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Growth and Characterization of Dichloro Tris(Triphenyl Phosphine Oxide)Cadmium(II) —Second Harmonic Generation from a Centrosymmetric Crystal

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ABSTRACT

The title compound dichloro tris(triphenyl phosphine oxide)cadmium(II) were grown by slow cooling method from aqueous solution. The title compound was synthesized and purified by repeated crystallization process. Grown crystals were characterized by X-ray diffraction and FTIR analysis. The range of optical transmission was determined by recording UV-Vis-NIR spectrum. Thermal properties were investigated by DTA and TGA analyses. Its mechanical hardness was estimated by Vickers microhardness method.

Keywords: Crystal Growth; Single Crystal X-Ray Diffraction; Ultraviolet Spectra; Nonlinear Optical Crystals

1. Introduction

Growth of single crystals of semi organics has been a subject of perennial concern in order to use the materials for device application. Due to this, the new semi-organic crystals have higher mechanical strength and chemical stability [1]. Metals with d^{10} configuration like Zinc, Cadmium, Mercury readily combines with organic materials resulting in stable compounds with good physic chemical behaviour. Triphenylphosphine is an interesting candidate as it binds well to most of the transition metals of group VII-X [2]. The basic structure of organic NLO Materials is based on the π bond system, due to the overlap of π orbital delocalization of electronic density [3]. On the basis of this, in the present investigation, we report for the first time, the synthesis, growth, crystal structure and characterization of the title compound dichloro tris(triphenyl phosphine oxide)cadmium(II).

2. Experimental Section

2.1. Synthesis of $CdCl_2$ $(TPPO)_4$

The title compound was synthesized by dissolving analytical reagent grade cadmium chloride ($CdCl_2$) (HIMEDIA) and triphenyl phosphine oxide (TPPO) (Chanshu Yangvan Chemical China) in absolute ethanol in stoichiometric ratio. The temperature of the solution was maintained at about 50˚C and $CdCl_2$ $(TPPO)_4$ was obtained by the evaporation of the solvent. Purity of the compound was increased by successive recrystallization.

$$CdCl_2 + 2\left[\left(C_6H_5\right)_3 PO\right] \rightarrow CdCl_2\left[\left(C_6H_5\right)_3 PO\right]_4$$

2.2. Crystal Growth

$CdCl_2$ $(TPPO)_4$ crystals were grown by slow evaporation technique. The precipitate was taken as raw material. Saturated $CdCl_2$ $(TPPO)_4$ solution was prepared at room temperature with ethanol and Dimethyl sulfoxide (DMSO) of 1:1 ratio as solvent. DMSO was added to improve the crystallization. The prepared transparent solution was filtered. The pH of the solution is 5. The solution was taken in glass beaker and closed with perforated covers and kept in a dust free atmosphere. The transparent crystals were harvested after 35 days when it attained a size of 7 × 2 × 2 mm^3. The as grown crystal is shown in **Figure 1**.

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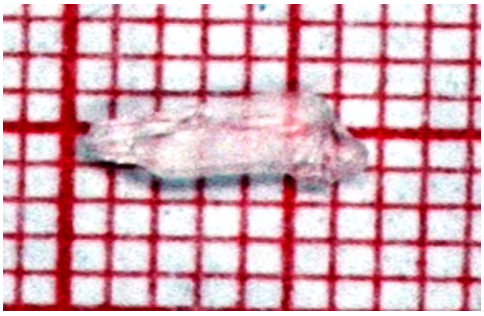

Figure 1. The as grown crystal of dichloro tris(triphenylphosphine oxide)cadmium(II)crystal.

2.3. Characterization of $CdCl_2$ $(TPPO)_4$

The single-crystal XRD data of the grown $CdCl_2$ $(TPPO)_4$ crystal was obtained using accurate unit cell parameters and orientation matrix were obtained by least-square fit of several high angle reflection in the range $1.5^\circ \leq \theta \leq 25^\circ$ using Mo K_α radiation on BRUKER SMART APEX CCD area detector using ω scan mode. X-ray powder pattern of the crystal was recorded on a Rigaku DMaxic computer controlled X-ray powder diffractometer with copper (K alpha 1) radiation of wavelength 1.54056 Å. The scanning rate was maintained at 1.6˚/min over a 2θ range of 10˚ to 70˚ employing reflection mode of scanning. The elemental analysis of the synthesized $CdCl_2(TPPO)_4$ was carried out by JSM energy dispersive X-ray microanalyzer equipped with JEOL-6360 SEM.

The functional groups of vibration of $CdCl_2$ $(TPPO)_4$ crystal were identified by FTIR technique using a Perkin Elmer spectrophotometer using KBr pellet technique in the range of 400 - 4000 cm^{-1}. The UV-Vis-NIR absorption spectrum of the $CdCl_2$ $(TPPO)_4$ crystal was examined in the wavelength range of 450 - 1000 nm using Lambda 35 (Instrument Model) UV-Vis-NIR spectrophotometer. Thermogravimetric analysis was carried out for the as grown crystals of $CdCl_2$ $(TPPO)_4$ using PYRIS thermal analyzer. The NLO property of $CdCl_2$ $(TPPO)_4$ crystal was confirmed by Kurtzpowder SHG test using Nd-YAG laser (1064 nm). The pulse width and repetition rate of the laser pulses were 8 ns with a repetition rate of 10 Hz respectively at 1064 nm radiation. The microhardness studies of single crystal was carried out using a Vickers microhardness tester fitted with a diamond pyramidal indentor.

3. Results and Discussions

3.1. X-Ray Diffraction Analysis

Unit cell parameters of the grown $CdCl_2$ $(TPPO)_4$ crystals were obtained using the single crystal diffractometer and are given in **Table 1**. It is found that $CdCl_2$ $(TPPO)_4$ crystallizes in orthorhombic system with centrosymmetric space group Pbca and V = 6608.4(7) $Å^3$. The crystallinity of the grown crystals was checked by taking the X-ray diffraction pattern of powder samples of $CdCl_2$ $(TPPO)_4$. The ORTEP plot of the molecule is shown in **Figure 2**.

3.2. Energy Dispersive X-Ray Analysis

The determination of elemental composition of the single crystal was done using energy dispersive analysis for confirming stoichiometry. The energy spectrum of the crystal is shown in **Figure 3**. In the present study, the grown $CdCl_2$ $(TPPO)_4$ single crystal was analyzed by JSM energy dispersive X-ray micro analyzer equipped with JEOL-6360 SEM. The energy spectrum confirms the presence of cadmium chloride and triphenyl phosphine oxide.

3.3. Fourier Transform Infrared (FTIR) Analysis

The Fourier Transform Infrared spectrum (FTIR) of

Table 1. Single crystal X-ray data of $CdCl_2$ $(TPPO)_4$.

CCDC Number	CCDC 893123
Empirical formula	$C_{72}H_{60}Cd_2Cl_4O_4P_4$
Formula weight	1479.68
Crystal system	Orthorhombic
Space group	Pbca
Unit cell dimensions	a = 11.1658(7) Å; $\alpha = 90^\circ$.
	b = 22.0016(14) Å; $\beta = 90^\circ$.
	c = 26.8999(16) Å; $\gamma = 90^\circ$.

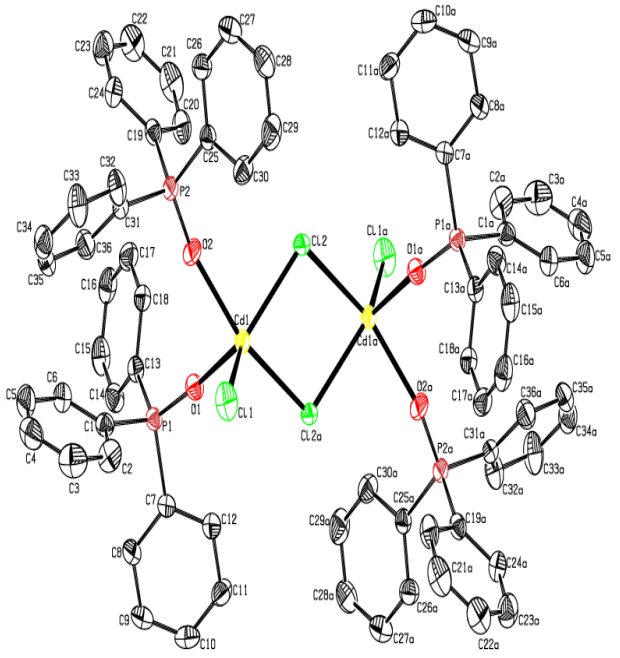

Figure 2. ORTEP plot of the molecule drawn at 30% probability level.

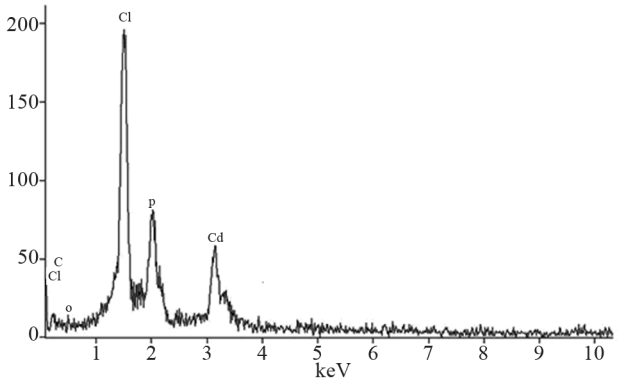

Figure 3. Energy spectrum of dichloro tris(triphenyl phosphine oxide)cadmium(II)single crystal.

$CdCl_2$ $(TPPO)_4$ crystal was recorded on PerkinElmer FTIR spectrophotometer using KBr pellet technique in the range of 400 - 4000 cm^{-1}. The recorded FTIR spectrum of $CdCl_2$ $(TPPO)_4$ depicts that stretching vibration of P=O (~1187 cm^{-1}) shifts to lower frequency (~1160 cm^{-1}) which clearly indicates influence of Cd. Also, frequency 537 cm^{-1} indicates the influence of metal-oxygen vibrational modes [4]. The peak at ~3456 cm^{-1} is assigned for the stretching vibrations of the O-H bond of the water molecules absorbed by KBr. The vibrational frequencies of $CdCl_2$ $(TPPO)_4$ are compared with that of the FTIR spectrum of $ZnCl_2$ $(TPPO)_2$ [5] and $CdBr_2$ $(TPPO)_2$ [6] in **Table 2**.

3.4. UV-Vis-NIR Analysis

The absorption spectrum of $CdCl_2$ $(TPPO)_4$ was recorded in the wavelengths range of 450 - 1000 nm using Lambda 35 (Instrument Model). UV-Vis-NIR spectrometer. A crystal with the thickness of about 2 mm was used for this measurement. From the spectrum, it is evident that the compound has a very low cut off at ~390 nm, and the crystal is found to be transparent in the region of 350 - 900 nm, which is an essential requirement for frequency doubling process.

3.5. Thermal Analysis

Thermogravimetric and differential thermal analysis of $CdCl_2$ $(TPPO)_4$ were carried out using a PYRIS thermal analyzer. A ceramic crucible was used for heating the sample and the analyses was carried out in an atmosphere of nitrogen at a heating rate of 10 K/min in the temperature range of 309 - 1136 K. The initial mass of the material subjected to analysis was 4.5 mg. A sharp endothermic peak at ~463 K depicts a phase transition of the material. Thermal studies show that the crystal is stable without decomposition upto ~573 K and an endothermic peak observed at ~723 K represents the melting point of $CdCl_2$ $(TPPO)_4$.

Table 2. Comparison of vibrational frequencies (cm^{-1}) of $CdCl_2$ $(TPPO)_4$ with reported works.

Assignments	$ZnCl_2$ $(TPPO)_2$ [5]	$CdBr_2$ $(TPPO)_2$ [6]	$CdCl_2$ $(TPPO)_4$ (present work)
ν (P=O)	1155	1157	1160
ν (P-C)	1437	1432	1433
ν (C=C)	1588	1589	1586
ν (C-H)	3055	3052	3058
ν (O-H)	3436	3456	3458

(ν) Symmetric stretching

3.6. Microhardness Studies

Vickers microhardness test was carried out on the prominent face of $CdCl_2$ $(TPPO)_4$ crystal using microhardness tester fitted with a diamond indenter. The indentation was made using a Vickers Pyramidal indentor for various loads. The indentation time was kept at 25 s for all the loads. From the Vicker's microhardness studies, it is observed that at lower load, there is an increase in the work hardening of the surface layers. For load above 70 g crack started developing around the indentation mark, which may be due to the release of internal stresses [7].

3.7. NLO Activity

The study of SHG conversion efficiency of the grown crystal was carried out using the modified experimental setup of Kurtz and Perry [8]. A Q-switched Nd-YAG laser beam of wavelength 1064 nm, with an input power of 4.9 mJ, and pulsewidth of 8 ns with a repetition rate of 10 Hz was used. The grown single crystal of was powdered with a uniform particle size and then packed in a microcapillary of uniform bore and exposed to lase radiations. The output from the sample was monochromated to collect the intensity of 532 nm component. The generation of the second harmonics was confirmed by the emission of green light. A sample of potassium dihydrogen phosphate (KDP), also powdered to the same particle size of the experimental sample, was used as the reference material in the present measurement. Second harmonic generation efficiency of the powdered $CdCl_2$ $(TPPO)_4$ is ~0.94 times that of potassium dihydrogen phosphate. The comparison of conversion efficiency of $CdCl_2$ $(TPPO)_4$ has been compared with other reported centrosymmetric materials and is given in **Table 3**.

4. Conclusion

Optical quality single crystals of dichloro tris(triphenyl phosphine oxide)cadmium(II) ($CdCl_2$ $(TPPO)_4$) have been grown from aqueous solution by slow cooling method. The lattice parameters have been calculated by X-ray diffraction studies. Elemental analysis of the synthesized

Table 3. Comparitive study of SHG efficiencies of different centrosymmetric crystals.

Compound	Space group	SHG SHG efficiency in comparison with KDP(in times)
R,S-serine [9]	$P2_1/a$	0.02
(p-Nitrophenol, hexamethyltetramine, phosphoric acid and water) super molecular crystal [10]	$P2_1/c$	3.1
Glycine picrate [11]	$P2_1/a$	2.34
$CdCl_2$ $(TPPO)_4$ [present work]	Pbca	0.94

material was confirmed by EDAX analysis. The functional groups were identified using FTIR analysis. The UV-Vis-NIR spectrum reveals the wider transmission window of $CdCl_2$ $(TPPO)_4$. Thermal analysis indicates that $CdCl_2$ $(TPPO)_4$ is thermally stable upto ~573 K. The powder SHG efficiency of this $CdCl_2$ $(TPPO)_4$, a centrosymmetric crystal is ~0.94 times that of the efficiency of KDP and can be used in photonics device fabrication. The mechanical stability of $CdCl_2$ $(TPPO)_4$ has been determined using Vickers microhardness studies.

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