# Chapter VIII

Growth and Characterization of Struvite Family Crystals

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8.1 Introduction

This chapter deals with the growth and characterization of two struvite family crystals, namely, Potassium Magnesium Phosphate Hexahydrate (PMPH) or struvite-K and Sodium Magnesium Phosphate Heptahydrate (SMPH) or struvite-Na. Both struvite-K and struvite-Na crystals were grown by single diffusion gel growth technique in silica hydro gel medium. The grown crystals were characterized by powder XRD, FT-IR, Thermal analysis and dielectric study. The kinetic parameters as well as thermodynamic parameters were calculated by applying well known formulae. The results are discussed.

8.2 Struvite Family Crystals

Struvite type compound can be represented by $X^+Y^{2+}PO_4.nH_2O$, where $n = 6$ to $8$. It contains one monovalent cation $X^+$ and one divalent cation $Y^{2+}$. Among phosphate containing bio-minerals, struvite has attracted considerable attention, because of its common occurrence in a wide variety of environments. Some of the struvite type compounds and their structural relationships have been reported by Dickens and Brown [1].

Struvite analog $X^+Y^{2+}PO_4.nH_2O$ compounds with $X = \text{Rb}$ and Tl and $Y = \text{Mg}$ were obtained by means of the gelatine-gel diffusion technique by Weil [2]. Moreover, struvite type compounds $M[Mg(H_2O)_6](XO_4)$, where $M = \text{Rb}$, Tl and $X = \text{P}$, As were reported by the same author [3]. Crystal chemistry of struvite analog $X^+Y^{2+}PO_4.6H_2O$ compounds with $X = \text{K}$, Rb, Cs, Tl, NH$_4$ and $Y = \text{Mg}$ were reported by Banks et al [4]. Erdmann and Kothner [5] prepared rubidium magnesium phosphate hexahydrated {RbMgPO$_4$.6H$_2$O}, by mixing solutions of magnesium sulphate and of
rubidium phosphate. Struvite analogs with $Y^{2+} = $ Co and Ni were also reported by various researchers [6-10].

Recently, Yang and Sun [11] reported the formation of new struvite type phosphate compound hazenite {KNaMg\(_2\)(PO\(_4\))\(_2\).14H\(_2\)O}, which contains both K and Na as univalent cations. Recently, Yang et al [12] found hazenite mineral on completely dried-out or decomposed green algae (cyanobacteria) on porous calcium-carbonate (mainly calcite and aragonite) substrates on the shoreline in Mono Lake, California. There are many structural similarities between hazenite and struvite-type materials, which have been of great interest because of their broad and important biological, agricultural, and industrial implications [2, 4, 9, 10, 13-16]. Takagi et al [17] synthesized struvite-type compound Mg\(_2\)KH(PO\(_4\))\(_2\).15H\(_2\)O using different combinations of magnesium salts, concentrations (0.05-0.20 M), temperature (278-298 K) and pH (6.5-7.5).

Very few attempts were made to grow struvite-K and struvite-Na crystals in laboratory conditions. Earlier only needle type struvite-K crystals were grown by gel diffusion technique by Banks et al [4].

8.2.1 Struvite-K Crystals

Potassium magnesium phosphate hexahydrate {KMgPO\(_4\).6H\(_2\)O}, also known as struvite-K, is new inorganic phosphate mineral approved by the Commission on New Minerals and Mineral Names, International Mineralogical Association (CNMMN-IMA) in the year 2003 [18]. Struvite-K is the natural potassium equivalent to struvite \{NH\(_4\)MgPO\(_4\).6H\(_2\)O\}, since the crystals of struvite-K are rich in potassium and similar to struvite.
Struvite-K is a well-defined potassium analogue of struvite; where monovalent cation K\(^+\) replaces the NH\(_4\)\(^+\) ammonium cations. This ion replacement is possible, as the ionic radii of K\(^+\) (1.33 Å) and NH\(_4\)\(^+\) (1.43 Å) are almost identical [19]. Earlier, both the struvite and struvite-K were reported as iso-structural compounds [20,21].

Struvite-K was identified as a mineral at two different locations [22]: (i) at the famous sulphosalt locality of Lengenbach in Binntal, Switzerland, in a dolomitic rock of Triassic age, (ii) at Rossblei, Austria, in an abandoned galena mine. The mineral occurs as pseudomorphous aggregates of dirty white colour reaching up to several millimeter in size. The aggregates represent close intergrowths of fine-grained struvite-K and newberyite. Moreover, struvite-K was also found as urinary calculi in the animals like dogs [23], goats [24] and buffalo calves [25] fed with the high-level cottonseed meal diet. Recently, Zheng-Shun Wen et al [26] checked the effect of dietary cottonseed meal on the occurrence of urolithiasis in Chinese merino sheep and concluded that addition of high level cottonseed meal increased remarkably the levels of blood magnesium, potassium, phosphorus which further promoted the formation of struvite-K. Tay et al [27] reported that nonporous struvite-K can be used in teeth root-end filling material as the primary ceramicrete binder phase.

8.2.2 Struvite-Na Crystals

Sodium magnesium phosphate heptahydrate (NaMgPO\(_4\).7H\(_2\)O), also known as struvite-Na is the sodium analog to struvite in spite of the excess of water molecule. In struvite-Na, the monovalent Na\(^+\) cations replace the NH\(_4\)\(^+\) (ammonium) cations. Previously the struvite structure was thought to be
unable to accommodate univalent cations smaller than K⁺ ion (1.33 Å). But a sodium analog of struvite was first synthesized by Mathew et al [28]. In fact, the natural formation of the struvite analog hazenite {KNaMg₂(PO₄)₂.14H₂O} from Mono Lake, California, and synthesis of struvite-Na invalidates this hypothesis. One explanation for this is that the smaller ionic size of Na⁺ in struvite-Na is effectively compensated by the Na⁺–H₂O pair.

Alkemper and Fuess [29] synthesized sodium magnesium phosphate crystals with orthorhombic structure by heating an equimolar mixture of NaPO₃ and MgO to 1273 K, cooling to 873 K (5 K / min) and holding for 10 h. Whereas, Mathew et al [28] synthesized MgNaPO₄.7H₂O crystals with tetragonal structure from a batch initially set up for the preparation of Mg₃(PO₄)₂.8H₂O by following the procedure of Kanazawa et al [30], where the crystals of Mg₃(PO₄)₂.22H₂O were allowed to stand in water and the pH was adjusted to 9.0 by the addition of Na₂CO₃.

### 8.3 Growth of Struvite Family Crystals

The gel growth technique and its advantages are described in great detail in chapter III. The single diffusion gel growth technique was used to grow both the struvite-K as well as struvite-Na crystals. To grow these crystals almost same steps – such as (i) preparation of sodium meta-silicate (SMS) stock solution, (ii) preparation of SMS solution with definite specific gravity (SG), (iii) preparation of gel, and (iv) the pouring of supernatant solutions (SS) were followed as precisely described in section 5.2 of chapter V and hence repetitions are avoided in this chapter. The only change was diverse selection of reactant - I during the preparation of gel. Reactant – I, i.e. ADP was replaced by potassium dihydrogen phosphate (KDP) – {KH₂PO₄} and sodium
dihydrogen orthophosphate (SDO) – \{\text{NaH}_2\text{PO}_4.2\text{H}_2\text{O}\} for the growth of struvite-K and struvite-Na, respectively. Since the growth conditions, for instance, the SG of SMS solution, the gel pH, the concentrations of reactants, etc., play important role in the growth of crystals; in the present study, different growth parameters were used to grow struvite-K and struvite-Na crystals. Table 8.1 and 8.2 show the growth parameters for struvite-K and struvite-Na crystals, respectively.

### 8.3.1 Growth Parameters for Struvite-K

**Table : 8.1 : Different Growth Parameters Used to Grow Struvite-K Crystals**

<table>
<thead>
<tr>
<th>Set</th>
<th>Specific Gravity of SMS</th>
<th>Concentration of KDP (Reactant I) (M)</th>
<th>pH value of the Gel</th>
<th>Concentration of supernatant solution of magnesium acetate (Reactant II) (M)</th>
<th>Liesegang Rings observed having pH values</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.04</td>
<td>1.00</td>
<td>6.0 to 8.0</td>
<td>1.00</td>
<td>8.0</td>
</tr>
<tr>
<td>2</td>
<td>1.04</td>
<td>1.50</td>
<td>6.0 to 8.0</td>
<td>1.50</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>1.05</td>
<td>0.25</td>
<td>6.0 to 8.5</td>
<td>1.00</td>
<td>&gt; 7.0</td>
</tr>
<tr>
<td>4</td>
<td>1.05</td>
<td>0.50</td>
<td>6.0 to 7.5</td>
<td>1.00</td>
<td>&gt; 7.5</td>
</tr>
<tr>
<td>5</td>
<td>1.05</td>
<td>1.00</td>
<td>5.5 to 8.5</td>
<td>1.00</td>
<td>&gt; 8.0</td>
</tr>
<tr>
<td>6</td>
<td>1.05</td>
<td>1.50</td>
<td>6.0 to 8.0</td>
<td>1.00</td>
<td>&gt; 7.5</td>
</tr>
<tr>
<td>7</td>
<td>1.05</td>
<td>0.50</td>
<td>6.0 to 9.0</td>
<td>0.50</td>
<td>-</td>
</tr>
<tr>
<td>8</td>
<td>1.06</td>
<td>0.50</td>
<td>6.0 to 8.5</td>
<td>1.00</td>
<td>&gt; 8.0</td>
</tr>
<tr>
<td>9</td>
<td>1.06</td>
<td>1.00</td>
<td>6.0 to 8.0</td>
<td>1.00</td>
<td>8.0</td>
</tr>
<tr>
<td>10</td>
<td>1.07</td>
<td>1.50</td>
<td>5.8 to 7.0</td>
<td>1.00</td>
<td>-</td>
</tr>
</tbody>
</table>

The following reaction is expected to occur in the gel between the two reactants, namely, KDP as a reactant - I present in the gel and magnesium acetate as a reactant - II present in the SS.

\[
\text{KH}_2\text{PO}_4 + \text{Mg(CH}_3\text{COO)}_2.4\text{H}_2\text{O} + 2\text{H}_2\text{O} \rightarrow \text{KMgPO}_4.6\text{H}_2\text{O} + 2\text{CH}_3\text{COOH} \quad (8.1)
\]

Reactant - I + Reactant - II \rightarrow Struvite-K
8.3.2 Growth Parameters for Struvite-Na

Table 8.2: Different Growth Parameters Used to Grow Struvite-Na Crystals

<table>
<thead>
<tr>
<th>Set</th>
<th>Specific Gravity of SMS</th>
<th>Concentration of SDO (Reactant I) (M)</th>
<th>pH value of the Gel</th>
<th>Concentration of supernatant solution of magnesium acetate (Reactant II) (M)</th>
<th>Liesegang Rings observed having pH values</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.04</td>
<td>1.00</td>
<td>5.5 to 8.0</td>
<td>1.00</td>
<td>8.0</td>
</tr>
<tr>
<td>2</td>
<td>1.04</td>
<td>1.50</td>
<td>5.5 to 8.0</td>
<td>1.50</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>1.05</td>
<td>0.50</td>
<td>6.0 to 8.0</td>
<td>0.50</td>
<td>&gt; 7.5</td>
</tr>
<tr>
<td>4</td>
<td>1.06</td>
<td>0.75</td>
<td>6.0 to 8.0</td>
<td>0.75</td>
<td>&gt; 6.8</td>
</tr>
<tr>
<td>5</td>
<td>1.06</td>
<td>1.00</td>
<td>6.0 to 8.5</td>
<td>1.00</td>
<td>&gt; 7.0</td>
</tr>
<tr>
<td>6</td>
<td>1.06</td>
<td>1.50</td>
<td>6.0 to 7.5</td>
<td>1.00</td>
<td>&gt; 7.0</td>
</tr>
</tbody>
</table>

The following reaction is expected to occur in the gel between the two reactants, namely, SDO as a reactant - I present in the gel and magnesium acetate as a reactant - II present in the SS.

\[
\text{NaH}_2\text{PO}_4.2\text{H}_2\text{O} + \text{Mg(CH}_3\text{COO)}_2.4\text{H}_2\text{O} + 2\text{H}_2\text{O} \rightarrow \text{NaMgPO}_4.7\text{H}_2\text{O} + 2\text{CH}_3\text{COOH} \quad (8.2)
\]

Reactant - I + Reactant - II \rightarrow Struvite-Na

As a result of reactions (8.1) and (8.2) struvite-K and struvite-Na crystals were grown in the gel media of respective test tubes. It was found that the growth of these struvite type crystals completed within 12 days after the pouring of supernatant solution. It was also observed that both the struvite-K and struvite-Na types of crystals grew very rapidly near the gel - liquid interface, whereas they grew slowly at substantial depths from the gel - liquid interface which might be due to decreasing nature of concentration gradients with depth. The grown crystals were carefully removed from the gel medium, quickly rinsed in distilled water and then dried on a filter paper. The grown crystals were kept in airtight bottles and used for further investigation.
8.3.3 Morphology of Gel Grown Struvite-K Crystals

It was noticed that morphology of gel grown struvite-K crystals was dependent on growth parameters. By changing the growth parameters, struvite-K crystals with different morphologies like prismatic type, star type, rectangular platelet type, elongated platelet type, coffin shaped and dendritic type were grown by single diffusion gel growth technique.

![Figure 8.1 Struvite-K Crystals Grown in Gel Medium for 1.05 SG of SMS, 0.5 M KDP and SS of 0.5 M Magnesium Acetate with different pH values as (a) 6.5 pH, (b) 7.0 pH, (c) 7.5 pH, (d) 8.0 pH, (e) 8.5 pH and (f) 9.0 pH](image)

It was observed that pH values of the gel played an important role in the growth of the struvite-K crystals. Figure 8.1 shows the photographs of the struvite-K crystals grown in the gel medium for the growth parameters as 1.05 SG of SMS solution, 0.5 M KDP solution as reactant - I and SS of 0.5 M magnesium acetate with different pH values. As shown in figure 8.1 (a) transparent prismatic type struvite-K crystals are observed for 6.5 pH. Here, it is noticed that number density and the apparent size of the grown crystals decreases, whereas transparency increases with increasing depth of gel column. For 7.0 pH of the gel, the number density of the grown prismatic struvite-K crystals are decreased, whereas the apparent crystal size increases as shown in figure 8.1 (b). For higher values of the gel pH, the settled gels were found denser and as a result comparatively poor crystals were grown.
The dense gels have small pore sizes and do not readily facilitate the movements of supernatant solution ions for the reaction and also the dense gel put constraints on the growth of crystals.

It was also observed that the number density of the grown crystals increased with the increasing concentrations of either the first reactant, i.e. KDP or the second reactant magnesium acetate in SS. For instance, figure 8.2 shows the photographs of the test tubes with fixed values of 1.05 SG and 7.0 pH of gel with diverse concentration of both the reactants. Moreover, as shown in figure 8.2 (d), for certain higher concentrations of reactants star type bunch of poly-crystals are found to grow in the gel instead of prismatic single crystals.
The variation in the specific gravity of the gel also played important role in the growth phenomenon of the struvite-K crystals. For example figure 8.3 shows the photographs of the test tubes with the fixed growth parameters as 1 M concentration of each of the reactants and 7.0 pH of gel but the SG of the gel was varied. As shown in figure 8.3 (b) and (c), very few star type poly-crystals are noticed in the case of 1.04 and 1.06 SG of gel, whereas the maximum number of single crystals were grown in the case of 1.05 SG of gel as seen in figure 8.3 (a).

As shown in figure 8.4 (a), the dendritic type growth is observed for the SMS solution of SG 1.04, 1.5 M KDP solution, 1.5 M magnesium acetate SS and 6 pH value of the gel, which might be due to the higher concentration of the reactants. But when gel pH was increased from 6.0 to 6.5, few poly-crystals were observed instead of dendritic crystals as can be seen in figure 8.4 (b).

Prismatic type struvite-K crystals with different diaphaneity and diverse apparent size ranging from 1 to 8 mm were found in all the sets (set number - 3 to 7) with 1.05 SG of SMS solutions with the pH range of 6.5 to 8.0. However, the good quality transparent prismatic type struvite-K crystals with...
optimum apparent size were observed only for the growth parameters as SMS of SG 1.05, 0.5 M KDP, 0.5 M SS with 6.5 pH value of the gel. It was remarkably noticed that as the pH value of the gel increased, the transparency of the grown crystals decreased. Moreover, transparent prismatic crystals were also noticed in the gel column at higher depth from the gel liquid interface. Figure 8.5 (a) and (b) shows transparent and opaque prismatic type struvite crystals, respectively. Comparatively large, opaque, prismatic type crystals having apparent size of 5 to 9 mm were observed for the growth parameters as 1.06 SG of SMS, 1 M KDP, 1 M SS and 7.5 pH value of the gel.

As mentioned earlier, pH values of the gel played an important role in the growth morphology of the crystals, for example, with the growth parameters having 1.05 SG of SMS solution, 0.25 M KDP and 1 M SS, the rectangular platelet type \{figure 8.5 (c)\} as well as coffin shaped crystals \{figure 8.5 (d)\} were observed for 6.0 pH, the star type crystals were observed for 6.5 pH and prismatic type crystals were observed for 7.0 and 7.5 pH.

8.3.4 Morphology of Gel Grown Struvite-Na Crystals

Struvite-Na crystals were grown by changing different growth parameters as mentioned in table 8.2. Figure 8.6 shows the photographs of Struvite-Na crystals grown in the gel medium.

![Figure: 8.6 Struvite-Na Crystals Grown in Gel Medium for growth conditions as](image)
Crystals with different morphologies like prismatic type, star type and dendritic type were grown in the gel. More or less, most of the findings for the growth of struvite-Na crystals were identical to those obtained for struvite and struvite-K crystals, and hence reported briefly to avoid repetitions.

![Figure 8.7 Prismatic Type Struvite-Na Crystals Grown with the Conditions as 1.05 SG of SMS, 0.5 M SDO, 0.5 M SS and pH Value of Gel as (a) 6.0 pH, (b) 6.5 pH, (c) 7.0 pH and (d) 7.5 pH](image)

Crystallization of struvite-Na was found to be possible within the range of 6 to 7.5 pH of gel, whereas crystallization was not obtained below 6 pH and Liesegang rings were obtained along with few crystals above 7 pH of the gel. The grown struvite-Na crystals had transparent, translucent and opaque diaphaneity, depending upon the location and the growth conditions. As illustrated in figure 8.7, prismatic type struvite-Na crystals with different diaphaneity and diverse apparent size ranging from 1 to 5 mm were found in the cases with 1.05 SG of SMS solutions within the pH range of 6.0 to 7.5. It was noticed that transparency of the grown crystals gradually decreased with the increasing pH value of the gel. Moreover, good quality transparent prismatic crystals were noticed at higher depth from the gel - liquid interface as shown in figure 8.8.

![Figure 8.8 Prismatic Type Struvite-Na Crystals](image)
As shown in figure 8.6 (c), star type poly-crystals were noticed in the cases of 1.04 and 1.06 SG of gel, whereas the maximum number of single crystals was grown in the case of 1.05 SG of gel. Star type clustered patterns of crystals were developed as a result of diffusion of highly concentrated nutrients near the gel-liquid interface.

### 8.3.5 Formation of Liesegang Rings

The Liesegang rings are typical periodic precipitation pattern of rings or bands formed during diffusion process of chemical reactants in gel. A brief introduction including the formation, types and the parameters affecting the development of Liesegang rings are previously discussed in section 3.11 of the chapter III.

The Liesegang rings were observed for 7.0 and higher pH values of the gel in case of struvite-K crystal growth. Such patterns arise from the interplay between the reaction kinetics and the diffusion of chemical species. Table 8.1 demonstrates the cases for which Liesegang rings are observed. Figure 8.9 (a to c) shows the formation of Liesegang rings in the test tubes with the growth parameters as 1.05 SG of SMS solution, 0.25 M KDP, 1.0 M magnesium acetate for 7.0 pH, 7.5 pH and 8.0 pH values of the gel, respectively. It was observed that as the pH of the gel increased, the number of Liesegang rings increased. The spacing between the Liesegang rings in the gel column increased with the depth. Moreover, the thickness of the Liesegang rings also increased with the depth. Joseph and Joshi [31] have discussed the effect of various parameters on the formation of Liesegang rings during the growth of calcium hydrogen phosphate dihydrate crystals. The crystals in the Liesegang rings are of the order of micrometer size. It is clear from the figure 8.9 (a) that
struvite-K crystals were grown with prismatic morphology having apparent length of 3 to 5 mm; and they also formed a ring structure under the last Liesegang ring.

Figure : 8.9 Formation of Liesegang Rings in the experiments of Struvite-K with growth parameters : 1.05 SG of SMS, 0.25 M KDP, 1.0 M SS and Gel pH as (a) 7.0 pH, (b) 7.5 pH and (c) 8.0 pH

The Liesegang rings were also observed for 6.8 and higher pH values of the gel for the experiments of struvite-Na crystal growth. Table 8.2 illustrates the cases for which Liesegang rings were observed. Figure 8.10 (a to c) shows the formation of distinct thick Liesegang rings at the top of the gel column near the gel-liquid interface in the test tube with the growth parameters as 1.06 SG of SMS solution, 1.0 M SDO, 1.0 M SS for 7.0 pH, 7.5 pH and 8.0 pH
values of the gel, respectively. Struvite-Na crystals with star as well as prismatic morphology were also observed along with Liesegang rings.

8.4 Powder XRD study

A detailed description of the powder XRD is already mentioned in the section 4.2 of Chapter-IV. The powder XRD study of grown struvite family crystals was carried out to confirm the crystalline material as well as to verify the structure. It was found that both of the struvite analogues under investigation, i.e., struvite-K and struvite-Na, exhibited orthorhombic crystal structure similar to struvite crystal structure.

8.4.1 Powder XRD of Struvite-K

Figure 8.11 exhibits the powder XRD pattern of struvite-K crystals. The crystal structure of struvite-K was found to be orthorhombic with unit cell parameters as, \(a = 6.893 \text{ Å}, b = 6.141 \text{ Å}, c = 11.222 \text{ Å}\) and \(\alpha = \beta = \gamma = 90^\circ\). The values are closely matching with the reported values by Mathew and Schroeder [20], and recently reported values by Graeser et al [22].

![Figure : 8.11 Powder XRD Pattern of Struvite-K Crystals](image)
The struvite-K crystal structure consists of two structural units (functional groups), namely, (i) PO$_4$ tetrahedron, and (ii) Mg.6H$_2$O octahedron. Figure 8.12 shows the structural units of struvite-K. Mg$^{2+}$ cations are all coordinated octahedrally by six H$_2$O molecules whose H atoms are strongly bonded to oxygen atoms in (PO$_4$)$_3^{-}$ groups. Figure 8.13 demonstrates the crystal structure of struvite-K as explained by Graeser et al [22].
8.4.2 Powder XRD of Struvite-Na

Crystal structure of KNaMg$_2$(PO$_4$)$_2$.14H$_2$O has been recently reported. However, no major work on struvite-Na is reported. Figure 8.14 exhibits the powder XRD pattern of struvite-Na crystals. The crystal structure of struvite-Na was found to be orthorhombic with cell parameters as, $a = 6.893$ Å, $b = 6.124$ Å, $c = 11.150$ Å and $\alpha = \beta = \gamma = 90^\circ$.

![Figure 8.14 Powder XRD Pattern of Struvite-Na Crystals](image)

8.5 FT-IR Spectroscopic Study

Many common minerals exhibit unique spectra in the mid-infrared range, which extends from 400 cm$^{-1}$ to 4000 cm$^{-1}$. Details of the FT-IR technique are previously discussed in section 4.3 of chapter IV. The FT-IR spectra of both the struvite analogue crystals are presented in figure 8.15, which depict that both the struvite-K and struvite-Na have more or less identical spectrum. The vibrational band assignments according to literature and experimental data are summarized in table 8.3.
Figure: 8.15 (a) FT-IR Spectrum of Struvite-K (b) FT-IR Spectrum of Struvite-Na

Table 8.3: Assignments of Absorption Bands in the FT-IR Spectrum of Struvite

<table>
<thead>
<tr>
<th>Assignments</th>
<th>Reported IR frequencies From Other Minerals wavenumbers (cm⁻¹)</th>
<th>Observed IR frequencies wavenumbers (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Absorption peaks due to water of crystallization</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H–O–H stretching vibrations of water crystallization</td>
<td>3280 to 3550</td>
<td>3276.7, 3389.9, 3521.6</td>
</tr>
<tr>
<td>Absorption peaks due to water of crystallization</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H–O–H stretching vibrations of cluster of water molecules of crystallization</td>
<td>2060 to 2460</td>
<td>2375, 2480.5</td>
</tr>
<tr>
<td>Absorption peaks due to PO₄³⁻ units</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ν₁ symmetric stretching vibration of PO₄³⁻ units</td>
<td>930 to 995</td>
<td>1023.5</td>
</tr>
<tr>
<td>ν₂ symmetric bending vibration of PO₄³⁻ units</td>
<td>404 to 470</td>
<td>421.8</td>
</tr>
<tr>
<td>ν₃ asymmetric stretching vibration of PO₄³⁻ units</td>
<td>1017 to 1163</td>
<td>1066.8, 1168.6, 1239.4</td>
</tr>
<tr>
<td>ν₄ asymmetric bending modes</td>
<td>509 to 554</td>
<td>507.8</td>
</tr>
<tr>
<td>Metal-Oxygen bonds</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Metal-Oxygen bonds</td>
<td>400-650</td>
<td>687.6</td>
</tr>
<tr>
<td>Deformation of OH linked to Mg²⁺</td>
<td>847</td>
<td>894</td>
</tr>
</tbody>
</table>

Growth and Characterization of Struvite and Related Crystals 378
It was found that both the struvite analogs have characteristic FT-IR spectra, since they have distinguishing positions of the absorption bands occurred due to vibrations of water of crystallization, tetrahedral $\text{PO}_4^{3-}$ units and metal oxygen bonds.

There are four regions found in the FT-IR spectrum depicting the absorptions due to water of crystallization in both the struvite analog crystals under investigation as shown in table 8.3, which closely matched to the previously reported peaks in several inorganic hydrated compounds [32-39].

Intense bands appeared between the $3275 \text{ cm}^{-1}$ and $3522 \text{ cm}^{-1}$ indicate H–O–H stretching vibrations of water of crystallization. Here, the position of relatively broad band peak near $3275 \text{ cm}^{-1}$ suggests that the water is strongly hydrogen bonded to the Mg cations. The weak bands appeared within $2375 \text{ cm}^{-1}$ to $2480.5 \text{ cm}^{-1}$ in the spectrum can be assigned due to H–O–H stretching vibrations of cluster of water molecules of crystallization. The medium intense bands appeared nearly at $1655 \text{ cm}^{-1}$ and $1704 \text{ cm}^{-1}$ in the spectrum indicate the H–O–H bending modes of vibrations suggesting the presence of water [40]. A medium absorption band at $894 \text{ cm}^{-1}$ indicates the wagging modes of vibration of the coordinated water and the Metal–Oxygen bond in the complex.

Vibrational modes of tetrahedral $\text{XY}_4$ molecules are well known [41]. Julien et al [42] had described the vibrational modes of the materials containing $\text{PO}_4^{3-}$ anions. In the FT-IR spectrum, the $\nu_1$ symmetric stretching vibration of tetrahedral $\text{PO}_4^{3-}$ anions units was found to be at medium band at $894 \text{ cm}^{-1}$ in case of struvite-K and 893.2 cm$^{-1}$ in case of struvite-Na correspond to the previously reported values for different phosphate minerals.
The position of the symmetric stretching vibrations is mainly dependent on the type of mineral, the cation present and crystal structure. While, the positions of the asymmetric stretching vibrations $\nu_3$ of phosphate $\text{PO}_4^{3-}$ anion units in struvite were found at the strongest peaks between $1065.9 \text{ cm}^{-1}$ and $1239.5 \text{ cm}^{-1}$, which are in accordance with the values reported earlier [40, 43, 45, 46]. The symmetric bending vibrations $\nu_2$ of $\text{PO}_4^{3-}$ units were observed nearly at the starting points of spectrum correspond to the previously reported values for various phosphate minerals [43]. Moreover, the asymmetric bending vibrations $\nu_4$ of $\text{PO}_4^{3-}$ units in struvite were observed around $507 \text{ cm}^{-1}$. Here, $\nu_1$ and $\nu_3$ involve the symmetric and asymmetric stretching mode of the P–O bonds, whereas $\nu_2$ and $\nu_4$ involve mainly O–P–O symmetric and asymmetric bending mode with a small contribution of P vibration. The absorption peaks near $687 \text{ cm}^{-1}$ ascribe the presence of oxygen-metal bond.

Thus, the FT-IR spectra of both struvite-K and struvite-Na prove the presence of water of hydration, P–O bond, $\text{NH}_4^+$ ion and $\text{PO}_4^{2-}$ ion and metal-oxygen bond.

### 8.6 Thermal Studies

The thermal studies, such as TGA, DTA and DSC of powdered samples of struvite-K as well as struvite-Na were carried out using Linseis Simultaneous Thermal Analyzer (STA) PT-1600, in the atmosphere of air from $25 ^\circ\text{C}$ to $900 ^\circ\text{C}$ at a heating rate of $15 ^\circ\text{C}/\text{min}$ using $\alpha$-$\text{Al}_2\text{O}_3$ as standard reference. Details of the techniques used for the thermal study are elaborately discussed in section 4.4 of chapter IV as well as section 5.6 of chapter V.
8.6.1 Thermal Study of Struvite-K

Figure 8.16 shows the TGA, DTA and DSC profiles obtained for the gel grown struvite-K as curves (a), (b) and (c), respectively. The graph of mass loss in mg on the Y-axis plotted versus temperature at a fixed rate of change of temperature in °C on the X-axis gives the TGA curve (thermo-gram).

From TGA curve it was found that the struvite-K started dehydrating and decomposing from just above the room temperature and finally at 600 °C it became 64.14% of the original weight and remained almost constant up to the end of analysis. Mass loss in a TGA analysis of sample at temperatures above 100 °C indicates association of water molecules with the Struvite-K chemical structure. A continuous loss of mass in the TGA curve can be attributed to the dehydration of the sample. From the TGA curve, the number
of water molecules associated with the crystal was estimated to be 5. In the temperature range 650–900 °C, no further weight loss occurred and the sample remained almost stable.

From the TGA, total mass loss is found to be 35.86 %, which may be due to the loss of water of crystallization. This weight loss corresponds to the following reaction for struvite-K:

\[
\text{KMgPO}_4\cdot6\text{H}_2\text{O} \rightarrow \text{KMgPO}_4 + 6\text{H}_2\text{O}
\]  

(8.3)

Table 8.4 indicates the TGA results of struvite-K crystals along with the theoretically calculated and experimentally obtained percentage weight.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Substance</th>
<th>Theoretical weight (%) (Calculated)</th>
<th>Practical weight (%) (from TGA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Room Temperature</td>
<td>KMgPO₄·6H₂O (Struvite-K)</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>900 °C</td>
<td>KMgPO₄ (Dehydrated Struvite-K)</td>
<td>63.76</td>
<td>64.14</td>
</tr>
</tbody>
</table>

The graph of DTA signal, i.e. differential thermocouple output in microvolts on the Y-axis plotted versus the sample temperature in °C on the X-axis gives the results of DTA. The transition temperatures were measured precisely using DTA curve. In the DTA curve an endothermic peak was observed at 180 °C, which might be due to release of crystalline water. Processes involving a loss of mass usually give rise to endothermic nature in DTA trace because of the work of expansion. During this endothermic process, the amount of heat change was found to be 406.75 μVs/mg. On further heating at higher temperatures, anhydrate struvite-K was obtained. In the DTA curve of struvite-K crystals, two exothermic peaks were observed, one medium peak at 110 °C and the second strong one at 677.8 °C. Second
exothermic peak might be due to high temperature phase transition. During this exothermic process at 677.8 °C, the amount of heat change was found to be – 22.63 µVs/mg.

The graph of heat flow in mJ/s on the Y-axis plotted versus temperature at a fixed rate of change of temperature in °C on the X-axis shows the output of the DSC. The DSC curve exhibited peaks at the same temperatures as peaks were obtained in DTA curve. In the TGA curve, no remarkable change was observed for the peak which was noticed at 677.8 °C in DTA and DSC curves due to the possible phase transition, since no change took place in the mass of the specimen.

8.6.2 Thermal Study of Struvite-Na

Figure 8.17 shows the TGA, DTA and DSC profiles obtained for the gel grown struvite-Na by the curves (a), (b) and (c), respectively. From the TGA curve, it was found that the struvite-Na started dehydrating and decomposing just above the room temperature and finally at 600°C it became 63.9 % of the original weight and remained almost constant up to the end of analysis.

Mass loss in a TGA analysis of sample at temperatures above 100°C indicates association of water molecules with the struvite-Na chemical structure. A continuous loss of mass in the TGA curve can be attributed to the dehydration of the sample. From TGA, the number of water molecules associated with the crystal was estimated to be 5. In the temperature range 600–900°C, no further weight loss occurred and the sample remained stable.

From the TGA, total mass loss is found to be 36.1 %, which may be due to the loss of water of crystallization. This weight loss corresponds to the following reaction for struvite-Na:
NaMgPO$_4$.7H$_2$O $\rightarrow$ NaMgPO$_4$ + 7H$_2$O \hspace{1cm} (8.4)

Table 8.5 indicates the TGA results of struvite-Na crystals along with the theoretically calculated and experimentally obtained percentage weight.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Substance</th>
<th>Theoretical weight (%) (Calculated)</th>
<th>Practical weight (%) (from TGA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Room Temperature</td>
<td>NaMgPO$_4$.7H$_2$O (Struvite-Na)</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>900 °C</td>
<td>NaMgPO$_4$ (Dehydrated Struvite-Na)</td>
<td>61.25</td>
<td>63.9</td>
</tr>
</tbody>
</table>

Figure 8.17 TGA, DTA and DSC Profiles for the Gel Grown Struvite-Na Crystal

In the DTA curve an endothermic peak was observed at 183.4°C, which might be due to release of crystalline water. Processes involving a loss of mass usually give rise to endothermic nature in DTA trace because of the work of expansion. During this endothermic process, the amount of heat change was found to be 403.10 µVs/mg. On further heating at higher
temperatures, anhydrate struvite-Na was obtained. In the DTA curve of struvite-Na crystals, two exothermic peaks were observed, one medium peak at 100°C and the second strong one at 674°C. Second exothermic peak might be due to high temperature phase transition. During this exothermic process at 674 °C, the amount of heat change was found to be – 28.40 µVs/mg.

The DSC curve exhibited peaks at the same temperatures as peaks were obtained in DTA curve. In TGA curve, no remarkable change was observed for the peak which was noticed at 674°C in DTA and DSC curves due to the possible phase transition, since no change took place in the mass of the specimen.

The thermodynamic parameters obtained from the thermal analysis of both the struvite-K and struvite-Na are tabulated in table 8.6.

<table>
<thead>
<tr>
<th>Table : 8.6 : Thermodynamic Parameters of Struvite-K and Struvite-Na</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Compound</strong></td>
</tr>
<tr>
<td><strong>Reaction → Unit ↓</strong></td>
</tr>
<tr>
<td>Temperature °C</td>
</tr>
<tr>
<td>Enthalpy (ΔH) J / g</td>
</tr>
<tr>
<td>Specific Heat Capacity J / g °C</td>
</tr>
<tr>
<td>Amount of Heat Change µVs/mg</td>
</tr>
<tr>
<td>Heat Flow Rate mJ / s</td>
</tr>
</tbody>
</table>

8.6.3 Kinetic Parameters of Dehydration and Decomposition

The kinetic parameters of both the struvite-K and struvite-Na were evaluated from the respective TGA curves by applying Coats and Redfern relation [47] as depicted by equation (5.4) in chapter V. Figure 8.18 (a) and (b) illustrate the Coats and Redfern plot for struvite-K and struvite-Na.
respectively. The values of activation energy were obtained from the slope of the best linear fit plot. The values of activation energy \( E \), frequency factor \( A \) and order of reaction \( n \) were obtained as tabulated in table 8.7.

\[
y = -\log_a \left( \frac{(1 - (1 - a)^{-n}} {r^{(1 - a)}} \right)
\]

![Figure: 8.18 Coats and Redfern Plots for (a) Struvite-K, (b) Struvite-Na](image)

Table: 8.7 : Kinetic Parameters of Struvite-K and Struvite-Na

<table>
<thead>
<tr>
<th>Kinetic Parameters</th>
<th>Symbol</th>
<th>Struvite-K</th>
<th>Struvite-Na</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activation Energy</td>
<td>( E )</td>
<td>83.21 kJ Mol(^{-1})</td>
<td>102.66 kJ Mol(^{-1})</td>
</tr>
<tr>
<td>Frequency Factor</td>
<td>( A )</td>
<td>( 4.64 \times 10^{10} )</td>
<td>( 4.17 \times 10^{13} )</td>
</tr>
<tr>
<td>Order of Reaction</td>
<td>( n )</td>
<td>2</td>
<td>2</td>
</tr>
</tbody>
</table>

It is noticed that the values of activation energy is slightly higher in struvite-Na than struvite-K. Which indicates that struvite-Na is slightly more stable than struvite-K. This is also reflected from DTA and DSC curves where first endothermic reaction is observed at 183.4°C for struvite-Na and for struvite-K at 180°C. This clearly suggests slightly higher stability of struvite-Na.

8.6.4 Thermodynamic Parameters of dehydration and Decomposition

Various thermodynamic parameters such as standard entropy of activation \( \Delta^\ddagger S^\circ \), standard enthalpy of activation \( \Delta^\ddagger H^\circ \), standard Gibbs energy of activation \( \Delta^\ddagger G^\circ \) and standard internal energy of activation \( \Delta^\ddagger U^\circ \) were calculated by applying well known formulae, as described in detail by
Laidler [48] and mentioned in section 5.6.5 of chapter V. Table 8.8 gives the values of thermodynamic parameters of dehydration and decomposition for both the struvite analog crystals under present investigation.

**Table : 8.8 : Thermodynamic Parameters of Dehydration and Decomposition**

<table>
<thead>
<tr>
<th>Thermodynamic Parameters</th>
<th>Symbol</th>
<th>Struvite-K</th>
<th>Struvite-Na</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard Entropy of activation</td>
<td>(\Delta^\dagger S^\circ)</td>
<td>(-43.00 \text{ JMol}^{-1}\text{K}^{-1})</td>
<td>(13.76 \text{ JMol}^{-1}\text{K}^{-1})</td>
</tr>
<tr>
<td>Standard Enthalpy of activation</td>
<td>(\Delta^\dagger H^\circ)</td>
<td>(76.67 \text{ kJ Mol}^{-1})</td>
<td>(96.28 \text{ kJ Mol}^{-1})</td>
</tr>
<tr>
<td>Standard Gibbs Energy of activation</td>
<td>(\Delta^\dagger G^\circ)</td>
<td>(93.57 \text{ kJ Mol}^{-1})</td>
<td>(91.02 \text{ kJ Mol}^{-1})</td>
</tr>
<tr>
<td>Standard Internal Energy of activation</td>
<td>(\Delta^\dagger U^\circ)</td>
<td>(79.94 \text{ kJ Mol}^{-1})</td>
<td>(99.47 \text{ kJ Mol}^{-1})</td>
</tr>
</tbody>
</table>

Here, negative value of \(\Delta^\dagger S^\circ\) for struvite-K shows that the process is non-spontaneous, whereas positive value of the struvite-Na depicts spontaneous process. For both the struvite analog crystals the values of standard enthalpy of activation \(\Delta^\dagger H^\circ\) are positive, which show that the enthalpy is increasing during the process and such process is an endothermic process. Positive values of \(\Delta^\dagger G^\circ\) demonstrate that both the struvite-K and struvite-Na are thermodynamically unstable.

**8.7 Dielectric Studies**

Every material has a unique set of electrical characteristics which are dependent on its dielectric properties. The dielectric constant of a material is associated with the energy storage capability in the electric field in the material and the loss factor is associated with the energy dissipation, conversion of electric energy to heat energy in the material. The experimental technique used for the dielectric study was described earlier in section 4.5 of the chapter IV. The dielectric constants, dielectric loss, a.c. conductivity \((\sigma_{ac})\) and a.c. resistivity \((\rho_{ac})\) were evaluated with the frequency of applied field at
room temperature using well known formulae as depicted by equations (4.4), (4.6), (4.7) and (4.8) in section 4.5 of chapter IV.

Figure 8.19 (a) shows the variations in the dielectric constant of both the struvite-K and struvite-Na with the frequency of applied field from 400 Hz to 100 kHz at room temperature. The value of dielectric constant for struvite-K at 400 Hz frequency was found as 19.88, which was finally reduced to 10.82 at 100 kHz frequency of applied field. Initially, the dielectric constant remained almost constant up to 1 kHz frequency, thereafter it decreased rapidly with increasing frequency up to 20 kHz and then slowly decreased at higher frequency. This type of behavior indicated higher space charge polarizability of the material in the low frequency region. As the frequency increased, a point was reached where the space charge could not sustain and complied with the external field, and hence the polarization decreased and exhibited the reduction in the values of dielectric constant as frequency increased. This was discussed in detail elsewhere [49-51]. For struvite-Na the value of dielectric constant at 400 Hz frequency was found as 22.09, which was decreased rapidly initially then reduced slowly and finally reduced to 12.31 at 100 kHz frequency of applied field rapidly. It was noticed for both the struvite analog
crystals that the dielectric constant decreased with the increasing value of frequency of applied field.

It is noticed that the value of dielectric constant is maximum at lower frequencies for both the struvite-K as well as struvite-Na, since all mechanisms such as space charge, orientation, ionic and electronic polarizations are operative at lower frequencies of applied electric field. But at higher frequencies, these mechanisms cannot follow the frequency of applied electric field and hence the values of dielectric constant are low.

Figure 8.19 (b) shows the variations in the dielectric loss for both the struvite analog with the frequency of applied field. From the data of the variation of dielectric loss (D = tan δ) with frequency of applied field for struvite-K, it was surprisingly observed that dielectric loss increased up to 2 kHz and followed by decreasing nature with higher frequency, whereas in case of struvite-Na the value of dielectric loss decreased with the increasing value of frequency of applied field. Dielectric loss behaviour of struvite-K is unusual. Similar nature of dielectric loss is reported for plasticized polymer nanocomposite electrolytes by Pradhan et al [52]. Some of the possible reasons for such frequency response to dielectric loss are as under:

(i) Such increase of dielectric loss at lower frequencies is attributed to oscillation of dipoles. Moreover, since at higher frequencies all the polarization mechanisms are not operative; hence energy need not to be spent to rotate dipoles, and consequently the dielectric loss also decreases.

(ii) It is known that the dielectric loss is defined as \( \varepsilon'' / \varepsilon' \). A maximum in dielectric loss at a certain frequency can be observed when \( \varepsilon' \) has a minimum value i.e. a minimum stored energy at that frequency.
(iii) The occurrence of peak in the frequency response of dielectric loss can be observed when the hopping frequency is approximately equal to that of the externally applied electric field, i.e., when resonance phenomena takes place.

![Figure 8.20 (a) Variation in a.c. Conductivity and (b) a.c. Resistivity with Frequency of Applied Field](image)

Figure 8.20 (a) and (b) show the nature of variation of a.c. conductivity and a.c. resistivity with frequency of applied field for both the material. It was found that for struvite-K a.c. conductivity increased and consequently the a.c. resistivity decreased with the increasing value of frequency of applied field. The frequency dependence of a.c. conductivity of struvite-K follows the Jonscher's [53] universal power law, known as “Universal Dielectric Response” (UDR).

Whereas for struvite-Na initially a.c. conductivity increased with the increasing frequency but it was reduced after 40 kHz frequency, which may be due to the mismatch of dipole frequency and applied field frequency. The a.c. resistivity of struvite-Na decreased up to 40 kHz of applied frequency followed by increasing nature.
8.8 Conclusions

1. Both the struvite analogs struvite-K and struvite-Na can be grown by using single diffusion gel growth technique.

2. Growth conditions, i.e., the SG of SMS solution, gel pH, the concentrations of reactants, etc., play important role in the growth of struvite-K as well as struvite-Na crystals.

3. The crystal morphology of both the struvite analogs was strongly dependent on growth parameters. By changing the growth parameters, struvite-K crystals with different morphologies like prismatic type, star type, rectangular platelet type, elongated platelet type, coffin-lid shaped and dendritic type can be grown. Whereas struvite-Na crystals of prismatic type, star type and dendritic type can be grown.

4. The grown struvite-K and struvite-Na crystals had transparent, translucent and opaque diaphaneity, depending upon the location and the growth conditions.

5. The phenomenon of the formation of Liesegang rings were observed in the gel growth experiments of both the struvite analogs. The numbers of formation of Liesegang rings were increased with the increasing value of the gel pH. The thickness as well as spacing between the Liesegang rings in the gel column increased with the depth.

6. The powder XRD studies confirmed the structural similarity of the grown struvite-K and struvite-Na crystals with struvite. It was found that both struvite-K and struvite-Na crystallized in the orthorhombic Pmn2₁ space group with unit cell parameters as follows
Struvite-K: $a = 6.893 \, \text{Å}, b = 6.141 \, \text{Å}, c = 11.222 \, \text{Å}, \alpha = \beta = \gamma = 90^\circ$

Struvite-Na: $a = 6.893 \, \text{Å}, b = 6.124 \, \text{Å}, c = 11.150 \, \text{Å}, \alpha = \beta = \gamma = 90^\circ$.

7. FTIR spectra of both the struvite analog crystals revealed the presence of functional groups. The spectra confirmed the presence of water of hydration, $P - O$ bond and $PO_4^{3-}$ ion and metal-oxygen bond.

8. Both the struvite-K and struvite-Na crystals were found to be thermally unstable. From the TGA curves of struvite-K and struvite-Na, it was found that these struvite analogs started dehydrating and decomposing just above the room temperature and, finally, at 600 °C it became 64.14 % and 63.9 % of the original weight, respectively. A continuous loss of mass in the TGA curve depicted the simultaneous dehydration and decomposition of the material. Mass loss in a TGA analysis at temperatures above 100 °C proved the association of water molecules with these crystals. From the TGA, the numbers of water molecules associated with both the crystal were estimated to be 5.

9. In the DTA curve of struvite-K, two remarkable peaks were observed. A very strong endothermic peak observed at 180 °C attributed to release of crystalline water and the amount of heat change was found to be 406.75 µVs/mg during this endothermic process. A medium exothermic peak observed at 677.8 °C attributed to high temperature phase transition and the amount of heat change was found to be – 22.63 µVs/mg. Similarly in the DTA curve of struvite-Na two remarkable peaks were observed. A very strong endothermic peak observed at 183.4 °C attributed to release of crystalline water and the amount of heat change was found to be 403.10 µVs/mg. A medium exothermic peak observed at 674 °C attributed to high
temperature phase transition and the amount of heat change was found to be – 28.40 µVs/mg.

10. By applying the Coats-Redfern relation to the dehydration along with decomposition stage in the respective thermograms, the values of kinetic parameters were calculated. For struvite-K the values of activation energy $E$, frequency factor $A$ and order of reaction $n$ were found to be 83.21 kJ Mol$^{-1}$, $4.64 \times 10^{10}$ and 2, respectively. While for struvite-Na the values of $E$, $A$ and $n$ were found to be 102.66 kJ Mol$^{-1}$, $4.17 \times 10^{13}$ and 2, respectively. The high value of activation energy indicated more stable nature of struvite-Na which can also be confirmed from the thermograms.

11. The thermodynamic parameters for the dehydration and decomposition process were also evaluated for both struvite-K and struvite-Na. For both the struvite analog crystals the values of standard enthalpy of activation $\Delta^\ddagger H°$ are positive, which show that the enthalpy is increasing during the process and such process is an endothermic process. Positive values of $\Delta^\ddagger G°$ demonstrate that both the struvite-K and struvite-Na are thermodynamically unstable.

12. For both struvite-K and struvite-Na, the dielectric constant as well as dielectric loss was found to be dependent on the frequency of applied field at room temperature. It was noticed for both the struvite analog crystals that the dielectric constant decreased with the increasing value of frequency of applied field. For struvite-K the variation of dielectric loss increased up to 2 kHz and followed by decreasing nature with higher frequency. Such increase of dielectric loss at lower frequencies may be attributed to oscillation of dipoles as well as the matching of hopping
frequency and the frequency of the externally applied electric field. In case of struvite-Na the value of dielectric loss decreased with the increasing value of frequency of applied field.

13. It was found that for struvite-K a.c. conductivity increased and consequently the a.c. resistivity decreased with the increasing value of frequency of applied field. The frequency dependence of a.c. conductivity of struvite-K follows the Jonscher’s universal power law. Whereas for struvite-Na initially a.c. conductivity increased with the increasing frequency but it was reduced after 40 kHz frequency, which may be due to the mismatch of dipole frequency and applied field frequency. The a.c. resistivity of struvite-Na decreased up to 40 kHz of applied frequency followed by increasing nature.
References


