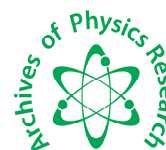




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Growth and characterization of α -hopeite single crystals in silica gel

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ABSTRACT

α -hopeite single crystals were grown for the first time by single diffusion gel growth technique in sodium metasilicate gel media. Structural characteristics of the grown crystals were investigated by powder X-ray diffraction analysis. Surface morphology and composition of materials were studied using scanning electron microscopy and energy dispersive analysis of X-rays. The presence of various functional groups in the grown crystals was identified by performing FTIR studies. Optical transmission study revealed the transparency of the crystal in the entire visible region. Differential thermal and thermo gravimetric analysis established the thermal stability of the α -hopeite crystal.

Keywords: Inorganic compound, optical material, Crystal growth, X-ray diffraction, diffusion.

INTRODUCTION

Recently chemists, physicists and material scientists have shown great interest in the development of crystal growth technology for the synthesis of new materials which plays an important role in pharmaceutical and chemical industries. Nowadays extensive studies have been carried out for the preparation and characterization of inorganic materials owing to their unique properties and intriguing applications in many areas. Specifically 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 [1]. α -hopeite (Zn₃(PO₄)₂·4H₂O) belongs to a family of inorganic phosphate. α -hopeite has gathered interest in recent years due to its industrial applications. Zinc phosphate is frequently used as pigments for coating products (iron and steel alloys), which possess good anticorrosive properties [2]. Due to its economy, speed of operation,

adhesion, lubricative properties and ability to withstand excellent corrosion resistance, zinc phosphate coatings have found wide spread application not only in electric motors and transformers, but also in the automotive industry [3]. And it has been extensively used as a better substitute for toxic and high cost cadmium coatings [4]. This environmentally friendly and anti-corrosive α -hopeite rescues our country from tremendous economic loss besides posing a serious threat to the national resources of a country [5].

Zinc phosphate coating on steel consists mainly of crystalline α -hopeite [6, 7]. In nature, zinc phosphate tetrahydrate ($\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$) exists in two structures, orthorhombic hopeite and parahopeite, its triclinic polymorph [8]. The α -form of hopeite occurs in nature [9]. There is a need for the growth of α -hopeite as a standard material for its application and industrial research or development. From the literature survey it has been concluded that the growth technology plays a principal role for the synthesis of α -hopeite crystal [10]. Gel growth overcomes these difficulties due to its simplicity and convenience, as it involves diffusion of two reagents in gel at a reasonably slow and controlled rate, it yield sparingly soluble reaction product. By preventing convection currents and remaining chemically inert, the gel medium on its own provides a soft three dimensional network in which the crystal nuclei are delicately held in the position of their formations. Moreover, since the crystals grow at near ambient temperature, the presence of minimum equilibrium defects are ensured [11, 12]. In the present work, α -hopeite crystal, $\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ (zinc phosphate tetra hydrate) were grown for the first time by single diffusion gel growth technique in sodium metasilicate gel media.

MATERIALS AND METHODS

Double distilled water, analytical grade Zinc nitrate $\text{Zn}(\text{NO}_3)_2$, orthophosphoric acid H_3PO_4 and sodium metasilicate Na_2SiO_3 were used for the growth of α -hopeite crystal. Inter diffusion technique was employed to grow single crystals in a gel medium. The growth experiment was carried out in test tubes using sodium metasilicate solution of density 1.035 g/cm^3 . 1M of orthophosphoric acid solution was added to the virgin gel solutions to form gels of pH values varying between 4 to 6. The gel was kept in undisturbed condition for 72 hrs. The inter diffusion process takes place by placing an aqueous solution of zinc nitrate $\text{Zn}(\text{NO}_3)_2$ of 1 M concentration on top of sodium metasilicate gel phase containing orthophosphoric acid. The controlled reaction between zinc nitrate and orthophosphoric acid takes place in the gel medium by single diffusion process. As zinc nitrate diffuses through the gel, a white thin film appears just below the gel surface. This sample was kept at 40°C in a constant temperature bath. A thick mass of polycrystalline material was formed within a day. Below the polycrystalline mass, tiny transparent X shaped crystals of dimension $8 \times 2 \times 2 \text{ mm}^3$ were grown within a period of 3 to 4 days.

After a period of two weeks, single crystals of α -hopeite of appreciable size appeared within the gel medium at certain distance below the polycrystalline precipitation zone. The size of the crystals was found to be varying depending on the factors like molarity, density of gel, pH value and gel age. Several experiments were performed by varying the growth parameters like gel age, gel pH, gel density, and molarity of lower and upper reactants, in order to establish the optimum conditions conducive for the growth of α -hopeite in the form of single crystals in a size suitable for scientific investigations. Table 1 depicts the optimum conditions for the growth of good

quality single crystals. The obtained crystal was found to be insoluble both in water and organic solvents as shown in figure 1.



Fig. 1 Photograph of the grown α - hopeite crystal

Table 1 Optimum conditions for the growth of α -hopeite crystal

Parameters	Optimum conditions
Density of Na_2SiO_3	1.035 g/cm ³
Inner reactant	10 ml H_3PO_4 with 1 M
Outer reactant	10 ml $\text{Zn}(\text{NO}_3)_2$ with 1 M
Temperature	30 – 40 degree
pH	4 – 5
Gel age	72hrs
Period of growth	2 weeks
Shape	X shape

RESULTS AND DISCUSSION

3.1. X-ray diffraction analysis: Single crystal X-ray diffraction study confirms that the crystal belongs to orthorhombic systems with space group $P2_12_12_1$. Lattice parameters of α -hopeite crystals were measured as $a = 5.0228\text{\AA}$, $b = 10.5906\text{\AA}$, $c = 18.3910\text{\AA}$, $\alpha = \beta = \gamma = 90^\circ$, cell volume $V = 971.9750\text{\AA}^3$. Powder X-ray diffraction spectrum of the grown crystal was also recorded on a REICH SIEFERT X-ray diffraction instrument using $\text{CuK}\alpha$ (1.540 \AA) radiation. The sample was scanned for a 2θ range 10-70° at a scan rate of 1°/min and the obtained diffraction pattern was indexed as shown in figure 2. Sharp peak intensities in the X-ray diffraction spectrum indicate its high crystallinity. These calculated (hkl) planes satisfy the general reflection condition of the space group observed from the structure determination of the

crystal. The unit cell parameters calculated from single crystal and powder XRD analysis agree well with that of the reported values [3, 13].

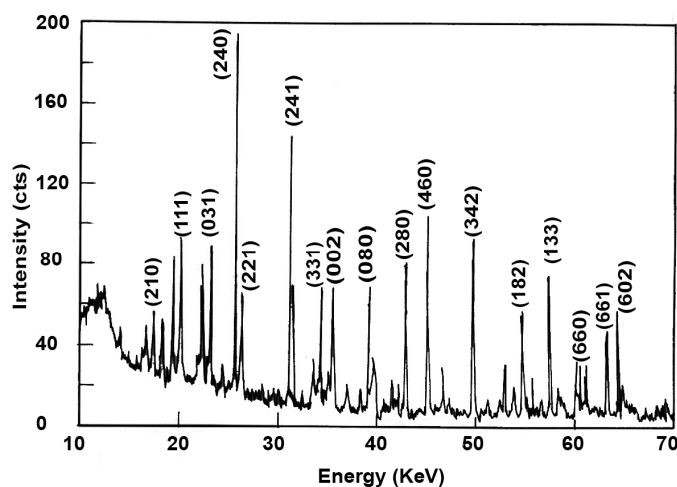


Fig. 2 Powder X-ray diffraction pattern of the grown α -hopeite crystal

3.2 FTIR analysis: Well grown crystals free from visible defects were selected and analyzed by FTIR spectroscopy. FTIR spectral analysis of the grown crystal was recorded in the middle IR range between 400 to 4000 cm^{-1} as shown in figure 3. The broad absorption peak between 3506-3400 cm^{-1} is due to O-H stretching vibration. A peak at 1645 cm^{-1} is due to water bonding. The sharp peak at 1107 cm^{-1} is assigned to stretching mode of P-O and plane bending mode of $(\text{PO}_4)^{3-}$. The PO_4^{2-} stretching mode is positioned at 1009 cm^{-1} . The stretching mode of P-O-H is observed at 948 cm^{-1} . Sharp peaks at 635 to 579 cm^{-1} are also assigned to symmetric bending mode of $(\text{PO}_4)^{3-}$. These peaks of phosphate show the incorporation of orthophosphoric acid in the lattice of the grown crystals.

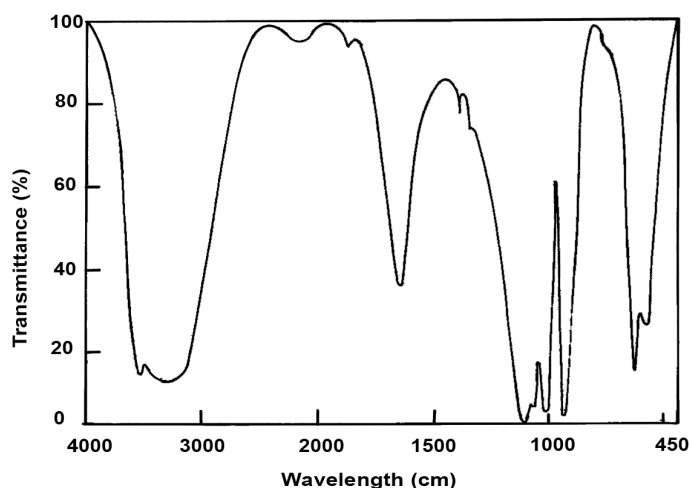


Fig. 3 FTIR spectrum of the grown α -hopeite crystal

3.3 DRS UV Spectral studies: Optical transmittance spectral analysis of α -hopeite crystal was carried out between 200-900 nm. From the spectrum shown in figure 4, the transmittance was

found to be very high in the entire visible region and it shows minimum absorption in the UV region. This is one of the most desirable properties of the crystal for the fabrication of potential devices [14]. The UV cut off wavelength of the crystal was found to be 230 nm with nearly 75 % transmittance.

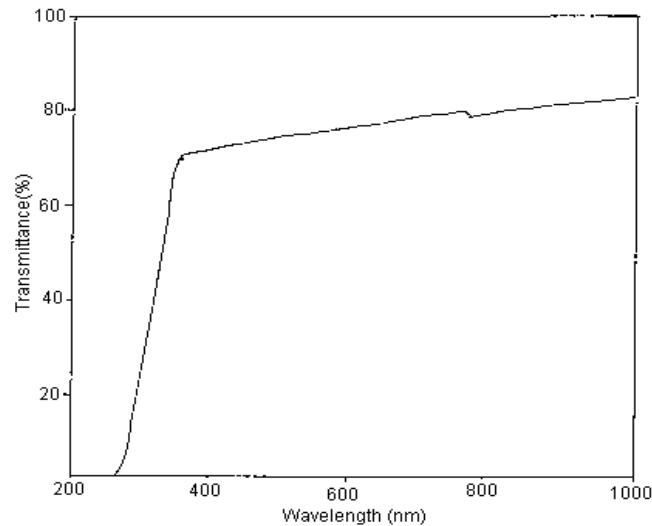


Fig. 4 UV spectrum of the grown α - hopeite crystal

3.4 Surface studies: SEM was carried out to visualize step growth patterns on the b-cut plate of α -hopeite single crystals by using the instrument JSM A40-A [15]. Cleaved plates, without any metallization was immediately loaded into the SEM for investigation. Charging effect was avoided by operating the SEM at very low magnification (25 x), low accelerating voltage 20 kV and low probe current (3 pA) in order to observe the domains in the static condition. SEM photograph of the α -hopeite crystal as shown in figures 5a and 5b gives the formation of the faces of the crystals. The presence of micro inclusion appears on the overlapped step pattern as shown in figure 5a. From figure 5b, it is observed that the growth surface shows screw dislocation which confirms the rectangular spiral growth-steps on the surface of the α -hopeite crystal.

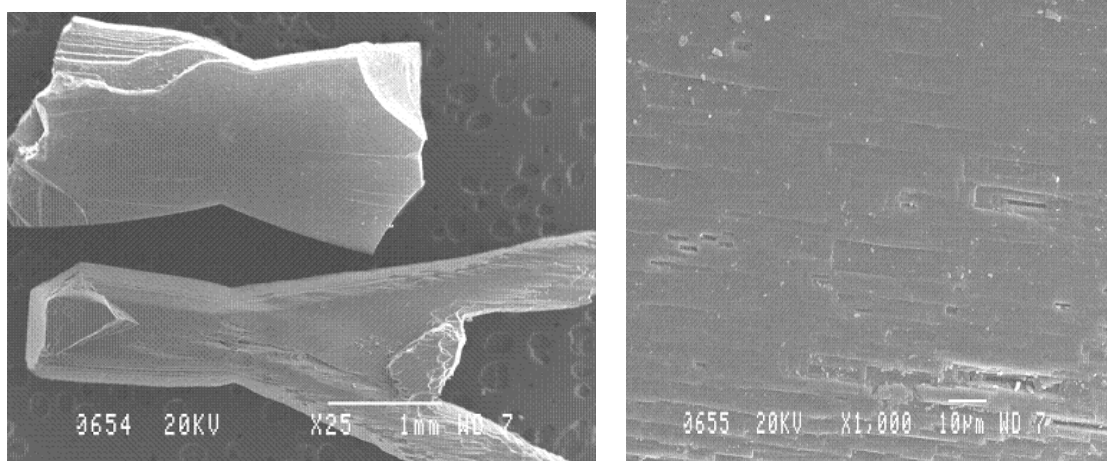


Fig. 5a SEM image at 1mm & 10 μ m magnification of the grown α - hopeite crystal

3.5 Energy Dispersive X-ray analysis: In order to verify the starting composition and the consequent reaction through diffusion, as controlled by the silica gel which yield crystals of the expected composition and these crystals were examined by EDX. Figure 6 shows counts per second against energy of the EDX spectrum of α -hopeite crystals. Elemental percentages for phosphorous is 56.75% and that for zinc is 43.25%. These peaks show the presence of phosphates and zinc in the grown crystals. It also indicate the absence of impurities in the grown α -hopeite crystals.

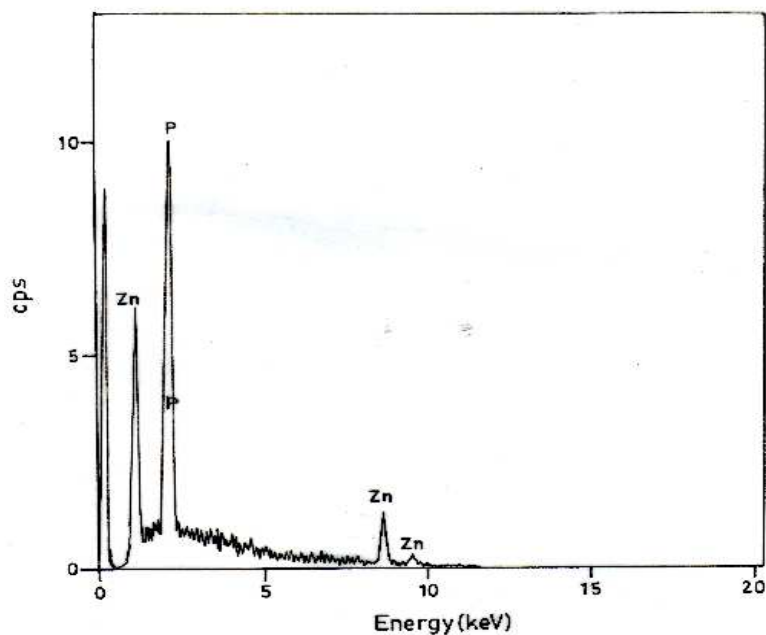


Fig. 6 EDAX spectrum of the grown α -hopeite crystal

3.6 Thermal analysis: Thermo gravimetric analysis of α -hopeite was carried out for sample weight of 4 mg between 50 °C to 800 °C at the rate of 20 °C /min in nitrogen atmosphere. The thermo gravimetric curves show that α -hopeite crystal loses water in two well defined steps. Heating of α -hopeite crystal to 142 °C was accompanied by the removal of two water molecules indicating that $Zn_3(PO_4)_2 \cdot 2H_2O$ is established at this temperature. The next stage of dehydration gave an anhydrous $Zn_3(PO_4)_2$ phase at 327 °C. Similarly DTA curve gives two well defined transitions at 140 °C and 327 °C, due to thermal dehydration of α -hopeite crystal. The DTA curve also shows an endothermic peak at 193 °C which corresponds to the first step decomposition of the TG curve in which loss of two water molecules takes place. The second endothermic peak at 297 °C corresponds to the second step decomposition. The sharpness of the thermogram is also illustrative of the crystal purity without the association of any impurity. The loss of water corresponds to mass loss of about 16 % resulting in 84 % of residue left at the final stage. [3].

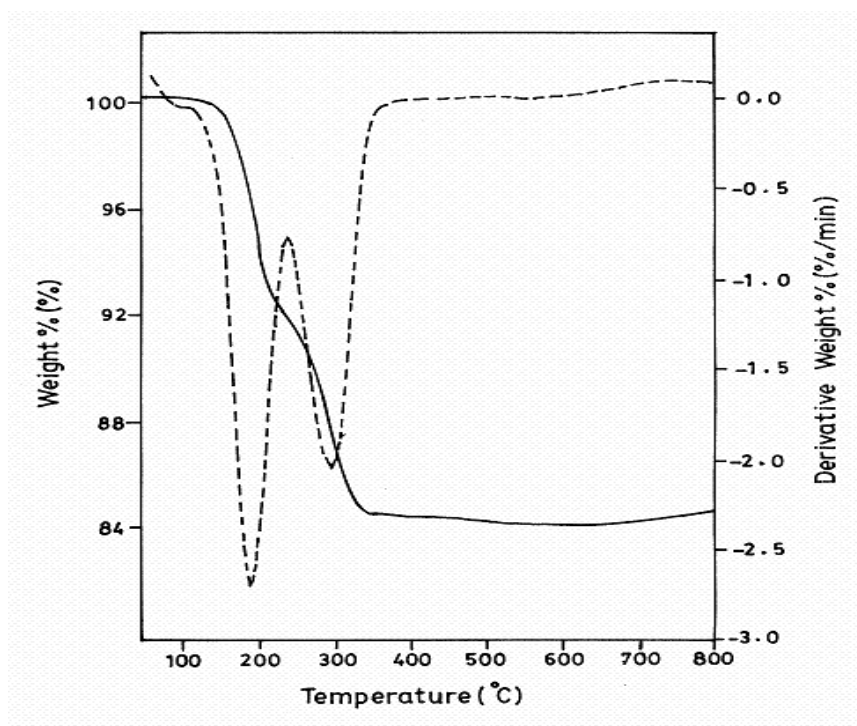


Fig. 7 TG/DTA spectrum of the grown α -hopeite crystal

CONCLUSION

Single crystals of α -hopeite (i.e., zinc phosphate tetrahydrate) were grown by the gel growth technique. Single crystal X-ray analysis reveals that the crystal belongs to orthorhombic system, which is in good agreement with the reported values. Crystal diffraction pattern was also observed using powder X-ray diffraction analysis. The presence of phosphate functional group in the grown crystals was identified by performing FTIR studies. The optical transmittance study reveals high transparency with a UV cut off at 230 nm. Thermo gravimetric and differential thermal analysis shows that the crystal is stable up to 130 °C. The SEM image of the crystal confirms the step like growth pattern of the crystals. The presence of zinc and phosphate in the grown crystal was confirmed using EDX spectral analysis.

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