

EXAFS Study of Pressure-Induced Phase Transition in SrWO₄

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Abstract

Pressure-induced scheelite-to-wolframite structural phase transition in SrWO₄ was studied using two complementary techniques – X-ray absorption spectroscopy and X-ray diffraction (XRD). In situ XRD and W L₃-edge EXAFS measurements were performed using the synchrotron radiation. The experiments were done at room temperature in the pressure range from 0 to 30 GPa using the diamond anvil cell. The XRD results unambiguously show that SrWO₄ transforms from the tetragonal scheelite phase to the monoclinic wolframite-type phase at about 11.7 GPa. Locally this transition appears as a change of the tungsten ions coordination from regular tetrahedral to distorted octahedral. The analysis of the EXAFS data suggests that tungsten ions displace from the centres of the tetrahedra by about 0.04 Å and some nearest oxygen atoms relax by about 0.23 Å.

1. Introduction

Strontium tungstate SrWO₄ belongs to scheelite-type ABO₄ compounds which are commonly used as solid-state laser hosts when doped with rare-earth ions [1]. In scheelites [2], tungsten ions are surrounded by four equidistant oxygen atoms, forming regular tetrahedra, whereas the A²⁺ ions are located between WO₄ units and are eight-fold coordinated by oxygen atoms.

At high pressure, the scheelite structure transforms into the wolframite one, in which both tungsten and A²⁺ ions are expected to be six-fold coordinated by oxygen atoms. Pressure-induced scheelite-to-wolframite phase transition in ABO₄ compounds has been studied for many years [2]. It is associated with a displacement of B cations, leading to the change of their coordination from tetrahedral to distorted octahedral (Fig. 1).

Until now most works on the scheelite-to-wolframite phase transition have been performed by Raman spectroscopy and X-ray diffraction. In particular, the Raman studies of tungstates indicate that the transition occurs at 6.5 GPa for BaWO₄ [3], at 10 GPa for CaWO₄ [4] and at 11.5 GPa for SrWO₄ [4, 5].

In this work we present for the first time in situ X-ray absorption spectroscopy (XAS) and X-ray diffraction (XRD) measurements of the high-pressure phase transition in SrWO₄. A combination of two complementary structural methods allowed us to follow precisely pressure-induced modifications of the SrWO₄ structure and to probe directly the transformation of WO₄ tetrahedron to WO₆ octahedron. Note that this work is the first observation of the scheelite-to-wolframite phase transition from the local viewpoint.

2. Experimental details and data analysis

In-situ pressure-dependent (0–30 GPa) energy-dispersive XAS and XRD experiments were performed at D11 (XAS10) and

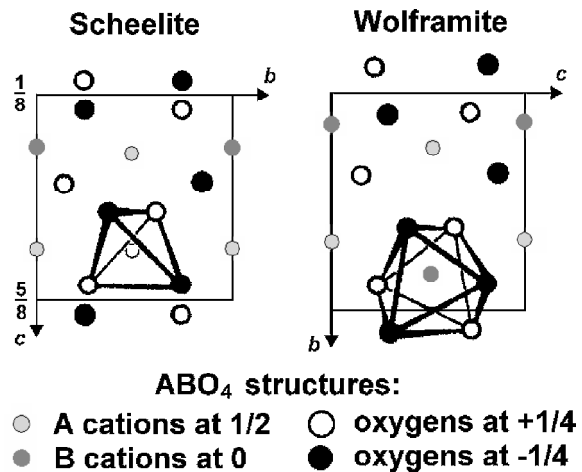


Fig. 1. Comparison of scheelite and wolframite ABO₄ structures [2].

DW11A (WDIS) beamlines using synchrotron radiation from the LURE DCI storage ring, operated at the energy 1.85 GeV and the current 230–300 mA. Polycrystalline SrWO₄ (99.9%) sample was commercial powder, obtained from Alfa Aesar. It was finely ground, and some quantity was placed together with few pieces of ruby into the standard diamond anvil cell. A water-ethanol-methanol mixture was used as a pressure-transmitting medium. Pressure was measured before and after pair of XAS and XRD experiments using the standard ruby fluorescence technique. The position of the cell was adjusted during each XAS experiment to improve the quality of the spectra, thus minimising the appearance of extra absorption peaks associated with Bragg reflections from the diamonds. The energy scale of the W L₃-edge XAS experiments was calibrated relative to the measurement of SrWO₄ powder in transmission mode on a conventional spectrometer (beamline D21 at LURE) with a double-crystal Si(311) monochromator. All experiments were done at room temperature.

After energy scale calibration [6], the W L₃-edge X-ray absorption spectra were analysed by the EDA software package [7, 8] following standard procedure. The EXAFS part of the spectra was singled out by the Fourier filtering procedure and best-fitted within the multi-shell Gaussian/cumulant model [7, 8]. Theoretical scattering amplitudes and phase shift functions, calculated by the FEFF8 code [9] for the SrWO₄ structure [10], were utilised in the model. The complex Hedin-Lundqvist exchange-correlation potential [11] was used to account for the inelastic losses of photoelectron, and the cluster potential was calculated self-consistently.

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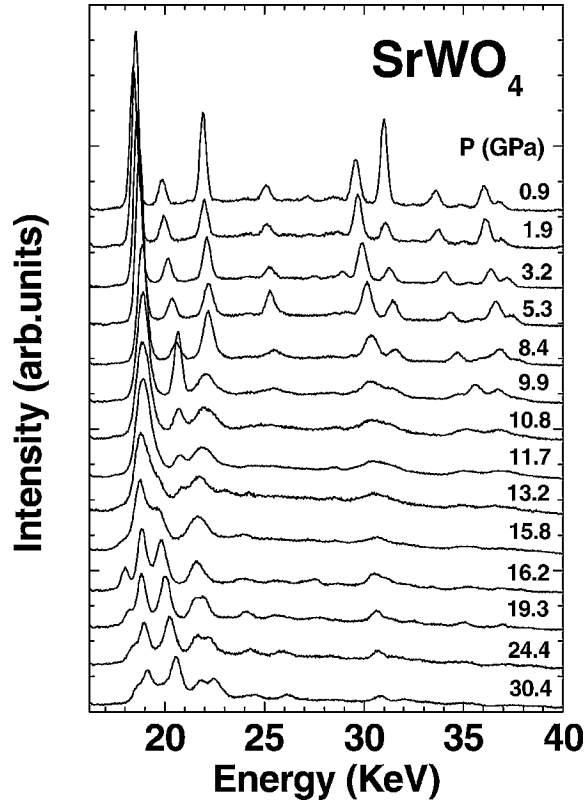


Fig. 2. Energy-dispersive X-ray powder diffraction patterns of polycrystalline SrWO₄. All visible peaks belongs to SrWO₄. Note a transition from tetragonal to monoclinic phase at about 11.7 GPa.

3. Results and discussion

XRD patterns of SrWO₄ at different pressures are shown in Fig. 2. The transition from tetragonal scheelite phase to monoclinic wolframite phase is observed at about 11.7 GPa, when a new peak starts to grow at 20 KeV on the right side of the first strong peak. This result is in perfect agreement with Raman studies in [4, 5].

The analysis of the W L₃-edge EXAFS spectra confirm and complements the results of XRD. The W L₃-edge EXAFS spectra are strongly sensitive to the local environment around tungsten atoms. In Fig. 3 we present two EXAFS spectra and their Fourier transforms (FTs), corresponding to the extreme points at 0 and 30 GPa. Large modifications caused by the phase transition are well visible. Comparison of the spectrum at 30 GPa with the one of monoclinic WO₃, in which tungsten atoms have distorted octahedral environment, shows their similarity. The FTs are dominated by the first coordination shell peak at 1.25 Å. The group of peaks located above the first one are due to outer coordination shells and multiple-scattering effects.

The best-fit analysis of the first peak at 1.25 Å (Fig. 4) within the multi-shell Gaussian/cumulant models allowed us to determine the variation of the local environment around tungsten atoms. The fits were performed using the one-shell and two-shells and three-shells models with and without the cumulants [7, 8]. We found that at low pressure the one-shell Gaussian model is adequate to describe the experimental EXAFS signal. Thus, in scheelite phase, tungsten atoms are four-fold coordinated by oxygen atoms with the mean distance $R(\text{W-O}) = 1.78 \text{ \AA}$ and the Debye-Waller (DW) factor $\sigma^2(\text{W-O}) = 0.002 \text{ \AA}^2$. Next nearest oxygen atoms are expected at 3.08 Å [10] and do not contribute under the first peak in FT. An increase of pressure results in the rise of the DW factor to

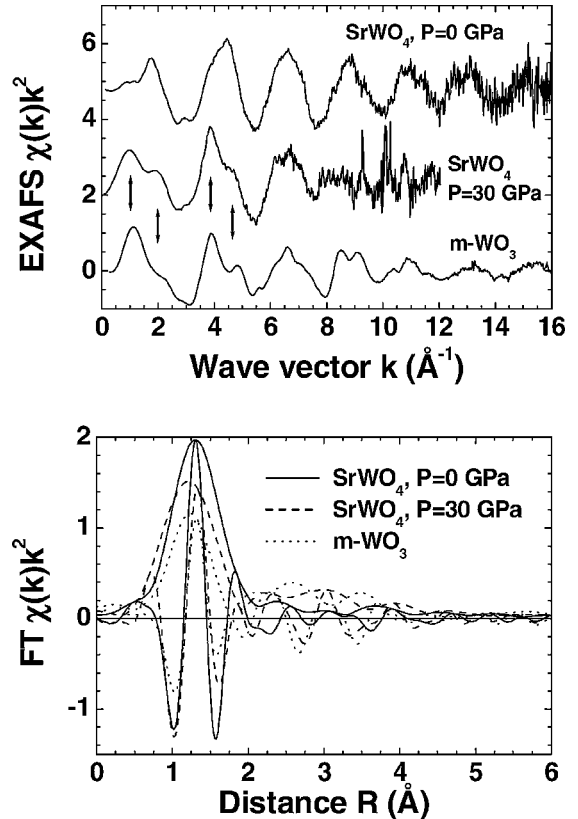


Fig. 3. The experimental W L₃-edge EXAFS $\chi(k)k^2$ signals and their FTs in SrWO₄ (at $P = 0$ and 30 GPa) and m-WO₃[12]. Arrows in the upper panel indicate well visible similarities in the EXAFS signals of SrWO₄ at 30 GPa and m-WO₃, in which tungsten ions are six-fold coordinated. Note that the FTs are not corrected for the phase shifts.

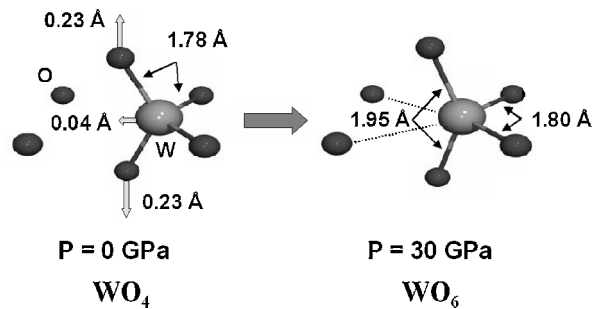


Fig. 4. Model of the local structure modification around tungsten atoms in SrWO₄ upon high-pressure phase transition. Large grey spheres are tungsten atoms, small black spheres are oxygen atoms. Wide arrows in the left part of the figure indicate directions of atomic displacements. The bonds of two weakly bound oxygen atoms, which complete the octahedron at high-pressure, are shown by dotted lines in the right part of the figure.

$\sigma^2(\text{W-O}) = 0.007 \text{ \AA}^2$, that indicates an increase of static disorder due to the beginning of tungsten atoms displacements.

Above the phase transition, the two-shells model becomes more adequate to describe the experimental EXAFS signals. The results suggest that there are two oxygen atoms at $R(\text{W-O}) = 1.80 \text{ \AA}$ with $\sigma^2(\text{W-O}) = 0.002 \text{ \AA}^2$ and two oxygen atoms at $R(\text{W-O}) = 1.95 \text{ \AA}$ with $\sigma^2(\text{W-O}) = 0.005 \text{ \AA}^2$ and $C_3 = 0.006 \text{ \AA}^3$.

Thus, the application of pressure forces tungsten atoms to displace by about 0.04 Å in the direction of the tetrahedron edge to reconstruct it till octahedron (Fig. 4). At the same time, two oxygen

atoms displace in opposite directions by about 0.23 Å, to allow for the tungsten to pass. As a result, the coordination of tungsten atoms at 30 GPa becomes distorted octahedral with two short (1.80 Å), two middle (1.95 Å) and two long bonds (not detectable in our experiment due to probably their large DW factors). The values of the W-O bonds in high-pressure phase are typical for octahedral coordination of tungsten atoms [13]. However, stronger bonding of tungsten atoms with four oxygen atoms show that tungstens tend to preserve tetrahedral-like environment. This conclusion is supported by recent high-pressure Raman studies [5]. It was found [5] that the frequency of the stretching $A_g(\nu_1)$ mode of the WO_4 tetrahedra changes smoothly across the phase transition pressure, suggesting sufficient stability of tetrahedral units.

4. Conclusions

The pressure-induced scheelite-to-wolframite structural transition in $SrWO_4$ was studied for the first time by in situ XAS and XRD techniques. We confirmed the occurrence of the phase transition at about 11.7 GPa. The analysis of the W L_3 -edge EXAFS spectra allowed us to follow in details a transformation of tungsten coordination polyhedron from regular tetrahedron in scheelite phase to distorted octahedron in wolframite phase.

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