

This article was downloaded by: [Universidad de Valencia]

On: 18 December 2008

Access details: Access Details: [subscription number 779262402]

Publisher Taylor & Francis

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



High Pressure Research

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smppt/title-content=t713679167>

Growth, characterization, and high-pressure optical studies of CuWO_4

J. Ruiz-Fuertes ^a; D. Errandonea ^a; A. Segura ^a; F. J. Manjón ^b; Zh. Zhu ^c; C. Y. Tu ^c

^a MALTA Consolider Team, Física Aplicada - ICMUV, Universidad de Valencia, Burjassot, Spain ^b MALTA Consolider Team, Física Aplicada - IDF, Universidad Politecnica de Valencia, València, Spain ^c Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fujian, Fuzhou, P.R. China

Online Publication Date: 01 December 2008

To cite this Article Ruiz-Fuertes, J., Errandonea, D., Segura, A., Manjón, F. J., Zhu, Zh. and Tu, C. Y. (2008) 'Growth, characterization, and high-pressure optical studies of CuWO_4 ', *High Pressure Research*, 28:4,565 — 570

To link to this Article: DOI: 10.1080/08957950802446643

URL: <http://dx.doi.org/10.1080/08957950802446643>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Growth, characterization, and high-pressure optical studies of CuWO_4

J. Ruiz-Fuertes^a, D. Errandonea^{a*}, †, A. Segura^a, F.J. Manjón^b, Zh. Zhu^c and C.Y. Tu^c

^aMALTA Consolider Team, Física Aplicada – ICMUV, Universidad de Valencia, Burjassot, Spain;

^bMALTA Consolider Team, Física Aplicada – IDF, Universidad Politecnica de Valencia, València, Spain;

^cFujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fujian, Fuzhou, P.R. China

(Received 16 June 2008; final version received 30 August 2008)

Copper tungstate (CuWO_4) crystals grown by the top-seeded solution growth method were characterized by X-ray diffraction, Raman scattering, and optical measurements. CuWO_4 has a triclinic structure ($P\bar{1}$) with $a = 4.709 \text{ \AA}$, $b = 5.845 \text{ \AA}$, $c = 4.884 \text{ \AA}$, $\alpha = 88.3^\circ$, $\beta = 92.5^\circ$, and $\gamma = 97.2^\circ$. It consists of corner-linked CuO_6 and WO_6 octahedra, the former having a pseudo-tetragonally elongated geometry caused by the Cu^{2+} Jahn–Teller effect. Fifteen out of the eighteen Raman modes of CuWO_4 are reported, discussed, and compared with those of other tungstates. We also determined the indirect band-gap energy of CuWO_4 (2.3 eV) and its negative pressure coefficient up to 25 GPa. The pressure evolution of the band-gap is discussed in terms of the electronic structure of CuWO_4 . Finally, no clear evidence of structural changes were found in our high-pressure experiments, but large amounts of defects are apparent beyond 18 GPa.

Keywords: CuWO_4 ; tungstates; scintillating material; crystal structure; electronic properties

1. Introduction

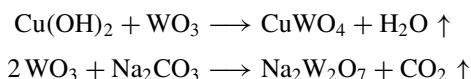
Orthotungstates are technologically important materials with special prominence in their use in scintillation detectors, lasers, photoanodes, and optical fibers. Copper tungstate (CuWO_4) has attracted increasing interest due to these applications [1] and its use as a semiconducting photoelectrode for photoelectrolysis [2]. Kihlberg et al. [3] determined that the crystal structure of CuWO_4 is triclinic ($P\bar{1}$) and X-ray photoelectron spectroscopy studies revealed information on its band-structure [4]. However, many physical properties of CuWO_4 remain unknown. In this paper we report results on X-ray diffraction, Raman-effect, and optical-absorption measurements. We also performed high-pressure (HP) optical studies up to 25 GPa. Results are discussed and compared with those obtained in tetragonal and monoclinic orthotungstates; e.g., PbWO_4 and ZnWO_4 .

*Corresponding author. Email: daniel.errandonea@uv.es

†Presently at the Fundación General de la Universidad de Valencia.

2. Experimental details

CuWO₄ crystals were prepared using the top-seeded solution growth technique. The growth was carried out in a vertical tubular muffle furnace using a Pt crucible and a Na₂W₂O₇ flux. The mixtures were synthesized according to the reactions:



The starting materials (analytical grade) of 80 mol% CuWO₄ and 20 mol% Na₂W₂O₇ were mixed, slowly heated to 1000 °C, and kept at this temperature for two days to homogenize the solution. By seeding several times, the saturation temperature (T_S) was determined. The outer surface of the seed was dissolved placing it into the melt at a temperature 20 °C higher than T_S for half an hour. The growing crystal was rotated at 10–25 rpm, and the cooling rate was 1–3 °C/day. The as grown crystal was drawn out of the melt and cooled down to room temperature (RT) at a rate of 50 °C/h.

To identify the crystallization phase an X-ray diffraction analysis was performed with a powder diffractometer (RIGAKU, DMAX2500PC) operated at 40 kV and 100 mA using Cu K_α radiation ($\lambda = 1.5405 \text{ \AA}$). The 2θ scan range was 5–90° with a step size of 0.05°. The diffraction patterns were analyzed using PowderCell. Raman measurements in single crystal CuWO₄ were performed in backscattering geometry with a Renishaw Invia micro-Raman setup equipped with notch filters. A 785 nm laser line at a power below 50 mW was used for excitation to avoid thermal effects. Raman spectra were obtained with a resolution of 3 cm⁻¹. The optical-absorption study was first carried out at ambient pressure to get a better estimation of the band-gap. The samples used were 10 to 30- μm thick platelets cleaved from the single crystal. HP optical-absorption measurements up to 25 GPa were carried out at RT in a membrane-type diamond-anvil cell equipped with 500- μm culet anvils. For these measurements 5 to 10- μm thick samples were loaded together with a ruby chip in a 200- μm diameter hole drilled in a 40- μm thick Inconel gasket. Methanol–ethanol–water (16:3:1) was used as a pressure transmitting medium and the pressure (P) was measured using the ruby fluorescence technique [5]. In both the ambient pressure and the HP experiments, the optical-absorption spectra were obtained from the transmittance spectra of the sample using the sample-in sample-out method in an optical setup similar to that described in [6]. Reflectance measurements were also performed in CuWO₄ working at normal incidence. Two independent sets of HP experiments were conducted in order to check the reproducibility of the reported results.

3. Results and discussion

Figure 1 shows an X-ray powder diffraction pattern obtained from CuWO₄. All the peaks on it can be indexed to a pure phase, corresponding to a triclinic structure with space group $P\bar{1}$. Its lattice parameters are $a = 4.709(7) \text{ \AA}$, $b = 5.845(9) \text{ \AA}$, $c = 4.884(7) \text{ \AA}$, $\alpha = 88.3(2)^\circ$, $\beta = 92.5(2)^\circ$, and $\gamma = 97.2(2)^\circ$. They are in good agreement with the literature [3,7]. The statistical parameters of the refinement are $R_{\text{WP}} = 2.04\%$, $R_p = 1.62\%$, and $R(F^2) = 1.85\%$ with background subtracted. There are 217 reflections. The structure of CuWO₄ is represented in Figure 1. The primitive cell contains two chemical formulas and consists of corner-linked CuO₆ and WO₆ octahedra, having the CuO₆ octahedra a pseudo-tetragonally elongated geometry caused by the Jahn–Teller effect of the Cu²⁺ cation. In the figure, it can be seen that although CuWO₄ is triclinic, its structure is topologically related to that of monoclinic wolframite ($P2/c$) [8]. The WO₆ octahedra are

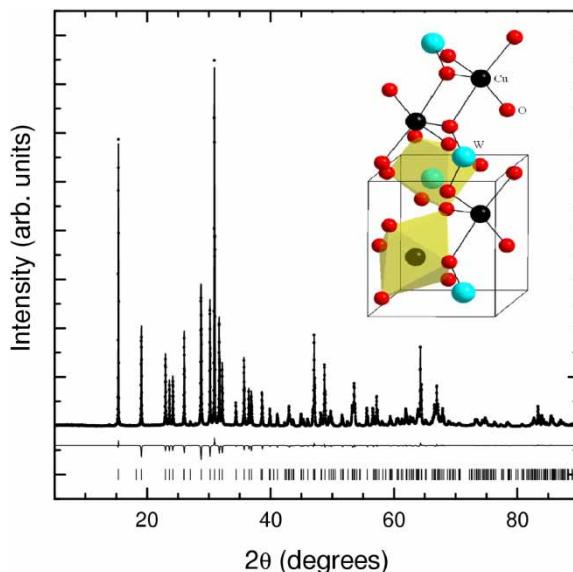


Figure 1. Diffraction pattern of CuWO_4 . Symbols: observations, line: refined model and residual, ticks: angular values of reflections. The inset shows the crystal structure of CuWO_4 , different atoms are indicated and CuO_6 and WO_6 octahedra shown.

slightly distorted as in wolframite with W-O distances ranging from 1.8 to 2.2 Å. However, the Jahn–Teller effect of Cu^{2+} , which reduces the degeneracy of $3d$ orbitals, is sufficient to cause a lowering of the monoclinic $P2/c$ symmetry to the triclinic $P\bar{1}$ symmetry. Consequently, the CuO_6 octahedra have a pseudo-tetragonally elongated geometry with four planar Cu-O distances close to 2 Å and two axial Cu-O distances around 2.4 Å.

The properties of CuWO_4 were also analyzed by means of Raman measurements. According to group theory, 18 zone-center Raman-active modes are expected in CuWO_4 ($\Gamma = 18A_g$). Figure 2 shows the Raman spectra of CuWO_4 measured at ambient pressure. Fifteen modes can be identified, one of them being observed as a shoulder of the peak near 398 cm^{-1} (see inset). The remaining three modes cannot be seen most probably because they are located below 150 cm^{-1}

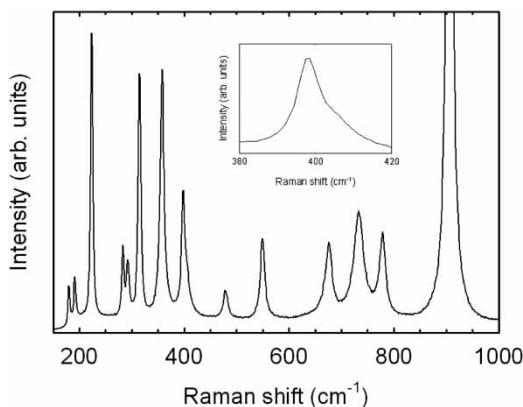


Figure 2. Raman spectrum of CuWO_4 . The inset shows that the band near 398 cm^{-1} can be decomposed into two modes, located at 398 and 405 cm^{-1} .

and consequently they are cut by the notch filter used to suppress the laser line and its Rayleigh scattering. The observed modes are located at 180, 192, 224, 283, 293, 315, 358, 398, 405, 479, 550, 676, 733, 779, and 906 cm^{-1} . The Raman spectra of CuWO_4 can be interpreted in terms of internal and external modes of the WO_6 octahedra. Internal modes correspond to vibrations of O atoms against W inside the WO_6 octahedra and external modes imply the movement of WO_6 octahedra as rigid units against Cu. Out of the internal modes of the WO_6 octahedra, we have shown in PbWO_4 [9] and ZnWO_4 [10], that according to Hardcastle and Wachs rules six modes can be considered as stretching modes related to the six W–O bonds inside the WO_6 octahedra. An estimation of these modes can be obtained by applying Hardcastle and Wachs formulae to check the total valence of W [9,10]. A calculation such as that performed for ZnWO_4 [10] suggests that the stretching modes of CuWO_4 are those at 405, 550, 676, 733, 779, and 906 cm^{-1} . Note that the stretching modes proposed for CuWO_4 are very similar to those of wolframite ZnWO_4 (407, 546, 678, 709, 786, and 907 cm^{-1}) [10]. The similarity in the internal frequencies of both compounds can be attributed to the similarity in masses between Cu and Zn and the similarity of the triclinic $P\bar{1}$ and monoclinic wolframite structures.

Figure 3 shows optical-absorption spectra of CuWO_4 obtained up to 18 GPa. The spectra exhibit a slow rise and the maximum value reached by the absorption coefficient, α , is around 8000 cm^{-1} . The quadratic dependence of the absorption energy on the photon energy suggests that the fundamental absorption of CuWO_4 has indirect character, as proposed by Pandey et al. from thin film studies [1]. The indirect band-gap was then determined from the $\alpha^{1/2}$ versus $h\nu$ plot, yielding $E_g = 2.3$ eV at ambient conditions. Reflectance measurements also support the indirect band-gap hypothesis as the reflectance spectrum does not exhibit any intense structure in the spectral range around the band-gap.

In Figure 3, it can be seen that the only change induced by pressure in the absorption spectra is a monotonic red-shift. As the shape of the spectra does not change up to 18 GPa, we assumed that CuWO_4 keeps its indirect character in this pressure range. Under this hypothesis, we determined the pressure dependence of E_g shown in Figure 3. We found that E_g decreases with P following a quadratic function. At ambient pressure the pressure coefficient is $dE_g/dP = -11$ meV/GPa, at 18 GPa it is -25 meV/GPa. In our analysis we only considered the absorption spectra collected up to 18 GPa because the quality of the spectra degrades beyond this pressure. A possible reason for this degradation is the introduction of defects in the sample that cause an irreversible change of the shape of the absorption edge, as observed in other tungstates. A consequence of the presence of defects is that the ambient-pressure absorption spectrum is not recovered when decompressing from $P > 20$ GPa; by contrast, the initial absorption spectrum is recovered when releasing

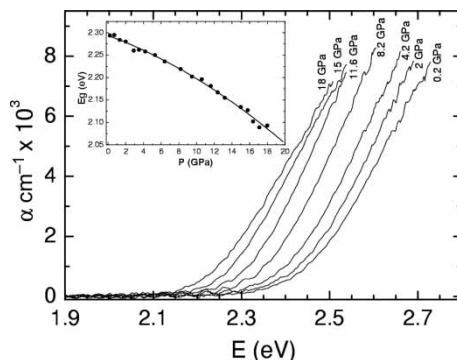


Figure 3. Absorption spectra of CuWO_4 single crystals for different pressures. The inset shows the pressure dependence of the absorption edge of CuWO_4 . Symbols: experimental results, line: quadratic fit.

pressure from $P < 20$ GPa. It is important to note here that the defect appearance on the samples beyond 18 GPa might be due to the non-hydrostatic stresses applied to them at these pressures as a consequence of the pressure medium used in the experiments [11]. The influence of such stresses in the results should not be neglected in view of the use of single crystals in our experiments. Indeed non-hydrostatic stresses could be also responsible for similar changes observed in single-crystalline CdWO_4 and ZnWO_4 [10]. To check this hypothesis, new experiments on CuWO_4 will be performed using neon as pressure medium.

According with the size criterion developed for AWO_4 compounds [12], a HP phase transition is predicted to take place in CuWO_4 beyond 21 GPa [13]. The HP phase would likely have a wolframite-type structure [13]. Up to 25 GPa we have not found any change in the absorption spectra or any shift in the evolution of the band-gap with P that pointed out to the occurrence of a phase transition. However, the defect creation observed beyond 20 GPa can be related to precursor effects of the predicted transition as observed in other semiconductors [14]. This conclusion about the HP structural stability of CuWO_4 is supported by a preliminary analysis of HP EXAFS measurements, which did not detect any phase transition up to 18 GPa.

To conclude, we will compare the pressure evolution of E_g in CuWO_4 and other tungstates. Contrary to CuWO_4 ($dE_g/dP = -11$ meV/GPa), wolframite ZnWO_4 and scheelite BaWO_4 ($I4_1/a$) have small but positive pressure coefficients (≈ 9 meV/GPa) [15]. On the other hand, scheelite-type PbWO_4 has a large negative pressure coefficient of -75 meV/GPa [16]. Curiously, in the HP phases of BaWO_4 and PbWO_4 $dE_g/dP \approx -20$ meV, being similar to dE_g/dP in CuWO_4 . Density-functional calculations on AWO_4 compounds ($A = \text{Ca}, \text{Cd}, \text{and Pb}$) [17] revealed that the bottom of the conduction band of orthotungstates are dominated by contributions of W $5d$ like states. On the other hand, the upper part of the valence band is mainly composed by O $2p$ states. In those compounds where the valence shell of bivalent cation A contains only s states there is a small contribution of them to the valence and conduction bands, but if the bivalent cations have a different electronic configuration (*e.g.*, Cu and Pb) a larger contribution of the metal A to the valence and conduction bands is expected [4,18,19]. Consequently, the decrease observed in E_g for CuWO_4 and PbWO_4 upon compression can be qualitatively explained by taking into account the pressure increase of the crystal field acting on W $5d$ and O $2p$ states and the consequent increase of their hybridization with metal A states [16]. In particular the valence band in CuWO_4 is expected to have a significant Cu $3d$ contribution, vanishing at the Γ point for symmetry reasons and being maximum at the zone edge. Apart from explaining the indirect character of CuWO_4 , it explains the negative pressure coefficient of E_g , since O $2p$ states (with some Cu $3d$ hybridization) shift towards high energies faster than the W $2d$ states, causing a reduction of the energy difference between the bottom of the conduction band and the top of the valence band [16]. The similitude of the pressure effects on the band-gap of CuWO_4 and that of the HP phases of BaWO_4 and PbWO_4 is consistent with this picture. These HP structures have a W–O coordination more similar to the coordination six of CuWO_4 than the low-pressure phases [20]. This makes them less compressible than the low-pressure phase of PbWO_4 (W–O coordination = 4). Therefore E_g is expected to close with P in a similar way than in CuWO_4 and much less than in scheelite PbWO_4 . Further experimental and theoretical studies are being conducted to clarify this interpretation of the reported results. An important issue to address by future studies is how the Jahn–Teller effect is affected by pressure in CuWO_4 .

Acknowledgements

Research supported by the Spanish MICINN (Grants MAT2007-65990-C03-01, MAT2006-02279, and CSD-2007-00045) and the Science & Technology Plan Project of Fujian, China (Grants 2005HZ1026, 2007H0037, and SZD08001-2). The authors thank F. Rey (ITQ, CSIC-UPV) for giving access to diffraction and Raman setups.

References

- [1] P.K. Pandey, N.S. Bhavne, and R.B. Kharat, *Spray deposition process of polycrystalline thin films of CuWO₄ and study on its photovoltaic electrochemical properties*, Mater. Lett. 56 (2005), pp. 3149–3155.
- [2] M.A. Buttler, *Photoelectrolysis and physical properties of the semiconducting electrode WO₂*, J. Appl. Phys. 48 (1997), pp. 1914–1920.
- [3] L. Kihlborg and E. Gerbert, *CuWO₄, a distorted wolfrannite-type structure*, Acta Crystallogr. B 26 (1970), pp. 1020–1026.
- [4] O.Y. Khyzhun, T. Strunskus, S. Cramm, and Y. M. Solonin, *Electronic structure of CuWO₄: XPS, XES and NEXAFS studies*, J. Alloys Compd. 389 (2005), pp. 14–20.
- [5] H.K. Mao, J. Xu, and P.M. Bell, *Calibration of the ruby pressure gauge to 800-Kbar under quasi-hydrostatic conditions*, J. Geophys. Res. 91 (1986), pp. 4673–4676.
- [6] A. Segura, J.A. Sanz, D. Errandonea, D. Martínez-García, and V. Fages, *High conductivity of Ga-doped rock-salt ZnO under pressure: Hint on deepultraviolet-transparent conducting oxides*, Appl. Phys. Lett. 88 (2006), p. 011910.
- [7] P.F. Schofield, K.S. Knight, S.A.T. Redfern, and G. Cressey, *Distortion characteristics across the structural phase transition in (Cu_{1-x}Zn_x)WO₄*, Acta Crystallogr. B 53 (1997), pp. 102–112.
- [8] D. Errandonea, J. Pellicer-Porres, F.J. Manjón, A. Segura, Ch. Ferrer-Roca, R.S. Kumar, O. Tschauer, P. Rodríguez-Hernández, *High-pressure structural study of the scheelite tungstates CaWO₄ and SrWO₄*, Phys. Rev. B 72 (2005), p. 174106.
- [9] F.J. Manjón, D. Errandonea, D. Errandonea, N. Garro, J. Pellicer-Porres, P. Rodríguez-Hernández, S. Radescu, J. Lopez-Solano, A. Mujica, A. Muñoz, *Lattice dynamics study of scheelite tungstates under high pressure. I. BaWO₄*, Phys. Rev. B 74 (2006), pp. 144111–144112.
- [10] D. Errandonea, F.J. Manjón, N. Garro, P. Rodríguez-Hernández, S. Radescu, A. Mujica, A. Muñoz, and C.Y. Tu, *Combined Raman scattering and ab initio investigation of pressure-induced structural phase transitions in the scintillator ZnWO₄*, Phys. Rev. B 78 (2008), p. 054116.
- [11] D. Errandonea, Y. Meng, M. Somayazulu, and D. Häusermann, *Pressure-induced alpha → omega transition in titanium metal: a systematic study of the effects of uniaxial stress*, Physica B 355 (2005), pp. 116–125.
- [12] D. Errandonea, F. J. Manjón, M. Soinayazulu, and D. Häusermann, *Effects of pressure on the local atomic structure of CaWO₄ and YLiF₄: mechanism of the scheelite-to-wolframite and scheelite-to-fergusonite transitions*, J. Sol. State Chem. 177 (2004), pp. 1087–1097.
- [13] D. Errandonea and F. J. Manjón, *Pressure effects on the structural and electronic properties of ABX₄ scintillating crystals*, Prog. Mater. Sci. 53 (2008), pp. 711–773.
- [14] F.J. Manjón, D. Errandonea, A. Segura, J.C. Chervin, and V. Muñoz, *Precursor effects of the rhombohedral-to-cubic phase transition in indium selenide*, High Pres. Res. 22 (2002), pp. 261–266.
- [15] R. Lacomba-Perales, M.Sc. thesis, Universitat de Valencia, 2007.
- [16] D. Errandonea, D. Martínez-García, R. Lacomba-Perales, J. Ruiz-Fuertes, and A. Segura, *Effects of high pressure on the optical absorption spectrum of scintillating PbWO₄ crystals*, Appl. Phys. Lett. 89 (2006), p. 091913.
- [17] Y. Zhang, N.A.W. Holzworth, and R.T. Williams, *Electronic band structures of the scheelite materials CaMoO₄, CaWO₄, PbMoO₄, and PbWO₄* Phys. Rev. B 57 (1998), pp. 12738–12750; Y. Abraham, N.A.W. Holzworth, and R.T. Williams, *Electronic structure and optical properties of CdMoO₄ and CdWO₄*, Phys. Rev. B 62 (2000), pp. 1733–1741.
- [18] M. Itoh, N. Fujita, and Y. Inabe, *X-ray photoelectron spectroscopy and electronic structures of scheelite- and wolframite-type tungstate crystals*, J. Phys. Soc. Japan 75 (2006), pp. 084705.1–084705.8.
- [19] R. Lacomba-Perales, J. Ruiz-Fuertes, D. Errandonea, D. Martínez-García, and A. Segura, *Optical absorption of divalent metal tungstates: Correlation between the band-gap energy and the cation ionic radius*, Eur. Phys. Lett. 83 (2008), p. 37002.
- [20] D. Errandonea, J. Pellicer-Porres, F.J. Manjón, A. Segura, Ch. Ferrer-Roca, R.S. Kumar, O. Tschauer, J. Lopez-Solano, P. Rodríguez-Hernández, S. Radescu, A. Mujica, A. Muñoz, and G. Aquilanti, *Determination of the high-pressure crystal structure of BaWO₄ and PbWO₄*, Phys. Rev. B 73 (2006), p. 224103.