Synthesis and comparative study of pure and calcium doped zinc hydrogen phosphate single crystal in silica gel medium at ambient temperature

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Synthesis of Zinc hydrogen phosphate ($ZnHPO_4$) and Calcium doped $ZnHPO_4$ single crystals were grown in silica gel at ambient temperature. Effect on various parameters like gel pH, and gel ageing, gel density and concentration of reactants on the growth of these crystals were studied. Crystals with different morphologies and habits were obtained. Some of them were transparent diamond, X - shaped and some are twinned. The crystals were characterized by X- Ray Diffraction (XRD), Scanning electron microscope (SEM), Fourier transform infra red (FTIR), Ultra violet (UV), Non – linear optical (NLO) and Thermo gravimetric analysis (TG-DTA). XRD study reveals that the crystal lattice of Calcium doped $ZnHPO_4$ is orthorhombic and crystalline perfection of the crystals were extremely good. SEM image showed plate like morphology and further plate like growth was observed on some plates.

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1. Introduction

Modern technologies based on optoelectronics, acoustic optics, optical fiber communication (OFC), optical computing, etc., have been exploited the versatile properties of the NLO crystals. The rapid advances in these technologies have been made possible due to the availability of a variety of single crystalline materials. This led the researchers to concentrate on the development of new variety of single NLO crystals with high purity [1].

The presence of dopant during the crystallization is one of the key factors that affect the morphology and physical properties of the crystal [2]. The amount of dopants present in a growth medium has been influenced more on the processes of nucleation of crystallizing phases of the same substance and the subsequent growth of the nucleated phase [3].

A single diffusion technique using silica gels in crystal growth at ambient temperature is another simplex technique to obtain perfection, pure crystals as reported by Henisch et al [4]. In conventional growth, pure $ZnHPO_4$ crystals were accomplished at 40ºC in a constant temperature bath have been already reported [5]. In this present work, we have attempted to grow pure calcium doped $ZnHPO_4$ crystals by single diffusion technique at ambient temperature [6-10]. The harvested crystals were characterized by X-ray diffraction technique, SEM analysis, FTIR, TGA, DTA and NLO studies.

2. Experimental

2.1 Materials

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

2.2 Preparation technique

The growth of crystals in a gel medium has been attracting the attention of many investigators [11-13]. Pure and Calcium doped Zinc hydrogen phosphate in the form of a single crystal is accomplished by using single diffusion technique. The silica gel was prepared by adding 284.20 g of Sodium meta silicate ($Na_2SiO_3.9H_2O$) to 1litre of double de-mineralized water, so as to have a gel concentration of 1M. This solution was kept undisturbed for five days and a clear stock solution was obtained on sedimentation. The density of the solution was determined by the specific gravity bottle method. The gel density values of 1.03 g/cc, 1.04 g/cc and 1.05 g/cc measurement was done very accurately since it has considerable influence on the gelation process and quality of the crystal. The pH of the silica gel was adjusted between the values of 5-7 by mixing the orthophosphoric acid (H_3PO_4) and stock solutions in various proportions. Continuous stirring is needed to avoid excessive local ion concentration, which may cause premature local gelling and make a final solution inhomogeneous. The desired value of the pH of the solution was transferred to several single glass test tubes 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 hrs to 48 hrs and 6 days, which depends upon the pH and environmental temperature. After the gel ageing, the supernatant solutions of $Zn(NO_3)_2.6H_2O$ (Zinc Nitrate – AR Grade) and $Ca(NO_3)_2.4H_2O$ (Calcium Nitrate – AR Grade) at a required mole solution was slowly added along the walls of the test tubes over the set goals and tightly closed to prevent evaporation. The experiment was conducted at ambient temperature. The following expected reaction takes place in the growth columns and growth procedure is listed in the Table 1 and 2.

$$Zn(NO_3)_2.6H_2O + H_3PO_4 \rightarrow ZnHPO_4 + 2HNO_3 + 6H_2O \quad (1)$$

$$Zn(NO_3)_2.6H_2O + Ca(NO_3)_2.4H_2O + H_3PO_4 \rightarrow$$

$$CaZnHPO_4 + 2(HNO_3)_2 + 10H_2O \quad (2)$$

Fig. 1 (a) and (b) shows the photograph of Pure and Calcium doped Zinc hydrogen phosphate crystals grown in the gel medium. Calcium ions diffuse through the gel and a thin white film in the form of a ring appeared known as Liesegang ring [14] [Fig. 1 (b)]. Crystals with different morphology like rectangular platelet type and star type were grown in the gel. Fig. 2 shows a different type of morphology of Pure and Calcium doped $ZnHPO_4$ grown crystals.

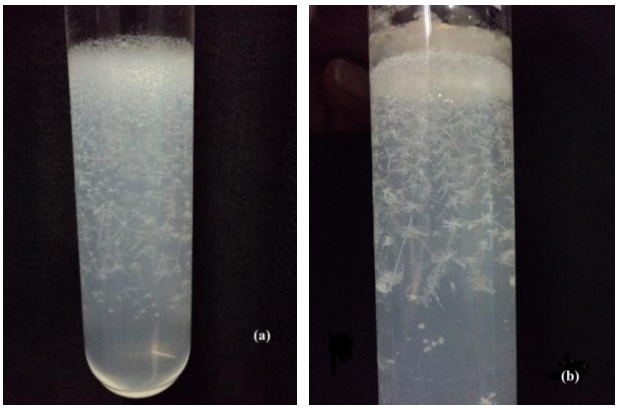

Fig. 1. (a) Pure $ZnHPO_4$ crystals grown in gel medium, (b) Liesegang rings observed for 1.04 silica gel density, 6.0 pH value and supernatant concentration of 1 N calcium doped $ZnHPO_4$

Table 1. Pure $ZnHPO_4$ crystal growth procedure

Silica Gel Density gm/cc	**H_3PO_4 Acid concentration in Normality**	**pH**	**Gel ageing**	**Supernatant concentration $Zn(NO_3)_2.6H_2O$ 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 M	12 hrs 24 hrs 38 hrs	244 days	pH = 5 – very tiny X shape pH = 6 – few X shape and platelet pH = 7 – 3x4mm Xshape single

Table 2. Calcium doped $ZnHPO_4$ crystal growth procedure

Silica Gel Density gm/cc	**H_3PO_4 Acid concentration in Normality**	**p^H**	**Gel ageing**	**Supernatant concentration $Zn(NO_3)_2.6H_2O$ + $Ca(NO_3)_2.4H_2O$ 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 – poly crystals pH = 6 – good needle and platelet pH = 7 – 2x3mm single Liesegang rings form

2.3 Characterization

Single crystal X-ray diffraction (XRD) analysis on $ZnHPO_4$ and the calcium doped ZnHPO4 crystal was carried out using Bruker Kappa Apex II. SEM technique examined using the instrument JEOL Model JSM 6390LV, USA. In order to confirm the presence of phosphate functional groups in the crystal lattice, FTIR spectra was recorded by a KBr pellet technique using BRUKKER 66v spectrometer in the wavenumber range 400-4000 cm^{-1}. The 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. The thermal behavior of the crystal was characterized using thermo gravimetric analysis (TGA) 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 $ZnHPO_4$ and $CaZnHPO_4$ single crystals

The single crystal XRD result reveals that the grown crystals of pure $ZnHPO_4$ and $CaZnHPO_4$ both belongs to the orthorhombic crystal system with space group Pnma. The lattice parameters obtained in case of pure $ZnHPO_4$ are: a = 10.59 Å, b = 18.25 Å, c = 5.02 Å, $\alpha = \beta = \gamma = 90^0$. The volume of the unit cell of the pure $ZnHPO_4$ crystal is A = 971.68$Å^3$. Similarly, the lattice parameters obtained in case of calcium doped $ZnHPO_4$ crystals are: a = 10.61 Å, b = 18.25 Å, c = 4.93 Å, $\alpha = \beta = \gamma = 90^0$. The volume of the unit cell of the $CaZnHPO_4$ crystal is A = 955.17$Å^3$.

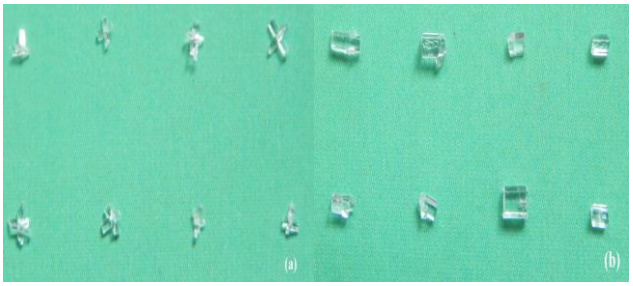

Fig. 2. (a) and (b) Different morphology of pure and calcium doped $ZnHPO_4$crystals

3.2 SEM analysis

The surface morphology of the powdered sample of Pure and Calcium doped $ZnHPO_4$ crystal was examined by using SEM technique. Fig. 3 (a) and 4 (a) illustrates SEM photographs of Pure and calcium doped $ZnHPO_4$ crystal. An enlarged SEM image is shown in Fig. 3 (b) and 4 (b). The crystal morphology seems to be thick and thin layered structures. The sample plates are flat with sharp edges and further platelike growth were observed.

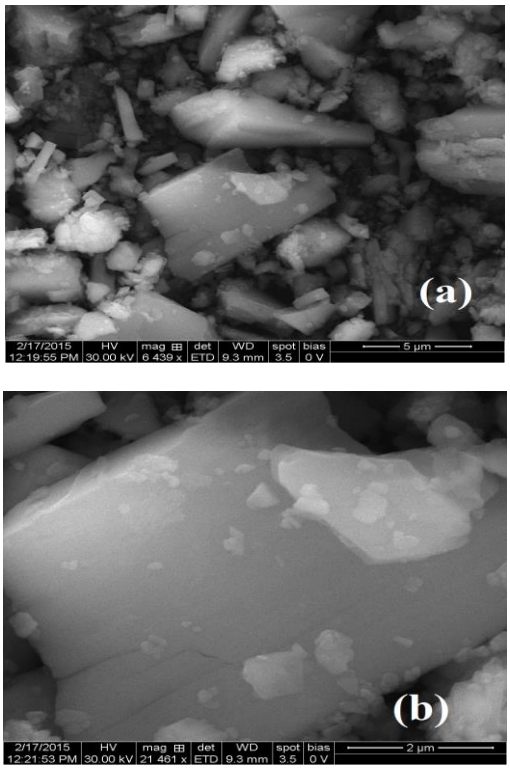

Fig. 3 (a). SEM image of pure $ZnHPO_4$ crystal (b) Magnified SEM image

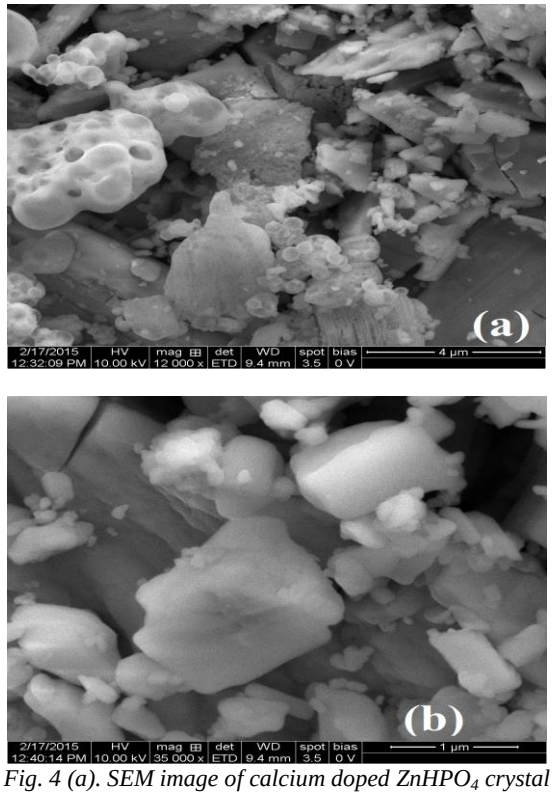

Fig. 4 (a). SEM image of calcium doped $ZnHPO_4$ crystal (b) Magnified SEM image

3.3 FTIR analysis

The FTIR absorption spectrum of pure and calcium doped $ZnHPO_4$ crystals were shown in Fig. 5 (a) and (b) respectively. The spectra show that the pure and Calcium doped $ZnHPO_4$ crystals show the spectra in the wavenumber range of 400 - 4000 cm^{-1}. The FTIR spectrum shows the identification of O – H bonding and P – O bonding. Some interesting features were revealed in a comparison of the bands and peaks of the FTIR spectra of pure and Ca doped $ZnHPO_4$ crystal. The presence of a broad absorption band between 3028 cm^{-1} to 3541 cm^{-1} for pure and 3033 cm^{-1} to 3544 cm^{-1} for Ca doped $ZnHPO_4$ indicates the presence of O – H stretching vibration (strong) in both crystals. The sharp peak at 1627 cm^{-1} for pure $ZnHPO_4$ and 1633 cm^{-1} for Ca doped $ZnHPO_4$ is assigned to H – O – H bending modes of vibrations. The phosphate group stretching mode HPO_4^{2-} is positioned at 1136 cm^{-1} for pure and 1110 cm^{-1} for Ca doped $ZnHPO_4$ crystal. The absorption peak between 617 to 557 cm^{-1} for pure and 601 to 559 cm^{-1} for Ca doped $ZnHPO_4$ is due to symmetric (O – P – O) bending modes of vibration of PO_4^{3-}. At Ca doped $ZnHPO_4$ the absorption between 959 cm^{-1} and 600 cm^{-1} is due to Ca – O [15]. A comparative assignment of absorption peaks of FTIR spectra is given in the Table 3.

Table 3. FTIR assignment of pure and calcium doped $ZnHPO_4$ crystals

Assignment	Reported frequency value cm^{-1}	Observed frequency value cm^{-1}		Intensity
		$ZnHPO_4$	$CaZnHPO_4$	
O – H stretching mode of vibration (H_2O)	3000 – 3600	3028 – 3541	3033 – 3544	Strong, Broad
H – O – H bending mode of vibration	1590 – 1650	1627	1633	Strong, Sharp
P = O stretching mode (Phosphate group)	1100 – 1200	1136	1110	Strong
P – H bending mode	950	951	959	Weak
P – OH stretching mode	900 – 1050	910	919	Strong
O – P – O symmetric bending mode of PO_4^{3-}	635 – 579	557 – 617	559 – 601	Medium
Metal – oxygen bonding (Ca and Zn)	400 - 600	422	424	Medium

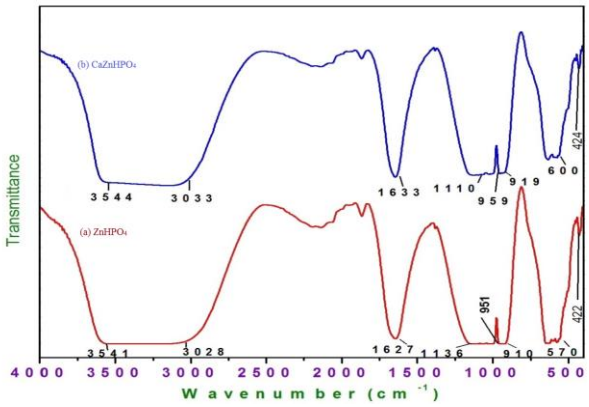

Fig. 5. FTIR Spectrum of (a) $ZnHPO_4$ (b) Calcium doped $ZnHPO_4$

3.4 UV spectral studies

The optical absorption spectral analysis of $ZnHPO_4$ and calcium doped $ZnHPO_4$ was carried out between 190-900 nm. As the crystal is colorless, its absorption is nearly equal to zero in the entire visible region and shows maximum absorption at UV region. This is one of the most desirable properties of the crystals for the fabrication of potential devices. The UV cutoff wavelength of pure $ZnHPO_4$ crystal and calcium doped $ZnHPO_4$ was found to be 236 nm and 231 nm. This transparent nature in the UV-Vis-NIR region can be used for various nonlinear optical applications . The UV absorption spectrum of $ZnHPO_4$ and calcium doped $ZnHPO_4$ is shown in Fig. 6.(a) and (b).

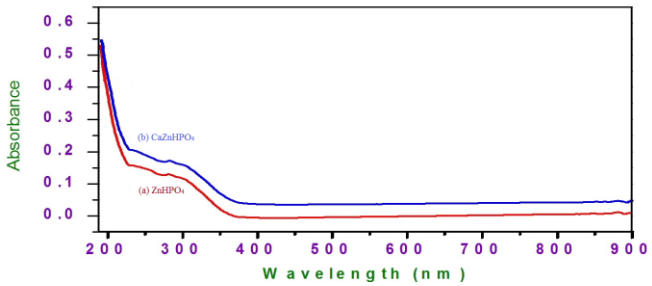

Fig. 6. UV absorption of (a) $ZnHPO_4$ (b) Calcium doped $ZnHPO_4$

3.5 NLO Study

The SHG test for the grown calcium doped $ZnHPO_4$ crystal was carried out by using powder Kurtz and Perry technique [16]. The crystal was ground into a homogenous powder and densely packed between two transparent glass slides. A Q-switched Nd:YAG laser beam of wavelength 1064 nm (pulse width 6 ns) was allowed to strike the sample cell normally. A sample of potassium dihydrogen phosphate (KDP) was also powdered and used for the same experiment as a reference material in the SHG measurement. The second harmonics generated by crystals were confirmed from output emission of green light of wavelength 532 nm. The second harmonic generation efficiency of pure $ZnHPO_4$ crystal and calcium doped $ZnHPO_4$ crystal was found to be nearly 1.32 times and 1.5 times greater than pure KDP crystal.

3.6 Thermal analysis

Thermal gravimetric analysis (TG) provides a quantitative measurement of any weight changes associated with thermally induced transitions and with the Differential thermal analysis (DTA), the difference in the temperature between the sample and the thermally inert reference material is measured as a function of temperature. Fig. 7 (a) shows simultaneously recorded TG and DTA curve for the pure $ZnHPO_4$ crystals. The curve shows that the material is thermally stable up to a temperature of 76°C and thereafter starts decomposing. The whole process of decomposition is completed in two steps. The first stage of decomposition begins from 76^0C and continues up to a temperature of 210°C resulting in a weight loss of 19.09% of the total weight. During the first step of decomposition, hydrated $ZnHPO_4$ crystal becomes anhydrous in nature. The second stage of decomposition starts from 211°C and ends at a temperature of 315°C leading to weight loss of 6.46%. This weight loss in the second stage of decomposition corresponds to the conversion of anhydrous $ZnHPO_4$ into pyrophosphate crystals. Fig. 7 (b) shows the simultaneously recorded TG and DTA curve for Ca doped $ZnHPO_4$ crystal. From the thermogram, it is clear that the doped crystal is thermally stable up to temperature of 92°C, which means that doped crystal is more stable than pure one. In case of Ca doped $ZnHPO_4$ crystal, the decomposition also takes place in two steps. The temperature for the formation of stable product after decomposition in case of pure one is 311°C whereas in case of doped one the stable product is formed at a temperature of 299°C. This means that the temperature for the formation of end product decreases with calcium substitution.

As seen from [Fig. 7(a)] the DTA curve in case of pure $ZnHPO_4$ and Calcium doped $ZnHPO_4$ [Fig. 7 (b)] there is well marked endothermic and exothermic peak corresponding to each stage of decomposition. For pure $ZnHPO_4$ irreversible endothermic transition at 123°C and 297°C and a sharp endothermic peak at 123°C shows the melting point of the crystal and Ca doped $ZnHPO_4$ irreversible endothermic transition at 240°C and 571°C. 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 necessarily not only depends on the amount of water loss on dehydration, but also on the structural factors.

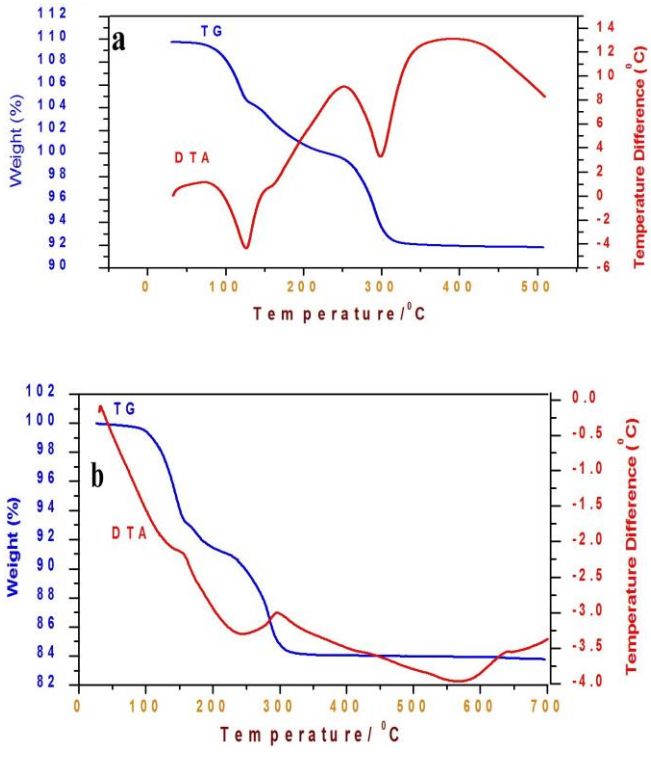

Fig. 7. Thermogram showing simultaneous recording of TG and DTA curves for (a) $ZnHPO_4$ (b) calcium doped $ZnHPO_4$

4. Conclusion

Synthesis of pure zinc hydrogen phosphate ($ZnHPO_4$) and calcium doped $ZnHPO_4$ crystals in the form of single

crystal were accomplished by single diffusion technique. Pure $ZnHPO_4$ and calcium doped $ZnHPO_4$ both belong to the orthorhombic crystal system. The lattice parameters of pure crystal are: a = 10.59 Å, b = 18.25 Å, c = 5.02 Å, $\alpha = \beta = \gamma = 90^o$ and volume of the unit cell is 971.68 $Å^3$. Similarly, the lattice parameters for calcium doped crystals are: a = 10.61 Å, b = 18.25 Å, c = 4.93 Å, $\alpha = \beta = \gamma = 90^0$ and volume of the unit cell is 955.17$Å^3$. SEM images show that both the crystals having a plate like surface morphology. The absorption peaks obtained in FT-IR spectrum confirmed the water of crystallization, symmetric as well as asymmetric stretching and bending vibration of PO_4 units and metal-oxygen bonds in pure $ZnHPO_4$ and calcium doped $ZnHPO_4$ crystals. The thermal studies suggest that pure $ZnHPO_4$ is stable up to temperature of 76°C whereas calcium doped $ZnHPO_4$ is stable up to a temperature of 92°C. This means that doping of Calcium increases their thermal stability. Also, temperature for the formation of end product decreases with calcium substitution.

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