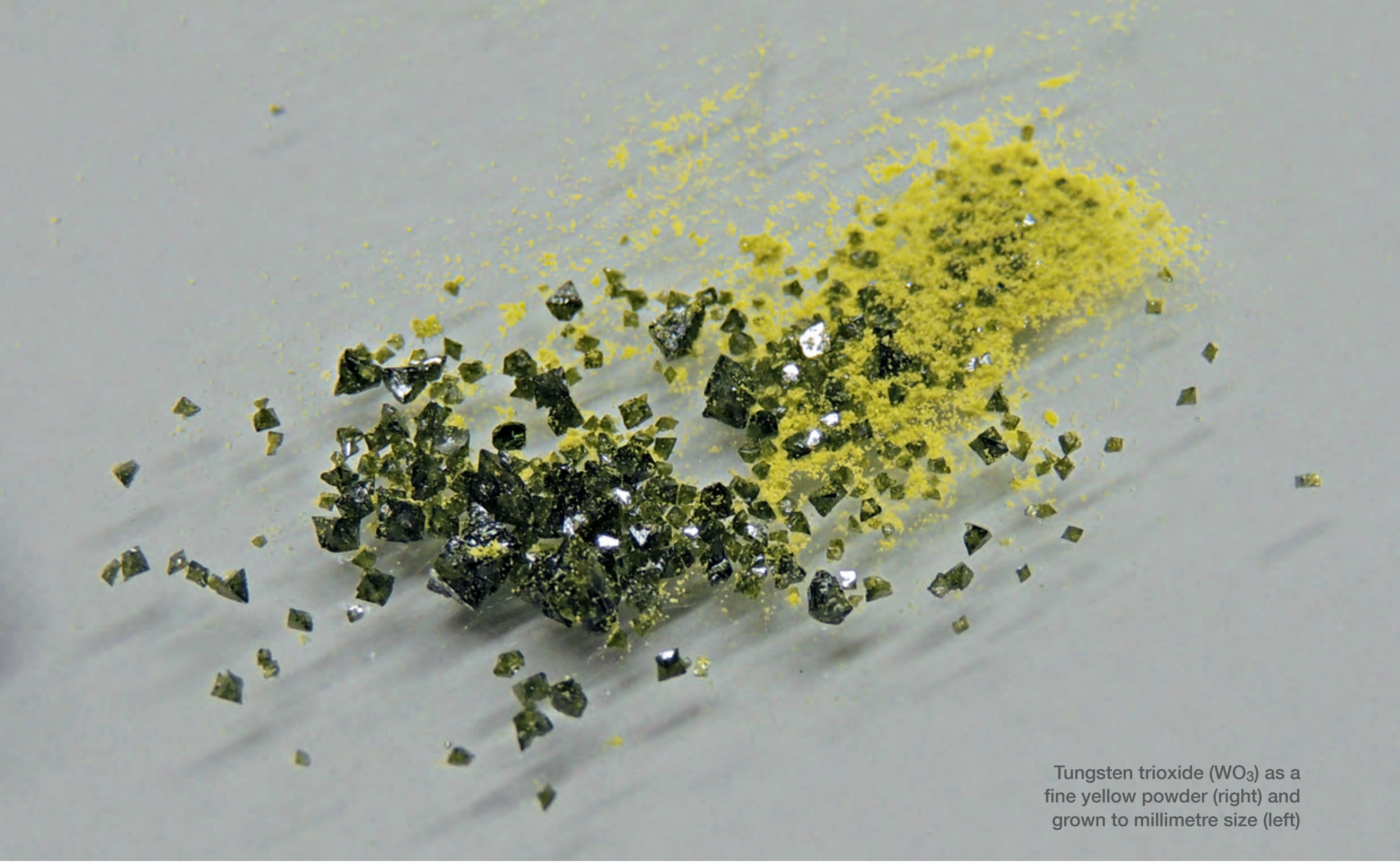


Tungsten trioxide (WO_3) as a fine yellow powder (right) and grown to millimetre size (left)

Wolf-Dieter Schubert needs no introduction to readers of these Newsletters as he is the Technical Consultant to ITIA and has contributed no less than 11 articles, beginning in 2003. This time, together with his colleague Matthias Weil of the Vienna University of Technology, he has been prompted by the spectacular colours of tungsten oxides to delve deeper into the science behind the phenomena.

Even before the discovery of tungsten metal in 1783 by the Spanish brothers Juan José and Fausto de Elhuyar, its yellow oxide was known to the scientists of that time as it formed as hydrated species (today: $WO_3{*}H_2O$) on the acidification of tungsten-bearing aqueous solutions (**Figure 1**). It was called tungstic acid by the Swedish chemist Carl Wilhelm Scheele [1] and its bright yellow colour fascinated his contemporaries. Rudolf Erich Raspe, a German Geologist and the famous author of *"The Adventures of Baron Munchausen"*, reported in 1795: *"In beauty it exceeds Turner's well-known yellow by far"*, and proposed its use as artists' colour [2].

The formation of a brown lower oxide of tungsten (WO_2) was mentioned for the first time in the Thesis Work of the de Elhuyar brothers in 1783 [3], and in 1816 the first systematic study of the reactions of tungsten with oxygen was published by the Swede Jöns Jacob Berzelius (known today as the "Father of Swedish Chemistry") [4]. In his famous textbook "Lärebok I Kemien" [5], Berzelius described two tungsten oxides, a yellow oxide with three atoms of oxygen per atom of tungsten (WO_3), and a brown oxide with two atoms per atom of tungsten (WO_2). He also observed that the yellow oxide easily changed its colour to green or even dark blue on *"exposing it to the sun for a longer time"*, or by adding zinc metal as a reducing species (**Figure 1**), without changing its weight considerably.

There are several tungsten oxides, but only four of them are of major importance. They all have attractive colours: the yellow WO_3, the dark blue $W_{20}O_{58}$ ($WO_{2.9}$), the violet $W_{18}O_{49}$ ($W_{2.72}$) and the chocolate brown WO_2. So-called higher tungsten oxides are structurally related to both the WO_3 and $W_{20}O_{58}$ structures and exhibit chemical formulas between $WO_{2.99}$ and $WO_{2.889}$. They belong to the group of non-stoichiometric tungsten oxides, and are of interest mainly to structural chemists. They exhibit colours from yellow to green to very dark blue (as already described by Berzelius). The colour changes are a result of a slight loss of oxygen which generates an additional valence state in the WO_3 parent structure, either W^{5+} or W^{4+}. Cation-to-cation charge transfer between the parent W^{6+} and a reduced ion is responsible for the change in colour [6].

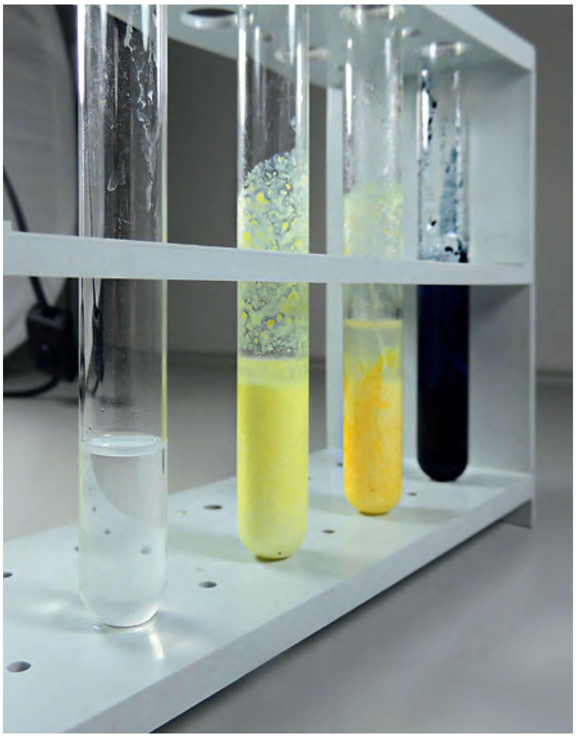


Figure 1: On acidification of tungsten-bearing aqueous solutions a yellow precipitate is formed, called tungstic acid. Transparent sodium tungstate solution to the left; yellow tungstic acid formed on acidification (in the middle); and dark blue precipitate which forms under reducing conditions (e.g. by adding zinc metal).

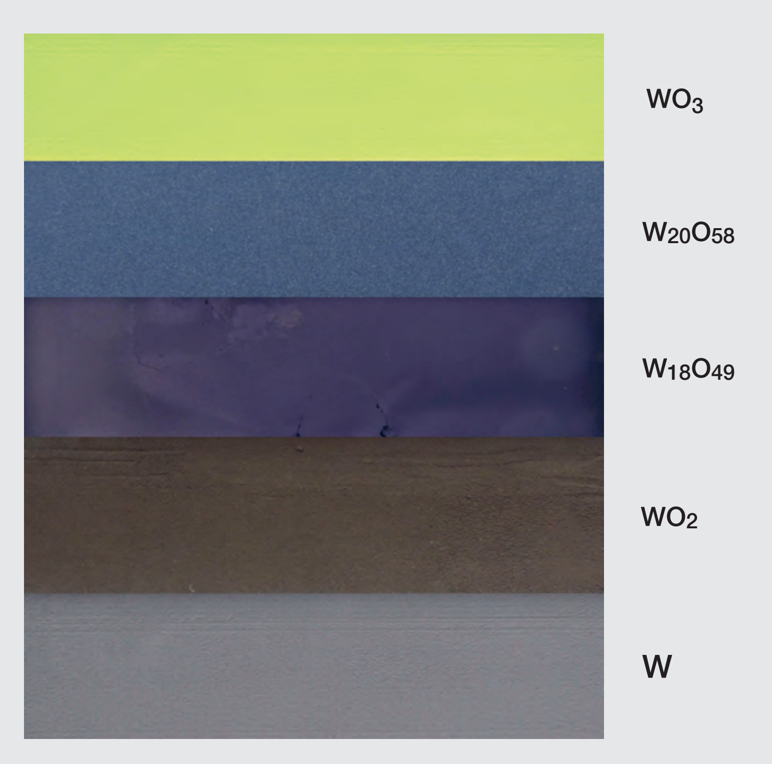


Figure 2: Colours of the tungsten oxides, prepared by interrupting the reduction process at selected reduction stages: yellow WO_3, blue $W_{20}O_{58}$, violet $W_{18}O_{49}$, chocolate-brown WO_2, and grey W metal. Note the green touch of WO_3, which is due to a slight oxygen deficiency.

Tungsten oxides are important starting materials for the production of tungsten metal powder by hydrogen reduction. These oxides are formed out of ammonium paratungstate by a thermal decomposition process called "calcination" and are, depending on the decomposition conditions (more or less reducing), a mixture of different higher tungsten oxides, including amorphous oxide phases. As described before, they exhibit colours between yellow and dark blue (TBO, "Tungsten Blue Oxide").

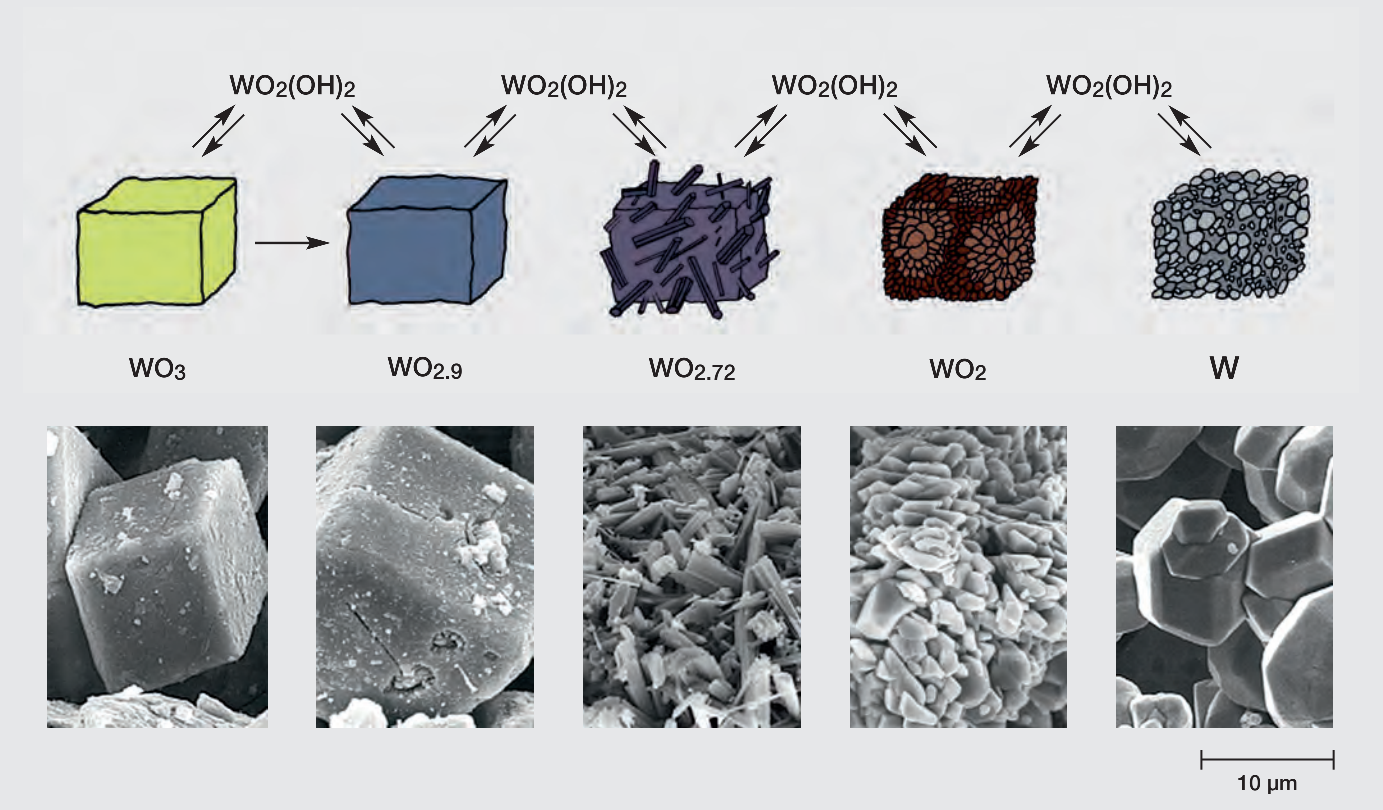


Figure 3: Electron-microscopical images of tungsten oxides and tungsten metal, formed during hydrogen reduction of WO_3. The reason for the significant change in form of the powder particles is a result of a chemical vapour transport (CVT) of tungsten via the volatile tungsten hydroxide $WO_2(OH)_2$; by courtesy of Prof. Roland Haubner; Vienna University of Technology.

Stoichiometric compounds such as $W_{20}O_{58}$, $W_{18}O_{49}$ or WO_2 are formed intermediately during the reduction process and can be isolated by interrupting the reduction process at the selected reduction state (**Figure 2**).

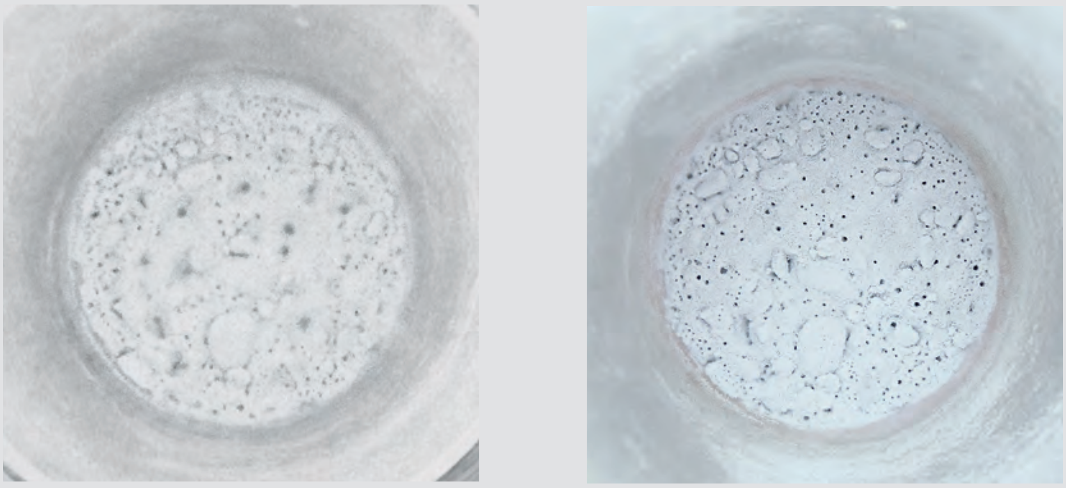
All tungsten oxides exhibit different colours, characteristic crystal symmetries, and also peculiar crystal forms. They are commonly not visible to the naked eye, as the powder particles are too small for a simple visual detection. However, they can be made visible by looking at the powders with the help of an electron microscope (**Figure 3**) where distinct differences of the crystal forms can be clearly recognised.

Inherent colours of the oxides due to absorption and selective reflection

The colours of the tungsten oxides are a result of the fact that the absorption and emission of photons (light) are dependent on wavelength. If the material has a low reflectivity at the short wavelength end of the spectrum (460 – 480 nm) it appears yellow to orange, because only the green and yellow part of the light is reflected. If it has a low reflectivity at the long wavelength end of the spectrum (550 – 700 nm), it appears blue or violet. If all components of the white light are absorbed and not re-emitted, the material appears black.

Colours can significantly change with different valence states within an oxide structure, although the parent structure of differently coloured oxides basically appears the same (due to changes in absorption and reflection and/or transmission). Inherent colours also change with the size of the particles, and the colours of powders therefore can significantly differ from those of single crystals. Thin films of tungsten trioxide are even transparent, but can be readily coloured by impurities which are used today for electronic devices [7].

Colours can also change with the temperature of the material due to alterations in the reflectivity of the oxides.



WO_3 < -50°C

WO_3 -50°C → -27°C

Figure 4: On cooling below -50°C the yellow oxide becomes white (left); between -50°C and -27°C it is bluish white (right). The crystal structure changes from monoclinic α-WO_3 (below -50°C) to triclinic β-WO_3 (above -50°C) [8].

Thermochromism of tungsten yellow oxide

Thermochromism is the property of substances to change colour due to a change in temperature and WO_3 is an attractive example for this property. On cooling the oxide by liquid nitrogen down to -196°C, a sudden change occurs from yellow to white, which then alters to a bluish-white colour between -50 and -27°C (**Figure 4**). At room temperature it becomes pale lemon-yellow again. On further heating to 200 – 300°C, WO_3 becomes dark yellow, changing to a deep orange colour at 400 to 500°C (**Figure 5**).

These reversible colour changes are linked to changes in the electronic properties of WO_3 which alter due to changes of the internal symmetry of the WO_3 crystals (through alterations of the lattice arrangements)*.

*Note: The idealised WO_3 structure (cubic symmetry; ReO_3-type) consists of a three-dimensional array of corner-sharing WO_6 octahedra. The real structure is distorted. This means that the relatively small tungsten atoms tend to be displaced from the octahedral centre and these displacements are temperature-dependent. Moreover, the symmetry can be influenced by small amounts of impurities [8].

WO_3 25°C

WO_3 200–300°C

WO_3 400–500°C

Figure 5: At elevated temperatures the colour of the WO_3 changes from pale lemon-yellow to dark yellow, and finally deep orange.

Crystal growth by Chemical Vapour Transport (CVT)

Since the different tungsten oxides exhibit interesting structural, optical and electronic properties, they are of interest to physicists. However, for investigation of the physical properties of the oxides, larger crystals must be prepared. The determination of the crystal structure and the measurement of (anisotropic) properties of a compound generally require high-quality single crystals. For crystal growth, numerous experimental methods are available, e.g. by means of crystallisation from solution, from the melt or under participation of the vapour phase. For each of the desired compounds the feasibility of a planned crystal growth method needs to be checked and the experimental conditions optimized. For example, crystal growth of elementary tungsten from the melt is hampered by the very high melting point of the metal (3422°C ± 15°C). Likewise, crystal growth of the tungsten oxides WO_3, $W_{20}O_{58}$, $W_{18}O_{49}$ and WO_2 requires a defined oxygen partial pressure which is difficult to adjust for most crystallisation procedures. A convenient laboratory method to overcome such problems is the application of chemical vapour transport (CVT) reactions for crystal growth. The principle of CVT is the volatilisation of a (polycrystalline) solid in the presence of a gaseous reaction partner, the so-called transport agent, whereby the solid is deposited elsewhere, frequently in the form of well-developed crystals.

The chemical transformation of the solid into the gas phase under formation of an intermediate product is called dissolution, the place of volatilization is called the *source region*, and the place of re-crystallisation is called the *sink region*. The dissolution and re-crystallisation will only take place if the external conditions, usually the temperatures, at the source and the sink region are different. This means that the chemical equilibrium between the involved phases can be influenced by application of a temperature gradient. If the sink region has a lower temperature than the source region, the CVT is *endothermic* (a process or reaction in which the system absorbs energy from its surroundings in the form of heat) and, in the opposite case, the CVT is *exothermic* (a reaction that releases energy from the system, usually in the form of heat).

Because the transport involves a chemical reaction between the solid in the sink and the transport agent, CVT is also associated with a purification effect which is industrially used in the Mond-Langer process for production of high-purity nickel or in the Van Arkel process for the purification of refractory metals (e.g. Ti, Zr, Hf, V, Ta, Re). Another practical application of CVT can be found in halogen lamps, where evaporating tungsten atoms are transported back to the hot zone (exothermic transport) as a volatile halogen compound, commonly formed with iodine or bromine and traces of oxygen, which enhances the working life time of the halogen lamp.

The first reaction based on CVT was observed and described by Robert Bunsen [9] who associated the fumarolic deposition of iron(III)-oxide crystals with the presence of hydrogen chloride as transport agent and the intermediate formation of gaseous $FeCl_3$ according to the following equilibrium equation (transport reaction):

$$Fe_2O_3\ (s) + 6\ HCl\ (g) \rightleftharpoons 2\ FeCl_3\ (g) + 3\ H_2O\ (g)$$

In the case of tungsten oxides and tungsten metal, halogens and/or water (or precursors thereof) can be used as transport agents. For example, the transport reaction of WO_2 can then be formulated as

$$WO_2\ (s) + X_2\ (g) \rightleftharpoons WO_2X_2\ (g) \qquad (X = Cl, Br, I)\ \text{or}$$
$$WO_2\ (s) + 2\ H_2O\ (g) \rightleftharpoons WO_2(OH)_2\ (g) + H_2\ (g)$$

In the case of tungsten metal the reaction can be formulated as

$$W\ (s) + TeCl_4 \rightleftharpoons WCl_4\ (g) + Te\ (g),\ \text{resp.}$$
$$W\ (s) + 4\ H_2O \rightleftharpoons WO_2(OH)_2\ (g) + 3\ H_2\ (g)$$

In the second half of the 20th century, the theory behind CVT was developed mainly by Harald Schäfer and co-workers, accompanied with systematic experimental investigations of various systems, including elementary, binary and ternary phases, which led to the first monograph on this method being published in 1962 [10]. In the meantime, theoretical models of CVT have improved and the number of practical applications of CVT for synthesis and crystal growth of numerous other systems has increased significantly. The most up-to-date reference and textbook on CVT has been published recently by Binnewies et al [11].

Table 1. Experimental details for crystal growth of elementary tungsten and tungsten oxides

Phase	Molar educt ratio W:WO_3	Transport agent	Temperature gradient (source → sink)	Reaction time
W [12]	1:0	$HgBr_2$	1000°C → 900°C	10 days
$W_{20}O_{58}$ [13]	0.3:19.7	$TeCl_4$	1000°C → 900°C	one week
$W_{18}O_{49}$ [13]	1.7:16.3	$TeCl_4$	1000°C → 900°C	one week
WO_2 [14]	1:2	I_2	1000°C → 900°C	one week
WO_3 [13]	0:1	$TeCl_4$	900°C → 800°C	five days

For crystal growth of elementary tungsten as well as of the oxides WO_3, $W_{20}O_{58}$, $W_{18}O_{49}$ and WO_2 using CVT, the reported experimental conditions as given in **Table 1** were adapted. For all experiments, high-purity tungsten and WO_3 powder were mixed in stoichiometric ratios for the desired phases. Together with small amounts of the respective transport agent, the mixtures were placed in a silica ampoule. Under cooling, the ampoule was then evacuated and subsequently sealed by using an oxyhydrogen burner (**Figure 6**) and finally placed in a two-zone furnace, schematically shown in **Figure 7**.

Figure 8 demonstrates a view into the hot zone of the furnace.

After the respective reaction time, the ampoules were pulled out from the furnace tube and quenched in water. If iodine was used as a transport agent, the ampoule still remained violet until the iodine vapour had condensed on quenching (**Figure 9, lower image**). If $TeCl_4$ was used as a transport agent, a metallic mirror formed on cooling in the source area of the ampoule, whereas tungsten oxide single crystals were formed in the sink area (**Figure 9; upper image**).

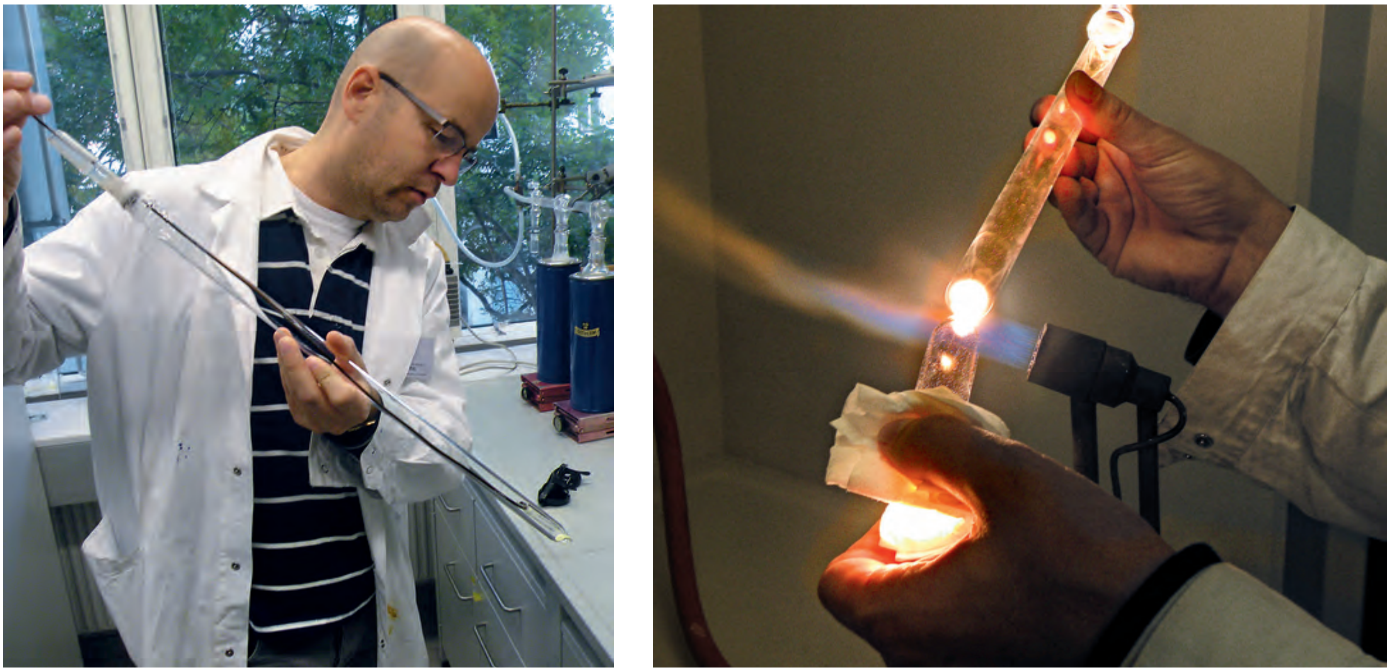


Figure 6: The powder mixtures (W, WO_3) are first placed in a half-ampoule together with a transport agent. The ampoules are then evacuated and subsequently sealed by using an oxyhydrogen burner. They are then placed in a two-zone furnace for CVT growth.

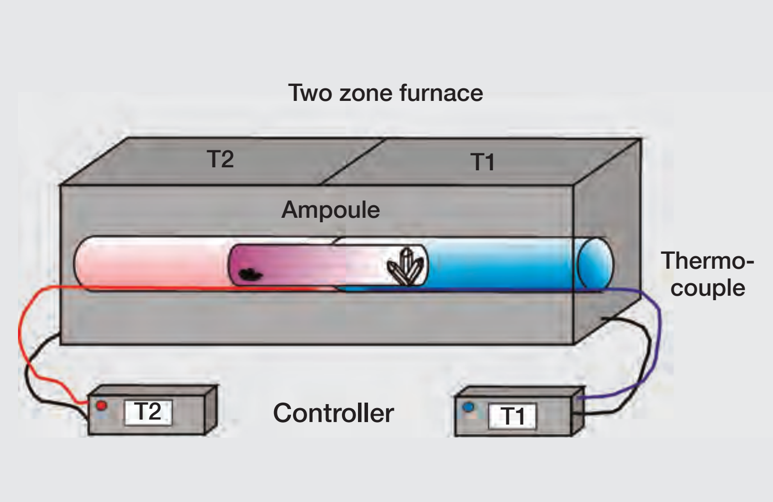


Figure 7: Schematic set-up for a CVT experiment using a sealed ampoule in a two-zone furnace; the red part of the furnace signifies the hot zone (source), the blue part the cooler sink zone where the crystals are deposited from the vapour phase.

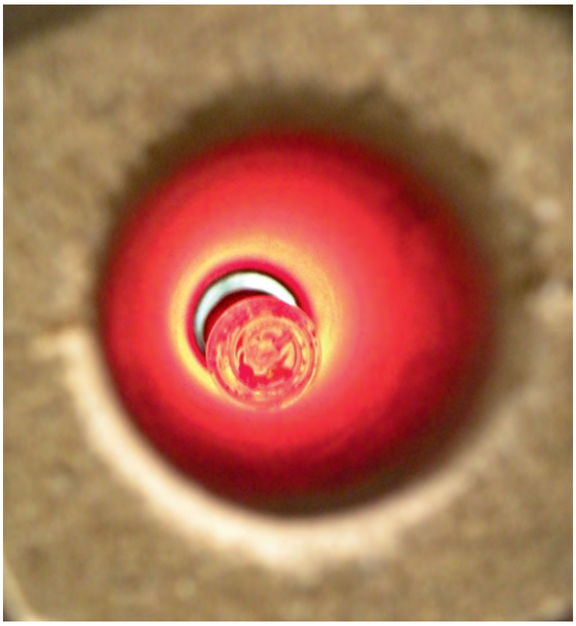


Figure 8: View into the hot zone of the furnace, showing the ampoule with crystals grown at its cooler end; the red colour stems from emission of light by the hot bodies (incandescence). The size of the ampoule is about 2 cm in diameter.

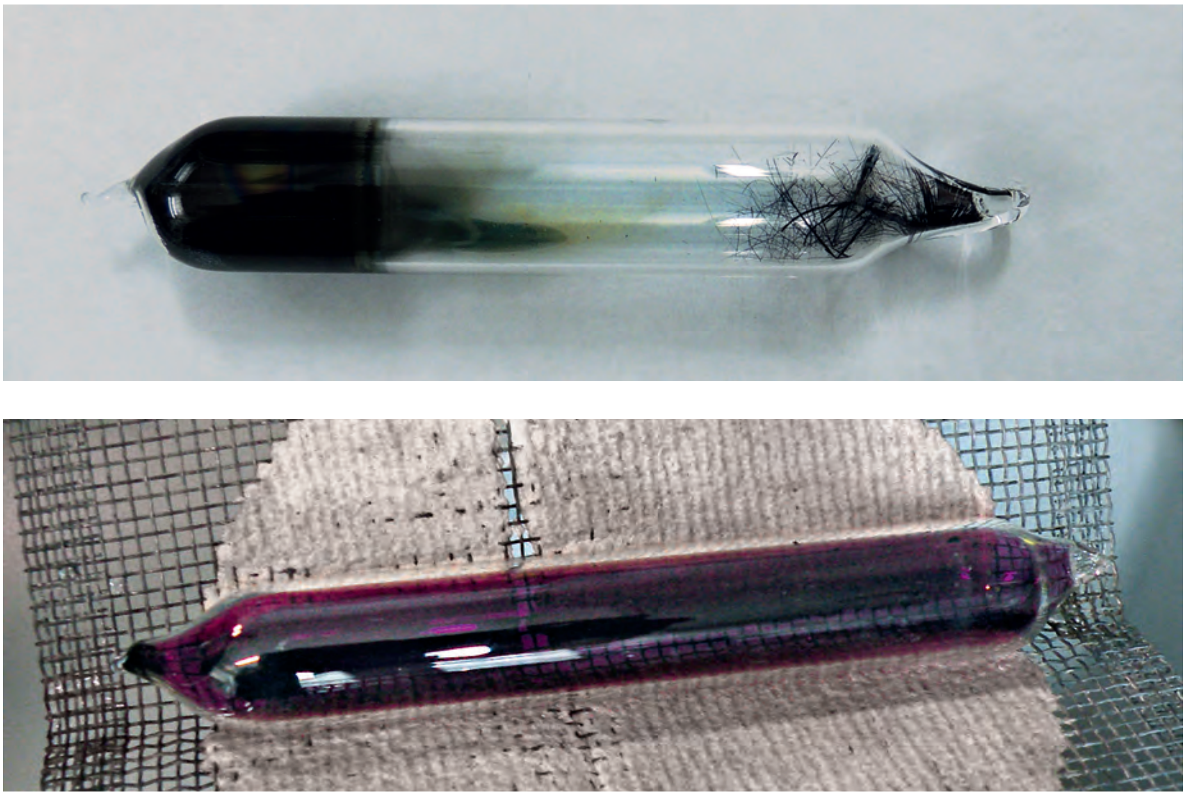


Figure 9: After the CVT experiments, the ampoules (length about 12 cm) are cooled down by water; if $TeCl_4$ is used as a transport agent, the primarily cooled source part turns black, due to the deposition of a thin metallic film of tellurium; in the sink part of the tube whisker-like $W_{18}O_{49}$ has formed (upper image); on working with iodine as a transport medium, the tube remains violet (iodine vapour) unless the iodine re-sublimes at lower temperatures.

Figure 10: Translucent WO_3 crystal formed by CVT (transport medium: $TeCl_4$); size of the crystal: 3 mm. The colour of the sample is yellow with a green touch, indicating a slight oxygen deficiency.

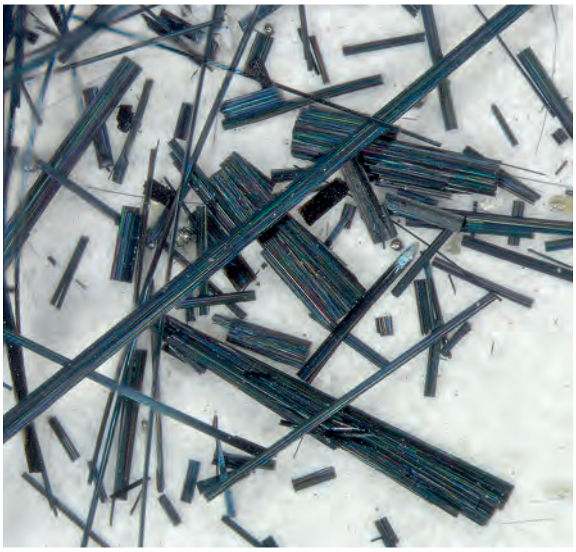


Figure 12: Whisker-like $W_{18}O_{49}$ crystals formed in the silica ampoule by CVT; (Transport medium: $HgBr_2$); width of the needles: 2–200 µm; needle length up to 20 mm; thin needles join together to form bundles of needles. Note the small droplets of metallic mercury formed on cooling by decomposition of $HgBr_2$.

The results of crystal growth experiments are demonstrated in **Figures 10–14**. The largest crystals were obtained in the case of WO_2, which turned out to be a rather simple procedure for crystal growth with crystal dimensions up to 4 mm. In comparison, the largest crystals in the case of WO_3, $W_{20}O_{58}$ and tungsten metal were in the 3 mm range. The most striking crystal form was obtained in the case of the violet oxide ($W_{18}O_{49}$), where a network of thin needles

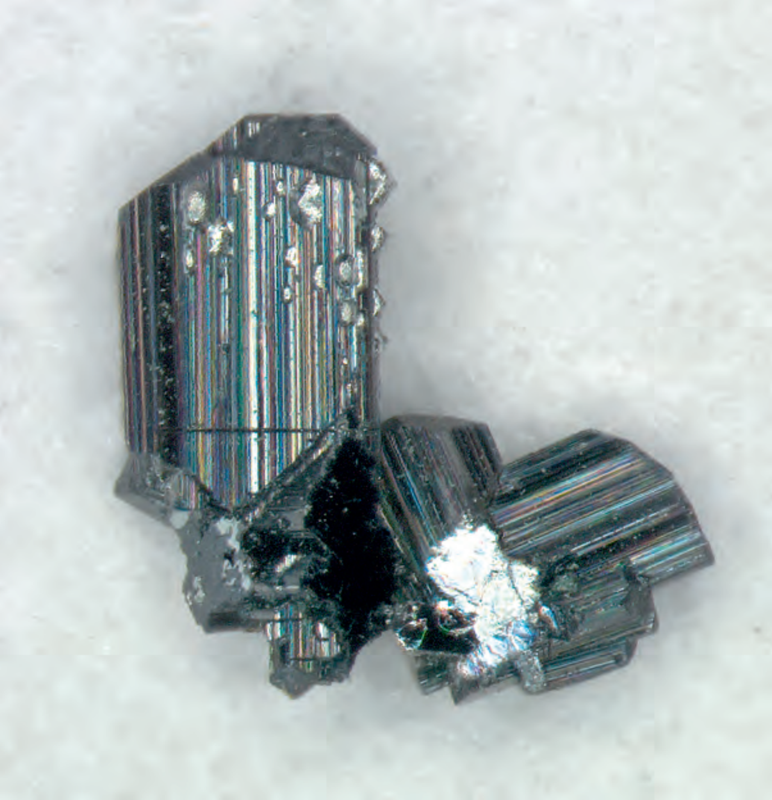


Figure 11: $W_{20}O_{58}$ single crystal formed by CVT (transport medium: $TeCl_4$); size of the crystal: 3 mm. The colour of the sample is black with a slight dark blue shine.

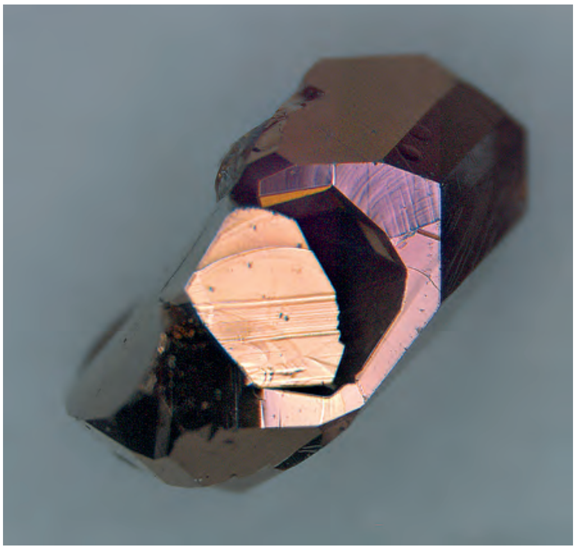


Figure 13: WO_2 single crystal formed by CVT (transport medium: I_2); size of the crystal: 4 mm. Unlike the colour of WO_2 powder, which is chocolate-brown, the colour of single crystals is bronze-like.

formed upon the deposition process, with needle diameters of 3 to 50 µm only, but needle length of up to more than 2 cm (**Figure 9; upper image**). This growth of the violet oxide is a well known peculiarity and reflects well the whisker-like growth of this monoclinic structure (the b-axis of the monoclinic cell is parallel to the needle axis).

Conclusion

The colours of tungsten oxides are due to light absorption and selective reflection (and/or transmission). This is called subtractive colouration. The colour of the oxides changes with the electronic properties of the oxides which, per se, are a result of the crystal symmetry of the solid. Changes in size, crystallinity or temperature can significantly change the colour, as demonstrated in this article. Chemical vapour transport of tungsten renders the preparation of single crystals of tungsten oxides, but also tungsten metal, to further exploit their interesting structural, optical and electronic properties.

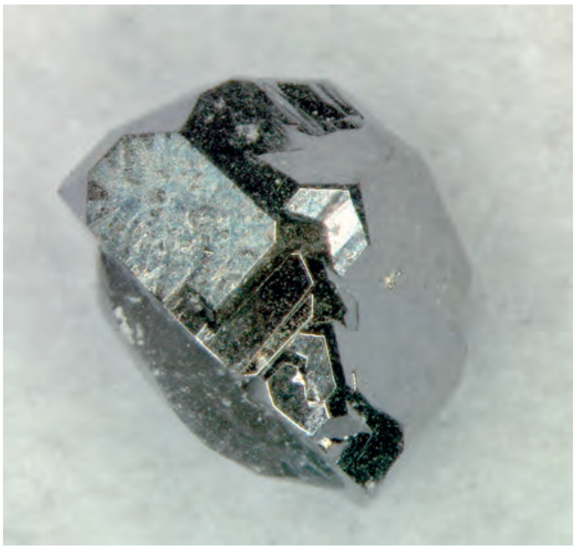


Figure 14: Tungsten metal single crystal formed by CVT (transport medium: $HgBr_2$); size of the crystal: 3 mm. The crystal has a grey, metallic shine. The white light is absorbed by the crystal but the metal piece appears reflective over the whole visible wavelength range.

Further Reading

R. Tilley: Colour and the optical properties of Materials, John Wiley & Sons, Ltd, England, 2000 (ISBN: 0-471-85197-3).

References:

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ITIA news

26th Annual General Meeting, Sydney, Australia

For the first time, the ITIA will hold its AGM in Australia. The 26th AGM will be held in the Westin Hotel in Sydney from Sunday 22 to Wednesday 25 September and will be generously hosted by Global Tungsten and Powders Corp and Wolfram Camp Mining Pty Ltd who have invited delegates to a dinner on Wednesday evening. The event will be followed by visits to the Wolfram Camp Mine, an open pit tungsten and molybdenum mine in Queensland, 90 km west of Cairns, and the Mt Carbine Tungsten Mine, 120 km north-west of Cairns.

The breathalyser ...

Delegates who decide to visit the mine sites should take care not to party for too long the night before as visitors are breathalysed on arrival! Fortunately, on an exploratory visit in January, Rose Maby (see pic) had retired to bed early and passed the test (just!).

There are 8 Australian members of ITIA (13% of the total) although the worldwide economic situation has imposed restrictions on ambitious plans to develop or reopen tungsten mines in various parts of the country. In 2008 there were 15 projects listed but the 2012 figure for production is

Wolfram Camp Mine

Carbine Tungsten Tailings

only 50 t W content judging by reported imports. Production peaked in 1981 at 3,300 t W content – nearly 14% of the total in the Western World – but declined over the next decade as the Western World's mines could not compete with China and, after 1990, production was negligible.

As always at these AGMs, the chance is taken to hear updates from experts in the principal market sectors as may be seen from the list of papers and speakers below:

- **History and Development of Tungsten Applications and Market, with Highlight on ITIA Members' Mining Projects in Australia**, Dr Burghard Zeiler, ITIA

- **Update on Russian Tungsten Market,** Mr Denis Gorbachev, Wolfram CJSC

- **EU Tungsten Market Update,** HC Starck GmbH

- **Tungsten Pricing Mechanisms,** Representatives from Metal Bulletin, Metal-Pages and Ryan's Notes/CRU

- **China Tungsten Market Update**, Xiamen Tungsten Co Ltd

- **Hardmetal Recycling Developments and Market with Emphasis on Zn-Process,** Dr Matti Kurkela, Tikomet Oy

- **US Tungsten Market Update,** Mrs Stacy Garrity, Global Tungsten & Powders Corp

- **Update on the Japanese Tungsten Market,** Mr Furkhat Faizulla, Advanced Material Japan Corp

It is expected that the session on Tungsten Pricing Mechanisms will attract a large audience and keep Counsel on his toes.

For the full programme, registration forms, hotel reservations and visa advice, readers should go to the ITIA website.

Sydney at night

Appointment of HSE Director

For many years, and not least during the last six years with the heavy workload resulting from compliance with REACH, the ITIA has been unique amongst metals' associations in not having a full-time HSE Director or Manager with the necessary scientific expertise.

All members of both the ITIA and the Tungsten Consortium have welcomed the decision to appoint Dr Ranulfo Lemus-Olalde as the ITIA HSE Director in February and he will also run the Technical Secretariat of the Tungsten Consortium.

Dr Lemus has attended most HSE and Consortium meetings as the Principal Toxicologist of Arcadis US Inc (scientific advisers to the ITIA and to the Tungsten Consortium) since 2007 and his expertise has been an invaluable asset to our HSE and REACH work programmes.

Having successfully completed his university education in Mexico and the USA to become a Doctor of Science in 1996, he then undertook post-doctoral studies at the University of Pittsburgh. His work for ITIA has focussed on conducting hazards classification for tungsten substances and hard-metal, whilst he was also responsible for the REACH testing programme and writing the Chemical Safety Reports which ultimately led to the successful registration of dossiers for 9 tungsten substances and one mixture.

The extensive HSE and Consortium work programmes for the future will mean that it will be Dr Lemus who interfaces with regulatory agencies and authorities on HSE matters relating to tungsten materials.

Dr Ranulfo Lemus-Olalde

ITIA tungsten consortium

Compliance with REACH – a service from the ITIA

After assisting companies to meet the second REACH deadline of 31 May to register their substances in the tonnage band 100 – 1,000 tpa, the Consortium Secretariat is now preparing updates to the Technical Dossiers for submission to ECHA later this year.

Two German companies, DURUM Verschleiss-Schutz GmbH and Sulzer Metco WOKA GmbH, have joined the Consortium this year.

For further details of the Consortium work programme, a list of members, and conditions for Membership and purchase of Letters of Access and Recyclers Agreements, please refer to the Consortium websites:

- www.tungstenconsortium.com
- www.sief.tungstenconsortium.com

ITIA membership

Welcome to:

Carbine Tungsten Ltd, Recovery of tungsten concentrates from the Mt Carbine Tungsten Mine in Queensland, Australia.

Noble Group – Hard Commodities, Located in Singapore with headquarters in Hong Kong the company manages global commodity supply chains.

Todd Corporation, The New Zealand based company holds 19.9% of Wolf Minerals developing the Hemerdon tungsten mine in the UK

Tungco Inc, A trading company involved in tungsten carbide recovery and recycling located in the US.

For a full list of ITIA members, contact details, and products or scope of business, please refer to the ITIA website – www.itia.info.

Dr Burghard Zeiler
Secretary-General