

## CHAPTER V

### CONCLUSION

The vibrational spectroscopy is the powerful method for studying of solid hydrates in terms of sample characterization, structural and bonding features. This study, the intermolecular interactions in  $\text{ZnHPO}_4 \cdot \text{H}_2\text{O}$ ,  $\text{Co}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{LiFePO}_4 \cdot 3\text{H}_2\text{O}$ ,  $\text{LiCoPO}_4 \cdot 3\text{H}_2\text{O}$ ,  $\text{LiNiPO}_4 \cdot \text{H}_2\text{O}$ ,  $\text{LiMnPO}_4 \cdot \text{H}_2\text{O}$  and  $\text{Li}_2\text{Zn}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$  were interpreted by using FTIR/ FT Raman spectroscopy. The FTIR spectra were recorded by KBr pellets techniques. Anion – water interactions were estimated from the observed uncoupled  $\nu_{\text{OH}}$  (HOD) vibration. The frequency shift  $\Delta\nu_{\text{OH}}$  (HOD) lead to the estimation of  $R_{\text{O} \dots \text{O}}$  distances and enthalpy of hydrogen bonding ( $-\Delta H_{\text{H}}$ ) by using equation:  $R_{\text{O} \dots \text{O}} = 3.764 - 0.169 \ln \Delta\nu_{\text{OH}}(\text{HOD}) / \text{cm}^{-1} \text{ \AA}$  and  $-\Delta H_{\text{H}} = 1.286 + 0.0418 \Delta\nu_{\text{OH}} (\text{HOD}) / \text{cm}^{-1} \text{ kJ mol}^{-1} \text{ OH}$ , respectively. The non-deuterated and deuterated analogues of the mentioned hydrates were synthesized in three replications. The factor group analyses were carried out for the vibrational bands assignment.

The thermal properties of all hydrates were studied by using TG/DTG/DTA and DSC techniques. The mole numbers of water of crystallization of these hydrates were determined by using TG/DTG/DTA and Karl Fischer methods. The metal stoichiometry was determined by using atomic absorption spectroscopy (AAS) and atomic emission spectroscopy. The mole numbers of water of crystallization and metal contents confirm the required formula of each hydrate.

#### 5.1 Zinc Hydrogen Phosphate Monohydrate ( $\text{ZnHPO}_4 \cdot \text{H}_2\text{O}$ )

The thermal decomposition of  $\text{ZnHPO}_4 \cdot \text{H}_2\text{O}$  was studied by using DSC techniques. DSC curves of  $\text{ZnHPO}_4 \cdot \text{H}_2\text{O}$  show two endothermic peaks corresponding to the dehydration (247 °C) and decomposition (346 °C) due to the elimination of water of constituent from anion. The corresponding enthalpies ( $\Delta H$ ) were found to be 391.823 and 316.188 J/g, respectively. The Karl Fischer method was used to confirm the water content in this hydrate and found to be 1 mole. The zinc ratio in

this hydrate determined by AAS and were found to 1 mole atom per formula. The results from all techniques confirm the formula of this hydrate to be  $\text{ZnHPO}_4 \cdot \text{H}_2\text{O}$ .

The vibrational band position at  $3535\text{ cm}^{-1}$  was assigned to  $\nu_{\text{as}}(\text{H-OP})$ , while those in the range of  $3376\text{--}1638\text{ cm}^{-1}$  are the water fundamental vibrations. The bands in the range of  $1110\text{--}1019\text{ cm}^{-1}$  were assigned to the terminal  $\text{PO}_3$  stretching.

Thermal decomposition kinetics of  $\text{ZnHPO}_4 \cdot \text{H}_2\text{O}$  was carried out by using Ozawa and Kissinger methods in order to calculate the activation energies. The activation energies for the first dehydration step were found to be  $252.340$  and  $239.340\text{ kJ mol}^{-1}$  from Ozawa and Kissinger method, respectively, while the second step were found to be  $258.693$  and  $241.469\text{ kJ mol}^{-1}$ , respectively. The pre-exponential factor was found to be  $4.91 \times 10^{17}$  and  $2.02 \times 10^{19}\text{ min}^{-1}$  for the first and second steps, respectively (Ozawa method). The pre-exponential factor was found to be  $4.39 \times 10^{17}$  and  $1.74 \times 10^{19}\text{ min}^{-1}$  for the first and second steps, respectively (Kissinger method).

## 5.2 Cobalt Dihydrogen Phosphate Dihydrate ( $\text{Co}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ )

The thermal dehydration of  $\text{Co}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$  was studied by using DSC techniques. DSC curves of  $\text{Co}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$  show two endothermic peaks of dehydration and decomposition at  $173$  and  $328^\circ\text{C}$ . The corresponding to enthalpies ( $\Delta H$ ) of dehydration and decomposition were found to be  $293.728$  and  $290.566\text{ J/g}$ , respectively. The Karl Fischer method was used to confirm the water content in this hydrate and found to be 2 moles. The cobalt ratio in this hydrate determined by AAS was found to be 1 mole atom per formula. The results from all techniques confirm the formula of this hydrate to be  $\text{Co}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ .

The vibrational band positions at  $3330$  and  $3290\text{ cm}^{-1}$  were assigned to  $\nu_{\text{as}}(\text{H-OP})$  and  $\nu_{\text{s}}(\text{H-OP})$ , while those in the range of  $3180\text{--}1610\text{ cm}^{-1}$  are the water fundamental vibrations. The bands in the range of  $1154\text{--}1040\text{ cm}^{-1}$  were assigned to the terminal  $\text{PO}_3$  stretching.

Thermal decomposition kinetics of  $\text{Co}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$  was carried out by using Ozawa and Kissinger methods in order to calculate the activation energies. The activation energies for the first dehydration step were found to be  $112.876$  and



104.464 kJ mol<sup>-1</sup> from Ozawa and Kissinger methods, respectively, while the second step were found to be 217.333 and 207.735 kJ mol<sup>-1</sup>, respectively. The pre-exponential factor (A) values were found to be  $9.13 \times 10^{12}$  and  $5.80 \times 10^{12}$  min<sup>-1</sup> for the first and second steps, respectively (Ozawa method). The A values were found to be  $8.59 \times 10^{12}$  and  $5.44 \times 10^{12}$  min<sup>-1</sup> for the first and second steps, respectively (Kissinger method).

### 5.3 Lithium Ferrous Phosphate Trihydrates (LiFePO<sub>4</sub>.3H<sub>2</sub>O)

The green precipitates of LiFePO<sub>4</sub>.3H<sub>2</sub>O were obtained from the preparation method as described in Chapter 3. Thermal property of LiFePO<sub>4</sub>.3H<sub>2</sub>O by TG/DTG/DTA measurement shows three steps of weight losses in the range of 80 – 600 C°, which are related to the elimination of water of crystallization. Three steps in thermograms are divided into the ranges: 80 – 120, 150 – 250 and 270-300 C°. The total percentage of weight losses from these three ranges are 24.68% corresponding to 3 moles of water of crystallization. The DSC thermogram of this hydrate shows three endothermic peaks at around 116, 190 and 290 °C which correspond to the dehydration of water of crystallization. The average of calculated mole number of water of crystallization from Karl Fischer method is 3 moles. Both lithium and iron stoichiometry in this hydrate were found to be 1 mole atom per hydrate formula. The results from TG/DTG/DTA, Karl Fischer, and AAS techniques confirm the formula of this hydrate to be LiFePO<sub>4</sub>.3H<sub>2</sub>O.

The vibrational band positions between 3600 – 1400 cm<sup>-1</sup> are the water fundamental vibrations. The vibrational bonds in the range of 1125 – 1043 cm<sup>-1</sup> were assigned to the terminal PO<sub>3</sub> stretching of PO<sub>4</sub><sup>3-</sup>. The P-OH vibrational bands can be observed at 939 and 819 cm<sup>-1</sup>, those correspond to  $\nu_{as}POH$  and symmetric ( $\nu_sPOH$ ), respectively. The shoulder bands at 3382 cm<sup>-1</sup> is the uncoupled  $\nu_{OH}(HOD)$  stretching in deuterated analogue sample.

The observed uncouple of  $\nu_{OH}(HOD)$  leads to the estimated enthalpy of hydrogen bonding ( $-\Delta H_H$ ) and R<sub>O...O</sub> distance of LiFePO<sub>4</sub>.3H<sub>2</sub>O to be 14.853 kJ mol<sup>-1</sup>OH and 2.787 Å, respectively.



Thermal dehydration kinetics of  $\text{LiFePO}_4 \cdot 3\text{H}_2\text{O}$  was studied by using Ozawa and Kissinger methods. The calculated activation energy values and pre-exponential factor by Ozawa method are found to be 97.986, 121.940 and 253.281  $\text{kJ mol}^{-1}$  for the first, second and third step of dehydration, respectively, while those calculated by Kissinger method for the dehydration are 91.405, 114.099 and 243.086  $\text{kJ mol}^{-1}$  for the first, second and third step of dehydration, respectively. The pre-exponential factor (A) values were found to be  $1.0230 \times 10^{13}$ ,  $3.5536 \times 10^{13}$  and  $2.7330 \times 10^{23} \text{ min}^{-1}$  for the first, second and third steps, respectively (Ozawa method). The A values were found to be  $9.6416 \times 10^{12}$ ,  $3.3238 \times 10^{13}$  and  $2.4615 \times 10^{23} \text{ min}^{-1}$  for the first, second and third steps, respectively (Kissinger method).

#### 5.4 Lithium Cobalt Phosphate Trihydrates ( $\text{LiCoPO}_4 \cdot 3\text{H}_2\text{O}$ )

The thermal dehydration of  $\text{LiCoPO}_4 \cdot 3\text{H}_2\text{O}$  was studied by using TG/DTG/DTA and DSC techniques. TG curves of  $\text{LiCoPO}_4 \cdot 3\text{H}_2\text{O}$  showed three endothermic peaks for the dehydration at about 100 – 160, 180 – 195 and 235 – 270  $^{\circ}\text{C}$  under the operation from 60 to 600  $^{\circ}\text{C}$ . The total weight losses was 23.06% corresponding to 3 moles of water. The Karl Fischer method was used to confirm the water content and found to be 3 moles. Both lithium and cobalt stoichiometries determined by AAS and AES methods are 1 mole atom per formula, respectively. The results from TG/DTG/DTA, Karl Fischer, AAS and AES techniques confirm the formula of this hydrate to be  $\text{LiCoPO}_4 \cdot 3\text{H}_2\text{O}$ . The DSC thermograms of  $\text{LiCoPO}_4 \cdot 3\text{H}_2\text{O}$  showed three endothermic peaks at 179  $^{\circ}\text{C}$  ( $\Delta H = 441.092 \text{ J/g}$ ), 198  $^{\circ}\text{C}$  ( $\Delta H = 9.704 \text{ J/g}$ ) and 215  $^{\circ}\text{C}$  ( $\Delta H = 12.861 \text{ J/g}$ ), respectively.

The vibrational band position at 3072  $\text{cm}^{-1}$  was assigned to the vibration of MO-H. The P-OH vibrational bands can be observed at 938 and 854  $\text{cm}^{-1}$  that correspond to asymmetric ( $\nu_{\text{as}}\text{POH}$ ) and symmetric ( $\nu_{\text{s}}\text{POH}$ ), respectively. The shoulder bands at 3372, 2540, 2403, 2315 and 1463  $\text{cm}^{-1}$  were assigned to the  $\nu_{\text{OH}}(\text{HOD})$ ,  $\nu_3(\text{B}_2)\text{D}_2\text{O}$ ,  $\nu_1(\text{A}_1)\text{D}_2\text{O}$  or  $\nu_{\text{OD}}(\text{HOD})$ ,  $\nu_1(\text{A}_1)\text{D}_2\text{O}$  or  $\nu_{\text{OD}}(\text{HOD})$  and  $\nu_2(\text{HOD})$  vibrations in deuterated analogue samples, respectively.



The observed uncouple of  $\nu_{\text{OH}}(\text{HOD})$  leads to the estimation of enthalpy of hydrogen bonding ( $-\Delta H_{\text{H}}$ ) and  $R_{\text{O} \dots \text{O}}$  distance and found to be  $15.271 \text{ kJ mol}^{-1} \text{ OH}$  and  $2.781 \text{ \AA}$ , respectively.

Thermal decomposition kinetics studies of  $\text{LiCoPO}_4 \cdot 3\text{H}_2\text{O}$  by using Ozawa and Kissinger methods were carried out to calculate the activation energies of dehydration. The activation energies calculated by Ozawa method for the dehydration in  $\text{LiCoPO}_4 \cdot 3\text{H}_2\text{O}$  were found to be  $117.027$ ,  $459.313$  and  $556.912 \text{ kJ mol}^{-1}$  for the first, second and third step of dehydration, respectively, while those obtained by Kissinger method are  $109.431$ ,  $450.797$  and  $548.759 \text{ kJ mol}^{-1}$ , respectively. The pre-exponential factor ( $A$ ) values were found to be  $2.2850 \times 10^{13}$ ,  $1.9257 \times 10^{51}$  and  $9.5759 \times 10^{59} \text{ min}^{-1}$  for the first, second and third steps, respectively (Ozawa method). The  $A$  values were found to be  $1.9864 \times 10^{13}$ ,  $1.6264 \times 10^{51}$  and  $9.2324 \times 10^{59} \text{ min}^{-1}$  for the first, second and third steps, respectively (Kissinger method).

## 5.5 Lithium Nickel Phosphate Monohydrate ( $\text{LiNiPO}_4 \cdot \text{H}_2\text{O}$ )

The thermal dehydration of  $\text{LiNiPO}_4 \cdot \text{H}_2\text{O}$  was studied by using TG/DTG/DTA and DSC techniques. TG curves of  $\text{LiNiPO}_4 \cdot \text{H}_2\text{O}$  show one endothermic peak of dehydration at  $226^\circ\text{C}$  (fig.4.3) under the operation from  $80$  and  $600^\circ\text{C}$ . The total weight loss is  $11.38\%$  by mass, which corresponds to 1 mole of water per formula. The Karl Fischer method was used to confirm the water content in this hydrate and found to be 1 mole per formula. Both lithium and nickel stoichiometries in this hydrate were determined by AAS and AES methods and found to be 1 mole atom per formula, respectively. The results from TG/DTG/DTA, Karl Fischer, AAS and AES techniques confirm the formula to be  $\text{LiNiPO}_4 \cdot \text{H}_2\text{O}$ . The DSC thermograms of  $\text{LiNiPO}_4 \cdot \text{H}_2\text{O}$  illustrate one endothermic peak of the dehydration at  $220^\circ\text{C}$  ( $\Delta H = 306.938 \text{ J/g}$ ).

The vibrational bands position at  $3044 \text{ cm}^{-1}$  is assigned to the vibration of  $\text{MO-H}$ , while the  $\text{P-OH}$  vibrational bands were observed at  $944$  and  $886 \text{ cm}^{-1}$  that correspond to asymmetric ( $\nu_{\text{as}}\text{POH}$ ) and symmetric ( $\nu_{\text{s}}\text{POH}$ ), respectively. The shoulder bands at  $3337$ ,  $2539$ ,  $2371$ ,  $2286$  and  $1421 \text{ cm}^{-1}$  are assigned to the

$\nu_{\text{OH}}(\text{HOD})$ ,  $\nu_3(\text{B}_2)\text{D}_2\text{O}$ ,  $\nu_1(\text{A}_1)\text{D}_2\text{O}$  or  $\nu_{\text{OD}}(\text{HOD})$ ,  $\nu_{\text{OD}}(\text{HOD})$  and  $\nu_2(\text{HOD})$  vibrations in deuterated analogue samples, respectively.

The observed uncouple  $\nu_{\text{OH}}(\text{HOD})$  leads to the estimation of enthalpy of hydrogen bonding ( $-\Delta H_{\text{H}}$ ) and  $\text{R}_{\text{O}}\dots\text{O}$  distance and found to be  $16.734 \text{ kJ mol}^{-1}\text{OH}$  and  $2.765 \text{ \AA}$ , respectively.

Thermal decomposition kinetics studies of  $\text{LiNiPO}_4\cdot\text{H}_2\text{O}$  by using Ozawa and Kissinger methods was carried out to calculate the activation energies of dehydration. The activation energies calculated by Ozawa and Kissinger method for the dehydration in  $\text{LiNiPO}_4\cdot\text{H}_2\text{O}$  were found to be  $142.486$  and  $134.090 \text{ kJ mol}^{-1}$ , respectively. The pre-exponential factor values were found to be  $5.3646 \times 10^{14}$  and  $4.4988 \times 10^{14} \text{ min}^{-1}$  for Ozawa and Kissinger method, respectively.

## 5.6 Lithium Manganese Phosphate Monohydrate ( $\text{LiMnPO}_4\cdot\text{H}_2\text{O}$ )

The thermal dehydration of  $\text{LiMnPO}_4\cdot\text{H}_2\text{O}$  was studied by using TG/DTG/DTA and DSC techniques. TG curves of  $\text{LiMnPO}_4\cdot\text{H}_2\text{O}$  shows one endothermic peak of dehydration at  $205^\circ\text{C}$  under the operation from  $80$  to  $600^\circ\text{C}$ . The total weight loss is  $9.41\%$  by mass, which corresponds to 1 mole of water per formula and the Karl Fischer method also confirm 1 mole of water per formula. Both lithium and manganese stoichiometries were confirmed by AAS and AES technique to be 1 mole atom per formula. All mentioned techniques confirm the hydrate formula to be  $\text{LiMnPO}_4\cdot\text{H}_2\text{O}$ . The DSC thermograms of  $\text{LiMnPO}_4\cdot\text{H}_2\text{O}$  show one endothermic peak at  $200^\circ\text{C}$  and the enthalpy change ( $\Delta H$ ) was found to be  $200.640 \text{ J/g}$ .

The vibrational bands in the range of  $3410\text{--}1609 \text{ cm}^{-1}$  are the water fundamental vibrations. The vibrational bands in the regions of  $1122\text{--}1023 \text{ cm}^{-1}$  are assigned to terminal  $\text{PO}_3$  stretching. The bands at  $3314$ ,  $2541$ ,  $2448$  and  $1302 \text{ cm}^{-1}$  are the  $\nu_{\text{OH}}(\text{HOD})$ ,  $\nu_3(\text{B}_2)\text{D}_2\text{O}$ ,  $\nu_1(\text{A}_1)\text{D}_2\text{O}$  or  $\nu_{\text{OD}}(\text{HOD})$ ,  $\nu_1(\text{A}_1)\text{D}_2\text{O}$  or  $\nu_{\text{OD}}(\text{HOD})$  and  $\nu_2(\text{HOD})$  vibrations in deuterated analogue sample.



The enthalpy of hydrogen bonding ( $-\Delta H_H$ ) and  $R_{O \cdots O}$  distance were calculated from the observed uncouple of  $\nu_{OH}(HOD)$  and found to be  $17.440 \text{ kJmol}^{-1}$  OH and  $2.755 \text{ \AA}$ , respectively.

Thermal decomposition kinetics studies of  $\text{LiMnPO}_4 \cdot \text{H}_2\text{O}$  were carried out using Ozawa and Kissinger methods in order to calculate the activation energies and found to be  $115.532$  and  $107.492 \text{ kJ mol}^{-1}$ , respectively, while the pre-exponential factor values were found to be  $3.1569 \times 10^{12}$  and  $2.4988 \times 10^{12} \text{ min}^{-1}$  for Ozawa and Kissinger method, respectively.

### 5.7 Dilithium Zinc Hydrogen Phosphate Monohydrate ( $\text{Li}_2\text{Zn}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ )

The thermal dehydration of  $\text{Li}_2\text{Zn}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$  was studied by using TG/DTG/DTA and DSC techniques. TG curves of  $\text{Li}_2\text{Zn}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$  showed two endothermic peaks of dehydration at  $187$  and  $286^\circ\text{C}$  over the range of  $80$  and  $600^\circ\text{C}$ . The weight loss of first step is  $7.44\%$  corresponding to the dehydration of water of crystallization and corresponding to  $1$  mole of water per formula. The second peak of weight loss of  $2.34\%$  corresponding to the elimination of water of constituent from anion. The Karl Fischer method was used to confirm the water content in this hydrate and found to be  $1$  mole per formula. The lithium to zinc ratio in this hydrate determined by AAS and AES were found to be  $2$  to  $1$  mole atom per formula. The results from all techniques confirm the formula of this hydrate to be  $\text{Li}_2\text{Zn}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ . The DSC thermogram of  $\text{Li}_2\text{Zn}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$  shows two endothermic peaks at  $180$  and  $280^\circ\text{C}$  corresponding to the enthalpy ( $\Delta H$ ) of dehydration of  $443.635$  and  $269.264 \text{ J/g}$ , respectively.

The vibrational band positions at  $3536$  and  $3481 \text{ cm}^{-1}$  are assigned to  $\nu_{as}(\text{H-OP})$  and  $\nu_s(\text{H-OP})$ , while those in the range of  $3462$ – $1609 \text{ cm}^{-1}$  are the water fundamental vibrations. The band in the range of  $1121$ – $1007 \text{ cm}^{-1}$  are assigned to the terminal  $\text{PO}_3$  stretching, while the bands at  $2573$  and  $1410 \text{ cm}^{-1}$  are the  $\nu_3(\text{B}_2)\text{D}_2\text{O}$  or  $\nu_{OD}(\text{HOD})$  and  $\nu_2(\text{HOD})$  vibrations in deuterated analogue samples.

Thermal decomposition kinetics study of  $\text{Li}_2\text{Zn}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$  was carried out by using Ozawa and Kissinger methods in order to calculate the activation energies. The activation energy values for the first dehydration step were found to be  $102.625$

and  $94.839 \text{ kJ mol}^{-1}$  from Ozawa and Kissinger method, respectively, while the second step were found to be  $213.451$  and  $204.046 \text{ kJ mol}^{-1}$ , respectively. The pre-exponential factor (A) values were found to be  $2.3213 \times 10^{11}$  and  $6.2434 \times 10^{19} \text{ min}^{-1}$  for the first and second steps, respectively (Ozawa method). The A values were found to be  $1.9681 \times 10^{11}$  and  $5.8683 \times 10^{19} \text{ min}^{-1}$  for the first and second steps, respectively (Kissinger method).

The water of crystallization of  $\text{Li}_2\text{Zn}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$  can be dehydrated and rehydration to the structure, provided that the temperature is lower than  $200^\circ\text{C}$

All the studied hydrates provide the kinetic parameters, those have never been reported before. The hydrate with single and simple dehydration can be used to test the kinetic model. The studied compounds can be the precursors for the production of pyrophosphate or polyphosphate using in various field of applications.