

Structure, thermal and magnetic characterization of hydrothermal synthesized $\text{Li}_2\text{CuP}_2\text{O}_7$ crystals

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Abstract

New lithium copper(II) pyrophosphate, $\text{Li}_2\text{CuP}_2\text{O}_7$ crystals were synthesized by the hydrothermal technique at moderate temperature and pressure conditions. The as-synthesized compound was characterized by DTA/TGA, infrared radiation, single crystal XRD and magnetic susceptibility measurement. The compound has crystallized in monoclinic system with $C2/c$ space group and cell parameters $a = 15.3360(14)$ Å, $b = 4.8733(13)$ Å, $\beta = 114.8(1)^\circ$, $V = 585.2(2)$ Å³, having tunnel type of cavities in the structure. Thermal behaviour and structural coordination of the prepared materials were investigated, respectively, using DTA/TGA and FTIR measurements. Magnetic results have revealed; it is a frequency and temperature dependent prospective paramagnetic materials.

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Keyword: D. Crystal structure

1. Introduction

The preparation of open framework metal phosphates is related to NASICON and LISICON analogues and have been extensively investigated, owing to their wide applications as prospective materials in technology, viz. in electronic device and as solid electrolyte with high thermal resistance in space application, sensors, laser materials, piezoelectric, luminescence, ceramics, ionic conductor and magnetic materials, etc. [1–9]. Introduction of alkaline ions, e.g., sodium and lithium in phosphate materials can be of interest for ion conduction properties such as rechargeable alkali batteries [10]. Owing to the low density and the high reductive power of lithium metal, a great deal of interest has been focused on the development of lithium batteries as power source for portable device or eclectic vehicle [11,12]. Recently, the authors have reported a number of pyrophosphates, whose structures are related to NASICON and their analogues [13–15]. Here, the authors are reporting a new group of $\text{Li}_2\text{CuP}_2\text{O}_7$ compound, developed in the form of single crystal by hydrothermal preparation at moderate temperature and pressure conditions and systematic characterization of structure and magnetic properties are examined.

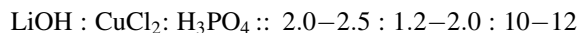
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2. Experimental procedure

2.1. Synthesis

$\text{Li}_2\text{CuP}_2\text{O}_7$ crystals were synthesized by adopting earlier reported hydrothermal techniques [13–15]. The source of all the reagents used in the experiments was from Glaxo chemicals and are analytically pure, used without further purification. A number of experiments were carried out using different ratios of LiOH, CuCl_2 , and 98% of H_3PO_4 at constant temperature in order to give a more detailed description of the phase stability and to optimize the growth condition of the compounds. The starting nutrients were thoroughly mixed at room temperature to form a homogenous, relatively less viscous solution and were transferred to a Teflon lined stainless steel autoclave of 50 mL capacity. The pH of starting reactants is maintained in the range of 4.06–4.32. The autoclaves were sealed and synthesis was carried out at 260 °C and auto generated pressure of 60–80 bar. The nucleation was spontaneous and it was minimized through slow rate of heating. Initially the temperature was boosted to 200 °C within an hour and further heated at the rate of 5 °C h^{-1} up to 260 °C. The experiments were run continuously for 8 days at peak temperature and followed by instant quenching to ambient conditions. The resultant product was in semisolid condition and the pH of the compound was in the range of 3.22–3.37. The product was thoroughly washed several times with double distilled water using ultrasonic cleaner and dried at 85 °C. The study crystals were obtained under following molar ratios:



Successful growth of technologically important phosphate crystals in the form of single crystals by hydrothermal method will depends on selection of starting reactants, suitable solvent, percent fill, temperature, pressure, etc. Among them, the selection of the reactant materials and the solvent is the most important criteria. In the present experiments, H_3PO_4 and NaOH solutions have been used as the solvents and copper chloride as solute. Based on the solute and solvents used, the following reactions could be proposed.



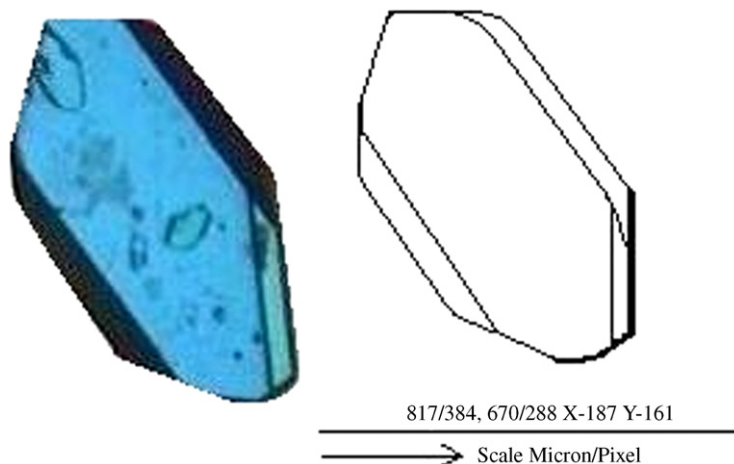
The morphology of the crystals varies according to the growth techniques, the physico-chemical conditions and concentration of the starting materials. On the whole, $\text{Li}_2\text{CuP}_2\text{O}_7$ crystals obtained by the hydrothermal methods were of good quality and exhibit smooth surface, sub vitreous luster, sub transparent, blue colour and having a size ranging from 0.5 to 2.5 mm (Fig. 1). Inclusions are also present.

2.2. Characterization methods

To understand the thermal properties of the compounds to provide more information on the technological importance, DTA and TGA analysis of $\text{Li}_2\text{CuP}_2\text{O}_7$ has recorded in the temperature range of 55–700 °C under the oxygen atmosphere using TGA 7 Perkin-Elmer, US analyzer. The heating rate was 10 °C/min. FTIR spectrum was registered in the range of 4000–400 cm^{-1} using a high resolution Perkin-Elmer Infrared Spectrophotometer. Magnetic susceptibility measurements were made using Gouy balance method by applying field strength of 0.5–3.0 kG at 300 K. The compound subjected to heat treatment for an hour in the range of 100–500 °C, again the magnetic susceptibility measurements were made by applying constant field strength (0.5 kG).

2.3. X-ray structure determination

A good single crystal of appropriate size was selected carefully under a polarizing microscope and glued to a thin glass capillary. Using CCD camera, crystal was made optically centered and the experiment was performed on a DIPLabo Kappa Imaging Plate Diffractometer equipped with normal focus, 3 kW sealed X-ray source (Mo K α

Fig. 1. Growth morphology of $\text{Li}_2\text{CuP}_2\text{O}_7$ crystal.

radiation, $\lambda = 0.71063 \text{ \AA}$). The crystal to detector distance was fixed at 120 mm with a detector area having $440 \text{ mm} \times 241 \text{ mm}$. Thirty-six frames of data were collected by oscillation method. Successive frames were scanned in steps of 3° min^{-1} with an oscillation range of 5° . Using Denzo programmer, image processing and data reduction was made [16]. The details of crystal and structure refinement are given in Table 1. The structure was solved by direct methods and expanded by Fourier techniques. Initial phase sets yielded a model with a minimum combined figure of merit, which gave the positions of all the non-hydrogen atoms in the first map it self. The model was subjected to full-matrix least-squares refinement by using SHELXS-97 [17] and SHELXL-97 [18]. Anisotropic refinement was started at this stage and after 8 cycles of refinement residual converged to 0.0746 for 1056 reflections and 58 parameters. Extinction correction was applied. The statistical weight factor was also included in the last cycle of refinement. Li and O atoms were found independently at the sites. But the refinement saturated with the same residual index.

Table 1
Crystal data and structure refinement table

Empirical formula	$\text{Cu}_2\text{Li}_4\text{O}_{14}\text{P}_4$
Formula weight	502.72
Wavelength	0.71069 \AA
Crystal system	Monoclinic
Space group	$C2/c$
Cell dimensions	$a = 15.3360(14) \text{ \AA}$; $b = 4.8733(13) \text{ \AA}$; $c = 8.6259(16) \text{ \AA}$; $\alpha = 90^\circ$; $\beta = 114.795(10)^\circ$; $\gamma = 90^\circ$
Volume	$585.2(2) \text{ \AA}^3$
Z	2
Density (calculated)	2.853 mg/m^3
Absorption coefficient	4.259 mm^{-1}
F0 0 0	484
Crystal size	$0.4 \text{ mm} \times 0.3 \text{ mm} \times 0.3 \text{ mm}$
Theta range for data collection	$2.93\text{--}32.46^\circ$
Index ranges	$0 \leq h \leq 22$; $0 \leq k \leq 7$; $-13 \leq l \leq 11$
Reflections collected	1087
Independent reflections	1056 [$R(\text{int}) = 0.0307$]
Refinement method	Full-matrix least-squares on F ²
Data/restraints/parameters	1056/0/58
Goodness-of-fit on F ²	1.477
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0746$, $wR2 = 0.1876$
R indices (all data)	$R1 = 0.0758$, $wR2 = 0.1889$
Extinction coefficient	$0.099(11)$
Largest diff. peak and hole	3.885 and -2.331 E. \AA^3

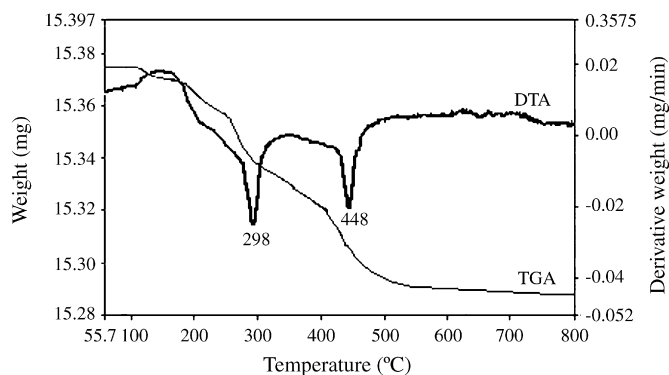


Fig. 2. DTA/TGA curve of Li₂CuP₂O₇ compound.

3. Results and discussion

The DTA/TGA results yielded two endothermic peaks at 298 and 448 °C (Fig. 2). The endothermic peak at 298 °C is attributed due to the chemical decomposition and releasing of ligands and the peak at 448 °C is due to the irreversible phase transition of the compound indicating, it has relatively moderate to high thermal stability.

FTIR spectrum of Li₂CuP₂O₇ shows a high degree of resolution of its absorption peaks especially in three frequency regions, that is at $\nu_1 = 2881.13 \text{ cm}^{-1}$, $\nu_2 = 1970.89\text{--}1482.03 \text{ cm}^{-1}$ and $\nu_3 = 1194.6\text{--}426.35 \text{ cm}^{-1}$ (Fig. 3). The stretching 2881.13 cm^{-1} is due to the presence of Cu–O molecules and at $1970.89\text{--}1482.03 \text{ cm}^{-1}$ is attributed due to the stretching of O–Li–O bonding. The strong bands in the range of $1194.6\text{--}426.35 \text{ cm}^{-1}$ are due to the presence of P–O–P and P–OH bonding. It has been reported, the degree of multiplication and fineness in the spectra of phosphates increases as the degree of polymerization increases in the [PO₄] tetrahedral [13–15]. It is clearly noticed, the study compounds have exhibited more number of splitting and sharpness, especially in the low frequency regions indicating polymerization of [PO₄]³⁻ to [P₂O₇]⁴⁻. It is more prominent in the compounds containing higher molar ratios of phosphorus.

ORTEP diagram of the molecule with 50% probability is shown in Fig. 4 [19] and Fig. 5 shows packing of the molecules down *b*-axis. Table 2 shows the atomic coordinates and equivalent thermal parameters of the molecule. The bonding between Cu1 and the four oxygen atoms, viz. O2a, O3b, O3d and O2e is perfectly planar. Tables 3 and 4 give the bond lengths and angles, respectively. The structure does show tunnel type of cavity or void space. The short contacts between Li—the asymmetric residue unit (ARU)-2, and atoms of the ARU-1 form an inter-molecular cluster that results in an infinite 3D network structure. The bond distances between O and P are in the range of 1.49–1.62 Å. Each Cu atom has coordination with six phosphate oxygen atoms i.e., two O-atoms of one terminal phosphate layer. This coordination environment resembles distorted hexahedron representation or six membered ring columns. Each such layer has been extended linearly and is interlinked through metal coordination at the terminal, which in turn exhibits three dimensional layer type polymer structures. Li atoms are crystallographically independent entity in the structure.

The magnetic moment (μ_{eff}) of copper derivatives generally with only one unpaired electron and are low spin tetrahedral or square planers having μ_{eff} in the range 1.90–2.50 BM [20,21]. It has been suggested, μ_{eff} of 1.83–1.86

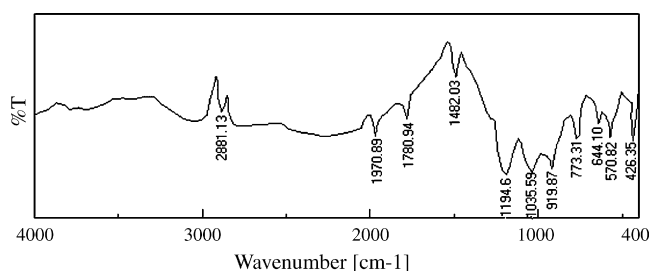


Fig. 3. FTIR spectrum of Li₂CuP₂O₇ compound.

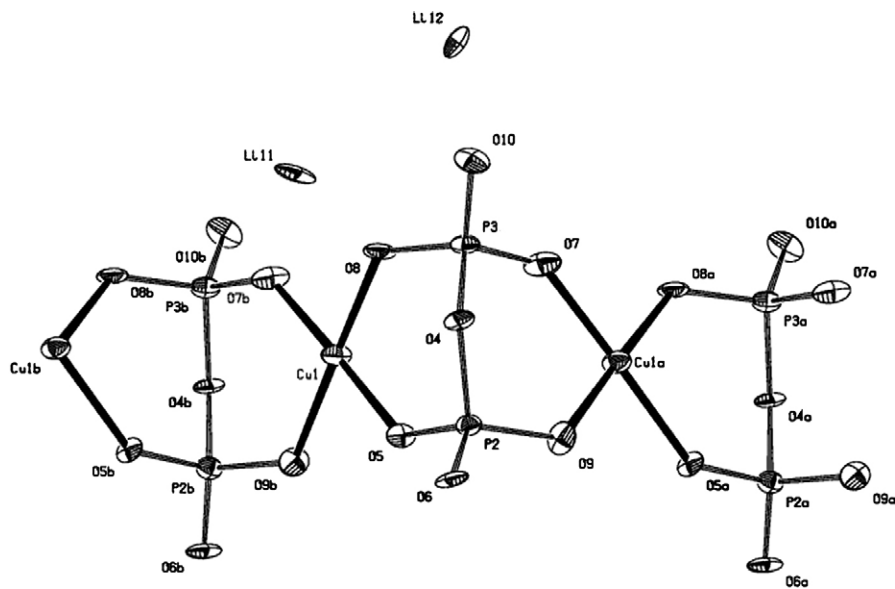


Fig. 4. ORPET perspective diagram of the molecule with thermal ellipsoids at 50% probability.

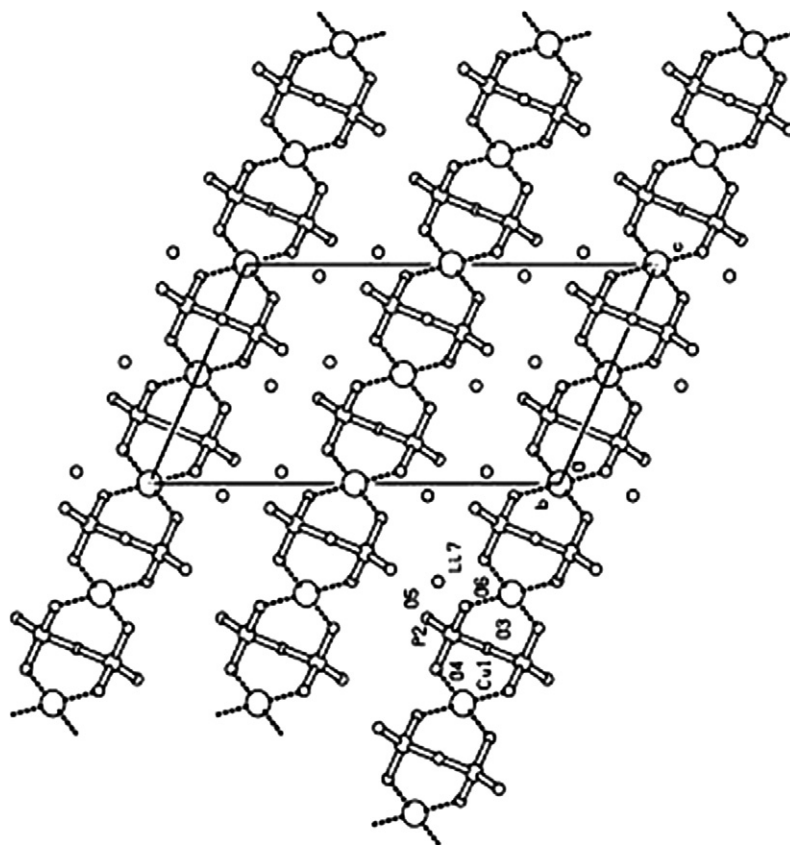


Fig. 5. Packing down *b*-axis.

Table 2
Atomic coordinates and equivalent thermal parameters of the non-hydrogen atoms

Atom	x	y	z	U_{eq}
Cu1	0.0000	0.0000	0.0000	0.0162(3)
O2	-0.1020(2)	0.2262(6)	-0.1567(3)	0.0186(6)
O3	0.0984(2)	0.1544(6)	-0.0578(4)	0.0189(6)
O4	0.1792(2)	-0.5752(6)	0.3889(4)	0.0180(5)
O5	0.0000	-0.5313(7)	0.2500	0.0152(7)
P6	0.10128(6)	-0.3664(2)	0.3146(1)	0.0129(3)
Li7	0.3090(5)	-0.6415(1)	0.4454(1)	0.0190(1)

Table 3
Bond lengths (Å)

Atoms	Length
Cu1–O2	1.928(2)
Cu1–O2 (i)	1.928(2)
Cu1–O3 (i)	1.929(3)
Cu1–O3	1.929(3)
O2–P6 (i)	1.528(3)
O3–P6 (ii)	1.524(3)
O4–P6	1.493(3)
O5–P6 (iii)	1.626(2)
O5–P6	1.626(2)
P6–O3 (iv)	1.524(3)
P6–O2 (i)	1.528(3)

BM for square planar, where as for tetrahedral configuration, it will be larger than 2.0 BM due to orbital contribution for the ground state configuration. Thus the μ_{eff} values of all the copper(II) compounds indicate them to be copper(II) octahedral (tetragonal geometry) [22,23]. Present investigation compound has exhibited paramagnetic with μ_{eff} values in the range of 1.54–2.18 BM (Fig. 6), lesser than the reported values. It could be attributed due to the bonding of diamagnetic P^{+5} ion with the paramagnetic Cu^{+2} ion through common oxygen ion (P–O–Cu) and could be resulted low spin octahedral stereochemistry around Cu(II) ions. It is also observed, the compound have shown positive correlation with the magnetic field strength. To unravel the thermal effect on the magnetic properties, the compound has been

Table 4
Bond angles (°)

Atoms	Angle
O2–Cu1–O2 (i)	180.0(2)
O2–Cu1–O3 (i)	84.9(1)
O2 (i)–Cu1–O3 (i)	95.1(1)
O2–Cu1–O3	95.1(1)
O2 (i)–Cu1–O3	84.9(1)
O3 (i)–Cu1–O3	180.0(2)
P6 (i)–O2–Cu1	125.0(2)
P6 (ii)–O3–Cu1	135.6(2)
P6 (iii)–O5–P6	120.8(2)
O4–P6–O3 (iv)	114.3(2)
O4–P6–O2 (i)	112.6(2)
O3 (iv)–P6–O2 (i)	110.7(2)
O4–P6–O5	106.7(2)
O3 (iv)–P6–O5	105.7(1)
O2 (i)–P6–O5	106.2(1)

Symmetry transformations used to generate equivalent atoms: (i) $-x, -y, -z$; (ii) $x, -y, (z - 1)/2$; (iii) $-x, y, (-z + 1)/2$; (iv) $x, -y, (z + 1)/2$.

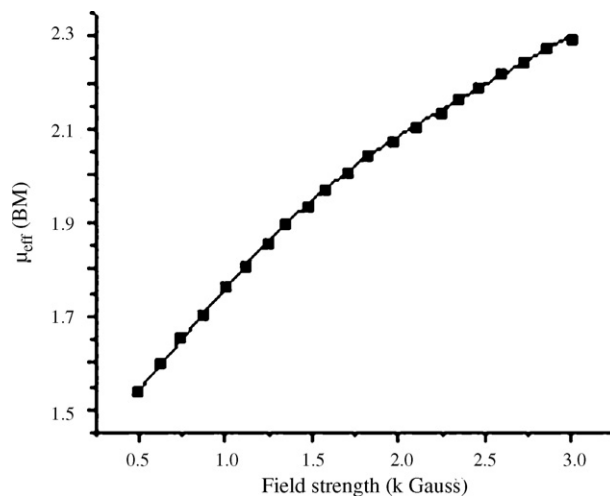


Fig. 6. Magnetic moment vs. magnetic field strength of Li₂CuP₂O₇ compound.

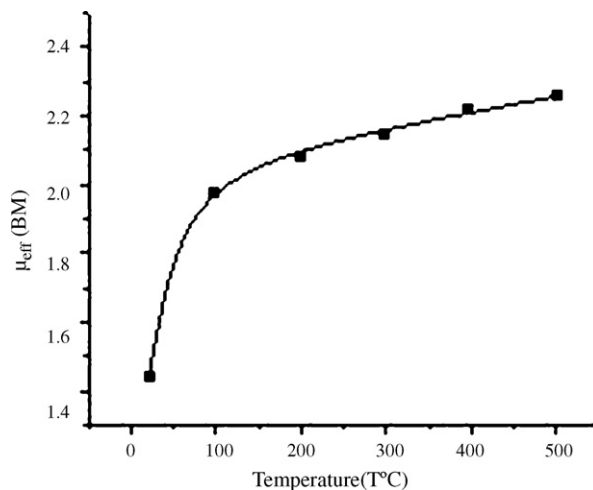


Fig. 7. Magnetic moment vs. temperature of Li₂CuP₂O₇ compound.

subjected to heat treatments for an hour at an interval of 100 °C up to 500 °C. After the thermal treatment, magnetic susceptibility measurements were made at constant field strength (0.5 kG). The corresponding μ_{eff} values were calculated and given in Fig. 7. The results of the thermally treated compound have shown positive correlation with the temperature. The μ_{eff} sharply increased as the compounds were subjected to heat treatment up to 100 °C. Further increase in the temperature resulted linearity in the increase of the μ_{eff} values. It could be attributed due to the liberation of the adsorbed water. However, neither breakdown of ligands nor phase transitions have affected magnetic properties of the compound. The magnetic result has shown, the study compound is a frequency and temperature dependent paramagnetic material.

4. Conclusions

Li₂CuP₂O₇ crystals were synthesized by hydrothermal method in the form of single crystals with well-developed morphology. Single crystal X-ray studies revealed, the compound crystallized in monoclinic system with tunnel type of framework structure. DTA and TGA results revealed it has relatively moderate to high thermal stability. The multiplication and fineness in the absorption bands, especially in the lower frequency region is due to the complexity

and polymerization of $[\text{PO}_4]^{3-}$ to $[\text{P}_2\text{O}_7]$ tetrahedron. Magnetic results revealed, the μ_{eff} of the compound is paramagnetic and exhibited positive correlation with the magnetic field strength and temperature.

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