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GROWTH AND CHARACTERISATION STUDIES OF PURE AND Mg DOPED $ZnHPO_4$ CRYSTALS BY GEL GROWTH METHOD

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Abstract: Zinc hydrogen phosphate (ZHP) and magnesium doped zinc hydrogen phosphate (MZHP) crystals are grown in silica gel medium with silica gel technique by the process of diffusion using different gel densities and various concentrations of orthoposphoric acid and supernatant solutions. The grown crystals were characterized by powder X – ray diffraction (PXRD) studies, whereas from single crystal X-ray diffraction (SXRD) the crystal system comes out to be orthorhombic. Fourier transform infrared spectroscopic (FTIR) studies signifies the presence of phosphate $(PO_4)^{2-}$ group and water of crystallization. Thermogravimetric analysis is undertaken to study the thermal stability of the grown crystals. Kurtz powder technique is employed to confirm their non – linear optic (NLO) behavior. The study of UV absorption spectra reveals that the value of band gap energy decreased slightly as the concentration of magnesium increased.
Keywords: Silica gel, Mg doping, SEM, NLO, Energy band gap.

1. Introduction

Studies on the preparation and characterization of zinc hydrogen phosphate have been widely investigated [1-4]. However, successful application of the required material depends on morphology and purity. Thus, a well-defined microstructure depends mainly on the conditions of synthesis [5]. The preparation of some transition metal phosphates by different synthesis conditions and medium agents had been reported, which give rise to final metal phosphates with cost effective method [6, 7]. Crystal defects are highly minimized in gel grown crystals as growth takes place due to the process of diffusion of the reactants at a slow rate without convection [8]. The growth of crystals in a gel medium has attracted the attention of many investigators [9-11]. 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 [12-15]. This technique appeared to be quiet attractive for growing crystals of alkaline earth metal compound like magnesium, calcium and barium has unique advantages in terms of crystals produced and simplicity of the process [16-18]. The alkaline earth phosphates have received enormous importance with respect to their use as phosphor matrices [19]. Several researchers have used gel technique to grow single crystals and also modified them by suitable substitution to determine the effect of modification on their substitution [20, 21].

Some of the single crystals like octa calcium phosphate (OCP), hydroxyapatite (HAP), calcium hydrogen phosphate (CHP), Zinc hydrogen phosphate (ZHP) and magnesium hydrogen phosphate (MHP) are grown in silica gel medium at room temperature [22, 23]. The next approach is to grow single crystal in silica gel medium at different environments, which contains one major mineral (phosphate), one minor mineral (zinc) and one inhibitor (magnesium). There is no study available on the growth of MZHP single crystals in gel medium. To increase MZHP crystals of more perfection and greater optical transparency our work was directed towards the growth of MZHP single crystals using gel technique. Various authors have done a series of experiments with silica gel at different pH values ranging from 5.5 to 11. One can obtained the periodic precipitation, Liesegang rings [24-26] of crystals named as hydroxyapatite (HAP), brushite, struvite, MZHP, etc. In the present study, MZHP crystals are grown in silica gel medium at same concentrations and different pH values at room temperature. The harvested crystals were characterized by X-ray diffraction technique, SEM, FTIR, SHG, UV, TG and DTA studies.

2. Experimental

2.1 Synthesis of ZHP and MZHP

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Synthesis of pure and magnesium doped zinc hydrogen phosphate (MZHP) single crystals were carried out using single diffusion gel growth method. The silica gel was prepared by dissolving 284.20 g of sodium metasilicate in 1000 ml of de mineralized water so as to obtain gel solution of 1M concentration. The gel density ranges from 1.03 g/cm^3 to 1.05 g/cm^3, and it is accurately measured since it has considerable influence on the gelation process and quality of the crystal. Gel was prepared by mixing stock solution with particular concentration of ortho phosphoric acid (1 and 2 Normality) which is act as a lower reactant. 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 hrs to 48 hrs and 6 days, which depends upon the pH and environmental temperature. After the gel ageing, the supernatant solutions of zinc nitrate and magnesium 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 pure and magnesium doped zinc hydrogen phosphate (MZHP) single crystals.

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

$$Zn(NO_3)_2.6H_2O + Mg(NO_3)_2.6H_2O + H_3PO_4 \longrightarrow MgZnHPO_4 + 2(HNO_3)_2 + 12H_2O \quad (2)$$

The diffusion of Zn^{2+} and Mg^{2+} ions leads to the reaction between these ions and the phosphate ions present in the gel as lower reactant. The reaction leads to the formation of Mg doped zinc hydrogen phosphate crystal (MZHP). Fig. 1(a) shows the growth of ZHP crystals in a crystallizer in which asterisk like crystals appear. The asterisk-like morphology is actually an agglomeration of large number of stacked crystal platelet. Once the upper reactant of 1 M concentration was poured on a perfectly set gel, then nucleation starts and the anions of zinc nitrate slowly diffused into the gel column containing phosphate ions. Magnesium doped zinc ions diffuse through the gel and a white thin film in the form of ring appeared known as Liesegang ring [24-26] [Fig. 1(b)] just below the gel surface. A thick mass of polycrystalline material was formed on the ring within a day and get spread in the downward direction. Below the thin polycrystalline mass, tiny transparent crystals were seen within a period of 3 days. Fig. 1(b) shows that along with Liesegang ring there are platelets crystals as well as spherulites growing in the gel media at different regions. The following expected reaction takes place in the growth columns and growth procedure is listed in the Table 1 and 2. Crystals with different morphologies like star type, and rectangular platelet type were grown in the gel. Fig. 1(c and d) shows a different type of morphology of Pure and magnesium doped ZHP grown crystals.

TABLE 1 ZINC HYDROGEN PHOSPHATE (ZHP) CRYSTAL GROWTH PROCEDURE

Silica Gel Density g/cm^3	H_3PO_4 acid concentration in Molarity	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 h 36 h 4 h	1M	12 h 24 h 38 h	244 days	pH = 5 – very tiny X - shape pH = 6 – Tiny needle and X shape crystals pH = 7 – 3x2mm X shape crystals

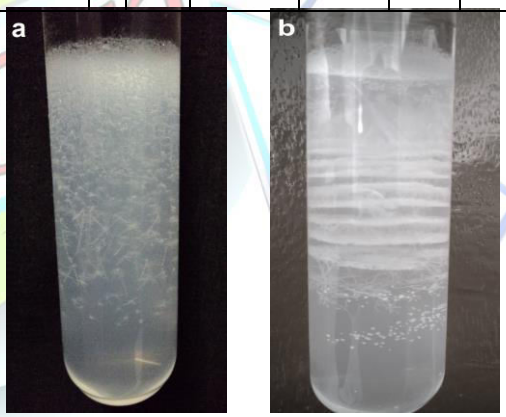

TABLE 2 MAGNESIUM DOPED ZINC HYDROGEN PHOSPHATE (MZHP) CRYSTAL GROWTH PROCEDURE

Silica Gel Density	H_3PO_4 acid concentration	pH	Gel ageing	Supernatant concentration (Zn $(NO_3)_2$. $6H_2O$ +	Nucleation Started	Growth Period	Nature of Crystal observed and Harvested crystal size

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g/cm^3	in Molarity			Mg$(NO_3)_2$.6H_2O in M			
1.04	1N	5 6 7	14 4 h 36 h 4 h	1 : 1 ratio	10 h 12 h 30 h	244 days	pH = 5 – Poly and sugar like crystals pH = 6 – Tiny needle crystals pH = 7 – Lissegang rings (8) and 5x1 needle single crystal

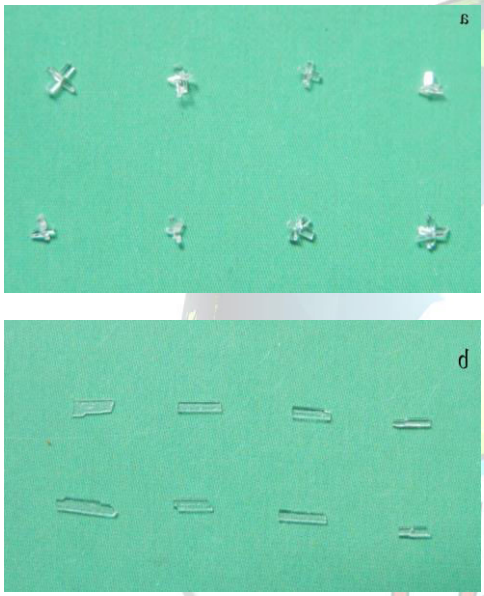

Fig. 1. (a) Asterisk and platelet crystals of zinc hydrogen phosphate (ZHP) (b) Liesegang ring formation along with growth of magnesium doped zinc hydrogen phosphate (MZHP) crystals in a crystallizer growing in silica gel medium. (c and d) Different morphology of pure and magnesium doped zinc hydrogen phosphate crystals.

2.2 Characterization

X – ray diffraction analysis on pure and magnesium doped zinc hydrogen phosphate single crystal was carried out by employing Bruker AXS D8 Advance X-ray diffractometer with Cu Kα (λ=1.5406) radiation using a tube voltage and current of 40 kV and 30 mA respectively. 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}. Optical absorption spectrum of the grown crystal was recorded using JASCO UV visible spectrometer in the wavelength range 190 nm - 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 mg was heated in a crucible between 30 °C to 700 °C at a heating rate of 20 K min^{-1} in nitrogen atmosphere.

3. Results and discussion

3.1 X-ray Diffraction analysis

The powder X-ray diffractogram for both ZHP and MZHP crystal is shown in Fig. 2 (a and b) respectively. The occurrence of highly resolved peak at specific 2θ Bragg angles in both the crystals indicates the crystalline nature of the grown crystals. The detail of the PXRD plot depicting interplanar 'd' spacing and corresponding {hkl} planes for ZHP and MZHP is given in the Table 3. Single crystal X-ray studies were also carried out which confirmed that ZHP and MZHP both belongs to orthorhombic crystal system with space group Pmna. The lattice parameters obtained in case of pure ZHP are: a = 10.59 Å, b = 18.25 Å, c = 5.02 Å, α = β = γ = 90^0 and volume of unit cell being A = 971.68 Å^3. Similarly, the lattice parameters obtained in case of doped MZHP crystals are: a = 10.46 Å, b = 18.09 Å, c = 4.92 Å, α = β = γ = 90^0 and volume of unit cell being A = 931.54 Å^3. Since the ionic radii of magnesium and zinc are comparable, one can expect identical crystal system for both ZHP and MZHP crystals. From single crystal XRD it has also been observed that because of Mg doping peak value shifts towards higher angle, indicating a decrease in the value of lattice constants. Which are matched with the standard XRD data of JCPDS file (Numbers: 33-1474) [27].

Table 3 Compiled data of various hkl planes corresponding to different Bragg angle and inter planer spacing'd' for zinc hydrogen phosphate (ZHP) and magnesium doped zinc hydrogen phosphate (MZHP).

d-spacing (A^0)		2 theta (θ)		[hkl] planes		Intensity (A.U)	
ZHP	MZHP	ZHP	MZHP	ZHP	MZHP	ZHP	MZHP
4.55	4.52	19.40	19.42	040	040	7146	3716

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2.82	2.80	31.40	31.35	241	241	453	1111
2.25	2.23	39.35	39.38	171	171	1000	345
1.83	1.80	49.95	49.93	402	402	297	86
1.52	1.50	60.7	60.65	303	303	1885	278

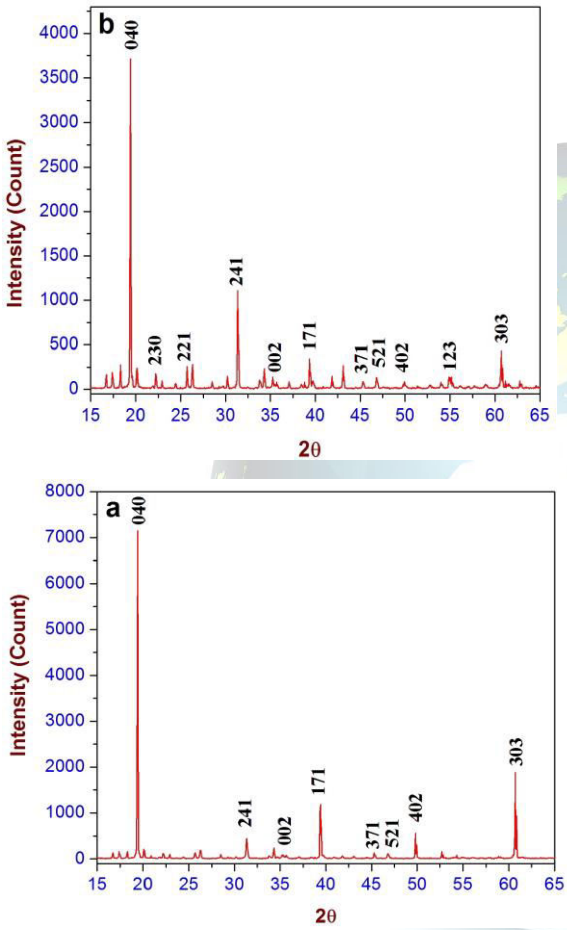

Fig. 2. X-ray diffractogram of (a) Zinc hydrogen phosphate (ZHP). (b) Magnesium doped zinc hydrogen phosphate (MZHP).

3.2 SEM analysis

Scanning electron microscopic studies were performed to see the surface morphologies on both ZHP and MZHP crystals. Pure and doped phosphate crystals assume various types of morphologies, which include spherulites, single crystals and needle shaped platelets. Fig. 3(a) represents platelet like morphology of ZHP crystal showing channels engraved on the surface, whereas Fig. 3(b) represents needle like MZHP crystal, which suggests growth hillock, elongated to an angle of 45^0 with reference to crystal edge. These types of morphologies [Fig. 3 (a and b)] are basically the consequence of growth instability caused by extremely high supersaturation. These surface features are found in accordance with the theories of growth of morphologically important faces of crystals. Fig. 3 (c and d) has shown magnified SEM images of ZHP and MZHP crystals.

Fig. 3. Scanning electron micrograph of (a) Zinc hydrogen phosphate (ZHP). (b) Magnesium doped zinc hydrogen phosphate (MZHP) crystal. (c and d) Magnified SEM image of ZHP and MZHP crystals.

3.3 FTIR analysis

Fig. 4 (a and b) shows FTIR spectrum of pure ZHP and doped MZHP crystals respectively. Fundamental IR frequencies observed in other phosphate compounds were also found in the present case, which confirms the presence of phosphate group in the grown crystal. The presence of water of crystallization is evidenced by the broadband at 3541, 3028, 1627 cm^{-1} for ZHP and 3577, 3066, 1627 cm^{-1} for MZHP crystals. The peaks occurring at 528, 503, 427 cm^{-1} in case of pure ZHP and at 422 cm^{-1} in case of doped MZHP are attributed to the presence of metal - oxygen bond. A slight shift in some of the characteristic vibration

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frequency of the MZHP spectrum was observed with respect to pure ZHP because of doping with magnesium. This is due to the lattice strain developed as a result of doping. The shift in the wave number was due to the difference in mass number of zinc (65.40) and magnesium (24.30) ion. It is reported in the literature [28], that the difference in mass of ion leads to a change in the molecular geometry and mechanical vibrations, which results in a shift in bands. The peaks corresponding to other functional groups were also present and comparative assignments of prominent peaks of FTIR spectra are given in the Table 4.

Table 4 Presence of various functional groups in case of pure zinc hydrogen phosphate (ZHP) and magnesium doped calcium hydrogen phosphate (MZHP) crystals.

Assignment	Reported frequency value cm^{-1}	Observed frequency value cm^{-1}	
		ZHP	MZHP
O – H stretching mode of vibration (H_2O molecule)	3000 – 3600	3541, 3028	3577, 3006
H – O – H bending mode of vibration (H_2O)	1590 – 1650	1627	1627
P = O stretching mode (Phosphate group - HPO_4^{2-})	1100 – 1200	1136	1128
P – OH stretching mode	900 – 1050	953	956, 923
O – P – O symmetric bending mode of PO_4^{3-}	635 – 579	617, 557	621
Metal Oxygen bond (Mg and Zn)	400 – 600	422	528, 503 and 437

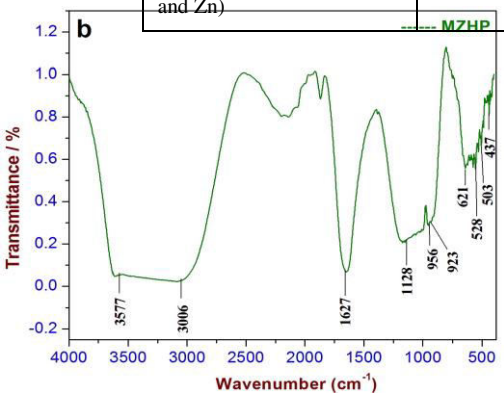
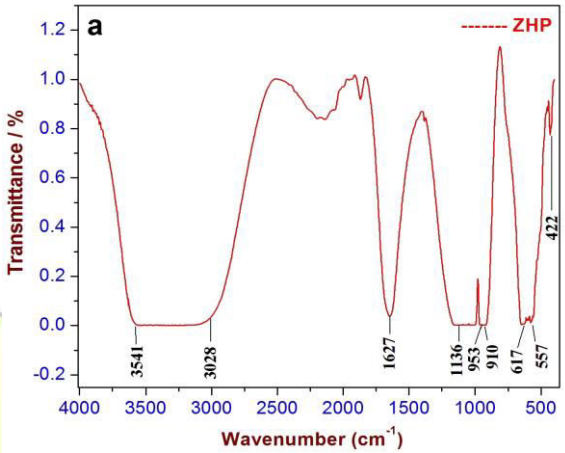


Fig. 4. FTIR



spectrum of the crystal depicting the various functional groups present in (a) Zinc hydrogen phosphate (ZHP). (b) Magnesium doped zinc hydrogen phosphate (MZHP).

3.4 UV spectral studies

The optical absorption spectral analysis of 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. Using the formula Eg = 1240/λ (nm) [29], the band gap energy is presented in the Table 5. The UV absorption spectrum of Zinc hydrogen phosphate (ZHP) and Magnesium doped zinc hydrogen phosphate (MZHP) are shown in Fig. 5.

Table 5 Band gap energy of pure zinc hydrogen phosphate (ZHP) and magnesium doped calcium hydrogen phosphate (MZHP)

Crystal	λ (nm)	Band gap energy (eV)
Zinc hydrogen phosphate (ZHP)	264.94	4.68

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Magnesium doped zinc hydrogen phosphate (MZHP)	275.72	4.49

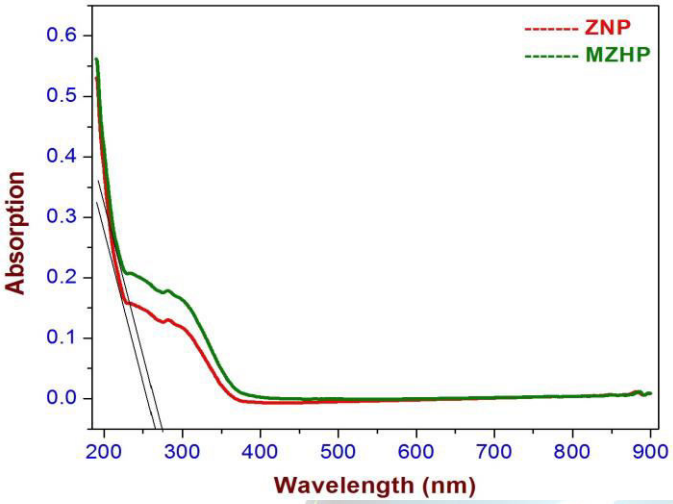

Fig.5 UV-vis absorption spectrum of Zinc hydrogen phosphate (ZHP) and Magnesium doped zinc hydrogen phosphate (MZHP).

3.5 SHG Studies:

The SHG test for the grown MZHP crystal was carried out by using powder Kurtz and Perry technique [30]. 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 MZHP. The output from the sample was monochromated to collect the intensity of 532 nm component and the fundamental was eliminated. KDP was used as a reference material for the present measurement. This confirms the NLO behavior 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 MZHP sample to that of the KDP signal amplitude recorded for the same input powder. The second harmonic generation efficiency of pure $ZnHPO_4$ crystal and magnesium doped $ZnHPO_4$ crystal was found to be nearly 1.32 times and 1.8 times greater than pure KDP crystal. It is very clear that this crystal has potential and prospects for frequency conversion applications.

3.6 Thermal Analysis:

Thermal gravimetric analysis (TG) provides a quantitative measurement of any weight changes associated with thermally induced transitions and in 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. 6 (a) shows simultaneously recorded TG and DTA curve for zinc hydrogen phosphate (ZHP) 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 completes 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 first step of decomposition, hydrated ZHP crystal becomes anhydrous in nature. The second stage of decomposition starts from 211°C and ends at a temperature of 365°C leading to weight loss of 6.46%. This weight loss in the second stage of decomposition corresponds to the conversion of anhydrous ZHP into zinc pyrophosphate crystals. Table 6(a) gives the compiled summary of the decomposition process of $ZnHPO_4.2H_2O$. It can be seen that the calculated weight loss is in close proximity with the observed values. Based on these thermal analyses, we confirm that the grown crystal is having a composition of $ZnHPO_4.2H_2O$.

Fig. 7 (b) shows the simultaneously recorded TG and DTA curve for MZHP crystals. From the thermogram, it is clear that the doped crystal is thermally stable up to temperature of 88°C, which means that doped crystal is more stable than pure one. In case of MZHP crystal, the decomposition also takes place in two steps. Table 6(b) gives detailed summary of the decomposition of $Mg_{(0.1)}Zn_{(0.9)}HPO_4.2H_2O$ along with observed as well as calculated weight loss. It is worth mentioning here that the temperature for the formation of stable product after decomposition in case of pure one is 365°C whereas in case of doped one the stable product is form at a temperature of 350°C. This means that the temperature for the formation of end product decreases with magnesium substitution. Above result suggests that the calculation of percentage of weight loss for pure and doped zinc hydrogen phosphate crystal contain water of hydration, which they lose at different temperature ranges. This study indicates that the compound could be used for any optical application below its melting point.

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Table 6 Results of thermal decomposition for different temperature ranges with observed and calculated weight loss in case of: (a) Zinc hydrogen phosphate (ZHP). (b) Magnesium doped zinc hydrogen phosphate (MZHP).

Stage	Temp. (°C)	Decomposition step	Weight loss (%)
(a) First	76 – 210	$ZnHPO_4.2H_2O \xrightarrow{\Delta} 2ZnHPO_4 + 2H_2O$	19.09
Second	211 – 365	$2ZnHPO_4 \xrightarrow{\Delta} Zn_2P_2O_7 + H_2O$	6.46
(b) First	88 – 250	$Mg{:}ZnHPO_4.2H_2O \xrightarrow{\Delta} Mg{:}2ZnHPO_4 + 2H_2O$	21.23
Second	251 – 350	$Mg{:}2ZnHPO_4 \xrightarrow{\Delta} Mg{:}\ Zn_2P_2O_7 + H_2O$	7.22

As seen from DTA curve in case of ZHP [Fig. 6(a)] and MZHP [Fig. 6(b)] there is well marked endothermic and exothermic peak corresponding to each stage of decomposition. The sharpness of endothermic peaks shows a good degree of crystallinity and purity of the sample. 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.

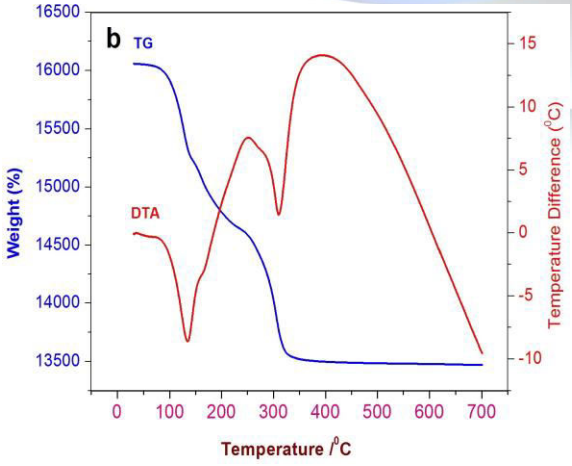
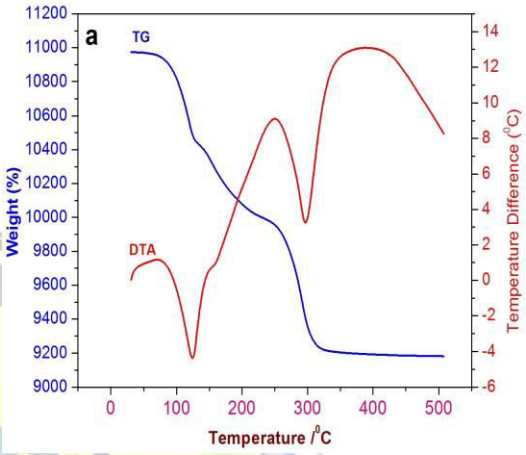


Fig.6. Thermogram showing simultaneous recording of TG and DTA curves for (a) Zinc hydrogen phosphate (ZHP). (b) Magnesium doped zinc hydrogen phosphate (MZHP).



4.

Conclusion

Synthesis of pure zinc hydrogen phosphate (ZHP) and magnesium doped zinc hydrogen phosphate (MZHP) single crystals have been achieved by single diffusion technique. X-ray analysis confirmed that ZHP and MZHP both belong to orthorhombic crystal system. The lattice parameters obtained in case of pure ZHP are: a = 10.59 Å, b = 18.25 Å, c = 5.02 Å, $\alpha = \beta = \gamma = 90^0$ and volume of unit cell being A = 971.68 $Å^3$. Similarly, the lattice parameters obtained in case of doped MZHP crystals are: a = 10.46 Å, b = 18.09 Å, c = 4.92 Å, $\alpha = \beta = \gamma = 90^0$ and volume of unit cell being A = 931.54 $Å^3$. SEM images show that both the crystals having needle shaped platelets like surface morphology. FTIR results support the presence of water of hydration and other functional groups in both pure and doped zinc hydrogen phosphate crystals. Both ZHP and MZHP absorption spectra recorded in solution form reveal that they possess low cut-off wavelengths. The SHG studies reveal that they are capable of realizing green light and their second harmonic efficiency is greater than that of KDP. Due to their excellent optical, thermal, and nonlinear properties, these crystals can be used for NLO applications. The thermal studies suggest that pure ZHP is stable up to temperature of 76^0C whereas MZHP is stable up to a temperature of 88^0C. This means that doping of Mg increases their thermal stability. Also, temperature for the formation of end product decreases with magnesium substitution.

5. References

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International Journal of Advanced Research Trends in Engineering and Technology (IJARTET)
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[1]. C. Justin Raj, G. Mangalam, S. Mari Navis Priya, J. Mary Linet., et al, Cryst. Rest. Technol, 42, (2007), pp 344 – 348.
[2]. T. Jayaprakash, and P. Kalugasalam, Journal of optoelectronics and advanced materials, 17, (2015) pp 1734 – 1738.
[3]. H. K. Hensisch, Crystal Growth in Gels, University Park, PA: The Pennsylvania University Press, (1973).
[4]. R. Mahalakshmi, S. X. Jesuraja, and S. Jerome Das, Cryst. Res. Technol. 41, 782 (2006).
[5]. Y. Han, S. Li, X. Wang, L. Jia, J. He, Mat. Res. Bull. 42 (2007) 1169.
[6]. S. Scaccia, M. Carewska, A. Di. Bartolomeo, P.P. Prosini, Thermochim. Acta 397 (2003) 135.
[7]. A. Manthiram, J. Kim, Chem. Mater. 10 (1998) 2895.
[8]. Santhana Raghavan, P. Ramasamy, Crystal Growth — Processes and Methods, KRU Publications, India, P-245.
[9]. H.K. Henisch, J. Dennis, H.I. Hanoka, J. Phy. Chem. Solids 26 (1965) 493.
[10]. K.C. Joseph, M.J. Joshi, Ind. J. Phys. 76A (2002) 159.
[11]. A. Elizabeth, C. Joseph, M.A. Ittyachen, Bull. Mater. Sci. 24 (2001) 431.
[12]. J.S. Soresen, E. Hans, L. Madsen, J. Cryst. Growth 216 (2000) 399.
[13]. R.V.S.S. N Ravikumar, Y.P. Reddy, K. Ikeda, B.J. reddy, A.V. Chandersekhar, Cryst. Res. Technol. 36 (2001) 1429.
[14]. E. Hans, L. Madsen, J. Cryst. Growth 244 (2002) 349.
[15]. C.C. Desai, M.S.V. Ramana, Bull. Mater. Sci. 11 (1988) 21.
[16]. Heinz K. Henisch, Crystal Growth in Gels, Dover Publications Inc, New York, 1996.
[17]. Z. Blank, D.M. Speyer, W. Brenner, Y. Okomoto, Nature 216 (1967) 1103.
[18]. C. Barta, J. Zemlicka, V. Rene, J. Cryst. Growth 10 (1971) 158.
[19]. H. Koelmans, A.P.M. Cox, J. Electrochem. Soc. 104 (1957) 442.
[20]. N. Dishovshy, Z. Boncheva-Mladenova, J. Cryst. Growth 51 (1981) 147.
[21]. J. Dennis, H.K. Henisch, J. Electrochem. Soc. 114 (1967) 263.
[22]. P. Sundaramoorthi, S. Kalainathan and G. Kanchana, National Conference on Recent Trends in Material Science and Technology, Proceeding, p. 72 (2005).
[23]. P. Sundaramoorthi, S. Kalainathan and G. Kanchana, Tenth National Seminar on Crystal Growth, Proceeding, p. 31 (2005).
[24]. Henisch H K et al 1965 J. Electrochem. Soc. 112 627.
[25]. R.E Liesegang, Naturewiss. Wochenschr., 11, 353 (1896).
[26]. H.K. Henisch and J.M. Garcia-Ruiz, J. Crystal Growth, 75, 195 (1986).
[27]. H.K. Henisch and J.M. Garcia-Ruiz, J. Crystal Growth, 75, 203 (1986).
[28]. S. P. Yan, W. He and C. Y. Sun, "The Biomimetic Synthesis of Zinc Phosphate Nanoparticles," *Dyes and Pig-ments*, Vol. 80, No. 2, 2009, pp. 254-258.
[29]. S.J. Joshi, B.B. Parekh, K.D. Vohra, M.J. Joshi, Bull. Mater. Sci. 29 (2006) 307.
[30]. P. Selvarajan, J. Glorium Arulraj, S. Perumal, Phys. B 405 (2010) 738–743.
[31]. S.K. Kurtz, T.T. Perry, J. Appl. Phys. 39 (1968) 3798–3813.

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