# An organometallic *chimie douce* approach to new Re$_x$W$_{1-x}$O$_3$ phases†

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Re$_x$W$_{1-x}$O$_3$·H$_2$O and Re$_x$W$_{1-x}$O$_3$ phases are prepared by a new organometallic *chimie douce* concept employing the organometallic precursor methyltrioxorhenium.

Crystalline WO$_3$ has found widespread interest as an electrochromic material, applied *e.g.* as thin film for "smart windows",[1] and as a gas sensor.[2] At room temperature monoclinic γ-WO$_3$ (P2$_1$/n) represents the thermodynamically most stable phase and consists of tilted WO$_6$ octahedra. Its structure is therefore related *via* group–subgroup relationships with cubic ReO$_3$ (Pm-3m), which represents the aristotype of the BO$_3$ perovskite family. Accordingly, it should be possible to form solid solutions of mixed Re$_x$W$_{1-x}$O$_3$ phases due to the structural resemblance of both parent oxides and the similar ionic radii of Re$^{VI}$ and W$^{VI}$.[3] While WO$_3$ is an insulator, ReO$_3$ displays metallic behaviour with a specific conductivity in the same range as crystalline copper.[4] Hence, solid solutions of both oxides might lead to new phases with interesting electronic properties like the related Na$_x$WO$_3$ phases, which are benchmark systems to study chemically-induced metal-to-insulator transitions.[5] However, up to now mixed Re$_x$W$_{1-x}$O$_3$ phases were only accessible in small quantities under extreme conditions at high pressure and high temperatures (65 kbar, 1200 °C).[6] Here, we propose a new organometallic *chimie douce* method which allows the synthesis of Re$_x$W$_{1-x}$O$_3$ phases in large quantities by a low temperature process at ambient pressure.

A convenient aqueous synthesis of WO$_3$·yH$_2$O (y = 1, 2, 1/3) from tungstates *via* tungstic acid has been reported and discussed earlier.[7–9] We found that mixed hydrated WO$_3$/ReO$_3$ phases are formed from sodium metatungstate containing the Keggin ion [H$_2$W$_{12}$O$_{40}$]$^{6-}$ and the organometallic precursor, CH$_3$ReO$_3$, (**m**ethyl**t**ri**o**xorhenium; MTO) in diluted HCl at 100 °C.[10] The new Re$_x$W$_{1-x}$O$_3$·H$_2$O phases are obtained as dark green to black micro-crystalline platelets, in contrast to WO$_3$·H$_2$O which shows a bright yellow colour when prepared under the same conditions (Fig. 1). The choice of the precursors is crucial; no mixed WO$_3$/ReO$_3$ phases are obtained from sodium tungstate Na$_2$WO$_4$·2H$_2$O which consists of isolated WO$_6$ octahedra. We interpret these observations as a kinetic effect: acidification of sodium tungstate initiates a fast condensation process[8] leading to WO$_3$·H$_2$O precipitates. This process, however, is apparently

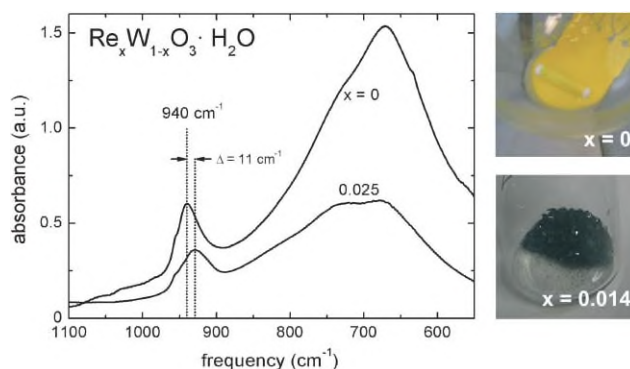[a] *Institut für Physik, Universität Augsburg, Universitätsstr. 1, D-86135, Augsburg, Germany. E-mail: wolfgang.scherer@physik.uni-augsburg.de; Fax: +49-(0)821-598-3227; Tel: +49-(0)821-598-3350*
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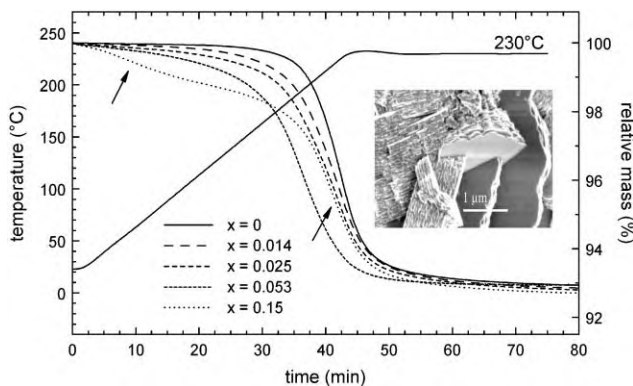† Electronic supplementary information (ESI) available: differential TGA curves. See http://dx.doi.org/10.1039/b506088e



**Fig. 1** IR spectra (KBr) of WO$_3$·H$_2$O and Re$_x$W$_{1-x}$O$_3$·H$_2$O with x = 0.025. The right hand side shows photographs of tungstite and a mixed phase (x = 0.014).

delayed when α-metatungstate is used instead as precursor. In this case, hydrolysis of the [H$_2$W$_{12}$O$_{40}$]$^{6-}$ ion to release the neutral monooxo precursor [WO(OH)$_4$(OH$_2$)] provides a sufficient time span for the preconditioning of our organometallic precursor (*e.g.* CH$_3$ReO$_2$(OH)$_2$ formation)[11] to take part in the following oxolation process. Once incorporated, MTO loses the methyl group, accompanied by reduction of Re$^{VII}$ to Re$^{VI}$.[11] We note that only pure WO$_3$·H$_2$O is precipitated when other inorganic Re$^{VII}$ species like perrhenate salts are added to the reaction mixture instead of MTO. Hence, the salient capability of our organometallic precursor to form Re$^{VI}$ oxide species by methane elimination in water appears to be crucial for successful tungsten/rhenium substitution.[12] The composition and homogeneity of the samples were ascertained by ICP, SEM-EDX, X-ray diffraction and microanalysis up to a Re content of 12%. For x larger than 0.12 phase separation *via* ReO$_3$ formation is observed.

IR spectroscopic studies (KBr pellets; Fig. 1) show a characteristic band at 940 cm$^{-1}$ in the parent tungstite, WO$_3$·H$_2$O, which shifts to lower frequency in our new Re$_x$W$_{1-x}$O$_3$·H$_2$O samples with increasing rhenium content. This mode can be assigned by the stretching mode of the W=O bond (see structural motif in Fig. 5) which appears to become softened by stepwise substitution of W(d$^0$) by the less Lewis-acidic Re(d$^1$) centres.[9,13] Hence, substitution of only 2.5% of tungsten atoms by rhenium lowers the corresponding W/Re=O streching frequency by 11 cm$^{-1}$.

A further indication of electronic changes induced by the rhenium content of the mixed phases can be found in the dehydration behaviour as studied by TGA using a temperature ramp from 25 to 230 °C during 45 minutes. As shown in Fig. 2, all phases lose a total of one molecule of water per formula unit (7%),

**Fig. 2** TGA dehydration curves of selected $Re_xW_{1-x}O_3 \cdot H_2O$ phases (right axis) and the respective temperature profile (left axis). The inset displays a typical SEM image for the sample $x = 0.014$ revealing a morphology typical for layered compounds.

but the ease of dehydration depends on the rhenium content. While significant water loss (5% of the total loss) of $WO_3 \cdot H_2O$ starts only above 180 °C,[9] the mixed phases with $x = 0.025$ (0.053) of rhenium content lose water already at 140 °C (90 °C). Hence, replacement of the $W(d^0)$ atoms by the more electron-rich and less Lewis-acidic $Re(d^1)$ centres facilitates the dehydration of water molecules which are interconnecting corner-sharing $WO_6$ layers *via* hydrogen bonding. The samples with rhenium contents $x > 0.12$, which show phase separation, lose water in two clearly distinguishable steps at different temperatures. The inflection points of the dehydration curve of the sample with 15% rhenium content are marked by arrows in Fig. 2.

Magnetisation measurements were performed for all $Re_xW_{1-x}O_3 \cdot H_2O$ samples presented in this paper. In Fig. 3 the inverse susceptibility $\chi^{-1}(T) = B/M$ is pictured, representatively for $x = 0.025$. Below 100 K $\chi(T)$ is well accounted for by a Curie–Weiss law $\chi(T) = C/(T - \theta) + \chi_0$ with a marginal itinerant
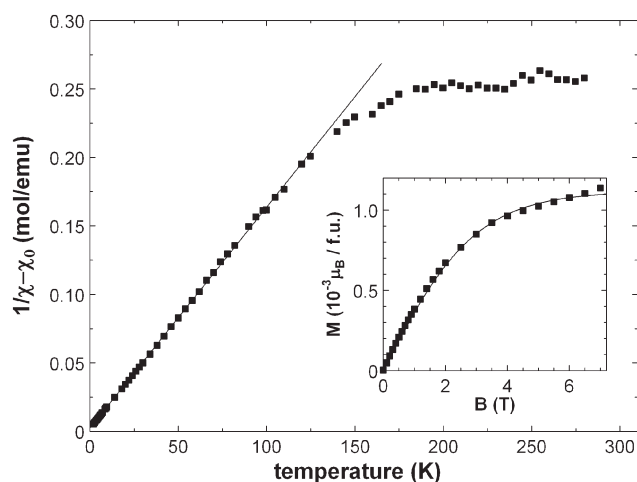


**Fig. 3** The inverse magnetic susceptibility $\chi^{-1}$ of $Re_xW_{1-x}O_3 \cdot H_2O$ ($x = 0.025$) measured in an external magnetic field $B = 1$ T. A diamagnetic core electron contribution $\chi_{Dia} = -68$ μemu/mol was subtracted from the data. The solid line is a linear fit with a Curie–Weiss law. The inset displays the field dependence of the magnetic moment $M$ per formula unit at 2 K together with a fitted Brillouin function (solid line).

contribution $\chi_0 \approx 0.03$ memu/mol and $\theta \approx 0$ K. The vanishing Curie–Weiss temperature $\theta$ indicates no correlations between the residual localised $d^1$ electrons at the Re atoms. The effective paramagnetic moment $\mu_{eff} = 0.06$ $\mu_B$ obtained from the Curie constant $C$ indicates that 0.1% of the metal sites carry a $d^1$ moment, which correspond to an amount of 4% of the Re atoms. In the inset of Fig. 3 the magnetisation $M(B)$ at 2 K is displayed. The fitted Brillouin function (solid line) takes into account a $d^1$ state with a quenched orbital moment ($L = 0$). The saturation magnetisation $M_{sat}$ is proportional to the quantity of the aligned local spins. The observed small saturation value of $M_{sat} \approx 10^{-3}$ $\mu_B$/f.u. corresponding to an amount of 0.1% $d^1$ moments at the metal sites corroborates our susceptibility results (for a single $d^1$ moment $M_{sat} = 1$ $\mu_B$/f.u.).

As one would expect from the marginal $\chi_0$ value, the resistivity $\rho$ of pressed powder samples of $Re_xW_{1-x}O_3 \cdot H_2O$ is generally high (about 10 Ωcm) and reveals an insulating temperature dependence ($d\rho/dT < 0$).

ESR spectra (9.35 GHz, 4 K) confirm the presence of localised $d^1$ moments at the Re atoms: a signal at $g = 2$ is observed, showing a hyperfine coupling (six lines) to rhenium ($I = 5/2$ for $^{185}Re$ and $^{187}Re$), with an average coupling constant $A \approx 620$ Oe (0.058 cm$^{-1}$; see Fig. 4).[14]

Finally, a strong indication for the change in the $WO_3 \cdot H_2O$ lattice due to rhenium doping is found by X-ray powder diffractometry. The mixed hydrated phases are isotypic to the orthorhombic $WO_3 \cdot H_2O$ tungstite structure (*Pmnb*). Fig. 5 shows an overlay of the diffraction pattern of $WO_3 \cdot H_2O$ and the phase with 2.5% rhenium content. Both patterns confirm the high crystallinity of our samples and do not hint at any parasitic phase.

However, closer inspection of the diffraction pattern (Fig. 5) reveals that some Bragg peaks of the rhenium substituted samples are slightly but significantly shifted to smaller angles (Bragg peaks (002) and (022) in Fig. 5) in comparison with the pattern of the parent compound $WO_3 \cdot H_2O$. Accordingly, Rietveld refinements reveal a widening of the $WO_3 \cdot H_2O$ lattice by 1.5 pm in the $c$ direction (from 5.1264(4) Å to 5.1416(1) Å) after Re doping ($x = 0.025$).

Analysis of the diffraction pattern of dehydrated $Re_xW_{1-x}O_3 \cdot H_2O$ samples, however, was complicated due to the partial amorphous character of the products (Fig. 6 (a)). The



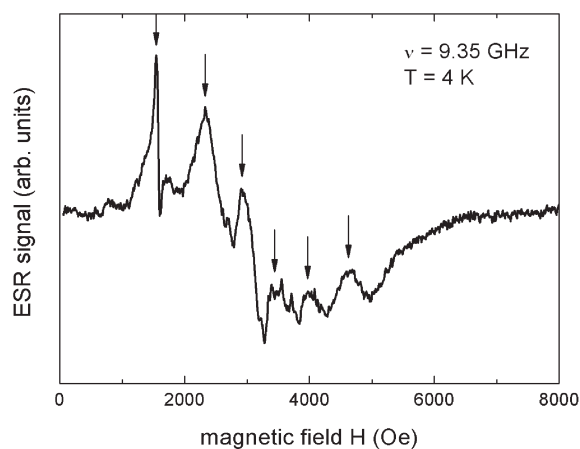**Fig. 4** An ESR spectrum of $Re_xW_{1-x}O_3$ ($x = 0.025$) at 4 K. The six lines indicate the hyperfine coupling of electron spins localised at $Re(d^1)$ centres.

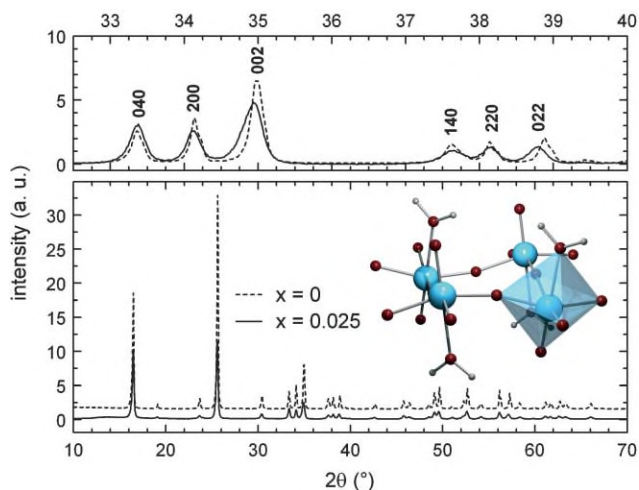**Fig. 5** X-ray powder diffraction pattern of WO₃·H₂O (tungstite) and Re$_x$W$_{1−x}$O₃·H₂O ($x$ = 0.025). The upper part is an enlargement of the diffraction range between 32 and 40°. The inset shows the structural motif of tungstite representing layers of corner-sharing polyhedra which are interconnected in the third dimension *via* hydrogen bonding.
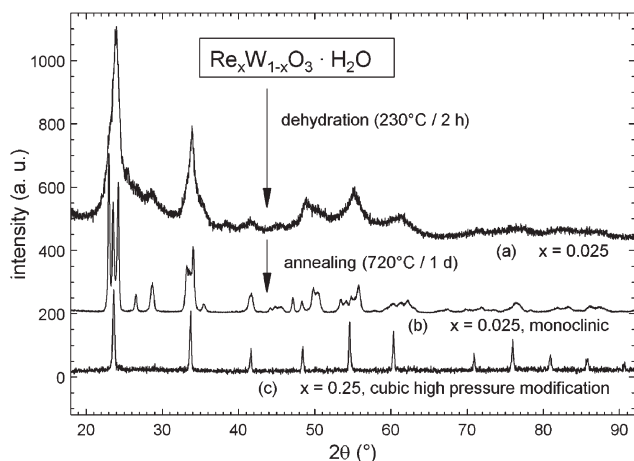


**Fig. 6** (a) X-ray powder diffraction pattern of dehydrated Re$_x$W$_{1−x}$O₃·H₂O ($x$ = 0.025) and (b) the annealed sample; (c) diffraction pattern of the cubic high pressure modification of Re$_{0.25}$W$_{0.75}$O₃.

resulting pattern closely resembles the ones found earlier for dehydrated WO₃·H₂O phases which were reported to represent the hitherto unknown metastable form of cubic WO₃.[15] However, a direct comparison with the cubic diffraction pattern of highly crystalline Re$_{0.25}$W$_{0.75}$O₃ powder obtained by bulk synthesis at 7.5 GPa and 1100 °C ($a$ = 3.7516(2) Å; Fig. 6 (c))[16] clearly reveals that the new Re$_x$W$_{1−x}$O₃ phases obtained by dehydration should be indexed rather by a monoclinic than by a cubic unit cell. Precise lattice parameters for the new monoclinic Re$_x$W$_{1−x}$O₃ phase ($x$ = 0.025, $a$ = 7.3165(4) Å, $b$ = 7.5131(4) Å, $c$ = 7.6911(5) Å, $β$ = 90.521(6)°, $P2_1/n$) could be obtained by Rietveld analysis of the annealed samples (720 °C, 1 day) (Fig. 6 (b)). Furthermore, a single crystal diffraction study on Re$_{0.02}$W$_{0.98}$O₃ ($a$ = 7.305(3) Å, $b$ = 7.534(2) Å, $c$ = 7.691(2) Å, $β$ = 90.88(3)°) which was alternatively synthesised by chemical transport methods at 1000 °C

clearly reveals the isotypic relationship between monoclinic Re$_x$W$_{1−x}$O₃ phases obtained by *chimie douce* and classical ceramic methods.

Hence, at this stage we can demonstrate that we succeeded in obtaining pure Re$_x$W$_{1−x}$O₃ phases by an organometallic *chimie douce* approach. An organometallic compound, methyltrioxorhenium, was found to be the only successful precursor suitable for the rhenium doping of WO₃ at low temperatures and ambient pressure. Diffraction studies reveal that the new Re$_x$W$_{1−x}$O₃ phases obtained by our *chimie douce* approach are not cubic but isotypic to monoclinic γ-WO₃. We could hence demonstrate that cubic phases of mixed Re/W trioxides still appear to remain a domain of high pressure/high temperature methods. As a result of our studies a fast and simple *chimie douce* pathway to mixed Re/W trioxides has been opened as an alternative to ceramic routes which warrants further exploitation with respect to electronic design (*e.g.* electrochromic and gas sensing properties) and chemical behaviour (*e.g.* intercalation chemistry, oxidation catalysis).

## Notes and references

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