Atklāta un izpētīta augsta spiediena fāžu pāreja izolators-metāls alvas volframātā

Sasniegumi teorētiskajā zinātnē

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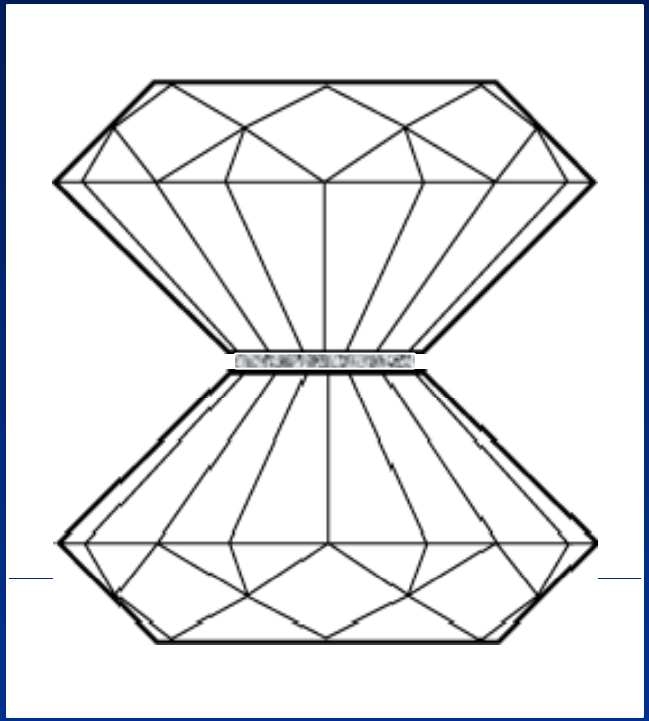
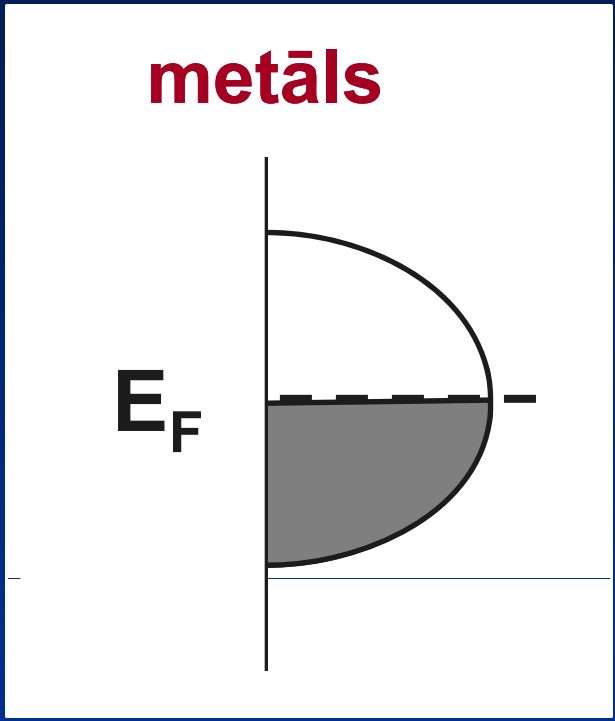
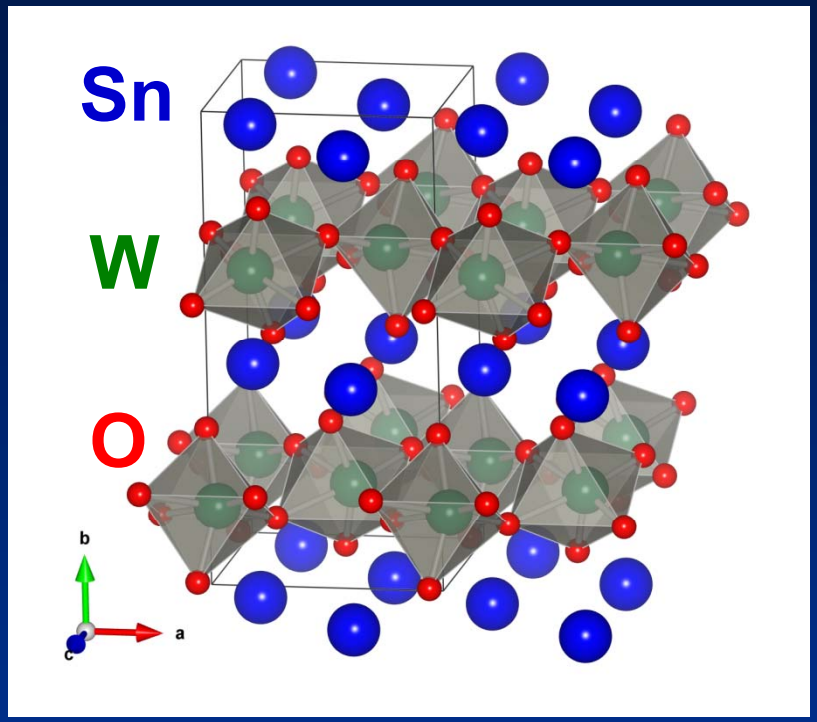
Fāžu pāreja izolators-metāls

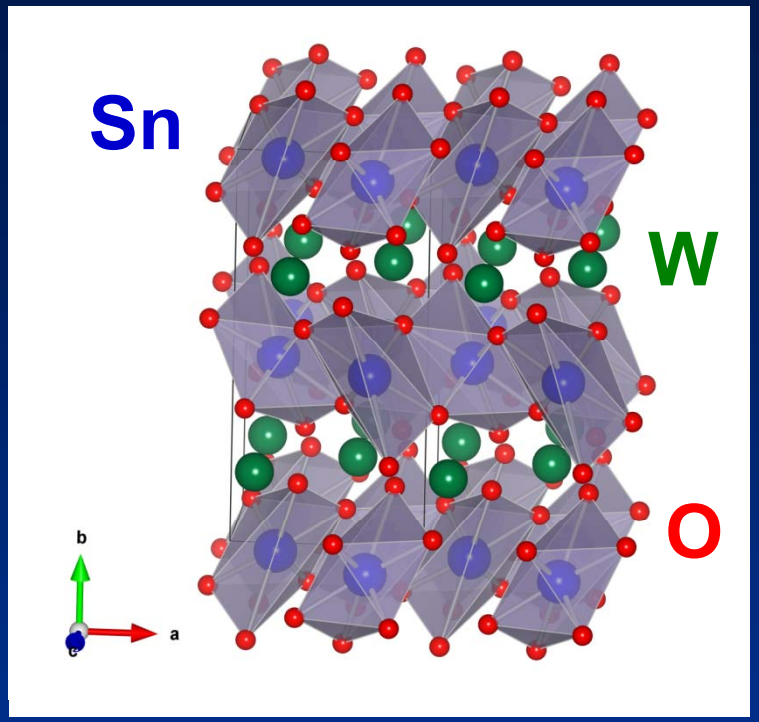




Pietiekami augstā spiedienā visas vielas pāriet metāliskā stāvoklī!

Alvas volframāta (α-$SnWO_4$) kristalogrāfiskā struktūra

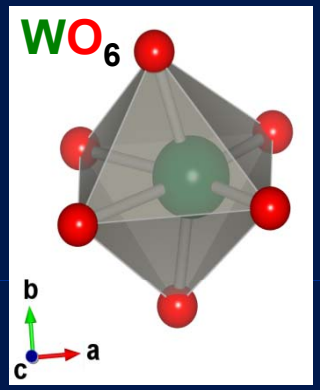




Pamata struktūrvienības:

WO_6 oktaedri ar no centra nobīdītu W

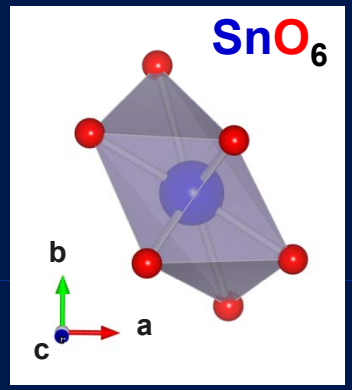
2× *R*(W-O) = 1.80 Å
2× *R*(W-O) = 1.89 Å
2× *R*(W-O) = 2.14 Å



+

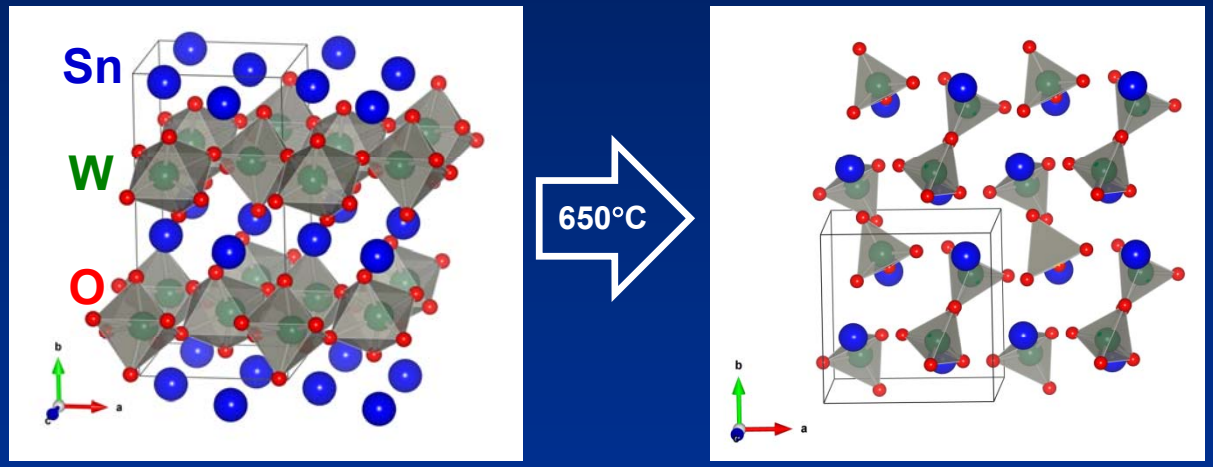
stipri izkropļoti SnO_6 oktaedri

2× *R*(Sn-O) = 2.18 Å
2× *R*(Sn-O) = 2.39 Å
2× *R*(Sn-O) = 2.83 Å



Alvas volframāta (α-$SnWO_4$) īpašības

- Ortorombiskā slāņaina struktūra (*Pnna*, no. 52)
- Aizliegtā zona $E_g \approx 1.7$ eV
- Fāžu pāreja α-$SnWO_4$ $\xrightarrow{650°C}$ β-$SnWO_4$

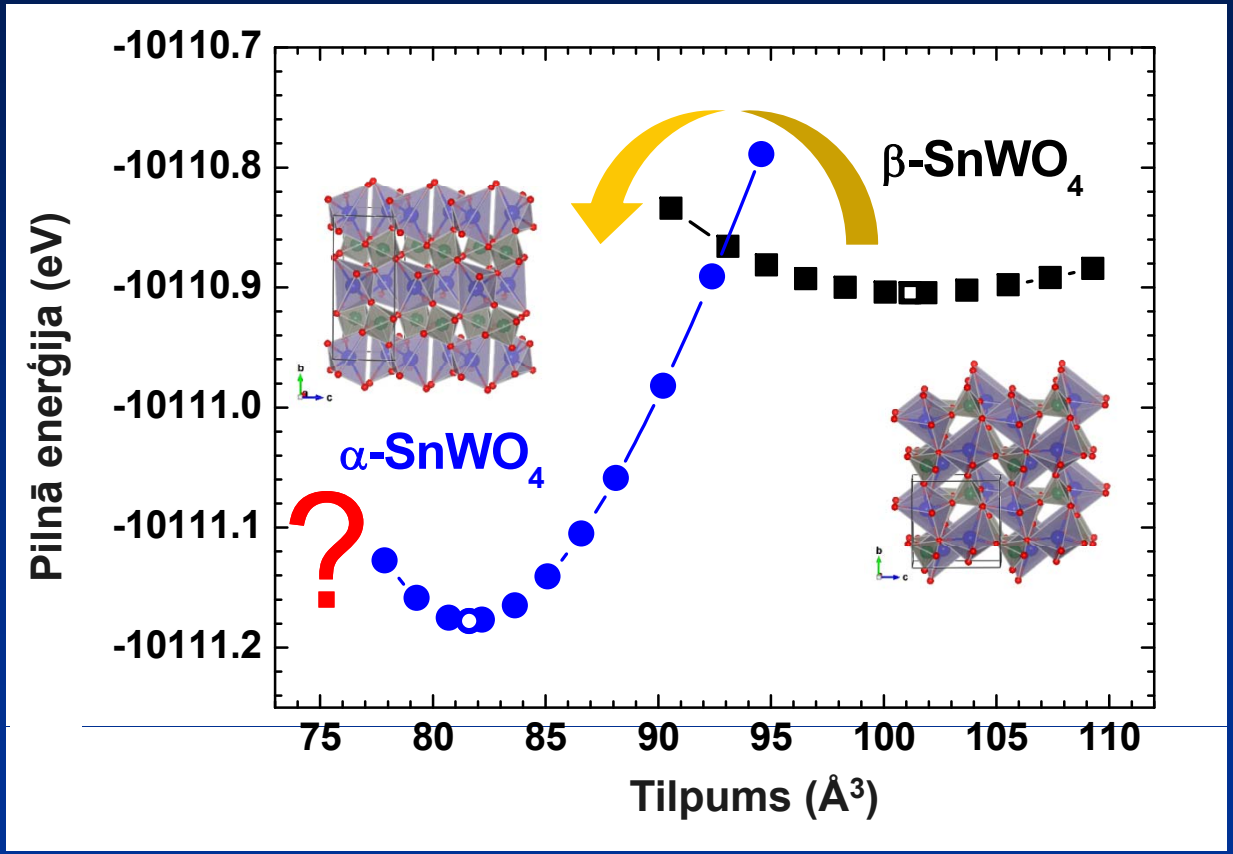


kubisks ($P2_13$, no. 198), $E_g \approx 2.6$ eV

Kas notiek zem augsta spiediena?

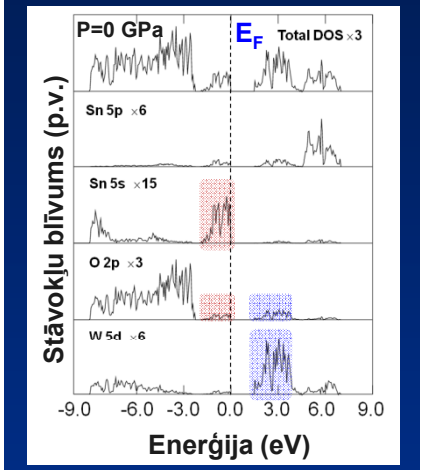
Teorētiskās modelēšanas rezultāti

Lielāks spiediens – mazāks tilpums

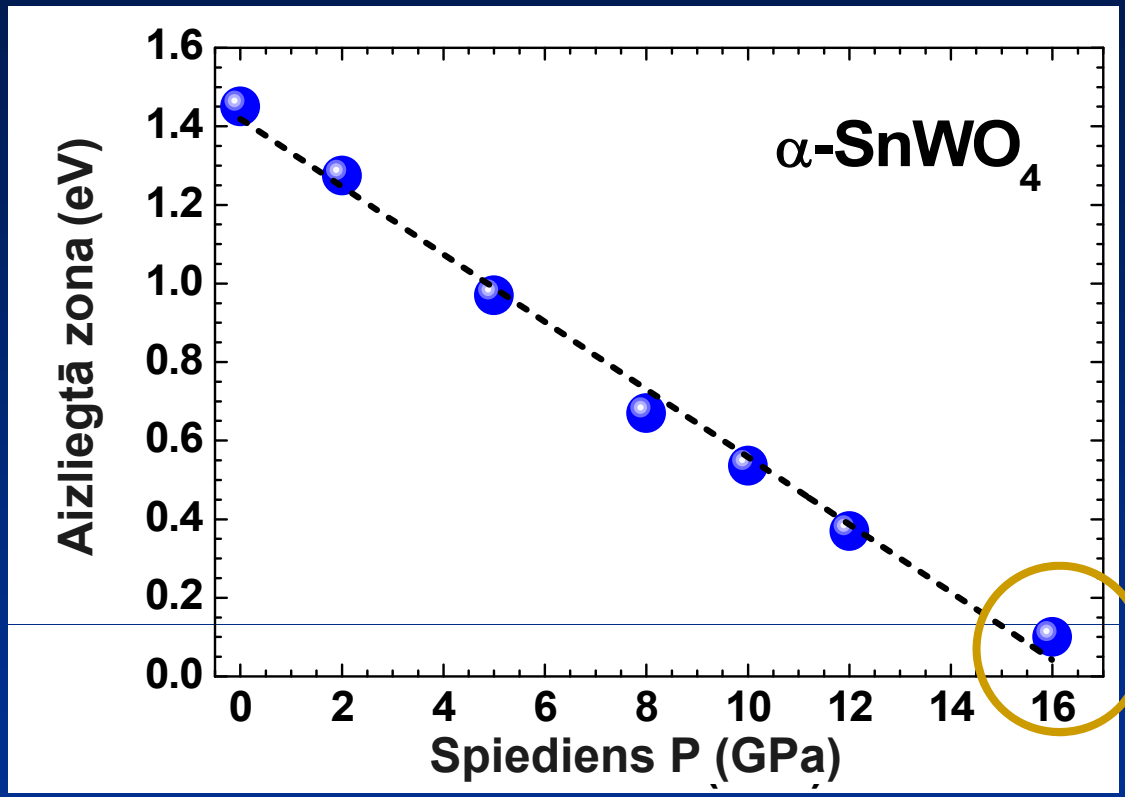


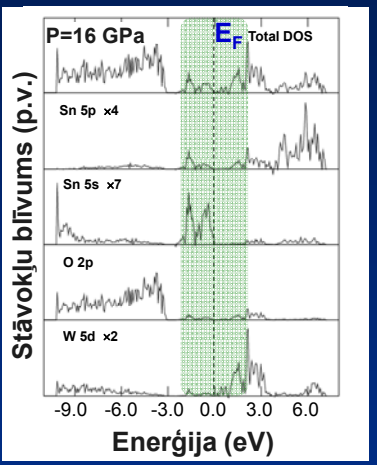
Kas notiek zem augsta spiediena ar α-$SnWO_4$?

Teorētiskās modelēšanas rezultāti



Valences zona: O 2p + Sn 5s
Vadāmības zona: W 5d + O 2p



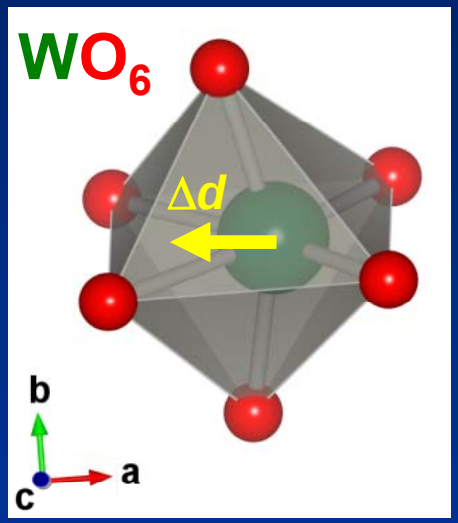


Notiek fāžu pāreja vadošā stāvoklī!

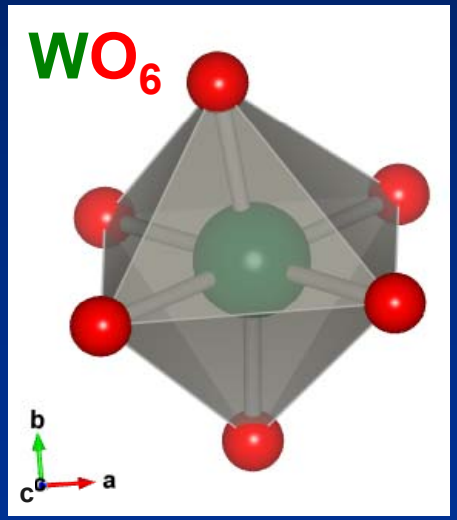
Kāpēc?

Teorētiskās modelēšanas rezultāti

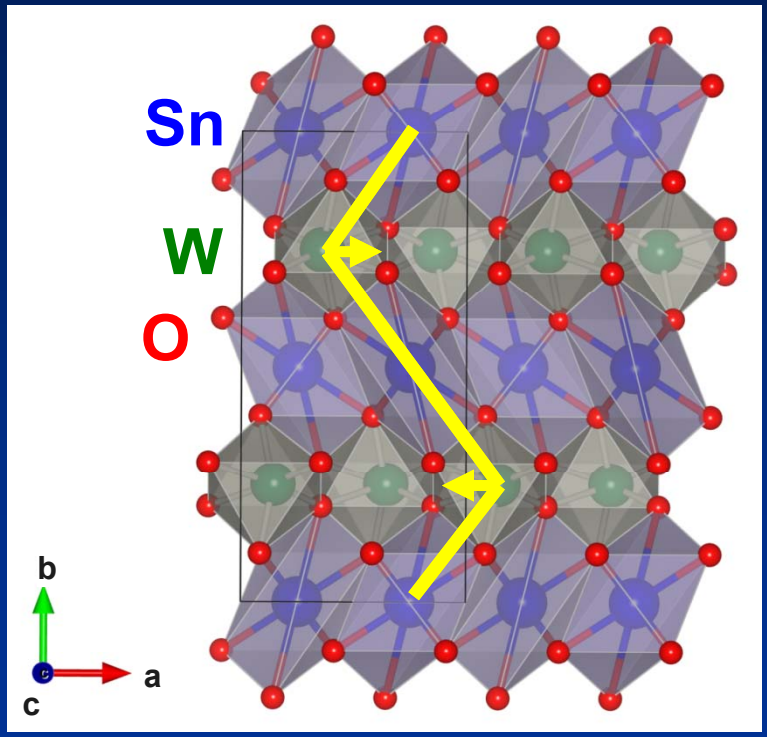
Volframa nobīde
$\Delta d \sim 0.2$ Å



Oktaedra simetrizācija



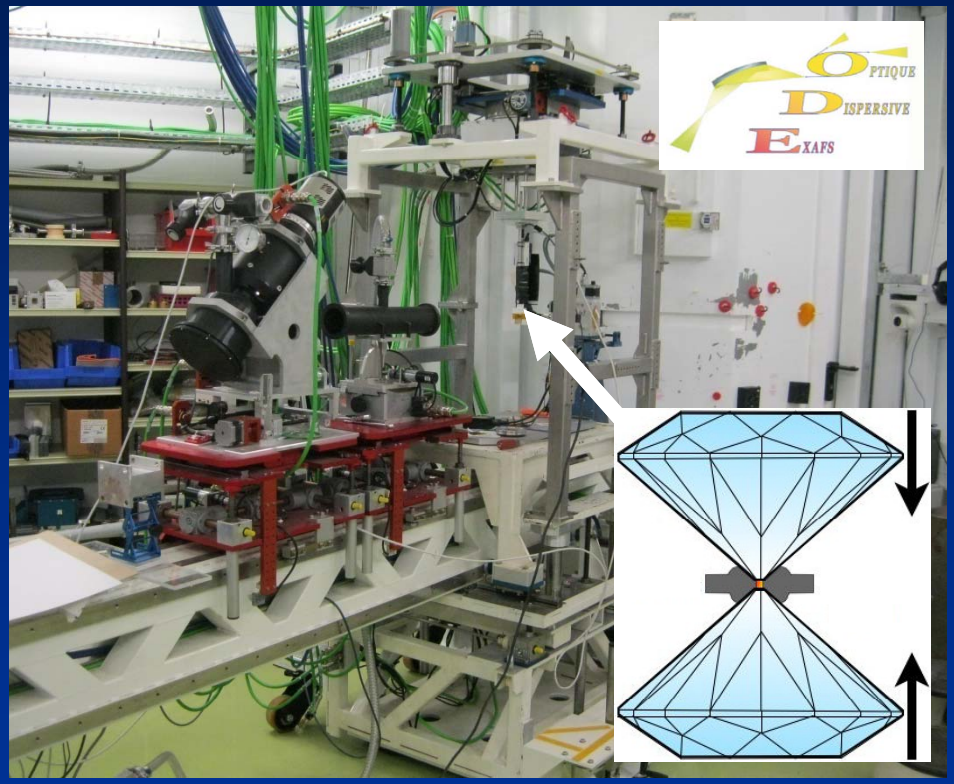
Elektronu delokalizācija *b*-ass virzienā



1 → 2 → 3

In-situ eksperimenti SOLEIL sinhrotrona centrā

Rentgenabsorbcijas spektroskopija

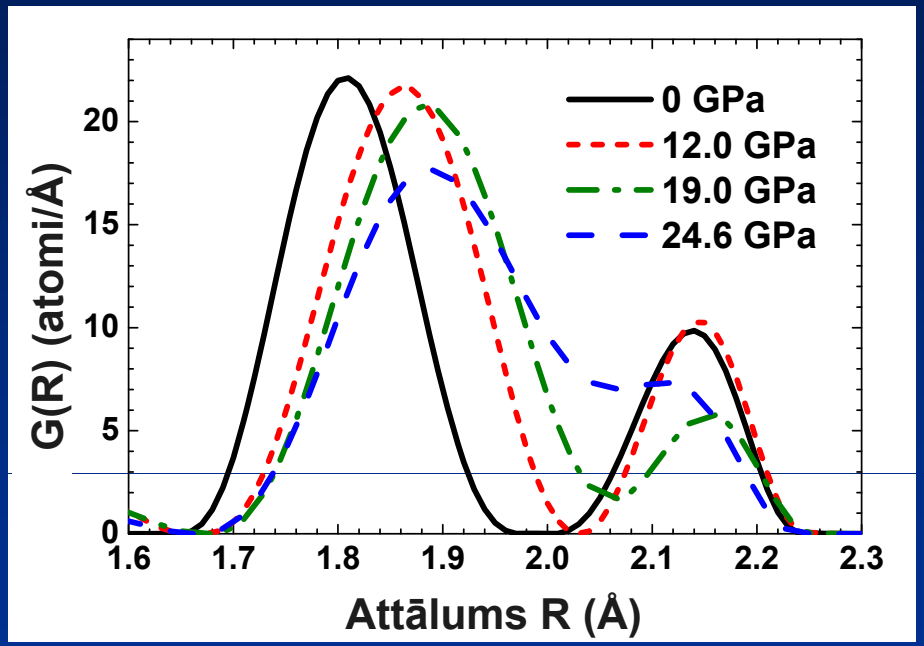


Infrasarkanā spektroskopija

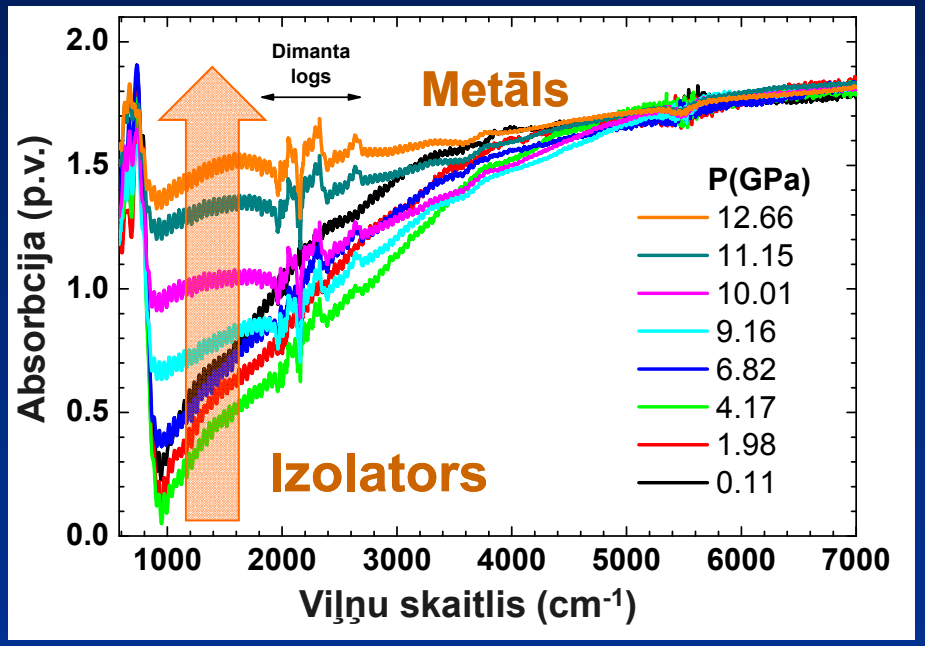
Spiediens P = 0 - 25 GPa (0 - 250 000 atm)

Galvenie eksperimentālie rezultāti

WO_6 oktaedra simetrizācija



Aizliegtās zonas kolapss infrasarkanā diapazonā



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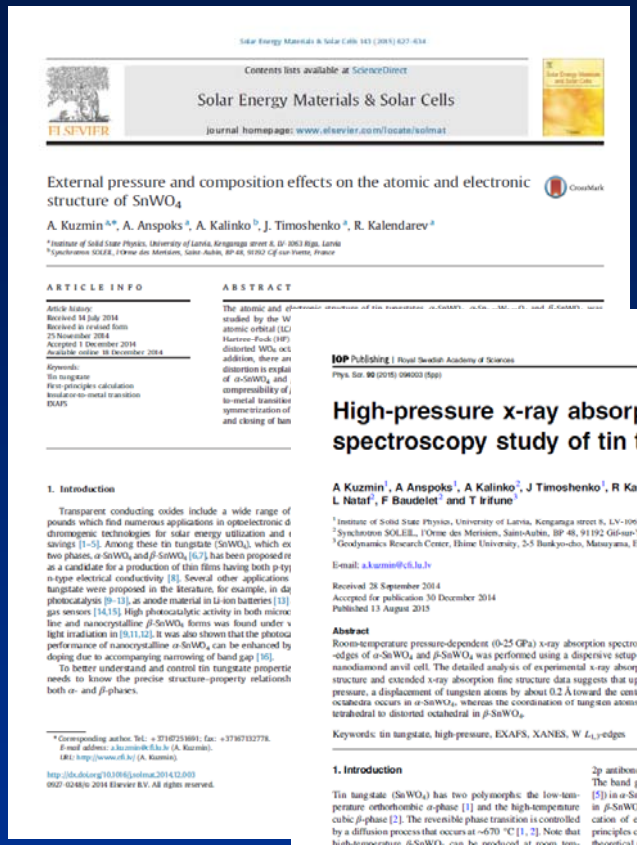
Sakrīt ar teoriju!

Publikācijas



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External pressure and composition effects on the atomic and electronic structure of $SnWO_4$

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EXAFS

ABSTRACT

1. Introduction

Transparent conducting oxides include a wide range of
pounds which find numerous applications in optoelectronic d
chromogenic technologies for solar energy utilization and
savings [1–5]. Among these tin tungstate ($SnWO_4$), which ex
two phases, α-$SnWO_4$ and β-$SnWO_4$ [6,7], has been proposed re
as a candidate for a production of thin films having both p-ty
n-type electrical conductivity [8]. Several other applications
tungstate were proposed in the literature, for example, in da
photocatalysis [9–13], as anode material in Li-ion batteries [13]
gas sensors [14,15]. High photocatalytic activity in both micro
line and nanocrystalline β-$SnWO_4$ forms was found under v
light irradiation in [9,11,12]. It was also shown that the photoca
performance of nanocrystalline α-$SnWO_4$ can be enhanced by
doping due to accompanying narrowing of band gap [16].
To better understand and control tin tungstate propertie
needs to know the precise structure–property relationsh
both α- and β-phases.

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High-pressure x-ray absorption spectroscopy study of tin tungstates

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Abstract

Keywords: tin tungstate, high-pressure, EXAFS, XANES, W $L_{1,3}$-edges

1. Introduction

Tin tungstate ($SnWO_4$) has two polymorphs: the low-tem-
perature orthorhombic α-phase [1] and the high-temperature
cubic β-phase [2]. The reversible phase transition is controlled
by a diffusion process that occurs at ~670 °C [1, 2]. Note that
high-temperature β-$SnWO_4$ can be produced at room tem-
perature by rapid cooling, so that both the α and β phases can
be studied at the same temperature and pressure.
The crystal structures of the two tungstates differ sig-
nificantly, although both are composed of metal-oxygen
polyhedra. Distorted WO_6 and SnO_8 octahedra are the
building blocks of α-$SnWO_4$, whereas slightly deformed WO_6
tetrahedral and strongly distorted SnO_8 octahedral units form
the β-$SnWO_4$ structure. The distortion of SnO_8 octahedra is
caused by a stereochemically active Sn $5s^2$ lone electron pair
via the second-order Jahn-Teller (SOJT) effect [3–5]. The
SOJT effect also causes a distortion of WO_6 octahedra due to
the partially covalent W-O bonding and W^{6+} ($5d^0$) electronic
configuration [5, 6].
Metal-oxygen interactions are responsible for the elec-
tronic structure of tin tungstates. The results of first-principles
calculations [4, 5] indicate that the valence band of both
tungstates is formed by strongly interacting O 2p and Sn 5s
states, whereas the conduction band originates from W 5d-O
2p antibonding states with some admixture of Sn 5p states.
The band gaps are rather small: indirect 1.7 eV [4] (1.45 eV
[5]) in α-$SnWO_4$ and direct 2.6–2.7 eV [3, 4, 7] (4.36 eV [5])
in β-$SnWO_4$. Therefore, they can be affected by the appli-
cation of external pressure. The results of our recent first-
principles calculations [8] suggest a band gap shrinkage under
theoretical pressure of about 16 GPa in α-$SnWO_4$, leading to
the insulator-to-metal transition, whereas no such effect was
found in β-$SnWO_4$. Note that the pressure dependence of the
electronic structure is accompanied by a change in the metal-
oxygen polyhedra distortion due to both charge transfer
effects and unit-cell volume reduction [8]. As a result, the
pressure-induced phase transition from β-$SnWO_4$ to α-
$SnWO_4$ is expected at room temperature and at a theoretical
pressure of about 2 GPa (figure 1).
In this study we used x-ray absorption spectroscopy
(XAS) at the W $L_{1,3}$-edges to probe the local environment in
α-$SnWO_4$ and β-$SnWO_4$ up to a pressure of 25 GPa. XAS is
well suited to follow local structure deformations under high
pressure due to its local order sensitivity and element selec-
tivity, as well as its ability to perform *in situ* experiments
using diamond anvil cells (DACs) [9, 10]. Our previous XAS
study allowed us to follow in detail the distortion of tungsten-
oxygen polyhedra in a $SrWO_4$ tungstate up to 30 GPa [11].
However, the use of conventional single-crystal DACs

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Pressure-induced insulator-to-metal transition in α-$SnWO_4$

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Abstract. In-situ high-pressure W L_1 and L_3 edges x-r
spectroscopies complemented by first-principles calculations
induced insulator-to-metal transition in α-$SnWO_4$ in the range
by a symmetrization of metal-oxygen octahedra due to a stron
O 2p states along the b-axis direction, leading to a collapse of

1. Introduction

Metal-insulator transitions in oxides are of considerable interest al
century [1, 2, 3]. The phenomenon finds applications in novel elect
thus stimulating the discovery of new functional materials [4, 5].
overview of recent experimental and theoretical findings on novel pr
metal transition in low-temperature α-phase of tin tungstate (α-Sn
Tin tungstate has two polymorphs, the low-temperature orthorh
Pnna, no. 52) and high-temperature cubic β-phase (space group $P2_1$
into each other by a diffusion-controlled phase transition mechanis
two phases have narrow band gaps (E_g=1.7 eV in α-$SnWO_4$ and
unique band structures, strongly influenced by the charge transfer
and tungsten atoms and the presence of the lone pair of Sn 5s elect
The crystal structure of α-$SnWO_4$ (Fig. 1) is composed of two-
octahedra, separated by layers of Sn^{2+} ions, which are also six-fold c
[6]. The WO_6 octahedra within a sheet are joined by four vertices, f
layer, and are distorted due to the second-order Jahn-Teller (SOJ
W^{6+} ($5d^0$) electronic configuration. This distortion is associated wit
of W^{6+} ions in the direction of the octahedron edge, so that the
bonds. The six-fold coordination of Sn^{2+} ($5s^26p^0$) ions is distorted
three different Sn–O bonds. The pair of stereochemically active Sn
for the lone pair distortion of the SnO_8 octahedron via the SOJT ef

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Phys. Scr. 89 (2014) 044005 (5pp) — doi:10.1088/0031-8949/89/04/044005

Extended x-ray absorption fine structure spectroscopy and first-principles study of $SnWO_4$

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Abstract

The local atomic structure in α- and β-$SnWO_4$ was studied by synchrotron radiation W L_3-edge x-ray absorption spectroscopy at 10 and 300 K. Strongly distorted WO_6 octahedra were found in α-$SnWO_4$, whereas nearly regular WO_4 tetrahedra were observed in β-$SnWO_4$, confirming previous results. The structural results obtained were supported by the first-principles calculations, suggesting that the second-order Jahn–Teller effect is responsible for octahedral distortion.

Keywords: tin tungstate, EXAFS, W L_3-edge, *ab initio* calculation, Jahn–Teller effect

(Some figures may appear in colour only in the online journal)

1. Introduction

Tin tungstate ($SnWO_4$) is an interesting compound, which
has rarely been studied. It has two polymorphs (figure 1):
the low-temperature orthorhombic α-phase (space group
Pnna, no. 52) [1] and the high-temperature cubic β-phase
(space group $P2_13$, no. 198) [2]. A diffusion-controlled
phase transition occurs at 670 °C [2]; metastable (at room
temperature) β-$SnWO_4$ can be prepared by a rapid quenching
from above 670 °C [3]. The crystal structure of orthorhombic
α-$SnWO_4$ [1] is composed of two-dimensional (2D) sheets
of WO_6 octahedra, separated by layers of Sn^{2+} ions, which
are six-fold coordinated by oxygens. The WO_6 octahedra
within a sheet are joined by four corners and are distorted
due to the second-order Jahn–Teller (SOJT) effect [4] because
of the W^{6+}($5d^0$) electronic configuration. This distortion is
associated with an off-center displacement of W^{6+} ions in
the direction of the octahedron edge, so that there are three
distinct W–O bonds (2 × 1.802, 2 × 1.889, 2 × 2.141 Å). The
six-fold coordination of Sn^{2+}($5s^26p^0$) ions is distorted even
more, leading to three different Sn–O bonds (2 × 2.184, 2 ×
2.392, 2 × 2.826 Å). The pair of stereochemically active Sn
5s electrons is responsible for the "lone pair" distortion of the
SnO_8 octahedron via the SOJT effect [5].
The structure of cubic β-$SnWO_4$ is built up of slightly
deformed WO_4 tetrahedra, which are interconnected with
SnO_8 octahedra. The latter are strongly distorted via the
SOJT effect [6] and have two different Sn–O bonds (3 ×
2.214 and 3 × 2.810 Å) [2]. The WO_4 tetrahedra have
three shorter (1.747 Å) and one longer (1.764 Å) W–O
bonds: the bond length depends on how many tin atoms
are bound to the oxygen atom. The distant oxygen atom
in the WO_4 tetrahedron is shared with three tin atoms,
whereas the other three oxygens bridge to one tin atom
each.
The recent applicative interest in tin tungstate is caused
by its possible use in day-light photocatalysis [5, 7–10] and
gas sensors [11, 12]. It was found that β-$SnWO_4$ exhibits high
visible-light photocatalytic activity in both microcrystalline
($d \sim 1\ \mu m$) and nanocrystalline ($d < 20$ nm) forms [5, 9, 10].
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($d \sim 1\ \mu m$) and nanocrystalline ($d < 20$ nm) forms [5, 9, 10].
The photocatalytic performance of nanocrystalline α-$SnWO_4$
can be enhanced by Zn^{2+} doping, inducing band gap
narrowing [13].
The photocatalytic activity of two tin tungstate phases
is strongly related to their small band gaps (indirect E_g =
1.64 eV in α-$SnWO_4$ [5] and direct E_g = 2.6–2.7 eV in
β-$SnWO_4$ [5, 6, 9]) and their unique band structures [5].
Results of density functional theory (DFT) calculations [5]
suggest that the valence band in both tungstates is mainly
composed of strongly interacting O 2p and Sn 5s states,
whereas the conduction band has a W 5d-O 2p antibonding
character with an admixture of Sn 5p states.

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Paldies par uzmanību !