

Article

An Investigation of the Pressure-Induced Structural Phase Transition of Nanocrystalline α -CuMoO₄

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Abstract: The structural behavior of nanocrystalline α -CuMoO₄ was studied at ambient temperature up to 2 GPa using in situ synchrotron X-ray powder diffraction. We found that nanocrystalline α -CuMoO₄ undergoes a structural phase transition into γ -CuMoO₄ at 0.5 GPa. The structural sequence is analogous to the behavior of its bulk counterpart, but the transition pressure is doubled. A coexistence of both phases was observed till 1.2 GPa. The phase transition gives rise to a change in the copper coordination from square-pyramidal to octahedral coordination. The transition involves a volume reduction of 13% indicating a first-order nature of the phase transition. This transformation was observed to be irreversible in nature. The pressure dependence of the unit-cell parameters was obtained and is discussed, and the compressibility analyzed.

Keywords: high pressure; phase transition; synchrotron radiation; X-ray diffraction



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1. Introduction

Nanomaterials play an important role in catalysis, optics, electricity, and other research fields due to their exclusive and typical characteristics. In the past decades, compared to bulk materials, their nanocrystalline counterparts have gained massive attention due to their novel properties such as thermal, electronic, and magnetic, owing to their specific shape, size, and surface to volume ratio. In addition to that, nanomaterials also find their application in the fields of biology, medicine, and chemical industry [1–4]. Metal molybdates (AMoO₄) are important inorganic materials which have gained enormous scientific importance due to their wide range of applicability, such as industrial catalysts, photoluminescence, microwave applications, optical fibers, humidity sensors, scintillator materials and due to their magnetic and electrochemical properties [5–8].

Among molybdates, CuMoO₄ is the compound with a very complex polymorphism [9–12]. Till date, six different polymorphs of CuMoO₄ have been identified in the literature: namely ambient condition α -CuMoO₄ [9], high temperature β -CuMoO₄ [10], low temperature γ -CuMoO₄ [11], high pressure (HP) CuMoO₄-II [12], distorted wolframite CuMoO₄-III [13] and monoclinic ϵ -CuMoO₄ [14]. Earlier, single-crystal high-pressure and low-temperature X-ray diffraction studies carried by Wiesmann et al. [15] found that phase α -CuMoO₄ undergoes a structural phase transition to γ -CuMoO₄. This occurs during cooling at 190 K at ambient pressure as well as under increasing pressure at 0.2 GPa and room temperature. Congruently, high pressure and low temperature optical-absorption measurements carried out by Rodriguez et al. [16] found that α -CuMoO₄ undergoes a first-order transition at 0.25 GPa to γ -CuMoO₄. They found the same transition by cooling α -CuMoO₄ to 200 K at ambient pressure. The α to γ phase transition involves a change of part of the copper coordination polyhedra, from square-pyramidal (C_{4v}) CuO₅ in α -CuMoO₄ to octahedral elongated (D_{4h}) CuO₆ in γ -CuMoO₄. The transition also involves a volume drop of 13%.

Many of the applications of CuMoO_4 involve its use in the form of nanoparticles [17–19]. However, the information available on the structural and mechanical properties of nanocrystalline CuMoO_4 is scarce. It is known that the high-pressure (HP) behavior of materials could be different for nanoparticles than for bulk materials [20–23]. In particular, transition pressures and compressibilities could be affected when the particle size is reduced [20–23]. To explore the structural and mechanical properties of nanocrystalline CuMoO_4 under compression, the performance of an HP X-ray diffraction (XRD) investigation is needed. However, such studies have not been carried out yet in nanocrystalline $\alpha\text{-CuMoO}_4$. In the present work we have investigated nanocrystalline $\alpha\text{-CuMoO}_4$ by high pressure powder X-ray diffraction up to a pressure of 2 GPa under hydrostatic conditions.

2. Experiment

CuMoO_4 nanoparticles were prepared following the method reported by Hassani et al. [20]. The chemical composition of the obtained CuMoO_4 nanoparticles was determined by energy-dispersive X-ray spectrometry (EDXS), which was recorded with a JEOL JEM-6700F device. A EDXS spectrum is shown in Figure 1. The analysis showed that the composition of the nanoparticles was 67 (3) atomic % oxygen, 16 (1) atomic % copper, and 17 (1) atomic % molybdenum, which agrees with the stoichiometry of CuMoO_4 .

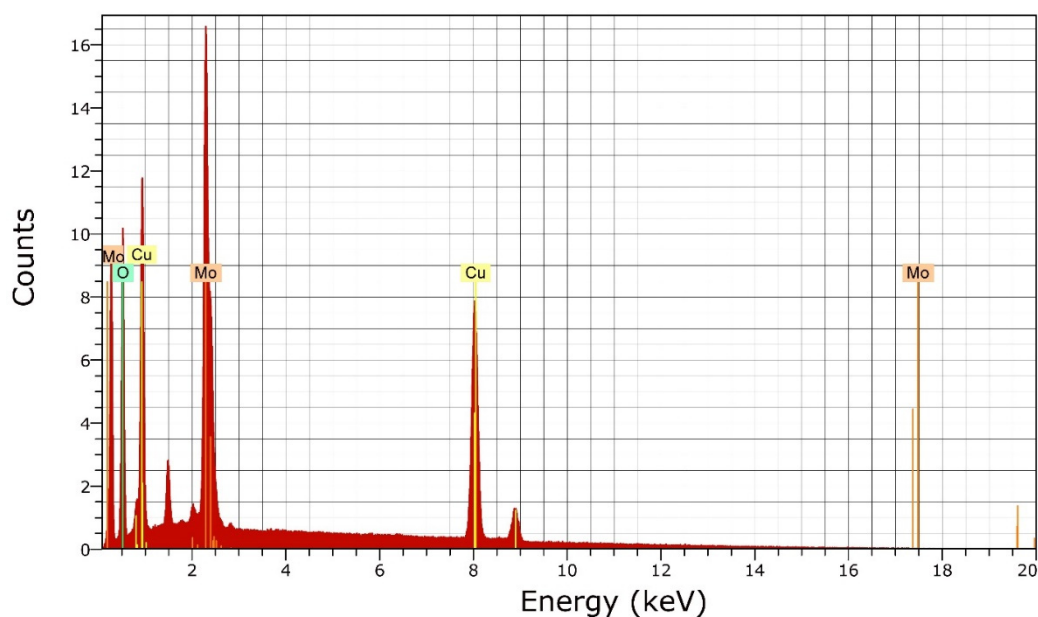


Figure 1. Energy dispersive X-ray analysis (EDXS) spectrum of nanocrystalline CuMoO_4 .

Ambient conditions powder XRD ($\lambda = 0.4246 \text{ \AA}$) performed in the same set up as high-pressure measurements confirmed that CuMoO_4 nanoparticles crystallize in the triclinic α polymorph (space group $P\bar{1}$). The average particle size was estimated from powder XRD using the Scherrer equation [24], to be 43 (7) nm. This value was confirmed using MAUD [25], which gave an average particle size of 40 (9) nm. Angle-dispersive powder HP-XRD measurements were performed at the BL04-MSPD beamline of ALBA synchrotron [26]. An incident monochromatic X-ray beam with a wavelength of $0.4246 \text{ \AA}$ was focused down to a spot size of $20 \mu\text{m} \times 20 \mu\text{m}$ (FWHM). Two-dimensional (2D) XRD data were recorded using a Rayonix SX165 CCD detector. The 2D images were integrated into one-dimensional intensity versus 2θ patterns using Dioptas [27]. The sample-to-detector distance along with detector parameters were determined using a LaB_6 calibrant. A pellet of CuMoO_4 nanocrystalline powder was loaded into a Boehler-Almax diamond-anvil cell (DAC) with diamond culets of $500 \mu\text{m}$ using a T301 stainless-steel gasket, pre-indented to a thickness of $50 \mu\text{m}$ and with a sample chamber of $200 \mu\text{m}$ diameter in the center. As pressure-

transmitting medium, we used a 4:1 methanol–ethanol to allow a direct comparison with previous HP studies performed in microscopic samples [15]. The pressure medium can be considered nearly hydrostatic within the pressure limit of the experiments [28]. Special attention was paid to occupy only a minor fraction on the pressure chamber with sample to avoid sample bridging between diamonds [29]. The pressure was determined using ruby fluorescence [30]. Small ruby spheres with a grain size of $\sim 1\ \mu\text{m}$ and concentration of 3000 ppm Cr^{3+} [31] were used for pressure calibration [31] based on the wavelength shift of the R1 fluorescence band of the trivalent Cr^{3+} [32,33]. The estimated relative error for all measured pressures was better than 1% [34]. The unit-cell parameters were initially determined using the Le Bail analysis incorporated in the GSAS software [35]. Using the same software, Rietveld analysis [36] was also carried out for the initial $\alpha\text{-CuMoO}_4$ phase and high pressure $\gamma\text{-CuMoO}_4$ phase.

3. Results and Discussion

At ambient conditions, CuMoO_4 crystallizes in a triclinic $\alpha\text{-CuMoO}_4$ structure (space group $P\bar{1}$, $Z = 6$). The $\alpha\text{-CuMoO}_4$ structure can be described by MoO_4 tetrahedra, CuO_5 square pyramidal polyhedra, and CuO_6 distorted octahedra, interconnected via common corners and edges forming layers as shown in Figure 2.

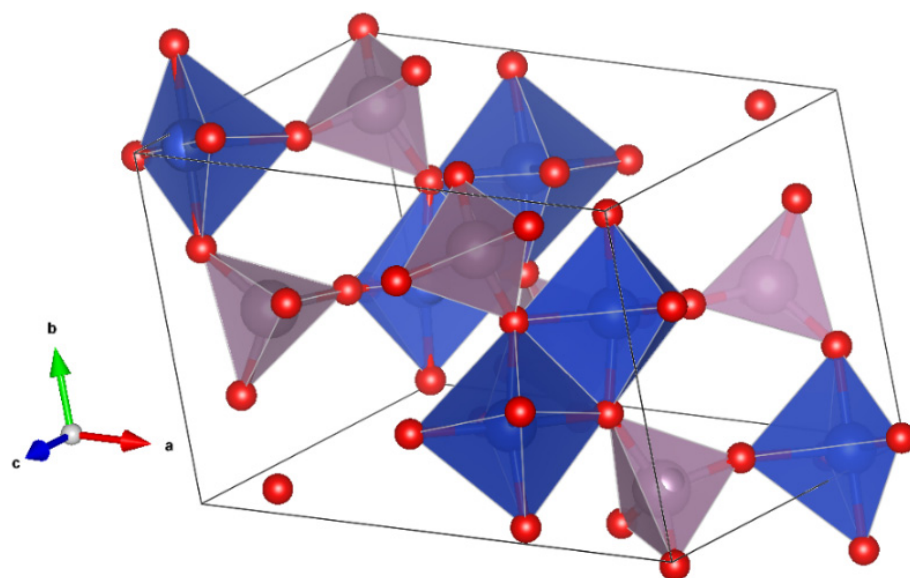


Figure 2. Crystal structure of $\alpha\text{-CuMoO}_4$. Blue solid spheres correspond to Cu atoms, gray solid spheres correspond to Mo atoms, and red solid spheres correspond to O atoms. The different coordination polyhedra are illustrated in the figure.

Figure 3 shows a selection of HP powder X-ray diffraction profiles of nanocrystalline $\alpha\text{-CuMoO}_4$ at representative pressures. There were no noticeable changes (other than typical peak shifts due to the changes induced by pressure in the unit-cell parameters) in the diffraction patterns up to 0.3 GPa and all the diffraction peaks could be indexed to $\alpha\text{-CuMoO}_4$ phase. At 0.5 GPa, the appearance of many weak extra diffraction peaks was observed at 2θ of 4.2, 4.7, 6.8 and 9.5° along with the diffraction peaks of the $\alpha\text{-CuMoO}_4$ phase. The red arrows in Figure 3 identify some of the additional peaks observed at 0.5 GPa. The red dashed lines show how these peaks evolve with pressure until the highest pressure corresponding to peaks of the γ -phase. In the pattern at 2.0 GPa (γ -phase) they are identified with asterisks.

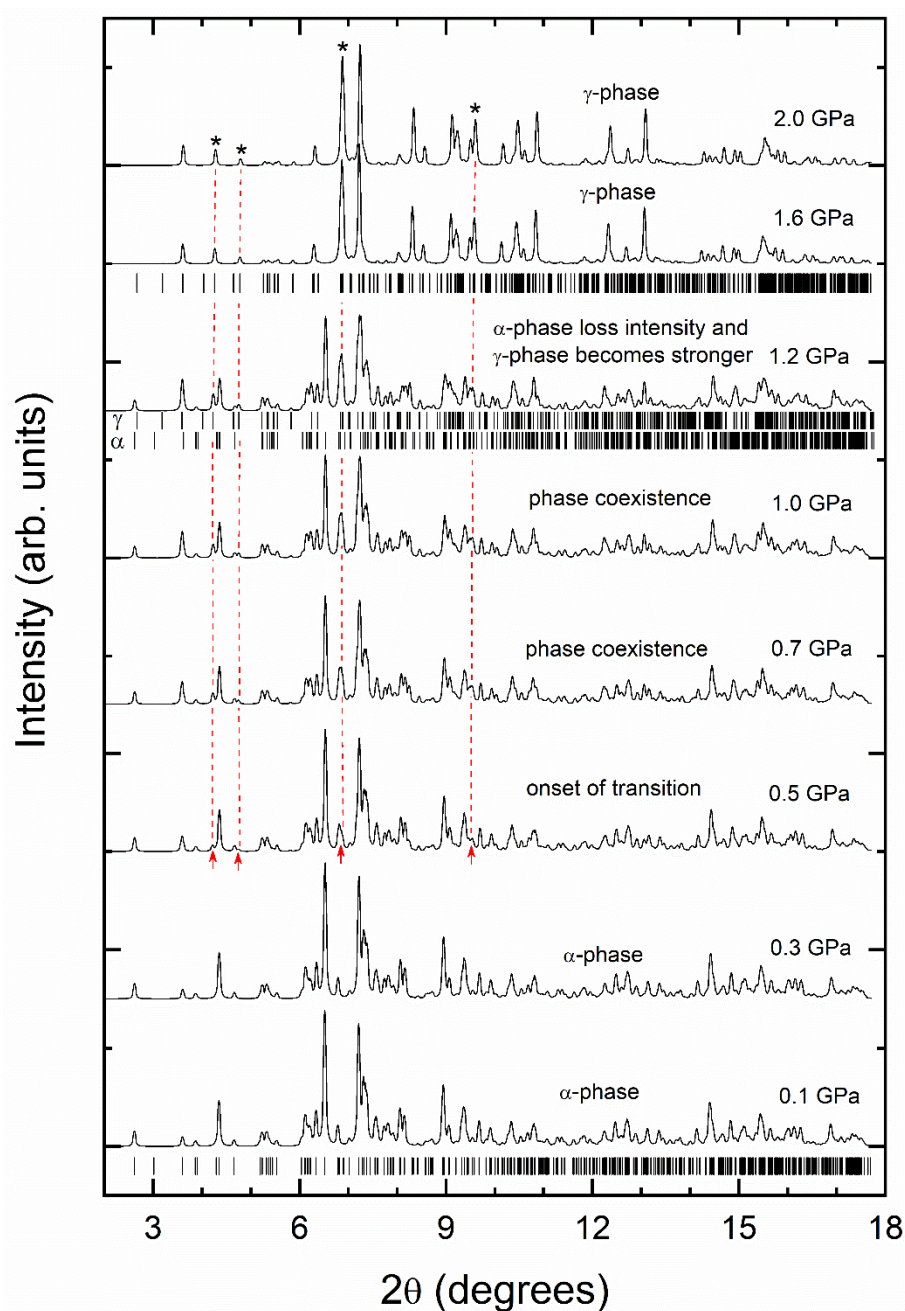


Figure 3. Evolution of the X-ray diffraction patterns of α -CuMoO₄ as a function of pressure. Pressures are provided in the figure. Red arrows indicate the appearance of extra diffraction peaks evidencing the onset of the transition to the γ -CuMoO₄ phase. Red dashed lines show how these peaks evolve under compression. The asterisks identify the peaks in the γ -phase. Ticks are the position of Bragg peaks for different structures.

These modifications in the diffraction pattern are indicative of the onset of a structural phase transition in α -CuMoO₄ at 0.5 GPa. The transition pressure observed in this study is almost double the transition pressure determined from earlier single-crystal high-pressure XRD measurements and optical studies on bulk samples, which identified the phase transition at 0.2 and 0.25 GPa, respectively [15,16]. The increase of the transition pressure could be explained in terms of an increase in surface energy in the newly formed high-pressure phase crystallites [37]. The coexistence of both the phases has been observed till 1.2 GPa. Beyond this pressure, all the diffraction peaks could be assigned to the triclinic γ -CuMoO₄ (space group $P\bar{1}$). On further increase of pressure, the γ -CuMoO₄ phase has

been found to remain stable up to 2 GPa, which is the highest pressure reached in our XRD measurements. On release of pressure, the γ -CuMoO₄ phase has been observed at ambient conditions, thus indicating the irreversible nature of the phase transition. In previous studies [15,16] the reversibility of the HP α - γ transition was not evaluated. However, it was shown that the γ -phase has a smaller band gap and different optical properties than the α -phase [16]. In particular, the band gap of γ -CuMoO₄ is close to 2 eV, making it ideal for hydrogen production via photocatalytic water splitting [38]. Given the low-pressure requested to obtain γ -CuMoO₄ as an ambient-conditions metastable polymorph, HP could be an efficient way to synthesize γ -CuMoO₄ for water splitting applications. The crystal structure of the HP γ -CuMoO₄ phase is represented in Figure 4. In this structure, all Cu atoms display an octahedral elongated coordination, and all Mo atoms have a distorted octahedral coordination. Rietveld refinements supporting the structural assignments are provided in Figure 5.

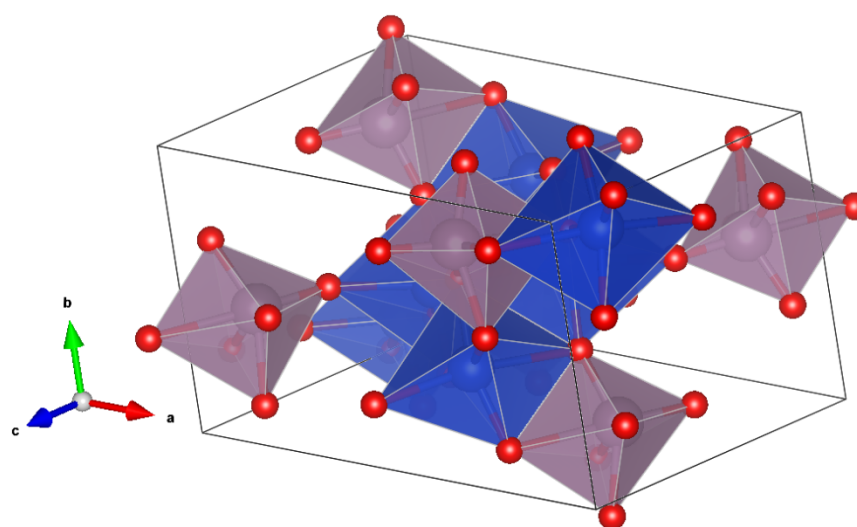


Figure 4. Crystal structure of γ -CuMoO₄. Blue solid spheres correspond to Cu atoms, gray solid spheres correspond to Mo atoms, and red solid spheres correspond to O atoms. The different coordination polyhedra are illustrated in the figure.

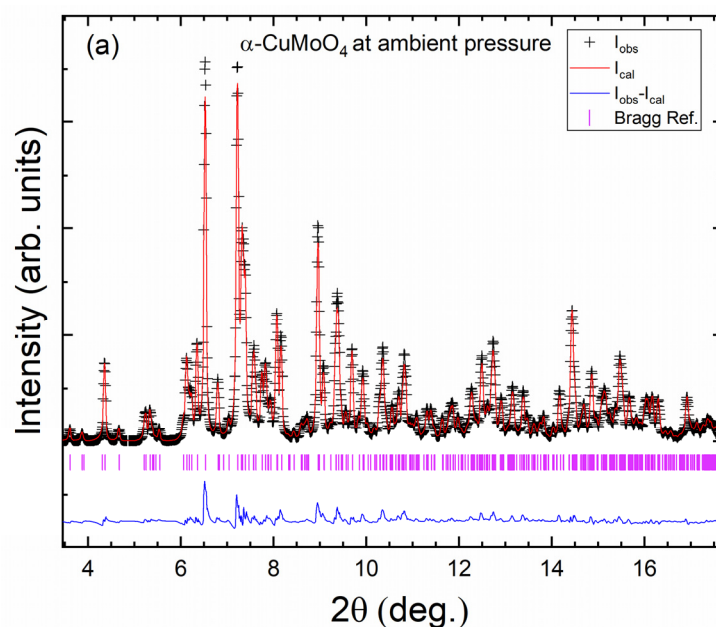


Figure 5. Cont.

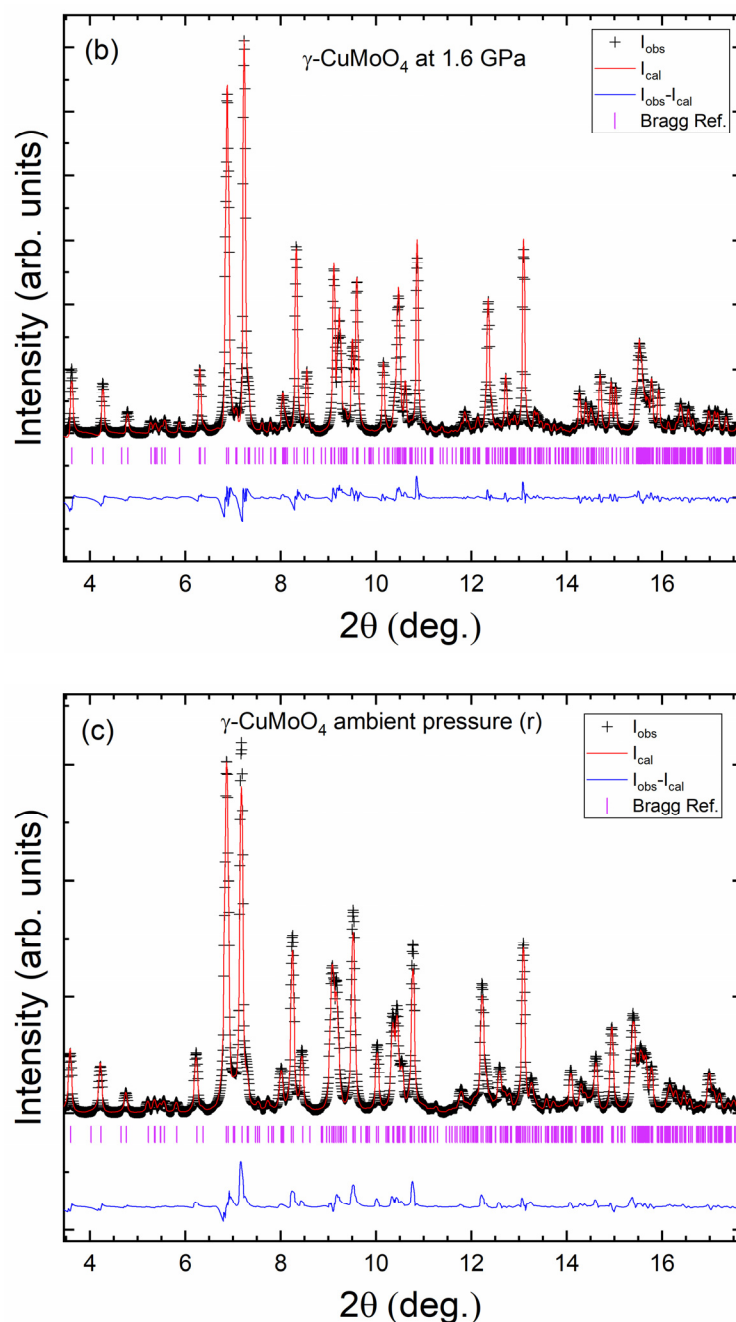


Figure 5. (a) XRD pattern and Rietveld refinement of α -CuMoO₄ at ambient pressure. (Rwp = 13.4%, Rp = 9.2%). (b) XRD pattern and Rietveld refinement of γ -CuMoO₄ at 1.6 GPa (Rwp = 11.4%, Rp = 6.8%). (c) XRD pattern and Rietveld refinement of γ -CuMoO₄ at ambient pressure after pressure release (Rwp = 12.4%, Rp = 8.0%), denoted by (r).

At ambient pressure, the lattice parameters for α -CuMoO₄ were refined as $a = 9.870$ (1) Å, $b = 6.764$ (1) Å, $c = 8.337$ (1) Å, $\alpha = 101.13$ (5)°, $\beta = 96.90$ (5)°, $\gamma = 107.03$ (5)°. The lattice parameters and fractional coordinates of the α -CuMoO₄ are given in Table 1. They are in good agreement with those reported in previous single-crystal high-pressure XRD measurements by Wiesmann et al., $a = 9.901$ (3) Å, $b = 6.786$ (2) Å, $c = 8.369$ (3) Å, $\alpha = 101.13$ °, $\beta = 96.88$ °, $\gamma = 107.01$ ° [15]. On the other hand, the lattice parameters of γ -CuMoO₄ phase at 1.6 GPa were found to be $a = 9.608$ (9) Å, $b = 6.219$ (7) Å, $c = 7.875$ (5) Å, $\alpha = 94.91$ (1)°, $\beta = 103.10$ (1)°, $\gamma = 102.48$ (9)°. The lattice parameters and fractional coordinates are summarized in Table 2. They are in good agreement with those reported in previous single crystal high-pressure XRD measurements by Wiesmann et al., $a = 9.708$ (3) Å, $b = 6.302$ (7) Å,

$c = 7.977$ (2) Å, $\alpha = 94.76^\circ$, $\beta = 103.35^\circ$, $\gamma = 103.26^\circ$ [15]. After release of pressure, the lattice parameters for γ -CuMoO₄ were found to be $a = 9.6605$ Å, $b = 6.2751$ Å, $c = 7.9334$ Å, $\alpha = 94.76^\circ$, $\beta = 103.29^\circ$, $\gamma = 103.14^\circ$. The unit-cell volume of the γ -phase was 11.5% smaller than the volume of the α -phase.

Table 1. Lattice parameters and fractional coordinates of α -CuMoO₄ at ambient conditions. Space group $P\bar{1}$, $Z = 6$, $a = 9.870$ (1) Å, $b = 6.764$ (1) Å, $c = 8.337$ (1) Å, $\alpha = 101.13$ (5) $^\circ$, $\beta = 96.90$ (5) $^\circ$, $\gamma = 107.03$ (5) $^\circ$.

Atoms	Sites	x	y	z
Cu1	2i	0.4054 (3)	0.7466 (3)	0.1983 (3)
Cu2	2i	0.9922 (3)	0.0472 (3)	0.2024 (3)
Cu3	2i	0.2365 (3)	0.4626 (3)	0.3853 (3)
Mo1	2i	0.3450 (2)	0.1970 (2)	0.0850 (2)
Mo2	2i	0.1064 (2)	0.4960 (2)	0.7776 (2)
Mo3	2i	0.2500 (2)	0.9927 (2)	0.4648 (2)
O1	2i	0.1425 (12)	0.9355 (12)	0.6056 (12)
O2	2i	0.2751 (12)	0.7459 (12)	0.3590 (12)
O3	2i	0.1839 (12)	0.1582 (12)	0.3414 (12)
O4	2i	0.1644 (12)	0.0642 (12)	0.9873 (12)
O5	2i	0.1846 (12)	0.5020 (12)	0.5974 (12)
O6	2i	0.3669 (12)	0.4518 (12)	0.2238 (12)
O7	2i	0.2405 (12)	0.5940 (12)	0.9484 (12)
O8	2i	0.4122 (12)	0.1567 (12)	0.5772 (12)
O9	2i	0.0039 (12)	0.2291 (12)	0.7692 (12)
O10	2i	0.0107 (12)	0.3455 (12)	0.2115 (12)
O11	2i	0.4463 (12)	0.2493 (12)	0.9330 (12)
O12	2i	0.4104 (12)	0.0335 (12)	0.1952 (12)

Table 2. Lattice parameters and fractional coordinates of γ -CuMoO₄ at 1.6 GPa. Space group $P\bar{1}$, $Z = 6$, $a = 9.608$ (9) Å, $b = 6.219$ (7) Å, $c = 7.875$ (5) Å, $\alpha = 94.91$ (1) $^\circ$, $\beta = 103.10$ (1) $^\circ$, $\gamma = 102.48$ (9) $^\circ$.

Atoms	Sites	x	y	z
Cu1	2i	0.4339 (3)	0.7158 (3)	0.2360 (3)
Cu2	2i	0.0069 (3)	0.0931 (3)	0.1939 (3)
Cu3	2i	0.3355 (3)	0.4240 (3)	0.5260 (3)
Mo1	2i	0.3481 (2)	0.2165 (2)	0.1269 (2)
Mo2	2i	0.1092 (2)	0.4145 (2)	0.8800 (2)
Mo3	2i	0.2269 (12)	0.9336 (2)	0.4583 (2)
O1	2i	0.1193 (12)	0.8973 (12)	0.6000 (12)
O2	2i	0.2951 (12)	0.6970 (12)	0.4544 (12)
O3	2i	0.1998 (12)	0.2082 (12)	0.3424 (12)
O4	2i	0.1546 (12)	0.1263 (12)	0.9699 (12)
O5	2i	0.1927 (12)	0.4514 (12)	0.7175 (12)
O6	2i	0.4765 (12)	0.4375 (12)	0.3011 (12)
O7	2i	0.2720 (12)	0.5024 (12)	0.0747 (12)
O8	2i	0.3863 (12)	0.1490 (12)	0.5890 (12)
O9	2i	0.9406 (12)	0.1831 (12)	0.7561 (12)
O10	2i	0.9744 (12)	0.3626 (12)	0.1078 (12)
O11	2i	0.4474 (12)	0.2102 (12)	0.9788 (12)
O12	2i	0.3568 (12)	0.9728 (12)	0.2219 (12)

From Rietveld refinements, we obtained the pressure evolution of the lattice parameters and equation of state of α -CuMoO₄ and γ -CuMoO₄. For the HP phase, they were obtained only for 0.7 GPa and higher pressures because at 0.3 and 0.5 GPa the fraction of γ -CuMoO₄ was too small to allow an accurate determination of unit-cell parameters (The peaks of γ -CuMoO₄ are too weak at these two pressures). For the low-pressure phase they were obtained up to 1.2 GPa. The pressure dependence of the lattice parameters and angles are plotted in Figure 6. From the figure, it can be seen the behavior under compression is anisotropic.

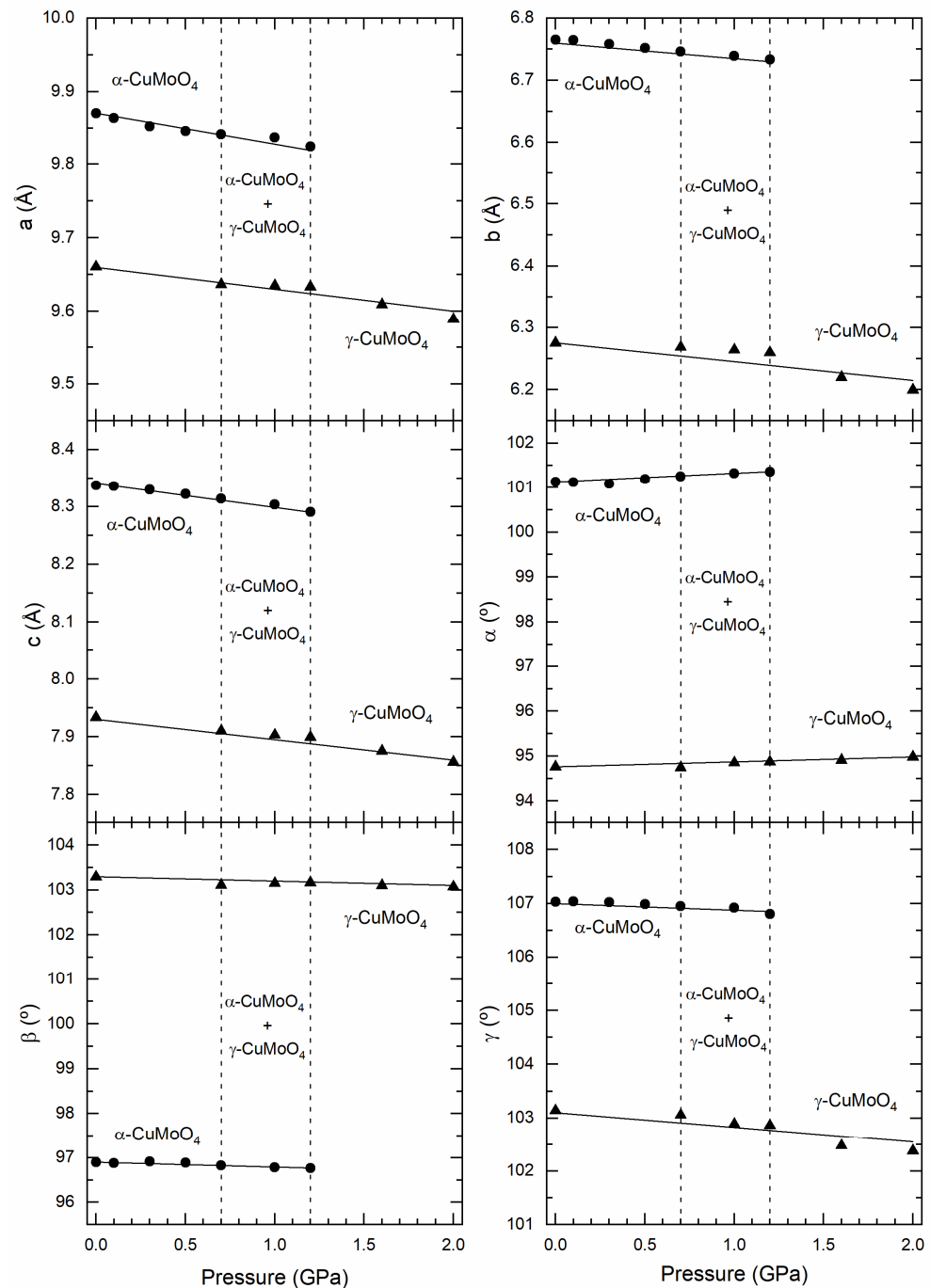


Figure 6. Pressure dependence of the lattice parameters and angles. Filled circles correspond to the α -CuMoO₄ phase and solid triangles corresponds to γ -CuMoO₄. Errors are smaller than symbol's size. The solid lines in the lattice-parameter plots are linear fits of the data. Vertical dashed lines delimit the region of phase coexistence.

For any triclinic structure, the description of the deformation of the unit cell under compression is provided by the compressibility tensor [39]; in particular, by its eigenvectors ($e_{\lambda i}$) and eigenvalues (λ_i). They give the principal axes of the compressibility and the compressibilities along them. We have obtained $e_{\lambda i}$ and λ_i for α -CuMoO₄ using PASCAL [40]. The results are given in Table 3.

Table 3. Eigenvalues, λ_i , and Eigenvectors, $e_{\lambda i}$, for the isothermal compressibility tensor of α -CuMoO₄.

Eigenvalues	Eigenvectors
$\lambda_1 = 4.2(8) \times 10^{-3} \text{ GPa}^{-1}$	$e_{\lambda 1} = (-0.8568, 0.0228, -0.2899)$
$\lambda_2 = 5.8(8) \times 10^{-3} \text{ GPa}^{-1}$	$e_{\lambda 2} = (-0.2653, -0.7825, 0.5632)$
$\lambda_3 = 7.1(8) \times 10^{-3} \text{ GPa}^{-1}$	$e_{\lambda 3} = (0.1237, 0.7819, 0.6110)$

The pressure dependence of volume of both the phases is plotted in Figure 7. From the plot, it can be seen that the phase transition from α -CuMoO₄ to γ -CuMoO₄ exhibits a volume collapse of $\sim 13\%$ at 0.7 GPa which is also in agreement with earlier XRD measurements [15]. The results of Figure 7 were fitted using second- and third-order Birch–Murnaghan equations of state. The fits were carried out using EOSFIT [41]. A fit of the volume vs. pressure data of the α -CuMoO₄ phase to a second-order Birch–Murnaghan equation of state ($B'_0 = 4$) gives a bulk modulus of 67 (2) GPa, if we use third order Birch–Murnaghan equation of state it gives bulk modulus of 62 (4) GPa with $B'_0 = 5.1$ (8) which is also in agreement with earlier XRD measurements [15]. A fit of the volume vs. pressure data of the γ -CuMoO₄ phase to a second-order Birch–Murnaghan equation of state ($B'_0 = 4$) gives bulk modulus of 62 (6) GPa, if we use third-order Birch–Murnaghan equation of state it gives bulk modulus of 68 (9) GPa with $B'_0 = 3.1$ (9). In the previous study, $B_0 = 44.0$ (3.4) GPa and $B'_0 = 15.3$ (3.0) were reported for γ -CuMoO₄. Such a large pressure derivative for the bulk modulus is unusual in oxides [42]. On the other hand, it is not reasonable to have a smaller bulk modulus for γ -CuMoO₄ than for α -CuMoO₄, because the first phase is denser than the second one. The mismatch of B_0 and B'_0 in the previous work could be related to the fact that volume at zero pressure (V_0) was unknown, being extrapolated from HP results. In our case, V_0 has been experimentally determined after decompression. V_0 , B_0 , and B'_0 are correlated parameters [43] and therefore an overestimation of V_0 (466 Å³ extrapolated in Ref. [15] and 454 Å³ here measured) could easily lead to inaccurate values of B_0 and B'_0 . Interestingly, our results indicate, that despite the volume collapse of the transition, the two phases of CuMoO₄ have comparable bulk moduli.

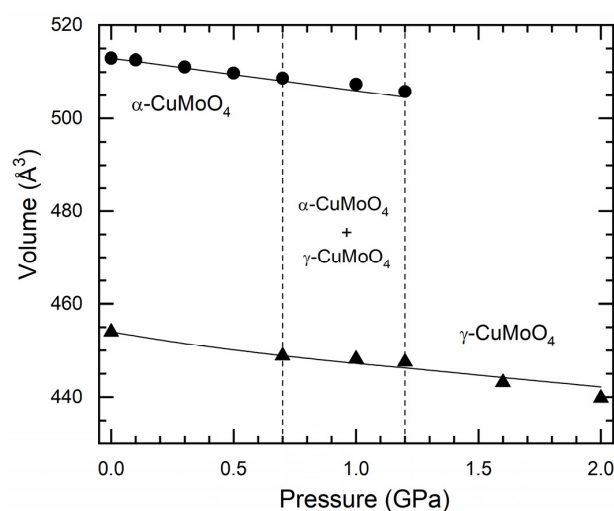


Figure 7. Pressure dependence of the volume. Filled circles correspond to the α -CuMoO₄ phase and solid triangles corresponds to γ -CuMoO₄. Errors are smaller than symbol size. The solid lines are linear fits of the data.

Interestingly, the two phases of CuMoO_4 have considerably smaller bulk moduli than CuWO_4 ($B_0 = 139$ GPa) [44]. This is related to the fact that CuMoO_4 has a much more open structure than CuWO_4 . This is a direct consequence of the way in which polyhedra are linked in CuMoO_4 , which gives to the structure of the two polymorphs a pseudo-layered characteristic. This feature makes the reduction of the “empty” space between layers easier and consequently leads to a smaller bulk modulus in CuMoO_4 . The second fact that facilitates the reduction of volume in CuMoO_4 is that it can be achieved by tilting of the polyhedra. It should be noted that with respect to its polyhedral constitution, CuMoO_4 is more similar to $\text{Cu}_3\text{V}_2\text{O}_8$ and $\text{Cu}_2\text{V}_2\text{O}_7$ [45,46] than to typical orthomolybdates [47,48]. This is consistent in that the two vanadates have bulk moduli of 52 and 64 GPa, respectively; values that are comparable to the bulk modulus of α - and γ - CuMoO_4 .

4. Conclusions

X-ray diffraction studies on nanocrystalline α - CuMoO_4 up to 2 GPa suggest that the low pressure α -phase undergoes an irreversible α - γ phase transition. The onset of phase transition occurs at 0.5 GPa, the coexistence of both phases was observed between 0.5 to 1.2 GPa, and the transition completes at 1.6 GPa, indicating a sluggish nature of the phase transition. The α to γ phase transition involves a change of part of the copper coordination polyhedra, from square-pyramidal (C_{4v}) CuO_5 in α - CuMoO_4 to octahedral elongated (D_{4h}) CuO_6 in γ - CuMoO_4 along with a reduction in volume by 13%, indicative of first-order phase transition. The transition pressure observed in this case is almost double compared to its bulk counterpart which can be attributed to an increase in surface energy in the newly formed high-pressure phase. In addition, we found that in nanocrystalline CuMoO_4 the high-pressure γ -polymorph can be recovered as a metastable phase upon decompression. Since the γ -phase has a smaller band-gap energy than the α -phase, our findings suggest that high pressure can be used to synthesize a metastable polymorph with a tailored band-gap energy for water splitting applications. Finally, we have also discussed the compressibility of both polymorphs and determined their equations of state.

Author Contributions: D.E. conceived the experiments. D.E. and C.P. conducted the experiments. V.P. analyzed the results. The manuscript was written through contributions of all authors. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare no conflict of interest.

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