CHAPTER III

EXPERIMENTAL

3.1 General Experimental

The selected phosphate hydrates of single and binary metal and their deuterated analogues were synthesized in three replications by using the available methods in the literatures and the modified ones for better conditions. The vibrational spectra of the synthesized hydrates were recorded on an FTIR/FT Raman spectrophotometer (Perkin Elmer Spectrum GX). The factor group analyses were carried out based on the reported crystallographic informations. The hydrate formula were confirmed by using atomic absorption spectrophotometry (AAS) and atomic emission spectrophotometry (AES), (Perkin Elmer, Analyst 100) for metal content. Karl-Fischer method (Metrohm 798 MPT Titrino) and thermal analysis [TG/DTG/DTA (Perkin Elmer, Pyris Diamond)] for water content. The XRD method was used to characterize their space group and structure. The thermal decomposition kinetic of some selected hydrates were studied by Ozawa and Kissinger methods by using Differential Scanning Calorimetry [DSC using Perkin Elmer Pyris 1].

Intermolecular interactions of selected hydrates were studied by FTIR and FT Raman spectroscopies and an isotopic dilution technique in form of HOD(D_2O). The FTIR spectra were recorded by KBr pellets technique at ambient condition and assigned based on the correlation field splitting analysis. Anion – water interaction was studied by observing the uncoupled ν_{OH} (HOD) vibration. The frequency shift $\Delta\nu_{OH}$ (HOD) leads to the estimation of $R_{O...O}$ distances [44] and enthalpy of hydrogen bonding, $-\Delta H_H$ [22] by using the equation $R_{O...O} = 3.764 - 0.169 \ln (\Delta\nu_{OH} / cm^{-1})$ Å and $-\Delta H_H = 1.268 + 0.0418 (\Delta\nu_{OH} (HOD)/cm^{-1})$ kJ/mol OH, respectively.

The structure and the space group of the prepared products were characterized by X-ray powder diffraction. Thermal behavior of the prepared samples was analyzed by using thermoanalytical techniques (TG/DTG/DTA and DSC).

3.2 Instruments and Chemicals

3.2.1 Instruments

3.2.1 FTIR/FT Raman spectrophotometer (Perkin Elmer Spectrum GX, Nd:YAG Laser, 1064 nm).

3.2.2 X-ray diffractometer (Bruker AXS, Karlsruhe, Germany).

3.2.3 Atomic absorption and Atomic emission spectrophotometer, AAS and AES (Perkin Elmer Analyst 100).

3.2.4 Differential scanning calorimeter, DSC (Perkin Elmer Pyris One).

3.2.5 Thermal gravimetric analysis and thermal differential analyzer, TG/DTG/DTA (Perkin Elmer Diamond).

3.2.6 Karl Fischer Automatic Titrator (Metrohm 798 MPT Titrino).

3.2.7 pH meter (Thermo Orion).

3.2.8 Hot plate stirrer (Electrothermal).

3.2.9 Analytical balance (Scaltec).

3.2.10 Oven (Memmert, 0 – 300°C).

3.2.11 Oven (Lindberg 0-1200°C).

3.2.12 Desiccators.

3.2.13 Suction pump (Eyela Aspirator A – 3s).

3.2.14 KBr hand press, agate mortar and pestle, and cesium iodide windows.

3.2.2 Chemicals

3.3.1 Acetone (C_3H_6O), 99.8 %, Carlo Erba.

3.3.2 Deuterium oxide (D_2O), 99.9 atom % D, Aldrich.

3.3.3 Ammonium phosphate diabasic ($(NH_4)_2HPO_4$), Riedel- deHaën.

3.3.4 Hydrochloric acid (HCl), 37% (w/ w), Merck.

3.3.5 Hydranal-composite 5, (one component reagent for volumetric Karl Fischer titration), Metrohm Ion Analysis.

3.3.6 Lithium hydroxide monohydrate ($LiOH.H_2O$), Fluka.

3.3.7 Lithium carbonate (Li_2CO_3), Fluka.

3.3.8 Manganese (II) dichloride tetrahydrate ($MnCl_2{\cdot}4H_2O$), Univar.

3.3.9 Manganese (II) nitrate tetrahydrate ($Mn(NO_3)_2{\cdot}4H_2O$), PRS panreac.

3.3.10 Manganese (II) sulphate monohydrate ($MnSO_4.H_2O$), Univar.

3.3.11 Iron (II) sulphate heptahydrate ($FeSO_4{\cdot}7H_2O$), Riedel- deHaën.

3.3.12 Iron (II) ammonium sulphate hexahydrate ($Fe(NH_4)_2(SO_4)_2.6H_2O$), Carlo Erba.

3.3.13 Manganese standard solution for AAS ($MnCl_2{\cdot}4H_2O$), Carlo Erba.

3.3.14 Cobalt (II) sulphate heptahydrate ($CoSO_4.7H_2O$), Sigma Aldrich.

3.3.15 Nikel (II) nitrate hexahydrate ($Ni(NO_3)_2.6H_2O$), Fluka.

3.3.16 Zinc acetylacetonate monohydrate ($C_{10}H_{14}O_4Zn.H_2O$), Fluka.

3.3.17 Methanol, CH_3OH, 99.9%, Carlo Erba.

3.3.18 Nitric acid, HNO_3, 70 % w/w, Lab-scan.

3.3.19 Nitrogen gas (dry N_2), 99.9%.

3.3.20 Potassium bromide (KBr), for IR- spectroscopy, Fluka.

3.3.21 Silica gel blue ($SiO_2{\cdot}H_2O$), drying agent, Merck.

3.3.22 Deionized (DI) water, Chemistry Department, Faculty of Science, Khon Kaen University.

3.3.23 Paraffin oil, Carlo Erba.

3.3 Preparation of the Selected Hydrates

3.3.1 Preparation of $ZnHPO_4.H_2O$

$ZnHPO_4.H_2O$ powder samples were prepared in three replications at room temperature in de-ionized water by mixing $Zn(C_5H_7O_2)_2.H_2O$ with H_3PO_4 (85 wt.% solution) with the molar ratio of the Zn:P of 1:1 upon stirring for about 20 min. Then, 0.1 M KOH was added dropwise into the solution mixture. The reaction mixture led to the formation of a gelatinous white precipitate (~20 min). The precipitate was recovered by filtration and dried at 110°C for 2 h.

3.3.2 Preparation of $Co(H_2PO_4)_2.2H_2O$)

$Co(H_2PO_4)_2.2H_2O$ powder samples were prepared in three replications by hydrothermal method in de-ionized water. Aqueous solution of $CoSO_4.7H_2O$

(99% Sigma Aldrich) as the Co^{2+} source was reacted with H_3PO_4 (85 wt.% solution Carlo Erba) with the mole ratio Co:P of 1:2 upon stirring for about 15 min, then 0.01 M of L-ascorbic acid was added as reducing agent and continue stirring for about 30 min, after that 0.1 M KOH was added dropwise into the solution mixture. The resulting violet gel was refluxed at 80 ± 5 °C for 8 h, then was filtered and washed with deionized water several times. Final precipitate was dried in desiccator.

3.3.3 Preparation of $Li_2Zn(HPO_4)_2.H_2O$

$Li_2Zn(HPO_4)_2.H_2O$ powder samples were also prepared in three replications at room temperature in de-ionized water by mixing $Zn(C_5H_7O_2)_2.H_2O$ (98% Fluka) with H_3PO_4 (85 wt.% solution Carlo Erba) , and $LiOH.H_2O$ (98% Fluka) with the mole ratio of the Li:Zn:P of 2:1:2 [4]. The reaction mixture led to the formation of a gelatinous white precipitate (~20 min). The precipitate was recovered by filtration and dried at 110°C for 2 h. Its deuterated analogue was prepared by the same crystallization procedure as the non deuterated one but replaced by 5-10 %D_2O. The precipitate was also dried in the evacuated desiccator.

3.3.4 Preparation of $LiFePO_4.3H_2O$

$LiFePO_4.3H_2O$ powder samples were prepared in three replications by the co-precipitation method in de-ionized water at room temperature [2]. Aqueous solution of $(NH_4)_2Fe(SO_4)_2.6H_2O$ (99% Carlo Erba), and H_3PO_4 (85 wt.% solution Carlo Erba) was added into the excess aqueous solution of $LiOH.H_2O$ (98% Fluka) in the molar ratio of Li:Fe:P of 3:1:1. The synthesis was conducted under a flow of nitrogen gas in order to prevent oxidation of iron [7] with the stirring time of about 30 min. The obtained green precipitate was washed by DI water several times and dried at 80°C for 3 h. The deuterated analogue samples of this compound were prepared by the method described for the non-deuterated one but using D_2O as solvent and the precipitatate was dried at 60°C for 6 h.

3.3.5 Preparation of $LiCoPO_4.3H_2O$

$LiCoPO_4.3H_2O$ powder samples were prepared in three replications by hydrothermal method in de-ionized water with the mole ratio of Li:Co:P of 3:1:1 [2].

Aqueous solution of $CoSO_4.7H_2O$ (99% Sigma Aldrich) as the Co^{2+} source was reacted with H_3PO_4 (85 wt.% solution Carlo Erba) upon stirring for about 15 min, then 0.01 M of L-ascorbic acid was added as reducing agent and continue stirring for about 30 min. After that, add an excess aqueous solution of $LiOH.H_2O$ (99% Fluka) of three time higher in mole than Co and P. The resulting pink gel was refluxed at 80 ± 5 °C for 8 h, then was filtered and washed with de-ionzed water several times. Final precipitate was dried in desiccator. The deuterated analogue samples of this salt were prepared by the same manner but using 5-10 %D_2O as solvent.

3.3.6 Preparation of $LiNiPO_4.H_2O$ and $LiMnPO_4.H_2O$

$LiNiPO_4.H_2O$ powder samples were synthesized in three replications by hydrothermal method in de-ionized water with the mole ratio of Li(exess):Ni:P of 3:1:1 [2]. Typical method was the reaction between aqueous solution of $Ni(NO_3)_2.6H_2O$ (99% Fluka) as the Ni^{2+}source and with H_3PO_4 (85 wt.% solution Carlo Erba) upon stirring for about 15 min, then 0.01 M of L-ascorbic acid was added as reducing agent and continue stirring for about 30 min. After that, add the excess aqueous solution of $LiOH.H_2O$ (99% Fluka). The resulting gel was reflux at 80 ± 5 °C for 15 h, then was filtered and washed with de-ionized water several times. Final precipitate was dried in desiccator. The deuterated analogue samples were prepared by the same manner but using 5-10 %D_2O as solvent.

$LiMnPO_4.H_2O$ powder samples were prepared in the same procedure by using $MnSO_4.H_2O$ (99% Univar) instead of $Ni(NO_3)_2.6H_2O$. The deuterated analogue samples were prepared using 5-10 %D_2O as solvent.

3.4 Determination of Water of Crystallization

The water of crystallization of each of selected hydrates was determined by using thermal analysis and Karl Fisher method, those can be briefly described as follow.

3.4.1 Karl Fischer Method

Karl Fischer method is a coulometric technique for determing the water of crystallization in the solid hydrates. Titration solution is Karl Fischer reagent (KF reagent free of pyridine). This reagent is available in form of one-component system. Methanol was used to calibrate the KF reagent titer. The equation for calibration of the KF reagent titer was given in section 2.9.4.

Blank Preparation

The blank solution was prepared by mixing between 1.0 to 1.2 g accurate of 0.15 M HNO_3 and 7.0 g accurate of methanol (CH_3OH) into a 10 mL volumetric flask and adjusted to the mark by using methanol.

Sample Preparation

Solid phosphate hydrate samples, those are insoluble in the working medium are previously extracted by the following procedure. Add about 0.1 g (accurate) of sample into a 10 mL volumetric flask, then add blank solution and mix thoroughly by shaking until the hydrated samples was dissolved and adjusted by the blank solution to the mark. This mixture, (hydrate sample + blank solution) was called "a working solution.

Procedure

1. Calibration of the Karl Fischer Reagent or the Titrating Solution

Transfer 10 to 25 mL of methanol (depending on the size of titration chamber) into the titration chamber, then titrate with the KF reagent until a stable end point was automatically obtained. This operation is intended to remove any moisture from the titration chamber. The known weight of de-ionzed water (~10 μL) was injected into the titration chamber. The water equivalents (WE) of the titrant are calculated in form of titer value. Repeat the calibration of an instrument three time and average the value and will be referred to as "titer".

2. Analysis of Samples

The known weight of sample (working solution or blank) was injected into the chamber and titration was automatically run until the stable end point was obtained. The percentage of water equivalent of the Karl Fischer reagent was calculated by the instrument. Repeat the injection of sample at least three times for averaging of the result in term of percentage of water equivalent.

3.4.2 Thermal Analysis (TG/DTA/DTG Method)

Thermal analyses were carried out using a thermogravimetric/ differential thermal analyzer (PerkinElmer Pyris Diamond, TG/DTA/DTG). The analytical reagent grade alumina (α-Al_2O_3) was used as a reference standard. The alumina pans was contained ca. 5-6 mg of powder samples were used. The thermal behavior of each sample was investigated from room temperature to about 600 °C under N_2 flow rate of 100 $cm^3 min^{-1}$ with the heating rate of of 10 °C min^{-1}.

3.5 Determination of Metal Content in Hydrates by AAS Technique

Iron, manganese, zinc, cobalt and nickel content in hydrates were determined by using AAS method, whereas lithium content was determined by using AES method.

3.5.1 Determination of Iron Content in Hydrates

The 1000 ppm of iron standard solution ($FeCl_3.6H_2O$) was diluted to 2.0, 4.0, 6.0, 8.0 and 10.0 ppm by using 0.15 M of HNO_3 as solvent. The approximately 0.02-0.10 gram accurate of $LiFePO_4.3H_2O$ was weighed, dissolved in 2.5 mL of concentrated nitric acid (65 % HNO_3) and adjusted volume to 100 mL by using 0.15 M HNO_3. Pipette 5.0 mL of this solution into a 100 mL volumetric flask and adjusted volume to the mark by using 0.15 M HNO_3. Three replications were required. The hallow cathode lamp and air acetylene burner were used for the determination of the iron at 248.3 nm and fuel flow rate of 1.0 L min^{-1}. The percentage of iron content was calculated and converted to iron stoichiometry of formula in the investigated hydrate.

3.5.2 Determination of Manganese Content in Hydrates

The 1000 ppm of manganese standard solution ($MnCl_2{\cdot}4H_2O$) was diluted to 1.0, 2.0, 3.0 and 4.0 ppm by using 0.15 M HNO_3 as solvent. The approximately 0.02-0.10 g accurate of $LiMnPO_4.H_2O$ was weighed, dissolved in 2.5

mL of concentrated nitric acid (65 % HNO_3) and adjusted the volume to 100 mL in volumetric flask by using 0.15 M HNO_3. Pipette 5.0 mL of this solution into a 25 mL volumetric flask and adjusted to the mark by using 0.15 M HNO_3. Three replications were needed for sample preparation. The hallow cathode lamp and air acetylene burner were used for the determination of the manganese at the wavelength of 279.5 nm and fuel flow rate of 1.0 L min^{-1}. The percentage of manganese content was calculated and converted to manganese stoichiometry of formula in each hydrates sample.

3.5.3 Determination of Zinc Content in Hydrates

The 1000 ppm of zinc standard solution ($ZnCl_2$) was diluted to 10.0, 20.0, 30.0, 40.0 and 50.0 ppm by using 0.15 M HNO_3 as solvent. The approximately 0.02-0.10 g accurate of $Li_2Zn(HPO_4)_2.H_2O$ was dissolved in 2.5 mL of concentrated nitric acid (65 % HNO_3 in a 100 mL volumetric flask and adjusted to the mark by 0.15 M HNO_3. Pipette 5.0 mL of this solution into a 25 mL volumetric flask and adjusted to the mark by using 0.15 M HNO_3. The sample preparations were carried out in three replications. The hallow cathode lamp and air acetylene burner were operated at the wavelength of 213.9 nm and fuel the flow rate of 1.0 L min^{-1}. The percentage of manganese content was calculated and converted to zinc stoichiometry of formula in each hydrates.

3.5.4 Determination of Cobalt Content in Hydrates

The 1000 ppm of cobalt carbonate ($CoCO_3$) standard solution was diluted to 2.0, 4.0, 6.0, 8.0 and 10.0 ppm by using 0.15 M HNO_3 as solvent. The approximately 0.02-0.10 g accurate of $LiMnPO_4.H_2O$ was dissolved in 2.5 mL of concentrated nitric acid (65 % HNO_3) and adjusted the volume to 50 mL in volumetric flask by using 0.15 M HNO_3. Then, pipette 5.0 mL of this solution into a 100 mL volumetric flask and adjusted to the mark by using 0.15 M HNO_3. Three replications of sample preparation are needed. The hallow cathode lamp and air acetylene burner were operated at 240.7 nm and the fuel flow rate of 1.0 L min^{-1}. The percentage of cobalt content was calculated and converted to cobalt stoichiometry of formula in each hydrates.

3.5.5 Determination of Nickel Content in Hydrates

The 1000 ppm of nickel standard solution ($Ni(NO_3)_2.6H_2O$) was diluted to 2.0, 4.0, 6.0, 8.0 and 10.0 ppm by using 0.15 M HNO_3 as solvent. The approximately 0.02-0.10 g accurate of $LiMnPO_4.H_2O$ was weighed, dissolved in 2.5 mL of concentrated nitric acid (65 % HNO_3) and adjusted the volume to 50 mL in volumetric flask by using 0.15 M HNO_3. Pipette 5.0 mL of this sample into a 100 mL volumetric flask and adjusted volume to the mark by using 0.15 M HNO_3. Three replications of sample preparation were needed. The hallow cathode lamp at 232.0 nm and air acetylene burner with 1.0 L min^{-1} of fuel flow rate were used for the determination of the nickel. The nickel stiochiometry of each hydrate can be evaluated.

3.5.6 Determination of Lithium Content in Hydrates

3.5.6.1 $LiFePO_4.3H_2O$, $LiMnPO_4.H_2O$ and $Li_2Zn(HPO_4)_2.H_2O$

The 1000 ppm of lithium chloride ($LiCl.H_2O$) standard solution was diluted to 1.0, 1.5, 2.0, 2.5 and 3.0 ppm by using 0.15 M HNO_3 as solvent. The approximately 0.02-0.10 g accurate weight of samples was dissolved in 2.5 mL of concentrated nitric acid (65 % HNO_3) and adjusted the volume to 100 mL in volumetric flask by using 0.15 M HNO_3. Then 5.0 mL of this solution was pipetted into a 100 mL volumetric flask and adjusted to the mark by using 0.15 M HNO_3. The samples was prepared in three replications. The lithium content in samples were determined by using AES technique. The percentage of lithium content was converted to the lithium stoichiometry of formula in each hydrates.

3.5.6.2 $LiCoPO_4.3H_2O$ and $LiMnPO_4.H_2O$

The determination of lithium content were prepared by a method similar to that described above. However, in these two cases the standard solution was diluted to 0.2, 0.4, 0.6, 0.8 and 1.0 ppm. About 0.02-0.10 g accurate of samples was dissolved in 2.5 mL of concentrated nitric acid (65 % HNO_3) in a 50 mL volumetric flask and adjusted to the mark by using 0.15 M HNO_3.

3.6 Vibrational Spectroscopic Method

Middle infrared absorption spectra of synthesized hydrates were measured on a Perkin Elmer Spectrum GX FTIR/FT Raman spectrophotometer at a resolution of 4.0 in the range of 4000-370 cm^{-1} using KBr pellet.

The calibration of FTIR spectrophotometer was carried out by using a polystyrene film in the 4000 – 370 cm^{-1} region. The spectra of the polystyrene reference film were recorded three times (see Figure 3.1). The standard bands positions at 3027.1, 2924.0, 2850.7, 1944.0, 1601.4, 1154.3, 1028.0, 906.7 and 698.9 cm^{-1} are compared with the average observed values, Table 3.1 [111].

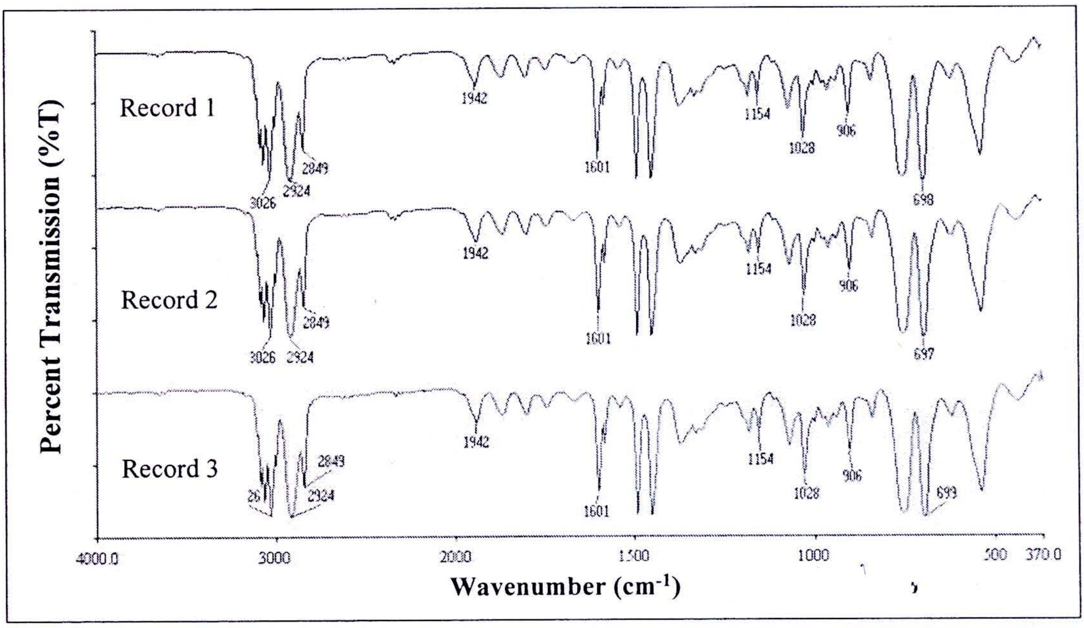

Figure 3.1 FTIR spectra of standard polystyrene film

Table 3.1 FTIR band positions of polystyrene reference film (cm^{-1})

Observed band positions (cm^{-1})			Average (cm^{-1})	$\nu_{reference}$ of band positions (cm^{-1})	Difference of band positions (cm^{-1}) ($\nu_{ref.} - \nu_{obs.}$)
$\nu_{obsrved}$ record 1	$\nu_{obsrved}$ record 2	$\nu_{obsrved}$ record 3			
3026	3026	3026	3026	3027.1	-1.1
2924	2924	2924	2924	2924.0	0.0
2849	2849	2849	2849	2850.7	-1.7
1942	1942	1942	1942	1944.0	-2.0
1601	1601	1601	1601	1601.4	+0.4
1154	1154	1154	1154	1154.3	+0.3
1028	1028	1028	1028	1028.0	0.0
906	906	906	906	906.7	+0.7
698	697	699	698	698.9	+0.9

3.6.1 KBr Pellet Technique

About 5 to 10 mg of solid sample was mixed with spectroscopic grade KBr with approximately sample: KBr of about 1:10. The mixture was ground to fine powder, then press in a KBr hand press. A transparent KBr pellet will be obtained and then the FTIR spectrum can be recorded. The FTIR spectrum of the spectroscopic grade of KBr pellet was recorded for comparison and is shown in Figure 3.2

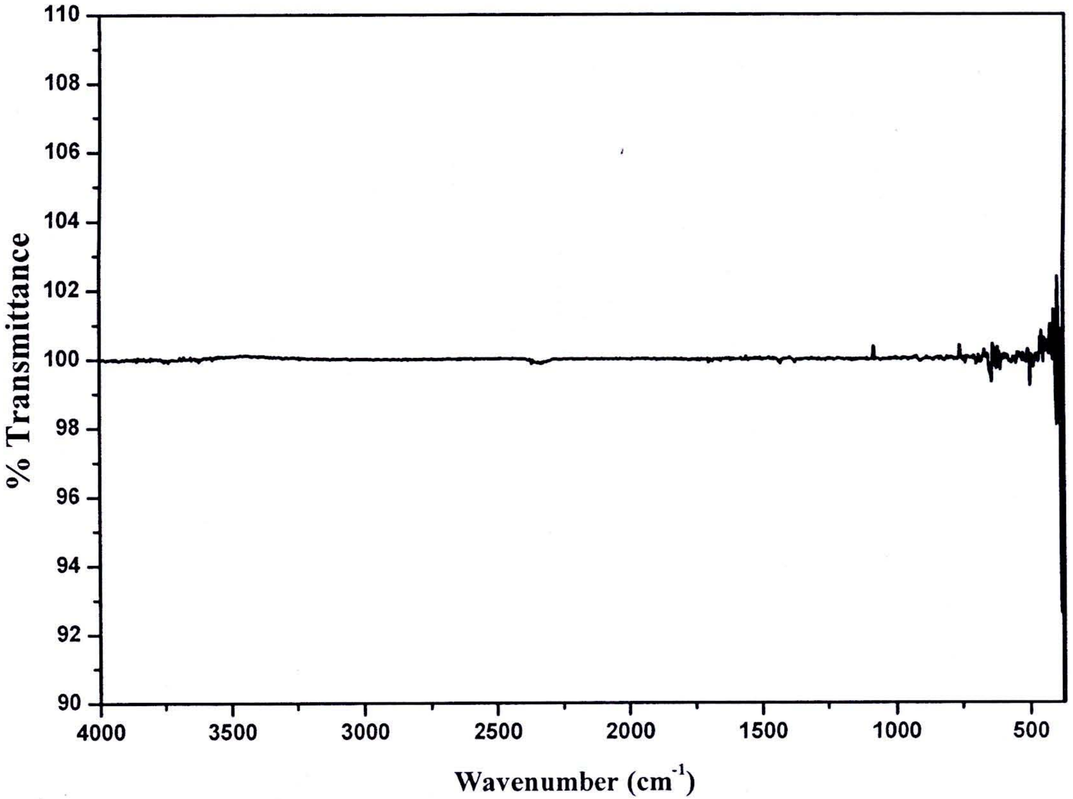

Figure 3.2 FTIR spectrum of KBr powder in the region 4000-370 cm^{-1}.

3.7 The Study on the Thermal Decomposition Kinetics of Selected Hydrates

The thermal decomposition of selected hydrates were carried out on a differential scanning calorimeter (Perkin Elmer Pyris One, DSC). The,approximately 40-70 mg of sample hydrates were weighed and filled in an aluminium pan (sample pan). The sample pan and reference pan (empty aluminium pan) were placed on the pan of DSC instrument and then the lid was closed. Samples were analyzed under an atmosphere of oxygen free nitrogen (OFN), over the temperature range (60-600 °C) with various heating rates. The thermal decomposition kinrtics were carried out to determine the activation energies by Ozawa and Kissinger methods, while the pre-exponential factor was determined by Ozawa equation.

3.8 The Study on the Reversible Hydration of $Li_2Zn(HPO_4)_2.H_2O$

The study of the dehydration and rehydration processes of $Li_2Zn(HPO_4)_2.H_2O$ illustrated that the water molecules can be removed and rehydrated without disrupting the structure of the material under the temperature not higher than 200°C. The dehydration was performed by heating the sample at the specific temperature to remove the water of crystallization. Then and the rehydration was performed by exposing the dehydrated sample to water for 2 h under the ambient temperature. The surface water or adsorbed water was removed from the rehydrated sample by drying at 100 °C for 2 h. The dehydration and rehydration processes of $Li_2Zn(HPO_4)_2.H_2O$ were confirmed by the FT-IR and DSC methods. The water content of the rehydrated sample was confirmed by using the Karl Fischer method.