

**Determination of the high-pressure crystal structure of BaWO<sub>4</sub> and PbWO<sub>4</sub>**D. Errandonea,<sup>1,\*</sup> J. Pellicer-Porres,<sup>1</sup> F. J. Manjón,<sup>2</sup> A. Segura,<sup>1</sup> Ch. Ferrer-Roca,<sup>1</sup> R. S. Kumar,<sup>3</sup> O. Tschauer,<sup>3</sup> J. López-Solano,<sup>4</sup> P. Rodríguez-Hernández,<sup>4</sup> S. Radescu,<sup>4</sup> A. Mujica,<sup>4</sup> A. Muñoz,<sup>4</sup> and G. Aquilanti<sup>5</sup><sup>1</sup>*Departamento Física Aplicada-ICMUV, Universitat de València, Edificio de Investigación, C/Dr. Moliner 50, 46100 Burjassot (Valencia), Spain*<sup>2</sup>*Departamento Física Aplicada, Universitat Politècnica de València, Camino de Vera s/n, 46022 València, Spain*<sup>3</sup>*High Pressure Science and Engineering Center, Department of Physics, University of Nevada, 4505 Maryland Parkway, Las Vegas, Nevada 89154-4002, USA*<sup>4</sup>*Departamento Física Fundamental II, Universidad de La Laguna, La Laguna, Tenerife, Spain*<sup>5</sup>*European Synchrotron Radiation Facility, BP 220, Grenoble, F-38043 France*

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We report the results of both angle-dispersive x-ray diffraction and x-ray absorption near-edge structure studies in BaWO<sub>4</sub> and PbWO<sub>4</sub> at pressures of up to 56 GPa and 24 GPa, respectively. BaWO<sub>4</sub> is found to undergo a pressure-driven phase transition at 7.1 GPa from the tetragonal scheelite structure (which is stable under normal conditions) to the monoclinic fergusonite structure whereas the same transition takes place in PbWO<sub>4</sub> at 9 GPa. We observe a second transition to another monoclinic structure which we identify as that of the isostructural phases BaWO<sub>4</sub>-II and PbWO<sub>4</sub>-III (space group  $P2_1/n$ ). We have also performed *ab initio* total-energy calculations which support the stability of this structure at high pressures in both compounds. The theoretical calculations further find that upon increase of pressure the scheelite phases become locally unstable and transform displacively into the fergusonite structure. The fergusonite structure is, however, metastable and can only occur if the transition to the  $P2_1/n$  phases were kinetically inhibited. Our experiments in BaWO<sub>4</sub> indicate that it becomes amorphous beyond 47 GPa.

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**I. INTRODUCTION**

Research and development are underway for the implementation of new instrumentation in low-background particle-physics experiments. Event-type discrimination measurements could be possible in the near future by means of simultaneous measurements of a combination of phonon and scintillation signals from cryogenic phonon-scintillation detectors.<sup>1</sup> These detectors provide unique advantages in experiments searching for rare events; i.e., interactions with weakly-interactive massive particles,<sup>2</sup> double-beta decays,<sup>3</sup> and radioactive decays of very long-living isotopes.<sup>4</sup> Both CaWO<sub>4</sub> and PbWO<sub>4</sub> are promising materials for the next generation of cryogenic phonon-scintillation detectors.<sup>2,5,6</sup> This has motivated a renewed interest in the fundamental physical properties of the AWO<sub>4</sub> tungstates (with A=Ca, Sr, Ba, Pb, Eu) which under normal conditions crystallize in the tetragonal scheelite structure [space group (SG):  $I4_1/a$ , No. 88, and number of formula units per crystallographic cell  $Z=4$ ].<sup>7</sup> The scheelite tungstates are in fact technologically important materials within a wider scope, having been used during the last years as solid-state scintillators<sup>8-10</sup> and in other optoelectronic devices.<sup>11-13</sup> A significant amount of research work on the structural behavior of AWO<sub>4</sub> compounds exists<sup>14-23</sup> and this corpus forms a solid background for understanding the main physical properties of these materials.

We have recently established by means of angle-dispersive x-ray diffraction (ADXRD) experiments, x-ray absorption near edge structure (XANES) measurements, and *ab initio* total-energy calculations,<sup>20,21</sup> that upon compression CaWO<sub>4</sub> and SrWO<sub>4</sub> undergo a scheelite-to-fergusonite phase transition. In the present work we report a similar combined

study in BaWO<sub>4</sub> and PbWO<sub>4</sub>. This allows us to get a more complete picture of the structural behavior of the AWO<sub>4</sub> scheelite tungstates and improves our understanding of their physical properties.

The existence of high-pressure (HP) high-temperature (HT) phases in BaWO<sub>4</sub> and PbWO<sub>4</sub> has been known since the 1970s. The crystallographic structure of the HP-HT phase BaWO<sub>4</sub>-II (SG:  $P2_1/n$ , No. 14,  $Z=8$ ) was resolved by Fujita *et al.*<sup>24</sup> and Kawada *et al.*<sup>25</sup> The same structure was also found by Richter *et al.*<sup>26</sup> for the phase III of PbWO<sub>4</sub> previously discovered by Chang<sup>27</sup> (as in the case of BaWO<sub>4</sub>-II, by combining high pressure and high temperature). For PbWO<sub>4</sub> another monoclinic phase, phase II (raspite, SG:  $P2_1/a$ , No. 14,  $Z=4$ ), is known to occur in nature as a metastable and minority form under normal conditions.<sup>28</sup> On the other hand, the occurrence of a pressure-driven phase transition at room temperature (RT) and 6.5 GPa in BaWO<sub>4</sub> and 4.5 GPa in PbWO<sub>4</sub> was observed in Raman experiments performed by Jayaraman *et al.*<sup>29,30</sup> These authors suggested that for both materials the high-pressure forms had the monoclinic HgWO<sub>4</sub>-type structure (SG:  $C2/c$ , No. 15,  $Z=4$ ).<sup>31</sup> However, in the single-crystal ADXRD experiments carried out by Hazen *et al.* in PbWO<sub>4</sub> no phase transition was observed up to 6 GPa.<sup>19</sup> In more recent high-pressure powder ADXRD experiments Panchal *et al.* observed that scheelite-BaWO<sub>4</sub> transforms to a high-pressure phase at 7 GPa and on the basis of the quality of the unit-cell fit these authors suggested that the structure of this phase could be fergusonite and not HgWO<sub>4</sub>-type.<sup>16</sup> They also found evidence that beyond 14 GPa BaWO<sub>4</sub> undergoes another transition to an unidentified new phase. A single total-energy calculation has considered the possibility of the PbWO<sub>4</sub>-III phase.<sup>32</sup> These facts show that despite the experimental and theoretical efforts

made we have not yet achieved a full understanding of the effect of pressure on the structure of  $\text{BaWO}_4$  and  $\text{PbWO}_4$ .

The goal of the present study is to examine comprehensively the crystal stability of  $\text{BaWO}_4$  and  $\text{PbWO}_4$  up to approximately 20 GPa. In order to improve the current understanding of the structural behavior of these compounds we have performed ADXRD and XANES measurements in a diamond-anvil cell (DAC) at RT as well as *ab initio* total-energy calculations on a number of phases. From our ADXRD measurements we find that both compounds undergo a scheelite-to-fergusonite phase transition (at 7.1 GPa in  $\text{BaWO}_4$  and 9 GPa in  $\text{PbWO}_4$ ). These transitions are supported by our high-pressure XANES measurements. In addition, we find that  $\text{BaWO}_4$  and  $\text{PbWO}_4$  undergo a second transition to the monoclinic  $\text{BaWO}_4$ -II and  $\text{PbWO}_4$ -III isostructural phases near 10 and 15 GPa, respectively. The *ab initio* calculations find that the fergusonite phase can only occur as a metastable phase in both compounds and that the  $\text{BaWO}_4$ -II and  $\text{PbWO}_4$ -III phases are respectively stable at pressures above 7 and 9 GPa. We think that the intermediate fergusonite phase was experimentally observed due to a kinetic hindrance of the  $I4_1/a$ -to- $P2_1/n$  transformation. We also find that amorphization occurs in  $\text{BaWO}_4$  at pressures exceeding 47 GPa.

The details of the experimental methods are described in Sec. II and those of the *ab initio* theoretical calculations in Sec. III. Our experimental ADXRD results (including the evolution of the crystalline structures of both compounds under pressure) are given in Sec. IV A, the results of the XANES study in Sec. IV B, and the results of the theoretical study in Sec. IV C. We summarize our conclusions in Sec. V.

## II. EXPERIMENTAL DETAILS

$\text{BaWO}_4$  and  $\text{PbWO}_4$  crystals were grown with the Czochralski method starting from raw powders having 5N purity.<sup>8,11</sup> Samples were prepared as fine ground powders from the single crystals. High-pressure ADXRD measurements were carried out in a 400  $\mu\text{m}$  culet Mao-Bell DAC. Powder samples were loaded together with a ruby chip into a hole 100  $\mu\text{m}$  in diameter drilled on a 40  $\mu\text{m}$  thick rhenium gasket. For the XANES measurements under pressure, fine powder samples were loaded together with a ruby chip into a hole 200  $\mu\text{m}$  in diameter drilled on a 50  $\mu\text{m}$  thick Inconel gasket and inserted between the diamonds of a 400  $\mu\text{m}$  culet membrane-type DAC. Silicone oil was used as pressure-transmitting medium in all the experiments. The pressure was measured by the shift of the  $R1$  photoluminescence line of ruby.<sup>33</sup>

The ADXRD data shown in the present paper are based on three independent runs on  $\text{BaWO}_4$  (up to 9, 25, and 56 GPa) and one run on  $\text{PbWO}_4$  (up to 19.5 GPa). ADXRD experiments were performed at the 16-IDB beamline of the HPCAT facility at the advanced photon source (APS). Monochromatic synchrotron radiation at  $\lambda=0.3679$  Å (on the  $\text{BaWO}_4$  samples) or  $\lambda=0.3888$  Å (on the  $\text{PbWO}_4$  samples) was used for data collection on a Mar345 image plate. The x-ray beam was focused down to  $10 \times 10$   $\mu\text{m}^2$  using Kickpatrick-Baez mirrors. The diffraction images were inte-

grated and corrected for distortions using FIT2D<sup>34</sup> to yield intensity versus  $2\theta$  diagrams. Indexing, structure solution, and refinements were performed using the GSAS<sup>35</sup> and POWDERCELL<sup>36</sup> program packages. XANES experiments were conducted at the ID24 energy-dispersive x-ray absorption station of the European Synchrotron Radiation Facility (ESRF).<sup>37,38</sup> Experiments were performed at the W  $L_3$ -edge (10.207 keV). A curved Si (111) monochromator<sup>39</sup> and a vertically focusing mirror defined a focus spot of  $30 \times 20$   $\mu\text{m}^2$ . The reference standard for the energy calibration was metallic W. A detailed description of the ADXRD and XANES experiments is given in Ref. 20.

## III. DETAILS OF THE TOTAL-ENERGY CALCULATIONS

Further to the ADXRD and XANES experiments the structural phase stability of  $\text{BaWO}_4$  and  $\text{PbWO}_4$  was theoretically studied by means of total-energy calculations performed within the framework of the density functional theory (DFT) with the Vienna *ab initio* simulation package (VASP).<sup>40</sup> The exchange and correlation energy was dealt within the generalized gradient approximation (GGA).<sup>41</sup> A review of DFT-based total-energy methods as applied to the theoretical study of phase stability can be found in Ref. 42. For the present calculations on  $\text{PbWO}_4$  we used ultrasoft Vanderbilt-type pseudopotentials<sup>43</sup> while for  $\text{BaWO}_4$  we adopted the projector augmented wave (PAW) scheme.<sup>44</sup> Both the semicore  $5d$  electrons of Pb and the semicore  $5s$  and  $5p$  electrons of Ba were dealt with explicitly in the calculations. We used basis sets of plane waves up to a kinetic-energy cutoff of 692.5 eV for  $\text{PbWO}_4$  and 875 eV for  $\text{BaWO}_4$ , and Monkhorst-Pack grids for the Brillouin-zone integrations which ensure highly converged and precise results (to about 1 meV per formula unit). At each selected volume the structure of the phases considered was relaxed through the calculation of the forces on the atoms and the components of the stress tensor, which in the equilibrium yielded the values of the internal and cell parameters of the structural phases. Various structural information (equilibrium volume, bulk modulus, etc.) for each phase was obtained from the calculated energy-volume curves after a Birch-Murnaghan fitting.

## IV. RESULTS AND DISCUSSION

### A. ADXRD measurements at high pressures

#### 1. Low-pressure phase and phase transition

The *in situ* ADXRD data measured at different pressures are shown in Fig. 1(a) for  $\text{BaWO}_4$  and Fig. 1(b) for  $\text{PbWO}_4$ . The x-ray patterns could be indexed within the scheelite structure (stable at normal conditions) up to 6.9 GPa in  $\text{BaWO}_4$  and up to 8.1 GPa in  $\text{PbWO}_4$ . For  $\text{BaWO}_4$ , splitting and broadening of the diffraction peaks are observed at 7.3 GPa together with the appearance of new reflections [depicted by arrows in Fig. 1(a)], in particular the weak peaks observed at  $2\theta \approx 3.5^\circ$  and at  $2\theta \approx 9.5^\circ$ . These facts are indicative of a structural phase transition around 7.1(2) GPa which is in agreement with previous observations.<sup>16,29</sup> In the

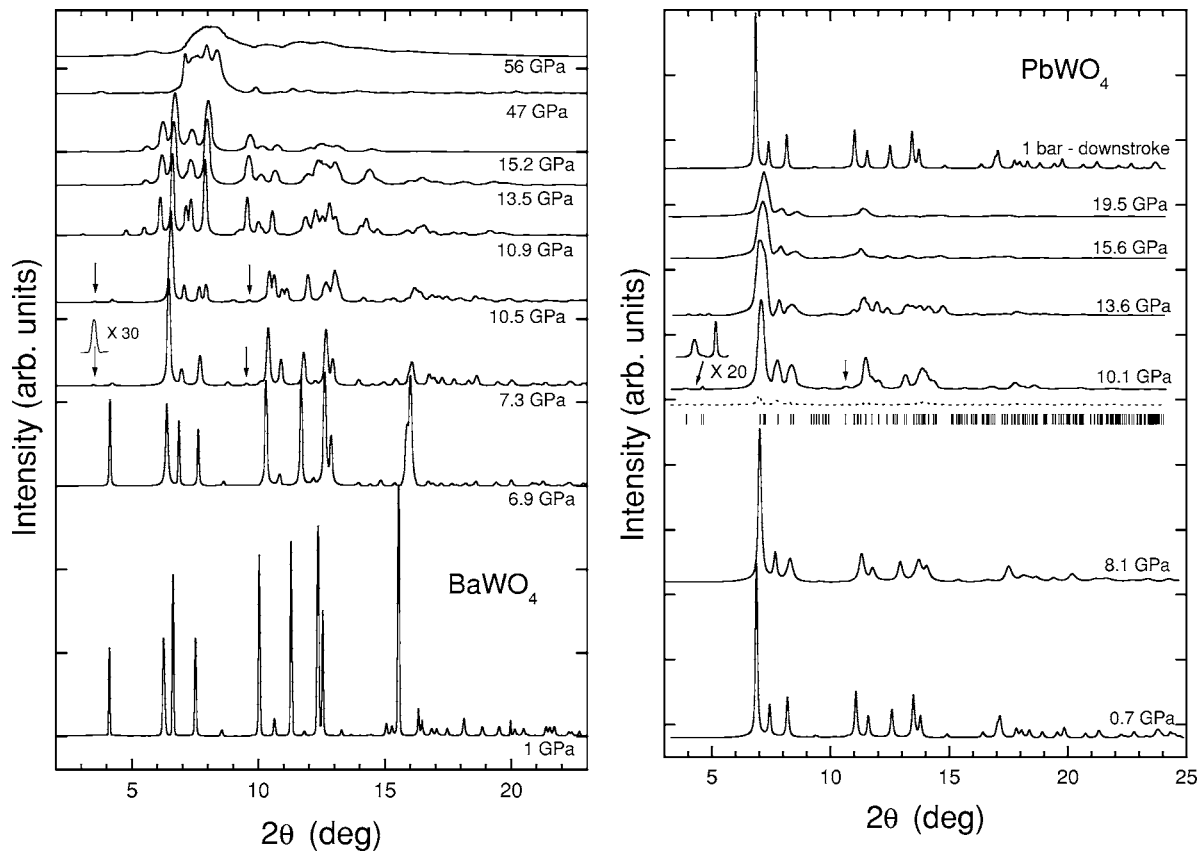


FIG. 1. Room-temperature ADXRD data of (a)  $\text{BaWO}_4$  and (b)  $\text{PbWO}_4$  at different pressures. In all diagrams the background was subtracted. To better illustrate the appearance of the (020) Bragg reflection of the fergusonite structure around  $2\theta \approx 4^\circ$  a section of one of the fergusonite patterns is enlarged and shown in the inset. In (b) to illustrate the quality of the Le Bail refinement obtained for the fergusonite structure at 10.1 GPa the difference between the measured data and the refined profile is shown (dotted line). The bars indicate the calculated positions of the reflections of the fergusonite structure.

case of  $\text{PbWO}_4$ , a broadening of the Bragg peaks is observed together with the appearance of new reflections in the x-ray pattern measured at 10.1 GPa. The same low-angle reflections found in  $\text{BaWO}_4$  and previously observed in the ADXRD patterns of the high-pressure phases of  $\text{CaWO}_4$  and  $\text{SrWO}_4$  (Ref. 20) were also present in  $\text{PbWO}_4$ . In spite of the typical broadening of the diffraction peaks observed in all scheelite-type tungstates (independent of the pressure-transmitting medium used in the experiments) we are able to place the threshold of a structural phase transition in  $\text{PbWO}_4$  at 9.1(10) GPa.

The value of 7.1(2) GPa for the transition pressure in  $\text{BaWO}_4$  compares well with that of 6.5 GPa reported by Jayaraman *et al.*<sup>29</sup> in their Raman study. (Values of transition pressures obtained from Raman scattering tend to be slightly lower than those obtained by x-ray diffraction on the same material.<sup>45</sup>) However, the observed pressure of 9.1(10) GPa for the phase transition in  $\text{PbWO}_4$  is much larger than the value of 4.5 GPa reported in another previous Raman study by Jayaraman *et al.* on this material.<sup>30</sup> Using the same technique, the authors of Ref. 30 found a value of 9 GPa for the transition in  $\text{PbMoO}_4$ , a material that should have a similar behavior than  $\text{PbWO}_4$  on account of the similarities in their mean Pb-O distances and the  $\text{WO}_4/\text{Pb}$  and  $\text{MoO}_4/\text{Pb}$  radii ratios.<sup>18</sup> Application of the size criterion proposed in Ref. 18

to  $\text{PbWO}_4$  leads to a transition pressure of 7.9(13) GPa which is close to our measured value. The fact that Hazen *et al.*<sup>19</sup> did not observe any phase transition in their x-ray diffraction experiments performed up to 6 GPa further suggests that the transition pressure of  $\text{PbWO}_4$  was probably underestimated in the Raman study of Ref. 30. As we will see below, our XANES measurements and *ab initio* total-energy calculations further support this conclusion.

The pressure dependence of the lattice parameters, cell volume, and axial ratios for both  $\text{BaWO}_4$  and  $\text{PbWO}_4$  are shown in Figs. 2(a)–2(d), where we also compare with previous high-pressure measurements<sup>16,19</sup> and data at ambient conditions.<sup>7</sup> The pressure-volume curves shown in Fig. 2(c) were obtained from fitting of the experimental data using a third-order Birch-Murnaghan equation of states (EOS). The bulk modulus, its pressure derivative, and the atomic volume at zero pressure obtained for the scheelite phase of  $\text{BaWO}_4$  and  $\text{PbWO}_4$  are summarized and compared with those of other scheelite tungstates in Table I. The values of these parameters are in good agreement with previously reported data<sup>16,19</sup> and indicate that  $\text{BaWO}_4$  is the most compressible scheelite-like orthotungstate. This is expected since the average Ba-O distance at ambient conditions (2.768 Å) is larger than the average A-O distance ( $d_{\text{A-O}}$ ) in any of the other  $\text{AWO}_4$  compounds, and the bulk modulus is known to be proportional to  $(d_{\text{A-O}})^{-3}$  (Ref. 20).

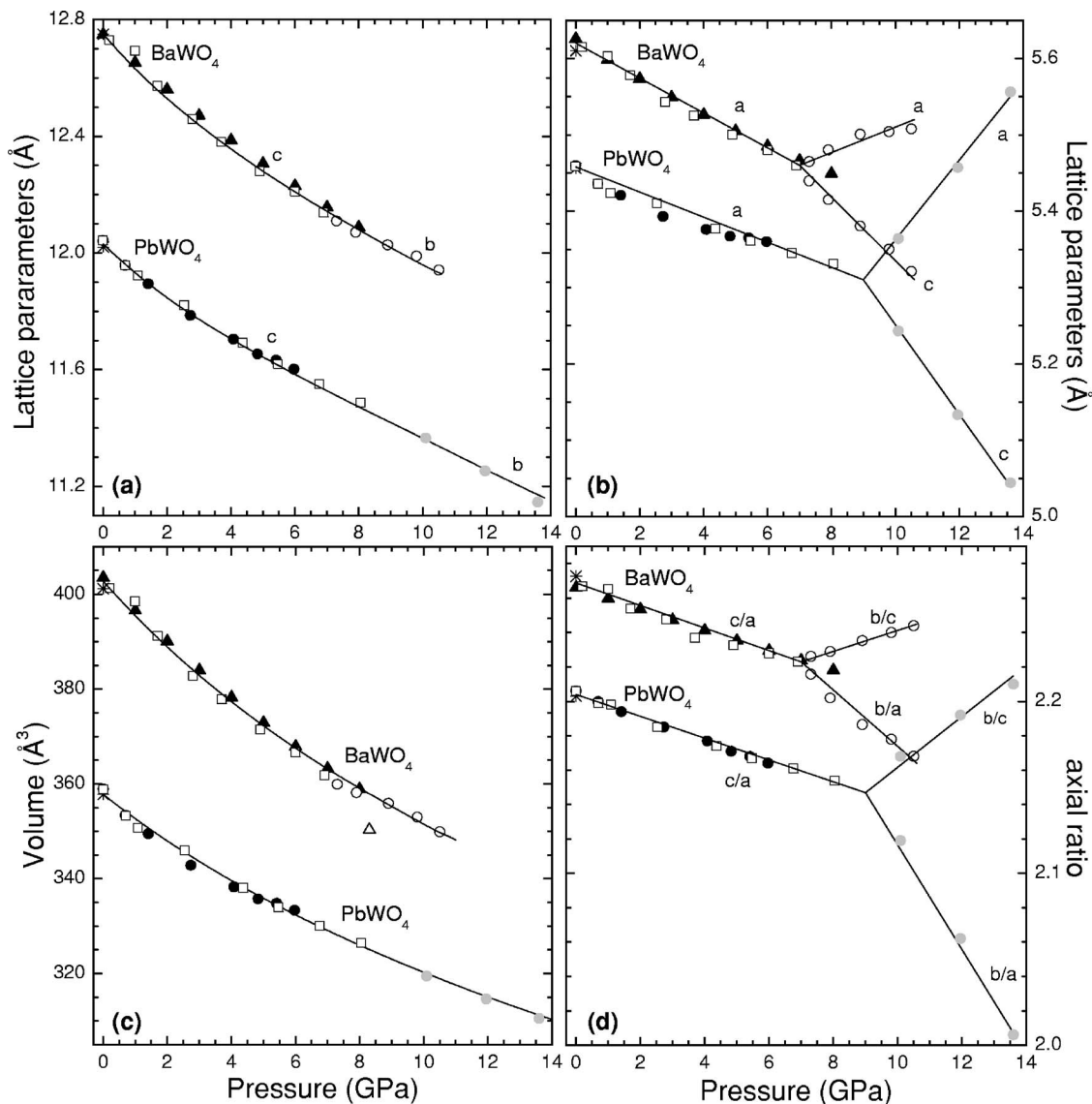


FIG. 2. Evolution of the lattice parameters (a) and (b), volume (c), and axial ratios (d) of  $\text{BaWO}_4$  and  $\text{PbWO}_4$  under pressure. Empty squares correspond to data of the scheelite phase and empty (gray) circles to data of the fergusonite phase of  $\text{BaWO}_4$  ( $\text{PbWO}_4$ ). Solid circles,<sup>19</sup> solid triangles,<sup>16</sup> and crosses<sup>7</sup> illustrate the data of the scheelite phase obtained from the literature. Empty triangles are the fergusonite data reported in Ref. 16. In (c) the solid lines represent the EOS described in the text. In (a), (b), and (d) they are just a guide to the eye. The plotted EOS corresponds to the true compressibility of the scheelite phase. However, it represents very well also the pressure dependence of the volume of the fergusonite phase.

Figures 2(a), 2(b), and 2(d), show that for the scheelite phases the compressibility along the  $c$  axis is larger than that along the  $a$  axis. This observation extends to  $\text{CaWO}_4$ ,  $\text{SrWO}_4$ , and  $\text{EuWO}_4$  [Refs. 20 and 22] and can be related to the fact that when pressure is applied to the scheelite structure the  $\text{WO}_4$  tetrahedra remain essentially undistorted while the volume of the  $\text{AO}_8$  bisdisphenoids is largely reduced. Thus, the  $a$  axis is expected to be less compressible than the  $c$  axis because the  $\text{WO}_4$  units are directly aligned along the  $a$  axis whereas along the  $c$  axis there is an  $A$  cation between the  $\text{WO}_4$  tetrahedra (see Fig. 1 of Ref. 20). From the present ADXRD results we further obtain that for both scheelite- $\text{BaWO}_4$  and scheelite- $\text{PbWO}_4$  the W-O distances are more rigid than the Ba-O and Pb-O distances (see Fig. 3). In particular, the W-O distance in  $\text{BaWO}_4$  decreases from 1.838 Å

TABLE I. Bulk modulus ( $B_0$ ), first pressure derivative of the bulk modulus ( $B_0'$ ), and equilibrium volume ( $V_0$ ) all at normal conditions for different  $\text{AWO}_4$  compounds.

Compound	$V_0$ [Å <sup>3</sup> ]	$B_0$ [GPa]	$B_0'$
$\text{CaWO}_4^a$	312(1)	74(7)	5.6(9)
$\text{SrWO}_4^a$	347.4(9)	63(7)	5.2(9)
$\text{BaWO}_4^c$	402.8(9)	52(5)	5(1)
$\text{PbWO}_4^c$	357.8(6)	66(5)	5.6(9)
$\text{EuWO}_4^b$	348.9(8)	65(6)	4.6(9)

<sup>a</sup>Reference 20.

<sup>b</sup>Reference 22.

<sup>c</sup>Present work.

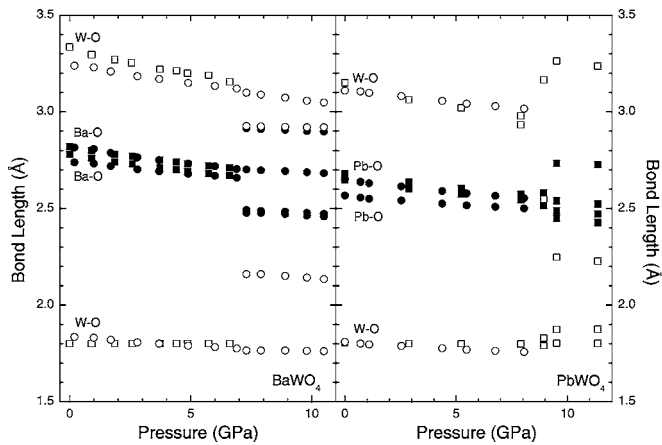


FIG. 3. Pressure dependence of the interatomic bond distances in the scheelite and fergusonite phases of  $\text{BaWO}_4$  and  $\text{PbWO}_4$ . Squares represent the calculated distances and circles the distances extracted from the present experiments.

at 1 bar to  $1.785 \text{ \AA}$  at 6.9 GPa and the average Ba-O distance decreases from  $2.768 \text{ \AA}$  at 1 bar to  $2.653 \text{ \AA}$  at 6.9 GPa. Similar differences between the changes of the W-O and Pb-O distances upon compression are observed in  $\text{PbWO}_4$ . These features are consistent with the previous argument about the anisotropic compressibility of the  $\text{AWO}_4$  compounds.<sup>20</sup>

## 2. High-pressure phases

The ADXRD spectra of  $\text{BaWO}_4$  exhibit a change around 7.3 GPa, while in the spectra of  $\text{PbWO}_4$  a similar change occurs near 10 GPa, see Figs. 1(a) and 1(b). These changes are completely reversible upon pressure release but significant hysteresis was observed. In both compounds the increase of pressure above the threshold of the transition leads to an increase of the broadening of the Bragg peaks. Splitting of the Bragg peaks is clearly observed in  $\text{BaWO}_4$  above the phase transition [cf. the ADXRD patterns in Fig. 1(a) collected at 7.3 GPa and 10.5 GPa: the (200) and (002) peaks located near  $2\theta \approx 8^\circ$  split, as well as the (240) and (042) peaks near  $2\theta \approx 10.5^\circ$  and the  $(\bar{2}02)$  and (202) peaks near  $2\theta \approx 11^\circ$ ]. The same splitting is not clearly observed in  $\text{PbWO}_4$  because of the broadening of the diffraction peaks. We note that the broadening and splitting of Bragg peaks in  $\text{BaWO}_4$  is observed because of the increase of the monoclinic distortion: both the monoclinic angle  $\beta$  and the difference between the  $b/a$  and  $b/c$  axial ratios increases. In particular,  $\beta$  goes from  $90.08^\circ$  at 7.3 GPa to  $90.98^\circ$  at 10.5 GPa.

Figures 1(b) and 4 show the LeBail refinement<sup>46</sup> of the ADXRD pattern of  $\text{PbWO}_4$  measured at 10.1 GPa and the Rietveld refinement of the experimental spectra of  $\text{BaWO}_4$  measured at 7.3 GPa assuming the fergusonite structure. A good fitting is obtained for both tungstates, with residuals  $R_{\text{wp}}=1.9\%$ ,  $R_p=1.6\%$ , and  $R(F^2)=1.2\%$  for  $\text{BaWO}_4$  at 7.3 GPa (242 reflections) and  $R_{\text{wp}}=2.35\%$ ,  $R_p=2.2\%$ ,  $R(F^2)=1.8\%$  for  $\text{PbWO}_4$  at 10.1 GPa (210 reflections). The new characteristic peaks of the fergusonite structure observed for  $\text{CaWO}_4$  and  $\text{SrWO}_4$  (Ref. 20) are here also ob-

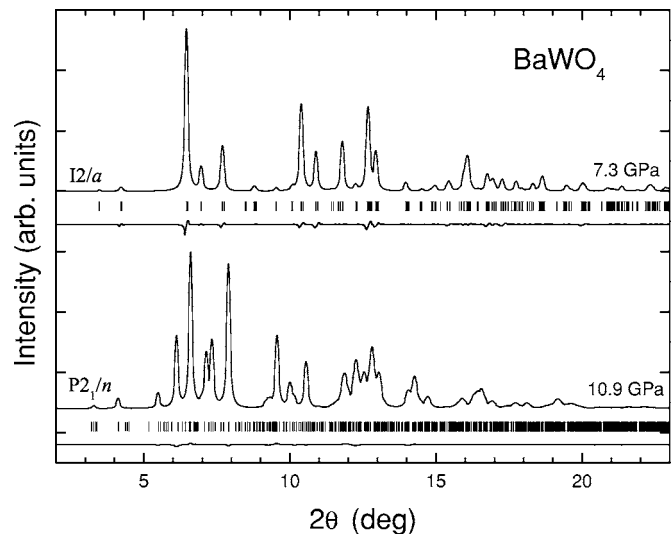


FIG. 4. ADXRD pattern of  $\text{BaWO}_4$  at 7.3 GPa and 10.9 GPa. The background was subtracted. The dotted lines represent the difference between the measured data and the refined profiles. The bars indicate the calculated positions of the reflections.

served in  $\text{PbWO}_4$  close to  $2\theta=4^\circ$  and  $2\theta=10^\circ$  at 10.1 GPa and in  $\text{BaWO}_4$  close to  $2\theta=3.5^\circ$  and  $2\theta=9.5^\circ$  at 7.3 GPa. Table II summarizes the lattice parameters and atomic positions of  $\text{BaWO}_4$  at 1 GPa and 7.3 GPa, and of  $\text{PbWO}_4$  at 0.7 GPa. The lattice parameters of fergusonite- $\text{PbWO}_4$  at 10.1 GPa are:  $a=5.376(6) \text{ \AA}$ ,  $b=11.495(5) \text{ \AA}$ ,  $c=5.273(7) \text{ \AA}$ , and  $\beta=91.57(9)^\circ$ . The atomic positions of fergusonite- $\text{PbWO}_4$  at 10.1 GPa cannot be extracted from the experimental data because of the impossibility of performing a Rietveld refinement of the spectrum. The parameters obtained for fergusonite- $\text{BaWO}_4$  at 7.3 GPa [ $a=5.465(7) \text{ \AA}$ ,  $b=12.109(3) \text{ \AA}$ ,  $c=5.439(7) \text{ \AA}$ ,  $\beta=90.087(9)^\circ$ ] agree reasonably well with those reported by Panchal *et al.* at 8.3 GPa ( $a=5.444 \text{ \AA}$ ,  $b=12.290 \text{ \AA}$ ,  $c=5.236 \text{ \AA}$ ,  $\beta=89.56^\circ$ ).<sup>16</sup> Our high-resolution synchrotron ADXRD experiments allowed us a large access to the reciprocal space and the possibility of performing Rietveld refinements, while Panchal *et al.*<sup>16</sup> performed quite valuable ADXRD measurements using a rotating anode machine that only allowed them to perform Le Bail refinements with a lower resolution and smaller access to the reciprocal space than ours. Panchal *et al.*<sup>16</sup> also concluded that the high-pressure phase of  $\text{BaWO}_4$  is fergusonite but with a larger uncertainty in the lattice parameters.

In  $\text{BaWO}_4$  evidence of the occurrence of a second phase transition is observed at 10.9 GPa. At this pressure we observed an extra broadening of the diffraction peaks, accompanied by several changes in the diffraction pattern [see Fig. 1(a)]. Upon further increase of pressure the broadening of the peaks further increases, however, at least up to 15.2 GPa all the ADXRD patterns can be assigned to the same phase observed at 10.9 GPa. Evidence of the occurrence of a second pressure-induced phase transition was previously observed by Panchal *et al.*<sup>16</sup> albeit at the larger pressure of 14 GPa. However, these authors did not report any x-ray diffraction pattern between 9.3 and 14 GPa. The results of our XANES

TABLE II. Structural parameters of the different structures of BaWO<sub>4</sub> and PbWO<sub>4</sub> as obtained from the present Rietveld refinements.

Structural parameters of scheelite BaWO <sub>4</sub> at 1 GPa:				
$I4_1/a$ , $Z=4$ , $a=5.603(4)$ Å, $c=12.693(7)$ Å.				
	Site	$x$	$y$	$z$
Ba	4b	0	0.25	0.625
W	4a	0	0.25	0.125
O	16f	0.2336(4)	0.0976(6)	0.0499(6)
Structural parameters of scheelite BaWO <sub>4</sub> at 6.9 GPa:				
$I4_1/a$ , $Z=4$ , $a=5.460(4)$ Å, $c=12.138(7)$ Å.				
	Site	$x$	$y$	$z$
Ba	4b	0	0.25	0.625
W	4a	0	0.25	0.125
O	16f	0.2222(4)	0.1087(6)	0.0499(6)
Structural parameters of fergusonite BaWO <sub>4</sub> at 7.3 GPa:				
$I2/a$ , $Z=4$ , $a=5.465(7)$ Å, $b=12.109(3)$ Å, $c=5.439(7)$ Å, $\beta=90.087(9)^\circ$ .				
	Site	$x$	$y$	$z$
Ba	4e	0.25	0.6131(9)	0
W	4e	0.25	0.1282(7)	0
O <sub>1</sub>	8f	0.9493(49)	0.9765(23)	0.2538(34)
O <sub>2</sub>	8f	0.4666(36)	0.2225(37)	0.8826(37)
Structural parameters of scheelite PbWO <sub>4</sub> at 0.7 GPa:				
$I4_1/a$ , $Z=4$ , $a=5.436(7)$ Å, $c=11.957(9)$ Å.				
	Site	$x$	$y$	$z$
Pb	4b	0	0.25	0.625
W	4a	0	0.25	0.125
O	16f	0.2482(6)	0.1073(6)	0.0510(9)

study and *ab initio* calculations (see below) further locate the occurrence of a second transition around 10 GPa in BaWO<sub>4</sub>. We think that the onset of this transition was previously overestimated in Ref. 16.

The quality of the ADXRD patterns collected from the new phase of BaWO<sub>4</sub> did not allow a Rietveld refinement. Therefore, we analyzed them using the Le Bail extraction technique considering the following candidate structures: raspite, HgWO<sub>4</sub>, BaWO<sub>4</sub>-II, wolframite (SG:  $P2_1/c$ , No. 13,  $Z=2$ ) (Ref. 47),  $\alpha$ -MnMoO<sub>4</sub> (SG:  $C2/m$ , No. 12,  $Z=8$ ) (Ref. 15), LaTaO<sub>4</sub> (SG:  $P2_1/c$ , No. 14,  $Z=4$ ) (Ref. 48), BaMnF<sub>4</sub> (SG:  $A2_1/am$ , No. 36,  $Z=4$ ) (Ref. 49), SrUO<sub>4</sub> (SG:  $Pbcm$ , No. 57,  $Z=4$ ) (Ref. 50),  $Cmca$  (SG:  $Cmca$ , No. 64,  $Z=8$ ) (Ref. 20), zircon (SG:  $I4_1/amd$ , No. 141,  $Z=4$ ) (Ref. 51), and pseudo-scheelite (SG:  $Pnma$ , No. 62,  $Z=4$ ) (Ref. 52). The most likely space group was found to be  $P2_1/n$  corresponding to the BaWO<sub>4</sub>-II-type structure. In the spectrum collected at 10.9 GPa the Le Bail extraction technique converged to the structure of BaWO<sub>4</sub>-II with residuals  $R_{WP}=2.2\%$ ,  $R_p=1.6\%$ , and  $R(F^2)=1.2\%$  for 909 reflections. The lattice parameters obtained for this structure at 10.9 GPa are  $a=12.841(9)$  Å,  $b=7.076(6)$  Å,  $c=7.407(6)$  Å,  $\beta=93.0(9)^\circ$ . Figure 4 shows the refined structure models and the residual

of the refinement procedure. All the ADXRD patterns measured up to 15.2 GPa can also be assigned to the BaWO<sub>4</sub>-II-type structure. From our data we conclude that the transition from the fergusonite phase to the BaWO<sub>4</sub>-II phase occurs at 10.7(2) GPa together with a large volume collapse  $\Delta V/V=8\%$ . This volume collapse reflects the fact that the structure of BaWO<sub>4</sub>-II consists of densely packed networks of distorted WO<sub>6</sub> octahedra. We note here that although we propose the identification of the new phase as BaWO<sub>4</sub>-II, the LaTaO<sub>4</sub>-type and the BaMnF<sub>4</sub>-type structures were in close competence with it giving only slightly larger residuals in our analysis. Peak intensities can be slightly distorted in DAC experiments (Refs. 53 and 54) and thus an analysis based on residuals alone is not enough in this case to discriminate between the crystal structures. However, both the BaMnF<sub>4</sub>-type and LaTaO<sub>4</sub>-type structures fail to account for the presence of the peaks located at  $2\theta \approx 3.3^\circ$ ,  $4.1^\circ$ , and  $5.5^\circ$  [assigned to the (200), (011), and (211) Bragg peaks of the BaWO<sub>4</sub>-II structure, respectively].

The x-ray patterns of BaWO<sub>4</sub> measured beyond 15.2 GPa keep slowly changing up to 47 GPa. In particular, the continuous broadening of the Bragg peaks observed from 15.2 GPa to 47 GPa suggests that beyond 15.2 GPa there is a substantial increase of the disorder in the crystalline phase.

At 56 GPa all the peaks finally disappear under a broad diffuse scattering. We think that these two facts indicate that at such high compression  $\text{BaWO}_4$  amorphizes, similarly to what has been observed in  $\text{CaWO}_4$  (Ref. 14). The occurrence of this kind of pressure-induced amorphization is sometimes related to a frustrated solid-solid phase transition. In the present study all the changes observed up to 25 GPa were reversible although showing significant hysteresis. However, the changes observed beyond 47 GPa were *not* reversible, a fact which is consistent with pressure-induced amorphization. Another possibility for the appearance of the broad features in the ADXRD patterns is the occurrence of a pressure-induced chemical decomposition of  $\text{BaWO}_4$  as observed in  $\text{LiGdF}_4$  (Ref. 55). This is however, not likely the case for  $\text{CaWO}_4$  since annealing at 45 GPa and 477 K during two hours led to the nucleation of a new crystalline structure of  $\text{CaWO}_4$  (Ref. 15) Most likely the loss of the Bragg peaks in the ADXRD patterns of  $\text{BaWO}_4$  and  $\text{CaWO}_4$  (near 47 GPa and 40 GPa, respectively) is the result of the frustrated transformation of their high-pressure crystalline phases into a noncrystalline solid. The irreversible nature of the amorphization implies that beyond 47 GPa the polyhedra not only deform and interconnect probably differently, but also that the structural changes are significantly larger to hinder the reversal of deformations upon release of pressure. Amorphization can be understood in terms of the packing of the anionic  $\text{WO}_4$  units around the  $A$  cations (size criterion).<sup>18</sup> When the ionic radii of the  $\text{WO}_4$  groups is small relative to that of the  $A$  cations, increasing repulsive and steric stresses induced by pressure can be accommodated by deformation of the cation outer shell as opposed to significant changes in its average position, thereby favoring the transformation to a high-pressure crystalline phase. In contrast to this, if the ratio between the ionic radii ( $\text{WO}_4/A$ ) is large the material will accommodate increased stresses through larger and more varied displacements from their average positions resulting in a subsequent loss of translational periodicity at high pressure. The lower pressure for the onset of amorphization in  $\text{CaWO}_4$  as compared to  $\text{BaWO}_4$  is consistent with the larger  $\text{WO}_4/A$  ratio for the Ca compound ( $\text{WO}_4/\text{Ca}=1.89$  and  $\text{WO}_4/\text{Ba}=1.47$ ). A direct conclusion can be drawn for  $\text{SrWO}_4$  and  $\text{PbWO}_4$  for which the ratios  $\text{WO}_4/\text{Sr}=1.76$  and  $\text{WO}_4/\text{Pb}=1.66$  imply that they should amorphize at pressures around 43 and 45 GPa, respectively.

In the case of  $\text{PbWO}_4$  the broadening of the diffraction peaks continuously increases from the transition pressure of 9.1 up to 19.5 GPa, the maximum pressure achieved in our experiments on  $\text{PbWO}_4$ . One of the possible reasons for the broadening of the Bragg peaks of the fergusonite structure is the continuous increase of the monoclinic distortion. At 13.6 GPa, the splitting and broadening of the Bragg peaks has increased considerably, but the ADXRD pattern can still be assigned to a strongly distorted fergusonite structure. In particular the low-angle peaks are still present. However, we have also observed some reversible changes in the features of the diffraction pattern at 15.6 GPa. The intensity of the pattern decreases, the two weak peaks at low  $2\theta$  angles apparently disappears, and the strong peaks observed near  $11.5^\circ$  at 10.1 GPa shifts to lower  $2\theta$  angles. The patterns collected above 15.6 GPa show the same features than the

one collected at 15.6 GPa. The observed changes may relate to the occurrence of a structural change in  $\text{PbWO}_4$  at 15.6 GPa. As we will show below, this hypothesis is confirmed by the present XANES results. We think that the continuous broadening observed in the ADXRD patterns of  $\text{PbWO}_4$  beyond 10.1 GPa may be caused by an increase of the disorder in the crystalline structure of  $\text{PbWO}_4$ . This result suggests that perhaps  $\text{PbWO}_4$  will also amorphize at a pressure higher than the maximum pressure reached in our experiments, as it occurs in  $\text{BaWO}_4$  and  $\text{CaWO}_4$ . The fact that the broadening observed up to 19.5 GPa is reversible [see Fig. 1(b)] would then indicate that the pressure-induced structural disorder did not develop enough at 19.5 GPa to avoid the reversion to the original structure upon decompression.

## B. XANES measurements at high pressures

XANES measurements provide information about the geometrical arrangement of the atoms surrounding the absorbing atom. XANES spectra do not depend on long range order, so the information that they provide is complementary to the one yielded by x-ray diffraction. As a sensitive tool XANES can be used to obtain information about pressure-driven structural changes. For the present study we have carried out high-pressure XANES experiments on  $\text{BaWO}_4$  and  $\text{PbWO}_4$  in order to study the evolution of the W environment under compression. We use XANES spectra as a footprint to help identifying the occurrence of high-pressure phases. Specifically, we compare experimental spectra with those calculated for a given phase using the real-space multiple-scattering code implemented in the FEFF8 package.<sup>56</sup>

The XANES simulations use as input the structural information provided by *ab initio* calculations or x-ray diffraction. The self-consistent potential was calculated using 6.5 Å clusters and the Hedin-Lundqvist energy-dependent self-energy. Full multiple scattering calculations were performed with the same cluster size. No pseudo Debye-Waller factor has been considered in our simulations.

We have performed simulations considering several structures, including fergusonite, wolframite,  $\text{LaTaO}_4$ ,  $\text{BaMnF}_4$ ,  $\text{HgWO}_4$ , *Cmca*, and  $\text{BaWO}_4$ -II (or  $\text{PbWO}_4$ -III), see Fig. 5. The structural data used were taken from the literature in the case of the  $\text{HgWO}_4$  (Ref. 31), wolframite,<sup>47</sup> and  $\text{PbWO}_4$ -III structures.<sup>26</sup> For the rest of the structures considered they were obtained either from the present Rietveld refinements (see Table II) or from our *ab initio* calculations (see Table III). As previously observed in  $\text{CaWO}_4$  and  $\text{SrWO}_4$ , (Ref. 20), the  $B$  resonance is very sensitive to the W-O coordination. In those structures where W is fourfold coordinated by O atoms, as the scheelite and the fergusonite structures, the  $B$  resonance is clearly visible. On the other hand, when W atoms approach a sixfold coordination (wolframite,  $\text{LaTaO}_4$ ,  $\text{BaMnF}_4$ ,  $\text{HgWO}_4$ , and  $\text{BaWO}_4$ -II) the  $B$  resonance disappears. Differences between the spectra corresponding to structures where W is sixfold coordinated by O atoms are more subtle.

### 1. Low-pressure phase

Experimental XANES spectra of  $\text{BaWO}_4$  and  $\text{PbWO}_4$  at the W  $L_3$ -edge (10.207 keV) are shown in Fig. 6. The

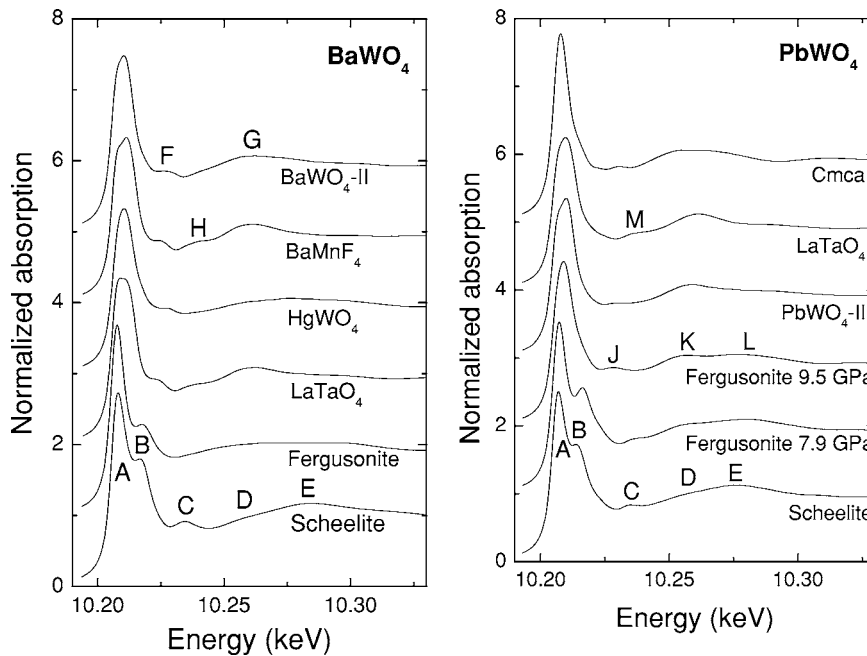


FIG. 5. *Ab initio* simulation of XANES spectra at the W  $L_3$ -edge of BaWO<sub>4</sub> (a) and PbWO<sub>4</sub> (b) in several different phases. The structural data used in simulations are taken from Tables II and III, and from Refs. 26, 31, and 47 (see text for details). Resonance B is present when the W coordination is fourfold, but it is not present when the W coordination is sixfold.

scheelite spectra of both compounds are quantitatively similar, with five evident resonances. Similar features were present in a previous study on CaWO<sub>4</sub> and SrWO<sub>4</sub> (Ref. 20). We find a tendency in the AWO<sub>4</sub> series that the intensity of the *E* resonance slightly increases whereas the resonances *B*, *C*, and *D* become less pronounced as the *A* cation becomes heavier. The calculated position and relative intensity of the resonances (Fig. 5) agrees qualitatively with the experimental spectra. (The resonances in the theoretical spectra are more pronounced because the pseudo Debye-Waller factor has not been considered in the simulations.)

## 2. High-pressure phases

The high-pressure XANES spectra of BaWO<sub>4</sub> remain essentially unchanged up to 7.8 GPa. At this pressure the *B* and *C* resonances loose intensity, whereas the white line (*A*) starts to broaden. These changes stabilize at 9.8 GPa, at which pressure the *B* resonance has disappeared. In the downstroke the scheelite phase is recovered, although with significant hysteresis.

We interpret the changes observed at 7.8 GPa as the beginning of a change in the W-O coordination from four to six, which is completed at 9.8 GPa. With respect to the possible candidates to the high-pressure phase observed beyond 9.8 GPa, the observation of resonances *F* and *G*, as well as their relative intensity and energy points to the BaWO<sub>4</sub>-II, BaMnF<sub>4</sub>-type, and LaTaO<sub>4</sub>-type structures. On the other hand, in the XANES simulations corresponding to the BaMnF<sub>4</sub> and LaTaO<sub>4</sub> structures a weak resonance *H* is present, but it is not clearly evidenced in the experimental spectra. Thus, we conclude that from the XANES point of view the BaWO<sub>4</sub>-II structure is the most convincing candidates for the crystalline structure of BaWO<sub>4</sub> beyond 9.8 GPa.

Apparent discrepancies arise here between XANES and ADXRD (and Raman) experiments. According to the present and previous ADXRD experiments<sup>15</sup> the structural sequence

of BaWO<sub>4</sub> is scheelite → fergusonite → BaWO<sub>4</sub>-II. The first transition occurs at around 7 GPa according to Raman and ADXRD measurements, and the second one occurs around 11 GPa. However, our XANES measurements cannot confirm the existence of the fergusonite phase and suggests the presence of the BaWO<sub>4</sub>-II structure at 9.8 GPa. There is a fact that can be argued against these apparent discrepancies. The distortion of the W-O tetrahedra at the scheelite-to-fergusonite transition is subtle. In fact, in AWO<sub>4</sub> scheelite compounds the transition is caused by displacements of the *A* cations from their high-symmetry positions. Therefore, the XANES spectrum of the fergusonite phase should not differ much from that of the scheelite phase (see Fig. 5 and Ref. 20). In fact only small changes of intensities in the resonances *B*, *C*, *D*, and *E* are expected. As we mentioned above, these resonances become less pronounced as the *A* cation atomic number increases. This fact makes the transition more difficult to detect in BaWO<sub>4</sub> than in CaWO<sub>4</sub> and SrWO<sub>4</sub>. In fact, in Ref. 20 the XANES measurements detected the transition in CaWO<sub>4</sub> at the *same* pressure than the ADXRD measurements, but in SrWO<sub>4</sub> XANES detected the transition at *higher* pressures than ADXRD; only after the monoclinic distortion is enhanced under compression. In BaWO<sub>4</sub> a second transition occurs quite close to the scheelite-to-fergusonite transition (before the monoclinic distortion is enhanced). We think that probably because of all these reasons the presence of the fergusonite phase was not detected in our XANES experiments.

As regards PbWO<sub>4</sub>, the spectra in Fig. 6(b) show a decrease in the intensity of the *B* resonance starting at 9.0 GPa. At 10.9 GPa the *B* resonance fades out and new weak resonances *J*, *K*, and *L* appear. The absence of the *B* resonance in the high-pressure phase seems to contradict ADXRD measurements, since ADXRD indicates a scheelite-fergusonite transition near 9 GPa and, according to the trend followed by simulations and experiments in CaWO<sub>4</sub> and SrWO<sub>4</sub>, as well as the result of fergusonite simulations in PbWO<sub>4</sub>, resonance



TABLE III. Calculated structural parameters of different structures of BaWO<sub>4</sub> and PbWO<sub>4</sub>.

BaWO <sub>4</sub> in the BaMnF <sub>4</sub> -type structure at 9.1 GPa:				
<i>A</i> 2 <sub>1</sub> / <i>am</i> , <i>Z</i> =4, <i>a</i> =5.8252 Å, <i>b</i> =13.8973 Å, <i>c</i> =3.9528 Å.				
	Site	<i>x</i>	<i>y</i>	<i>z</i>
Ba	4a	0.9959	0.1315	0
W	4a	0.4962	0.6015	0
O <sub>1</sub>	4a	0.7240	0.6896	0
O <sub>2</sub>	4a	0.2681	0.6894	0
O <sub>3</sub>	4a	0.7470	0.5002	0
O <sub>4</sub>	4a	0.4565	0.0862	0
BaWO <sub>4</sub> in the LaTaO <sub>4</sub> -type structure at 8.9 GPa:				
<i>P</i> 2 <sub>1</sub> / <i>c</i> , <i>Z</i> =4, <i>a</i> =7.2255 Å, <i>b</i> =5.7858 Å, <i>c</i> =8.0620 Å, β=106°.				
	Site	<i>x</i>	<i>y</i>	<i>z</i>
Ba	4e	0.2707	0.7500	0.0760
W	4e	0.2003	0.2500	0.3241
O <sub>1</sub>	4e	0.1721	0.2500	0.0466
O <sub>2</sub>	4e	0.0004	0.5007	0.2502
O <sub>3</sub>	4e	0.3769	0.4781	0.3472
O <sub>4</sub>	4e	0.3767	0.0216	0.3472
BaWO <sub>4</sub> -II phase at 9.3 GPa:				
<i>P</i> 2 <sub>1</sub> / <i>n</i> , <i>Z</i> =8, <i>a</i> =12.7173 Å, <i>b</i> =6.9816 Å, <i>c</i> =7.4357 Å, β=91.22°.				
	Site	<i>x</i>	<i>y</i>	<i>z</i>
Ba <sub>1</sub>	4e	0.1617	0.6555	0.1633
Ba <sub>2</sub>	4e	0.1349	0.9574	0.6316
W <sub>1</sub>	4e	0.0825	0.1633	0.0836
W <sub>2</sub>	4e	0.0912	0.4609	0.6497
O <sub>1</sub>	4e	0.1078	0.0279	0.2876
O <sub>2</sub>	4e	0.1845	0.6029	0.7777
O <sub>3</sub>	4e	0.0490	0.6510	0.4746
O <sub>4</sub>	4e	0.2128	0.2676	0.0618
O <sub>5</sub>	4e	0.0579	0.2693	0.8168
O <sub>6</sub>	4e	0.1783	0.3319	0.5103
O <sub>7</sub>	4e	0.0198	0.3756	0.1829
O <sub>8</sub>	4e	0.0789	0.9201	0.9539
Fergusonite PbWO <sub>4</sub> at 7.9 GPa:				
<i>I</i> 2/ <i>a</i> , <i>Z</i> =4, <i>a</i> =5.415 Å, <i>b</i> =11.661 Å, <i>c</i> =5.385 Å, β=90.11°.				
	Site	<i>x</i>	<i>y</i>	<i>z</i>
Pb	4e	0.25	0.6246	0
W	4e	0.25	0.1263	0
O <sub>1</sub>	8f	0.9021	0.9598	0.2308
O <sub>2</sub>	8f	0.4806	0.2113	0.8455

TABLE III. (*Continued.*)

Fergusonite PbWO <sub>4</sub> at 9.5 GPa:				
$I2/a$ , $Z=4$ , $a=5.900$ Å, $b=11.090$ Å, $c=4.923$ Å, $\beta=96.601^\circ$ .				
	Site	$x$	$y$	$z$
Pb	4e	0.25	0.6175	0
W	4e	0.25	0.1521	0
O <sub>1</sub>	8f	0.9049	0.9554	0.2246
O <sub>2</sub>	8f	0.4528	0.2126	0.7674
PbWO <sub>4</sub> in the LaTaO <sub>4</sub> -type structure at 10 GPa:				
$P2_1/c$ , $Z=4$ , $a=7.4233$ Å, $b=5.6241$ Å, $c=7.9757$ Å, $\beta=106.5^\circ$ .				
	Site	$x$	$y$	$z$
Pb	4e	0.3355	0.7593	0.0718
W	4e	0.1809	0.2521	0.2634
O <sub>1</sub>	4e	0.1688	0.2226	0.0346
O <sub>2</sub>	4e	0.0186	0.5338	0.2390
O <sub>3</sub>	4e	0.3765	0.4768	0.3334
O <sub>4</sub>	4e	0.3580	0.0169	0.3456
PbWO <sub>4</sub> -III phase at 12 GPa:				
$P2_1/n$ , $Z=8$ , $a=12.2171$ Å, $b=6.8146$ Å, $c=7.2069$ Å, $\beta=89.63^\circ$ .				
	Site	$x$	$y$	$z$
Pb <sub>1</sub>	4e	0.1591	0.6760	0.1645
Pb <sub>2</sub>	4e	0.1356	0.9576	0.6238
W <sub>1</sub>	4e	0.0850	0.1680	0.0824
W <sub>2</sub>	4e	0.0968	0.4637	0.6444
O <sub>1</sub>	4e	0.1036	0.0197	0.2883
O <sub>2</sub>	4e	0.1941	0.6057	0.7748
O <sub>3</sub>	4e	0.0474	0.6587	0.4739
O <sub>4</sub>	4e	0.2228	0.2676	0.0661
O <sub>5</sub>	4e	0.0663	0.2606	0.8137
O <sub>6</sub>	4e	0.1836	0.3375	0.4863
O <sub>7</sub>	4e	0.0209	0.3894	0.1801
O <sub>8</sub>	4e	0.0824	0.9126	0.9489
PbWO <sub>4</sub> in the $Cmca$ -type structure at 11.7 GPa:				
$Cmca$ , $Z=8$ , $a=7.8152$ Å, $b=13.3597$ Å, $c=5.3635$ Å.				
	Site	$x$	$y$	$z$
Pb	8e	0.25	0.8313	0.25
W	8f	0.5	0.5859	0.2841
O <sub>1</sub>	8e	0.25	0.1352	0.25
O <sub>2</sub>	8f	0.5	0.7977	0.9619
O <sub>3</sub>	8d	0.1450	0	0.5
O <sub>4</sub>	8f	0.5	0.9134	0.4396

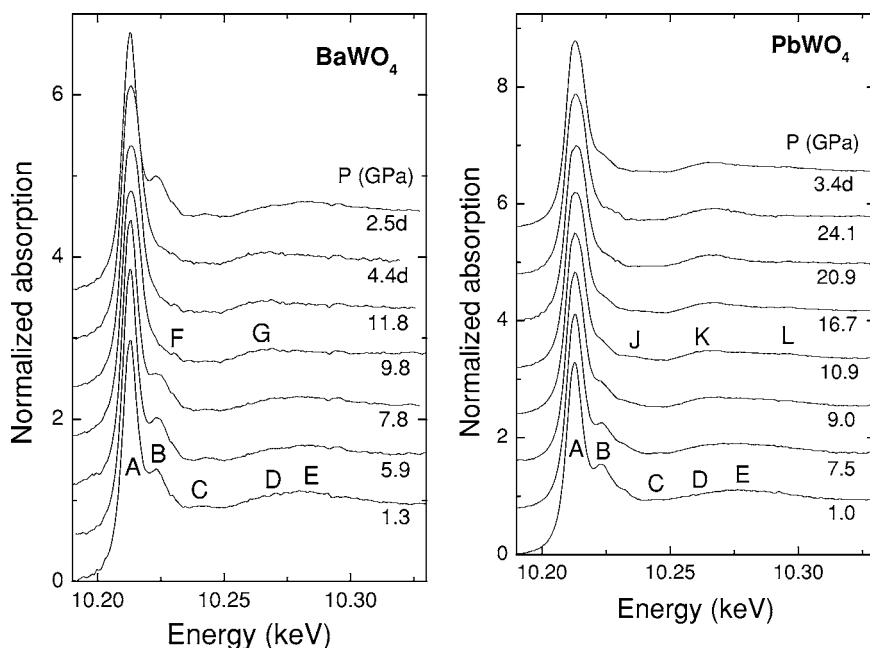


FIG. 6. Experimental XANES spectra ( $W L_3$ -edge) of  $BaWO_4$  (a) and  $PbWO_4$  (b) at different pressures. The spectra collected on pressure release are marked with *d*. The analysis of the spectra (see text) reveals a coordination change at 9.8 GPa in the case of  $BaWO_4$ . In its turn,  $PbWO_4$  transits to a sixfold coordinated fergusonite between 9 and 10.5 GPa. Subtle changes in the spectra suggest a second phase transition in  $PbWO_4$  at 16.7 GPa.

*B* should not disappear. The apparent discrepancy is solved thanks to the *ab initio* computations. Its results will be fully discussed in the next section. Now we would like only to point out that, following the calculations, the internal parameters of the fergusonite structure change between 7.9 and 9.5 GPa, implying a change in the W coordination from four oxygen atoms to 4+2 (see Fig. 3). This means that in  $PbWO_4$  the fergusonite structure would play the role of bridge phase between the scheelite structure, composed of  $WO_4$  tetrahedra, and a high-pressure structure containing  $WO_6$  octahedra. The FEFF simulations carried out with the two sets of internal parameters, and thus the two different coordinations, are shown in Fig. 5(b). As expected, in the fourfold coordinated version of the fergusonite structure the *B* resonance is present, whereas in the sixfold coordinated version the *B* resonance is absent. We thus conclude that at 9 GPa a phase transition takes place in  $PbWO_4$  towards a fergusonite structure, being upon further compression the W environment is distorted in such a way that the W atoms are surrounded by six O atoms in a 4+2 configuration at 10.9 GPa.

At 16.7 GPa there are new, subtle changes in the spectra. Resonances *J* and *L* lose intensity, whereas resonance *K* becomes enhanced. These changes are compatible with a second phase-transition towards the  $PbWO_4$ -III or  $LaTaO_4$  structures. The occurrence of this second transition is not only in agreement with our ADXRD experiments, but also with recent Raman<sup>57</sup> and optical absorption measurements<sup>58</sup> which detected the occurrence of two phase transitions located at 7 and 12 GPa. The absence of the weak *M* resonance in the experimental spectra is not a definitive argument but suggests that the  $PbWO_4$ -III phase is the more likely candidate for the third high-pressure phase.

To close this section we would like to comment that in  $PbWO_4$  the spectra collected at 3.4 GPa in a sample recovered from 24.1 GPa differs from that of the scheelite phase. However, when releasing the pressure from 19.5 GPa the

scheelite structure was recovered at ambient pressure in our ADXRD experiments. The origin of this discrepancy remains unknown.

### C. *Ab initio* calculations at high pressures

We now turn our attention to the results of our *ab initio* study on the energetics of the structural phases of  $BaWO_4$  and  $PbWO_4$  and comparison with the experimental data reported in the previous sections. On account of either its present observation or its previous consideration within the family of scheelite compounds to which  $BaWO_4$  and  $PbWO_4$  belong, we have considered the following structures in our calculations: the scheelite structure itself, raspite (observed in  $PbWO_4$  as a metastable phase under normal conditions), fergusonite, the  $BaWO_4$ -II-type (or  $PbWO_4$ -III-type) quenched from HP-HT conditions in both compounds, wolframite,  $HgWO_4$ -type,  $LaTaO_4$ -type,  $BaMnF_4$ -type,  $SrUO_4$ -type, zircon, and the orthorhombic *Cmca* structure previously proposed by us in Ref. 20 as a very high-pressure phase in  $SrWO_4$  and  $CaWO_4$ . We will comment only on the most relevant aspects of the theoretical results.

Figure 7 shows the energy-volume curves obtained for each of the structures considered in  $BaWO_4$  and  $PbWO_4$ . The relative stability and coexistence pressures of the phases can be obtained from these curves by the common-tangent construction.<sup>42</sup> Figure 7 shows the scheelite phases of both compounds as being stable at zero and low pressure, with values of the volume per formula unit (pfu), bulk modulus and pressure-derivative of the bulk modulus in the equilibrium of, respectively,  $V_0=105.2 \text{ \AA}^3$ ,  $B_0=52 \text{ GPa}$ , and  $B'_0=5$  for  $BaWO_4$  and  $V_0=94.0 \text{ \AA}^3$ ,  $B_0=66 \text{ GPa}$ , and  $B'_0=4.7$  for  $PbWO_4$ . These values are in good agreement with our experimental results, see Table I. Our calculated values of the structural parameters for scheelite- $BaWO_4$  [O(16f) at (0.2315, 0.1234, 0.0461) and  $c/a=2.25$  at 0.9 GPa] and for scheelite- $PbWO_4$  [O(16f) at (0.2334, 0.1114, 0.0436) and

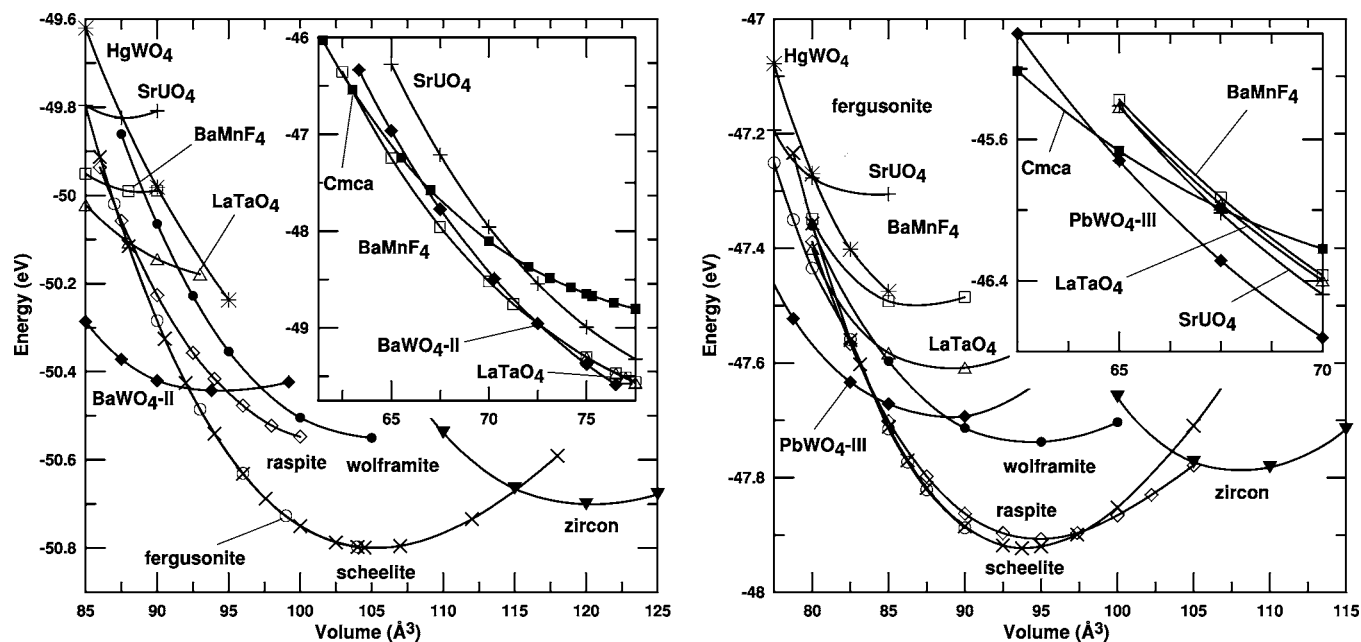


FIG. 7. Total-energy versus volume *ab initio* calculations for  $\text{BaWO}_4$  (a) and  $\text{PbWO}_4$  (b) in different structures. The insets extend the pressure range to the region where the  $\text{BaWO}_4\text{-II}$  and  $\text{PbWO}_4\text{-III}$  structures becomes unstable.

$c/a=2.21$  at 0 GPa] are also in good agreement with the experimental values, see Table II.

For  $\text{PbWO}_4$  we find the raspite structure to be very close in energy and equilibrium volume to the scheelite structure, with raspite slightly higher by about 20 meV pfu, which is in perfect agreement with raspite- $\text{PbWO}_4$  (or  $\text{PbWO}_4\text{-II}$ ) being found in nature as a metastable form under normal conditions.<sup>28</sup> This result disagrees with a previous theoretical calculation that obtained the raspite form lower in energy than the scheelite structure<sup>32</sup> (a similar disagreement exists for the  $\text{PbWO}_4\text{-III}$  phase which in Ref. 32 is shown much lower in energy than the scheelite form.). However, in our study the raspite structure is placed significantly higher in energy in  $\text{BaWO}_4$ , for which such structure has not been reported experimentally: from our present results this form is not expected to occur in this material.

As pressure increases scheelite- $\text{BaWO}_4$  becomes unstable against  $\text{BaWO}_4\text{-II}$  and similarly scheelite- $\text{PbWO}_4$  becomes unstable to  $\text{PbWO}_4\text{-III}$  (isomorphous to  $\text{BaWO}_4\text{-II}$ ). The unit-cell parameters and atomic positions of both phases are given in Table III. The calculated values of the coexistence pressures between both structures are about 5 GPa for both materials which is smaller than the experimental transition pressure at room temperature. It is however, very likely that at RT kinetic barriers preclude the transition at such pressure: the first observations of these phases required heating to 400–600 °C as well as application of high pressure.<sup>24–27</sup>

At pressures around 7.5 GPa in  $\text{BaWO}_4$  and 8 GPa in  $\text{PbWO}_4$  the scheelite phases of these compounds become locally unstable and undergo a distortion into the fergusonite structure with none or very little volume collapse. At such pressures however, the stable phase (the one with lower enthalpy) is the  $P2_1/n$  structure of  $\text{BaWO}_4\text{-II}$  and  $\text{PbWO}_4\text{-III}$ . From our calculations there is thus no true range of stability for the fergusonite phase in either compound, and this can

exist only as a metastable phase in the case that the transition to the monoclinic structure with space group  $P2_1/n$  were inhibited. The fergusonite distortion of the scheelite structure is particularly small both structurally and energetically in  $\text{BaWO}_4$  and thus the energy-volume curves for these phases are not distinguishable in Fig. 7.

The transitions from the low-pressure scheelite phases to the high-pressure  $P2_1/n$  phases ( $\text{BaWO}_4\text{-II}$  and  $\text{PbWO}_4\text{-III}$ ) are first-order reconstructive transformations with a large associated change in volume (about 12% for  $\text{BaWO}_4$  and 9% for  $\text{PbWO}_4$ , in good agreement with the experiments Ref. 25 and 26) and involve extensive rearrangement of the crystal structure. Because of this, the rate at which these transformations occur may be very slow and unstable (metastable) polymorphs may exist for very long periods of time at room temperature. This may be in the origin of the observation of the fergusonite structure in the ADXRD experiments under compression. The fact that  $\text{PbWO}_4\text{-III}$  and  $\text{BaWO}_4\text{-II}$  exists at high pressure above 350 °C and 600 °C, and are quenchable to ambient conditions<sup>25,26</sup> supports the idea that in the experiments fergusonite is observed instead of  $\text{PbWO}_4\text{-III}$  ( $\text{BaWO}_4\text{-II}$ ) due to a kinetic hindrance of the equilibrium phase transformation. On the other hand, the scheelite-to-fergusonite transition is a displacive transformation involving only small adjustments to the crystal structure. Such barrierless continuous or quasicontinuous transformations with none or very little change in volume are fully reversible, as observed in the experiments.

On further pressure increase in  $\text{BaWO}_4\text{-II}$  we find that this phase becomes unstable to the  $\text{BaMnF}_4$ -type structure around 27 GPa. (This  $\text{BaMnF}_4$ -type structure is related to the  $\text{LaTaO}_4$ -type structure, which turns out to be rather close in energy, and we find that one transforms continuously into the other as the compression progresses—such transition has indeed been reported as induced by temperature in the case of

the compound  $\text{LaTaO}_4$  itself.<sup>59</sup>) On further increase of pressure we find that the orthorhombic  $Cmca$  structure (or *silvanite*) that we proposed in a previous study for  $\text{CaWO}_4$  and  $\text{SrWO}_4$  (Ref. 20) becomes favored above around 56 GPa. In the case of  $\text{PbWO}_4$  the  $Cmca$  structure becomes favored over the  $P2_1/n$  phase ( $\text{PbWO}_4\text{-III}$ ) around 35 GPa.

Now, we would like to discuss the evolution of the fergusonite phase of  $\text{PbWO}_4$  under compression. From our calculations we obtain that, due to the change of the internal parameters, in this structure the W-O coordination changes gradually from 4 to 4+2. Figure 3 gives the evolution obtained for the Pb-O and W-O bond distances of  $\text{PbWO}_4$  under compression. There it can be clearly seen that theoretical calculations predict a change in the W coordination for  $\text{PbWO}_4$  as already comment when discussing the XANES results. No similar evolution in the internal parameters exists in  $\text{CaWO}_4$ ,  $\text{SrWO}_4$  or  $\text{BaWO}_4$ ; however, a similar evolution of the internal parameters has been found in  $\text{YLiF}_4$  according to recent *ab initio* calculations.<sup>60</sup>

An interesting further result of our study is the fact that at expanded volumes (and corresponding *negative* pressures) the zircon structure becomes stable against the scheelite structure in both materials. Mineral zircon ( $\text{ZrSiO}_4$ ) transforms under pressure to a structural phase isomorphous with scheelite<sup>61</sup> which is in agreement with our findings for  $\text{BaWO}_4$  and  $\text{PbWO}_4$  (though here of course the coexistence pressure is negative). Thus, including the expanded region (negative pressures) in the picture the following systematics arise for the first steps of the structural sequence undergone by these materials upon pressure increase:  $I4_1/amd(\text{zircon}) \rightarrow I4_1/a(\text{scheelite}) \rightarrow I2/a(\text{fergusonite}) \rightarrow P2_1/n$ . The zircon structure transforms by means of a *translationgleiche* transition into the scheelite structure [twining zircon on (200), (020), and (002) generates the scheelite-type]. This structure is transformed into the fergusonite structure by means of another *translationgleiche* transition that involves a lowering of the point-group symmetry from  $4/m$  to  $2/m$ . And finally the  $P2_1/n$  structure is naturally obtained by a *klassengleiche* transition from fergusonite. This systematics may have important implications for a number of  $\text{ABX}_4$  structures, especially those with a large difference between the sizes of the  $A$  and  $B$  atoms, which include some important minerals in addition to zircon and scheelite.

In order to better understand the structural behavior of  $\text{ABX}_4$  structures under compression a parallel can be drawn between high-pressure transformations in the  $\text{ABO}_4$  and  $\text{MO}_2$  ( $\text{MMO}_4$ ) octahedral structures. The rutile ( $\text{MO}_2$ ) structure consists of infinite rectilinear rods of edge-sharing  $\text{MO}_6$  octahedra parallel to the  $c$  axis, united by corner sharing to the octahedra in identical corner rods. If  $M$  is alternatively substituted by bigger and smaller cations  $A$  and  $B$  and the cations are shifted in each rod then the zircon structure is obtained. Under compression rutile transforms to the  $\alpha$ - $\text{PbO}_2$ -type structure<sup>62</sup> and both scheelite and fergusonite can be thought as distorted superstructures of  $\alpha$ - $\text{PbO}_2$ . Additionally, the monoclinic post-fergusonite structure that we ob-

served in  $\text{BaWO}_4$  and  $\text{PbWO}_4$  is related to a baddeleyite, post- $\alpha$ - $\text{PbO}_2$  structure of rutile-type  $\text{TiO}_2$  (Ref. 63). Thus the crystal chemistry systematics of  $\text{MO}_2$  compounds provides additional support to the structural sequence that we extract for  $\text{ABO}_4$  compounds from our results.

## V. CONCLUDING REMARKS

We have studied the high-pressure behavior of  $\text{BaWO}_4$  and  $\text{PbWO}_4$  and have found that both compounds undergo a scheelite-to-fergusonite phase transition. On further increase of pressure both compounds transform to a monoclinic structure with space group symmetry  $P2_1/n$ . According to our *ab initio* calculations the scheelite structure is predicted to transform under compression directly to  $P2_1/n$ . We attribute the occurrence of the fergusonite phase in the sequence of structural transitions to the existence of a kinetic barrier that prevents the  $I4_1/a$ -to- $P2_1/n$  from taking place. These conclusions may have important geophysical and geochemical implications since the scheelite-structured orthotungstates are common accessory minerals in various kinds of rocks in the Earth's upper mantle. Pressures of 7 to 10 GPa and temperatures higher than 500 °C are found at a depth of <100 km in the upper mantle.<sup>64</sup> Therefore, this family of minerals that in the Earth's surface are isomorphous to scheelite are likely expected to be isostructural to  $\text{BaWO}_4$ -II in the Earth's upper mantle. Finally, we have found that further increase of pressure leads to amorphization of  $\text{BaWO}_4$  in a similar way to that found previously for  $\text{CaWO}_4$  Ref. 14.

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