

# Dielectric behavior of mixed cadmium magnesium hydrogen phosphate crystal

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## ABSTRACT

Magnesium hydrogen phosphate (MHP) and transition metal doped cadmium magnesium hydrogen phosphate (CdMHP) was synthesized in the form of crystalline material by room temperature solution technique known as gel encapsulation technique. The synthesized crystals were then characterized for their structural, mechanical and electrical investigations using various chemical and physical methods. X - ray diffraction analysis (XRD) establishes magnesium hydrogen phosphate and cadmium magnesium hydrogen phosphate belonging to orthorhombic crystal system with space group Pbc<sub>a</sub>. The mechanical behaviour of these crystals was studied by calculating Vicker's hardness number. The behaviour of microhardness with applied load was observed to be complex. The electrical behaviour was carried out by calculating dielectric constant at different temperatures and for different frequencies. The dielectric constant ( $\epsilon'$ ) was found to be strongly dependent on temperature and frequency. The transition metal doping of cadmium in magnesium hydrogen phosphate remarkably decrease the value of dielectric constant from 68 to 23. The transition temperature also decreases from 330°C in case of magnesium hydrogen phosphate to 310°C in case of cadmium magnesium hydrogen phosphate. Copyright © 2014 VBRI press.

**Keywords:** Crystal growth; X-ray diffraction; microhardness; dielectric constant.



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## Introduction

Phosphates are considered as the most interesting class of materials which have attracted more and more interest on synthesis, crystallography, electro-optical properties and so on [1, 2]. Over the past few decades, the technology and science of materials has advanced rapidly for the synthesis and characterization of new non-linear optical materials. Potassium dihydrogen phosphates (KDP), an important class of material belonging to phosphate group have gained special interest due to their wide applications as ferroelectric, piezoelectric, pyroelectric as well as laser modulator [3, 4]. Studies on the preparation and characterization of calcium phosphate have been widely investigated [5-8]. Synthesis of some transition metal phosphates by different synthesis conditions and medium agents have been reported [9,10]. The precipitation of calcium phosphates in the presence of increasing cadmium amount was studied at 25°C in dilute ammonia solutions [11]. An amorphous precipitate, an apatite – calcium phosphate and the compound  $Cd_5H_2(PO_4)_4 \cdot 4H_2O$  are formed according to pH and cadmium concentration. The effect of cadmium substitution on various properties of pure calcium hydrogen phosphate has been studied by Bamzai et al [12]. Recently, effect of rare earth on thermo luminescence properties of  $CaSO_4$  phosphors have been investigated by Wani et al [13]

The alkaline earth phosphates have received enormous importance with respect to their use as phosphor matrices [14]. The effect of doping on gel grown crystals has been studied by many investigators [15-17]. Inorganic phosphates encompass a large class of diverse materials with a wide range of applications which includes catalysts, linear and non – linear optical components, solid electrolytes for batteries, in synthetic replacement for bone and teeth and many more [18, 19]. Magnesium hydrogen phosphate also known as Newberyite ( $MgHPO_4 \cdot 3H_2O$ ) has interesting application as far as their bioactivity is concerned [20]. Newberyite ( $MgHPO_4 \cdot 3H_2O$ ), together with another phosphate mineral brushite ( $CaHPO_4 \cdot 2H_2O$ ) have contributed to pre-enzymatic phosphorylation and thus to the development of life itself. Single crystals of anhydrous magnesium hydrogen phosphate ( $MgHPO_4$ ) are of considerable interest, especially in fundamental studies of phase transitions and because of their important dielectric, ferroelectric, piezoelectric and optical properties. Kanchana et al [21] carried out the growth of strontium chromium magnesium hydrogen phosphate ( $SrCrMHP$ ) crystals by silica gel method. They extended their research work and reported the growth of  $SrCaMHP$  crystals [22].

In the present investigations, the main objective of the work is to report growth, characterization, mechanical and dielectric behavior of pure and cadmium (Cd) mixed magnesium hydrogen phosphate crystals. Growth of mixed crystals is interesting because their characteristics change from those of the crystals of single components grown separately, e.g., mixed crystals are found to be harder than pure ones [23, 24]. Cadmium ( $Cd^{2+}$ ) ion which is transition metal has been selected for the modified magnesium hydrogen phosphate because its ionic radius ( $0.97\text{Å}$ ) is very close to that of magnesium ( $0.65\text{Å}$ ) ion. According to

Goldsmith rule, the dopant cation enters into the sites if the radius of the substituted ion and the replaced ion does not differ by 15 – 20%. Also, literature survey unfolds that no work has so far been reported on growth of mixed crystal of Cd modified magnesium hydrogen phosphate in gels at room temperature. The effect of substitution on various characteristics of the parent material has been investigated by carrying out systematic study on the crystal of the modified composition.

## Experimental

### Materials

To carry out the growth of magnesium hydrogen phosphate and cadmium magnesium hydrogen phosphate, the starting materials were the following: orthophosphoric acid ( $H_3PO_4$ ) from Loba Chemie (AR Grade 98%); sodium metasilicate ( $Na_2SiO_3 \cdot 5H_2O$ ) from s d Fine-chem Limited (LR Grade 97%); magnesium chloride ( $MgCl_2 \cdot 6H_2O$ ) from s d Fine-chem Limited (AR Grade 98%) and cadmium chloride ( $CdCl_2 \cdot H_2O$ ) from s d Fine-chem Limited (AR Grade 99%).

### Method

The growth of magnesium hydrogen phosphate (hereafter referred as MHP) and cadmium mixed magnesium hydrogen phosphate (referred as CdMHP) has been carried out by using room temperature solution technique i.e., gel encapsulation technique. The method involves incorporating one reactant called the lower reactant into the gelling mixture and later diffusing another reactant called the upper reactant into the gel medium. This leads to a very high supersaturation condition initiating the nucleation necessary for the growth of crystals.

### Preparation of hydrosilica gel

In order to grow crystals from silica gel, first of all silica gel solution of desired molarity was prepared by dissolving sodium metasilicate (SMS) powder in distilled water. The pH of the SMS solution must be lowered in order to have proper gelation. This can be achieved by mixing an acid with the solution. Since in the present case phosphate crystals are to be grown, therefore, orthophosphoric acid of desired molarity was added gently to the prepared SMS solution with constant stirring to adjust the pH of the solution and also as the source of anions for crystallization of the compound. The dissociation of orthophosphoric acid system can be represented by three dissociation equilibrium and the presence of various ions at various pH values [25]. Based on these results, the gel pH in the range 5-7 has been used in which the  $HPO_4^{2-}$  ions dominate or exist alone. The acidified gel was then poured into the test tube. This gel was allowed to set in the crystallizer and then aged for desired time. In our experiments, we used gels of ages 72, 96, 120, 144 and 198 h.

### Synthesis of pure MHP

After the gel was set and aged, the supernatant (magnesium chloride) solution of desired molarity was poured along the

sides of the tube, ensuring that this process does not break the gel. As soon as upper reactant comes in contact with the lower reactant, precipitation starts immediately suggesting spontaneous nucleation. All the experiments were conducted in the room temperature range 30-40°C. The expected chemical reaction in case of magnesium hydrogen phosphate (where lower reactant is orthophosphoric acid and upper reactant is magnesium chloride) is:



#### Synthesis of CdMHP

For the growth of 10% cadmium mixed magnesium hydrogen phosphate crystals, lower reactant remains the same. However, for upper reactant a mixture of CdCl<sub>2</sub> and MgCl<sub>2</sub> in proper ratio was used. The diffusion of Cd<sup>2+</sup> and Mg<sup>2+</sup> ions through narrow pores of silica gel leads to the reaction between these ions and HPO<sub>4</sub><sup>2-</sup> ions of lower reactant already present in the gel suggesting spontaneous nucleation and the expected chemical reaction is:



In order to obtain the optimum conditions conducive for the growth of MHP and CdMHP, number of experiments were carried out by varying the various growth parameters including upper reactant concentration, lower reactant concentration, gel concentration, gel pH and gel ageing. The optimum condition for the growth of good quality single crystal is given in **Table 1**.

**Table 1.** Optimum conditions for the growth of magnesium hydrogen phosphate (MHP) and cadmium magnesium hydrogen phosphate (CdMHP) crystals.

Varying parameter	MHP	CdMHP
Lower reactant concentration	0.5 M	0.5 M
Upper reactant concentration	0.5 M	1 M
Gel pH	7	6
Gel ageing	96 h	198 h
Gel concentration	0.5M	0.5M
Temperature	30-40°C	30-40°C

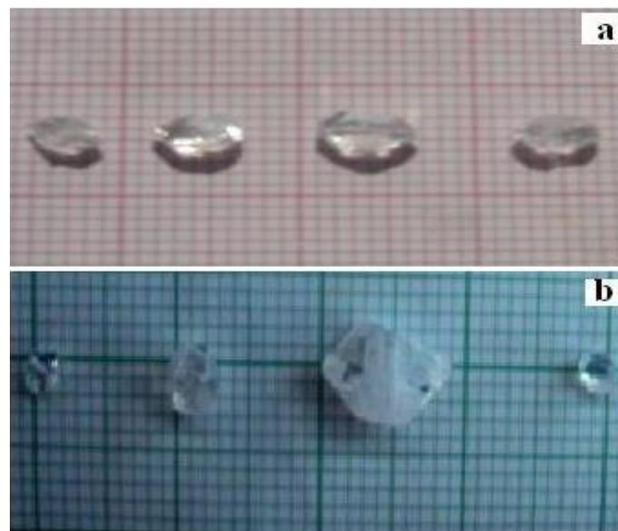
#### Characterization

The incident light microscope “EPIGNOST” was used for the rapid examination of the grown crystals. Single crystal X’Calibur Oxford X-ray diffractometer was used to find out the crystal system, whereas the powder pattern was also obtained using powder X-ray diffractometer (Rigaku Co. Ltd. Japan) with Cu K $\alpha$  radiation ( $\lambda = 1.5406\text{\AA}$ ) with a scanning rate of 2°/min. Hardness studies have been carried out by using auto detection microhardness analyzer (HVM-2 of Shimadzu, Japan). The dielectric measurements were recorded with the help of automated impedance analyzer (4192A LF model) interfaced with USB – GPIB converter 82357 (Agilent) and further automated by using a computer for data recording, storage and analysis.

## Results and discussion

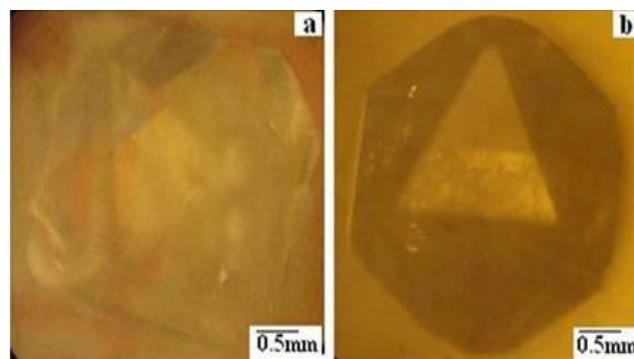
### Structural characterization

Some of the good quality single crystals of MHP and CdMHP placed on a microslide is shown in **Fig. 1 (a & b)** respectively.



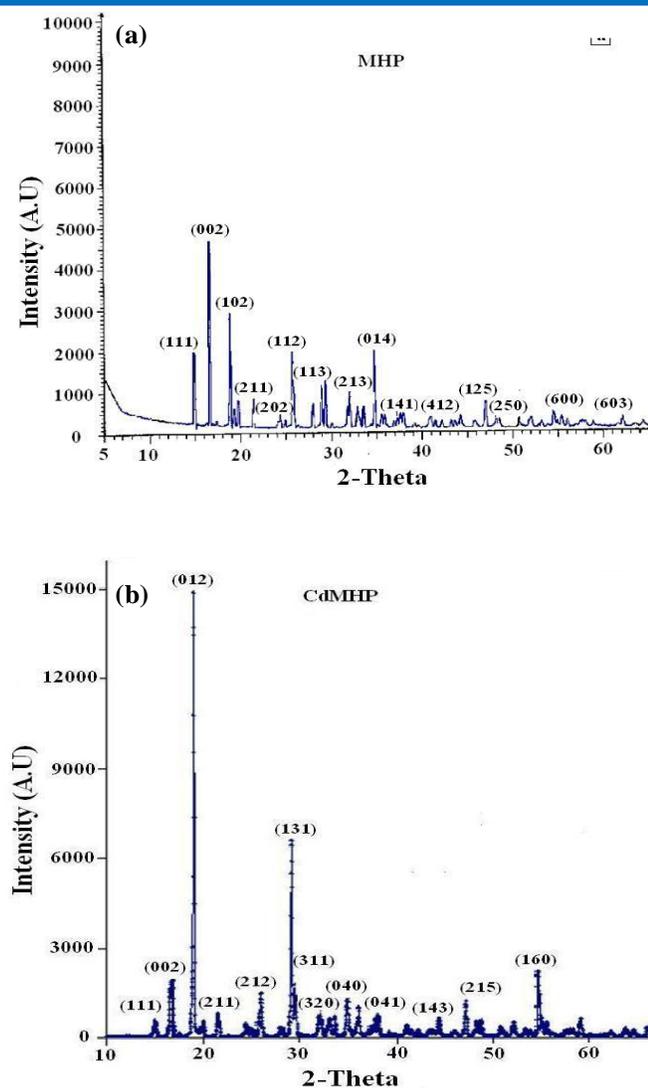
**Fig. 1.** Some of the good quality single crystals of (a) magnesium hydrogen phosphate (MHP) and (b) cadmium magnesium hydrogen phosphate (CdMHP) placed on a microslide.

For the micromorphological studies, the crystals were placed under the incident light microscope “EPIGNOST”. The optical micrographs of MHP and CdMHP is shown in **Fig. 2 (a & b)** respectively. **Fig. 2 (a)** shows the formation of a given plane on the surface of pure MHP crystal, whereas **Fig. 2 (b)** represents the optical micrograph of CdMHP crystal showing clearly the hexagonal morphology along with a clear plane.



**Fig. 2.** Optical micrograph showing (a) formation of a given plane on the surface of magnesium hydrogen phosphate crystal and (b) hexagonal morphology on the surface of cadmium magnesium hydrogen phosphate crystal.

The powder X – ray diffraction pattern for MHP and CdMHP is shown in **Fig. 3 (a & b)** respectively. The occurrence of highly resolved intense peaks at specific 2 $\theta$  Bragg angles indicates the crystallinity of the grown material.



**Fig. 3.** (a) Powder X-ray diffraction pattern of magnesium hydrogen phosphate (MHP) and (b) Powder X-ray diffraction pattern of cadmium magnesium hydrogen phosphate (CdMHP).

The details of the X – ray diffraction plot depicting  $d$  - spacing and corresponding  $[hkl]$  planes for MHP and CdMHP crystal is given in **Table 2**.

**Table 2.** Compiled data of various  $hkl$  planes corresponding to different Bragg angle and interplaner spacing for magnesium hydrogen phosphate (MHP) and cadmium magnesium hydrogen phosphate (CdMHP).

d-Spacing/Å		2 $\theta$ /°		[hkl]Planes		Intensity/counts	
MHP	CdMHP	MHP	CdMHP	MHP	CdMHP	MHP	CdMHP
5.9496	5.8939	14.878	15.019	111	111	46.30	3.6
5.3474	5.2677	16.564	18.817	002	002	100	12.6
4.1482	4.1218	21.403	21.542	211	211	17.2	5.2
3.6558	3.4298	24.327	25.958	202	212	10.2	9.8
2.7926	2.7997	32.023	31.940	213	320	21.4	5.6
2.5808	2.5687	34.732	34.901	014	040	41.5	9.6
1.9301	1.9248	47.042	47.181	125	215	15.1	8.0
1.6566	1.6795	55.417	54.600	600	160	7.2	14.1

From the diffraction pattern, it can be clearly seen that the substitution of Cd in place of Mg ions in pure MHP crystals lead to shift in the positions of peaks indicating a

change in the internal structure of crystals due to change in bond lengths as a result of doping. Thus, it has been observed that doping shifts peak value towards higher angle, indicating an increase in the value of lattice constants. Single crystal X - ray analysis establishes that MHP and CdMHP belong to orthorhombic crystal system. The lattice parameters obtained for both the systems is given in **Table 3**. From the powder as well as single crystal X – ray diffraction results, it can be concluded that MHP and CdMHP have the orthorhombic crystal system with space group Pbc<sub>a</sub>. Thus, it is clear that doping of about 10% Cd into MHP does not change the crystal system.

**Table 3.** Lattice parameters for magnesium hydrogen phosphate (MHP) and cadmium magnesium hydrogen phosphate (CdMHP) crystals.

Lattice parameter	MHP	CdMHP
$a$	9.9445(18) Å	10.0147(2) Å
$b$	10.2080(2) Å	10.2179(2) Å
$c$	10.6636(10) Å	10.6819(2) Å
$\alpha$	90.024(13)°	90°
$\beta$	89.824(12)°	90°
$\gamma$	89.905(15)°	90°
Volume, $V$	1082.45(10) (Å) <sup>3</sup>	1093.07(03) (Å) <sup>3</sup>
Space group	Pbc <sub>a</sub>	Pbc <sub>a</sub>

#### Mechanical characterization

The mechanical strength of the grown crystals was done by microhardness measurement technique. For carrying out the hardness studies on MHP and CdMHP, smooth and clean face of the crystal was selected and subjected to indentation test at room temperature. Loads ranging from 0.2452 N to 1.961 N were used for indentation keeping the indenter at right angles to the surface of the crystal for 10 sec in all cases. The distance between any two consecutive indentations was suitably adjusted in order to ensure that the effects were independent of each other. The Vicker's microhardness value ( $H_v$ ) was calculated using the formula:

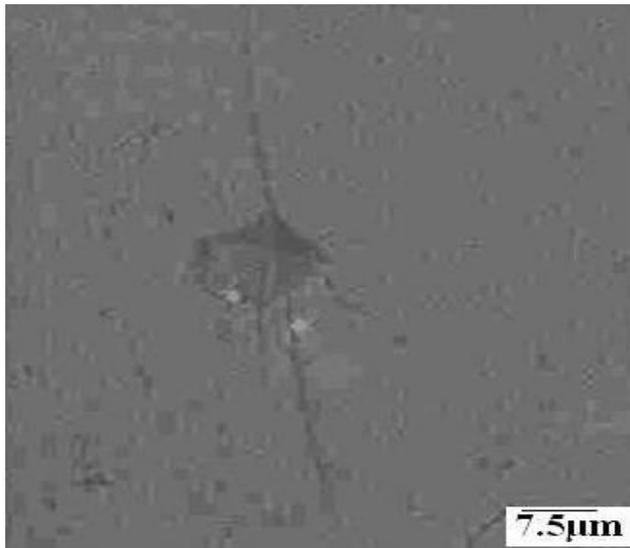
$$H_v = (2 \sin 68^\circ) P/d^2 \quad \text{or} \quad H_v = 1.8544P/d^2$$

where 'P' is the applied load in Newton and 'd' is the diagonal length of the indentation mark in micrometer. The error in  $H_v$  was estimated through the relation:

$$\Delta H_v = 1.8544 [(\Delta P/Y)^2 + (P\Delta Y/Y^2)^2]^{1/2}$$

where  $Y = d^2$ ,  $\Delta Y = 2d\Delta d$ ,  $\Delta P$ ,  $\Delta Y$  and  $\Delta d$  being error in P, Y, and d respectively. The study on variation of microhardness with applied load for MHP crystals has already been carried out and reported [26]. It was found that microhardness value first increases and then becomes independent of load. However, there is no report regarding the microhardness behaviour with applied load for CdMHP crystals. A survey of literature suggests that different materials behave differently so far their dependence of microhardness on applied load is concerned. It is reported that microhardness is: i) independent of load [27]; ii) increase or decrease with load [28, 29]; and iii) shows complex variation with change in load [30].

Therefore, it is interesting to see how Cd doping in MHP system responds to the indentation. **Fig. 4** shows the indentation impression at a load of 0.49 N. **Table 4** gives the compiled data on the microhardness studies of CdMHP crystal. The behaviour of Vicker's hardness number with applied load is somewhat complex.



**Fig. 4.** Shows indentation impression at a load of 0.49N for cadmium magnesium hydrogen phosphate.

**Table 4.** Results of microhardness studies on cadmium magnesium hydrogen phosphate (CdMHP) crystal.

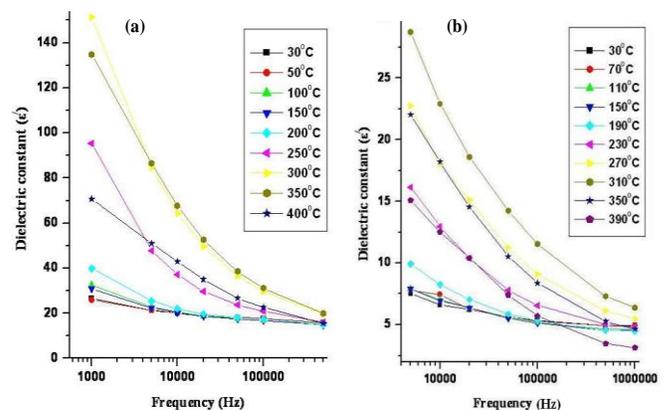
S.No.	Load (P) (N)	Average length (d) (in m)	Hardness ( $H_v$ ) $H_v = 1.8544P/d^2$ (MN/m <sup>2</sup> )	$\Delta H_v = 1.8544$ $(\Delta P/Y)^2 +$ $(\Delta Y/Y^2)^2]^{1/2}$
1.	0.245	$10.26 \times 10^{-6}$	4319	401
2.	0.490	$12.38 \times 10^{-6}$	5928	335
3.	0.980	$16.55 \times 10^{-6}$	6634	235
4.	1.961	$16.55 \times 10^{-6}$	13276	418
5.	2.942	$16.45 \times 10^{-6}$	20161	626
6.	4.903	$16.84 \times 10^{-6}$	32061	959
7.	9.807	$18.58 \times 10^{-6}$	52680	1420

It shows increasing trend with increase in applied load, where at first, the increase for smaller loads is less as compared to the higher load. The value of Vicker's hardness ranges from 4319 – 52680 MN/m<sup>2</sup> in the load ranging from 0.245 – 9.807 N, respectively. The explanation for the variation of  $H_v$  with load in complex fashion can be given on the basis of role played by the surface layer in deciding its hardness property. The diamond pyramid indenter used in the present investigation for calculating microhardness values penetrate considerably deeper than the thickness of the surface layer. However, as the depth of penetration increases with increasing load, the effect of the surface layer of the crystal becomes less marked, thereby, indicating the increase in the hardness value. For much larger loads, when the indenter reaches a depth at which undistorted layers of the material exists and the elastic properties of the inner material predominate over the surface properties, the microhardness is expected to cease its dependence on load

which in the present case, for CdMHP has not been obtained. Berzina et al [31] reported for various alkali halide crystals, the anomalous behaviour of microhardness at low loads is greatest in crystals with large surface energy and thus related the microhardness particularly, in low load region on the surface energy of the solids. Thus, we can say that in the present case also, the surface energy plays an important role for the increase in the values of microhardness.

#### Electrical characterization

The electric characterization includes the response of dielectric constant to an applied electric field. The variation of dielectric constant ( $\epsilon'$ ) can be attributed to different types of polarization which comes into play at different stages of its response to varying temperature and frequency of the applied alternating field. A study of variation of dielectric constant with temperature and frequency of the applied electric field is very useful in the study of phase transitions taking place in materials. For MHP and CdMHP, the dependence of dielectric constant on temperature was studied in the temperature range of 30 - 400°C and in the frequency range of 1 – 1000 kHz of the applied a.c field.



**Fig. 5.** (a) Plot showing variation of dielectric constant with temperature in case of magnesium hydrogen phosphate (MHP) and (b) variation of dielectric constant with temperature in case of cadmium magnesium hydrogen phosphate (CdMHP).

#### Variation of dielectric constant with frequency at different temperature

The dependence of dielectric constant on frequency of the applied a.c field in case of MHP and CdMHP is shown in **Fig. 5 (a & b)** respectively. It can be seen from the figure that the dielectric constant decreases continuously with increasing frequency and attains almost saturation at higher frequencies. The decrease in the value of dielectric constant with increasing frequency is a normal dielectric behaviour and has been reported earlier [32-35]. At each particular temperature, the dielectric constant has a maximum value at lower frequency. This type of behaviour indicates higher space charge polarizability in the low frequency region. As the frequency increases, the dipole do not comply with the varying external field resulting in the decrease in polarization which, in turn results in the decrease in the value of dielectric constant with increasing frequency [36].

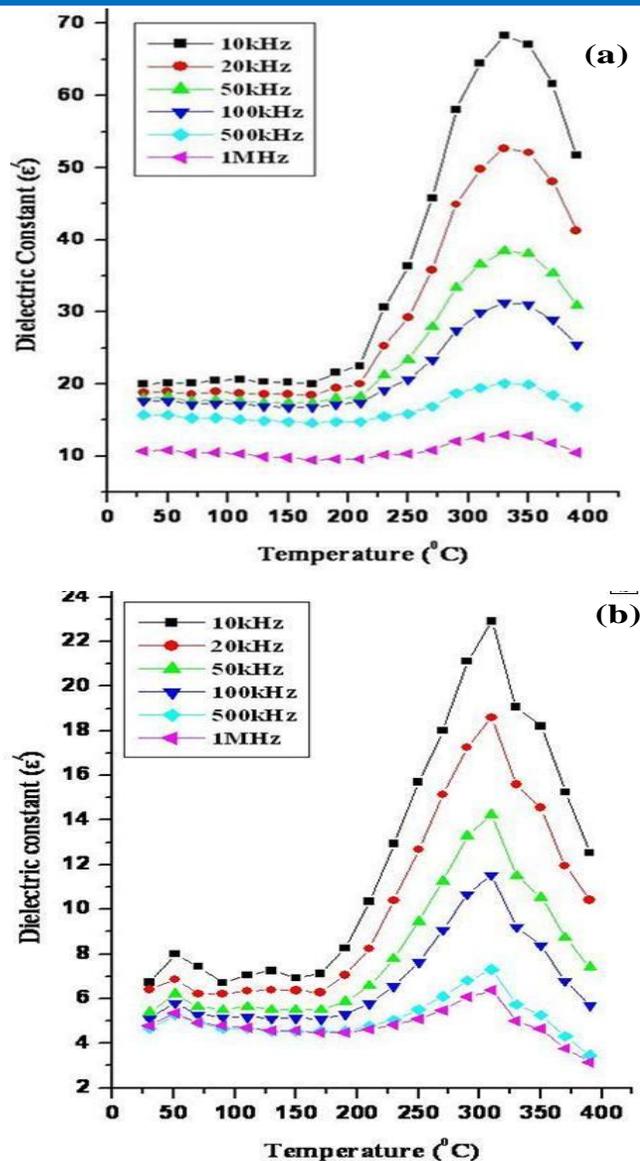


Fig. 6. (a) Plot showing variation of dielectric constant with temperature in case of magnesium hydrogen phosphate (MHP) and (b) variation of dielectric constant with temperature in case of cadmium magnesium hydrogen phosphate CdMHP.

Table 5. Data regarding dielectric constant and their corresponding transition temperature in case of magnesium hydrogen phosphate (MHP) and cadmium magnesium hydrogen phosphate (CdMHP) crystals.

Frequency	MHP		CdMHP	
	$\epsilon'$	$T_c$	$\epsilon'$	$T_c$
10kHz	68.3	330°C	22.91	310°C
100kHz	31.3	330°C	11.54	310°C
1MHz	12.9	330°C	6.37	310°C

Variation of dielectric constant with temperature at different frequencies

Fig. 6 (a & b) shows the behaviour of dielectric constant ( $\epsilon'$ ) with temperature in case of MHP and CdMHP

respectively. From the graph, it is clear that MHP has a high dielectric constant as compared to CdMHP. In case of MHP, the dielectric constant ( $\epsilon'$ ) under the application of frequency varies little upto the temperature of 200°C. As the temperature increases, the value of dielectric constant increases and reaches a maximum value of 68 for a frequency of 10 kHz at a temperature of 330°C. The value of  $\epsilon'$  decreases after 330°C and reaches upto a value of 52 at 390°C. For other frequencies i.e., from 20 kHz – 1 MHz, the peak value of dielectric constant is also observed at a temperature of 330°C. Thus, the peak value of 330°C is observed for all the frequencies considered, thereby, suggesting that the transition temperature in case of MHP is 330°C. In case of CdMHP, the variation of dielectric constant with frequency of applied ac field is very little upto the temperature of 190°C. As the temperature increases, the value of dielectric constant increases and reaches a maximum value of 23 for a frequency of 10 kHz at a temperature of 310°C. Beyond 310°C, the value of  $\epsilon'$  decreases and reaches upto a value of 13 at 390°C. For other frequencies i.e., from 20 kHz – 1 MHz, the peak value of dielectric constant is also observed at a temperature of 310°C. Thus, the peak value of 310°C is observed for all the frequencies considered, thereby suggesting that the transition temperature in case of CdMHP is 310°C. Table 5 gives the data regarding dielectric constant and their corresponding transition temperature in case MHP and CdMHP. From the above observation, it is clear that the transition metal (Cd) doping in MHP system decreases the transition temperature and also its dielectric constant.

## Conclusion

Growth of magnesium hydrogen phosphate (MHP) and cadmium mixed magnesium hydrogen phosphate (CdMHP) was accomplished by employing room temperature solution technique i.e., gel encapsulation technique. Optimum conditions for successful growth of good quality single crystals have been worked out. The crystals of MHP and CdMHP belong to orthorhombic crystal system with space group Pbc<sub>a</sub>. A slight change in the lattice parameters takes place on incorporation of Cd into the lattice of MHP system. Doping of cadmium does not change the crystal structure of MHP. Cadmium doping plays an important role in the mechanical properties of MHP crystals. The behavior of Vicker's hardness number with applied load is somewhat complex where the increase for smaller load is less as compared to the higher loads. The value of Vicker's hardness number ranges from 4319 – 52680 MN/m<sup>2</sup> in the load range of 0.245 – 9.807 N respectively. The dielectric constant decreases continuously with increasing frequency and attains almost saturation at higher frequencies for MHP and CdMHP crystals. The decrease in the value of dielectric constant with increasing frequency is a normal dielectric behavior. The transition metal doping of cadmium in MHP decrease remarkably the value of dielectric constant from 68 to 23 at a frequency of 10 kHz. Also the doping of cadmium affects the transition temperature of MHP system. The transition temperature

values decrease from 330°C in case of MHP to 310°C in case of CdMHP.

## Reference

- Dinamani, M.; Kamath, P. V. *Mat. Res. Bull.* **2001**, 36, 2043.  
DOI: [10.1016/S0025-5408\(01\)00682-1](https://doi.org/10.1016/S0025-5408(01)00682-1)
- Sales, B. C.; Chaoumakos, B. C. J. *Non – Cryst. Sol.* **1993**, 159, 121.  
DOI: [10.1016/0022-3093\(93\)91289-F](https://doi.org/10.1016/0022-3093(93)91289-F)
- Mullin, J. W.; Amatavivadhana, A. *J. Appl. Chem.* **1967**, 17, 151.  
DOI: [10.1002/jctb.5010170508](https://doi.org/10.1002/jctb.5010170508)
- Joshi, M. S.; Paul, B. K. J. *Cryst. Growth.* **1974**, 22, 323.  
DOI: [10.1016/0022-0248\(74\)90078-5](https://doi.org/10.1016/0022-0248(74)90078-5)
- Kumar, R.; Prakash, K. H.; Cheang, P.; Khor, K. A. *Langmuir* **2004**, 20, 5196.  
DOI: [10.1021/la049304f](https://doi.org/10.1021/la049304f)
- Bose, S.; Saha, S. K. *J. Chem. Mater.* **2003**, 15, 4464.  
DOI: [10.1021/cm0303437](https://doi.org/10.1021/cm0303437)
- Sadasivan, S.; Khushalani, D.; Mann, S. *Chem. Mater.* **2005**, 17, 2765.  
DOI: [10.1021/cm047926g](https://doi.org/10.1021/cm047926g)
- Wojciech, L. S.; Pavel, S.; Byrappa, K.; Richard, E. R.; Kevor, S. T.; Victor, F. J. *Biomaterials* **2002**, 23, 699.
- Scaccia, S.; Carewska, M.; Bartolomeo, A. D.; Prosini, P. P. *Thermochim. Acta* **2003**, 397, 135.  
DOI: [10.1016/S0040-6031\(02\)00292-7](https://doi.org/10.1016/S0040-6031(02)00292-7)
- Manthiram, A.; Kim, J. *Chem. Mater.* **1998**, 10, 2895.  
DOI: [10.1021/cm980241u](https://doi.org/10.1021/cm980241u)
- Lundager Madsen, H. E.; Abbona, F.; Barrase E. *Crys. Res. Tec.* **2004**, 39, 235.  
DOI: [10.1002/crat.200310176](https://doi.org/10.1002/crat.200310176)
- Bamzai, K. K.; Suri, S.; Singh, V. *Mater. Chem. & Phys.* **2012**, 135, 158.  
DOI: [10.1016/j.matchemphys.2012.04.040](https://doi.org/10.1016/j.matchemphys.2012.04.040)
- Wani, J. A.; Atone, M. S.; Dhoble, S. J. *Adv. Mat. Lett.* **2013**, 4, 363.  
DOI: [10.1088/0022-3727/24/3/020](https://doi.org/10.1088/0022-3727/24/3/020)
- Koelmans, H.; Cox, A. P. M. J. *Electro Chem. Soc.* **1957**, 104, 442.  
DOI: [10.1149/1.2428621](https://doi.org/10.1149/1.2428621)
- Dishovsky, N.; Boncheva-Mladenova, Z. J. *Crys. Growth* **1981**, 51, 147.  
DOI: [10.1016/0022-0248\(81\)90020-8](https://doi.org/10.1016/0022-0248(81)90020-8)
- Dennis, J.; Henisch, H. K. *J. Electro Chem. Soc.* **1967**, 114, 263.  
DOI: [10.1149/1.2426564](https://doi.org/10.1149/1.2426564)
- Gits, S.; Robert, M. C.; Lefauchaux, L. *J. Cryst. Growth* **1985**, 71, 203.  
DOI: [10.1016/0022-0248\(85\)90063-6](https://doi.org/10.1016/0022-0248(85)90063-6)
- Van Wazer, G. R. Phosphorus and its compounds, in: Chemistry, Interscience, New York, **1958**, 1.
- Kanazawa, T. Inorganic Phosphate Materials, Elsevier, New York, 1989.
- Sutor, D. J.; *Nature* **1968**, 218, 295.  
DOI: [10.1038/2189295a0](https://doi.org/10.1038/2189295a0)
- Kanchana, G.; Suresh, P.; Sundaramoorthi, P.; Kolainathan, S.; Jayanthi, G. P. *J. Min. and Mat. Charact. and Eng.* **2008**, 7, 215.
- Kanchana, G.; Sundaramoorthi, P.; Jayanthi, G. P. *J. Min. and Mat. Charact. and Eng.* **2009**, 81, 37.
- Dharma Prakash, S. M.; Rao, M. *Cryst. Res. Technol.* **1987**, 22, 1095.  
DOI: [10.1002/crat.2170220816](https://doi.org/10.1002/crat.2170220816)
- Kotru, P. N.; Razdan, A. K.; Wanklyn, B. M. *J. Mater. Sci.* **1989**, 24, 2401.  
DOI: [10.1007/BF01174502](https://doi.org/10.1007/BF01174502)
- Pecsok, R. L.; Shields, L. D.; Cairns, T.; Mc William L. C. Modern Methods of Chemical Analysis (1976). John Wiley, New York.
- Desai, C. C.; Patel, K. N. *Cryst. Res. and Technol.* **1989**, 24, 681.  
DOI: [10.1002/crat.2170240709](https://doi.org/10.1002/crat.2170240709)
- Ascheron, C.; Huse, C.; Kuhn, G.; Neumann H., *Cryst. Res. Technol.* **1989**, K 33, 24.  
DOI: [10.1002/crat.2170240226](https://doi.org/10.1002/crat.2170240226)
- Kotru, P. N.; Razdan, A. K.; Waanklyn, B. N. J. *Mater. Sci.* **1989**, 24, 793.  
DOI: [10.1007/BF01148759](https://doi.org/10.1007/BF01148759)
- Balakrishnan, K.; Vengatesan, B.; Kanniah, N.; Ramaswamy, P. J. *Mater. Sci. Lett.* **1990**, 9, 7866.  
DOI: [10.1007/BF00720158](https://doi.org/10.1007/BF00720158)
- Bhatt, V. P.; Patel, R. M.; Desai, C. F. *Cryst. Res. Technol.* **1983**, 18, 9.  
DOI: [10.1002/crat.2170180919](https://doi.org/10.1002/crat.2170180919)
- Berzina, J. G.; Berman, J. B.; Savintsev, P. A. *Sov. Phys. Cryst.* **1965**, 9, 483.
- Matthew, J. A.; Micheal G. B.; Drew; Susan Morris; David, A. R. *Polyhedron.* **1996**, 15, 3377.  
DOI: [10.1016/0277-5387\(96\)00044-7](https://doi.org/10.1016/0277-5387(96)00044-7)
- Pike, G. E. *Phys. Rev.* **1972**, B 6, 1572.  
DOI: [10.1103/PhysRevB.6.1572](https://doi.org/10.1103/PhysRevB.6.1572)
- Amin, B.; Kothari, A. *J. Phys. Chem. Solids*, **2004**, 65, 965.  
DOI: [10.1016/j.jpcs.2003.10.058](https://doi.org/10.1016/j.jpcs.2003.10.058)
- Politova, E. D.; Ivanova, V. V.; Kaleva, G. M. A.; Mosunov, V.; Segalla, A. G.; Yustefanovich, S.; Shvastsman, V. V.; Kholkin, A. L. *Ferroelectrics* **2004**, 313, 129.  
DOI: [10.1080/00150190490903847](https://doi.org/10.1080/00150190490903847)
- Reicha, F. M.; El-Hi, M.; El-Sonabati, A. Z.; Diab, M. A. *J. Phys.* **1991**, D 24, 369.  
DOI: [10.1088/0022-3727/24/3/020](https://doi.org/10.1088/0022-3727/24/3/020)

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