



(RESEARCH ARTICLE)



Crystal growth and characterization of Cd doped copper tartrate crystals in silica gel

Lakshmichhaya Ramkrishna Patil ^{1,*}, Arun Madhukar Patil ¹ and Sharda Jayantrao Shitole ²

¹ Department of Physics, R.C. Patel Arts Science & Commerce College, Shirpur-425405, Maharashtra, India.

² Smt. H.R. Patel Mahila College, Shirpur-425405, Maharashtra, India.

World Journal of Advanced Engineering Technology and Sciences, 2024, 13(02), 013–021

Publication history: Received 15 September 2024; revised on 29 October 2024; accepted on 31 October 2024

Article DOI: <https://doi.org/10.30574/wjaets.2024.13.2.0532>

Abstract

Cd doped Copper tartrate crystals were grown by the 'Single diffusion' method in silica gel. In 'gel growth technique' the parameters of crystal growth such as pH and aging were optimized in this work. Concentration of cadmium chloride as outer reactant was also optimized. Using 'Powder X-Ray Diffraction', the determined Orthorhombic crystal structure has volume 621.022080\AA^3 . Many peaks of maximum intensity match to that of copper tartrate crystal and XPS counts has shown presence of 0.02 % atomic weight of Cd doped into copper tartrate crystals. The Fourier transform infrared spectrum in the range $400\text{--}4,000\text{ cm}^{-1}$ was recorded to assign the vibrational bands to corresponding functional groups and bonds. It has confirmed the carboxyl as functional group and the other bonds between atoms. X ray Photoelectron Spectroscopy has concluded paramagnetic nature and the presence of Cu^{2+} ion and also the presence of carboxyl group by its binding energy peak.

Keywords: PXRD; XPS; FTIR; Sodium Meta Silicate; Doping

1. Introduction

Single Crystals grown in gel find important uses in research and development for their quality and XRD compatible size. Synthesis and analysis of useful single crystalline material is significant to understand physical and chemical properties of a solid material. Hence, growing crystals under controlled conditions has become a necessity.[1]

When a crystal is grown in solution, it takes the solute from the solution. Thus, reducing the concentration of the solution around it. To allow the crystal to keep growing, fresh solute concentrations must be withdrawn from the bulk of the solution, and lead molecules have to move toward the crystal surface of the growing crystal. This motion of the solute is usually referred to as the mass transfer process. In the absence of convection in the bulk of the solution for a gelled system, these molecular motion processes cause mass transference in a controlled manner [2].

Basic research on anisotropic physical properties requires crystalline samples of high quality. Crystal growth in gels is an ideal method to provide this kind of specimen, mostly when the salts to be grown are sparingly soluble in water. The nucleation kinetics and the crystal growth itself depend on gel characteristics such as density, pH, aging time, and salt concentrations. It is important to note that Sodium meta silicate (SS) is one of the most popular gels used to grow crystals of inorganics (low-molecular-weight compounds). In general, the gel from SS shows some general features: pH ranging from 3 to 5 and density between 1.03 and 1.06 g/ml [3].

Various pure and doped materials like oxalates, tartrates, phosphates in single crystalline form were grown in Silica gel medium by single diffusion. [4]. New materials are grown by 'Reaction method' and by single diffusion as silica gel is the hydrogel.

* Corresponding author: Lakshmichhaya Ramkrishna Patil

Gelation is one of step of a sol-gel process to prepare a gel. A sol-gel process occurs in several steps:

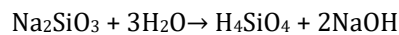
- Hydrolysis and condensation of molecules.
- Gelation (sol-gel transformation)
- Ageing.
- Drying

The sol-gel process may be described as:

” Formation of an oxide network through polycondensation reactions of a molecular precursor in a liquid.”

In most gel systems used for materials synthesis, the interactions are of a covalent nature and the gel process is irreversible [5].

The synthetic pathways to obtain hydrogels from the neutralization of sodium metasilicate (SS) solution are as follows:



Copper tartrate have been reported to be grown in silica gel find applications related to electrical, magnetic, Opto-electronic and medicinal properties [6]. Also, several doped copper tartrate crystals were grown by the gel technique, for example, sodium modified, iron doped and manganese doped copper tartrate crystals and cadmium doped copper tartrate [6]. Crystals are transparent to visible light. This allows them to be used for window applications, where the crystalline perfection and optical transparency is essential. As crystals behave as insulators and are suitable for the fabrication of materials for opto-electronic devices. They can be used to develop copper clad laminates in PCBs and also various application of in the electronic industries. [7].

In this study Cd doped copper tartrate grown in Silica gel and parameters of growth like pH and aging were varied at specific gravity of 1.04 g/ml of sodium metasilicate.

2. Material and methods

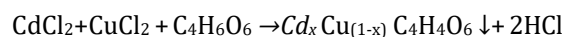
Cadmium doped Copper tartrate ($\text{Cd}_x\text{Cu}_{(1-x)}\text{C}_4\text{H}_4\text{O}_6$) crystals were grown by the gel growth method in silica gel by single diffusion technique. For doping, 1M Copper Chloride (CuCl_2) is mixed with 0.5M CdCl_2 used poured as a supernatant or outer reactant over the set gel. Sodium metasilicate (Na_2SiO_3) is used to prepare silica gel by neutralization method by tartaric acid. Tartaric acid ($\text{C}_4\text{H}_6\text{O}_6$) is used as an inner reactant. All chemicals were of analytical grade. Specific gravity of silica gel was measured.

For silica gel setting 1 M sodium metasilicate solution was added to a 1 M tartaric acid solution in a test tube until the pH value reached 4.0. After a firm gel setting, gel was aged for four days. Cadmium doped Copper tartrate ($\text{Cd}_x\text{Cu}_{(1-x)}\text{C}_4\text{H}_4\text{O}_6$) crystals were grown by the gel growth method in silica gel by single diffusion technique. 1M Copper Chloride (CuCl_2) is mixed with 0.5M CdCl_2 . This mixture was poured as an supernatant or outer reactant over the set gel dropwise (along the walls of the tube to avoid any gel breakage) and allowed to diffuse into the gel. Next day, pure copper tartrate crystals of bluish color were seen growing (Fig. 1). Within 30-45 days crystal growth is complete any gel structure holding crystals seems sinking to bottom of the test tube.

The pH, aging and concentration of cadmium chloride were varied in this work to optimize crystal growth conditions.

Silica gel is a 3D skeleton of Silicic acid. It is inert -Si-O-Si network. Within this crucible crystal growth takes place. Within its pore nucleation takes place. Diffusion of copper ions mixed with cadmium ions and tartrate ions lead to mass transport and react to produce greenish blue, moderately transparent and prismatic Cd doped copper tartrate crystals. The size of crystal grown is 2 mm x 4 mm x 0.500 mm.

The chemical reaction inside the silica gel growth for the doping of cd into copper tartrate crystal can be represented by,



At higher pH values gel becomes rigid. At low pH, gel is weaker to hold crystals. The pH of value 3.5,4,4.2 are suitable for growth. Aging of 3,4 days after firm gel setting is suitable for the growth of crystals. The concentration of 0.5 M cadmium chloride is optimized for 1M copper chloride concentration. The most optimized value of pH is 4 and aging is also 4 days. Aging is related to chemical reactions like hydrolysis and condensation. It affects crystal shape. At lower concentration of outer reactant size of crystals is small and habit is leaflike. At higher concentration size of crystals is large and leaflike. At optimum concentration habit is found to be cuboid.

For 30% volume in ml of 0.5 M CdCl_2 solution has produced crystals with $x=0.02$ i.e. 2% atomic weight percentage as detected by XPS spectroscopy.



Figure 1 $\text{Cd}_x\text{Cu}_{(1-x)}\text{C}_4\text{H}_4\text{O}_6$ crystal growth in Silica gel

3. Results and discussion

The structure of a crystal constitutes its unit cell, constituent atoms and its functional group. These parameters are found using techniques by analysis of received data presented as below:

3.1. Powder X-ray Diffraction:

Powder X-ray diffraction (PXRD) was performed by MeasSrv(B2)/250242.

The PXRD data of Cd doped copper tartrate is collected in the form of intensity and 2θ as shown in figure 2. Maximum intensity peaks match with the JCPDS card number is 01-0158. [8] and COD ID 7023997 [9] of copper tartrate and the corresponding observed maximum 'd' values from the author has received PXRD data are used to calculate dimensions of unit cell of Cd doped Copper tartrate crystal. Author's received data is matched and indexing of copper tartrate is presented in the table2. The edge lengths a, b, c of unit cell calculated from indexing of PXRD data of Cd doped copper tartrate are, $a = 5.47 \text{ \AA}$, $b = 11.76 \text{ \AA}$, $c = 9.20 \text{ \AA}$ and volume of unit cell is, $V = 621.02208 \text{ \AA}^3$.

Doping of Cd in Copper tartrate has affected dimension 'a'. The value of edge length 'a' of copper tartrate crystal is 8.67 \AA and dimensions b, c of unit cell are nearly same as the reported ones [8],[6] as JCPDS card number 01-0158. Author has matched intensity data with COD ID 7023997.

The intensity peaks match with Copper tartrate. Other peaks in Copper tartrate are absent. One may conclude that Cd is doped or occupy lattice of Copper tartrate. 'd' plane indexing is as illustrated in table 1 and peaks are shown in figure 2.

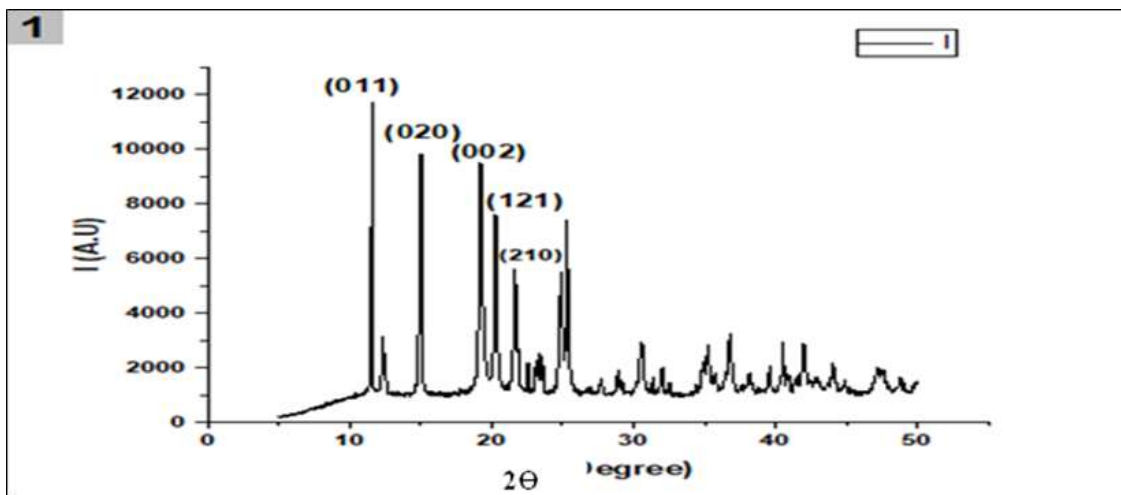


Figure 2 Powder X-Ray diffraction $Cd_xCu_{(1-x)}C_4H_4O_6$ crystal

Table 1 PXRD Indexing Of $Cd_xCu_{(1-x)}C_4H_4O_6$

Obs.Max($2\theta^\circ$)	d(Obs.Max in Å)	Corresponding (h,k,l) value
11.590 ^o	7.62927	(0,1,1)
15.045	5.88381	(0,2,0)
19.279	4.60033	(0,0,2)
20.311	4.36877	(1,2,1)
21.893	4.05646	(2,1,0)
25.335	3.51268	(2,2,0)

Table 2 PXRD Indexing Of $CuC_4H_4O_6$

Obs_ Max ($2\theta^\circ$)	d (Å) (Obs_ Max)	Indices of Plane (h, k, l)
11.587	7.63119	011
12.374 0	7.14750	110
15.042 0	5.88499	020
19.263 0	4.60391	002
20.285 0	4.37429	121
21.655 0	4.10057	210
24.901 0	3.57295	130
25.316 0	3.1520	220
30.571 0	2.92188	003
36.787 0	2.44121	321
35.242 0	2.54459	240

3.2. X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) is performed by K ALPHA+ made at M/s Thermo Fisher Scientific Instruments at NCL, Pune.

XPS spectra was done as Cu2P scan,Cd 3d scan,O 1s scan, C1S scan.The splitting of levels characteristics to cd doped copper tartrate were detected as Shown in Figure 3,4,5,6

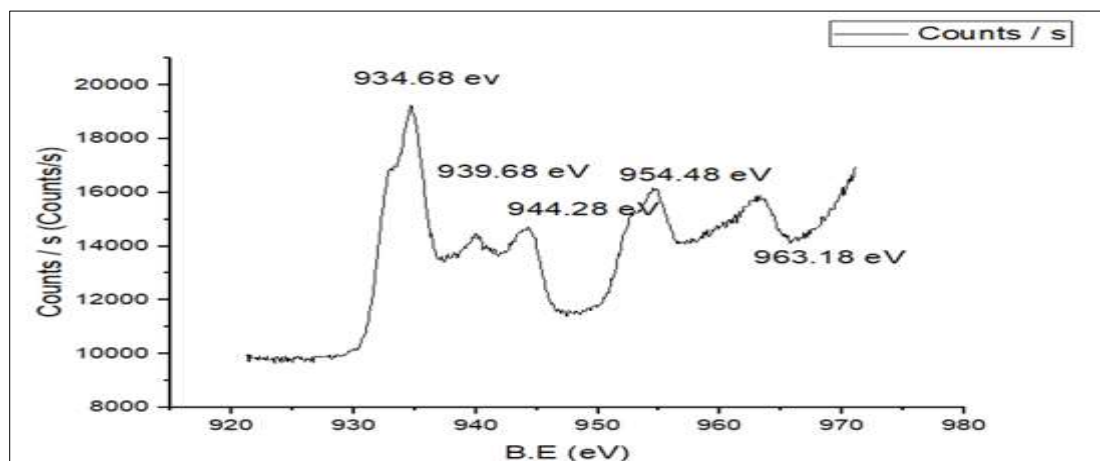


Figure 3 Cu₂P Scan of Cd doped Copper tartrate

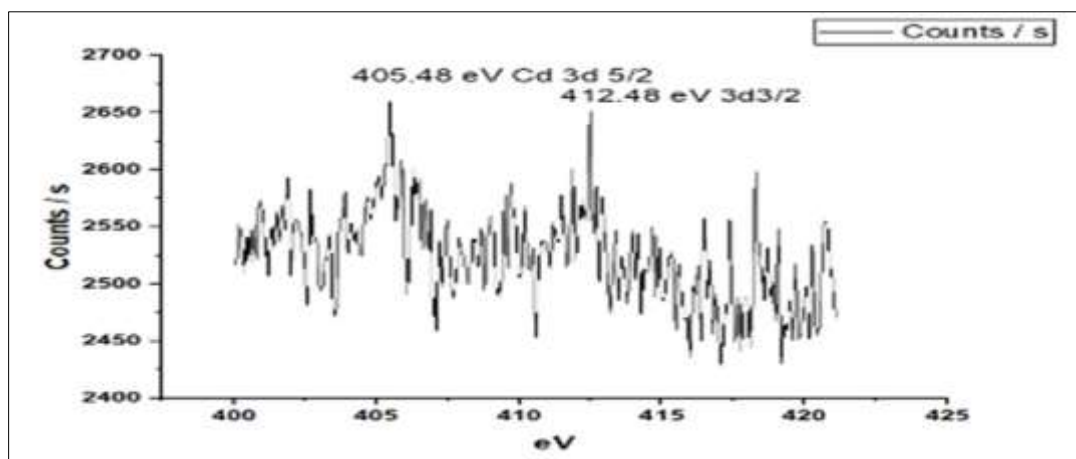


Figure 4 Cd 3d Scan of Cd doped Copper tartrate

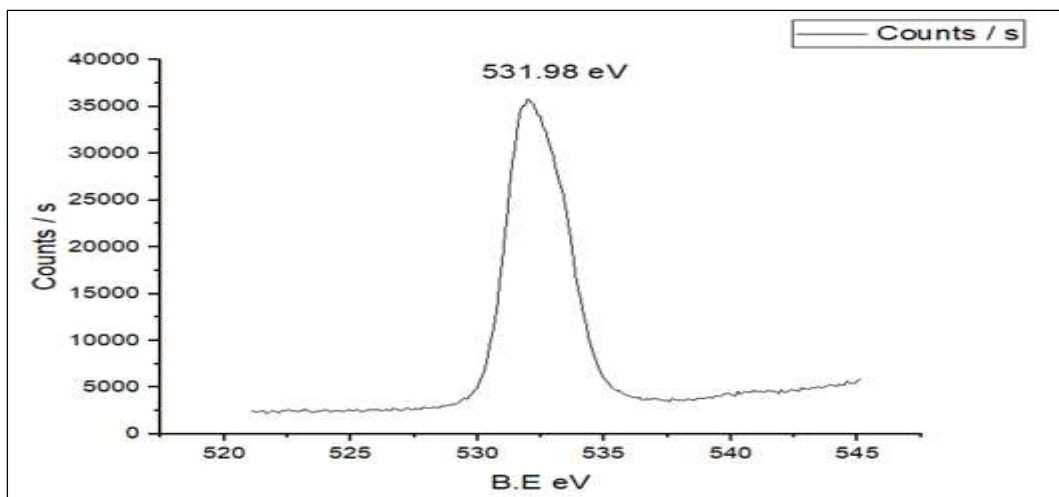


Figure 5 O 1S Scan of Cd doped Copper tartrate

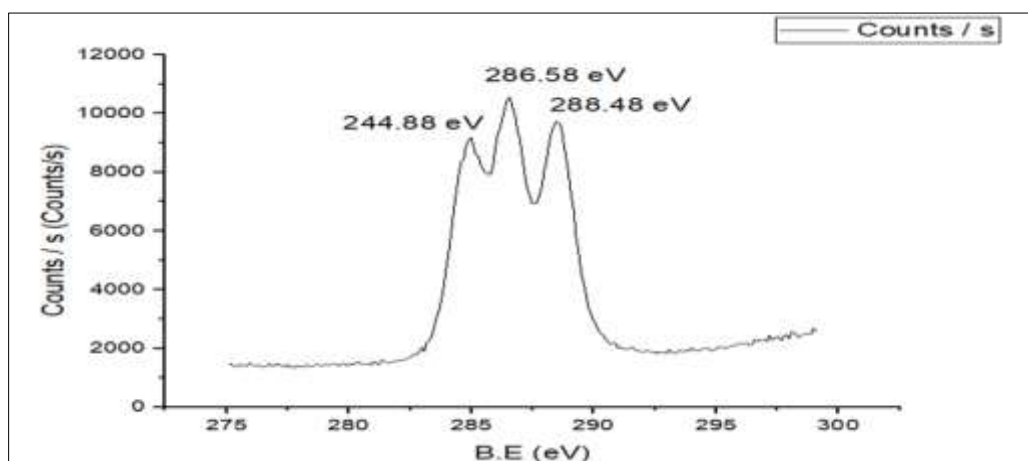


Figure 6 C 1S Scan of Cd doped Copper tartrate

The copper 2P scan electron binding energy spectrum of copper tartrate is shown in Figure 5. The Binding energy peak of $2P_{3/2}$ peak at 933.30 eV is observed. The spectrum consists of spin-orbit-split $2P_{3/2}$ and $2P_{1/2}$ peaks and satellites. These peaks seem to be sensitive in deducing the charge valency of copper ions in copper tartrate. The peaks $2P_{3/2}$ and $2P_{1/2}$ observed at 934.66 eV and 954.48 eV respectively, in Figure 5 are assigned to the Cu^{2+} ions. The Cu 2P peak has a significantly split spin-orbit component with $\Delta = 19.82$ eV close to a value $\Delta = 19.72$ eV. A broad satellite peak is observed near 944.48 eV and these are strong Cu^{2+} satellites of $2P_{3/2}$ state 945.2 eV. It has been reported that strong satellite peaks appear in the XPS spectrum of transition-metal elements with unpaired electrons, but not for a closed-shell structure. In other words, Cu^+ (d^{10}) configuration does not show satellite peaks and Cu^{2+} (d^9) shows such peaks. Therefore, the observed satellite peak at 945.2 eV is ascribed to Cu^{2+} ions [10,8]. Moreover, it has been reported that for transition metals, the absence of the satellite peaks is the fingerprint for elemental or diamagnetic lines. The occurrence of prominent satellites corresponds to the existence of the paramagnetic state [11,12]. This confirms the paramagnetic state of the Cd doped copper tartrate crystal.

The oxygen 1S scan electron binding energy spectrum of copper tartrate is shown in Figure 6. The spectrum consists of the 1S peak at about 531.98 eV, 531 eV are assigned to C-O organic bond [13].

The carbon 1S scan electron binding energy spectrum of copper tartrate is shown in Figure 6. It shows the three 1S peaks at about 288.48 eV, which is ascribed to carbonyl, that is, carbon with oxygen [14].

In chemical state O-C=O has B.E approximately 288.5 eV. 288.38 eV peak of B.E in C1S scan in Figure 6 shows this Chemical state [15].

CuLM2 scan is assigned to $\text{Cu}(\text{OH})_2$ [10].

In Cd 3d scan 405.48 eV and 412.48 eV can be assigned to $\text{Cd } 3d_{5/2}$ and $\text{Cd } 3d_{3/2}$ peaks [16]. Counts per second are less as compared to Copper, Oxygen and carbon and 0.02% weight of cadmium is detected.

3.3. Fourier Transform Infrared Spectroscopy

The Fourier Transform Infrared Spectroscopy (FTIR) spectrum was recorded using a Bruker ALPHA II model of spectrophotometer by the KBr pellet technique.

FTIR is the fingerprint of materials. FTIR analysis of single crystal Cadmium doped Copper tartrate is preliminary method of identifying a grown material. Functional group of a material, bonds in molecule of material are investigated. FTIR spectrum is recorded and analysed. Wavenumbers in spectrum below 1500 cm^{-1} represent 'fingerprint Region' of molecule and wavenumbers above it represent the 'Functional Group' region. Recorded FTIR spectra of single crystals of Copper tartrate are as Shown in figure 7 and analyzed in table 3.

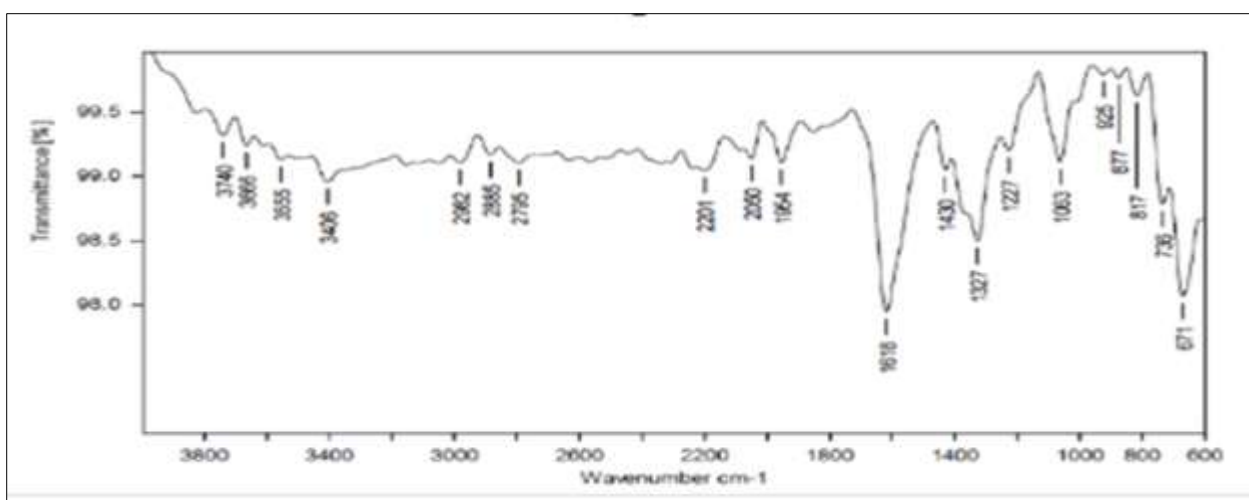


Figure 7 FTIR Spectra of Cd doped Copper tartrate ($\text{Cd}_x\text{Cu}_{(1-x)}\text{C}_4\text{H}_4\text{O}_6$)

Table 3 FTIR analysis of $\text{Cd}_x\text{Cu}_{(1-x)}\text{C}_4\text{H}_4\text{O}_6$

Absorption in Wavenumber (cm^{-1})	Assignment
3405.8331, 3555.0867	OH-Stretching due to water bands
1618.2504	$\text{C} = \text{O}$ due to oscillations of Carboxyl group
1327.4724, 1227.4625	C-O Stretching vibration
1062.8985	C-H stretching vibration
1062.8985	O-H stretching out of plane vibration
736.001, 817.1281, 876.6513	Metal Oxygen bond stretching Vibrations (CuO and Cd doped CuO)
1618.2504, 1327.4724, 1429.9304, 670.5868	Absorptions corresponding to Carboxyl group oscillations

Sheveheko studied [6] the IR spectra of both normal and partially deuterated compounds of some tartrates and found absorptions at 600 cm^{-1} and 400 cm^{-1} due to COO^- group in metal tartrates.

Moreover, Kirschner and Kiesling studied the infrared spectrum of Cu (II) tartrates tri-hydrate [6]. They found that tartrate was coordinated to Cu (II) through hydroxyl and 2-carboxylate groups [6].

In the FTIR analysis of Cd doped Copper tartrate Carboxyl ion frequencies are noticed at 1618.2504 cm^{-1} . This wave number is assigned to C=O due to oscillations of Carboxyl group [17].

CuO bond wavenumber is also noticed.

4. Conclusion

Cd doped Copper tartrate crystals were grown by the gel Growth method. From PXRD data I-2 θ values unit cell dimensions, structure of unit cell is confirmed to be an orthorhombic structure. The edge lengths a, b, c of unit cell calculated from the observed PXRD data of Cd doped copper tartrate are, $a = 5.47\text{ \AA}$, $b = 11.76\text{ \AA}$, $c = 9.20\text{ \AA}$ and volume of unit cell is, $V = 621.02208\text{ \AA}^3$. FTIR confirmed the presence of the copper metal ion complex and Carboxyl ion frequency. XPS study has shown paramagnetic nature and the presence of Cu^{2+} ion (d^9) state and 0.02 % atomic weight percentage of Cd in copper tartrate lattice.

Compliance with ethical standards

Acknowledgments

We acknowledge for the coordination for characterization work performed at Kavayitri Bahinabai Chaudhari North Maharashtra University Jalgaon India, NCL Pune and R.C. Patel Pharmacy College, Shirpur. We also acknowledge our thanks to the department of Physics of R.C. Patel Arts Science & Commerce College, Shirpur where the work of crystal growth is done. This is our original work for the degree of Doctor of Philosophy of Physics. This is self-funded work

Disclosure of conflict of interest

All authors declare that there is no conflict of interest.

Data Availability Statement

All datasets for this research are available upon request from the corresponding author.

Author Contributions

All authors contributed equally to the writing of this paper, and have read and approved the final draft.

References

- [1] Bhat H. L. Introduction to crystal growth: principles and practice. CRC Press, 2014.
- [2] Moreno, Abel, and Ma Eugenia Mendoza "Crystallization in gels." In Handbook of Crystal Growth, pp. 1277-1315 Elsevier, 2015.
- [3] Rudolph, Peter, ed. Handbook of crystal growth: Bulk crystal growth. Elsevier, 2014.
- [4] Patel, Ambalal Ranchhodhbhai and A. Venkateswara Rao. "Crystal growth in gel media" Bulletin of Materials Science 4 (1982) 527-548.
- [5] Aguilar, Guadalupe Valverde. " Introductory chapter: a brief semblance of the sol-gel method in research." Sol-Gel Method-Design and Synthesis of New Materials with Interesting Physical, Chemical and Biological Properties (2018).
- [6] Jethva, H. O., R M. Dabhi, and M. J. Joshi. "Structural, spectroscopic, magnetic and thermal studies of gel-grown copper levo-tartrate and copper dextro-tartrate crystals." IOSR Journal of Applied Physics 8, no. 3 (2016): 33-42.
- [7] Pradeepkumar, K V_, N. Jagannatha, P. S. Rohith, and Delma D'Souza and KL Susheela "Growth, Characterization and Nucleation Reduction Mechanism of CCT Crystals in Silica Gel Medium at Different Environments." J Apple Chem 8, no. 4 (2019): 1893-1899.
- [8] Aripnammal S, and R Velvizhi. "Structural, spectroscopic, and magnetic studies on copper tartrate crystals." Zeitschrift für Natufforschung A 74, no. 9 (2019) 813-819.
- [9] Crystallography Open Database: Information Card for Entry 7023997, n.d. [https:// www.crystallography.net/cod/7023997.html](https://www.crystallography.net/cod/7023997.html).

- [10] 'Copper | Periodic Table | Thermo Fisher Scientific - IE', n.d. <https://xpssimplified.com/elements/copper.php>.
- [11] Biesinger, Mark C. "Advanced analysis of copper X-ray photoelectron spectra." *Surface and Interface Analysis* 49, no 13 (2017) 1325-1334.
- [12] Ivanova TM, Maslakov KI, Sidorov AA, Kiskin MA, Linko RV, Savilov SV, Lunin VV, Eremenko IL. XPS detection of unusual Cu (II) to Cu (I) transition on the surface of complexes with redox-active ligands. *Journal of Electron Spectroscopy and Related Phenomena*. 2020 Jan 1; 238:146878.
- [13] "Oxygen." n.d. Cardiff University. <https://sites.cardiff.ac.uk/xpsaccess/reference/oxygen/>.
- [14] Chastain, Jill, and Roger C. King Jr. "Handbook of X-ray photoelectron spectroscopy" Perkin-Elmer Corporation 40 (1992): 221
- [15] Carbon | XPS Periodic Table | Thermo Fisher Scientific - IE', n.d. <https://www.thermofisher.com/in/en/home/materials-science/learning-center/periodic-table/non-metal/carbon.html>.
- [16] Cadmium | XPS Periodic Table | Thermo Fisher Scientific - US." 2024. Thermofisher.com. 2024. <https://www.thermofisher.com/in/en/home/materials-science/learning-center/periodic-table/transition-metal/cadmium.html>.
- [17] Padmanabhan, V. M. "Raman spectra of sodium and potassium tartrates_" In *Proceedings of the Indian Academy of Sciences-Section A*, vol. 28, no. 5, 485 New Delhi: Springer India, 1948