



Synthesis, Crystal Structure and Characterization of $\text{Cu}_2(\text{PO}_4)(\text{OH})$

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Abstract

This paper reports the hydrothermal synthesis and crystal structure refinement of cuivre phosphate hydroxide, $\text{Cu}_2(\text{PO}_4)(\text{OH})$, obtained at 453 K.

Its structure consists of chains of edge-sharing, distorted $[\text{CuO}_4(\text{OH})_2]$ octahedral extending parallel to $[001]$. These chains are cross linked by isolated PO_4 tetrahedra through corner-sharing, forming channels in which dimers of edge-sharing $[\text{CuO}_4(\text{OH})]$ trigonal bipyramids are located. The structure is stabilized by medium to weak O-H...O hydrogen bonds. In contrast to the previous refinement single crystal X-ray and analysis of data from vibrational spectroscopy, all non-H atoms were refined with anisotropic displacement parameters and the H atom was located.

KEYWORDS: Inorganic compounds; X-ray diffraction; Infrared spectroscopy; Raman spectroscopy.

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1. Introduction

The isostructural $M'M''$ $PO_4 \cdot H_2O$ type compounds ($M'=K^+$, NH_4^+ ; $M''=Mg^{2+}$, Mn^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+}) crystallize in the orthorhombic space group $Pmn2_1$ (C_{2v}) with $Z=2$ [1].

Crystal structure data from single monocrystal x-ray measurements are available for $NH_4 M'' PO_4 \cdot H_2O$ ($M'' = Co, Ni$) [2-4] and $K Mg PO_4 \cdot H_2O$ [5].

Olivenite, ideally $Cu_2 (AsO_4) (OH)$, is a common secondary mineral of the oxidized zone of hydrothermal deposits. It crystallizes with monoclinic symmetry in space group $P 2_1/n$ with a pseudo-orthorhombic cell ($\beta=90^\circ$). Several arsenates and phosphates belong to the olivenite mineral group, including adamite, $Zn_2 (AsO_4) (OH)$ eveite, $Mn^{2+}_2(AsO_4) (OH)$, zincolibethenite, $Cu Zn (PO_4)(OH)$ and zinc Olivenite $Cu Zn (AsO_4)(OH)$. Interestingly, except olivenite, all other minerals in this group display orthorhombic symmetry and crystallize in space group $Pnmm$. The first approximate structure determination of olivenite was reported by Heritsch [6] in space group $Pnmm$. Subsequent studies on olivenite, however, proposed various other space groups: $P2_1 2_1 2_1$ [7], $Pnmm$ [8], and $Pn2_1m$ [9].

Toman [10] proposed that olivenite has actually monoclinic symmetry, and that most of the crystals are twinned. However, Toman [10] did not report any atomic displacement parameters or the position of the H atoms. To avoid the complication of interpreting X-ray diffraction intensity data due to twinning, Burns and Hawthorne [11] performed structure refinements of olivenite using the Rietveld method from powder X-ray diffraction data. By assuming a single isotropic displacement parameter for all O atoms and no H atom position, they attempted refinement both in space group $Pnmm$ and $P 2_1/n$ and obtained nearly identical R_{Bragg} factors ($= 0.074$) and goodness-of-fit values ($= 2.30$). During the course of sample identification for the RRUFF project, we discovered an untwinned and phosphate-containing single-crystal of olivenite from Majuba Hill, Pershing County, Nevada, USA, and conducted a detailed structure refinement.

This paper reports the crystal structure of the monoclinic monophosphate hydroxide $Cu_2 (PO_4) (OH)$. This has been synthesized hydrothermally at 453 K for 72 hours.

2. Experiment

The single crystal of $Cu_2 (PO_4) (OH)$ is prepared hydrothermally from acidic phosphoric.

The reaction mixture was homogenized in 5 ml water.

The crystal structure has been refined in the space group $Pnmm$ and the lattice parameters

$$a = 8.07(1) \text{ \AA}; b = 8.37(1) \text{ \AA}; c = 5.859(10) \text{ \AA}.$$

In case of the Kappa CCD-based measurements, the corresponding software was Denzo-SMN (processing) [12] and HKL-SCALEPACK (multi-scan absorption correction) [13], respectively. All crystal structures were solved using direct methods and were subsequently refined with full matrix least squares refinements on F^2 with the SHELXTL software suite [14]. In the final refinement cycles the displacement parameters of all atoms were refined anisotropically.

The Fourier transform infrared (FT-IR) measurements were performed at room temperature. On a JASCO FT-IR 420 spectrometer over the $4000 - 400 \text{ cm}^{-1}$ region, in a KBr pellet. Furthermore, Raman spectra were measured with a LABRAMHR 800 triple monochromator at room temperature under a $50 \times$ LF objective microscope, a He-Ne ion laser operating at about 300 mW was used (on the triple) as an excitation source (514.532 nm), with a spectral step of 3 cm^{-1} .

3. Results and discussion

3.1 Refinement of the structure

The refinement was achieved on the basis of 2090 independent reflections with $I > 2\sigma(I)$. Atomic positions of Cu_1 , Cu_2 and P were determined using the heavy atom method.

Fourier difference allows oxygen ions to be localized. In addition, the Fourier map has clearly shown that two Cuivre positions.

Detailed conditions of collection and structure refinement are summarized in table 1.

Selected bond lengths, angles, the atomic positions and Thermal anisotropic are reported in tables 2, 3 and 4 respectively.

The structure of $Cu_2 (PO_4)(OH)$ consists of chains of edge-sharing $[Cu_2O_4(OH)_2]$ octahedra extending parallel to [001] that are cross-linked by sharing corners with isolated PO_4 tetrahedra to form an open framework. Channels in the framework contain dimers of edge-sharing $[Cu_1O_4(OH)]$ trigonal bipyramids that share corners with the $[Cu_2O_4(OH)_2]$ octahedral and PO_4 tetrahedra (Fig. 1.) Although the average $\langle P-O \rangle$, $\langle Cu_1-O \rangle$ and $\langle Cu_2-O \rangle$ distances of our study agree well with those given by Toman [10] and Burns and Hawthorne [11], the corresponding individual bond distances and angles from the three structure refinements (including ours) vary significantly. For example, the shortest and longest P-O bond distances within the PO_4 tetrahedra are 1.618 \AA ($As-O_5$) and 1.731 \AA ($As-O_4$), respectively, from Toman [10], 1.640 \AA ($As-O_4$) and 1.702 \AA ($As-O_1$) from [11], and $1.520(2) \text{ \AA}$ ($P-O_4$) and $1.562(3) \text{ \AA}$ ($P-O_1$) from this study. The shortest Cu-O bond length within the $[Cu_1O_4(OH)]$ trigonal bipyramid is $1.928(3) \text{ \AA}$ (Cu_1-O_3) from this study, but is 1.917 \AA (Cu_1-O_3) from [10] and 1.938 \AA from [11].



The structure consists of infinite Cu-O edge-sharing octahedral chains running parallel to the c axis. Cu-O trigonal bipyramids alternating with tetrahedral from ladders with the edge sharing trigonal bipyramids as rungs. The ladders run parallel to the c axis and link to the octahedral chains by corner sharing to form a three dimensional structure with strong chain character. Relationship with sarkinite. Sarkinite is the dimorph of eveite and structure cell data suggest that it belongs to the wagnerite, $Mg_2(PO_4)F$ structure type. As shown in fig. 2 the cation Cu (1) is coordinated to five oxygen anions. Each polyhedron is linked to four PO_4 tetrahedrons via corners and two other tetrahedrons via edges. Fig. 3 presents the Cu (2) cation is inserted into six fold sites. Each polyhedron is linked to three PO_4 tetrahedrons via corners.

The H atoms is bonded to O_3 , at a separation of 0.899 (9) Å. This distance is in fairly agreement with that (0.77 Å) reported for adamite [16].

Table. 1. Procedures for data collection and refinement of $Cu_2(PO_4)(OH)$.

The crystallographic characteristics and conditions for data collection	
Compound	$Cu_2(PO_4)(OH)$
System	orthorhombique
Space group	$Pn\bar{1}m$
Cell dimensions	a = 8.07 (1) Å b = 8.37 (1) Å c = 5.859 (10) Å
Volume	395.7(10) Å ³
Z	4
$\theta_{min.} / \theta_{max.}$ (°)	4.25 / 49.95
Temperature (K)	298(2)
ρ calc (g.cm ⁻³)	3.931
μ (m m ⁻¹)	4.55
Diffractometre	kappa CCD
Nombre of refined parametres	56
Standard reflections	4023
Reflections with $I > 2\sigma(I)$	2090
R	0.0763

Table. 2. Main interatomic distances and bond angles obtained for $\text{Cu}_2(\text{PO}_4)(\text{OH})$.

Atoms	Distances (Å)
$\text{Cu}_1\text{-O}_3$	1.928(3)
$\text{Cu}_1\text{-O}_2^{\text{I}}$	1.944(3)
$\text{Cu}_1\text{-O}_4^{\text{II}}$	2.047(3)
$\text{Cu}_1\text{-O}_4^{\text{III}}$	2.048(2)
$\text{Cu}_1\text{-O}_4$	2.048(2)
$\text{Cu}_2\text{-O}_1^{\text{IV}}$	1.9642(19)
$\text{Cu}_2\text{-O}_1$	1.9642(19)
$\text{Cu}_2\text{-O}_3^{\text{V}}$	1.922(2)
$\text{Cu}_2\text{-O}_3$	1.977(2)
$\text{Cu}_2\text{-O}_4^{\text{VI}}$	2.376(2)
$\text{Cu}_2\text{-O}_4^{\text{VII}}$	2.376(2)
$\text{P-O}_4^{\text{VIII}}$	1.520(2)*2
P-O_2	1.545(3)
P-O_1	1.562(3)

Atoms	Angles(°)
$\text{O}_3\text{-Cu}_1\text{-O}_2^{\text{I}}$	176.16(13)
$\text{O}_3\text{-Cu}_1\text{-O}_4^{\text{III}}$	88.51(8)
$\text{O}_2^{\text{I}}\text{-Cu}_1\text{-O}_4^{\text{III}}$	95.89(9)
$\text{O}_2^{\text{I}}\text{-Cu}_1\text{-O}_4^{\text{III}}$	95.89(9)
$\text{O}_2^{\text{II}}\text{-Cu}_1\text{-O}_4^{\text{III}}$	124.36(8)
$\text{O}_4^{\text{III}}\text{-Cu}_1\text{-O}_4$	111.28(15)
$\text{O}_{4\text{vi}}\text{-Cu}_2\text{-O}_2^{\text{II}}$	92.51(12)
$\text{O}_3\text{-Cu}_2\text{-O}_3$	95.13(10)
$\text{O}_1^{\text{IV}}\text{-Cu}_2\text{-O}_1$	83.85(12)
$\text{O}_1^{\text{IV}}\text{-Cu}_2\text{-O}_3^{\text{V}}$	96.20(9)
$\text{O}_1^{\text{IV}}\text{-Cu}_2\text{-O}_3$	175.63(11)
$\text{O}_1\text{-Cu}_2\text{-O}_3$	96.20(9)
$\text{O}_3^{\text{V}}\text{-Cu}_2\text{-O}_3$	84.08(12)
$\text{O}_1^{\text{IV}}\text{-Cu}_2\text{-O}_4^{\text{VI}}$	93.08(10)
$\text{O}_3\text{-Cu}_2\text{-O}_4^{\text{VII}}$	91.27(10)
$\text{O}_3^{\text{V}}\text{-Cu}_2\text{-O}_4^{\text{VI}}$	80.48(10)
$\text{O}_3\text{-Cu}_2\text{-O}_4^{\text{VII}}$	80.49(10)
$\text{O}_4^{\text{IV}}\text{-Cu}_2\text{-O}_4^{\text{VII}}$	168.94(10)
$\text{O}_1^{\text{IV}}\text{-Cu}_2\text{-O}_4^{\text{VII}}$	95.15(11)



$O_1-Cu_2-O_4^{VII}$	93.08(10)
$O_3^V-Cu_2-O_4^{VII}$	91.27(10)
$O_4^{VIII}-P-O_4$	109.3(2)
$O_4^{VIII}-P-O_2$	109.71(13)
$O_4^{VIII}-P-O_1$	110.99(10)
O_4-P-O_1	110.99(10)
O_2-P-O_1	106.16(17)
$P-O_4-Cu_1$	132.63(13)
$P-O_4-Cu_2^I$	116.78(11)
$Cu_1-O_4-Cu_2^I$	110.17(9)

Symmetry codes :

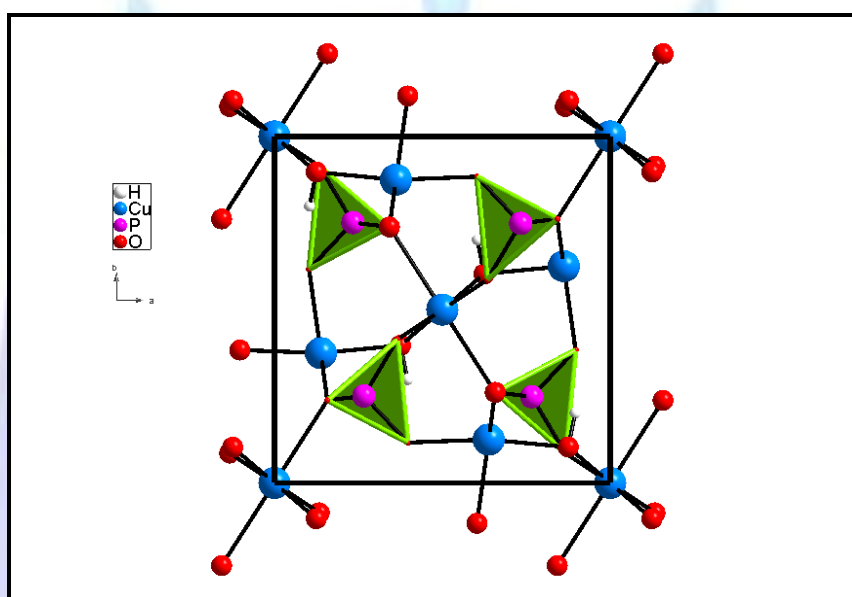
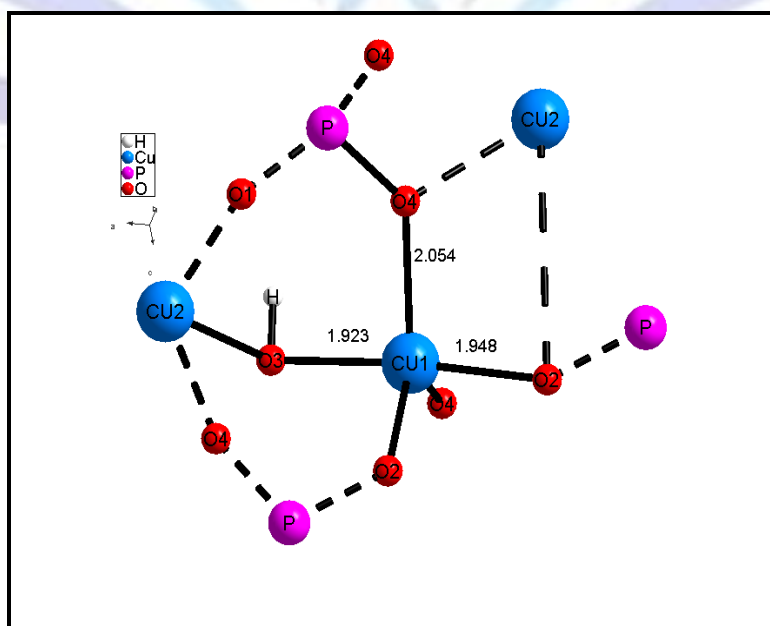
- (i) $x-1/2, -y+1/2, -z+1/2$
- (ii) $x-1/2, -y+1/2, -z+1/2$
- (iii) $x, y, -z$
- (iv) $-x+2, -y, -z+1$
- (v) $-x+2, -y, -z$
- (vi) $-x+3/2, y-1/2, -z+1/2$
- (vii) $x+1/2, -y+1/2, -z+1/2$
- (viii) $x, y, -z+1$
- (ix) $-x+3/2, y+1/2, z+1/2$

Table. 3. Atomic coordinates for $Cu_2(PO_4)(OH)$.

	X	Y	Z	Uiso* / Ueq
P	0.76665(11)	0.24873(10)	0.5000	0.00124(14)
O1	0.8657(3)	0.0884(3)	0.5000	0.0030(3)
O2	0.8974(4)	0.3836(4)	0.5000	0.0123(6)
O3	0.8759(3)	0.1034(3)	0.0000	0.0022(3)
O4	0.6586(3)	0.2624(3)	0.2885(3)	0.0081(3)
Cu1	0.63815(5)	0.12570(6)	0.000	0.00506(11)
Cu2	1.00000	0.00000	0.25058(7)	0.00449(12)
H	1.022(15)	0.058(14)	0.500	0.02(3)*

Table 4. Thermal anisotropic of $\text{Cu}_2(\text{PO}_4)(\text{OH})$.

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
P	0.000 (3)	0.0037(3)	0.000(3)	0.00087(19)	0.000	0.000
O1	0.0039(8)	0.0051(7)	0.000 (6)	0.0039(6)	0.000	0.000
O2	0.000	0.0062(9)	0.031 (2)	-0.0005(6)	0.000	0.000
O3	0.0002(6)	0.0063(7)	0.000 (6)	-0.0001(5)	0.000	0.000
O4	0.0107(7)	0.0137(7)	0.0000(5)	0.0084(6)	-0.0057(5)	-0.0039(5)
Cu1	0.00001(16)	0.00818(18)	0.00700(19)	0.00049(10)	0.000	0.000
Cu2	0.00388(18)	0.0096(2)	0.00001(19)	0.00484(11)	0.000	0.000


Figure 1. Projection of $\text{Cu}_2(\text{PO}_4)(\text{OH})$.


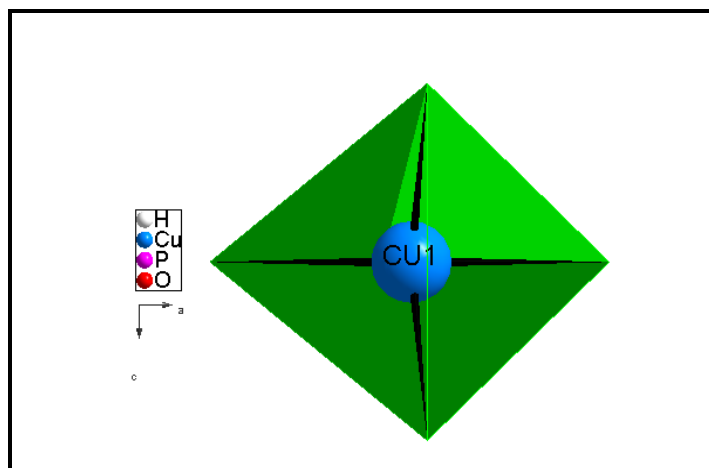


Figure. 2. Coordination of the metal Cu (1).

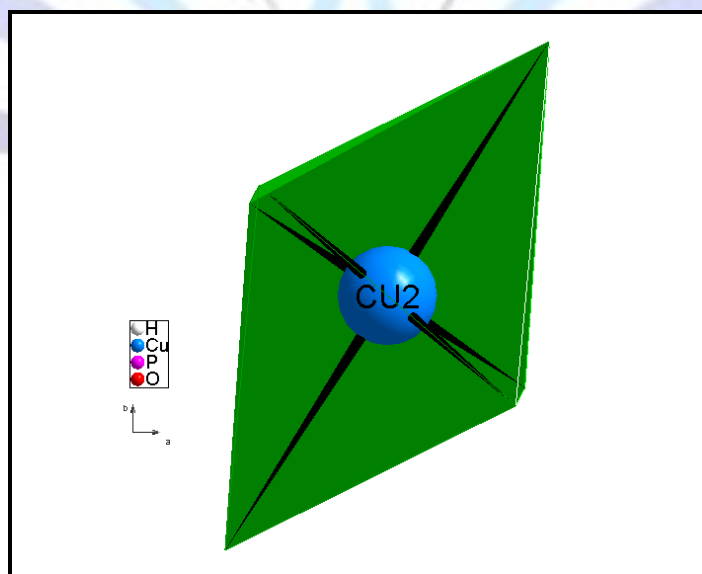
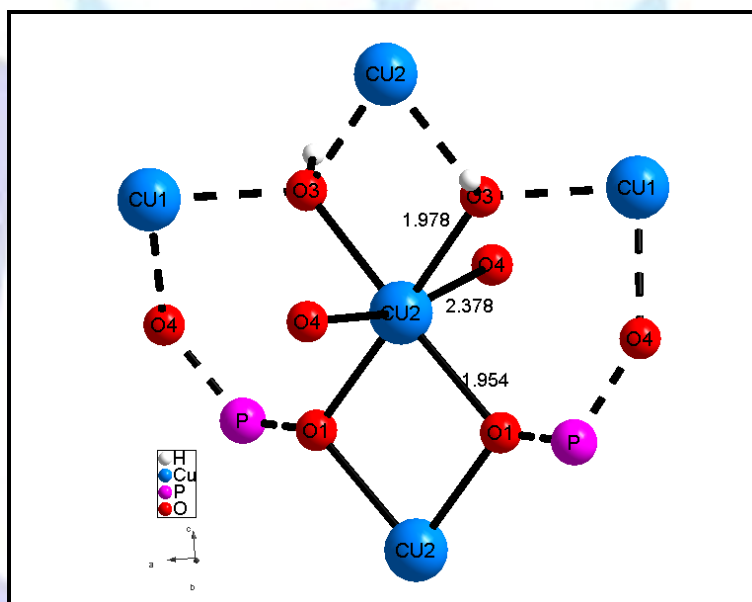


Figure. 3. Coordination of the metal Cu (2).

4. Spectroscopy analysis

FT-IR is one of the most general spectroscopic techniques used to identify the functional groups in materials. It is an important and popular tool for structural exposition and compound identification. The infrared spectra of the compounds obtained from the thermal vibration of $\text{Cu}_2(\text{PO}_4)(\text{OH})$ is shown in fig. 4. The presence of a sharp vibrational band at approximated 3535 cm^{-1} for $\text{Cu}_2(\text{PO}_4)(\text{OH})$ is attributed to the stretching mode of the O-H band.

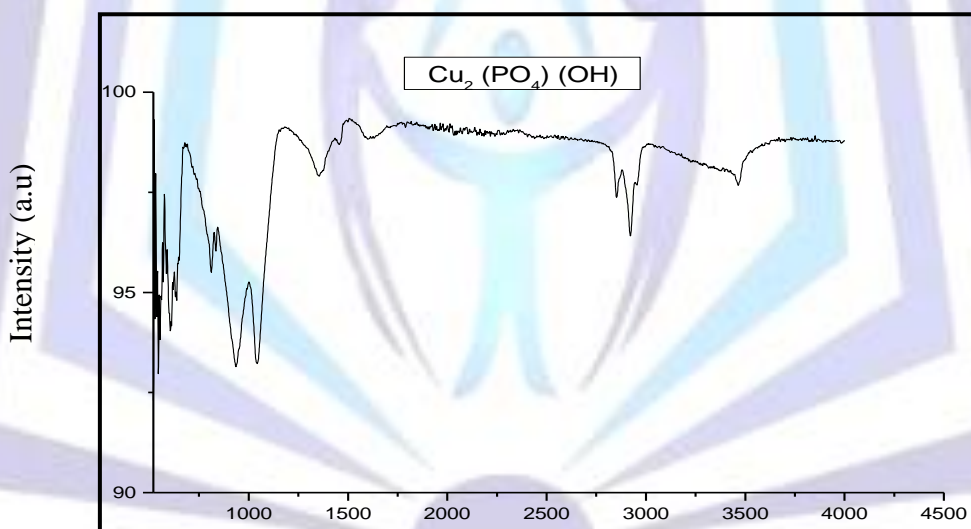
The band observed between 936 cm^{-1} ν_1 and 650 cm^{-1} ν_4 are attributed to the stretching vibration mode of the $(\text{PO}_4)^{3-}$ groups the position of these bands were similar to those (950 and 700 cm^{-1}) previously reported by I. De Pedro and all [15].

The ν_{as} asymmetrical stretching mode ν_{as} (P-O) appears at frequencies 881 , 837 and 812 cm^{-1} for $\text{Cu}_2(\text{PO}_4)(\text{OH})$.

The peak observed at 605 cm^{-1} characteristic of the symmetric ν_s (P-O) stretch. This band appears when $\text{Cu}_2(\text{PO}_4)(\text{OH})$.

The single-crystal laser Raman spectra of both $\text{Cu}_2(\text{PO}_4)(\text{OH})$ is given in Fig. 5. Two major bands in the hydroxyl stretching (ν_{OH}) region: one at 3445 cm^{-1} and the other at 3463 cm^{-1} .

Similar wavenumbers ($\nu_{\text{OH}} = 3437\text{ cm}^{-1}$ and 3464 cm^{-1}) were also obtained by Frost et al [17]. Given the correlation between ν_{OH} and O-H...O distances in minerals (libowitzky) [18], one would expect two O-H...O distances between 2.8 and 2.9 \AA in olivenite. Our structural data indeed show that $\text{O}_3 (= \text{OH})$ atom is at a distance of 2.79 \AA from O_1 and 2.838 \AA from O_4 . Nevertheless, the angles $\text{O}_3\text{-H...O}_4$ (110°) and $\text{O}_3\text{-H...O}_1$ (90°) appear to be too small for hydrogen bonding. Note that, based on the structure refinement of liberthenite, the phosphate analogue of olivenite, Cordsen [19] proposed a bifurcated hydrogen bonding model for this mineral, in which there are two O-H...O bonds at the same distance of 2.84 \AA and two bonding angles of 110° . Raman spectra of the tetrahedral anions in aqueous systems are well known. The symmetric stretching vibration of the dicuivre (II) monophosphate hydroxide anions (ν_1) is observed at 954 cm^{-1} and coincides with the position of the asymmetric stretching mode (ν_3). The symmetric bending mode (ν_2) is observed at 407 cm^{-1} and the out-of-plane bending modes (ν_4) is observed at 501 cm^{-1} . Of all the tetrahedral oxyanions spectra, the positions of phosphate vibrations occur at lower wavenumbers than any of the other naturally occurring mineral oxyanions spectra. The ν_1 and ν_3 bands of $\text{Cu}_2(\text{PO}_4)(\text{OH})$ were observed at 890 , 813 , 887 cm^{-1} and 1322 and 2645 cm^{-1} respectively. The bending modes were found at 407 cm^{-1} and 413 cm^{-1} .



Wavenumber (cm^{-1})

Figure 4. Infrared spectrum of $\text{Cu}_2(\text{PO}_4)(\text{OH})$.

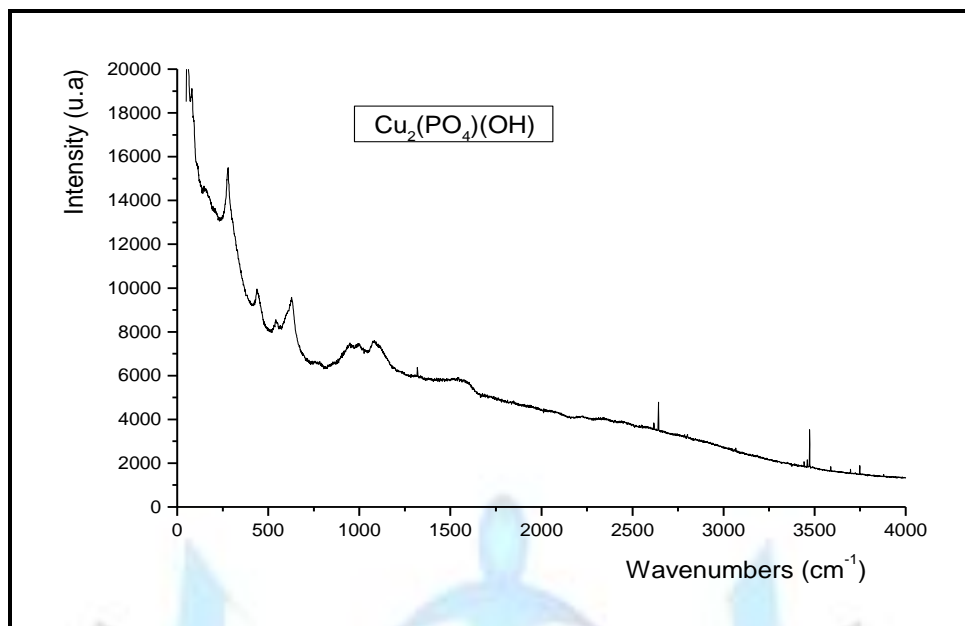


Figure. 5. Raman spectrum of $\text{Cu}_2(\text{PO}_4)(\text{OH})$.

Table. 5. Spectral data and band assignments Raman and IR of $\text{Cu}_2(\text{PO}_4)(\text{OH})$.

IR	Raman	Assignments
>500	141 242 407 413	$V_2(\text{PO}_4)$
612	573	$V_4(\text{PO}_4)$
935	790 813 887 954	$V_1(\text{PO}_4)$
3466	3445 3463 3476 3590 3698 3745	$V_S(\text{OH})$



5. Conclusion

The results from X-ray diffraction (XRD) as shown that formula was $\text{Cu}_2(\text{PO}_4)(\text{OH})$. The analysis of data from vibrational spectroscopy has also provided support for the high symmetry $Pn\bar{m}$ space group.

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