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LASER RAMAN, THERMAL, EDAX AND PHOTOLUMINESCENCE STUDIES OF MAGNESIUM DOPED ZINC HYDROGEN PHOSPHATE CRYSTALS IN SILICA GEL MEDIUM USING SINGLE DIFFUSION TECHNIQUE

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In the single diffusion method, Magnesium doped zinc hydrogen phosphate (MZHP) crystals grow in the silica gel medium using different gel densities and various concentrations of orthoposphoric acid and supernatant solutions. Silica gel obtained from sodium Metasilicate with a strongly acidic cation exchange in the H-form, was used for crystal growth experiments. The influence of pH, gel concentration and concentration of upper and lower reactants on the size, quality and nucleation density of the crystals is discussed. The techniques of concentration programming and seeded growth are used to enhance the crystal size. The pH range in which HPO_4^{2-}ions dominates were considered which in turn is necessary for the growth of Magnesium doped zinc hydrogen phosphate (MZHP) crystals. The thermogravimetric studies, Energy dispersive X-ray analysis (EDAX), Laser Ramanspectroscopy, Photoluminescence have been made to find the stoichiometric composition of the crystals and its structure.

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1. Introduction

Zinc hydrogen phosphate, Cadmium doped Zinc hydrogen phosphate are grown in silica gel medium at room temperature and reported [1,2]. The next approach is to grow Magnesium doped Zinc hydrogen phosphate crystal in silica gel medium at ambient temperature, which contains one major element (phosphate), one trace element (Zinc) and one inhibitor (magnesium). A room temperature solutiontechnique, popularly known as the gel technique, hasbeen used by a large number of researchers and a gooddeal of information pertaining to the scientific data ofseveral crystals is available [3-26]. Very little attention,however, has been paid to the growth of phosphate crystals at ambient temperatures using the geltechnique, which is not only very simple but inexpensiveas well. Nowadays more studies have been carried out for the preparation and characterization of inorganic materials owing to their unique properties and applications in many areas. Especially inorganic phosphate materials have attracted the attention of a large number of researchers due to the excellent property of the adaptability of PO4 tetrahedron in bonding to other diverse structural units. Because of their fundamental properties, inorganic phosphate materials find wide applications such as catalysts, ion exchange materials, chelating agents, corrosion-resistant coatings, glass ceramics, biomedical cements and high-quality fertilizers. Hence single crystals of such type of compounds cannot be grown by either slow evaporation or melt technique. In this situation single diffusion technique is the appropriate one for their growth. The purpose of the present article is to report for the first time the growth of magnesium doped single crystals in

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silica gel medium by using single diffusion technique at room temperature. These crystals have identified and characterized by TG/DTA, EDAX, Laser RAMAN, and PL.

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 Magnesium doped zinc hydrogen phosphate (MZHP) 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 silica gel 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 sedimentation. 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 ranges from 1.03 g/cc to 1.04 g/cc, and it is accurately measured since it has considerable influence on the gelation process and quality of the crystal. The gel was prepared by mixing stock solution with a particular concentration of ortho phosphoric acid (1 N & 2 N) which is acting 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 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 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 in the atmosphere.

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 a pipette. The supernatant solution diffuses through the set gel, which reacts with phosphoric acid present in the gel leading to the growth of magnesium doped zinc hydrogen phosphate (MZHP)single crystals.

$$Zn\,(NO_3)_2.6H_2O + Mg\,(NO_3)_2.6H_2O + H_3PO_4 \longrightarrow MgZnHPO_4 + 2(HNO_3)_2 + 12H_2O \quad (1)$$

In order to grow magnesium doped zinc hydrogen phosphate crystals, zinc nitrate are mixed with magnesium nitrate. 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).

Table 1 Magnesium doped zinc hydrogen phosphate (MZHP)Crystal Growth Procedure

Silica Gel Density gm/cc	**H_3PO_4 acid concentr -ation in Molarity**	**p^H**	**Gel ageing**	**Supernatant concentration (Zn $(NO_3)_2$. $6H_2O$ + Mg $(NO_3)_2$. $6H_2O$ in M**	**Nucle ation Starte d**	**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	10 hrs 12 hrs 30 hrs	244 days	pH = 5 – Poly & sugar like crystals pH = 6 – Tiny needle crystals pH = 7 –5mm x1 mm needle single crystal

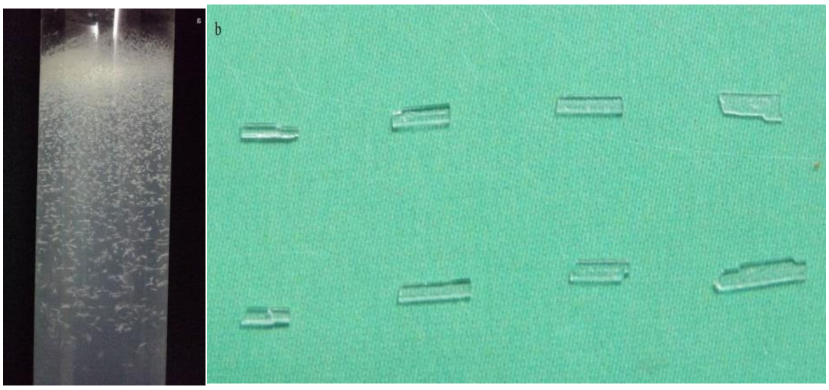

Fig. 1 (a) Magnesium doped $ZnHPO_4$ crystals grown in gel medium &
(b) Morphology of Magnesium doped $ZnHPO_4$ crystals

2.3 Characterization

Raman spectra were recorded using Laser Raman spectrometer (Renishaw Invia) with laser excitation lines of 488 and 514 nm respectively at room temperature with power of 15mW and acquisition of 6 seconds applied for the individual samples. The thermal behavior of thecrystal was characterized using thermo gravimetric analysis (TGA) and differential thermo gravimetric (DTA) analysis by Perkin Elmer STA 6000 thermal analyzer. A platinum crucible was used for heating the sample of weight 4.091 mg and analyses were carried out in nitrogen atmosphere at a heating rate of 20°C/min in the temperature range 30°C to 700°C. EDAX (FEI-Quanta 250) was used for the analysis of determine the chemical composition of the elements present in the material. In this work, the photoluminescence spectra of samples were recorded with Cary EcliseWinFLRphotoluminescence devices.

3. Results and discussion

3.1 Laser Raman studies of Magnesium doped $ZnHPO_4$ crystal

The recorded Raman spectrum of Magnesium doped zinc hydrogen phosphate is shown in Figure 2 Laser Raman analyses are effective scientific technique broadly used to identify the functional units, internal structure of molecules and chemical bonds of a compound. Raman spectroscopy is widely used for receiving information about various modes in crystals. Fig. 2 was the Raman spectrum for the Mg doped $ZnHPO_4$ crystals. The Raman spectrum shows effective band splits with clearly resolved bands. When we compare the intensity with other peaks, it was very low observed at 176 cm^{-1} where there is metal-metal stretching mode. The absorption bands at 312 cm^{-1} were attributed to P-O bending vibration, respectively. The most intense band in the Raman spectrum is identified at 941 cm^{-1} and is assigned to the ν_s (PO_4) symmetric stretching mode. Other Raman bands are found out at 1150, 1059, 1000 and 995 cm^{-1} and are assigned to the $\nu_{as}(PO_4)$ anti symmetric stretching modes.

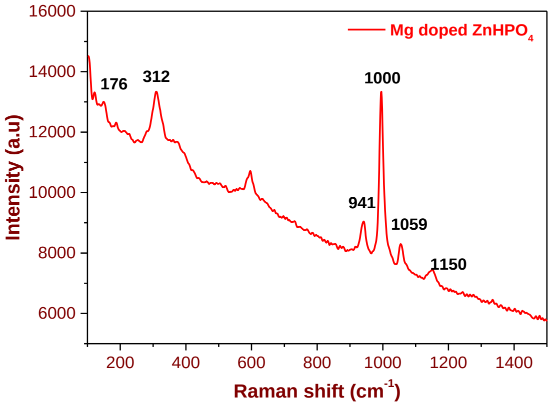

Fig. 2 Laser Raman spectrum of Mg doped $ZnHPO_4$

3.2 Thermal analysis of $MgZnHPO_4$ crystals

Thermogravimetric analysis is a technique to assess the stability of various substances. The Mg doped $ZnHPO_4$ of 16.05 mg sample was taken for the TG process. The sample was scanned at the rate of 20°C/minute in nitrogen atmosphere in the temperature range 30–700°C. Fig. 3 show the simultaneously recorded thermogravimetric analysis (TG) and differential thermogravimetric analysis (DTA) curve for Mg doped $ZnHPO_4$ sample. Thermograms were first analyzed to obtain information about the percentage mass loss at different temperatures and hence about the thermal stability and kinetics of dissociation of samples. From the thermograms, it is clear that the doped sample is thermally stable up to temperature of 81°C, which means that doped sample is more stable than pure one. In case of Mg doped $ZnHPO_4$, the whole process of decomposition undergoes in two steps. Table 2 gives detailed summary about the decomposition of $MgZnHPO_4.4H_2O$calculated weight losses. It is worth mentioning here that the temperature for the formation of stable product after decomposition in case of pure one is 312°C, whereas in case of doped one the stable product is formed at a temperature of 330°C. This means that the temperature for the formation of end product increases with magnesium substitution. Above result suggested that the calculation of percentage of weight loss for Mg doped $ZnHPO_4$ contain water, which they lose at different temperature ranges.

As seen from DTA curve in case of Mg doped $ZnHPO_4$ (Fig. 3) there is well marked endothermic and exothermic peak corresponding to each stage of dehydration and decomposition. 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. Table 3 gives the compiled summary of the data of DTA of Mg doped $ZnHPO_4$. DTA plot exhibits a smooth endotherm at 123 and 304°C. These values correspond to the thermal decomposition process in the ranges 82-234 and 234–330°C, respectively. The sharpness of endothermic peaks shows that the good degree of crystallinity and purity of the sample. The decomposition process agrees fairly well with Mg doped $ZnHPO_4$.

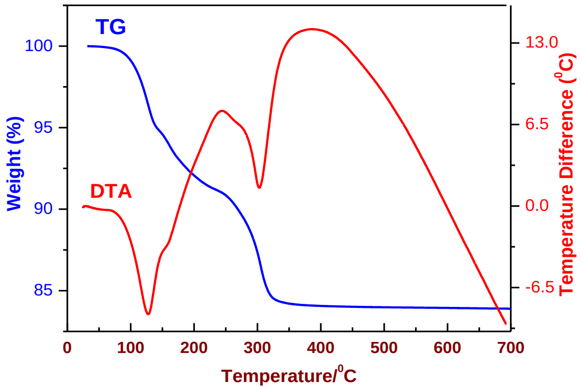

Fig 3 Thermogram showing simultaneous recording of TGA and DTA curves for Mg doped $ZnHPO_4$ crystal.

Table 2 Results of thermal decomposition for different temperature ranges with calculated weight loss in case of Mg doped $ZnHPO_4$.

Stage	**Temperature (°C)**	**Decomposition Steps**	**Weight loss (%)**
First	82-234	$Mg{:}ZnHPO_4.4H_2O \rightarrow MgZnHPO_4+4H_2O$	20
Second	234-330	$2MgZnHPO_4 \rightarrow 2MgZnO + P_2O_5 + H_2O_{(g)}$	13

Table 3 DTA data of Mg doped $ZnHPO_4$ crystal

Peak recorded	**Peak height**	**Nature**	**On set temperature**
123°C	-8.5	Endothermic	120°C
304°C	1.7	Exothermic	301°C

3.3 EDAX studies of Magnesium doped $ZnHPO_4$ crystals

In order to confirm the elemental composition of magnesium doped $ZnHPO_4$crystals, qualitative and quantitative elemental analysis were done on the application of EDAX. The spectrum obtained from EDAX analysis of Magnesium doped $ZnHPO_4$ is shown in Fig. 4. The EDAX spectrum connecting to Mg doped $ZnHPO_4$ shows peaks corresponding to all the major elements, that is, zinc, phosphorous and oxygen along with magnesium by suggesting that Mg^{2+} has entered into the lattice of $ZnHPO_4$ system. In magnesium doped$ZnHPO_4$, (Mg+Zn)/P ratio was estimated to be 1.85. The experimental calculated atomic and weight percentages of the individual elements are shown in table 4 respectively. The existence of water molecules in Mg doped $ZnHPO_4$ was further confirmed by thermo analytical observation.

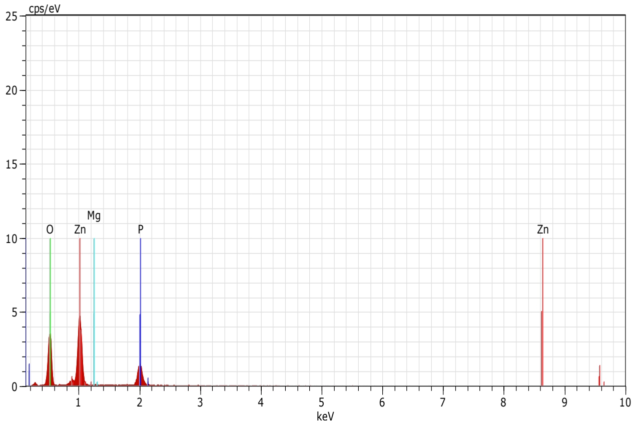

Fig 4 EDAX spectra showing the presence of major elements for magnesium doped $ZnHPO_4$.

Table 4 Experimental calculated composition obtained from energy dispersive X-ray analysis (EDAX) of various constituent elements present in case of magnesium doped $ZnHPO_4$.

Element	Weight %	Atomic %
Zn	48.23	20.48
P	12.32	11.05
Mg	0.02	0.03
O	39.43	68.44

3.4 Photoluminescence analysis

The Photoluminescence spectrum is shown in Figure 5. The luminescent emission of the Magnesium doped zinc hydrogen phosphate (MZHP) crystal is determined at room temperature. For the unirradiated MZHP crystal, the intensity pattern displays significantly high intensity band around ultra violet region at 304 nm. The emission spectrum shows the peaks particularly at 304nm, 376nm, 432nm and 467 nm when excited with 270 nm. Of these, the ultra violet emission at 304nm is the most intense of all emissions. In the PL spectra a UV emission peak centered at 304 nm and a broad peak in the visible emission region with higher wavelength of 300-350nm has been identified. The peak in the UV region corresponds to near band edge emission (NBE), because this peak is located near to the band gap energy (~4.08 eV), of $MgZnHPO_4$ at room temperature. The UV emission is attributed to the radiative recombination of a hole in the valence band with an electron in the conduction band. It is quite remarkable that ultra violet PL emission peak for the pure and doped sample was broad and asymmetric in shape and bears a shoulder on the lower energy side.

Using the photoluminescence spectrum band gap will be calculated using the formula.

$E_g = h\upsilon$

The curve can be observed for magnesium doped zinc hydrogen phosphate crystal at 307nm implying the band gap $E_g$is 4.086 eV.

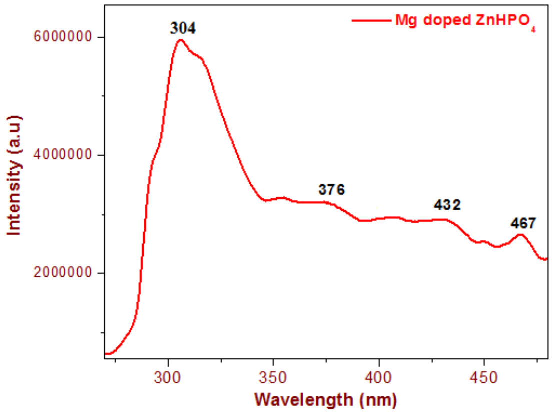

Fig 5 Photoluminescence spectrum of Magnesium doped ZHP crystal

4. Conclusion

Optical good quality single crystals of Magnesium doped zinc hydrogen phosphate have been grown by single diffusion method in silica gel medium at room temperature. Laser Raman spectroscopy analysis shows that there are different vibrational modes (Functional groups) present in the material. The TG–DTA analyses show that they possess high thermal stability. The thermal analysis reveals that there is 20% weight loss and crystal observed to decompose without melting. The qualitative and quantitative elemental analysis adopting the EDAX technique, confirms the presence of major elements present in the crystal. Photoluminescence spectra peaks can be obtained for magnesium doped zinc hydrogen phosphate crystal at 307nm implying the band gap $E_g$is 4.086 eV.

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