Crystal stability and pressure-induced phase transitions in scheelite AWO$_4$ (A = Ca, Sr, Ba, Pb, Eu) binary oxides. I: A review of recent *ab initio* calculations, ADXRD, XANES, and Raman studies

J. López-Solano[1], **P. Rodríguez-Hernández**[1], **S. Radescu**[1], **A. Mujica**[1], **A. Muñoz**[1], **D. Errandonea**[2], **F. J. Manjón**[3], **J. Pellicer-Porres**[2], **N. Garro**[2], **A. Segura**[2], **Ch. Ferrer-Roca**[2], **R. S. Kumar**[4], **O. Tschauner**[4], and **G. Aquilanti**[5]

[1] Dpto. de Física Fundamental II, Universidad de La Laguna, 38205 La Laguna, Tenerife, Spain
[2] Dpto. de Física Aplicada-ICMUV, Univ. de València, C/Dr. Moliner 50, 46100 Burjassot, Spain
[3] Dpto. de Física Aplicada, Univ. Politècnica de València, Cno. de Vera s/n, 46022 Valencia, Spain
[4] HiPSEC, Univ. of Nevada, 4505 Maryland Parkway, Las Vegas, NV 89154-4002, USA
[5] European Synchrotron Radiation Facility, BP 220 Grenoble 38043, France

The structural properties of CaWO$_4$, SrWO$_4$, BaWO$_4$, PbWO$_4$, and EuWO$_4$ scintillating crystals under pressure have been studied by X-ray powder diffraction, X-ray absorption near-edge structure measurements, Raman spectroscopy, and *ab initio* density functional theory calculations. The results obtained from these studies will be reviewed here and their differences and similitudes discussed.

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1   Introduction

At ambient conditions CaWO$_4$, SrWO$_4$, BaWO$_4$, PbWO$_4$, and EuWO$_4$ crystallize in the tetragonal scheelite structure ([SG] I4$_1$/a space group No. 88, $Z = 4$) [1]. These materials have attracted a great deal of interest in the last years due to their use as laser host materials [2], as scintillators in high-energy physics detectors [3], and as oxide ion conductors [4]. Understanding the electro-optical properties of these compounds is important for these applications, a prerequisite for which is the detailed knowledge of their crystal structure. In this contribution we review our recent studies on the effects of pressure in the crystal structure of these scheelite-structured orthotungstates via a combination of *ab initio* calculations [5–9], Raman spectroscopy [5, 6], and X-ray diffraction and absorption measurements [8–12], which have allowed us to establish the sequence of their pressure-driven structural phase transitions.

2   *Ab initio* calculations

Our calculations have been performed within the framework of the density functional theory via a plane-wave basis scheme and ultrasoft pseudopotentials (though the Projector Augmented Wave scheme was used in the case of BaWO$_4$) [13] as implemented in the Vienna *Ab initio* Simulation Package (VASP) [14]. A more detailed description of the calculations can be found in Refs. [5–9].

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* Corresponding author: e-mail: javierl@marengo.dfis.ull.es, Phone: +34 922 318 275, Fax: +34 922 318 320
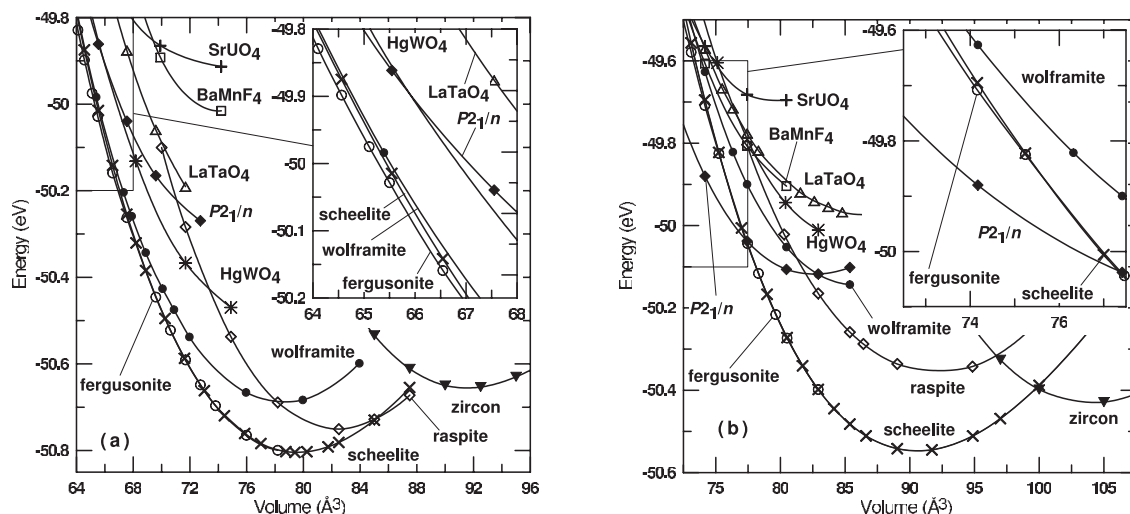
Fig. 1 Calculated energy-volume per formula unit curves for (a) $CaWO_4$ and (b) $SrWO_4$.

Figure 1 shows the calculated energy-volume curves of $CaWO_4$ and of $SrWO_4$ (which is similar to those of $PbWO_4$ and $BaWO_4$, see Ref. [9]). In order to establish the sequence of stable phases, we have considered several structures which have been observed in these or related compounds, like the fergusonite structure (SG I2/a No. 15, $Z = 4$), the structure of the isomorphous phases $PbWO_4$-III and $BaWO_4$-II (SG $P2_1/n$ No. 14, $Z = 8$, hereafter refered to as "$P2_1/n$"), and the $BaMnF_4$-type structure (SG $Cmc2_1$ No. 36, $Z = 4$). Further analysis of the structures with SG No. 14 and $Z = 4$ has led us to propose a novel structure, with $Cmca$ symmetry and $Z = 8$, as stable at higher pressures in the four tungstates studied (see Ref. [8, 9] for full structural data). To complement these static calculations and help in the identification of the Raman modes observed in our experiments (see Section 4) we have also performed lattice dynamics calculations at selected pressures for the Gamma point of the scheelite, fergusonite, and $P2_1/n$ structures of $PbWO_4$ and $BaWO_4$ [5, 6] using the direct, small displacements method [15, 16].

The calculated sequences of transitions are summarized in Table 1, together with the experimentally observed ones. Our theoretical results show that the scheelite phases have the lowest energy at ambient pressure in all four compounds. On increasing pressure, a fergusonite-type distortion of the scheelite structure becomes increasingly more noticeable from the structural point of view, and its energy becomes lower than that of the ambient pressure phase. Thus we find a second order, slow and continuous, phase transition from scheelite to fergusonite, in good agreement with the ADXRD and XANES experiments.

However, our calculations in $SrWO_4$, $BaWO_4$, and $PbWO_4$ show that the $P2_1/n$ structure ($BaWO_4$-II-type) has indeed lower enthalpy than the fergusonite structure, and thus the transition should be from scheelite to $P2_1/n$. It should be stressed that the previous experimental observations of the $P2_1/n$ phases in $PbWO_4$ and $BaWO_4$ [17, 18] required the application of both high pressure and high temperature to the respective scheelite phases, whereas our present calculations have been performed at 0 K. The scheelite-to-$P2_1/n$ transitions are strongly first order with large density changes (9–12%) and involve extensive rearrangement of the crystal structure, in contrast to the second-order scheelite-to-fergusonite transitions. Thus, the barrierless transition to the fergusonite structure may happen at pressures at which the first-order transition to the $P2_1/n$ structure is kinetically hindered. The presence of kinetic barriers may also explain the need for high temperature in the previous experimental observations of this phase in $PbWO_4$ and $BaWO_4$. In support of this picture, our X-ray experiments in $BaWO_4$ and $PbWO_4$ [9] find indications of $P2_1/n$ as post-fergusonite stable phases at higher pressures than our calculated coexistence pressures (see Section 3). Our more recent Raman experiments [5, 6] have found a mixture of the $P2_1/n$ and fergusonite phases at pressures slightly above the theoretical ones, whereas as pressure further increases only the $P2_1/n$ phase was observed, again in agreement with the theoretical picture.

Though there is no experimental confirmation of a P2$_1$/n structure in SrWO$_4$, the position of this compound in Bastide's diagram close to PbWO$_4$ and BaWO$_4$ supports its existence (see part II of this paper [19]). On the other hand, CaWO$_4$ is quite apart from the other three tungstates in Bastide's diagram, and its $E-V$ diagram shows the fergusonite structure as more stable than the P2$_1$/n structure.

For all four compounds we predict a further transition (around 30 GPa in CaWO$_4$, SrWO$_4$, and PbWO$_4$ and at rather larger pressures in BaWO$_4$) to a structure with Cmca symmetry which to our knowledge has not been previously considered either theoretically or experimentally [8, 9]. In BaWO$_4$, a structure similar to that of BaMnF$_4$ is found as an intermediate phase between the BaWO$_4$-II and Cmca phases [9].

Table 1 Room temperature (RT) structural sequence and transition pressures of AWO$_4$ orthotungstates according to different experimental and theoretical studies. The following notation is used: scheelite (S), fergusonite (F).

material	technique	structural sequence	Ref.
CaWO$_4$	ADRXD	10.5(8) GPa scheelite → fergusonite	[8, 21]
	XANES	11.3(10) GPa scheelite → fergusonite	[8]
	Raman	10 GPa scheelite → monoclinic	[26]
	theory	8 GPa 29 GPa scheelite → fergusonite → Cmca	[8]
SrWO$_4$	ADXRD	9.9(2) GPa scheelite → fergusonite	[8, 22]
	XANES	13.7(17) GPa scheelite → fergusonite	[8]
	Raman	11.5 GPa scheelite → monoclinic	[27]
	theory	9.8 GPa 32 GPa 10 GPa scheelite → P2$_1$/n → Cmca scheelite → fergusonite	[8]
BaWO$_4$	ADXRD	7.1(2) GPa 10.7(2) GPa scheelite → fergusonite → BaWO$_4$-II	[9, 20]
	XANES	9.8 GPa scheelite → BaWO$_4$-II	[9]
	Raman	6.9(4) GPa 7.5(3) GPa 9.5(5) GPa scheelite → S + BaWO$_4$-II → S + F + BaWO$_4$-II → BaWO$_4$-II	[5, 24]
	theory	5.1 GPa 27 GPa 57 GPa 7.5 GPa scheelite → BaWO$_4$-II → BaMnF$_4$ → Cmca scheelite → fergusonite	[9]
PbWO$_4$	ADXRD	9(1) GPa 14.6(10) GPa scheelite → fergusonite → PbWO$_4$-III	[9]
	XANES	9 GPa 16.7 GPa scheelite → fergusonite → PbWO$_4$-III	[9]
	Raman	6.2(3) GPa 7.9(3) GPa 9.5(5) GPa 14.6(6) GPa S → S + PbWO$_4$-III → S + F + PbWO$_4$-III → F + PbWO$_4$-III → PbWO$_4$-III	[6, 25]
	theory	5.3 GPa 35 GPa 8 GPa scheelite → PbWO$_4$-III → Cmca scheelite → fergusonite	[9]
EuWO$_4$	EDRXD	8.5(5) GPa scheelite → fergusonite	[10]

3   X-ray diffraction and absorption measurements

We have studied $CaWO_4$, $SrWO_4$, $BaWO_4$ and $PbWO_4$ under compression up to 25 GPa by means of angle-dispersive X-ray powder diffraction (ADXRD) and X-ray-absorption near-edge structure (XANES) measurements [8, 9]. $EuWO_4$ was also studied, but only up to 12 GPa by energy-dispersive X-ray powder diffraction (EDXRD) [9]. A synchrotron source was used in both cases. ADXRD and XANES experiments were performed in a diamond-anvil cell (DAC) at the APS (16-IDB beamline) and the ESRF (ID24 beamline), respectively. EDXRD measurements were conducted in a DAC at the NSLS (X-17C beamline). The experimental procedures have been previously described in detail [8–10].

In the X-ray diffraction studies we observed that the scheelite phase remains stable up to 7–10 GPa when a reversible phase transition took place (see Table 1 for details). This transition is characterized by the splitting of several Bragg peaks and the appearance of new reflections [8–10]. The structural refinements of the diffraction patterns of the high-pressure phases show that for all five compounds studied they correspond to the monoclinic fergusonite structure [8–10]. These results agree with those reported by Panchal et al. [20] and Grzechnik et al. [21, 22]. The scheelite-to-fergusonite transition pressures compare well with those estimated from a systematic analysis of the packing ratio of the anionic WO_4 units around the A cations [23]. We find that the fergusonite-type phase remains stable up to 20 GPa in $CaWO_4$ and $SrWO_4$ and up to 12 GPa in $EuWO_4$ but a second transition is observed in $BaWO_4$ and $PbWO_4$ near 10 GPa and 15 GPa, respectively. This transition occurs together with a large volume collapse and the diffraction patterns can be reasonably fitted with the $P2_1/n$ structure of the $BaWO_4$-II and $PbWO_4$-III phases [9].

XANES measurements give information about the local arrangement of the atoms surrounding the absorbing atom, so they complement the information yielded by ADXRD. We have used XANES experiments (WL_3-edge) to investigate changes in the W coordination under pressure [8, 9]. The results of our study support the existence of a scheelite-to-fergusonite transition. We find that the monoclinic distortion triggered at the phase transition increases upon compression. The small changes of the local environment around the absorbing atom make XANES sensitive to the phase transition at slightly higher pressures than ADXRD. Because of this and the proximity of the first and second transitions in $BaWO_4$, our XANES experiments in this material were unable to clearly distinguish the fergusonite phase [9]. However, the resonances of the XANES spectra of $BaWO_4$ loose intensity at 7.8 GPa which is close to the expected scheelite-to-fergusonite transition pressure. The XANES spectra show that the second transition to the $P2_1/n$ structure ($BaWO_4$-II and $PbWO_4$-III phases) leads to an increase in the W−O coordination from 4 to 6, which reflects the fact that these high-pressure phases consist of densely packed networks of distorted WO_6 octahedra [9].

4   Raman spectroscopy

Raman spectroscopy is a subtle tool capable of distinguishing small traces of various local phases coexisting in a compound. In order to obtain a deeper understanding of the structural behaviour of scheelite-type AWO_4 scintillating crystals under pressure we have performed lattice dynamics studies comprising both Raman measurements in single crystals of $BaWO_4$ and $PbWO_4$ in a DAC and *ab initio* lattice dynamics calculations [5, 6]. For $BaWO_4$ [5] we observed the coexistence of weak peaks assigned to the $BaWO_4$-II phase with the scheelite peaks already at 6.9 GPa. Additionally, from 7.5 GPa to 9.0 GPa we found a mixture of the scheelite, $BaWO_4$-II, and fergusonite phases, with the fergusonite phase being dominant in this pressure range. The sample completely transformed to the $BaWO_4$-II phase at 9.5 GPa. Figure 2 shows the measured Raman spectra of $BaWO_4$ at 300 K at three different pressures. At 7.5 GPa the dominant structure is fergusonite but there is in fact a strong mixture with the other two structures evidenced by the extra peaks in the spectrum.

For $PbWO_4$ [6] we observed a similar behaviour; weak peaks assigned to $PbWO_4$-III coexist with the scheelite peaks from 6.2 GPa to 9 GPa. At 7.9 GPa the fergusonite phase appears and becomes dominant, but the $PbWO_4$-III and scheelite phases are also present. Above 9.5 GPa the scheelite phase disappears
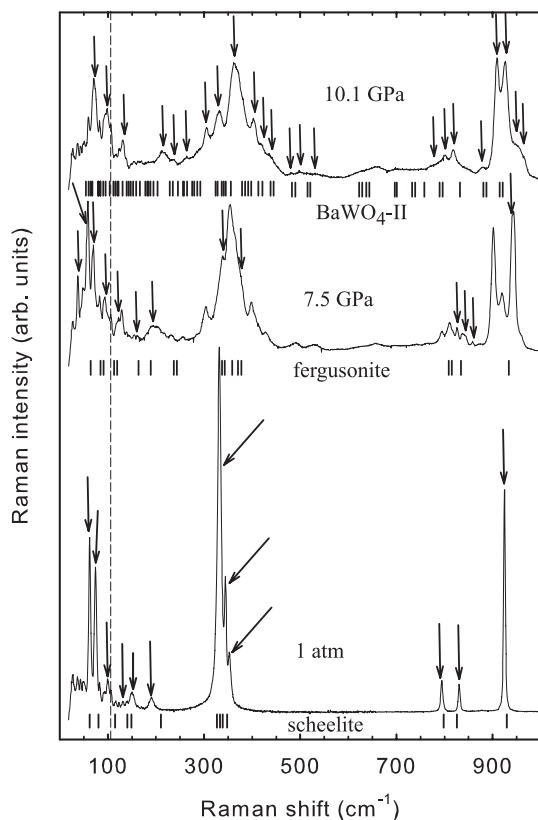
Fig. 2 Measured Raman spectra of $BaWO_4$ at pressures of 1 atm, 7.5 GPa, and 10.1 GPa. At each of these pressures the dominant structures are scheelite, fergusonite, and $BaWO_4$-II, respectively. The small vertical lines under the Raman spectra correspond to the calculated frecuencies for the dominant structures. The arrows indicate the peaks asigned to the dominant structures after the analysis described in Ref. [5].

and the fergusonite phase dominates up to 12.6 GPa. Above 14.6 GPa the sample transforms completely to the $PbWO_4$-III phase. The observed coexistence of the fergusonite and $P2_1/n$ phases supports the idea that there is a kinetic hindrance that prevents the $I4_1/a$-to-$P2_1/n$ phase transition for taking place. This also explains the observation of scheelite-to-fergusonite as the first phase transition in ADXRD experiments [8, 9, 20, 22]. The results of our high pressure Raman study are in good agreement with previous Raman experiments on $CaWO_4$, $SrWO_4$, $BaWO_4$, and $PbWO_4$ under pressure [24–27]. Furthermore, based upon our lattice dynamics studies we conclude that the Raman spectra of the high-pressure phases of $CaWO_4$ and $SrWO_4$, previously supposed to be of an unknown monoclinic structure [25, 26], correspond in fact to the fergusonite structure [5].

5   Concluding remarks

We have experimentally and theoretically studied the pressure behaviour of scheelite AWO_4 compounds (A = Ca, Sr, Ba, Pb, Eu) and find that $CaWO_4$ and $EuWO_4$ undergo a scheelite-to-fergusonite transition, while $SrWO_4$, $BaWO_4$, and $PbWO_4$ undergo a scheelite-to-$P2_1/n$ transition. This last transition is kinetically hindered and consequently the second-order scheelite-to-fergusonite transition is also observed in $BaWO_4$, $SrWO_4$, and $PbWO_4$. At higher pressures our calculations predict transitions to denser orthorhombic phases.

References

[1] A.W. Sleigth, Acta Cryst. B **28**, 2899 (1972).
[2] W. Chen, Y. Inagawa, T. Omatsu et al., Opt. Commun. **194**, 401 (2001).
[3] P. Lecoq, I. Dafinei, E. Auffray et al., Nucl. Instrum. Methods Phys. Res. A **365**, 291 (1995).
[4] S. Takai, K. Sugiura, and T. Esaka, Mater. Res. Bull. **34**, 193 (1999).
[5] F. J. Manjón, D. Errandonea, N. Garro et al., Phys. Rev. B **74**, 144111 (2006).
[6] F. J. Manjón, D. Errandonea, N. Garro et al., Phys. Rev. B **74**, 144112 (2006).
[7] P. Rodríguez-Hernández, J. López-Solano, S. Radescu et al., J. Phys. Chem. Solids **67**, 2164 (2006).
[8] D. Errandonea, J. Pellicer-Porres, F. J. Manjón et al., Phys. Rev. B **72**, 174106 (2005).
[9] D. Errandonea, J. Pellicer-Porres, F. J. Manjón et al., Phys. Rev. B **73**, 224103 (2006).
[10] D. Errandonea, phys. stat. sol. (b) **242**, R125 (2005).
[11] D. Errandonea, M. Somayazulu, and D. Häusermann, phys. stat. sol. (b) **231**, R1 (2002).
[12] D. Errandonea, M. Somayazulu, and D. Häusermann, phys. stat. sol. (b) **235**, 162 (2003).
[13] G. Kresse, and D. Joubert, Phys. Rev. B **59**, 1758 (1999).
[14] G. Kresse et al., computer code VASP. For more information, visit http://cms.mpi.univie.ac.at/vasp.
[15] D. Alfè, G. D. Price, and M. J. Gillan, Phys. Rev. B **64**, 045123 (2001).
[16] G. Kresse, J. Furthmüller, and J. Hafner, Europhys. Lett. **32**(9), 729 (1995).
[17] I. Kawada, K. Kato, and T. Fujita, Acta Cryst. B **30**, 2069 (1974).
[18] P. W. Richter, G. J. Kruger, and C. W. F. T. Pistorius, Acta Cryst. B **32**, 928 (1976).
[19] F. J. Manjón, D. Errandonea, J. López-Solano et al., phys. stat. sol. (b) **244**, No. 1 (2007). This issue.
[20] V. Panchal, N. Garg, A. K. Chauhan, Sangeeta, and S. M. Sharma, Solid State Commun. **130**, 203 (2004).
[21] A. Grzechnik, W. A. Crichton, M. Hanfland, and S. Van Smaalen, J. Phys.: Condens. Matter **15**, 7261 (2003).
[22] A. Grzechnik, W. A. Crichton, and M. Hanfland, phys. stat. sol. (b) **242**, 2795 (2005).
[23] D. Errandonea, F. J. Manjón, M. Somayazulu, and D. Häusermann, J. Solid State Chem. **177**, 1087 (2004).
[24] A. Jayaraman, B. Batlogg, and L. G. Van Uitert, Phys. Rev. B **28**, 4774 (1983).
[25] A. Jayaraman, B. Batlogg, and L. G. Van Uitert, Phys. Rev. B **31**, 5423 (1985).
[26] D. Christofilos, S. Ves, and G. A. Kourouklis, phys. stat. sol. (b) **198**, 539 (1996).
[27] D. Christofilos, K. Papagelis, S. Ves et al., J. Phys.: Condens. Matter **14**, 12641 (2002).