Optical and structural study of the pressure-induced phase transition of CdWO₄

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The optical absorption of CdWO₄ is reported at high pressures up to 23 GPa. The onset of a phase transition was detected at 19.5 GPa, in good agreement with a previous Raman spectroscopy study. The crystal structure of the high-pressure phase of CdWO₄ was solved at 22 GPa employing single-crystal synchrotron x-ray diffraction. The symmetry changes from space group P2/c in the low-pressure wolframite phase to P2₁/c in the high-pressure post-wolframite phase accompanied by a doubling of the unit-cell volume. The octahedral oxygen coordination of the tungsten and cadmium ions is increased to [7]-fold and [6+1]-fold, respectively, at the phase transition. The compressibility of the low-pressure phase of CdWO₄ has been reevaluated with powder x-ray diffraction up to 15 GPa finding a bulk modulus of B₀ = 123 GPa. The direct bandgap of the low-pressure phase increases with compression up to 16.9 GPa at 12 meV/GPa. At this point an indirect bandgap crosses the direct bandgap and decreases at -2 meV/GPa up to 19.5 GPa where the phase transition starts. At the phase transition the bandgap collapses by 0.7 eV and another direct bandgap decreases at -50 meV/GPa up to the maximum measured pressure. The structural stability of the post-wolframite structure is confirmed by ab initio calculations finding the post-wolframite-type phase to be more stable than the wolframite at 18 GPa. Lattice dynamic calculations based on space group P2₁/c explain well the Raman-active modes previously measured in the high-pressure post-wolframite phase. The pressure-induced bandgap crossing in the wolframite phase as well as the pressure dependence of the direct bandgap in the high-pressure phase are further discussed with respect to the calculations.

I. INTRODUCTION

Nowadays used as a scintillating detector in x-ray tomography, high-energy particle physics, and dosimetry devices, the wide-bandgap (4 eV) semiconductor cadmium tungstate (CdWO₄) has been extensively studied during the last three decades. It possesses a high light yield emission when hit by γ particles or x-rays and despite its long scintillation time (12-15 μs), it played a key role in the discovery of the natural alpha activity in 180W. Also, the long decay time of the radiation created by self-trapped Frenkel excitons of CdWO₄ makes this material a test bench for studying exciton-exciton interactions in semiconductors. In order to improve the versatility of CdWO₄ as a scintillating material, understanding how doping or externally modifying its interatomic distances affect its electronic structure, are of interest. In this context, pressure is an efficient tool to correlate changes in the bond distances with electronic properties.

CdWO₄ crystallizes in a wolframite-type structure (space group P2/c) at ambient conditions in which both Cd and W atoms are octahedrally coordinated (Fig. 1). Such a structure confers CdWO₄ a direct bandgap along the Z direction of the Brillouin zone. At high pressures, the conduction band, mainly contributed by the 5d W levels, moves up as a result of the increase of repulsion, giving rise to a widening of the band gap at 12(1) meV/GPa up to at least 9.9 GPa. Previous high-pressure polarized optical microscopic studies showed the emergence of aligned color domains at around 10 GPa in CdWO₄, probably due to the low-hydrostatic conditions. However, high-pressure Raman spectroscopy studies revealed that CdWO₄ remains in the wolframite-type structure up to at least 20 GPa. Above this pressure the number of Raman-active modes abruptly increases as a consequence of a phase transition, interpreted by the coexistence of a triclinic CuWO₄-type structure and a tetragonal scheelite-type structure, according to the predictions. The proposed formation and coexistence of the two energetically similarly stable high-pressure phases at the same pressure, though explained the number of the observed Raman modes, is controversial since those Raman spectroscopy experiments were performed using a single crystal. In order to study such a phase transition one should employ a structural technique on a single crystal at the same experimental conditions. However, previous single-crystal x-ray diffraction (SXRD) has been limited to 8.2 GPa. Furthermore, previous electronic band structure calculations have indicated a band crossing in CdWO₄ at 16 GPa, a pressure not experimentally explored yet with optical absorption.

In this work we present a powder XRD and a SXRD study of CdWO₄ up to 15 GPa and 22 GPa, respectively, to solve the structure of its high-pressure phase, and an optical absorption study up to 23 GPa to investigate the effect that the structural phase transition has on the optical properties of CdWO₄. Finally, the stability of the high-pressure phase of CdWO₄, the frequencies of its Raman modes, and its electronic properties
have been investigated using \textit{ab initio} calculations.

II. EXPERIMENTAL DETAILS

For the non polarized optical absorption experiments at high pressure two 10-\(\mu\)m-thick samples of CdWO\(_4\) were cleaved along the (010) plane from a large single crystal obtained from the MTI Corporation. In this orientation the cross-polarization terms of the complex reflection are both zero\(^{14}\). The samples were loaded in Neon pressure medium together with a ruby chip and Neon was used as pressure medium in Boehler-Almax DACs equipped with diamond culets of 350 \(\mu\)m diameter and tungsten gaskets preindented to 45 \(\mu\)m thickness with a hole of 160-\(\mu\)m diameter. The experiments were carried out at 15 and 22 GPa at the Extreme Conditions Beamline at PETRA III (\(\lambda = 0.2925\) Å and 0.2904 Å, respectively) using a PerkinElmer 1621 detector with a 8.3 \(\times\) 9.6 \(\mu\)m\(^2\) and 4 \(\times\) 8 \(\mu\)m\(^2\) beam and a sample to detector distance of 402.5 mm and 430.6 mm, respectively. The diffraction images were collected by \(1^\circ\) \(\omega\)-scanning. The image format was converted according to the procedure described by Rothkirch et al.\(^{16}\) for further processing with the CrysAlisPro software\(^{17}\) for indexing reflections and intensity data reduction. The crystal structure of the high-pressure phase of CdWO\(_4\) exhibits a pseudo-orthorhombic metric at 22 GPa. However, attempts to solve the crystal structure in an orthorhombic space group were unsuccessful. Finally, the crystal structure was successfully solved in space group \(Pc\) with SHELXS97-2\(^{18}\) using direct methods and was subsequently converted to space group \(P2_1/c\) using PLATON\(^{19}\). A pseudo-merohedral 2-component twin (55 \%) related via a twin plane perpendicular to the \(c\)-axis with the twin matrix \((1 0 0, 0 1 0, 0 0 -1)\) was refined with SHELXL97-2\(^{19}\). The programs were used with the WinGX interface\(^{20}\). The final refinements were carried out with anisotropic displacement parameters for the tungsten and cadmium atoms and isotropic ones for the oxygen atoms. The final residual value \(R1\) of the post-wolframite structure converged to 6.34 \% at a data:parameter ratio of \(\approx\) 26, which are excellent values for single-crystal structure refinements of high-pressure data, and even more for a twinned high-pressure phase.

III. COMPUTATIONAL DETAILS

First principles calculations of the total-energy to study electronic structure and lattice dynamics were done within the framework of the density-functional theory (DFT)\(^{21}\) and the pseudo-potential method using the Vienna \textit{ab initio} simulation package (VASP)\(^{22–24}\). The exchange and correlation energy were used in the generalized gradient approximation (GGA) with the PBE functional\(^ {25}\). The projector-augmented wave (PAW) scheme\(^{26,27}\) was adopted and the semicore 5\(p\) \(W\) electrons were also explicitly included in the calculations. The considered valence electron configuration was \(Cd\ 4d^{10}5s^2, O\ 2s^22p^4, \) and \(W\ 5d^46s^2\). The set of plane waves employed extended up to the kinetic energy cutoff of 530 eV to deal with the O atoms in order to have highly accurate results. The Monkhorst-Pack\(^ {28}\) grid used for Brillouin-zone integrations ensured converged results to about 1 meV per formula unit. To perform the geometrical optimization we used 20 special \(k\)-points of the reciprocal space with symmetry \(P2_1/c\) 14 \(k\)-points with \(P2_1/c\) and 36 and 39 \(k\)-points for \(P1\) and \(I4_1/a\) symmetries, respectively. In our simulations we obtain not only the energy and volume, we also obtain derivatives of the energy, forces, and stresses. Hence, we also obtain the pressure from the \textit{ab initio} simulations. In fact when we relax for a volume a structure, the relaxed structure should have diagonal...
stress tensor (hydrostatic), and zero forces on the atoms. In the relaxed equilibrium configuration the forces on the atoms were lower than 0.002 eV/Å and the deviation of the stress tensor from a diagonal hydrostatic form was less than 0.1 GPa. Lattice dynamic calculations were carried out at \( \Gamma \) using the direct forces constant approach. This method involves the construction of the dynamical matrix, that requires highly converged results on forces. Diagonalization of the dynamical matrix provides both the frequencies of the normal modes and their polarization vectors. This allows us to identify the irreducible representation and the character of the phonon modes at the zone center. More details of the calculations can be found in Refs.\(^{10,12,29} \)

**IV. EXPERIMENTAL RESULTS**

**A. Optical Absorption**

A selection of absorption-coefficient (\( \alpha \)) spectra of CdWO\(_4\) at different pressures can be found in Fig. 2. At ambient pressure the absorption edge shows a steep increase up to a maximum value of \( \alpha \approx 6 \times 10^3 \) cm\(^{-1}\), in good agreement with a direct band gap\(^{10} \). As observed in previous results up to 10 GPa\(^{10} \), as pressure increases, the absorption edge keeps the same shape and shifts from 4 eV to higher energies up to 15 GPa. At 16.9 GPa the absorption edge reduces its steepness and starts to downshift to lower energies with increasing pressure up to 19.5 GPa when the sample exhibits a subtle color change and a low-absorbance step-like absorption spectrum emerges at lower energy (≈ 3.5 eV) in coexistence with the main absorption edge (Fig. 2). The shape of the newly emerged absorption spectrum indicates the contribution of two distinct electronic transitions with different absorbances. CdWO\(_4\) undergoes a structural phase transition at 20 GPa according to Raman Spectroscopy\(^{12} \). Therefore, the existence of an additional low-absorbance absorption edge at 19.5 GPa can be attributed to the onset of the phase transition to the high-pressure phase, which at this pressure is a minor component. This is confirmed at 20.3 GPa with the loss of the high-energy absorption edge and an abrupt increase in the absorbance of the low-energy absorption edge (\( \alpha \approx 4 \times 10^3 \) cm\(^{-1}\)), indicating the end of the phase transition. At higher pressures the absorption edge of the high-pressure phase of CdWO\(_4\) decreases in energy with further compression.

The steep-shaped absorption edges observed in the low-pressure phase absorption edge up to 15 GPa and in the high-pressure phase above 20.3 GPa are typical of direct bandgaps. We have analyzed the absorption spectra in both phases employing the direct-bandgap Urbach’s rule \( \alpha = A_0 \exp (h \nu - E_g)/E_U \), where \( E_g \) is the bandgap, \( E_U \) is Urbach’s energy and is related to the steepness of the absorption tail, and \( A_0 \) is an intrinsic constant of the sample that accounts for the absorption of defects\(^{30} \). The fits to spectra of the low- and high-pressure phases (Fig. 3) confirm the indirect nature of the bandgaps in both phases (except at 16.9 and 19.5 GPa). In hydrostatic conditions\(^{31} \), where uniaxial stresses do not deteriorate the sample, \( E_U \) and \( A_0 \) can be assumed to remain constant under pressure as long as the structure of the compounds and the density of defects remain constant\(^{32} \). In the case of CdWO\(_4\) we have obtained an \( A_0 \) value of 600 cm\(^{-1}\) for both phases in good agreement with other wolframite-type compounds (\( A_0 \approx 500 \) cm\(^{-1}\) for MgWO\(_4\))\(^{10} \). For the \( E_U \), it takes a value of 0.056 eV in the low-pressure phase and 0.082 eV in the high-pressure phase. The higher value observed for \( E_U \) in the high-pressure phase indicates an increase of point defects usually observed after a structural phase transition\(^{33-35} \). Regarding the absorption edges at 16.9 GPa and 19.5 GPa, in Fig. 2 we can see that they lose steepness, redshift with pressure, and cross the absorption edges measured at lower pressures. The linear dependence of \( \alpha^{-1/2} \) with the photon energy (Fig. 3) confirms the indirect nature of the bandgap at 16.9 and 19.5 GPa. After releasing pressure the recovered sample shows an absorption edge recovers the shape and energy of the measured spectra on pressure increase for the low-pressure phase. This confirms the reversibility of the phase transition and the fact that pressure apparently does not induce defects in the used hydrostatic conditions.

The values of the bandgap energy obtained from the analysis of all measured spectra are shown in Fig. 4 together with the data from Ref.\(^{10} \). We show that in the wolframite-type phase, the bandgap increases up to 15 GPa with a pressure coefficient \( dE_g/dp \) of 12 meV/GPa in good agreement with previous data\(^{10} \). Above 15 GPa, the change from a direct to an indirect bandgap, associated to a band crossing previously reported\(^{10} \) and observed in other wolframites before the phase transition\(^{36} \), implies a negative pressure coefficient of -2 meV/GPa. At the phase transition the bandgap collapses by 0.7 eV, with the direct bandgap of the high-pressure phase showing a negative pressure dependence of -50 meV/GPa.
\( \alpha \) (cm\(^{-1/2}\))
B and gap (eV)

\[ \frac{1}{2} \]
\[ 2 \]
\[ 4 \]
\[ 6 \]
\[ 3 \]
\[ .03 \]
\[ .54 \]
\[ .04 \]
\[ .50 \]
\[ 2 \]
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TABLE I: Lattice parameters, atomic coordinates, and equivalent or isotropic displacement parameters, respectively, of the experimental and calculated wolframite-type and post-wolframite-type structures of CdWO₄. The lattice parameters are in Å, the β angle is in degrees, the unit-cell volume is in Å³, and the displacement parameters are in Å².

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<th>P2₁/c</th>
<th>P2₁/c</th>
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<td></td>
<td>15 GPa Exp.</td>
<td>16 GPa Exp.</td>
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<tr>
<td></td>
<td>22 GPa Exp.</td>
<td>22.9 GPa Exp.</td>
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<tr>
<td>Uᵢₒ</td>
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organized at the phase transition, which is also expressed in a strong broadening of the single crystal reflections in the high-pressure phase. At the phase transition, the oxygen coordinates of cadmium and tungsten cations are increased from [6] to [6+1] and [7], respectively (Fig. 1).

Our crystal structure solution of the post-wolframite phase of CdWO₄ from single-crystal x-ray diffraction clearly contradicts the earlier assumption of the coexistence of two high-pressure phases by Lacomba-Perales et al. 12. In that work the formation of both a high-pressure phase with a CuWO₄-type structure (S. G. P1) and another one of the scheelite-type (S. G. I4₁/a) had been proposed using ab initio calculations in order to interpret the experimentally observed Raman modes12. Using our experimentally determined crystal structure, the Raman-mode assignment is revisited in section V B and the calculation of the electronic band structure is presented in section V C, where it is discussed with respect to the pressure-induced behavior of the bandgap across the phase transition.
V. THEORETICAL RESULTS

A. Phase Stability

The calculated enthalpy differences of CdWO$_4$ for the scheelite-type (S. G. $I4_1/\alpha$), CuWO$_4$-type (S. G. $P\bar{1}$), and post-wolframite phase (S. G. $P2_1/c$) as solved in this study are plotted with respect to the enthalpy of the wolframite-type structure (S. G. $P2/c$) in Fig. 6.

At high pressures, Lacomba-Perales et al. $^{12}$ reported from their calculations that the scheelite-type structure would become slightly more stable than the wolframite above 21.2 GPa. This is a pressure slightly higher than that of the phase transition onset (19.5 GPa) observed in the optical absorption study, but can be considered as a reasonable agreement. However, our calculations show that the post-wolframite structure of CdWO$_4$, solved with SXRD at 22 GPa in this work, becomes more stable at 18 GPa than both the wolframite-type structure and the CuWO$_4$-type structure, supporting our experimental structural solution.

In order to obtain the bulk moduli of both low- and high-pressure phases from the calculated data, we have also employed second order Birch-Murnaghan fits for a better comparison with the experimental data. The bulk modulus of the wolframite phase of CdWO$_4$ from the calculations is $B_0 = 111$. This is 9% lower than our updated value using combined experimental data from our study up to 15 GPa and from Macavei and Schulz $^{13}$, and 18% lower than the $B_0$ obtained by Macavei and Schulz $^{13}$ up to 8.2 GPa. The bulk modulus obtained in our calculations for the post-wolframite phase it is $B_0 = 114.5$ GPa.

B. Raman modes

Since the previous structural prediction of the post-wolframite phase of CdWO$_4$ had been based on the assignment of experimentally observed Raman modes, we have calculated frequencies and pressure coefficients ($\partial\omega/\partial P$) of the Raman active modes of CdWO$_4$ at 26.1 GPa in the post-wolframite phase. They are presented in Table II together with the experimental values measured with Raman spectroscopy by Lacomba-Perales et al. $^{12}$ at 26.9 GPa.

With the point group $C_{2h}$ and $Z = 4$, the post-wolframite structure of CdWO$_4$ (S.G. $P2_1/c$) presents 36 Raman-active modes at zone center $\Gamma = 19A_g + 17B_g$. 26 out of those modes had been experimentally observed$^{12}$. The agreement between the calculated and the experimental frequencies is excellent as can be directly observed in Fig. 7. In respect of the pressure coefficients the calculated and experimental values compare very well for most of the modes if we consider the overlapping and low intensity of many of the Raman modes that were measured in the earlier Raman-spectroscopy study$^{12}$. This confirms that after the phase transition all the observed Raman modes belong to the single high-pressure post-wolframite phase and not to two phases as proposed previously$^{12}$.

C. Electronic Structure

Previous calculations had proposed a band crossing in CdWO$_4$ above 10 GPa$^{10}$. However, the experimental data had been limited to 9.9 GPa. In this work we have increased the experimental range to 23 GPa to explore this crossing. As shown in previous works$^{8,10}$, the direct band gap of CdWO$_4$ occurs along the $Z$ point of the Brillouin zone. Calculations underestimate the direct band gap of the wolframite phase by 1.11 eV, as expected by DFT-GGA method and predict an-
TABLE II: Calculated and experimental phonon frequencies at \( \approx 26 \) GPa and pressure coefficients of the Raman modes for the high-pressure structure of CdWO\(_4\).

<table>
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<th>symm.</th>
<th>( \omega_{\text{calc}} ) (cm(^{-1}))</th>
<th>( d\omega_{\text{calc}}/dP ) (cm(^{-1}/)GPa(^{-1}))</th>
<th>( \omega_{\text{exp}} ) (cm(^{-1}))</th>
<th>( d\omega_{\text{exp}}/dP ) (cm(^{-1}/)GPa(^{-1}))</th>
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FIG. 8: Calculated pressure dependence of the direct (\( Z \rightarrow Z \)) and indirect (\( \Gamma B \rightarrow Z \)) bandgaps of the low-pressure phase of CdWO\(_4\). Other indirect band gap \( \Gamma B \rightarrow Z \). Ground states are considered to be accurately determined by the DFT-GGA. Since both the direct (\( Z \rightarrow Z \)) and indirect (\( \Gamma B \rightarrow Z \)) bandgaps share the same final state we can assume that the underestimation (1.11 eV) is the same for both the direct and indirect transitions. Therefore, at ambient pressure the indirect band gap of CdWO\(_4\) should be at around 4.05 eV, 0.03 eV above the direct band gap and therefore, the indirect transition cannot be experimentally observed. As pressure is increased (Fig. 8) the O 2\( p \) states (which contribute to the valence band\(^{10}\)) move downwards in energy almost symmetrically at both \( Z \) and \( \Gamma B \) points of the Brillouin zone up to 6 GPa. This results in a parallel energy increase of both direct and indirect transitions. Above 6 GPa, the energy of the O 2\( p \) orbitals continue decreasing at \( Z \) but slow down notably at \( \Gamma B \). Above 12 GPa the energy at \( \Gamma B \) increases. This behavior produces an energy degeneracy of the valence band at both points of the Brillouin zone at 17 GPa. The result is a band crossing of both direct and indirect transitions in agreement with the experimental observation at 16.9 GPa (Fig. 4).

With respect to the high-pressure phase, in Fig. 9 we show the electronic band structure at 18 and 22.8 GPa. Since in the post-wolframite phase there are two additional non-equivalent positions for the O atoms and the formula units per unit cell double from \( Z = 2 \) to \( Z = 4 \), the number of symmetry directions of the Brillouin zone increases in two points to \( A \) and \( E \) giving rise to a more complex band structure with respect to the wolframite phase. Regarding the electronic contribution to the valence and conduction bands they are formed by the O 2\( p \) and the W 5\( d \) orbitals, respectively, as in the low pressure wolframite phase\(^{10}\).

In spite of the low dispersion of the bands, as a result of the \( d \) electrons, a close inspection to the calculated electronic band structure of the post-wolframite indicates that the maximum of the valence band is located along \( \Gamma A \) and the minimum of the valence band is found along the \( CY \) direction of the Brillouin zone. This would result into an indirect
FIG. 9: Electronic-band structure of the post-wolframite phase of CdWO$_4$ at 18 (black) and 22.8 GPa (red). The Fermi level is shown as a dotted line. The right panel shows the corresponding partial and total electron density of states at 18 GPa.

A bandgap which would widen with a pressure coefficient of 7.7 meV/GPa as the result of the pressure-induced increase in energy of the conduction band. This value contrasts with the experimental results that indicate a direct bandgap which has a negative pressure coefficient. In fact, the only point of the conduction band that moves downwards in energy with pressure is the point at the $\Gamma A$ direction of the Brillouin zone. When a direct and an indirect bandgap are very close in energy, usually the direct one is favored. Since the direct transition in $\Gamma A$ is only 0.1 eV higher in energy than the indirect $\Gamma A \rightarrow CY$, decreases in energy with pressure, and is allowed, we conclude that this direct bandgap is the only one observed experimentally. The calculations underestimate the experimental bandgap in $\sim$1 eV similarly to the underestimation of the bandgap of the low-pressure phase.

VI. CONCLUSIONS

The high-pressure post-wolframite structure of CdWO$_4$ has been solved at 22 GPa using single-crystal x-ray diffraction. It is a single phase with monoclinic structure and space group $P2_1/c$. Our result contradicts the previous proposal of two coexisting structures$^{12}$. Density-Functional-Theory based calculations support our structural solution which is more stable than the wolframite-type one above 18 GPa and provides a reliable assignment to the Raman modes observed by Lacomba-Perales et al.$^{12}$ for the high-pressure phase. Moreover, optical absorption experiments have been extended to 23 GPa confirming previous results$^{10}$ up to 10 GPa. At 16.9 GPa a band crossing of an indirect bandgap previously proposed by electronic band structure calculations$^{10}$ within the low-pressure wolframite phase was observed. With regards to the high-pressure phase our optical absorption calculations show a bandgap collapse of 0.7 eV as the result of the phase transition to a direct bandgap of 3.55 eV at 20 GPa. The experimental observation of a strong redshift (-50 meV) of this high-pressure phase bandgap and its direct nature indicate that the calculated indirect $\Gamma A \rightarrow CY$ bandgap in post-wolframite is not experimentally observed and instead a direct bandgap at $\Gamma A$ appears.

Acknowledgments

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