Theoretical and experimental study of CaWO$_4$ and SrWO$_4$ under pressure

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Abstract

In this paper, we combine a theoretical study of the structural phases of CaWO$_4$ and SrWO$_4$ under high pressure along with the results of angle-dispersive X-ray diffraction (ADXRD) and X-ray absorption near-edge structure (XANES) measurements of both tungstates up to approximately 20 GPa. The theoretical study was performed within the *ab initio* framework of the density functional theory (DFT) using a plane-wave basis set and the pseudopotential scheme, with the generalized gradient approximation (GGA) for the exchange and correlation contribution to the energy. Under normal conditions, CaWO$_4$ and SrWO$_4$ crystallize in the scheelite structure. Our results show that in a hydrostatic environment, both compounds undergo a scheelite-to-fergusonite phase transition with increasing pressure. We present a comparison of the evolution of the structural parameters, equation of state, and of the features of the transition, finding an overall excellent agreement between the experimental and theoretical results.
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1. Introduction

The scheelite ABX$_4$ compounds, of which the tungstates AWO$_4$ are a sub-branch, constitute a large family of materials that are important from a technological point of view, with applications as solid-state lasers [1] and scintillators [2], in optoelectronic devices [3–5], and as promising candidates to be superhard materials [6].

In the past years, there has arisen a renewed interest in ABX$_4$ compounds and the evolution of their properties under high pressure, and in particular, several experimental and theoretical works on the pressure behavior of scheelite oxides and fluorides have been performed (see Refs. [7–21] and references therein). Upon compression, most of these compounds have been reported to undergo structural transitions to monoclinic structures. However, several of these low-symmetry structures have proved difficult to characterize in high-pressure X-ray diffraction (XRD) experiments and it has been further suggested that their formation could be sensitive to the stress conditions in the pressure chamber.

The occurrence of a pressure-driven phase transition in CaWO$_4$ was first reported in the Raman study of Nicol and Durana [7], who proposed that the high-pressure phase had the wolframite structure. Energy-dispersive X-ray powder diffraction (EDXRD) experiments in CaWO$_4$ were recently performed for the first time by Errandonea and coworkers [8]. These authors examined several monoclinic structures previously suggested for the high-pressure phase of CaWO$_4$ [7,9–11] in order to index their EDXRD powder patterns. On the basis of the quality of the fit, they concluded that

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the most likely structure of the high-pressure phase of $CaWO_4$, among those considered, was that of the wolframite type [8]. However, Grzechnik et al. [12] have recently performed a high-resolution angle-dispersive X-ray powder diffraction (ADXRD) measurements on $CaWO_4$ and found the high-pressure structure to be fergusonite-like. Later measurements in $BaWO_4$ have further reported a scheelite-to-fergusonite transition in this material [11]. To the best of our knowledge, no high-pressure XRD study has been performed yet for $SrWO_4$. Some theoretical support to a pressure-driven scheelite-to-fergusonite-like transition in ABX_4 scheelite compounds has been given after the works by Sen et al. [13,14]. The theoretical results of Li et al. [15] suggest a higher-pressure (post-fergusonite) wolframite structure in $YLiF_4$.

In order to shed light on the pressure behavior of these materials, we report here the results of high-pressure ADXRD and X-ray absorption near-edge structure (XANES) measurements in $CaWO_4$ and $SrWO_4$ up to nearly 20 GPa, together with state-of-the-art *ab initio* total energy calculations for both compounds. Our ADXRD measurements confirm that under hydrostatic conditions, both compounds undergo a scheelite-to-fergusonite transition with increasing pressure. This phase transition is also supported by the high-pressure XANES measurements and the *ab initio* total energy calculations.

2. Overview of the experiments

High-pressure ADXRD measurements in high-purity powder samples were carried out in a Merrill-Basset diamond-anvil cell (DAC) in the case of $CaWO_4$, and in a Mao-Bell DAC in the case of $SrWO_4$. For the XANES measurements, a membrane-type DAC was used in both cases. Silicon oil was employed as pressure-transmitting medium. The pressure was measured with the ruby technique. The maximum pressure achieved in the experiments was about 20 GPa.

The ADXRD experiments were performed at the 16-IDB beamline of the HPCAT facility at the Advanced Photon Source (APS) using a monochromatic synchrotron radiation source ($\lambda = 0.3679$ Å). Diffraction images were recorded using an image plate detector and then integrated and corrected for distortions using the FIT2D software [22]. The indexing, structure solution, and refinement were carried out using the GSAS [23] and POWDERCELL [24] codes. XANES experiments at the W L_3-edge (10.207 keV) were conducted at the ID24 energy-dispersive X-ray absorption station of the European Synchrotron Radiation Facility (ESRF). We used metallic W as reference material for the energy calibration. More details of the experiments can be found in Ref. [21].

3. Details of the total-energy calculations

The energetics and the relative structural stability of the different phases of $CaWO_4$ and $SrWO_4$ were studied by

means of total energy calculations performed within the framework of the density functional theory (DFT) and the computational plane-wave pseudopotential scheme. We used the "Vienna *ab initio* simulation package" (VASP) [25] together with ultrasoft pseudopotentials of the Vanderbilt-type [26]. The exchange and correlation energy was evaluated within the generalized gradient approximation (GGA) [27]. Basis sets including plane waves up to a cutoff in their kinetic energy of 850 and 495 eV for $CaWO_4$ and $SrWO_4$, respectively, were used in order to achieve highly converged results. The tetrahedron method combined with the Bloechel corrections were employed for the Brillouin-zone integrations [28]. The total energy was converged with respect to the basis set size and the k-points set employed to about less than 1 meV per atom. Our theoretical results are for zero temperature and perfectly hydrostatic conditions. The effect of zero-point motion has not been taken into account.

In the theoretical study that we present here, we have focused in the relevant suspect structures at low and moderately high pressures for $CaWO_4$ and $SrWO_4$, scheelite (space group $I4_1/a$, with Ca/Sr at 4b, W at 4a, and O at 16f positions), fergusonite ($I2/a$; Ca/Sr(4e), W(4e), O_1 (8f), and O_2(8f)), and wolframite ($P2/c$; Ca/Sr(2f), W(2e), O_1(4g), and O_2(4h)), of which a detailed description may be found in Refs. [16,17]. All the structural phases considered were fully relaxed at a given compression both in the shape of their unit cell and in the position of the atoms within the cell. The minimum-energy configuration for a given structure was located by means of the calculated values of the components of the stress tensor and of the components of the forces on the atoms. Such a structural relaxation took the anisotropy in the diagonal components of the stress tensor to below 0.1 GPa and the forces on the atoms to below 0.005 eV/Å.

4. Results and discussion

Both ADXRD diffraction patterns and XANES spectra were recorded at small pressure intervals as the load was increased up to about 20 GPa, covering the whole region of stability of the low-pressure (scheelite) phase and the appearance and full development of the high-pressure phase. Typical ADXRD diffraction patterns of $CaWO_4$ and $SrWO_4$ at selected pressures for each region are plotted in Fig. 1, whereas the results of the XANES study are depicted in Fig. 2. Fig. 3 shows the energy–volume ($E–V$) curves for the phases considered in this study as stem from our *ab initio* calculations. Figs. 1–3 jointly contain the main information of both our experimental and theoretical study. We will next address the implications and consistency of these results, first in what pertains to the structural properties of the low-pressure scheelite phases and then for the high-pressure phase.
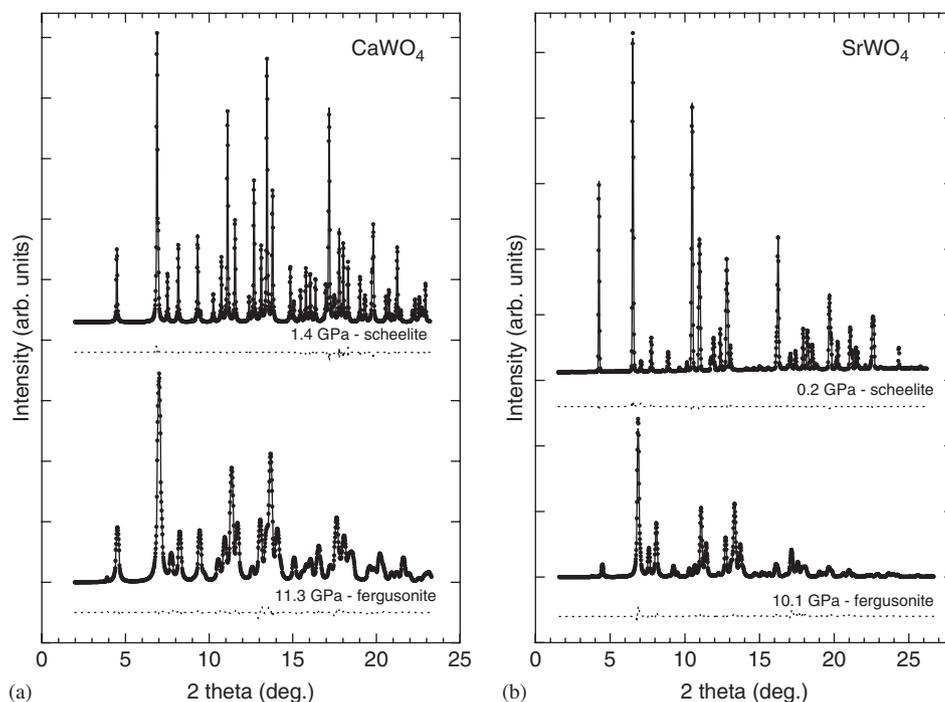
Fig. 1. ADXRD data (symbols) and Rietveld refinements (solid curves) of (a) $CaWO_4$ and (b) $SrWO_4$ in the low-pressure (scheelite) phase and the high-pressure (fergusonite) phase. The dashed curves below the profiles show the difference between the measured data and the refined profile. In all patterns the background has been subtracted. The values obtained for the structural parameters are: for scheelite-$CaWO_4$: $a = 5.205(5)$ Å, $c = 11.275(7)$ Å, $x(O) = 0.2289(3)$, $y(O) = 0.0910(4)$, $z(O) = 0.0421(5)$; For fergusonite-$CaWO_4$: $a = 5.069(2)$ Å, $b = 10.851(5)$ Å, $c = 5.081(7)$ Å, $\beta = 90.091(9)°$, $y(Ca) = 0.6100(8)$, $y(W) = 0.1325(3)$, $x(O_1) = 0.9309(39)$, $y(O_1) = 0.9684(23)$, $z(O_1) = 0.2421(24)$, $x(O_2) = 0.4850(35)$, $y(O_2) = 0.2193(31)$, $z(O_2) = 0.8637(37)$; for scheelite-$SrWO_4$: $a = 5.391(8)$ Å, $c = 11.893(7)$ Å, $x(O) = 0.2497$, $y(O) = 0.0925$, $z(O) = 0.0421(6)$; for fergusonite-$SrWO_4$: $a = 5.263(9)$ Å, $b = 11.182(6)$ Å, $c = 5.231(6)$ Å, $\beta = 90.35(1)°$, $y(Sr) = 0.6027(9)$, $y(W) = 0.1243(8)$, $x(O_1) = 0.9309(49)$, $y(O_1) = 0.9598(53)$, $z(O_1) = 0.2619(42)$, $x(O_2) = 0.4903(39)$, $y(O_2) = 0.2278(35)$, $z(O_2) = 0.8779(32)$.
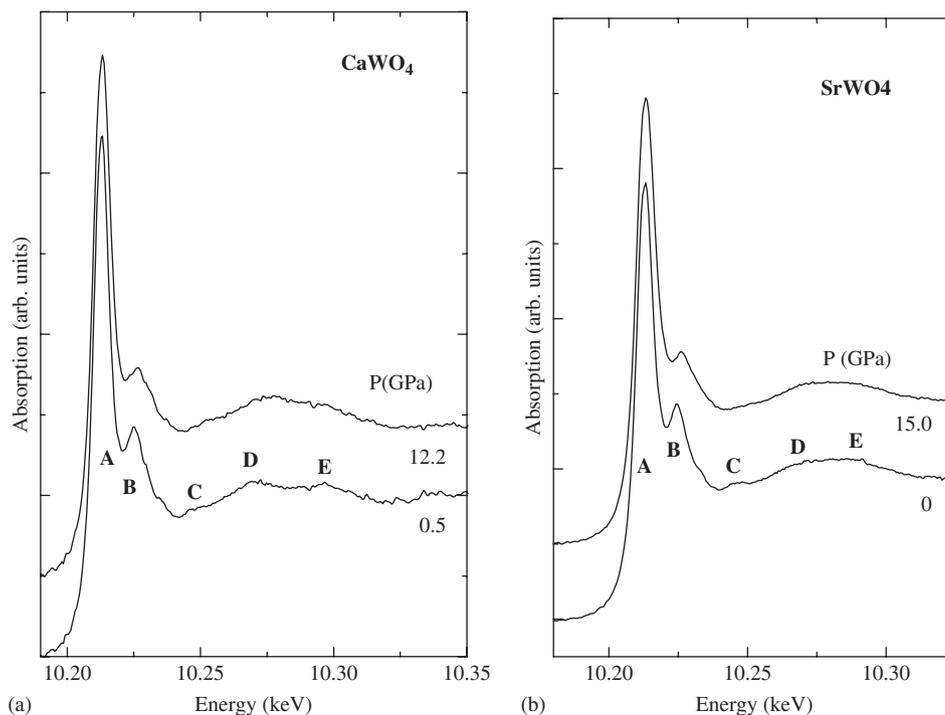

Fig. 2. Experimental XANES spectra of (a) $CaWO_4$ and (b) $SrWO_4$ at low and high pressures.
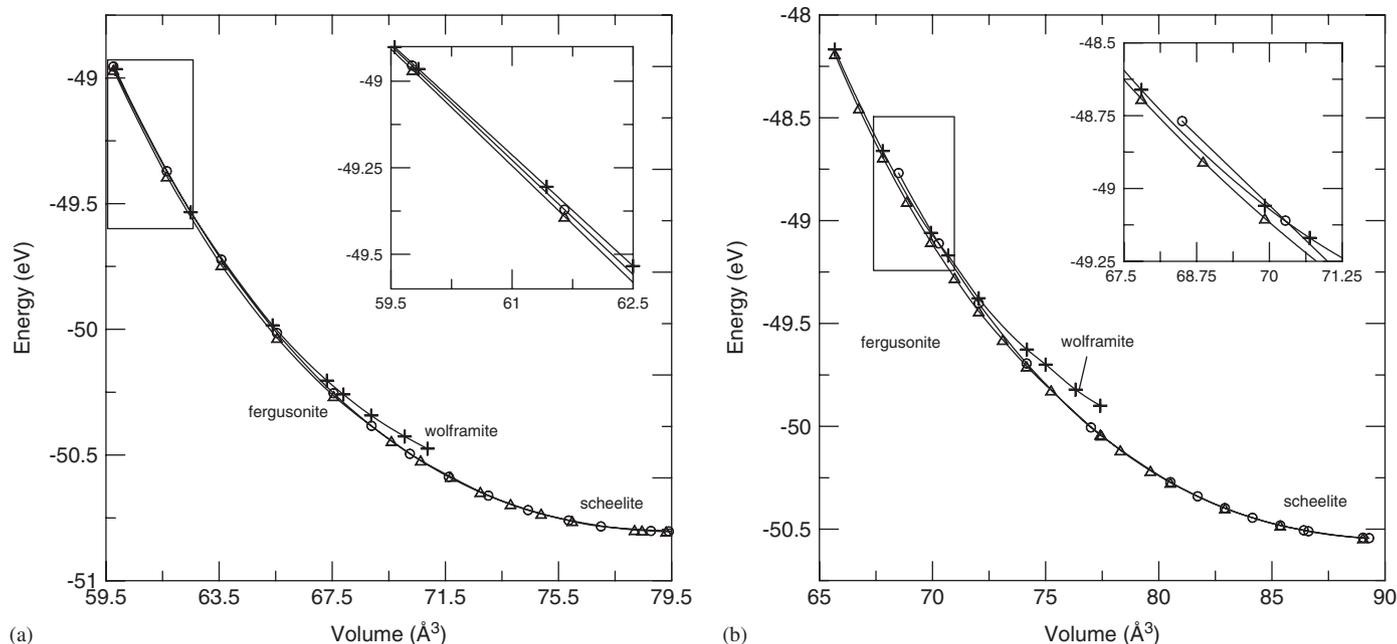
Fig. 3. Calculated energy–volume curves for the scheelite (circles), fergusonite (triangles), and wolframite (crosses) structures of (a) CaWO$_4$ and (b) SrWO$_4$ as result of our DFT–GGA calculations. Both the volume and the energy are given per formula unit.

4.1. The scheelite low-pressure phases

For both materials, the Rietveld refinements of the ADXRD data for the low-pressure scheelite phases shown in Fig. 1 can be seen to be very good. The theoretical E–V curves of Fig. 3 show that the scheelite phases have the lowest minimum energy, and are thus the stable phases at zero pressure. The pressure evolution of the cell parameters of the scheelite structure as obtained from the ADXRD measurements are given in Fig. 4, where we also compare with the theoretical results obtained upon full relaxation of all the scheelite structural degrees of freedom (both internal and cell parameters). The calculated lattice parameters tend to be larger than the experimental values, a well-known feature of the DFT–GGA calculations, which result in somewhat higher equilibrium volumes than experimentally reported, whereas the change with pressure is well reproduced. As can be seen, the compressibility of the c-axis is larger for SrWO$_4$ than for CaWO$_4$, while the a-axis compresses in about the same way in the two compounds. The larger compressibility of the c-axis in SrWO$_4$ is related to the difference in size of the Ca^{2+} and Sr^{2+} cations, which leads to a larger charge density around the Ca cations than around the Sr cations. The different behavior of the c- and a-axes is further connected to their different thermal expansion [29], as well as to the evolution of the c/a ratio along a cationic A series [30].

Calculated and experimental pressure–volume (P–V) curves are given in Fig. 5. The results for CaWO$_4$ agree with previously reported values for this material [8,12,18,30,31]. After fitting of the P–V data with the Birch–Murnaghan equation of state (EOS), we obtain the

following values for the equilibrium volume, V_0, the bulk modulus at zero pressure, B_0, and the pressure derivative of the bulk modulus at zero pressure, B_0': for scheelite-CaWO$_4$, $V_0 = 78.0(2)\,\text{Å}^3$, $B_0 = 74(7)\,\text{GPa}$, and $B_0' = 5.6(9)$; for scheelite-SrWO$_4$, $V_0 = 86.9(2)\,\text{Å}^3$, $B_0 = 63(7)\,\text{GPa}$, and $B_0' = 5.2(9)$. These are in good agreement with our theoretical values of $V_0 = 79.58\,\text{Å}^3$, $B_0 = 72\,\text{GPa}$, and $B_0' = 4.3$ (for scheelite-CaWO$_4$) and of $V_0 = 90.55\,\text{Å}^3$, $B_0 = 62\,\text{GPa}$, and $B_0' = 4.9$ (for scheelite-SrWO$_4$), and also with previously reported experimental values [8,12,18]. The smaller bulk modulus of scheelite-SrWO$_4$ is related to the different compressibility of the c-axis in the two compounds.

The analysis of the evolution of the atomic distances in both compounds supports the established picture of AWO$_4$ tungstate scheelites in terms of hard WO$_4$ tetrahedra surrounded by charge-compensating cations, the volume reduction of the unit cell being mainly related to the compression of the polyhedral environment of the A cation [18]. The different arrangement of hard WO$_4$ tetrahedra along the c- and a-axes may account for the different compressibility along each axis.

4.2. The high-pressure phases

Our theoretical results indicate that the scheelite phases of both compounds become unstable with respect to a fergusonite-like distortion as pressure increases. In fact, relaxation of the fergusonite structure at low pressures result in the scheelite structure (or a tiny distortion of this structure that within the error of the calculation cannot be resolved from it either structurally or energetically),
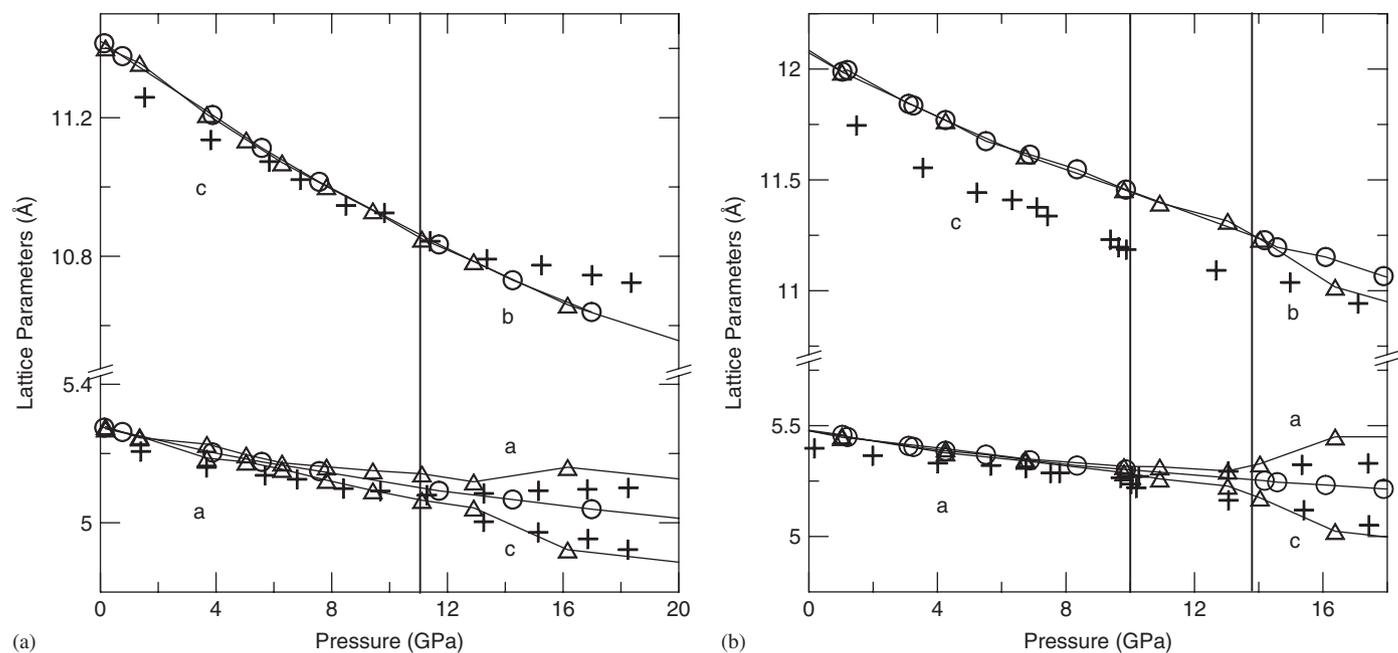
Fig. 4. Pressure evolution of the calculated and experimental lattice parameters of the (tetragonal) scheelite and (monoclinic) fergusonite phases of (a) $CaWO_4$ and (b) $SrWO_4$. The experimental values of the lattice parameters are indicated by crosses. The calculated values of the parameters for the scheelite structure are represented by circles and those of the fergusonite structure by triangles. For the calculated values a solid line has been used as a guide to the eye. The experimental transition pressures are indicated by vertical lines. In the case of $SrWO_4$ for which the experimental onset obtained using XANES is somewhat higher than the ADXRD onset, two vertical lines have been depicted indicating this fact (see text).
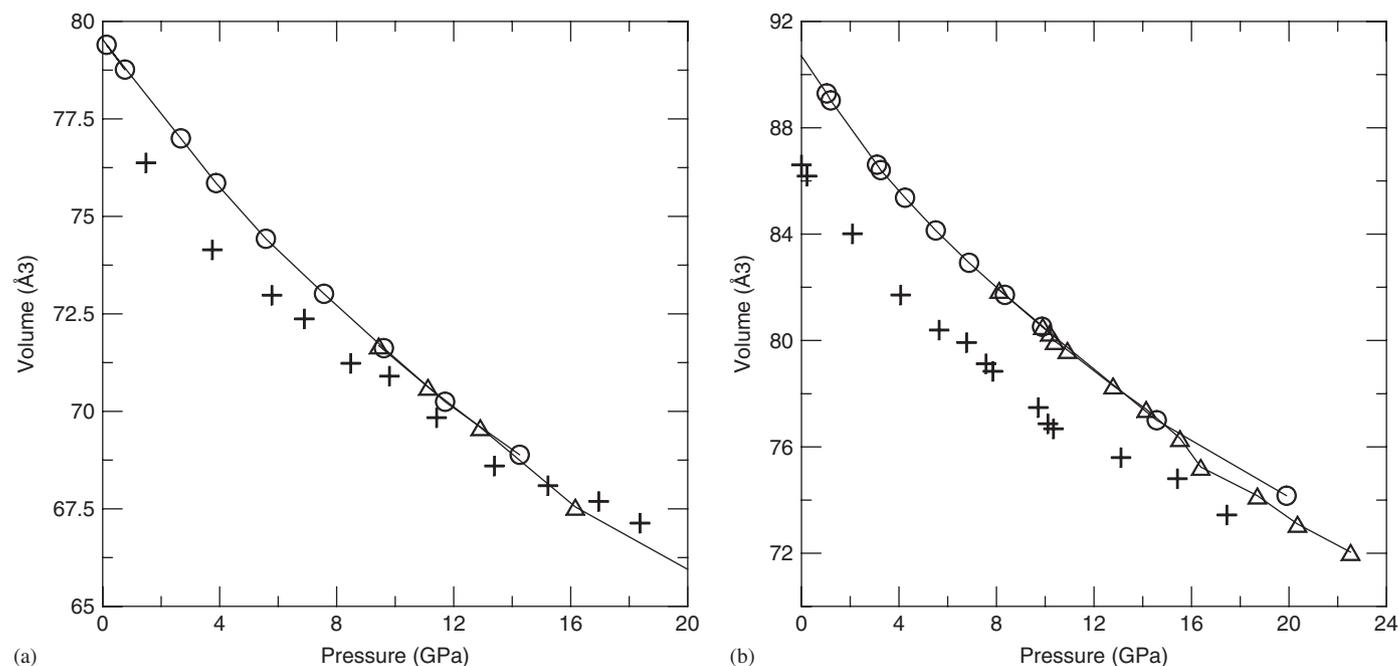

Fig. 5. Calculated and experimental pressure–volume curves for (a) $CaWO_4$ and (b) $SrWO_4$. The crosses correspond to the experimental values obtained from the ADXRD study. Circles and triangles correspond to the calculated values for the scheelite and fergusonite structures, respectively. The volume is given per formula unit.

whereas at higher pressures there is an increasing structural and energetical difference between the two phases. The onset of the distortion is difficult to place precisely, but at around 11 GPa it is already distinguishable in both materials. The wolframite structure is very close to the fergusonite structure though higher in energy (by about 41 meV per formula unit in $CaWO_4$ at a volume of 68.8 Å^3 (140 meV for $SrWO_4$ at 77.4 Å^3)) in the whole range of

relevant pressures, and the difference in energy between both structures decreases as the volume decreases. The scheelite/wolframite coexistence pressure is higher than the onset of the fergusonite structure. It may be speculated that a change in the conditions (non-hydrostaticity or uniaxial stress, high temperature, etc.) could change this state of affairs but we have not pursued this investigation here. As we will see, these theoretical results are in very good agreement with the experimental results.

As the pressure is increased, the diffraction peaks in the ADXRD spectra shift smoothly until 11.3 GPa in $CaWO_4$ and 10.1 GPa in $SrWO_4$. At these pressures and above, some of the diffraction peaks split and additional peaks emerge, which signal the formation of a new high-pressure structural phase. These changes are completely reversible upon pressure release.

For both materials, the ADXRD patterns of the high-pressure phases are well accounted for by the fergusonite structure. In particular, the appearance of a new peak around $2\theta \approx 3.8°$ is clearly distinguishable and corresponds to the $(0\,2\,0)$ reflections of the fergusonite structure. The results of the Rietveld refinement at 11.3 GPa for fergusonite-$CaWO_4$ and at 10.1 GPa for fergusonite-$SrWO_4$ are shown in Fig. 1. The quality of the fit is similar to what was obtained for the scheelite structures at lower pressures.

The observation of a high-pressure fergusonite phase in $CaWO_4$ agrees with the results of Grzechnik et al. [12] and differs from a previous suggestion of this phase as having the wolframite structure [8]. For both $CaWO_4$ and $SrWO_4$, there are two features of the present ADXRD spectra that rule out the wolframite structure. First, two of the stronger Bragg peaks of the wolframite structure, viz. the $(0\,1\,1)$ and $(1\,1\,0)$ peaks, expected at $2\theta \approx 5.7°$ are absent in the measured diffraction patterns of both compounds. Secondly, the $(1\,0\,0)$ reflection of the wolframite structure is not present at $2\theta \approx 4.15°$. It may be possible that in the EDXRD study reported in Ref. [8], the highly non-hydrostatic conditions in the pressure chamber (derived from the lack of pressure-transmitting medium) would have favored the formation of the wolframite structure, whereas in the present ADXRD study, the conditions in the cell are quasi-hydrostatic. In fact, a scheelite-to-wolframite transition has been reported for $CdMoO_4$ in experiments performed without a pressure-transmitting medium [19], and in the seminal work of Nicol and Durana [7]—using NaCl as pressure medium—the wolframite structure was first suggested for the high-pressure phase of $CaWO_4$.

Theoretically, the scheelite-to-fergusonite transition is a continuous or quasi-continuous displacive transition with no appreciable change in volume, which is confirmed by the ADXRD results. The transition implies a slight distortion of the WO_4 tetrahedra accompanied by a small shear distortion of alternate $(1\,0\,0)$ cation planes in the $[0\,0\,1]$ direction, while the AO_8 polyhedra undergo a rather larger distortion. The calculated and experimental pressure

evolution of the cell parameters of the fergusonite phases are shown in Fig. 4. From the values shown in this figure, one extracts immediately an increase in the *difference* between the b/a and b/c axial ratios as the pressure increases. The monoclinic angle β of fergusonite-$CaWO_4$ increases with pressure from 90.854° at 13.3 GPa to 93° at 18.3 GPa (from 90.57° at 10.3 GPa to 91.95° at 17.5 GPa in fergusonite-$SrWO_4$). Both the increase in the angle β and the increase in the differences between the axial ratios imply an increase in the monoclinic distortion with pressure.

Let us finish this section by mentioning that we have pursued the theoretical study of the phase stability of these compounds to higher pressures. Our preliminary results suggest that at pressures in the range 20–30 GPa, the fergusonite structure becomes thermodynamically unstable to a structural phase with space group *Cmca*. However, such high pressures have not yet been achieved in high-pressure experiments and further theoretical and experimental work is still needed in the post-fergusonite behavior of these materials.

4.3. XANES measurements at high pressures

The XANES part of the absorption spectrum can be used as a tool to detect structural changes in high-pressure experiments as it is very sensitive to modifications in the neighborhood of the absorbing atom. For both $CaWO_4$ and $SrWO_4$, we have performed XANES measurements for the low- and high-pressure phases in the 0–20 GPa pressure interval, as well as simulations of the XANES spectrum for the scheelite, fergusonite, and wolframite structures as a guide to the interpretation of the experimental data.

The simulations were carried out using the real-space multiple-scattering FEFF8 code [32] with a self-consistent potential calculated using a cluster of 120 atoms (14 shells) and Hedin–Lundqvist self-energy. Full multiple-scattering XANES calculations were performed using 87-atom clusters (11 shells). For both tungstates, the simulated spectra for the scheelite and fergusonite structures turn out to be qualitatively quite similar, displaying five resonances named A to D in order of increasing energy. The most significant difference between these spectra and that for the wolframite structure corresponds to the absence of the second (B) resonance at around 10.22 keV in the wolframite spectrum, as well as in the intensity and width of the white line (A resonance).

In the scheelite structure, the W environment consists of four O atoms in tetrahedral configuration. In the fergusonite structure, this tetrahedron is somewhat distorted, giving rise to two slightly different W–O distances, but otherwise the changes in the W environment are qualitatively small. We would then expect small changes in the XANES spectra between both structures. On the other hand, the quasi-six-fold coordination of W in the wolframite structure would lead to considerable changes

in the XANES spectrum with respect to that of the scheelite structure.

Fig. 2 shows the experimental XANES spectra at different pressures for $CaWO_4$ and $SrWO_4$. The low-pressure spectra of both compounds display the five resonances predicted by our simulations for the scheelite structure. The position and intensity of each feature agree qualitatively with that of the simulation. For $CaWO_4$, the spectra show no significant changes up to about 11 GPa. At this pressure, the B resonance looses intensity and the ratio of the intensities of the D and E resonances also decreases. Regarding $SrWO_4$, the XANES spectra initially show a slight reduction of the intensity of the B resonance as pressure increases but the onset of the phase transition is not as clear as in $CaWO_4$, and the distortion of the W tetrahedral environment is not evident up to 13.7(17) GPa. At 15.0 GPa, an acceleration in the decrease of the B resonance is accompanied by the progressive disappearance of the C resonance and the increment of the D resonance. The white line remains essentially unchanged as pressure is increased.

In both $CaWO_4$ and $SrWO_4$, the changes observed in the spectra continue up to the maximum pressures achieved, of about 20 GPa, suggesting that the structural distortions leading to the fergusonite structure become more pronounced with the increase in pressure. At this pressure the B resonance is still visible. The changes in the XANES spectra are reversible upon decrease of pressure, which agrees with the reversible character of the scheelite-to-fergusonite transition in these compounds.

5. Conclusions

We have performed ab initio total energy calculations on the scheelite, fergusonite, and wolframite structures of $CaWO_4$ and $SrWO_4$ along with ADXRD and XANES studies in $CaWO_4$ and $SrWO_4$ up to pressures of about 20 GPa, ensuring quasi-hydrostatic conditions. We have found that both compounds undergo a scheelite-to-fergusonite phase transition, confirming in the case of $CaWO_4$ the results of a previous ADXRD study [12]. Our own ADXRD study locates the onset of the phase transition at 10.8(5) GPa in $CaWO_4$ and at 9.9(2) GPa in $SrWO_4$, pressures which are in very good agreement with our theoretical results. The monoclinic distortions leading to the phase transition continue up to the maximum pressures achieved in the experiments. The small changes of the local environment around the absorbing atom make XANES sensitive to the phase transition at somewhat higher pressures than in the ADXRD study. In the case of $SrWO_4$, precursor effects of the transition appear at 10 GPa but the transition is not completed until 15 GPa. From our theoretical study, the wolframite structure (previously proposed for the high-pressure phase of $CaWO_4$) turns out to be close though higher in energy than the fergusonite structure in the whole range of pressures investigated for both compounds. The structural

properties of the scheelite and fergusonite phases obtained from the experimental measurements and those from our first-principles calculations are in excellent agreement.

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