Structural, FTIR, UV, thermal and SHG studies of silica gel grown cadmium doped zinc hydrogen phosphate crystals

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Single crystals of Cadmium doped $ZnHPO_4$ were grown by using single diffusion technique at ambient temperature. Crystals with different morphologies and effect on various parameters like gel pH, and gel ageing, gel density and concentration of reactants on the growth of $CdZnHPO_4$ crystals were studied. The crystals grown were characterized by XRD, SEM, FTIR, UV, SHG and TG-DTA. XRD studies reveal that the crystal lattice of the Cadmium doped ZnHPO4 is orthorhombic and crystalline perfection. Functional groups were identified by FTIR analysis. Cadmium doped ZnHPO4 is stable up to a temperature of 110 °C.

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1. Introduction

Dopant plays a vital role in different spheres of our day-to-day life. Trace amounts of dopant present in crystalline solids have an extremely influence on their mechanical, electrical, thermal and optical properties [1]. Additives or Dopants present in the medium used for the growth of a variety of various substances have long been recognized to have a profound influence on the growth morphology of crystals [1, 2]. Second order NLO materials have the ability to double the frequency of incident light and have important commercial applications [3]. Nonlinear optical materials will be the key elements for future photonic technologies based on the fact that photons are capable of processing information with the speed of light. These are used in optical switching, frequency conversion (SHG, wave mixing), electro-optic applications, and EO modulators [4]. The growth of single crystals in silica gel medium has attracted the attention of many researchers [5-7]. Most of the phosphate crystals are insoluble in water and decompose before melting. Hence, single crystals of such materials cannot be grown by either slow evaporation or melt method but can be grown by the gel method. A number of phosphate crystals grown by the gel method have been reported [8-11]. The reason for doping Cadmium with pure zinc hydrogen phosphate crystal is to analyze their composition and variation in unit cell dimensions. Also to find out the thermal stability and optical behavior of cadmium doped zinc hydrogen phosphate crystals [12]. In this present investigation, we have attempted to grow cadmium doped $ZnHPO_4$ crystals by single diffusion technique at ambient temperature [13-15]. The harvested crystals were characterized by X-ray diffraction technique, SEM analysis, FTIR, SHG, TG and DTA studies.

2. Experimental

2.1 Materials

All reagents used were of analytical grade purity and were produced from Merck Chemical Reagent Co. Ltd. India.

2.2 Preparation Technique

Synthesis of cadmium zinc hydrogen phosphate single crystals was carried out using single diffusion gel growth method. The silica gel, also known as water glass was used in the present work as an intermediate growth medium. The chemicals used for growth of $CdZnHPO_4$ crystals were, Zn $(NO_3)_2.6H_2O$, Cd $(NO_3)_2.4H_2O$, H_3PO_4 and $Na_2SiO_3.9H_2O$ all chemicals were of AR grade. Water glass was prepared by dissolving 284.20 g of sodium meta silicate in 1000 ml of de mineralized water so as to obtain gel solution of 1M concentration. The sodium meta silicate solution was kept undisturbed for five days and a clear solution was obtained on decantation. The clear solution was filtered by using Whatman Grade No. 1 Filter Paper and it is stored in a glass container and this solution is called stock solution. The gel density used in this work ranges from 1.03 g/cc to 1.05 g/cc, and it is accurately measured by using specific gravity bottle method. Gel was prepared by mixing stock solution with particular concentration of ortho phosphoric acid (1N & 2 N) which is act as a lower reactant. The solution was constantly

stirring in a beaker by magnetic stirrer. Stirring is done to avoid the excessive local ion concentration, which may otherwise cause premature local gelling and make the final medium inhomogeneous and turbid. The pH of the gel was medium adjusted between values 5 to 7. The solution was transferred to several single glass test tube of length 20 cm and diameter 2.5 cm. The silica gel of the desired pH was then allowed to set and ageing for a specific time of 4 h to 48 h & 6 days, which depends upon the pH and environmental temperature. Test tubes were then closed with rubber corks to prevent evaporation and contamination of the exposed surface by dust particles of the atmosphere. After the gel set, the supernatant solutions of Zinc nitrate and Cadmium nitrate (1:1 Molar concentration) were added slowly along the walls of the test tubes by using pipette. The supernatant solution diffuses through the set gel, which reacts with phosphoric acid present in the gel leading to the growth of Cadmium doped $ZnHPO_4$ single crystals. The experiment was conducted at room temperature. The following expected reaction takes place in the growth columns and growth procedure is listed in the table 1.

$$Zn(NO_3)_2.6H_2O + Cd(NO_3)_2.4H_2O + H_3PO_4 \longrightarrow CdZnHPO_4 + 2(HNO_3)_2 + 10H_2O$$

Table 1. Cadmium doped $ZnHPO_4$ Crystal Growth Procedure

Silica Gel Density gm/cc	H_3PO_4 Acid concentration in Normality	pH	Gel ageing	Supernatant concentration ($Zn(NO_3)_2.6H_2O$ + $Cd(NO_3)_2.4H_2O$) in M	Nucleation Started	Growth Period	Nature of Crystal observed and Harvested crystal size
1.04	1N	5 6 7	144 hrs 36 hrs 4 hrs	1 : 1 ratio	8 hrs 12 hrs 24 hrs	244 days	pH = 5 – sugar like crystals pH = 6 – good X shape & few platelet crystals pH = 7 – 3x4mm X shape crystals

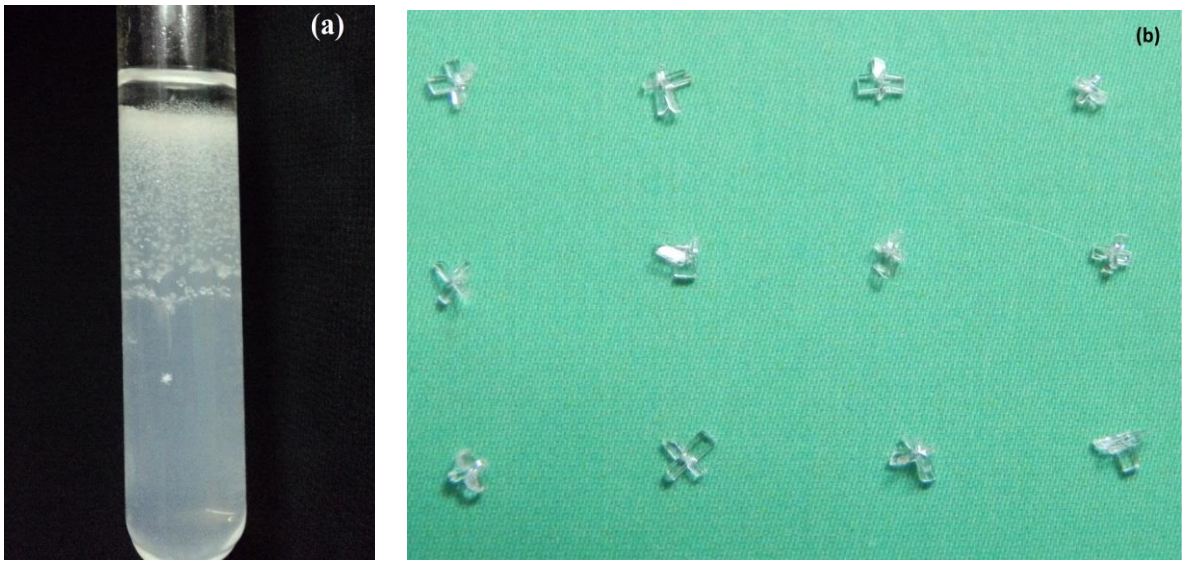

Fig. 1 (a) cadmium doped $ZnHPO_4$ crystals grown in gel medium & (b) Morphology of cadmium doped $ZnHPO_4$ crystals

2.3 Characterization

Single crystal X-ray diffraction (XRD) analysis on cadmium doped $ZnHPO_4$ crystal was carried out using Bruker Kappa Apex II, Cochin University STIC Laboratory, Kerala. SEM technique examined by (JEOL Model JSM 6390LV, USA) Cochin University STIC Laboratory, Kerala. In order to confirm the presence of phosphate functional groups in the crystal lattice, FTIR spectra was recorded by KBr pellet technique using

BRUKKER 66v spectrometer in the wave number range 400-4000 cm^{-1}. Optical absorption spectrum of the grown crystal was recorded using JASCO UV visible spectrometer in the wavelength range 190-900 nm. NLO property of the crystal was confirmed using Kurtz and Perry powder test at the Indian Institute of Science, Bangalore. The thermal behavior of the crystal was characterized using thermo gravimetric analysis (TG) and differential thermo gravimetric (DTA) analysis by NETZSCH STA 449F3 thermal analyzer. The sample of weight 4.091 mg was heated in a crucible between 50 to 800 °C at a heating rate of 20 K min^{-1} in nitrogen atmosphere.

3. Results and discussion

3.1 X-ray Diffraction of $CdZnHPO_4$ Single Crystal

The single crystal XRD result reveals that the grown crystals of Cadmium doped $ZnHPO_4$ belong to orthorhombic crystal system with space group Pmna. The lattice parameters obtained in case of cadmium doped $ZnHPO_4$ crystals are: a = 10.61 Å, b = 18.26 Å, c = 4.94 Å, $\alpha = \beta = \gamma = 90^0$. The volume of the unit cell of the $CdZnHPO_4$ crystal is A = 958.3943 $Å^3$.

3.2 SEM analysis

Surface morphology of the powdered sample of Cadmium doped $ZnHPO_4$ crystal was examined by using SEM technique. The study of the surface of the crystal gives valuable information about its internal structure. Fig. 2(a) illustrates SEM photographs of cadmium doped $ZnHPO_4$ crystal. An enlarged SEM image is shown in Fig. 2(b). It shows plate like crystal morphology. These crystals are grown by layer deposition. Thick and thin layers are seen in figure. The individual plates of samples are flat and the plates with the sharp edges were observed. On some plates further plate like growth was observed.

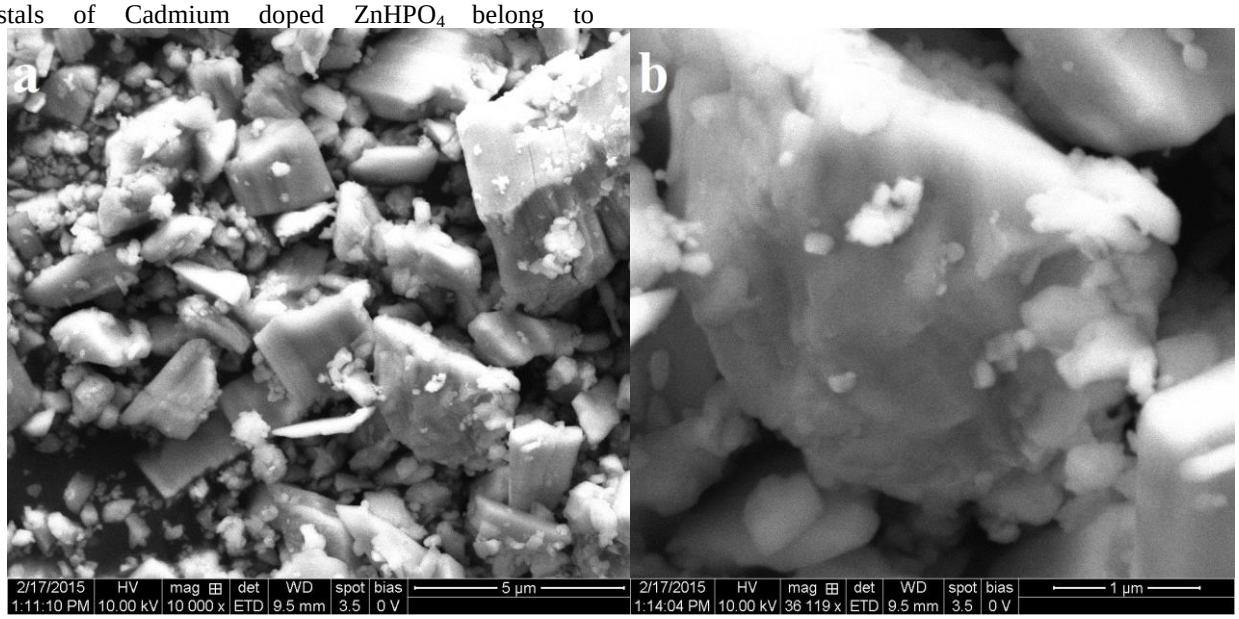

Fig. 2 (a): SEM image of cadmium doped $ZnHPO_4$ crystal (b) Magnified SEM image

3.3 FTIR analysis

The FTIR absorption spectrum of Cadmium doped ZnHPO4 crystal was shown in Fig. 3 and the assignment of various absorption peaks were given in the table (2). The FTIR spectrum shows the identification of O – H bonding and P – O bonding. The absorption peaks were identified and are in good agreement with earlier literature [2-6]. The presence of broad absorption band between 3080 cm^{-1} to 3504 cm^{-1} for Cd doped crystal indicates the presence of O – H stretching vibration (strong). The sharp peak at 1635 cm^{-1} for $CdZnHPO_4$ is assigned to H – O – H strong bending mode of vibrations. The phosphate group stretching mode HPO_4^{2-} is positioned at 1093 cm^{-1} for $CdZnHPO_4$ crystal. The absorption peak at 921 & 997 cm^{-1} is due to P – OH stretching mode strong vibration. The symmetric (O – P – O) bending modes of vibration of PO_4^{3-} are located at 563 & 626 cm^{-1}. The metal – oxygen bonding is positioned at 422 cm^{-1}.

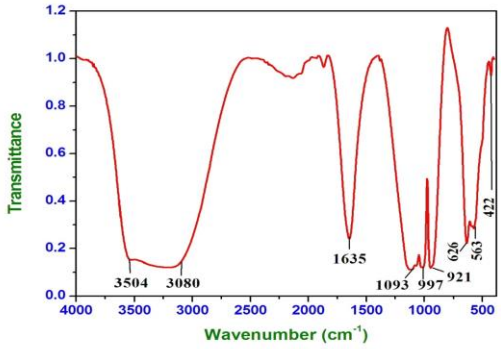

Fig. 3 FTIR Spectrum of Cadmium doped $ZnHPO_4$

Table 2. FTIR assignment of Cadmium doped $ZnHPO_4$ crystals

Assignment	Reported frequency value cm^{-1}	Observed frequency value cm^{-1} $CdZnHPO_4$	Intensity
O – H stretching mode of vibration (H_2O molecule)	3000 – 3600	3080 – 3504	Strong, Broad
H – O – H bending mode of vibration (H_2O)	1590 – 1650	1635	Strong, Sharp
P = O stretching mode (Phosphate group - H PO_4^{2-})	1100	1093	Strong
P – OH stretching mode	900 – 1050	997 & 921	Strong
O – P – O symmetric bending mode of PO_4^{3-}	635 – 579	563 & 626	Medium
Metal Oxygen bond	400 – 600	422	Medium

3.4 UV spectral studies

The optical absorption spectral analysis of cadmium doped $ZnHPO_4$ was carried out between 190-900 nm. As the crystal is colorless, Low absorption in the entire visible and near infrared region with the low cut-off wavelength in the UV region suggests that the sample is suitable for optoelectronic applications. The UV cutoff wavelength of the crystal was found to be 235 nm. The UV absorption spectrum of cadmium doped $ZnHPO_4$ is shown in Fig. 4.

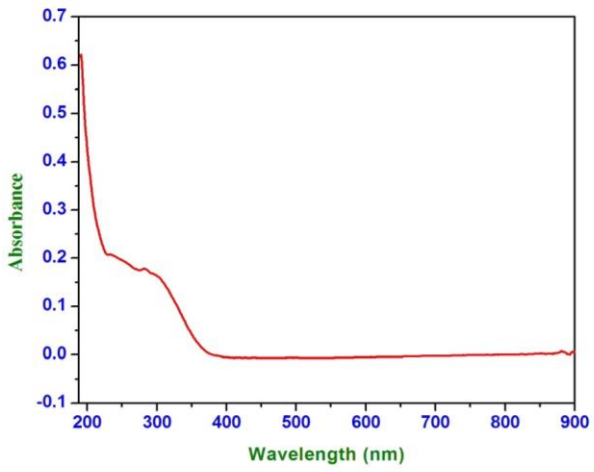

Fig. 4 UV absorption of Cadmium doped $ZnHPO_4$

3.5 SHG Studies

The SHG test for the grown cadmium doped $ZnHPO_4$ crystal was carried out by using powder Kurtz and Perry technique [16]. It is a popular method to evaluate conversion efficiency of a nonlinear optical material. In this experiment Q-switched pulses were obtained from a Q-switched Nd–YAG laser of wavelength 1064 nm and pulse width of 8 ns (spot radius of 1 mm) on the powder sample of cadmium doped $ZnHPO_4$. The output from the sample was monochromated to collect the intensity of 532 nm component and the fundamental was eliminated. Urea was used as a reference material for the present measurement. This confirms the NLO behaviour of the material. The green light intensity was registered by a photomultiplier tube and converted into an electrical signal. This signal was displayed on the oscilloscope screen. The sample was replaced by potassium dihydrogen orthophosphate (KDP) and the signal was displayed in the oscilloscope screen. SHG conversion efficiency was computed by the ratio of signal amplitude of the $CdZnHPO_4$ sample to that of the KDP signal amplitude recorded for the same input powder. The SHG efficiency of the grown cadmium doped $ZnHPO_4$ crystal was found to be 1.2 times greater than that of KDP.

3.6 Thermal Analysis

The analysis of recorded curve is quiet helpful in determining the thermal stability, composition and solid-state kinetics of dissociation of the grown material. Fig. 5 gives simultaneously recorded TG and DTA curve for cadmium doped $ZnHPO_4$ crystal. From the curve, it is clear that when the material is heated at uniform rate, it loses weight as a continuous function of temperature. The curve shows that the material is thermally stable up to a temperature of 110 °C and thereafter starts decomposing. The whole process of decomposition completes in two steps. The first stage of decomposition begins from 110 ^{0}C and continues up to a temperature of 220 °C resulting in a weight loss of 19.09% of the total weight. During first step of decomposition, hydrated cadmium doped $ZnHPO_4$ crystal become anhydrous in nature. The second stage of decomposition starts from 220 °C and ends at a temperature of 325 °C leading to weight loss of 6.46%. This weight loss in the second stage of decomposition corresponds to the conversion of anhydrous cadmium doped $ZnHPO_4$ into pyrophosphate crystals. This study indicates that the compound could be used for any optical application below its melting point.

As seen from Fig. 5 the DTA curve in case of Cadmium doped $ZnHPO_4$ there is well marked endothermic and exothermic peak corresponding to each stage of decomposition. For Cadmium doped $ZnHPO_4$ irreversible endothermic transition at 137 °C and 280 °C and a sharp endothermic peak at 137 °C show the melting point of the crystal. The DTA thermogram also reveals that the sharp endothermic peak coinciding with that of TG confirms the thermal stability of the crystal. Since peaks in DTA curve correspond to weight loss in TG curve

thereby suggesting some structural changes taking place in the material beside weight loss in the material. The existence of these peaks can be explained in terms of energy requirements. The energy of peaks does not necessarily depend only on the amount of water loss on dehydration but also depends on the structural factors.

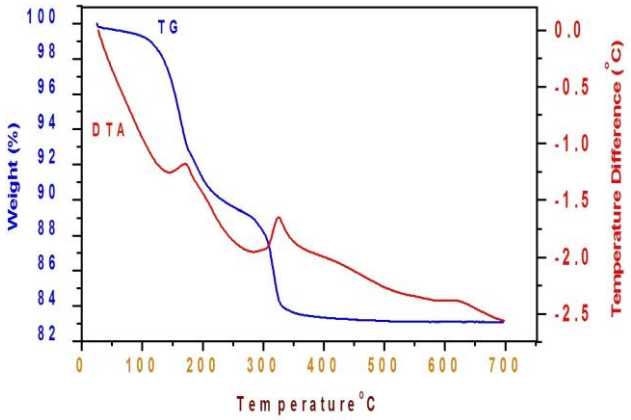

Fig. 5 Thermogram showing simultaneous recording of TG and DTA curves for Cadmium doped $ZnHPO_4$

4. Conclusion

Growth of cadmium doped $ZnHPO_4$ single crystals have been achieved by gel technique. The X-ray diffraction studies reveal that cadmium doped $ZnHPO_4$ both belong to orthorhombic crystal system and doping has not altered the crystal structure. The lattice parameters obtained in case of cadmium doped $ZnHPO_4$ crystals are: a = 10.61 Å, b = 18.26 Å, c = 4.94 Å, $\alpha = \beta = \gamma = 90^0$. The volume of the unit cell of the $CdZnHPO_4$ crystal is A = 958.3943 $Å^3$. SEM images show that the crystals having plate like surface morphology. The FTIR spectra confirm the presence of all possible functional groups. The absorption spectra recorded in solution form reveal that they possess low cut-off wavelengths. The TG–DTA analyses reveal that they possess high thermal stability. The NLO studies reveal that they are capable of realizing green light and their second harmonic efficiency is greater than that of urea. Due to their excellent optical, thermal, mechanical and nonlinear properties, these crystals can be used for NLO applications.

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