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High-pressure theoretical and experimental study of HgWO₄

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High-pressure theoretical and experimental study of HgWO₄

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HgWO₄ at ambient pressure is characterized using a combination of *ab initio* calculations, X-ray diffraction and Raman scattering measurements. The effect of low pressure and temperature on the structural stability is analysed. Extending our *ab initio* study to the range of higher pressures, a sequence of stable phases up to 30 GPa is proposed.

Keywords: phase transitions; tungstates; *ab initio* calculations; Raman scattering; X-ray diffraction

1. Introduction

In spite of the interest that ABO₄ compounds have attracted in recent years, the pressure behavior of mercury tungstate remains largely unknown. It is, however, a rather interesting compound, since it does not crystallize in the scheelite (CaWO₄-type, space group (SG) no. 88, *I*2/*a*, *Z* = 4) nor in the wolframite (NiWO₄-type, SG no. 12, *P*2/*c*, *Z* = 2) structures, the two most usual ambient-pressure structures for tungstates [1]. The HgWO₄-type (SG no. 15, *C*2/*c*, *Z* = 4) structure has some similarities with the wolframite, but in particular the cationic environments are different, as reflected by the coordinations: [6,6] for wolframite and [6 + 2, 6] for HgWO₄-type, where the first number in brackets is the oxygen coordination of the Hg cation and the second that of the W. Thus, the sequence of stable phases under pressure of HgWO₄ can be expected to have notable differences with respect to the ones proposed for compounds with the scheelite or wolframite structure, scheelite → fergusonite → BaWO₄-II-type [1] and wolframite → CuWO₄-type → Cmca [2–4], respectively.

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In this paper, we study the pressure behavior of HgWO_4 . Although we include some results of our X-ray diffraction and Raman scattering measurements, we will focus on our theoretical *ab initio* calculations. Further details of our experimental work can be found in [5].

2. Method

All the *ab initio* calculations presented in this work have been performed with the VASP [6,7] code, which works within the density functional theory framework, using the plane-waves basis and pseudopotentials. Projector augmented-wave [8] pseudopotentials and the recently proposed PBEsol [9] approximation for the exchange and correlation energy have been adopted. The latter is a generalized gradient approximation (GGA) form tuned to produce a good description of the structural equilibrium properties of solids and surfaces.

An energy cut-off of 530 eV for the plane-waves basis and dense Monkhorst and Pack [10] reciprocal space grids ensure an energy convergence of 1 meV per formula unit. For each structure and volume considered, a full optimization of the lattice parameters and atomic positions was performed until the components of the stress tensor differed from the isotropic diagonal form in less than 0.1 GPa, and the maximum atomic force was lower than 0.001 eV/Å.

The energy and volume data were fitted with a fourth-order Birch–Murnaghan equation of state to obtain the pressure, equilibrium volume (V_0), bulk modulus (B_0) and the first and second derivatives of the latter (B'_0 and B''_0 , respectively). From the values of energy, volume and pressure, the enthalpy of each structure was calculated to determine the most stable phase among the ones considered at each pressure and zero temperature (zero-point motion effects were also not included). The Gibbs free energy was calculated within the quasi-harmonic Debye approximation with the GIBBS [11] code to estimate the effect of temperature on the HgWO_4 -type \rightarrow wolframite transition. Phonon frequencies at the Γ point of the HgWO_4 -type structure were calculated using the direct force constant method [12], as implemented in the PHONON code [13].

3. Results and discussion

Figure 1 shows the energy as a function of volume curves for all the structures considered as possible stable phases of HgWO_4 . Among these structures, the calculations find the HgWO_4 -type as the lowest-energy phase at zero pressure, in agreement with the experimental observations. The calculated values of V_0 , B_0 , B'_0 and B''_0 are, respectively, 81.61 Å³ per formula unit, 60.6 GPa, 8.9 and -0.8 GPa^{-1} . The experimental values of V_0 , B_0 and B'_0 are, respectively, 81.01 Å³, 72.7 GPa, and 5.1 [5], so that there is a reasonable agreement between theory and experiment.

In Table 1, calculated Raman frequencies are presented together with the data from our Raman experiments. The overall agreement is quite reasonable, with a small underestimation of the theoretical values with respect to the experimental ones which has been related to the GGA approximation [14]. X-ray diffraction patterns can also be indexed with an HgWO_4 -type structural model (see Figure 2(a) in [5]). Thus, the ambient-pressure phase of HgWO_4 is unequivocally determined.

Upon an increase in pressure, the wolframite structure becomes more stable than the HgWO_4 -type, as shown by the free energy as a function of pressure curves of Figure 2. As pointed out in [15], both structures are very similar. In the $I2/a$ setting, the HgWO_4 -type structure features lattice parameters very close to those of a wolframite $P2/c$ supercell doubled along its c -axis, as shown in Figure 3. The atomic positions are also similar, the most noticeable difference being in the stacking of the oxygens [15], which produces rather different environments around both

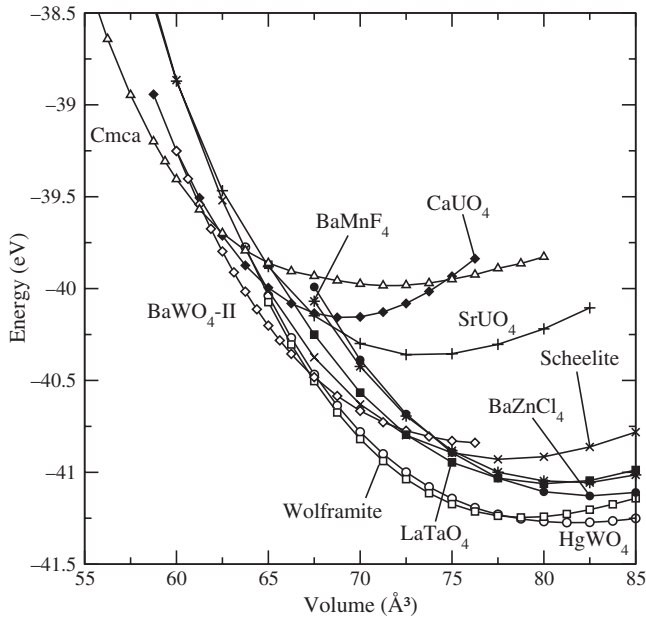


Figure 1. *Ab initio* calculated energy as a function of volume curves for the HgWO₄-type (empty circles), wolframite (empty squares), BaWO₄-II-type (empty diamonds), Cmca (empty triangles), BaZnCl₄-type (filled circles), LaTaO₄-type (filled squares), scheelite (crosses), CaUO₄-type (filled diamonds), BaMnF₄-type (stars) and SrUO₄-type (plus signs) structures. The fergusonite structure was found to be identical to the scheelite and the CuWO₄-type to the wolframite. Energy and volume are written per formula unit.

Table 1. *Ab initio* calculated and experimental Raman frequencies ω (cm⁻¹) for the HgWO₄-type structure at ambient pressure.

Mode	ω (<i>ab initio</i>)	ω (experiment)	Mode	ω (<i>ab initio</i>)	ω (experiment)
B _g	87	89	A _g	353	374
B _g	133	139	B _g	491	508
A _g	141	145	A _g	525	537
A _g	184	193	A _g	683	698
B _g	200	204	B _g	695	715
B _g	216	228	B _g	827	842
A _g	268	278	A _g	907	924
B _g	280	292			

cations. Despite all these similarities, which explain their proximity in energy, it should be stressed that in our calculations the two structures are markedly different.

It should also be noted that in our experiments at ambient temperature we did not find indications of the wolframite structure up to the maximum pressure reached of 16 GPa for X-ray diffraction experiments and 25 GPa for Raman scattering measurements (although the quality of the Raman spectra above 16 GPa is poor [5]). To estimate the effect of the temperature on these energetically close phases, we have calculated the Gibbs free energy of the HgWO₄-type and wolframite structures at 300 K within the Debye approximation. The difference in free energy between both phases is marked by the dashed line of Figure 2(b). As shown, temperature makes the wolframite phase more unfavourable with respect to the HgWO₄-type, and the transition pressure is increased from ~ 2 GPa at 0 K to ~ 11 GPa at 300 K. This pressure is rather close to the

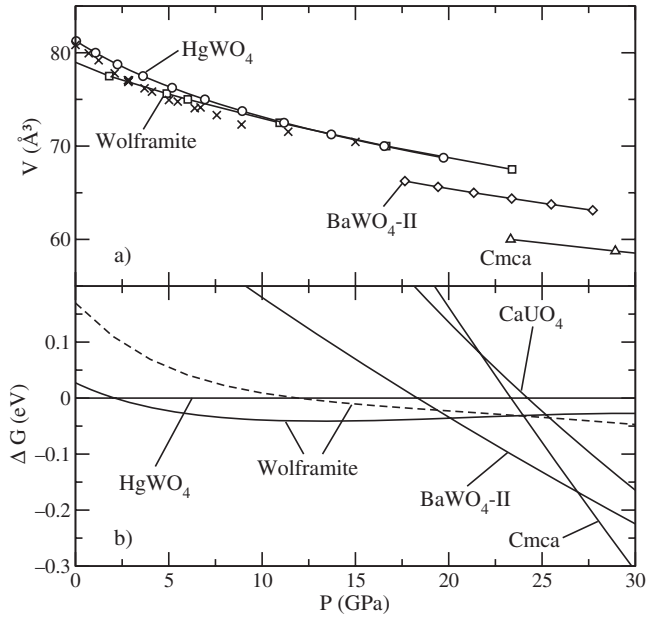


Figure 2. (a) Volume as a function of pressure and (b) Gibbs free energy as a function of pressure. In (a), the theoretical data for the HgWO₄-type (circles), wolframite (squares), BaWO₄-II (diamonds) and Cmca (triangles) are shown; crosses correspond to experimental data of the HgWO₄-type structure. In (b), continuous lines are used for calculations at 0 K without zero-point motion effects, and a dashed line for the calculation at 300 K. At each pressure and temperature, the free energy is measured with respect to that of the HgWO₄-type phase. Volume and free energy are written per formula unit.

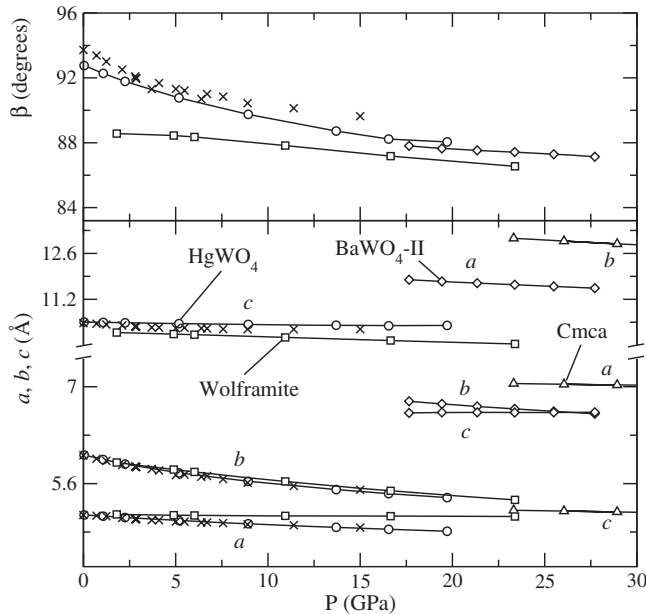


Figure 3. Calculated lattice parameters a , b , c and β of the HgWO₄-type (circles), wolframite (squares), BaWO₄-II-type (diamonds) and Cmca (triangles) structures. Experimental data of the HgWO₄-type structure are marked by crosses. For an easier comparison with the $P2/c$ wolframite, the HgWO₄-type structure is shown in the $I2/a$ setting. The c -axis of the wolframite is shown multiplied by 2.

maximum reached in experiments, where measurements are of lower quality, and this may justify the lack of experimental observations of the wolframite phase.

As a final comment with regard to the stability at lower pressures, we note that in the present calculations a full optimization of the lattice and atomic parameters of the triclinic CuWO_4 -type (SG no. 2, $P-1$, $Z = 2$) structure have lead to the wolframite structure. This is in marked contrast to the situation found in the Mg, Zn and Cd tungstates [2–4]. Also, the fergusonite (YNbO_4 -type, SG no. 15, $I2/a$, $Z = 4$) structure has been found to be identical to the scheelite.

Extending our *ab initio* study to higher pressures, we have considered several candidates for stable phases: BaWO_4 -II-type (SG no. 14, $P2_1/n$, $Z = 8$), Cmca (SG no. 64, Cmca , $Z = 8$), BaZnCl_4 -type (SG no. 60, $Pbcm$, $Z = 4$), LaTaO_4 -type (SG no. 14, $P2/c$, $Z = 4$), CaUO_4 -type (SG no. 166, $R-3m$, $Z = 1$), BaMnF_4 -type (SG no. 36, $A2_1am$, $Z = 4$) and SrUO_4 -type (SG no. 57, $Pbcm$, $Z = 4$) structures. Some of these structures have been found to be energetically competitive in previous works and all are likely high-pressure phases on the basis of crystal-chemical considerations [1]. Although ambient temperature can affect energetically close phases at low pressures, it is unlikely that it will completely modify the sequence of stable phases under high pressure, and thus we have performed only zero-temperature calculations. As shown in Figure 2(b), the BaWO_4 -II-type structure becomes the most stable after the wolframite and HgWO_4 -type structures. Increasing the pressure further, the BaWO_4 -II-type structure becomes unstable with respect to the Cmca . In these two first-order transitions, the coordination changes first from $[6 + 2, 6]$ to $[8, 6]$, and then to $[11, 6 + 1]$. The sequence HgWO_4 -type \rightarrow BaWO_4 -II-type \rightarrow Cmca of transitions under pressure bears similarities to the sequences of both the scheelite and the wolframite compounds.

4. Concluding remarks

The *ab initio* and experimental results presented in this work for the stability at low pressures and low temperatures are in agreement and show that the HgWO_4 -type is the stable phase in these conditions. At high pressures, the BaWO_4 -II-type and Cmca phases found stable in our *ab initio* calculations have been reported in previous works on other ABO_4 compounds. Further experimental work at high pressures is needed to confirm the high-pressure behavior of HgWO_4 .

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