

Pressure-induced insulator-to-metal transition in α -SnWO₄

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Abstract. In-situ high-pressure W L₁ and L₃ edges x-ray absorption and mid-infrared spectroscopies complemented by first-principles calculations suggest the existence of pressure-induced insulator-to-metal transition in α -SnWO₄ in the range of 5-7 GPa. Its origin is explained by a symmetrization of metal-oxygen octahedra due to a strong interaction of Sn 5s, W 5d and O 2p states along the *b*-axis direction, leading to a collapse of the band gap.

1. Introduction

Metal-insulator transitions in oxides are of considerable interest already for more than half a century [1, 2, 3]. The phenomenon finds applications in novel electronic and photonic devices, thus stimulating the discovery of new functional materials [4, 5]. In this study we present an overview of recent experimental and theoretical findings on novel pressure-induced insulator-to-metal transition in low-temperature α -phase of tin tungstate (α -SnWO₄).

Tin tungstate has two polymorphs, the low-temperature orthorhombic α -phase (space group *Pnna*, no. 52) and high-temperature cubic β -phase (space group *P2₁3*, no. 198), which transform into each other by a diffusion-controlled phase transition mechanism at about 670°C [6]. The two phases have narrow band gaps (E_g =1.7 eV in α -SnWO₄ and 2.6 eV in β -SnWO₄) and unique band structures, strongly influenced by the charge transfer phenomena between oxygen and tungsten atoms and the presence of the lone pair of Sn 5s electrons [7, 8].

The crystal structure of α -SnWO₄ (Fig. 1) is composed of two-dimensional sheets of WO₆ octahedra, separated by layers of Sn²⁺ ions, which are also six-fold coordinated by oxygen atoms [6]. The WO₆ octahedra within a sheet are joined by four vertices, forming a 2D perovskite-like layer, and are distorted due to the second-order Jahn-Teller (SOJT) effect [9] because of the W⁶⁺(5d⁰) electronic configuration. This distortion is associated with an off-center displacement of W⁶⁺ ions in the direction of the octahedron edge, so that there are three distinct W–O bonds. The six-fold coordination of Sn²⁺(5s²6p⁰) ions is distorted even more, leading also to three different Sn–O bonds. The pair of stereochemically active Sn 5s electrons is responsible for the lone pair distortion of the SnO₆ octahedron via the SOJT effect [7, 8].



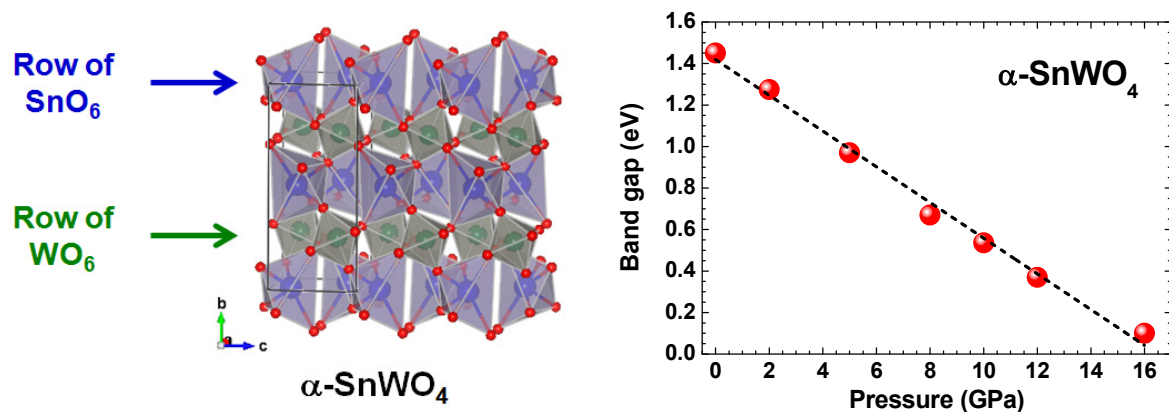


Figure 1. Crystal structure of α -SnWO₄ [6] and pressure dependence of band gap according to first-principles linear combination of atomic orbital (LCAO) calculations [10].

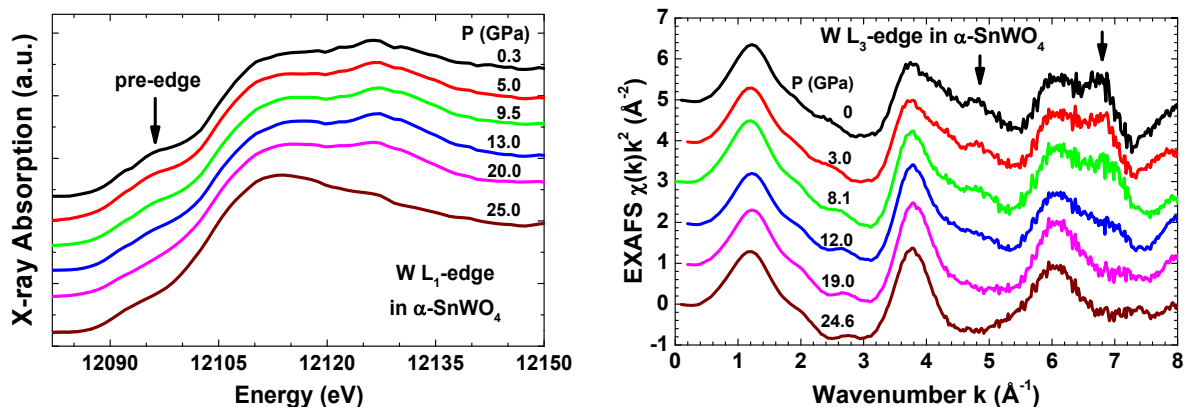


Figure 2. Pressure dependence of the W L₁-edge XANES and W L₃-edge EXAFS in α -SnWO₄.

Narrow band gap and easily deformable metal-oxygen octahedra make α -SnWO₄ a good candidate for pressure-induced insulator-to-metal transition. Here we have tackled this issue by in-situ high-pressure x-ray absorption and infrared spectroscopies complemented by first-principles calculations.

2. Experimental and calculation details

The synthesis of polycrystalline α -SnWO₄ was performed by solid-state reaction: an equimolar amount of SnO (99.99%) and WO₃ (99.9%) powders was placed in a sealed silica ampoule under a vacuum, annealed at 600°C for 8 hours and slowly cooled down to room temperature.

Room-temperature pressure-dependent x-ray absorption spectroscopy study was performed in the pressure range from 0 to 25 GPa at the W L₁ and L₃ edges using the dispersive set-up of the bending-magnet SOLEIL ODE beamline [11] and high-pressure nano-polycrystalline diamond anvil cell (DAC) [12]. The use of nano-polycrystalline DAC allowed us to eliminate spurious contributions from the Bragg peaks into the x-ray absorption spectra. Mid-infrared (550-8000 cm⁻¹) absorption measurements were performed in transmission mode using Bruker IFS 125MR spectrometer combined with recently developed high-pressure setup based on the DAC at the SOLEIL AILES beamline [13]. The sample pressure was monitored by the ruby

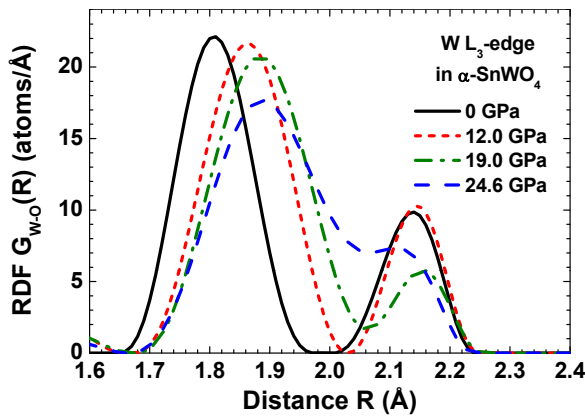


Figure 3. Pressure dependence of radial distribution functions (RDFs) $G_{W-O}(R)$ for the first coordination shell of tungsten in α -SnWO₄.

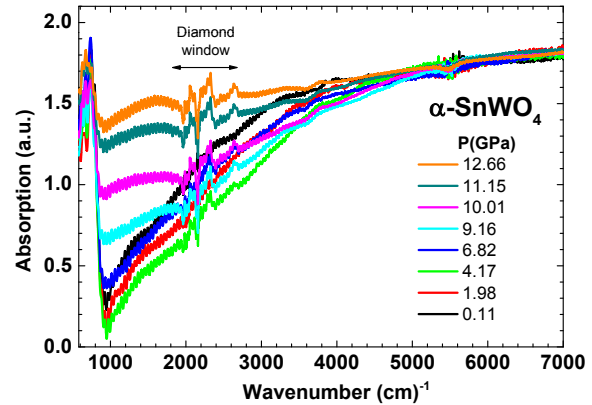


Figure 4. Pressure dependence of mid-infrared spectra of α -SnWO₄. The features between ~ 1830 and 2700 cm^{-1} are due to a diamond window.

luminescence in both experiments.

The W $L_{1,3}$ -edge x-ray absorption near edge structure (XANES) and L_3 -edge extended x-ray absorption fine structure (EXAFS) were extracted following the conventional procedure [14] using the EDA package [15] and are shown in Fig. 2. The radial distribution functions (RDFs) within the first coordination shell of tungsten (Fig. 3) were reconstructed from EXAFS by the regularization-like method [16, 17], which was successfully employed by us in the analysis of several tungstates [18, 19, 20]. Theoretical scattering amplitude and phase shift functions, calculated by the *ab initio* FEFF8 code [21] using the complex exchange-correlation Hedin-Lundqvist potential [22], were used in all simulations (see [8] for more details).

3. Results and discussion

Our first-principles linear combination of atomic orbital (LCAO) calculations [10] predict the existence of the insulator-to-metal transition in α -SnWO₄ (Fig. 1). Its origin is explained by a symmetrization of metal-oxygen octahedra due to a strong interaction of Sn 5s, W 5d and O 2p states, leading to a collapse of the band gap at about 16 GPa [10]. The evidence of this transition was experimentally observed in the mid-infrared region (Fig. 4). Here the contribution of lattice vibrations is responsible for the absorption bands below $\sim 850 \text{ cm}^{-1}$. An abrupt increase of the absorption, which is associated with optical indirect transition across the band gap [8, 10], was detected above $\sim 850 \text{ cm}^{-1}$ upon increasing pressure above 5-7 GPa. Lower value of the experimental transition pressure compared to the predicted one [10] can be attributed to possible non-stoichiometry of the sample.

The structural origin of the insulator-to-metal transition can be probed directly by studying the W $L_{1,3}$ -edges absorption spectra. The analysis of the W $L_{1,3}$ -edge XANES indicates that upon increasing pressure WO₆ octahedra become less distorted, as is evidenced from a decrease of the pre-edge peak due to $2s(W) \rightarrow 5d(W) + 2p(O)$ transition [23] (left panel in Fig. 2). This conclusion is well supported by the analysis of the W L_3 -edge EXAFS spectra (right panel in Fig. 2).

Pressure dependence of the radial distribution function (RDF) around tungsten $G_{W-O}(R)$ was reconstructed and is shown in Fig. 3. The RDF at 0 GPa consists of two well defined peaks located at 1.80 and 2.14 Å, which correspond to four nearest and two distant oxygen atoms of the WO₆ octahedra distorted due to the SOJT effect [9]. Upon increasing pressure a distortion

of the WO₆ octahedra decreases, affecting mainly the group of four nearest oxygen atoms: the average value of their W–O bond length becomes longer by ~ 0.09 Å. At the same time, the group of two distant oxygen atoms at 2.14 Å is less influenced by pressure, however their average W–O bond length decreases by ~ 0.03 Å above 19 GPa. Such pressure-induced reduction of the WO₆ octahedra distortion is compatible with a displacement of tungsten atoms towards the center of the WO₆ octahedra by about 0.2 Å at highest pressure. The observed symmetrization of the WO₆ octahedra correlates well with our results of first-principles LCAO calculations [10], which predict such behaviour for both WO₆ and SnO₆ octahedra upon increasing pressure.

4. Conclusions

X-ray absorption spectroscopy at the W L₁ and L₃-edges and infrared absorption spectroscopy were successfully applied to in-situ investigation of the pressure effect on the local atomic and electronic structure in α -SnWO₄. It is shown that a displacement of tungsten atoms by about 0.2 Å towards the center of the WO₆ octahedra occurs in α -SnWO₄ upon increasing pressure up to 25 GPa. The strong modification of α -SnWO₄ lattice is accompanied by the insulator-to-metal phase transition caused, according to the first-principles LCAO calculations [10], by interaction of Sn 5s, W 5d and O 2p states along the *b*-axis direction.

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