High-pressure theoretical and experimental study of HgWO₄

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Abstract

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 analyzed. 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

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1. Introduction

In spite of the interest ABO_4 compounds have attracted in recent years, the pressure behaviour 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, $I2/a$, $Z=4$) nor in the wolframite (NiWO₄-type, SG no. 12, $P2/c$, $Z=2$) structures, the two most usual ambient-pressure structures for tungstates [1]. The HgWO₄-type (SG no. 15, $C2/c$, $Z=4$) 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 HgWO$_4$-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 HgWO$_4$ can be expected to have notable differences with respect to the ones proposed for compounds with the scheelite or wolframite structure, scheelite→fergusonite→BaWO$_4$-II-type [1] and wolframite→CuWO$_4$-type→Cmca [2-4] respectively.

In this paper, we study the pressure behaviour 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 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 GGA approximation tuned to produce a good description of the structural equilibrium properties of solids and surfaces.

An energy cutoff of 530 eV for the plane-waves basis and dense Monkhorst-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^3.

The energy and volume data were fitted with a 4th order Birch-Murnaghan equation of state to obtain the pressure, equilibrium volume (V_0), bulk modulus (B_0) and the first derivative of the latter (B'_0). From the values of energy, volume and pressure, the enthalpy of each structure was calculated to determine the most stable phase amongst 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→wolframite transition. Phonon frequencies at the Γ point of the HgWO$_4$-type structure were calculated using the small displacements method [12].

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, and B'_0 are respectively 81.61 $Å^3$ per formula unit, 60.6 GPa, and 8.9, which are in good agreement with the experimental values of 81.01 $Å^3$, 72.7 GPa, and 5.1. In particular note that the PBEsol approximation overestimates V_0 by less than 1%, much lower than the usual 5% produced by other GGA approximations.

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 [13]. X-ray diffraction patterns can also be indexed with a $HgWO_4$-type structural model (see **Figure 2.(a)** in [5]). Thus, the ambient-pressure phase of $HgWO_4$ is unequivocally determined.

Upon increase of 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 [14], 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 [14], which produces rather different environments around both cations. Despite all these similarities, which justify 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 didn't found 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 $HgWO_4$-type and wolframite structures at 300 K within the Debye approximation. The difference in free energy between both phases is marked by the discontinuous line of **Figure 2.(b)**. As shown, temperature makes the wolframite phase more unfavourable with respect to the $HgWO_4$-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 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, *Pbcn*, 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 ones. 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→BaWO$_4$-II-type→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 pressure and low temperature are in agreement, and show that the HgWO$_4$-type is the stable phase in these conditions. At high pressure, 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 pressure would be needed to confirm the high pressure behaviour of HgWO$_4$.

References

[1] F.J. Manjón, and D. Errandonea, Phys. Status Solidi B **246**, 9 (2009).

[2] D. Errandonea, F.J. Manjón, N. Garro, P. Rodríguez-Hernández, S. Radescu, A. Mujica, A. Muñoz, and C.Y. Tu, Phys. Rev. B 78, 054116 (2008).

[3] J. Ruiz-Fuertes, S. López-Moreno, D. Errandonea, J. Pellicer-Porres, R. Lacomba-Perales, A. Segura, P. Rodríguez-Hernández, A. Muñoz, A.H. Romero, and J. González, J. Appl. Phys. **107**, 083506 (2010).

[4] R. Lacomba-Perales, D. Errandonea, D. Martínez-García, P. Rodríguez-Hernández, S. Radescu, A. Mújica, A. Muñoz, J.C. Chervin, and A. Polian, Phys. Rev. B **79**, 094105 (2009).

[5] F.J. Manjón, J. López-Solano, S. Ray, O. Gomis, D. Santamaría-Pérez, M. Mollar, V. Panchal, D. Errandonea, P. Rodríguez-Hernández, and A. Muñoz, accepted in Phys. Rev. B (2010).

[6] G. Kresse, and J. Hafner, Phys. Rev. B **47**, 558 (1993).

[7] G. Kresse, and J. Furthmüller, Phys. Rev. B 54, **11169** (1996).

[8] P. E. Blöchl, Phys. Rev. B **50**, 17953 (1994).

[9] J.P. Perdew, A Ruzsinsky, G.I. Csonka, O.A. Vydrov, G.E. Scuseria, L.A. Constantin, X. Zhou, and K. Burke, Phys. Rev. Lett. **100**, 136406 (2008).

[10] H.J. Monkhorst and J. D. Pack, Phys. Rev. B **13**, 5188 (1976).

[11] M.A. Blanco, E. Francisco, and V. Luaña, Comput. Phys. Comm. **158**, 57 (2004).

[12] K. Parlinski, computer code PHONON. Available at http://wolf.ifj.edu.pl/phonon

[13] R. Wahl, D. Vogtenhuber, and G. Kresse, Phys. Rev. B **78**, 104116 (2008).

[14] W. Jeitschko, and A.W. Sleight, Acta Cryst. B **29**, 869 (1973).

Tables

Table 1. *Ab initio* calculated and experimental Raman frequencies ω (cm^{-1}) for the HgWO$_4$-type structure at ambient pressure.

Mode	ω (*ab initio*)	ω (experiment)		Mode	ω (*ab initio*)	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				

Figure captions

Figure 1. *Ab initio* calculated energy as a function of volume curves for the $HgWO_4$-type (empty circles), wolframite (empty squares), $BaWO_4$-II-type (empty diamonds), Cmca (empty triangles), $BaZnCl_4$-type (filled circles), $LaTaO_4$-type (filled squares), scheelite (crosses), $CaUO_4$-type (filled diamonds), $BaMnF_4$-type (stars), and $SrUO_4$-type (plus signs) structures. The fergusonite structure was found to be identical to the scheelite, and the $CuWO_4$-type to the wolframite. Energy and volume are written per formula unit.

Figure 2.(a) Volume as a function of pressure and (b) Gibbs free energy as a function of pressure. In (a) theoretical data for the $HgWO_4$-type (circles), wolframite (squares), $BaWO_4$-II (diamonds), and Cmca (triangles) is shown; crosses correspond to experimental data of the $HgWO_4$-type structure. In (b) continuous lines are used for calculations at 0 K without zero-point motion effects, discontinuous ones for 300 K. At each pressure and temperature the free energy is measured with respect to that of the $HgWO_4$-type phase. Volume and free energy are written per formula unit.

Figure 3. Calculated lattice parameters a, b, c, and β of the $HgWO_4$-type (circles), wolframite (squares), $BaWO_4$-II-type (diamonds), and Cmca (triangles) structures. Experimental data of the $HgWO_4$-type structure is marked by crosses. For an easier comparison with the $P2/c$ wolframite, the $HgWO_4$-type structure is shown in the $I2/a$ setting. The c axis of the wolframite is shown multiplied by 2.
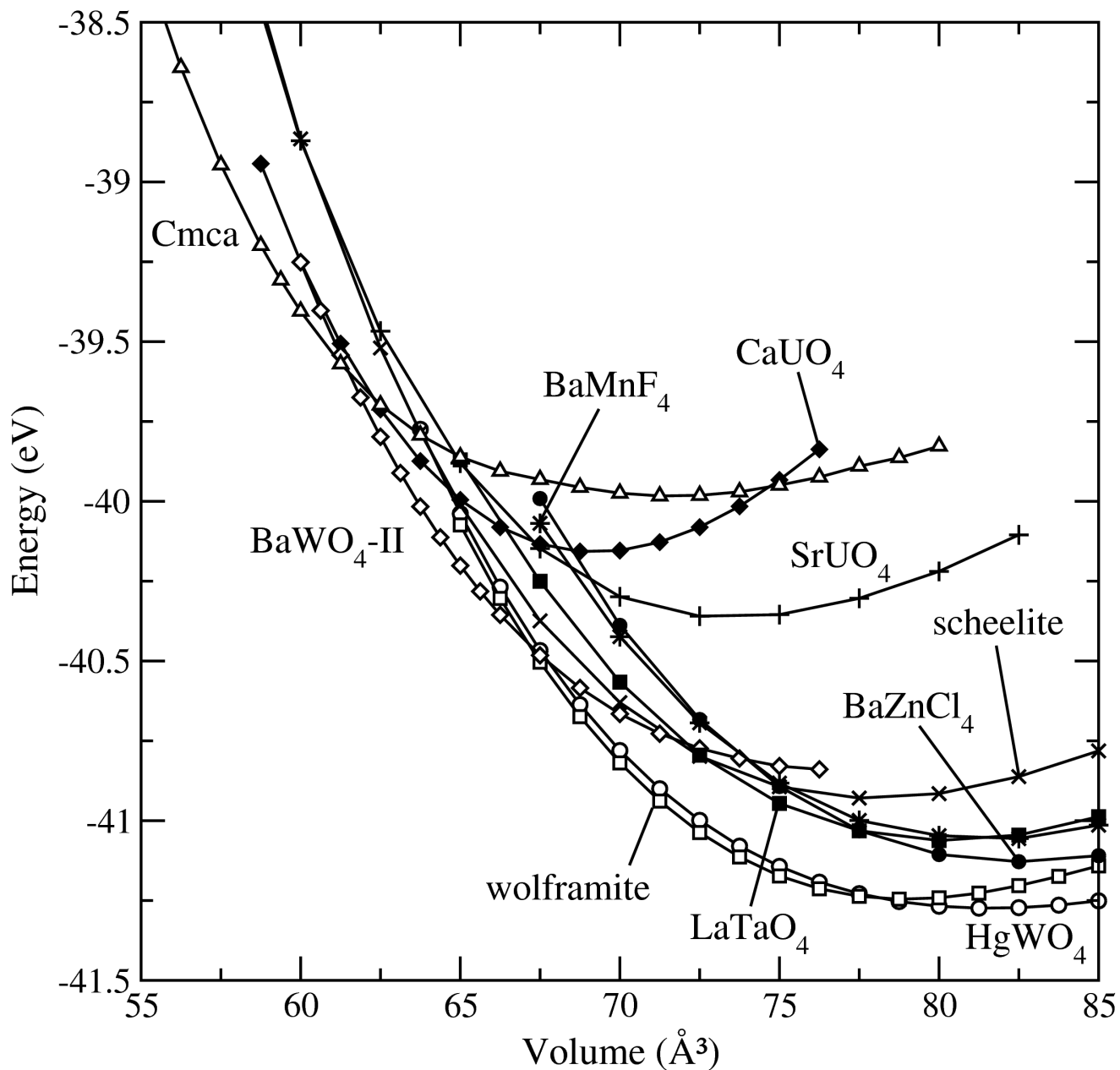
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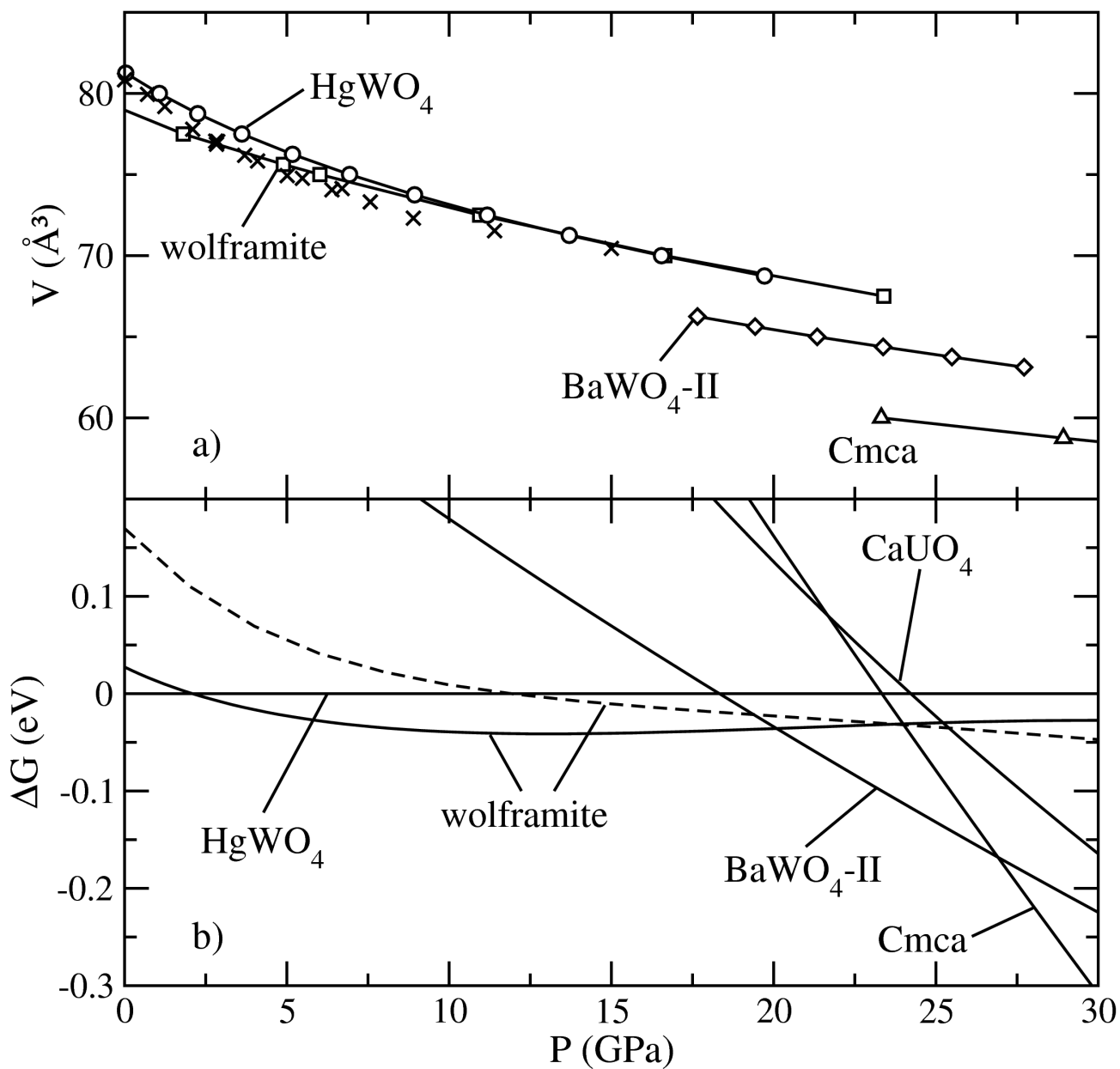
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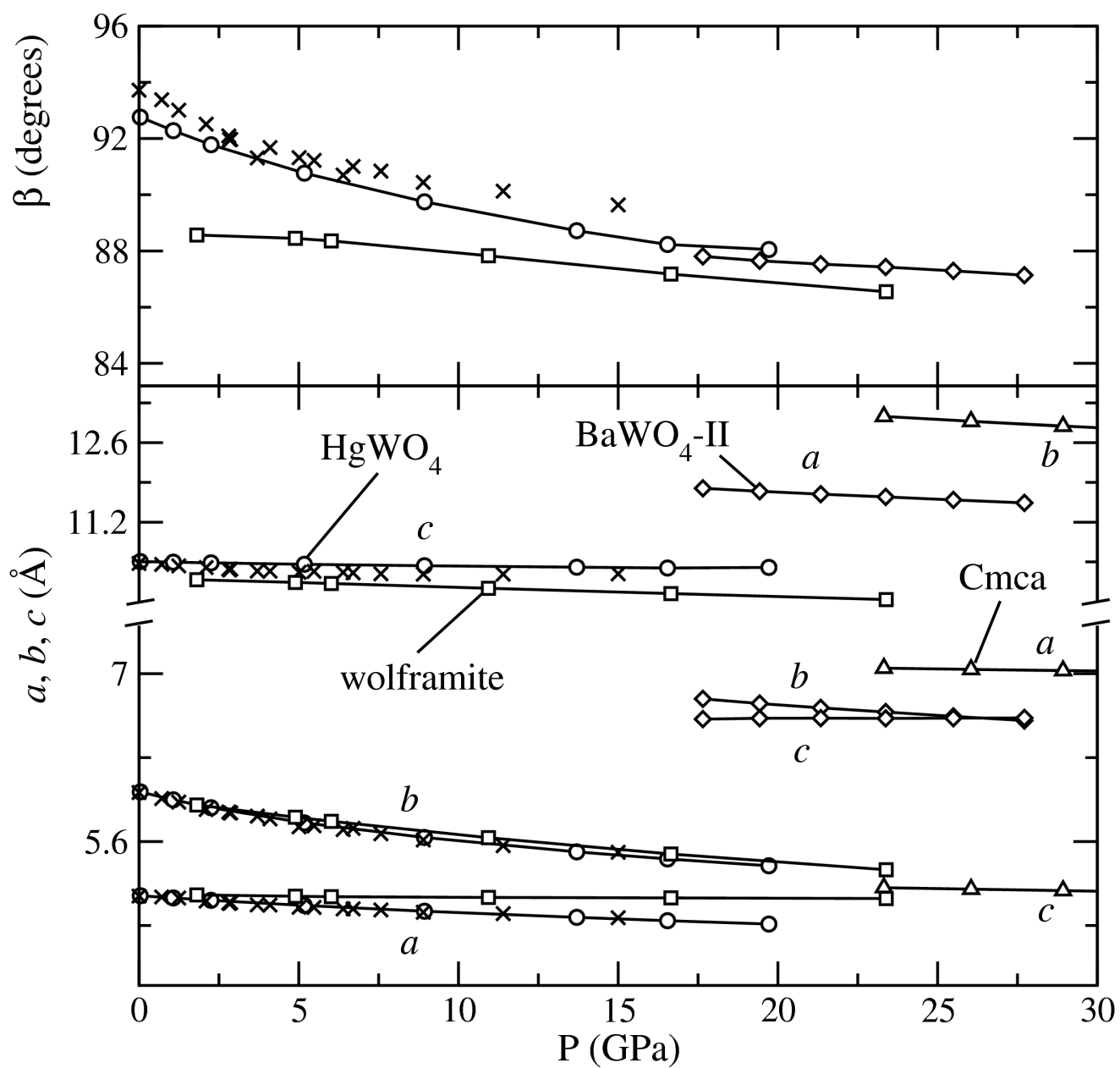
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