External pressure and composition effects on the atomic and electronic structure of SnWO₄

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The atomic and electronic structure of tin tungstates, α-SnWO₄, α-Sn(sub 1.03)WO₉O₄ and β-SnWO₄, was studied by the W L₃-edge X-ray absorption spectroscopy and first-principles linear combination of atomic orbital (LCAO) calculations based on the hybrid exchange-correlation density functional (DFT)/Hartree–Fock (HF) scheme. It was found that the crystal structure of both α-phases is built up of strongly distorted WO₆ octahedra, whereas that of β-SnWO₄ is composed of nearly regular WO₄ tetrahedra. In addition, there are distorted SnO₆ octahedra in both α- and β-phases. The metal–oxygen octahedra distortion is explained by the second-order Jahn–Teller effect. The influence of pressure on the structure of α-SnWO₄ and β-SnWO₄ was studied in detail based on the calculated equations of state. The compressibility of β-SnWO₄ was found to be larger than that of α-SnWO₄. The existence of the insulator-to-metal transition was theoretically predicted in α-SnWO₄ at about 16 GPa and was explained by a symmetrization of metal–oxygen octahedra leading to a strong interaction of Sn 5s, W 5d and O 2p states and closing of band gap.

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1. Introduction

Transparent conducting oxides include a wide range of compounds which find numerous applications in optoelectronic devices, chromogenic technologies for solar energy utilization and energy savings [1–5]. Among these tin tungstate (SnWO₄), which exists in two phases, α-SnWO₄ and β-SnWO₄ [6,7], has been proposed recently as a candidate for a production of thin films having both p-type and n-type electrical conductivity [8]. Several other applications of tin tungstate were proposed in the literature, for example, in day-light photocatalysis [9–13], as anode material in Li-ion batteries [13] and in gas sensors [14,15]. High photocatalytic activity in both microcrystalline and nanocrystalline β-SnWO₄ forms was found under visible-light irradiation in [9,11,12]. It was also shown that the photocatalytic performance of nanocrystalline α-SnWO₄ can be enhanced by Zn²⁺ doping due to accompanying narrowing of band gap [16].

To better understand and control tin tungstate properties, one needs to know the precise structure–property relationships in both α- and β-phases.

Crystal structure of orthorhombic α-SnWO₄ (Fig. 1) is built up of layers of WO₆ octahedra, separated by layers of Sn²⁺ ions, which are also six-fold coordinated by oxygen atoms [7]. The WO₆ octahedra are connected within a layer by four corners and are distorted due to the second-order Jahn–Teller effect (SOJT) [17] because of the W⁶⁺ (5d⁰) electronic configuration. The SOJT effect is also responsible for SnO₆ octahedra distortion and is caused by the pair of stereochemically active Sn 5s electrons (lone pair) [9].

The structure of cubic β-SnWO₄ (Fig. 1) is built up of slightly deformed WO₄ tetrahedra, which are interconnected with strongly distorted via SOJT effect SnO₆ octahedra [18]. The WO₄ tetrahedra are slightly distorted with three short (1.74 Å) and one long (1.76 Å) W–O bonds. The W–O bond lengths depend on how many tin atoms are bound to the oxygen atom: the distant oxygen atom is shared with three tin atoms, whereas nearest three oxygens are bridging to one tin atom each.

Small band gaps, indirect $E_g=1.64$ eV in α-SnWO₄ [9] and direct $E_g=2.6–2.7$ eV in β-SnWO₄ [9,11,18], and unique band structures [9] are responsible for the photocatalytic activity of tin tungstates [19]. The results of recent DFT calculations [9] suggest that the valence band in both tungstates is mainly composed of strongly interacting O 2p and Sn 5s states, whereas W 5d–O 2p antibonding states with some admixture of Sn 5p states contribute to the conduction band.

The use of tin tungstate in transparent electronics assumes its production as a thin film, whose conductivity type can be controlled...
The synthesis of polycrystalline $\alpha$-SnWO$_4$ and $\beta$-SnWO$_4$ was performed using the method described in [6,25]. First, an equimolar amount of SnO (99.99%) and WO$_3$ (99.9%) powders was mixed and sealed in a silica ampoule under vacuum. $\alpha$-SnWO$_4$ was obtained by heating at 600 °C for 8 h, whereas $\beta$-SnWO$_4$ was produced by heating at 800 °C followed by rapid quenching down to room temperature. $\alpha$-Sn$_{1.03}$W$_{0.99}$O$_4$ phase was produced using the procedure as for $\alpha$-SnWO$_4$ phase but modifying the proportion of starting SnO and WO$_3$ components. All samples were characterized by X-ray powder diffraction and micro-Raman spectroscopy.

The W L$_3$-edge (10207 eV) X-ray absorption spectra were measured in transmission mode at the HASYLAB/DESY C (CEMO) bending magnet beamline [26]. The storage ring DORIS-III was operated at the energy $E=4.44$ GeV and current $I_{\text{max}}=140$ mA. The X-ray beam intensity was measured by two ionization chambers filled with argon and krypton gases. The higher-order harmonics were effectively eliminated by detuning of the double-crystal monochromator Si(111) to 60% of the rocking curve maximum, using the beam-stabilization feedback control. The tin tungstate powder samples were deposited on Millipore filters and fixed by Scotch tape. Measurements were performed at 10 and 300 K using the Oxford Instruments liquid helium flow cryostat.

X-ray absorption spectra were analysed using the EDA software package [27] following conventional procedure [28,29]. The W L$_3$-edge EXAFS spectra $\chi(k)k^2$ and their Fourier transforms (FT's) for $\alpha$-SnWO$_4$, $\alpha$-Sn$_{1.03}$W$_{0.99}$O$_4$ and $\beta$-SnWO$_4$ are shown in Fig. 2. The first shell contributions into the total EXAFS spectra were isolated by Fourier filtering in the range of 0.8–2.2 Å, and the radial distribution functions (RDF's) $G(R)$ for the W–O bonds were obtained by the regularization-like method [30] (Fig. 3). Theoretical scattering

![Crystal structure of $\alpha$-SnWO$_4$ (space group Pnma) and $\beta$-SnWO$_4$ (space group P2$_1$). WO$_6$ and WO$_4$ polyhedra are shown. The unit cells are also indicated.](image)

Fig. 1. Crystal structure of $\alpha$-SnWO$_4$ (space group Pnma) and $\beta$-SnWO$_4$ (space group P2$_1$). WO$_6$ and WO$_4$ polyhedra are shown. The unit cells are also indicated.

by adjusting the composition. For example, the p-type conductivity has been reported for Sn$_x$W$_{4-x}$O$_4$ film with $x=1.02$ and $y=0.98$, whereas the n-type has been observed at $x=0.98$ and $y=1.02$ [8]. Note that a significant deviation from the tungstate composition leads to a formation of tin tungsten bronzes as Sn$_x$WO$_3$ ($x<0.3$) and Sn$_2$W$_2$O$_9$ with different crystal structures [20–23]. In addition to the effect of the composition, the genuine physical properties of tin tungstate can be affected by stress or strain due to lattice and thermal expansion mismatch between the thin film and the substrate. This can be realized by growing epitaxial thin films and varying both their thickness and the nature of the substrate. Externally applied high pressure is an alternative approach, allowing one to induce even larger strain [24].

In this study we have used the W L$_3$-edge extended X-ray absorption fine structure (EXAFS) spectroscopy to probe the behaviour of local atomic structure around tungsten atoms in $\alpha$-Sn$_{1.03}$W$_{0.99}$O$_4$ and two reference compounds $\alpha$-SnWO$_4$ and $\beta$-SnWO$_4$ at 10 and 300 K. The obtained experimental results are explained using the first-principles linear combination of atomic orbital calculations. The behaviour of $\alpha$- and $\beta$-phases under pressure was also studied based on the calculated equations of state and suggests the possible existence of the insulator-to-metal transition in $\alpha$-SnWO$_4$. 

2. Experimental and calculation details

The synthesis of polycrystalline $\alpha$-SnWO$_4$ and $\beta$-SnWO$_4$ was performed using the method described in [6,25]. First, an equimolar amount of SnO (99.99%) and WO$_3$ (99.9%) powders was mixed and sealed in a silica ampoule under vacuum. $\alpha$-SnWO$_4$ was obtained by heating at 600 °C for 8 h, whereas $\beta$-SnWO$_4$ was produced by heating at 800 °C followed by rapid quenching down to room temperature. $\alpha$-Sn$_{1.03}$W$_{0.99}$O$_4$ phase was produced using the procedure as for $\alpha$-SnWO$_4$ phase but modifying the proportion of starting SnO and WO$_3$ components. All samples were characterized by X-ray powder diffraction and micro-Raman spectroscopy.

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amplitude and phase shift functions, used in the EXAFS simulations, were calculated for α-SnWO₄ (β-SnWO₄) crystallographic structures [7,6] by the self-consistent, real space multiple-scattering FEFF8 code [31] using complex exchange-correlation Hedin–Lundqvist potential [32] and the following values of the atomic muffin-tin radii: Rₘₜ(Sn) = 1.58 Å (1.57 Å), Rₘₜ(W) = 1.23 Å (1.14 Å) and Rₘₜ(O) = 0.93 Å (0.92 Å) for α-SnWO₄ (β-SnWO₄).

The first-principles linear combination of atomic orbital (LCAO) calculations were performed by the CRYSTAL09 code [33] using the hybrid exchange-correlation density functional (DFT)/Hartree–Fock (HF) scheme. Such approach was successfully used by us recently for other tungstates as ZnWO₄ [34,35], CaWO₄ [35], NiWO₄ [36] and CuWO₄ [37]. Several hybrid functionals were tested, and the best agreement with the experimental structure was obtained for the PBE0-13% functional [38] (the percentage defines the HF admixture in the exchange part of DFT functional). Note that similar result was found by us previously for NiWO₄ [36] and CuWO₄ [37]. The core electrons of the tungsten atoms were excluded from consideration using the Hay–Wadt (HW) effective small-core pseudopotential and the corresponding atomic basis set, excluding diffuse Gaussian-type orbitals. Durand–Barthelat core pseudopotential [39], employed previously in the LCAO calculations of SnO₂ [40], and the corresponding atomic basis set were used for tin atoms. The all-electron basis set, optimized in earlier calculations of perovskites [41], was employed for oxygen atoms. In the CRYSTAL09 code [33], the accuracy in evaluation of the Coulomb series and of the exchange series is controlled by a set of tolerances, which were taken to be (10⁻⁶, 10⁻⁸, 10⁻⁶, 10⁻⁸, 10⁻¹⁰) hartree. The tolerance on the total energy change was set to 10⁻¹⁰ hartree. The Monkhorst–Pack scheme [42] for an 8 × 8 × 8 k-point mesh in the Brillouin zone was applied. The optimized structural parameters for α-SnWO₄ and β-SnWO₄ are reported in Table 1.

Next the dependence of the total energy on the unit cell volume was calculated for both tungstate phases and fitted to the third-order Birch–Murnaghan isothermal equation of state (EOS) (Fig. 4) [43,44] in order to compute bulk modulus B₀ and its first derivative with respect to the pressure B₁ (Table 1). The determined EOS was further used to calculate the dependence of the unit cell volume V = f(P, V₀, B₀, B₁) on the pressure P.

Finally, for each pressure value P in the range from 0 to 16 GPa the relaxed structure was obtained by minimizing the total energy at fixed unit cell volume V(P). During structure relaxation, the lattice parameters and the atomic fractional coordinates were allowed to vary. As a result, the pressure dependence of the atomic and electronic structure was determined. The calculated total and

Table 1

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<tr>
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<th>α-SnWO₄</th>
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<th>β-SnWO₄</th>
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<td>1.45 [18]</td>
<td>2.68 [9], 2.7 [11], 4.36</td>
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</table>

Fig. 4. Dependence of the total energy per formula unit on the unit cell volume for α-SnWO₄ (solid circles) and β-SnWO₄ (solid squares). The equilibrium volumes of two tungstates are indicated by open circle and open square. Solid lines correspond to the third-order Birch–Murnaghan isothermal equation of state (EOS). See text for details.
projected density of states (DOS) and band structure diagrams for α-SnWO4 are shown in Fig. 5, whereas the pressure dependencies of the band gap $E_g$ and of the lattice parameters, ion charges and first shell interatomic distances (W–O and Sn–O) are reported in Figs. 6 and 7, respectively. The results for β-SnWO4 are displayed in Figs. 8–10.

3. Results and discussion

3.1. Tungsten L$_3$-edge EXAFS spectroscopy

The low-temperature (10 K) experimental W L$_3$-edge EXAFS spectra $\chi(k)k^2$ of α-SnWO$_4$, α-Sn$_{1.03}$W$_{0.99}$O$_4$ and β-SnWO$_4$ are shown in Fig. 2. The EXAFS oscillations are well observed up to high-$k$ values indicating the high quality of experimental data and low thermal damping. The similarity of the local environment around tungsten in two α-phases is clearly observed. This conclusion is supported by Fourier transforms (FT’s) of the EXAFS spectra, measured at 10 and 300 K, which are rather close in α-SnWO$_4$ and α-Sn$_{1.03}$W$_{0.99}$O$_4$.

The coordination shells up to about 5 Å produce the main contribution into FT’s, however, the influence of the outer shells is also detectable, especially at 10 K. The first coordination shell (the peak at 1.4 Å), composed of oxygen atoms, dominates in FT’s and is weakly sensitive to the thermal disorder. The first shell peak is symmetric and has large amplitude for β-SnWO$_4$, because the WO$_4$ tetrahedra are nearly regular, and the short W–O bonds are strong. The distortion of the WO$_6$ octahedra in two α-phases is responsible for the asymmetric shape of the first shell peak, which is broadened and has a shoulder at ~2 Å. It is interesting that the main part of the peak practically does not change going from 10 K to 300 K, whereas the shoulder amplitude is reduced at 300 K: this fact indicates the difference in the strength of W–O bonding for the nearest and distant oxygen atoms within the WO$_6$ octahedra [45].

The origin of the next peak in FT’s at ~2.7 Å is due to the multiple-scattering (MS) effects generated within the tungsten–oxygen polyhedra [46]. Its amplitude is small for tetrahedral coordination of tungsten in β-SnWO$_4$, but is nearly twice larger for octahedral coordination in both α-phases, as expected [47]. The origin of the difference in the amplitude comes from the fact that the scattering events within the O–W–O chains produce the main contribution into this peak, which increases when the value of the angle $\theta_{OWO}$ approaches $90^\circ$, i.e., the chain becomes linear and intermediate tungsten atom focuses strongly the photoelectron wave [46]. In tetrahedral WO$_4$ units in β-SnWO$_4$ all angles...
OWO ≈ 109° [6], whereas there are two angles OWO ≈ 170° and one angle OWO ≈ 157° in the distorted WO₆ octahedra in α-SnWO₄ [7].

The results of the MS calculations, based on the crystallographic structures of tin tungstates [6,7], suggest that the peaks between 3 and 5 Å are due to the outer coordination shells. The dominant contribution in this range comes from the shells containing tungsten and tin atoms. In α-SnWO₄ a group of six tin atoms and four tungsten atoms is responsible for the peak at 3.6 Å, whereas two tin atoms contribute into the peak at 4.2 Å. In β-SnWO₄, seven tin atoms give origin to the peak at 3.6 Å, whereas the peak at 4.4 Å is due to six tungsten atoms.

As one can see in Fig. 2, the effect of thermal disorder in the outer coordination shells of tungsten is much stronger than in the first shell. The change of temperature from 10 to 300 K leads to a decrease of the peak amplitude between 3 and 5 Å in α-SnWO₄ and α-Sn₁₀₃W₀₉₉O₄, whereas the peaks disappear completely in β-SnWO₄. Such behaviour can be explained by the difference in the atomic structure of the α and β phases (Fig. 1). Tetrahedral WO₄ units in β-SnWO₄ behave as rigid and weakly interact with each other as well as with the nearest SnO₆ units. On the contrary, octahedral WO₆ units in α-phases are bound to each other via corners and form 2D sheets in the ac-plane. They are also connected to two nearest SnO₆ units through edges. Therefore, the crystal structure of α-phases assumes more rigid lattice dynamics than that of β-phase.

Next we will discuss the results of the detailed analysis of the first coordination shell of tungsten (Fig. 3). The first shell contributions into the total EXAFS spectra were best-fitted using the regularization-like method [30], which has an advantage over conventional multi-component fitting in the case of strong disorder and/or coordination polyhedra distortions [29]. Good agreement between experimental and model EXAFS was found for all tungstates and the obtained RDF’s G₆₀₅–O(R) for W–O bonds at 10 and 300 K are shown in Fig. 3.

RDF’s for α-SnWO₄ and α-Sn₁₀₃W₀₉₉O₄ consist of the two peaks centred at 1.82 Å and 2.14 Å at 10 K. They correspond to the two groups of four and two oxygen atoms, forming the distorted WO₆ octahedra. The W–O bonds with the four nearest oxygen atoms are relatively strong, therefore the first peak in the RDF decreases only slightly upon increasing temperature from 10 to 300 K. At the same time, the two distant oxygens are weakly bound, so that these two W–O bonds become longer at 300 K, and the peak maximum shifts to 2.17 Å. Also thermal disorder influences more the longer W–O bonds. The only difference in the RDF’s G₆₀₅–O(R) between α-SnWO₄ and α-Sn₁₀₃W₀₉₉O₄ is the larger static disorder present in the

Fig. 6. Dependence of the calculated band gap value on pressure in α-SnWO₄.

Fig. 7. Dependence of the calculated lattice parameters, ion charges from Mulliken population analysis and first shell interatomic distances (W–O and Sn–O) on pressure in α-SnWO₄.
latter: as a result, the two peaks at 1.82 Å and 2.14 Å are more broadened. In $\beta$-SnWO$_4$ the RDF $G_{\text{Sn}-\text{O}}(R)$ consists of only one narrow peak centred at 1.77 Å at 10 K, being in agreement with tetrahedral coordination of tungsten. The rigidity of the WO$_4$ tetrahedra due to strong W–O bonding is responsible for that the RDF remains nearly unchanged upon increasing temperature up to 300 K.

3.2. First-principles calculations

In this section we will first compare the results of our first-principles LCAO calculations, performed for fully relaxed geometry, with the available experimental data for $\alpha$-SnWO$_4$ and $\beta$-SnWO$_4$ (see Table 1). Next we will discuss for the first time the influence of pressure on the atomic and electronic structure of tin tungstates.

The use of hybrid functional allowed us to obtain good agreement between experimental and theoretical values of structural parameters and indirect band gap of $\alpha$-SnWO$_4$. However, the overestimated value of the lattice constant (by $\sim$ 0.1 Å) and the larger value of the direct (at the X point of the Brillouin zone) band gap were found for $\beta$-SnWO$_4$. This disagreement can be related to the fact that $\beta$-SnWO$_4$ phase is metastable at low temperature. The larger band gap value in $\beta$-SnWO$_4$ is a consequence of the stronger crystal field splitting, caused by the shorter W–O bond lengths (Fig. 3).

![Fig. 9. Dependence of the calculated band gap value on pressure in $\beta$-SnWO$_4$.](image-url)

Fig. 9. Dependence of the calculated band gap value on pressure in $\beta$-SnWO$_4$. 

![Fig. 8. Total and projected density of states (upper row) and band structure diagrams (lower row) for $\beta$-SnWO$_4$ calculated using the first-principles LCAO method at the pressure values $P=0$ and 16 GPa. The energy zero is set at the top of the valence band (Fermi energy position).](image-url)

Fig. 8. Total and projected density of states (upper row) and band structure diagrams (lower row) for $\beta$-SnWO$_4$ calculated using the first-principles LCAO method at the pressure values $P=0$ and 16 GPa. The energy zero is set at the top of the valence band (Fermi energy position).
The atomic charges \( q(Sn) \), \( q(W) \), \( q(O1) \) and \( q(O2) \) were obtained from Mulliken population analysis (Table 1) to estimate the charge transfer effects, related to a degree of bond covalency. Note that all charges in both tin tungstates deviate from the formal (ionic) ones. The charge values suggest that the W–O bonds are largely covalent, and the Sn–O bonds also have some degree of covalency. This fact explains the occurrence of the second-order Jahn–Teller effect effects in WO\(_6\) and SnO\(_6\) octahedra [17,18].

The calculated total energy dependence on the unit cell volume (Fig. 4) indicates unambiguously the stability of \( \alpha \)-SnWO\(_4\) versus \( \beta \)-SnWO\(_4\) and was used to find the equations of state for two polymorphs. This result suggests that a phase transition from \( \beta \)- to \( \alpha \)-phase can be induced by applying relatively small pressure of about 2 GPa, which corresponds to the intersection point of two dependencies in Fig. 4.

The calculated bulk moduli \( B_0 \) differ significantly in two tin tungstates (Table 1). The value \( B_0 = 13.75 \text{ GPa} \) for \( \beta \)-SnWO\(_4\) is about six times smaller than the value \( B_0 = 85.09 \text{ GPa} \) for \( \alpha \)-SnWO\(_4\), suggesting larger compressibility of \( \beta \)-SnWO\(_4\) than that of \( \alpha \)-SnWO\(_4\). Therefore, it is interesting to compare their atomic and electronic structure under external pressure.

We have performed LCAO calculations at selected values of pressure in the range from 0 to 16 GPa, fixing the unit cell volume according to the EOS relationship \( V = f(P) \) and allowing the lattice parameters \( (a, b, c) \) and the atomic fractional coordinates \( (x, y, z) \) to vary. As a result, we have obtained the pressure dependence of the electronic structure in terms of total and projected density of states, band structure and ion charges from Mulliken population analysis and of the atomic structure in terms of lattice parameters and first shell interatomic distances (W–O and Sn–O) (Figs. 5–10).

Calculated total and projected density of electronic states and band structure diagrams at representative pressures are shown in Fig. 5 for \( \alpha \)-SnWO\(_4\) and in Fig. 8 for \( \alpha \)-SnWO\(_4\). In both tungstates, the O 2p and Sn 5s states produce the main contribution into the top of the valence band with some small admixture of the Sn 5p states, whereas the bottom of the conduction band is composed mainly from the hybridized W 5d–O 2p states. However, there is also some additional admixture of the Sn 5p states in the conduction band, which is larger in \( \beta \)-SnWO\(_4\) than in \( \alpha \)-SnWO\(_4\). These results confirm previous finding, obtained by band structure DFT calculations [9,18], on the origin of the valence and conduction bands.

When pressure is applied, the behaviour of \( \alpha \)-SnWO\(_4\) and \( \beta \)-SnWO\(_4\) differs significantly. The main intriguing effect is related to the collapse of the band gap from 1.45 eV at \( P = 0 \) down to nearly zero at \( P = 16 \text{ GPa} \) in \( \alpha \)-SnWO\(_4\), giving strong evidence of possible insulator-to-metal transition (Fig. 6). Such modification of the electronic structure is accompanied by a particular change of the atomic structure (Fig. 7). Under pressure the lattice parameters \( a, b \) and \( c \) of \( \alpha \)-SnWO\(_4\) decrease linearly, and the variation of the ion charges is almost negligible. However, the position of atoms within the unit cell changes significantly, resulting in the symmetrization of metal–oxygen octahedra and significant changes in the local geometry. The largest effect is observed along the \( b \)-axis, i.e., perpendicular to the 2D layers formed by WO\(_6\) octahedra (Fig. 1): the distance between nearest W and Sn atoms is reduced from 3.62 Å at \( P = 0 \) to 3.49 Å at \( P = 16 \text{ GPa} \) suggesting an increase of interactions among W, O and Sn electronic states in this direction.

The effect of pressure on \( \beta \)-SnWO\(_4\) does not show any evidence of IMT (Fig. 8), even far beyond the expected transition pressure of about 2 GPa to \( \alpha \)-SnWO\(_4\) (Fig. 4). The material remains in insulating state, and the band gap is reduced just by \( \sim 0.6 \text{ eV} \) at \( P = 16 \text{ GPa} \) (Fig. 9). Under pressure the lattice parameter \( a \) decreases by \( \sim 0.63 \text{ Å} \), and the ion charges remain nearly constant (Fig. 10). The distortion of WO\(_4\) tetrahedra, having three slightly shorter W–O bonds at \( P = 0 \), first decreases up to \( P = 5 \text{ GPa} \), but appears again above \( P = 10 \text{ GPa} \). However, the difference between three short and one long W–O distances

![Fig. 10](attachment:image.png)
in the WO₄ tetrahedra is below 0.03 Å at all pressures, so that the tetrahedra can be considered to be fairly regular. At the same time, the distortion of SnO₆ octahedra is reduced under pressure mainly due to the three distant Sn–O bonds, which become shorter by ~0.36 Å.

4. Conclusions

Tin tungstates α-SnWO₄ metastable β-SnWO₄ and α-Sn₁₋₀.₃W₁₋₀.₃O₉, were studied. The second-order Jahn–Teller effect gives origin to WO₄ and SnO₆ octahedra distortion. Equations of state (EOS) were determined for the first time for α-SnWO₄ and β-SnWO₄ tungstates and support the stability of the α-phase. It was found that the compressibility of β-SnWO₄ is larger than that of α-SnWO₄. Based on the obtained EOS, the pressure influence on the atomic and electronic structure in both tin tungstate phases was studied. The possible existence of the insulator-to-metal transition was theoretically predicted in α-SnWO₄ upon increasing pressure at about 16 GPa. Its origin was explained by a symmetrization of metal–oxygen octahedra leading to a strong interaction of Sn–S, W–S and O–2p states and closing of band gap.

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