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Synthesis, Growth, Reinvestigation of crystal structure, Optical measurements of L-Proline Cadmium Chloride Monohydrate (LPCCM): a novel nonlinear optical material

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Abstract: L-proline cadmium chloride monohydrate (LPCCM) possesses excellent optical and nonlinear optical properties which motivate us for further study on some important properties from application point of view. Therefore in the present investigation, the authors have synthesized the titled material and grew its good quality single crystal by slow evaporation solution technique. The single crystal of appropriate size (0.25 mm x 0.30 mm x 0.40 mm) was chosen for reinvestigation of its crystal structural with more accuracy (R=0.0217 or 2.17%) in comparison of previous report with goodness of parameters 1.000 using single crystal X-ray diffraction, which is the main aim of the present study. The grown crystal belongs to orthorhombic structure and its lattice parameters are found to be a=7.28380(10), b=9.9966(2), c=13.5217(2) Å and V=984.56(3) Å^3 with space group P212121. The crystal system and lattice parameters were further confirmed by powder X-ray diffraction analysis. Additionally, the grown single crystal was subjected to optical absorbance and reflectance measurements in ultraviolet-visible-near infrared range. From the recorded optical data the values of various optical parameters such as, optical transparency (53%), cut off wavelength 233 nm, optical band gap (5.6 eV), optical refractive index (~2.1) and optical permittivity (~4.3) were calculated. The obtained results suggest that the grown crystals are of particular interest for nonlinear optical devices.

Keywords: Crystal growth; Single crystal X-ray diffraction; optical properties; nonlinear optical material

1. INTRODUCTION

In recent scenario the nonlinear optical (NLO) species that display huge optical nonlinearity are of prodigious importance for numerous optical uses[1–3]. There is a common acuity that an optical species should have less dislocation density with great charge transfer and optical transparency[4]. A class of new materials known as semiorganic which are having the potential of combining the high optical nonlinearity and chemical flexibility of organic with the physical strength of inorganics. There is a furthermost significant advantage of these materials that they can be effortlessly grown from solution in large 3D crystals since they are highly soluble in wide range of solvents. Here is the short but all highlights of L-Proline cadmium chloride monohydrate (LPCCM) which is a recognized semiorganic material in the current literature belongs to orthorhombic crystal structure with space group $P2_12_12_1$, it possess high second harmonic generation (SHG) efficiency (twice of KDP) and there are several reports available on different properties e.g.: synthesis, solubility, FT-IR, FT-Raman, growth, bulk growth by SR, structural, nucleation kinetics, UV–Vis, CHN, dielectric, microhardness and thermal[5-9]. The available literature shows that these classes of crystals are of specific attention for the photo-induced nonlinear optics[10,11]. The crystal structure of LPCCM was first reported by Yukawa et al., in 1983 with refinement factor (R factor) value 0.035 [5]. As it is necessary that the crystal structure of any materials should be obtained with less value of R factor which directly related to the reliability and the measure of the covenant amongst the crystallographic model and experimental X-ray diffraction data. Further is also a measure of how well the refined structure foretells the experiential results[12].

Therefore, keeping the above point in mind the authors have grown the good quality single crystal of different sizes and reinvestigation of its crystal structure by single crystal as well as powder XRD with more accuracy was achieved for the first time and further it was subjected to optical measurements and various optical parameters were

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calculated. The obtained results are analysed, discussed and compared with earlier reports on respective properties wherever available.

2. EXPERIMENTAL

Crystal growth

LPCCM was synthesized using L-Proline and cadmium chloride of 99% purity in stoichiometric ratio of 1:1 and were dissolved in double distilled water above the room temperature. To get the final product the dissolved solution was stirred well and dried in an oven at 60^0 C. The crude product of LPCCM was further liquefied in deionized water and further refinement was carried out by recrystallization. For single crystal growth the finally prepared saturated solution of the titled compound was
filtered in another good quality beaker. Further, the beaker having LPCCM solution was well covered with perforated lid and reserved in constant temperature bath of high accuracy at 28°C. The well faceted and bulk single crystal of LPCCM was harvested from the mother solution after a span of 12 days.

Characterizations

Single crystal X-ray diffraction analysis was used to determine the crystal structure of LPCCM. A colorless single crystal of suitable size (0.25 x 0.30 x 0.40 mm) was cut from a larger specimen obtained by slow evaporation technique. The crystal structure of LPCCM was determined using the intensity data collected using a Bruker Kappa Apex II diffractometer (graphite-monochromated, MoK_α = 0.71073Å) at 296 K. For further confirmation of crystal structure of LPCCM the Powder X-ray diffraction analysis was also carried out using BRUKER D8 ADVANCE powder X-ray diffractometer (PXRD) having CuK_α radiation at the scan rate of 0.02º/s over the angular range of 5-70° at 300K. For optical parameters analysis the optical absorption and reflectance spectra of LPCCM single crystal of thickness ~2 mm was recorded on a prominent face in the wavelength region 200-1200 nm at ambient temperature by using a Perkin-Elmer Lambda 1050 NB InGaAs, UV-VIS-NIR spectrophotometer. The recorded data was used to calculate various optical parameters.

3. RESULTS AND DISCUSSION

Structural analysis

1. Single crystal XRD analysis

The relevant crystallographic data and structure refinement parameters of LPCCM are given in Table 1. The titled compound crystallizes in the orthorhombic $P2_12_12_1$ space group with cell parameters a = 7.2838(1)Å, b = 9.9966(2) Å, c = 13.5217(2), V= 984.56(3) $Å^3$. It is interesting to note here that there is a difference in R factors of the present work (R = 0.0217) and the work reported by Yasuhiko Yukawa et al.[5] (R = 0.035). Therefor it is clear that the present investigation is more accurate than the previous report[5]. In literature the significance of R-factor known as residual factor or reliability factor or the R-value or R_{Work} is connected to the measure of the covenant among the crystallographic model and experimental X-ray diffraction data. It can also be understand as: it is a measure of how well the refined structure predicts the experiential data[12]. The R values is also sometimes called the discrepancy index, as it mathematically describes the variance among the experimental observations and the ideal calculated values. The atomic coordinates and equivalent isotropic atomic displacement parameters ($Å^2$) for LPCCM crystal are given in Table 2.

Table 1: Sample and crystal data and structure refinement for LPCCM

Identification code	00891_LPCCM	
Chemical formula	$CdCl_2.(C_5H_9NO_3).H_2O$	
Formula weight	314.43	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal size	0.25 x 0.30 x 0.40 mm	
Crystal habit	clear colorless prismatic	
Crystal system	orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 7.28380(10) Å	α = 90°
	b = 9.9966(2) Å	β = 90°
	c = 13.5217(2) Å	γ = 90°
Volume	984.56(3) $Å^3$	
Z	4	
Density (calculated)	2.121 Mg/cm^3	
Absorption coefficient	2.729 mm^{-1}	
F(000)	608	
Theta range for data collection	3.01 to 28.28°	
Index ranges	-9<=h<=9, -13<=k<=13, -18<=l<=18	

Reflections collected	20544	
Independent reflections	2453 [R(int) = 0.0331]	
Coverage of independent reflections	99.9%	
Absorption correction	multi-scan	
Max. and min. transmission	0.5500 and 0.5000	
Structure solution program	SHELXS-97 (Sheldrick, 2008)	
Refinement method	Full-matrix least-squares on F2	
Refinement program	SHELXL-97 (Sheldrick, 2008)	
Function minimized	Σ w(Fo2 - Fc2)2	
Data / restraints / parameters	2453 / 0 / 110	
Goodness-of-fit on F2	1.000	
Final R indices	2282 data; I>2σ(I)	R1 = 0.0217, wR2 = 0.0696
	all data	R1 = 0.0267, wR2 = 0.0824
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0642P)^2+0.0108P]$ where $P=(F_o^2+2F_c^2)/3$	
Absolute structure parameter	-0.0(1)	
Extinction coefficient	0.0433(19)	
Largest diff. peak and hole	0.651 and -0.610 eÅ^{-3}	
R.M.S. deviation from mean	0.258 eÅ^{-3}	

Table 2. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for LPCCM crystal (U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor)

	x/a	y/b	z/c	U(eq)
Cd1	0.16752(3)	0.253864(19)	0.002033(13)	0.03242(12)
Cl1	0.41669(10)	0.37252(9)	0.89718(6)	0.0450(2)
Cl2	0.41450(10)	0.06750(7)	0.03397(6)	0.03801(19)
C1	0.4197(4)	0.4168(3)	0.1547(2)	0.0345(6)
C2	0.4291(5)	0.5554(4)	0.2016(3)	0.0489(8)
C3	0.3657(8)	0.6611(4)	0.1305(5)	0.0901(18)
C4	0.5290(10)	0.6928(6)	0.0700(5)	0.105(2)
C5	0.6834(9)	0.6868(5)	0.1417(4)	0.095(2)
N1	0.6215(4)	0.5929(3)	0.2224(2)	0.0546(8)
O1	0.2622(3)	0.3706(3)	0.14043(19)	0.0527(6)
O2	0.5675(3)	0.3610(3)	0.13654(18)	0.0463(6)
O3	0.4110(5)	0.0951(4)	0.7448(3)	0.0928(11)

Some important bond lengths and bond angles in LPCCM are given in Table 3 and 4. The anisotropic atomic displacement parameters (Å^2) and Hydrogen atomic coordinates and isotropic atomic displacement parameters (Å^2) of the grown LPCCM crystal are presented in Table 5 and 6. Selected bond lengths (Å)

and hydrogen bonds found in the structure of LPCCM are given in Table 1S and R too (see the supplementary material).

Table 3. Bond lengths (Å) for LPCCM crystal

Cd1-O1	2.311(2)	Cd1-O2	2.315(2)
Cd1-Cl1	2.5906(8)	Cd1-Cl1	2.6060(8)
Cd1-Cl2	2.6120(7)	Cd1-Cl2	2.6255(8)
Cl1-Cd1	2.6061(8)	Cl2-Cd1	2.6120(7)
C1-O2	1.237(4)	C1-O1	1.252(4)
C1-C2	1.525(4)	C2-N1	1.477(5)
C2-C3	1.501(6)	C2-H2	0.98
C3-C4	1.478(8)	C3-H3A	0.97
C3-H3B	0.97	C4-C5	1.486(9)
C4-H4A	0.97	C4-H4B	0.97
C5-N1	1.509(5)	C5-H5A	0.97
C5-H5B	0.97	N1-H1A	0.9
N1-H1B	0.9	O2-Cd1	2.315(2)

Fig. 1 shows the thermal ellipsoid plot drawn at 50% probability level of the asymmetric unit of LPCCM along with the atom numbering scheme. The crystal contains infinite one-dimensional polymeric chains parallel to an axis where the cadmium atoms present an octahedrical coordination environment $CdCl_4O_2$ and are triply bridged by two chlorine atoms and the carboxylate group of the proline ligand (see figure 2). Each chain is joined to four adjacent ones through hydrogen bonds involving the water molecules located in the interstices (see figure 3). Each water molecule shows four interactions: with two oxygen atoms from adjacent carboxylate groups and one proline nitrogen atom belonging to the same chain, and one chlorine atom from a neighbor chain. There are also NH•••Cl interactions from adjacent chains, which contribute to stabilize the chain packing, and intra-chain hydrogen bonds between the nitrogen and one of the carboxylic oxygen atoms from the same proline ligand. All the angles nearby the Cd atom with

four Cl atoms and two carboxyl oxygen atoms are approximately 90^0 [Fig. 5, Table 4]. The average bond

lengths of Cd-Cl and Cd-O is found to be 2.61 and 2.31Å respectively [Table 3] which are very close to the reported values[5]. The bond angle Cd-Cl-Cd was found to be ~88^0. The calculated bond lengths of C-C are found to be 1.501 and 1.478Å [Table 3].

Table 4. Bond angles (°) for LPCCM crystal

O1-Cd1-O2	178.93(9)	O1-Cd1-Cl1	90.17(7)
O2-Cd1-Cl1	90.26(7)	O1-Cd1-Cl1	91.75(7)
O2-Cd1-Cl1	87.84(7)	Cl1-Cd1-Cl1	177.920(8)
O1-Cd1-Cl2	90.93(7)	O2-Cd1-Cl2	88.06(7)
Cl1-Cd1-Cl2	94.55(3)	Cl1-Cd1-Cl2	86.23(2)
O1-Cd1-Cl2	91.18(7)	O2-Cd1-Cl2	89.82(7)
Cl1-Cd1-Cl2	86.27(2)	Cl1-Cd1-Cl2	92.89(2)
Cl2-Cd1-Cl2	177.731(18)	Cd1-Cl1-Cd1	89.02(2)
Cd1-Cl2-Cd1	88.15(2)	O2-C1-O1	126.8(3)
O2-C1-C2	117.0(3)	O1-C1-C2	116.1(3)
N1-C2-C3	103.6(4)	N1-C2-C1	110.6(3)
C3-C2-C1	111.1(3)	N1-C2-H2	110.5
C3-C2-H2	110.5	C1-C2-H2	110.5
C4-C3-C2	104.9(4)	C4-C3-H3A	110.8
C2-C3-H3A	110.8	C4-C3-H3B	110.8
C2-C3-H3B	110.8	H3A-C3-H3B	108.8
C3-C4-C5	103.9(5)	C3-C4-H4A	111.0
C5-C4-H4A	111.0	C3-C4-H4B	111.0
C5-C4-H4B	111.0	H4A-C4-H4B	109.0
C4-C5-N1	105.7(5)	C4-C5-H5A	110.6
N1-C5-H5A	110.6	C4-C5-H5B	110.6
N1-C5-H5B	110.6	H5A-C5-H5B	108.7
C2-N1-C5	107.6(4)	C2-N1-H1A	110.2
C5-N1-H1A	110.2	C2-N1-H1B	110.2
C5-N1-H1B	110.2	H1A-N1-H1B	108.5
C1-O1-Cd1	125.8(2)	C1-O2-Cd1	131.2(2)

Table 6. Hydrogen atomic coordinates and isotropic atomic displacement parameters (Å^2) for LPCCM

	x/a	y/b	z/c	U(eq)
H2	0.3559	0.5582	0.2624	0.059
H3A	0.2667	0.6278	0.0894	0.108
H3B	0.3232	0.7398	0.1657	0.108
H4A	0.5189	0.7813	0.0410	0.125
H4B	0.5451	0.6277	0.0175	0.125
H5A	0.7090	0.7749	0.1684	0.114
H5B	0.7936	0.6532	0.1099	0.114
H1A	0.6930	0.5195	0.2234	0.065
H1B	0.6295	0.6335	0.2817	0.065

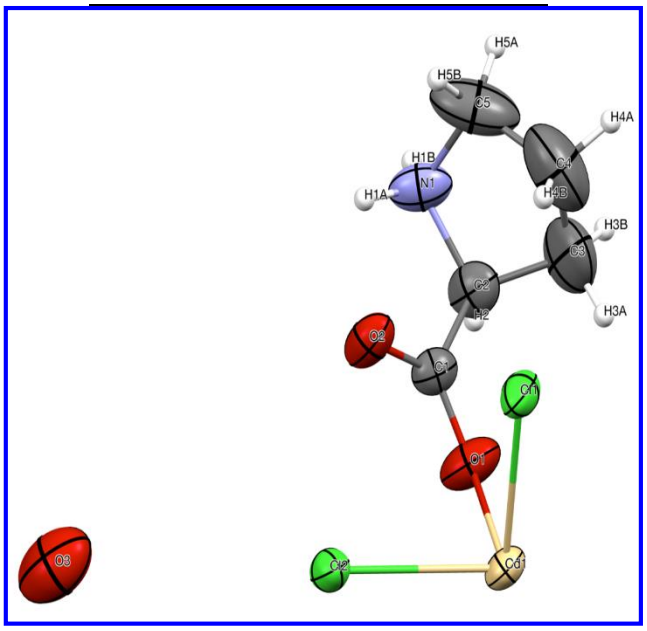

Figure 1. Thermal ellipsoid plot of the asymmetric unit (ellipsoids drawn at 50% probability).

Table 5. Anisotropic atomic displacement parameters factor exponent takes the form: -2π^2[h^2 a^{*2} U$_{11}$ + ... + 2 h k a* b* U$_{12}$] (Å^2) for LPCCM. The anisotropic atomic displacement

	U$_{11}$	U$_{22}$	U$_{33}$	U$_{23}$	U$_{13}$	U$_{12}$
Cd1	0.02106(16)	0.04174(17)	0.03447(16)	-0.00430(9)	-0.00161(6)	-0.00052(6)
Cl1	0.0288(3)	0.0571(5)	0.0489(4)	0.0177(4)	-0.0039(3)	-0.0035(4)
Cl2	0.0302(3)	0.0338(3)	0.0500(4)	-0.0007(3)	-0.0019(3)	-0.0015(3)
C1	0.0369(14)	0.0422(16)	0.0242(12)	-0.0082(11)	0.0016(12)	-0.0034(13)
C2	0.0466(18)	0.0470(18)	0.0531(19)	-0.0211(15)	0.0050(16)	0.0041(16)
C3	0.095(4)	0.046(2)	0.130(5)	-0.009(3)	-0.008(4)	0.023(3)
C4	0.158(6)	0.060(3)	0.096(4)	0.012(3)	0.008(5)	0.012(4)
C5	0.132(5)	0.081(3)	0.073(3)	-0.016(2)	0.045(4)	-0.052(4)
N1	0.0532(18)	0.0604(19)	0.0501(17)	-0.0228(15)	0.0075(15)	-0.0187(16)
O1	0.0337(12)	0.0743(15)	0.0499(14)	-0.0255(12)	0.0048(11)	-0.0094(12)
O2	0.0362(11)	0.0550(14)	0.0476(12)	-0.0240(11)	-0.0048(10)	0.0046(11)
O3	0.0638(19)	0.121(3)	0.094(2)	-0.040(2)	0.010(2)	0.002(2)

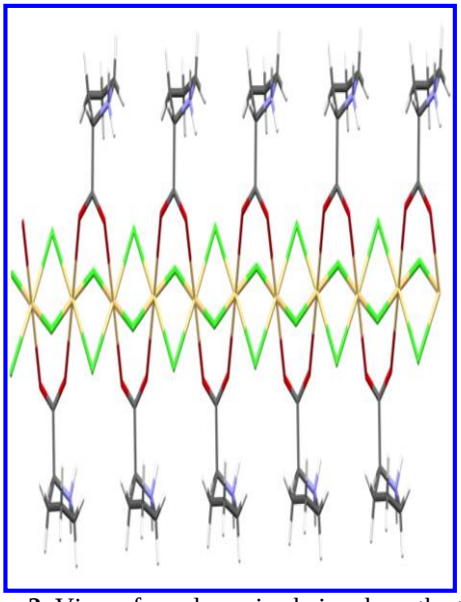

Figure 2. View of a polymeric chain where the triple bridge between cadmium atoms can be seen.

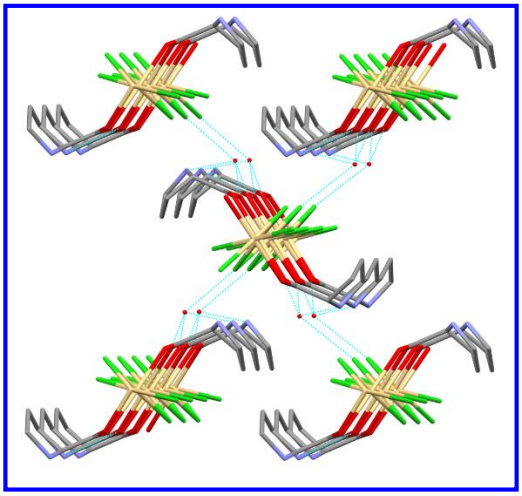

Figure 3. Hydrogen bonds from one chain to its four neighbors, involving the non-coordinated water molecules (hydrogen atoms have been omitted for clarity).

2. Powder XRD analysis

Powder X-ray diffraction pattern of LPCCM single crystals was recorded as shown in Fig. 4. The measured data was

used to compute lattice parameters using 'POWDERX' software from which it was established that the grown crystals belong to orthorhombic crystal system with space group $P2_12_12_1$. The determined lattice parameters were found to be a=7.213 Å, b=10.030 Å, c=13.541 Å, V=979.642 $Å^3$, and found to be in good agreement with the single crystal XRD results as well as with the earlier reported values[5-9]. Highly intensive peaks of powder XRD pattern show that the grown crystals are of good crystallinity.

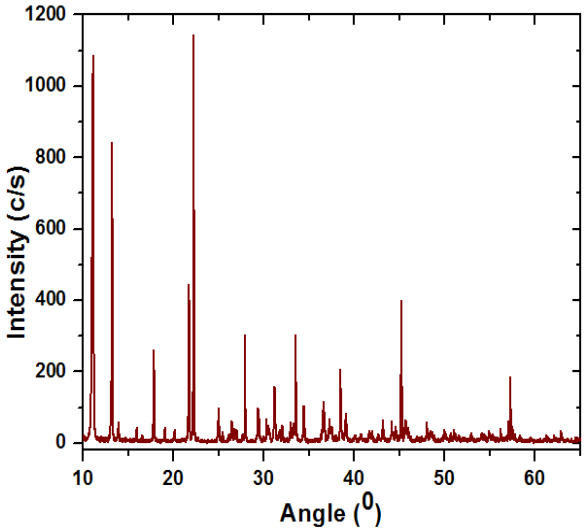

Figure 4. Powder XRD patterns of LPCCM crystals

Optical studies of LPCCM crystal

1. Optical absorption analysis

The measured optical absorption spectrum of LPCCM single crystal in wavelength region of 200-1200 nm is shown in Fig. 5. From figure it is clear that the grown crystal has low absorption which results in high transparency. It is necessary for any material who possessing nonlinear optical properties. The cut off wavelength of the grown crystal can be predicted as ~233 nm from figure 5.

2. Optical transmission analysis

It is very important and needful that we should grow a single crystal with high transparency in the considerable region of wavelength[13,14] for optoelectronic devices fabrication. Therefore, keeping such application and requirement in mind we have calculated the optical transmission of the grown crystal from absorbance data. From figure it is clear that the it has good optical transmittance in the entire tested region recommends its appropriateness for the fabrication of second harmonic generation devices[15-18] and found to be comparable with other reports on titled as well as with other reported materials[6-9, 19,20]. The transparency of the grown LPCCM single crystal was found to be ~53%.

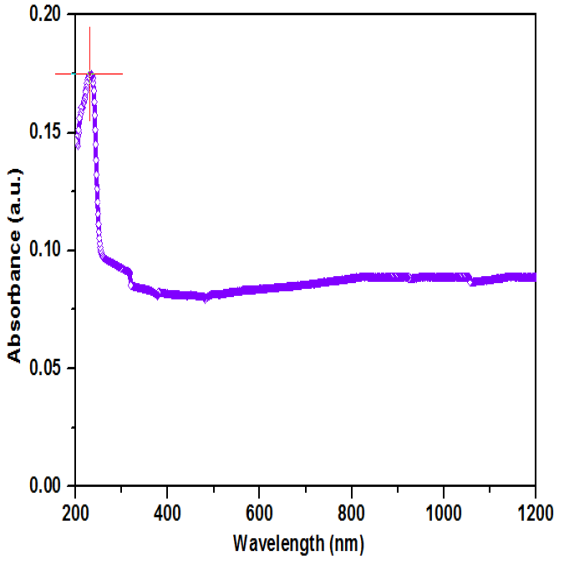

Figure 5. Optical absorption spectrum of LPCCM crystal.

3. Optical band gap, refractive index, permittivity analysis

It is well know that the dependence of optical absorption coefficient (α) with the photon energy (E) assists us to study the band structure and the type of transition[21]. To calculate the optical band gap of the grown single crystals the recorded absorbance data was used. For calculating the band gap of LPCCM the following procedure was opted:

Initially, the optical absorption coefficient (α_{cryst}) was determined by following relation:

$$\alpha_{cryst} = \frac{Absorbance\ (A)}{Thickness\ of\ the\ crystal\ (t_{cryst})} \qquad (1)$$

where t is the thickness of the used crystal (viz. 2×10^6 nm), Optical energy band gap (Eg_{cryst}) was alculated from the optical absorption coefficient (α) near the absorption edge from the following relation:

$$\alpha_{cryst} h\nu = A\,[h\nu - (Eg_{cryst})^r \qquad (2)$$

$$[(\alpha_{cryst})h\nu]^{\frac{1}{r}} = A\,[h\nu - (Eg_{cryst})] \quad (3)$$

where *A* is a constant, Eg_{cryst} is the optical band gap, *h* is the plank's constant and ν is the frequency of incident photon.

Eg_{cryst} was calculated by extrapolating the straight line to the *hν(eV)* [x-axis][22, 23], and found to be very high approximately 5.6 eV. As the band gap of the crystals is very large so it may be a suitable applicant for optoelectronic applications[24-26]. The refractive index of the titled materials was calculated from reflectance data and found to be ~2.1. Further the optical permittivity was also calculated and found to be ~4.3.

5. CONCLUSION

LPCCM single crystals of optical quality were grown successfully by slow evaporation solution technique. Single crystal X-ray diffraction analysis confirm that the grown crystal belongs to orthorhombic structure with space group $P2_12_12_1$ and the lattice parameters were found to be a=7.28380(10), b=9.9966(2), c=13.5217(2) Å and V= 984.56(3) Å^3. The goodness of parameters was found to be 1.000 and R1 = 0.0217, wR2 = 0.0696. Further the lattice parameters obtained from powder XRD results were found in good correlation with single crystals XRD results. The optical absorption spectrum confirms that the grown single crystal has very low absorption in the wavelength range of 250-1200 nm. Optical transmittances of the

Cccc grown crystal is found to be ~53% this indicates that the grown crystal have colorless nature and wide transparency range. The optical band gap was calculated and found to be 5.6 eV. The optical reflectance of the grown crystal was recorded and various optical constants such as optical refractive index, optical permittivity was determined and the results recommend that it can be a decent applicant for the building of various electro-optic devices..

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