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# APPENDICES

# Appendix A

- Calculation of Water of Crystallization from Karl Fischer Method
- Calculation of Water of Crystallization from Differential Thermal Gravimetry
- Calculation of Metal Content in Synthesized Hydrates from Atomic Absorption Spectroscopy (AAS) and Atomic Emission Spectroscopy (AES)

**Calculation of Water of Crystallization from Karl Fischer method**

**Calculation of water of crystallization in $ZnHPO_4.H_2O$**

$ZnHPO_4.H_2O$ was dissolved in the known weight of blank solution ($HNO_3$) for example 4.6118 grams and the known weight of substances for example 0.0422 grams were shown as following.

Example of the report data of $H_2O$ Titer

```
'fr
798 MPT Titrino          03211          798.0010
User                     0
Date  2009-02-11     time  11:42              4
U(init)            563 mV   SET  Ipol  H2OTriter
smpl size           10 µL
EP1                2.219 mL              237 mV
Titer              4.5065 mg/mL
                  mean (1)      +/-s          s/%
Titer              4.5065    0.00000 mg/mL    0.00
                  = = = = =

'fr
798 MPT Titrino          03211          798.0010
User                     0
Date  2009-02-11     time  11:48              5
U(init)            563 mV   SET  Ipol  H2OTriter
smpl size           10 µL
EP1                2.208 mL              209 mV
Titer              4.5290 mg/mL
                  mean (2)      +/-s          s/%
Titer              4.5177    0.00000 mg/mL    0.35
                  = = = = =

'fr
798 MPT Titrino          03211          798.0010
User                     0
Date  2009-02-11     time  11:52              6
U(init)            563 mV   SET  Ipol  H2OTriter
smpl size           10 µL
EP1                2.198 mL              226 mV
Titer              4.5496 mg/mL
                  mean (3)      +/-s          s/%
Titer              4.5284    0.00000 mg/mL    0.48
                  = = = = =
```

Example of the report data of percentage of water content in blank solution

```
'fr
798 MPT Titrino          03211          798.0010
User                     0
Date  2009-02-11    time  14.21              13
U(init)          568 mV   SET  Ipol          KF
smpl size      0.0444 g
EP1             0.772 mL                248 mV
Water           10.44 %
Titer          4.5284 mg/mL
                mean (1)       +/-s          s/%
Water            10.44         0.000 %       0.00
                =====
```

```
'fr
798 MPT Titrino          03211          798.0010
User                     0
Date  2009-02-11    time  14.32              14
U(init)          566 mV   SET  Ipol          KF
smpl size      0.0238 g
EP1             0.310 mL                250 mV
Water           10.38 %
Titer          4.5284 mg/mL
                mean (2)       +/-s          s/%
Water            10.41         0.057 %       0.60
                =====
```

```
'fr
798 MPT Titrino          03211          798.0010
User                     0
Date  2009-02-11    time  14.38              15
U(init)          566 mV   SET  Ipol          KF
smpl size      0.0368 g
EP1             0.873 mL                233 mV
Water           10.48 %
Titer          4.5284 mg/mL
                mean (3)       +/-s          s/%
Water            10.43         0.040 %       0.42
                =====
```

Example of the report data of percentage of water content in sample solution

'fr
798 MPT Titrino 03211 798.0010
User 0
Date 2009-02-11 time 16.59 19
U(init) 563 mV SET Ipol KF
smpl size 0.0468 g
EP1 1.192 mL 217 mV
Water 10.53 %
Titer 4.5284 mg/mL
mean (1) +/-s s/%
Water 10.53 0.000 % 0.00
=====

'fr
798 MPT Titrino 03211 798.0010
User 0
Date 2009-02-11 time 17.08 20
U(init) 559 mV SET Ipol KF
smpl size 0.0463g
EP1 1.165 mL 246 mV
Water 10.50%
Titer 4.5284 mg/mL
mean (2) +/-s s/%
Water 10.52 0.009 % 0.10
=====

'fr
798 MPT Titrino 03211 798.0010
User 0
Date 2009-02-11 time 17:17 21
U(init) 559 mV SET Ipol KF
smpl size 0.0473 g
EP1 0.811 mL 231 mV
Water 10.55 %
Titer 4.5284 mg/mL
mean (3) +/-s s/%
Water 10.52 0.011 % 0.13
=====

The percentage of water in blank solution = 10.43 %

The percentage of water $ZnHPO_4.H_2O$ solution = 10.53 %

The total percentage of water in hydrate sample = 10.53 – 10.43 = 0.10 %

100 gram of $LiFePO_4.3H_2O$ solution, the water content = 0.10 gram

0.0468 gram of $ZnHPO_4.H_2O$ solution (injected weight), the water content

$$= \frac{0.10 \times 0.0468}{100}$$

Mole of water = $4.6800 \times 10^{-4}$ gram

$$= \frac{4.6800 \times 10^{4}}{18} \text{ mole}$$

$$= 2.600 \times 10^{-6} \text{ mole}$$

4.6118 gram of $ZnHPO_4.H_2O$ solution, $ZnHPO_4.H_2O$

= 0.0422 gram

0.0468 gram of sample solution contains $ZnHPO_4.H_2O$

$$= \frac{0.0468 \times 0.0422}{4.6118} \text{ gram}$$

$$= 9.9744 \times 10^{-4} \text{ gram}$$

$ZnHPO_4$. anhydrous = $(9.744-4.6800) \times 10^{-4}$

$= 5.064 \times 10^{-4}$ gram

The mole number of anhydrous $ZnHPO_4$ = $\frac{5.064 \times 10^{4}}{179.32}$ mole

$= 2.824 \times 10^{-6}$ mole

$2.824 \times 10^{-6}$ mole of $ZnHPO_4.H_2O$.anhydrous, water content = $2.600 \times 10^{-6}$mole

1 mole of $ZnHPO_4.H_2O$ .anhydrous, water content = $\frac{2.600 \times 10^{6}}{2.824 \times 10^{6}}$ mole

= 0.92 mole

**Calculation of Water of Crystallization in $Co(H_2PO_4)_2.2H_2O$**

$Co(H_2PO_4)_2 \cdot 2H_2O$ was dissolved in the known weight of blank solution ($HNO_3$) and the know weight of solution were automatic titrated the weight of

$Co(H_2PO_4)_2 \cdot 2H_2O$ = 0.0364 gram, and the weight of sample solution = 3.9633 gram.

The typical result can be demonstrated as follow:

Example of the report data of $H_2O$ Titer

```
'fr
798 MPT Titrino          03211          798.0010
User                     0
Date  2009-02-14     time  12:10              4
U(init)            576 mV   SET  Ipol  H2OTriter
smpl size           10 µL
EP1               2.326 mL              195 mV
Titer             4.2992 mg/mL
                    mean (1)       +/-s          s/%
Titer             4.2992    0.00000 mg/mL      0.00
                    =====
```

```
'fr
798 MPT Titrino          03211          798.0010
User                     0
Date  2009-02-14     time  12:14              5
U(init)            574 mV   SET  Ipol  H2OTriter
smpl size           10 µL
EP1               2.313 mL              204 mV
Titer             4.3234 mg/mL
                    mean (2)       +/-s          s/%
Titer             4.3113    0.01711 mg/mL      0.40
                    =====
```

```
'fr
798 MPT Titrino          03211          798.0010
User                     0
Date  2009-02-14     time  12:17              6
U(init)            576 mV   SET  Ipol  H2OTriter
smpl size           10 µL
EP1               2.297 mL              196 mV
Titer             4.3535 mg/mL
                    mean (3)       +/-s          s/%
Titer             4.3254    0.02720 mg/mL      0.63
                    =====
```

Example of the report data of percentage of water content in blank solution

```
'fr
798 MPT Titrino          03211          798.0010
User                     0
Date  2009-02-14     time  15:50             10
U(init)            553 mV   SET  Ipol        KF
```

```
smpl size       0.0564 g
EP1              2.559 mL                219 mV
Water            12.65 %
Titer           4.3254 mg/mL
                   mean (1)       +/-s          s/%
      Water          12.65        0.000 %       0.00
                  =====
```

```
'fr
798 MPT Titrino          03211          798.0010
User                     0
Date  2009-02-14     time  15:57              11
U(init)           553 mV   SET  Ipol          KF
smpl size       0.0487 g
EP1              1.619 mL                243 mV
Water            12.70 %
Titer           4.3254 mg/mL
                   mean (2)       +/-s          s/%
      Water          12.67        0.035 %       0.21
                  =====
```

```
'fr
798 MPT Titrino          03211          798.0010
User                     0
Date  2009-02-14     time  16:06              12
U(init)           553 mV   SET  Ipol          KF
smpl size       0.0406 g
EP1              1.734 mL                243 mV
Water            12.74 %
Titer           4.3254 mg/mL
                   mean (3)       +/-s          s/%
      Water          12.69        0.093 %       0.55
                  =====
```

Example of the report data of percentage of water content in sample solution

```
'fr
798 MPT Titrino          03211          798.0010
User                     0
Date  2009-02-14     time  16:51              16
U(init)           551 mV   SET  Ipol          KF
smpl size       0.0481 g
EP1              1.455 mL                249 mV
Water            12.79 %
Titer           4.3254 mg/mL
                   mean (1)       +/-s          s/%
      Water          12.79        0.000 %       0.00
                  =====
```

'fr

| | | | |
|---|---|---|---|
| 798 MPT Titrino | 03211 | | 798.0010 |
| User | 0 | | |
| Date 2009-02-14 | time 16:58 | | 17 |
| U(init) | 551 mV | SET Ipol | KF |
| smpl size | 0.0477 g | | |
| EP1 | 2.654 mL | | 239 mV |
| Water | 12.77 % | | |
| Titer | 4.3254 mg/mL | | |
| | mean (2) | +/-s | s/% |
| Water | 17.88 | 0.113 % | 0.65 |

= = = = =

'fr

| | | | |
|---|---|---|---|
| 798 MPT Titrino | 03211 | | 798.0010 |
| User | 0 | | |
| Date 2009-02-14 | time 17:06 | | 18 |
| U(init) | 551 mV | SET Ipol | KF |
| smpl size | 0.0478 g | | |
| EP1 | 2.913 mL | | 243 mV |
| Water | 12.79 % | | |
| Titer | 4.3254 mg/mL | | |
| | mean (3) | +/-s | s/% |
| Water | 12.78 | 0.081 % | 0.46 |

= = = = =

The percentage of water in the blank solution = 12.69 %

The percentage of water of $Co(H_2PO_4)_2 \cdot 2H_2O$ solution = 12.79 %

The total percentage of water in hydrate sample = 12.79 – 12.69 = 0.10 %

100 gram of $Co(H_2PO_4)_2 \cdot 2H_2O$, the water content = 0.10 gram

0.0481 gram of $Co(H_2PO_4)_2 \cdot 2H_2O$ (injected weight), the water content

$$= \frac{0.0481 \times 0.10}{100}$$

$$= 4.8100 \times 10^{-5} \text{ gram}$$

Mole of water

$$= \frac{4.8100 \times 10^{5}}{18} \text{ mole}$$

$$= 2.6722 \times 10^{-6} \text{ mole}$$

3.9633 gram of $Co(H_2PO_4)_2 \cdot 2H_2O$ solution, $Co(H_2PO_4)_2 \cdot 2H_2O$

$$= 0.0364 \text{ gram}$$

0.0481 gram of sample solution contain $Co(H_2PO_4)_2 \cdot 2H_2O$

$$= \frac{0.0481 \times 0.0364}{3.9633} \text{ gram}$$

$$= 4.4176 \times 10^{-4} \text{ gram}$$

$Co(H_2PO_4)_2$. anhydrous $= (4.4176\text{-}0.4810) \times 10^{-4}$

$$= 3.9366 \times 10^{-4} \text{ gram}$$

The mole number of $Co(H_2PO_4)_2$.anhydrous $= \frac{3.9366 \times 10^{4}}{288.93}$ mole

$$= 1.3625 \times 10^{-6} \text{ mole}$$

$1.3625 \times 10^{-6}$ mole of $Co(H_2PO_4)_2$.anhydrous, water content $= 2.6722 \times 10^{-6}$ mole

1 mole of $Co(H_2PO_4)_2$ .anhydrous, water content $= \frac{2.6722 \times 10^{6}}{1.3625 \times 10^{6}}$ mole

$$= 1.96 \text{ mole}$$

**Calculation of Water of Crystallization in $LiFePO_4.3H_2O$**

$LiFePO_4.3H_2O$ was dissolved in the known weight of blank solution ($HNO_3$) for example 5.2144 grams and the known weight of substances for example 0.0388 grams were shown as following.

Example of the report data of $H_2O$ Titer

```
'fr
798 MPT Titrino          03211          798.0010
User                     0
Date  2009-02-11     time  11:42              4
U(init)            563 mV   SET  Ipol  H2OTriter
smpl size           10 µL
EP1               2.219 mL              237 mV
Titer             4.5065 mg/mL
                 mean (1)      +/-s          s/%
Titer             4.5065    0.00000 mg/mL    0.00
                 =====
```

```
'fr
798 MPT Titrino          03211          798.0010
User                     0
Date  2009-02-11     time  11:48              5
U(init)            563 mV   SET  Ipol  H2OTriter
smpl size           10 µL
EP1               2.208 mL              209 mV
```

```
Titer          4.5290 mg/mL
              mean (2)      +/-s          s/%
Titer          4.5177   0.00000 mg/mL    0.35
              =====

'fr
798 MPT Titrino          03211        798.0010
User                     0
Date  2009-02-11     time 11:52            6
U(init)          563 mV  SET  Ipol H2OTriter
smpl size         10 µL
EP1             2.198 mL              226 mV
Titer          4.5496 mg/mL
              mean (3)      +/-s          s/%
Titer          4.5284   0.00000 mg/mL    0.48
              =====
```

Example of the report data of percentage of water content in blank solution

```
'fr
798 MPT Titrino          03211        798.0010
User                     0
Date  2009-02-11     time 14.21           13
U(init)          568 mV  SET  Ipol        KF
smpl size      0.0375 g
EP1             0.782 mL              248 mV
Water            9.44 %
Titer          4.5284 mg/mL
              mean (1)      +/-s          s/%
Water            9.44       0.000 %       0.00
              =====

'fr
798 MPT Titrino          03211        798.0010
User                     0
Date  2009-02-11     time 14.32           14
U(init)          566 mV  SET  Ipol        KF
smpl size      0.0138 g
EP1             0.290 mL              250 mV
Water            9.52 %
Titer          4.5284 mg/mL
              mean (2)      +/-s          s/%
Water            9.48       0.057 %       0.60
        =====

'fr
798 MPT Titrino          03211        798.0010
User                     0
Date  2009-02-11     time 14.38           15
```

| | | | | |
|---|---|---|---|---|
| U(init) | 566 mV | SET | Ipol | KF |
| smpl size | 0.0398 g | | | |
| EP1 | 0.833 mL | | 233 mV | |
| Water | 9.48 % | | | |
| Titer | 4.5284 mg/mL | | | |
| | mean (3) | +/-s | | s/% |
| Water | 9.48 | 0.040 % | | 0.42 |

= = = = =

Example of the report data of percentage of water content in sample solution

'fr

| | | | | |
|---|---|---|---|---|
| 798 MPT Titrino | | 03211 | | 798.0010 |
| User | | 0 | | |
| Date 2009-02-11 | time | 16.59 | | 19 |
| U(init) | 563 mV | SET | Ipol | KF |
| smpl size | 0.0558 g | | | |
| EP1 | 1.192 mL | | 217 mV | |
| Water | 9.67 % | | | |
| Titer | 4.5284 mg/mL | | | |
| | mean (1) | +/-s | | s/% |
| Water | 9.67 | 0.000 % | | 0.00 |

= = = = =

'fr

| | | | | |
|---|---|---|---|---|
| 798 MPT Titrino | | 03211 | | 798.0010 |
| User | | 0 | | |
| Date 2009-02-11 | time | 17.08 | | 20 |
| U(init) | 559 mV | SET | Ipol | KF |
| smpl size | 0.0549 g | | | |
| EP1 | 1.165 mL | | 246 mV | |
| Water | 9.69 % | | | |
| Titer | 4.5284 mg/mL | | | |
| | mean (2) | +/-s | | s/% |
| Water | 9.68 | 0.009 % | | 0.10 |

= = = = =

'fr

| | | | | |
|---|---|---|---|---|
| 798 MPT Titrino | | 03211 | | 798.0010 |
| User | | 0 | | |
| Date 2009-02-11 | time | 17:17 | | 21 |
| U(init) | 559 mV | SET | Ipol | KF |
| smpl size | 0.0376 g | | | |
| EP1 | 0.811 mL | | 231 mV | |
| Water | 9.66 % | | | |
| Titer | 4.5284 mg/mL | | | |
| | mean (3) | +/-s | | s/% |
| Water | 9.68 | 0.011 % | | 0.13 |

= = = = =

The percentage of water in blank solution = 9.48 %

The percentage of water of $LiFePO_4.3H_2O$ solution = 9.67 %

The total percentage of water in hydrate sample = 9.67 – 9.48 = 0.19 %

100 gram of $LiFePO_4.3H_2O$ solution, the water content = 0.19 gram

0.0558 gram of $LiFePO_4.3H_2O$ solution (injected weight), the water content

$$= \frac{0.19 \times 0.0558}{100}$$

Mole of water = $1.0602 \times 10^{-4}$ gram

$$= \frac{1.0602 \times 10^{4}}{18} \text{ mole}$$

$= 5.8900 \times 10^{-6}$ mole

5.2144 gram of $LiFePO_4.3H_2O$ solution, $LiFePO_4.3H_2O$ content

= 0.0388 gram

0.0558 gram of sample solution contains $LiFePO_4.3H_2O$

$$= \frac{0.0558 \times 0.0388}{5.2144} \text{ gram}$$

$= 4.1520 \times 10^{-4}$ gram

$LiFePO_4$. anhydrous = $(4.1520\text{-}1.0602) \times 10^{-4}$

$= 3.0918 \times 10^{-4}$ gram

The mole number of anhydrous $LiFePO_4$

$$= \frac{3.0918 \times 10^{4}}{157.80} \text{ mole}$$

$= 1.9593 \times 10^{-6}$ mole

$1.9593 \times 10^{-6}$ mole of $LiFePO_4$.anhydrous, water content = $5.8900 \times 10^{-6}$mole

1 mole of $LiFePO_4$ .anhydrous, water content

$$= \frac{5.8900 \times 10^{6}}{1.9593 \times 10^{6}} \text{ mole}$$

= 3.006 mole

**Calculation of Water of Crystallization in $LiCoPO_4.3H_2O$**

$LiCoPO_4 \cdot 3H_2O$ was dissolved in the known weight of blank solution ($HNO_3$) and the know weight of solution were automatic titrated the weight of $LiCoPO_4 \cdot 3H_2O$ = 0.0661 gram, and the weight of sample solution = 3.2421 gram. The typical result can be demonstrated as follow:

Example of the report data of $H_2O$ Titer

```
'fr
798 MPT Titrino          03211          798.0010
User                     0
Date  2009-02-14      time  12:10              4
U(init)             576 mV   SET  Ipol H2OTriter
smpl size            10 µL
EP1                2.326 mL                195 mV
Titer              4.2992 mg/mL
                mean (1)       +/-s            s/%
Titer             4.2992    0.00000 mg/mL     0.00
                ======
```

```
'fr
798 MPT Titrino          03211          798.0010
User                     0
Date  2009-02-14      time  12:14              5
U(init)             574 mV   SET  Ipol H2OTriter
smpl size            10 µL
EP1                2.313 mL                204 mV
Titer              4.3234 mg/mL
                mean (2)       +/-s            s/%
Titer             4.3113    0.01711 mg/mL     0.40
                ======
```

```
'fr
798 MPT Titrino          03211          798.0010
User                     0
Date  2009-02-14      time  12:17              6
U(init)             576 mV   SET  Ipol H2OTriter
smpl size            10 µL
EP1                2.297 mL                196 mV
Titer              4.3535 mg/mL
                mean (3)       +/-s            s/%
Titer             4.3254    0.02720 mg/mL     0.63
                ======
```

Example of the report data of percentage of water content in blank solution

```
'fr
```

798 MPT Titrino 03211 798.0010
User 0
Date 2009-02-14 time 15:50 10
U(init) 553 mV SET Ipol KF
smpl size 0.0653 g
EP1 2.559 mL 219 mV
Water 16.95 %
Titer 4.3254 mg/mL
mean (1) +/-s s/%
Water 16.95 0.000 % 0.00
=====

'fr
798 MPT Titrino 03211 798.0010
User 0
Date 2009-02-14 time 15:57 11
U(init) 553 mV SET Ipol KF
smpl size 0.0412 g
EP1 1.619 mL 243 mV
Water 17.00 %
Titer 4.3254 mg/mL
mean (2) +/-s s/%
Water 16.97 0.035 % 0.21
=====

'fr
798 MPT Titrino 03211 798.0010
User 0
Date 2009-02-14 time 16:06 12
U(init) 553 mV SET Ipol KF
smpl size 0.0446 g
EP1 1.734 mL 243 mV
Water 16.82 %
Titer 4.3254 mg/mL
mean (3) +/-s s/%
Water 16.92 0.093 % 0.55
=====

Example of the report data of percentage of water content in sample solution

'fr
798 MPT Titrino 03211 798.0010
User 0
Date 2009-02-14 time 16:51 16
U(init) 551 mV SET Ipol KF
smpl size 0.0466 g
EP1 1.875 mL 249 mV
Water 17.40 %

| | | | |
|---|---|---|---|
| Titer | 4.3254 mg/mL | | |
| | mean (1) | +/-s | s/% |
| Water | 17.40 | 0.000 % | 0.00 |
| | = = = = = | | |

'fr

| | | | |
|---|---|---|---|
| 798 MPT Titrino | | 03211 | 798.0010 |
| User | | 0 | |
| Date 2009-02-14 | time 16:58 | | 17 |
| U(init) | 551 mV | SET Ipol | KF |
| smpl size | 0.0693 g | | |
| EP1 | 2.814 mL | | 239 mV |
| Water | 17.56 % | | |
| Titer | 4.3254 mg/mL | | |
| | mean (2) | +/-s | s/% |
| Water | 17.48 | 0.113 % | 0.65 |
| | = = = = = | | |

'fr

| | | | |
|---|---|---|---|
| 798 MPT Titrino | | 03211 | 798.0010 |
| User | | 0 | |
| Date 2009-02-14 | time 17:06 | | 18 |
| U(init) | 551 mV | SET Ipol | KF |
| smpl size | 0.0687 g | | |
| EP1 | 2.773 mL | | 243 mV |
| Water | 17.46 % | | |
| Titer | 4.3254 mg/mL | | |
| | mean (3) | +/-s | s/% |
| Water | 17.47 | 0.081 % | 0.46 |
| | = = = = = | | |

The percentage of water in the blank solution = 16.92 %

The percentage of water of $LiCoPO_4.3H_2O$ solution = 17.40 %

The total percentage of water in hydrate sample = 17.40 – 16.92 = 0.48 %

100 gram of $LiCoPO_4.3H_2O$, the water content = 0.48 gram

0.0466 gram of $LiCoPO_4.3H_2O$ (injected weight), the water content

$$= \frac{0.48 \times 0.0466}{100}$$

$$= 2.2368 \times 10^{-4} \text{ gram}$$

Mole of water

$$= \frac{2.2368 \times 10^{-4}}{18} \text{ mole}$$

$$= 1.2426 \times 10^{-5} \text{ mole}$$

3.2421 gram of $LiCoPO_4.3H_2O$ solution, $LiCoPO_4.3H_2O$ content

$$= 0.0661 \text{ gram}$$

0.0466 gram of sample solution contain $LiCoPO_4.3H_2O = \frac{0.0466 \times 0.0661}{3.2421}$ gram

$$= 9.500 \times 10^{-4} \text{ gram}$$

$LiCoPO_4$. anhydrous $= (9.500\text{-}2.2368) \times 10^{-4}$

$$= 7.2632 \times 10^{-4} \text{ gram}$$

The mole number of $LiCoPO_4$.anhydrous $= \frac{7.2632 \times 10^{4}}{160.87}$ mole

$$= 4.5149 \times 10^{-6} \text{ mole}$$

$4.5149 \times 10^{-6}$ mole of $LiCoPO_4$.anhydrous, water content $= 1.2426 \times 10^{-5}$ mole

1 mole of $LiCoPO_4$ .anhydrous, water content $= \frac{1.2426 \times 10^{5}}{4.5149 \times 10^{6}}$ mole

$$= 2.75 \text{ mole}$$

**Calculation of Water of Crystallization in $LiNiPO_4.H_2O$**

$LiNiPO_4 \cdot H_2O$ was dissolved in the known weight of blank solution and the known weight of solution were automatic titrated. If the weight of $LiNiPO_4 \cdot H_2O$ = 0.0627 gram, and the weight of sample solution = 4.7125 gram. The typical result can be demonstrated as follow:

Example of the report data of $H_2O$ Titer


```
'fr
798 MPT Titrino          03211          798.0010
User                     0
Date 2009-02-14     time 12:10                4
U(init)            576 mV  SET  Ipol H2OTriter
smpl size           10 µL
EP1               2.326 mL                195 mV
Titer             4.2992 mg/mL
                 mean (1)     +/-s            s/%
Titer             4.2992   0.00000 mg/mL     0.00
                 = = = = =

'fr
798 MPT Titrino          03211          798.0010
User                     0
```

```
Date   2009-02-14      time  12:14              5
U(init)              574  mV   SET  Ipol  H2OTriter
smpl size             10  µL
EP1                2.313  mL                204  mV
Titer              4.3234  mg/mL
                 mean (2)       +/-s            s/%
Titer              4.3113    0.01711  mg/mL     0.40
        =====
'fr
798 MPT Titrino              03211          798.0010
User                         0
Date   2009-02-14      time  12:17              6
U(init)              576  mV   SET  Ipol  H2OTriter
smpl size             10  µL
EP1                2.297  mL                196  mV
Titer              4.3535  mg/mL
                 mean (3)       +/-s            s/%
Titer              4.3254    0.02720  mg/mL     0.63
                 =====
```

Example of the report data of percentage of water content in blank solution

```
'fr
798 MPT Titrino              03211          798.0010
User                         0
Date   2009-02-14      time  15.02              4
U(init)              560  mV   SET  Ipol       KF
smpl size         0.0699  g
EP1                1.298  mL                187  mV
Water               8.03  %
Titer              4.3254  mg/mL
                 mean (1)       +/-s            s/%
Water               8.03      0.000  %         0.00
                 =====

'fr
798 MPT Titrino              03211          798.0010
User                         0
Date   2009-02-14      time  15.13              5
U(init)              560  mV   SET  Ipol       KF
smpl size         0.0410  g
EP1                0.762  mL                187  mV
Water               8.04  %
Titer              4.3254  mg/mL
                 mean (2)       +/-s            s/%
Water               8.03      0.007  %         0.09
                 =====
```

```
'fr
798 MPT Titrino          03211          798.0010
User                     0
Date  2009-02-14     time  15.22              5
U(init)          557 mV   SET  Ipol         KF
smpl size     0.0980 g
EP1             1.810 mL              187 mV
Water           7.99 %
Titer         4.3254 mg/mL
          mean (3)      +/-s          s/%
Water          8.02       0.026 %       0.33
               =====
```

Example of the report data of percentage of water content in sample solution

```
'fr
798 MPT Titrino          03211          798.0010
User                     0
Date  2009-02-14     time  14:37             1
U(init)          566 mV   SET  Ipol         KF
smpl size     0.0206 g
EP1             0.390 mL              245 mV
Water           8.19 %
Titer         4.3254 mg/mL
             mean (1)      +/-s          s/%
Water          8.19       0.000 %       0.00
               =====

'fr
798 MPT Titrino          03211          798.0010
User                     0
Date  2009-02-14     time  14:41             2
U(init)          563 mV   SET  Ipol         KF
smpl size     0.0652 g
EP1             1.218 mL              173 mV
Water           8.08 %
Titer         4.3254 mg/mL
             mean (2)      +/-s          s/%
Water          8.14       0.078 %       0.96
               =====

'fr
798 MPT Titrino          03211          798.0010
User                     0
Date  2009-02-14     time  14:54             3
U(init)          563 mV   SET  Ipol         KF
smpl size     0.0355 g
```

| | | |
|---|---|---|
| EP1 | 0.675 mL | 228 mV |
| Water | 8.22 % | |
| Titer | 4.3254 mg/mL | |

| | mean (3) | +/-s | s/% |
|---|---|---|---|
| Water | 8.16 | 0.074 % | 0.90 |

= = = = =

The percentage of water in the blank solution = 8.02 %

The percentage of water of $LiNiPO_4.H_2O$ solution = 8.19 %

The total percentage of water in hydrate sample = 8.19 - 8.02 = 0.17 %

100 gram of $LiNiPO_4.H_2O$, the water content = 0.17 gram

0.0206 gram of $LiNiPO_4.H_2O$ (injected weight), the water content

$$= \frac{0.17 \times 0.0206}{100}$$

$$= 3.5020 \times 10^{-5} \text{ gram}$$

Mole of water $$= \frac{3.5020 \times 10^{5}}{18} \text{ mole}$$

$$= 1.9455 \times 10^{-6} \text{ mole}$$

4.7125 gram of $LiNiPO_4.H_2O$ solution, $LiNiPO_4.H_2O$ content

$$= 0.0627 \text{ gram}$$

0.0206 gram of sample solution contain $LiNiPO_4.H_2O$ $$= \frac{0.0206 \times 0.0627}{4.7125} \text{ gram}$$

$$= 2.7408 \times 10^{-4} \text{ gram}$$

$LiNiPO_4$. anhydrous $$= (2.7408\text{-}0.3502) \times 10^{-4}$$

$$= 2.3906 \times 10^{-4} \text{ gram}$$

The mole number of $LiNiPO_4$.anhydrous $$= \frac{2.3906 \times 10^{4}}{160.63} \text{ mole}$$

$$= 1.4882 \times 10^{-6} \text{ mole}$$

$1.4882 \times 10^{-6}$ mole of $LiNiPO_4$.anhydrous, water content $= 1.9455 \times 10^{-6}$mole

1 mole of $LiNiPO_4$ .anhydrous, water content $$= \frac{1.9455 \times 10^{6}}{1.4882 \times 10^{6}} \text{ mole}$$

$$= 1.31 \text{ mole}$$

**Calculation of Water of Crystallization in $LiMnPO_4.H_2O$**

$LiMnPO_4 \cdot H_2O$ was dissolved in the known weight of blank solution ($HNO_3$) and the known weight of solution were automatic titrated. If the weight of $LiMnPO_4 \cdot H_2O$ = 0.0404 gram, and the weight of sample solution = 3.3164 gram. The typical result can be demonstrated as follow:

Example of the report data of $H_2O$ Titer

```
'fr
798 MPT Titrino          03211          798.0010
User                     0
Date  2009-11-24     time  16:27              25
U(init)                647 mV   SET  Ipol  H2OTriter
smpl size               10 µL
EP1                  2.042 mL              124 mV
Titer                4.8972 mg/mL
                  mean (1)       +/-s          s/%
Titer                4.8972    0.00000 mg/mL    0.00
                  = = = = =

'fr
798 MPT Titrino          03211          798.0010
User                     0
Date  2008-11-24     time  16:32              26
U(init)                626 mV   SET  Ipol  H2OTriter
smpl size               10 µL
EP1                  2.032 mL              180 mV
Titer                4.9213 mg/mL
                  mean (2)       +/-s          s/%
Titer                4.9093    0.01704 mg/mL    0.35
                  = = = = =

'fr
798 MPT Titrino          03211          798.0010
User                     0
Date  2008-11-24     time  16:36              27
U(init)                611 mV   SET  Ipol  H2OTriter
smpl size               10 µL
EP1                  2.085 mL               42 mV
Titer                4.7962 mg/mL
                  mean (3)       +/-s          s/%
Titer                4.8716    0.06637 mg/mL    1.36
                  = = = = =
```

Example of the report data of percentage of water content in blank solution

```
'fr
798 MPT Titrino          03211          798.0010
User                     0
Date  2008-11-24    time  22:09              7
U(init)          588 mV   SET  Ipol         KF
smpl size      0.0315 g
EP1             0.442 mL              144 mV
Water            6.84 %
Titer          4.8716 mg/mL
               mean (1)      +/-s          s/%
Water             6.84       0.000 %       0.00
'fr
798 MPT Titrino          03211          798.0010
User                     0
Date  2008-11-24    time  22:19              8
U(init)          590 mV   SET  Ipol         KF
smpl size      0.0486 g
EP1             0.692 mL              139 mV
Water            6.94 %
Titer          4.8716 mg/mL
               mean (2)      +/-s          s/%
Water             6.89       0.071 %       1.03
               = = = = =

'fr
798 MPT Titrino          03211          798.0010
User                     0
Date  2008-11-24    time  22:30              9
U(init)          581 mV   SET  Ipol         KF
smpl size      0.0615 g
EP1             0.875 mL              236 mV
Water            6.93 %
Titer          4.8716 mg/mL
               mean (3)      +/-s          s/%
Water             6.90       0:055 %       0.80
               = = = = =
```

Example of the report data of percentage of water content in sample solution

```
'fr
798 MPT Titrino          03211          798.0010
User                     0
Date  2008-11-14    time  22:41             10
U(init)          582 mV   SET  Ipol         KF
smpl size      0.0498 g
EP1             0.718 mL               98 mV
```

| | | | |
|---|---|---|---|
| Water | 7.02 % | | |
| Titer | 4.8716 mg/mL | | |
| | mean (1) | +/-s | s/% |
| Water | 7.02 | 0.000 % | 0.00 |

= = = = =

'fr

| | | | |
|---|---|---|---|
| 798 MPT Titrino | | 03211 | 798.0010 |
| User | | 0 | |
| Date 2008-11-24 | time 22:50 | | 11 |
| U(init) | 584 mV | SET Ipol | KF |
| smpl size | 0.0361 g | | |
| EP1 | 0.519 mL | | 187 mV |
| Water | 7.00 % | | |
| Titer | 4.8716 mg/mL | | |
| | mean (2) | +/-s | s/% |
| Water | 7.01 | 0.014 % | 0.20 |

= = = = =

'fr

| | | | |
|---|---|---|---|
| 798 MPT Titrino | | 03211 | 798.0010 |
| User | | 0 | |
| Date 2008-11-24 | time 22:59 | | 12 |
| U(init) | 563 mV | SET Ipol | KF |
| smpl size | 0.0312 g | | |
| EP1 | 0.446 mL | | 187 mV |
| Water | 6.96 % | | |
| Titer | 4.8716 mg/mL | | |
| | mean (3) | +/-s | s/% |
| Water | 6.99 | 0.031 % | 0.44 |

= = = = =

The percentage of water in the blank solution = 6.90 %

The percentage of water of $LiMnPO_4.H_2O$ solution = 7.02 %

The total percentage of water in hydrate sample = 7.02 – 6.90 = 0.12 %

100 gram of $LiMnPO_4.H_2O$, the water content = 0.12 gram

0.0498 gram of $LiMnPO_4.H_2O$ (injected weight), the water content

$$= \frac{0.12 \times 0.0498}{100}$$

$$= 5.9760 \times 10^{-5} \text{ gram}$$

Mole of water

$$= \frac{5.9760 \times 10^{5}}{18} \text{ mole}$$

$$= 3.3200 \times 10^{-6} \text{ mole}$$

3.3164 gram of $LiMnPO_4.H_2O$ solution, $LiMnPO_4.H_2O$ content

$$= 0.0404 \text{ gram}$$

0.0498 gram sample solution contain $LiMnPO_4.H_2O$ $$= \frac{0.0498 \times 0.0404}{3.3164} \text{ gram}$$

$$= 6.6066 \times 10^{-4} \text{ gram}$$

$LiMnPO_4$. anhydrous $$= (6.6066-0.5976) \times 10^{-4}$$

$$= 6.0090 \times 10^{-4} \text{ gram}$$

The mole number of $LiMnPO_4$.anhydrous $$= \frac{6.0090 \times 10^{4}}{156.88} \text{ mole}$$

$$= 3.830 \times 10^{-6} \text{ mole}$$

$3.830 \times 10^{-6}$ mole of $LiMnPO_4$.anhydrous, water content $= 3.3200 \times 10^{-6}$mole

1 mole of $LiMnPO_4$ .anhydrous, water content $$= \frac{3.3200 \times 10^{6}}{3.8300 \times 10^{6}} \text{ mole}$$

$$= 0.86 \text{ mole}$$

**Calculation of Water of Crystallization in $Li_2Zn(HPO_4)_2.H_2O$**

$Li_2Zn(HPO_4)_2 \cdot H_2O$ was dissolved in the known weight of blank solution ($HNO_3$) and the known weight of solution were automatic titrated. If the weight of $Li_2Zn(HPO_4)_2 \cdot H_2O$ = 0.0324 gram, and the weight of sample solution = 3.9666 gram. The typical result can be demonstrated as follow:

Example of the report data of $H_2O$ Titer

```
'fr
798 MPT Titrino          03211          798.0010
User                     0
Date  2009-02-11    time  11:42              4
U(init)            563 mV  SET  Ipol  H2OTriter
smpl size           10 µL
EP1               2.219 mL              237 mV
Titer             4.5065 mg/mL
              mean (1)      +/-s          s/%
Titer             4.5065   0.00000 mg/mL   0.00
              = = = = =

'fr
798 MPT Titrino          03211          798.0010
User                     0
```

```
Date   2009-02-11      time  11:48              5
U(init)              563  mV   SET  Ipol  H2OTriter
smpl size             10  µL
EP1                2.208  mL              209  mV
Titer              4.5290  mg/mL
                 mean (2)      +/-s            s/%
Titer              4.5177   0.00000  mg/mL     0.35
'fr
798 MPT Titrino             03211        798.0010
User                        0
Date   2009-02-11      time  11:52              6
U(init)              563  mV   SET  Ipol  H2OTriter
smpl size             10  µL
EP1                2.198  mL              226  mV
Titer              4.5496  mg/mL
                 mean (3)      +/-s            s/%
Titer              4.5284   0.00000  mg/mL     0.48
                 = = = = =
```

Example of the report data of percentage of water content in blank solution

```
'fr
798 MPT Titrino             03211        798.0010
User                        0
Date   2009-02-11      time  13:45             10
U(init)              569  mV   SET  Ipol       KF
smpl size         0.0389  g
EP1                0.638  mL              233  mV
Water               7.43  %
Titer              4.5284  mg/mL
                 mean (1)      +/-s            s/%
Water                7.43     0.000  %         0.00
                 = = = = =

'fr
798 MPT Titrino             03211        798.0010
User                        0
Date   2009-02-11      time  14:01             11
U(init)              570  mV   SET  Ipol       KF
smpl size         0.0350  g
EP1                0.575  mL              225  mV
Water               7.44  %
Titer              4.5284  mg/mL
                 mean (2)      +/-s            s/%
Water                7.43     0.007  %         0.10
                 = = = = =

'fr
```

```
798 MPT Titrino          03211          798.0010
User                     0
Date  2009-02-11    time  14:13              12
U(init)          566 mV   SET  Ipol          KF
smpl size      0.0255 g
EP1              0.422 mL                237 mV
Water             7.49 %
Titer           4.5284 mg/mL
                mean (3)       +/-s          s/%
Water             7.45         0.032 %        0.43
                =====
```

Example of the report data of percentage of water content in sample solution

```
'fr
798 MPT Titrino          03211          798.0010
User                     0
Date  2009-02-11    time  19.46              25
U(init)          560 mV   SET  Ipol          KF
smpl size      0.0511 g
EP1              0.846 mL                246 mV
Water             7.50 %
Titer           4.5284 mg/mL
                mean (1)       +/-s          s/%
Water             7.50         0.000 %        0.00
                =====

'fr
798 MPT Titrino          03211          798.0010
User                     0
Date  2009-02-11    time  19.55              26
U(init)          560 mV   SET  Ipol          KF
smpl size      0.0639 g
EP1              1.062 mL                231 mV
Water             7.53 %
Titer           4.5284 mg/mL
                mean (2)       +/-s          s/%
Water             7.52         0.021 %        0.28
                =====
'fr
798 MPT Titrino          03211          798.0010
User                     0
Date  2009-02-11    time  20.03              27
U(init)          560 mV   SET  Ipol          KF
smpl size      0.0533 g
EP1              0.885 mL                245 mV
Water             7.52 %
Titer           4.5284 mg/mL
```

| | mean (1) | +/-s | s/% |
|---|---|---|---|
| Water | 7.52 | 0.015 % | 0.20 |
| | = = = = = | | |

The percentage of water in blank solution = 7.45 %

The percentage of water of $Li_2Zn(HPO_4)_2 \cdot H_2O$ solution = 7.50 %

The total percentage of water in hydrate sample = 7.50 – 7.45 = 0.05 %

100 gram of of $Li_2Zn(HPO_4)_2 \cdot H_2O$, the water content = 0.05 gram

0.0511 gram of of $Li_2Zn(HPO_4)_2 \cdot H_2O$ (injected weight), the water content

$$= \frac{0.05 \times 0.0511}{100}$$

$$= 2.555 \times 10^{-5} \text{ gram}$$

Mole of water $$= \frac{2.555 \times 10^{5}}{18} \text{ mole}$$

$$= 1.4194 \text{ X } 10^{-6} \text{ mole}$$

3.9666 gram of of $Li_2Zn(HPO_4)_2 \cdot H_2O$ solution, of $Li_2Zn(HPO_4)_2 \cdot H_2O$ content

= 0.0324 gram

0.0511 gram of of sample solution contain $Li_2Zn(HPO_4)_2 \cdot H_2O$

$$= \frac{0.0511 \times 0.0324}{3.9666} \text{ gram}$$

$$= 4.1739 \times 10^{-4} \text{ gram}$$

of $Li_2Zn(HPO_4)_2 \cdot$. anhydrous $= (4.1739\text{-}0.2555) \times 10^{-4}$

$$= 3.9184 \times 10^{-4} \text{ gram}$$

The mole number of $Li_2Zn(HPO_4)_2$.anhydrous $$= \frac{3.9184 \times 10^{4}}{271.27} \text{ mole}$$

$$= 1.4444 \times 10^{-6} \text{ mole}$$

$1.4444 \times 10^{-6}$ mole of $Li_2Zn(HPO_4)_2$.anhydrous, water content = $1.4194 \times 10^{-6}$mole

1 mole of $Li_2Zn(HPO_4)_2$ .anhydrous, water content $$= \frac{1.4194 \times 10^{6}}{1.4444 \times 10^{6}} \text{ mole}$$

= 0.98 mole

**Calculation of Water of Crystallization from Differential Thermal Gravimetric**

**Calculation of Water of Crystallization in $LiFePO_4.3H_2O$**

The dehydration step of $LiFePO_4 \cdot 3H_2O$ from the thermogram (Fig. 4.1) can be expressed as following.

The weight of $LiFePO_4 \cdot 3H_2O = 5.4000 \times 10^{-3}$ gram

From the TGA data, tatal weight loss of $LiFePO_4 \cdot 3H_2O = 24.68$ %

Calculation the mole numbers of crystallization water in step 1

The percentage of weight loss = 24.68 %

100 gram of $LiFePO_4 \cdot 3H_2O$, the weight loss = 24.68 gram

$5.4000 \times 10^{-3}$ gram of $LiFePO_4.3H_2O$, the weight loss $= \frac{(5.4000 \times 10^{-3}) \times 24.68}{100}$ gram

$= 1.3327 \times 10^{-3}$ gram

Mole equivalent of water $= \frac{1.3327 \times 10^{-3}}{18}$ mol

$= 7.4038 \times 10^{-5}$ mol

$LiFePO_4$.anhydrous $= (5.4000 \times 10^{-3}) - (1.3327 \times 0^{-3})$ gram

$= 4.0673 \times 10^{-3}$ gram

Mole equivalent of $LiFePO_4$.anhydrous $= \frac{4.0673 \times 10^{-3}}{157.80}$ mol

$= 2.5775 \times 10^{-5}$ mol

$2.5775 \times 10^{-5}$ mol of $LiFePO_4$.anhydrous, water content $= 7.4038 \times 10^{-5}$ mol

1.0 mol of $LiFePO_4$.anhydrous, water content $= \frac{7.4038 \times 10^{-5}}{2.5775 \times 10^{-5}}$ mol

$= 2.87$ mol

**Calculation of Water of Crystallization in $LiCoPO_4.3H_2O$**

The dehydration step of $LiCoPO_4 \cdot 3H_2O$ from the thermogram (Fig. 4.2) can be expressed as following.

The weight of $LiCoPO_4 \cdot 3H_2O = 5.7000 \times 10^{-3}$ gram

From the TGA data, tatal weight loss of $LiCoPO_4 \cdot 3H_2O = 23.06$ %

Calculation the mole numbers of crystallization water in step 1

The percentage of weight loss = 23.06 %

100 gram of $LiCoPO_4 \cdot 3H_2O$, the weight loss = 23.96 gram

$5.7000\times10^{-3}$ gram of $LiCoPO_4.3H_2O$, the weight loss $= \frac{(5.7000\times10^{-3})\times 23.96}{100}$ gram

$= 1.3657\times10^{-3}$ gram

Mole equivalent of water $= \frac{1.3657\times10^{-3}}{18}$ mol

$= 7.5873\times10^{-5}$ mol

$LiCoPO_4$.anhydrous $= (5.7000\times10^{-3}) - (1.3657\times 0^{-3})$ gram

$= 4.3856\times10^{-3}$ gram

Mole equivalent of $LiCoPO_4$.anhydrous $= \frac{4.3343\times10^{-3}}{160.87}$ mol

$= 2.6942\times10^{-5}$ mol

$2.6942\times10^{-5}$ mol of $LiCoPO_4$.anhydrous, water content = $7.5873\times10^{-5}$ mol

1.0 mol of $LiCoPO_4$.anhydrous, water content $= \frac{7.5873\times10^{-5}}{2.6942\times10^{-5}}$ mol

= 2.81 mol

**Calculation of Water of Crystallization in $LiNiPO_4.H_2O$**

The dehydration step of $LiNiPO_4 \cdot H_2O$ from the thermogram (Fig. 4.3) can be expressed as following.

The weight of $LiNiPO_4 \cdot H_2O = 5.8000\times 10^{-3}$ gram

From the TGA data, tatal weight loss of $LiNiPO_4 \cdot H_2O$ = 11.38%

Calculation the mole numbers of crystallization water in step 1

The percentage of weight loss = 11.38 %

100 gram of $LiNiPO_4 \cdot H_2O$, the weight loss = 11.38 gram

$5.80\times10^{-3}$ gram of $LiNiPO_4.H_2O$, the weight loss $= \frac{(5.8000\times10^{-3})\times 11.38}{100}$ gram

$= 6.6004\times10^{-4}$ gram

Mole equivalent of water $= \frac{6.6004\times10^{-4}}{18}$ mol

$= 3.6668\times10^{-5}$ mol

$LiNiPO_4$.anhydrous $= (5.8000\times10^{-3})- (6.6004\times 0^{-4})$ gram

$= 5.1399\times10^{-3}$ gram

Mole equivalent of $LiNiPO_4$.anhydrous $= \frac{5.1399\times10^{-3}}{160.63}$ mol

$= 3.1998\times10^{-5}$ mol

$3.1998\times10^{-5}$ mol of $LiNiPO_4$.anhydrous, water content $= 3.6668\times10^{-5}$ mol

1.0 mol of $LiNiPO_4$.anhydrous, water content $= \frac{3.6668\times10^{-5}}{3.1998\times10^{-5}}$ mol

$= 1.14$ mol

**Calculation of Water of Crystallization in $LiMnPO_4.H_2O$**

The dehydration step of $LiMnPO_4{\cdot}H_2O$ from the thermogram (Fig. 4.4) can be expressed as following.

The weight of $LiMnPO_4{\cdot}H_2O = 5.5000\times 10^{-3}$ gram

From the TGA data, tatal weight loss of $LiMnPO_4{\cdot}H_2O = 9.41$

Calculation the mole numbers of crystallization water in step 1

The percentage of weight loss = 9.41 %

100 gram of $LiMnPO_4{\cdot}H_2O$, the weight loss = 9.41 gram

$5.50 \times 10^{-3}$ gram of $LiMnPO_4.H_2O$, the weight loss $= \frac{(5.5000\times10^{-3})\times9.41}{100}$ gram

$= 5.1755\times10^{-4}$ gram

Mole equivalent of water $= \frac{5.1755\times10^{-4}}{18}$ mol

$= 2.8752\times10^{-5}$ mol

$LiMnPO_4$.anhydrous $= (5.5000\times10^{-3})- (5.1755\times 0^{-4})$ gram

$= 4.9824\times10^{-3}$ gram

Mole equivalent of $LiMnPO_4$.anhydrous $= \frac{4.9824\times10^{-3}}{156.88}$ mol

$= 3.1759\times10^{-5}$ mol

$3.1759\times10^{-5}$ mol of anhydrous $LiMnPO_4$, water content $= 2.8752\times10^{-5}$ mol

1.0 mol of $LiMnPO_4$.anhydrous, water content $= \frac{2.8752\times10^{-5}}{3.1759\times10^{-5}}$ mol

$= 0.90$ mol

**Calculation of Water of Crystallization in $Li_2Zn(HPO_4).H_2O$**

The dehydration step of $Li_2Zn(HPO_4)_2{\cdot}H_2O$ from the thermogram (Fig. 4.5) can be expressed as following.

The weight of $Li_2Zn(HPO_4)_2{\cdot}H_2O = 5.3000\times 10^{-3}$ gram

From the TGA data, weight loss of $Li_2Zn(HPO_4)_2{\cdot}H_2O$ (first step) = 7.44%

Calculation the mole numbers of crystallization water in step 1

The percentage of weight loss = 7.44 %

100 gram of $Li_2Zn(HPO_4)_2{\cdot}H_2O$, the weight loss = 7.44 gram

$5.3000\times10^{-3}$ gram of $Li_2Zn(HPO_4)_2{\cdot}H_2O$, the weight loss $= \frac{(5.3000\times10^{-3})\times7.44}{100}$ gram

$= 3.9432\times10^{-4}$ gram

Mole equivalent of water $= \frac{3.9432\times10^{-4}}{18}$ mol

$= 2.1906\times10^{-5}$ mol

$Li_2Zn(HPO_4)_2$.anhydrous $= (5.3000\times10^{-3}) - (3.9432\times 0^{-4})$ gram

$= 4.9056\times10^{-3}$ gram

Mole equivalent of $Li_2Zn(HPO_4)_2$.anhydrous $= \frac{4.9056\times10^{-3}}{271.04}$ mol

$= 1.8099\times10^{-5}$ mol

$1.8099\times10^{-5}$ mol of $Li_2Zn(HPO_4)_2$..anhydrous, water content $= 2.1906\times10^{-5}$ mol

1.0 mol of $Li_2Zn(HPO_4)_2$..anhydrous, water content $= \frac{2.1906\times10^{-5}}{1.8099\times10^{-5}}$ mol

$= 1.21$ mol

**Calculation of Metal Content in Synthesized Hydrates from Atomic Absorption Spectroscopy (AAS) and Atomic Emission Spectroscopy (AES).**

**Calibration Curves for Determination of Metals**

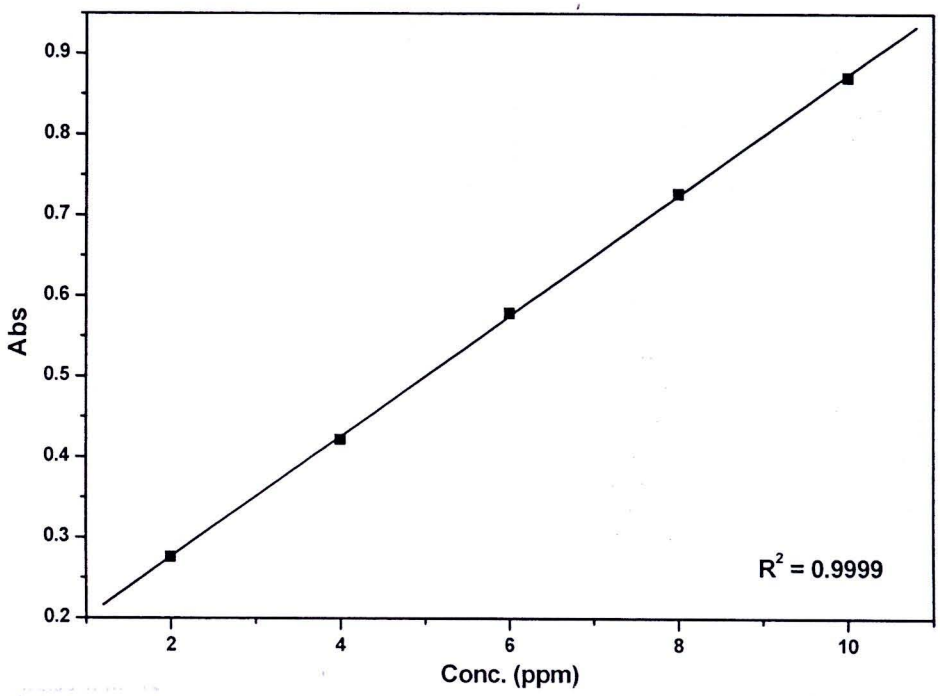


**Figure A.1** Calibration curve for the determination of iron by AAS.

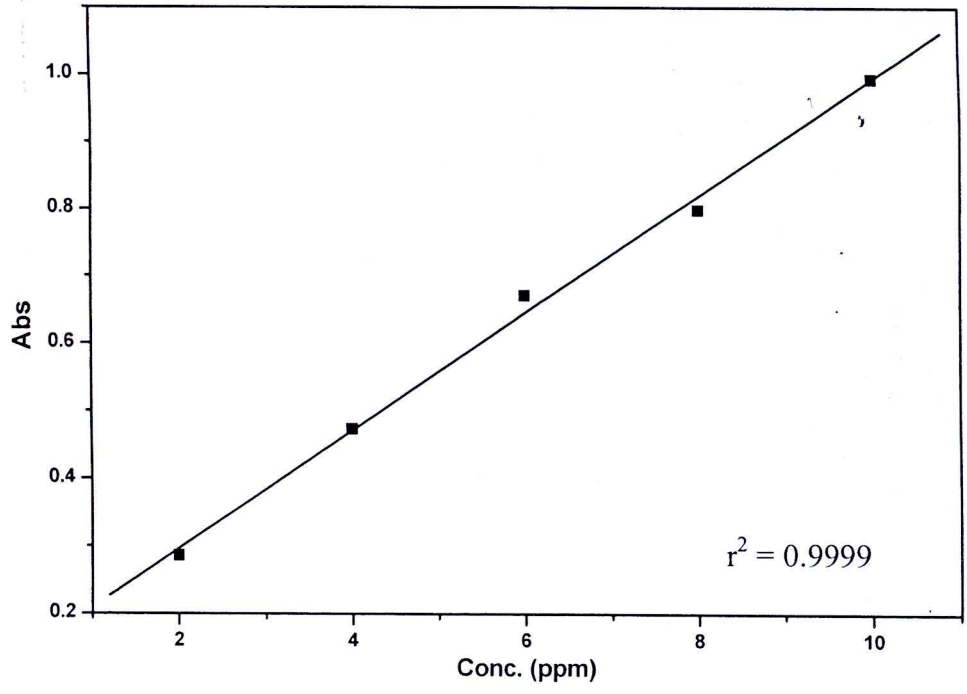


**Figure A.2** Calibration curve for the determination of cobalt by AAS.

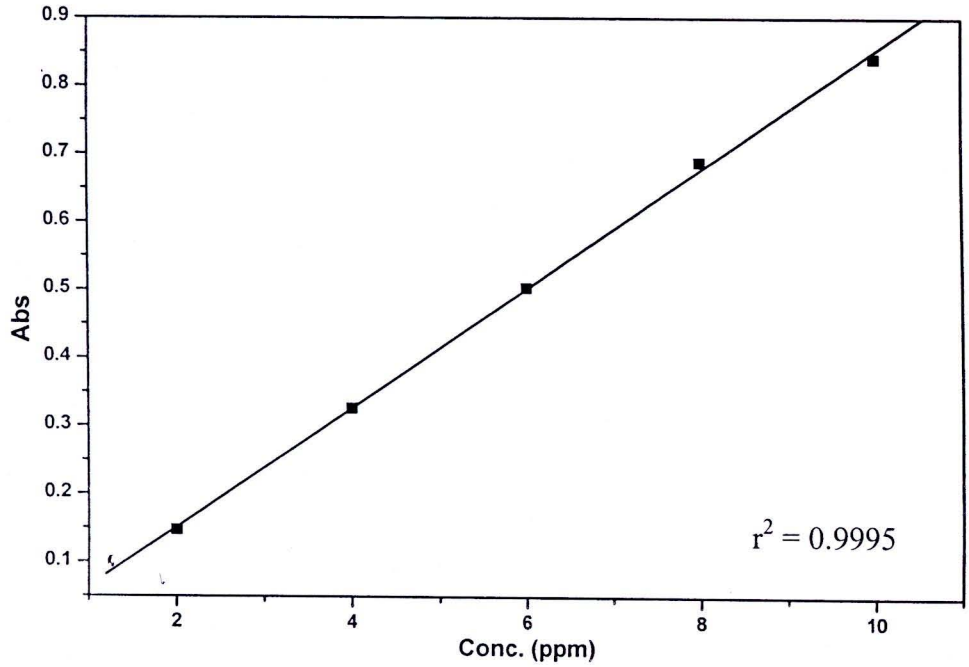


**Figure A.3** Calibration curve for the determination of nickel by AAS.

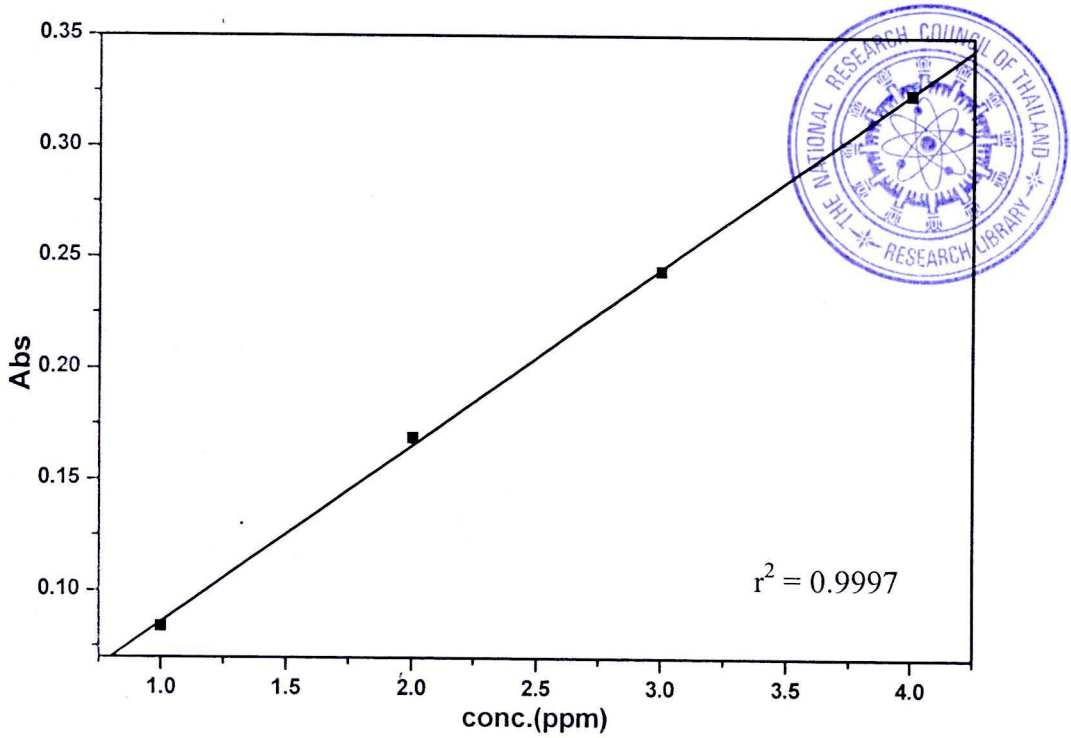




**Figure A.4** Calibration curve for the determination of manganese by AAS.

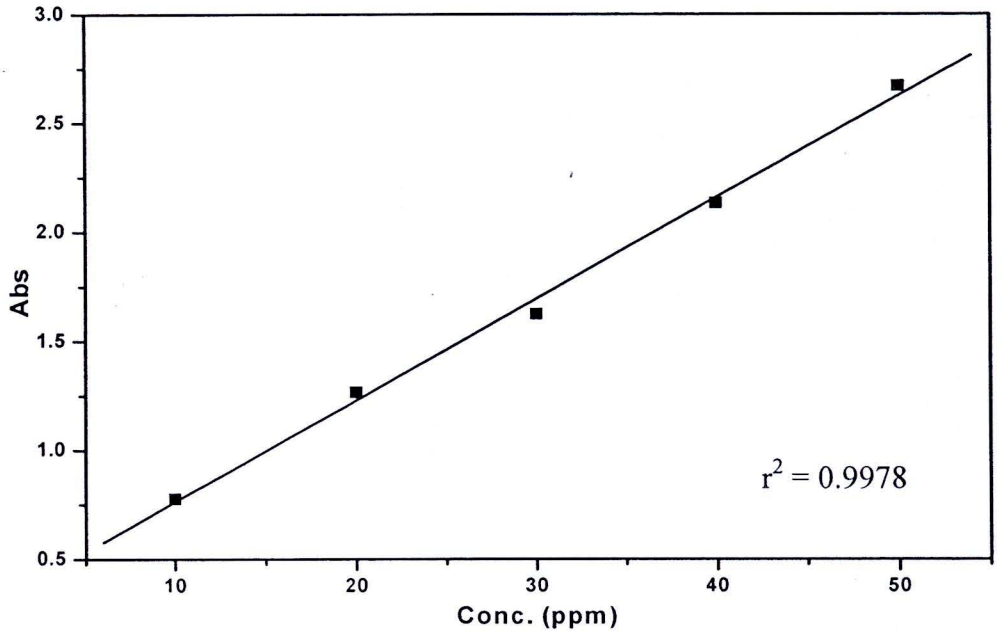


**Figure A.5** Calibration curve for the determination of zinc by AAS.

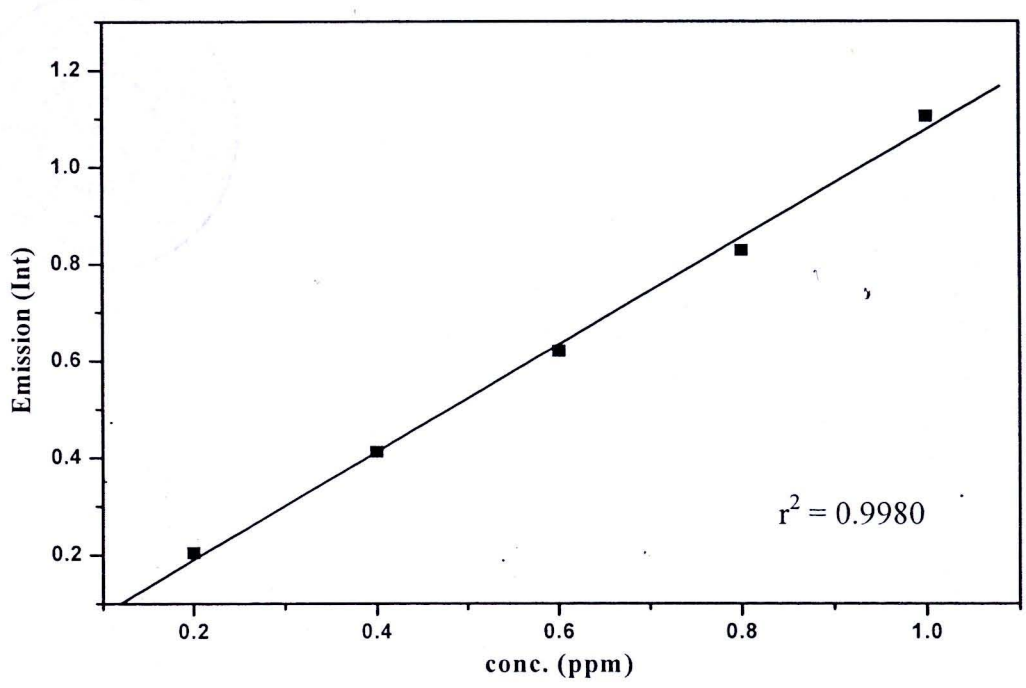


**Figure A.6** Calibration curve for the determination of lithium in $LiCoPO_4.3H_2O$ and $LiNiPO_4.H_2O$ by AES.

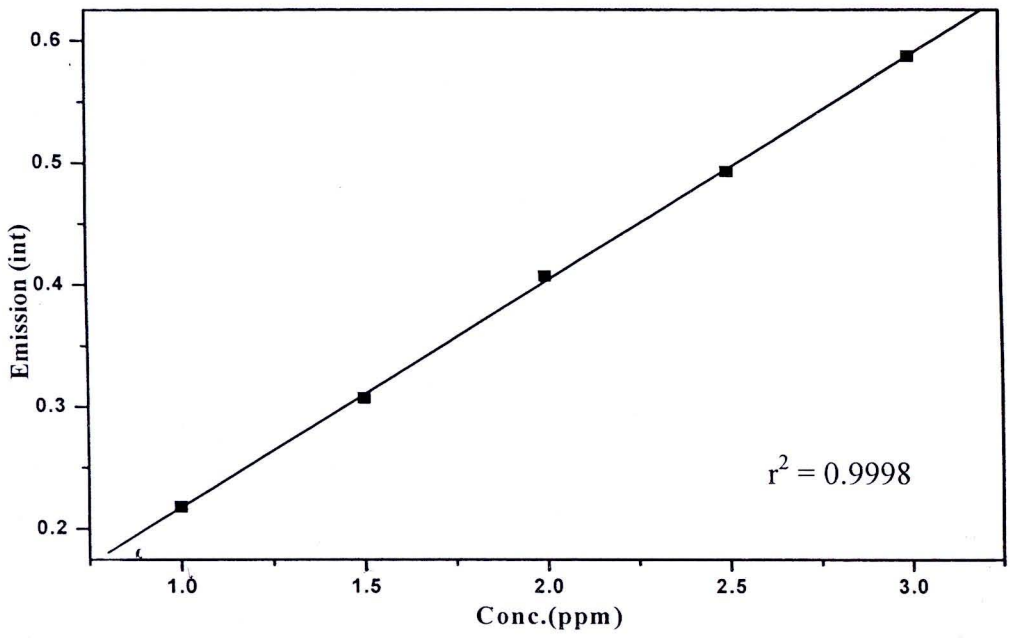


**Figure A.7** Calibration curve for determination of lithium of $LiFePO_4.3H_2O$, $LiMnPO_4.H_2O$ and $Li_2Zn(HPO_4)_2.H_2O$.

# Appendix B

- Mulliken Symbols
- Character Tables
- Correlation Tables
- Space Group and Site Symmetries
- Primitive and Centered Lattices

**Mulliken Symbols**

**Table A.1** Summary of Mulliken symbols used for various species of vibrations [63].

| Type | Symbol | Remarks |
|---|---|---|
| Nonlinear molecules | *A* | One-dimensional representations which are symmetric with respect to the rotation about the principal exis of rotation ($C_n = 1$) |
| | *B* | One-dimensional representations which are asymmetric with respect to the rotation about the principal exis of rotation ($C_n = 1$) |
| | *E* | Two-dimensional representations. Occur in molecules having an axis higher than $C_2$. |
| | *F* | Three-dimensional representations. Occur in molecules having an axis higher than two $C_3$ axes. |
| | Subscripts 1 and 2 to *A* and *B* | Symmetric or antisymmetric with respect to a $C_2$ axis (or a vertical plane of symmetry) perpendicular to the principal axis. |
| | Subscripts *g* and *u* to *A* and *B* | Symmetric or antisymmetric with respect to a center of symmetry (i). |
| | Primes and double primes with *A* and *B* | Symmetric or antisymmetric with respect to $\sigma_h$ |
| Linear Molecules | $\sigma^+$ or $\sum^+$ | Symmetric with respect to a plane of symmetric through the molecular axis. |
| | $\sigma^-$ or $\sum^-$ | Antisymmetric with respect to a plane of symmetry through the molecular axis. |
| | $\Delta$, $\varphi$, $\pi$ | Degenerate vibrations, with the degree of degeneracy increasing in this order. |

**Table A.2** Symmetry elements, symmetry operations, character Tables and correlation tables for point and space groups [63].

| Symmetry element | Symmetry Operation |
|---|---|
| 1. Identity (E or I) | 1. Molecule or cell unchanged |
| 2. Axis of rotation ($C_n$) | 2. Rotation about axis by 2 π/n |
| 3. Center of symmetry or inversion center (i) | 3. Inversion of all atoms through center |
| 4. Plane (σ) | 4. Reflection on the plane |
| 5. Rotation-reflection axis ($S_n$) | 5. Rotation about axis by 2 π/n followed by reflection in the plane perpendicular to the axis |
| 6. Screw axis ($n_p$) | 6. Rotation followed by a translation |
| 7. Glide plane (c) | 7. Reflection followed by a translation |

**Character Tables** [63]

Character tables are selected for the symmetry point groups those are relevant to the studied compounds. The components of the polarizability e.g, $\alpha_{yy}$, $\alpha_{zz}$ are listed in the row for a certain species in the last column for Raman active species. Similarly, the translation components $T_x$, $T_y$ and $T_z$ are listed in the third column for infrared active species.

**The $C_{2v}$ Group**

| $C_{2v}$ | $E$ | $C_2$ | $\sigma_v(xz)$ | $\sigma_v(yz)$ | Activity | |
|---|---|---|---|---|---|---|
| | | | | | **IR** | **Raman** |
| $A_1$ | 1 | 1 | 1 | 1 | $T_z$ | $\alpha_{xx}$, $\alpha_{yy}$, $\alpha_{zz}$ |
| $A_2$ | 1 | 1 | -1 | -1 | $R_z$ | $\alpha_{xy}$ |
| $B_1$ | 1 | -1 | 1 | -1 | $T_x$, $R_y$ | $\alpha_{xz}$ |
| $B_2$ | 1 | -1 | -1 | 1 | $T_y$, $R_x$ | $\alpha_{yz}$ |

**The $C_{2h}$ Group**

| $C_{2h}$ | $E$ | $C_2$ | $i$ | $\sigma_h$ | Activity | |
|---|---|---|---|---|---|---|
| | | | | | **IR** | **Raman** |
| $A_g$ | 1 | 1 | 1 | 1 | $R_z$ | $\alpha_{xx}$, $\alpha_{yy}$, $\alpha_{zz}$, $\alpha_{xy}$ |
| $A_u$ | 1 | 1 | -1 | -1 | $T_z$ | |
| $B_g$ | 1 | -1 | 1 | -1 | $R_x$, $R_y$ | $\alpha_{yz}$, $\alpha_{xz}$ |
| $B_u$ | 1 | -1 | -1 | 1 | $T_x$, $T_y$ | |

**The Cubic Group**

| $T_d$ | $E$ | $8C_3$ | $3C_2$ | $6S_4$ | $6\sigma_d$ | Activity | |
|---|---|---|---|---|---|---|---|
| | | | | | | **IR** | **Raman** |
| $A_1$ | 1 | 1 | 1 | 1 | 1 | | $\alpha_{xx} + \alpha_{yy} + \alpha_{zz}$ |
| $A_2$ | 1 | 1 | 1 | -1 | -1 | | |
| $E$ | 2 | -1 | 2 | 0 | 0 | | $\alpha_{xx} + \alpha_{yy} - 2\alpha_{zz}$, $\alpha_{xx} - \alpha_{yy}$ |
| $F_1$ | 3 | 0 | -1 | 1 | -1 | $R_x$, $R_y$, $R_z$ | |
| $F_2$ | 3 | 0 | -1 | -1 | 1 | $T_x$, $T_y$, $T_z$ | $\alpha_{xy}$, $\alpha_{yz}$, $\alpha_{xz}$ |

**Correlation Tables**

The correlation tables illustrate the correlation between the point group and site group of a particular vibrating species.

| $D_{2h}^{16}$ | $D_2$ | $C_2(z)$ $C_{2v}$ | $C_2(y)$ $C_{2v}$ | $C_2(x)$ $C_{2v}$ | $C_2(z)$ $C_{2h}$ | $C_2(y)$ $C_{2h}$ | $C_2(x)$ $C_{2h}$ |
|---|---|---|---|---|---|---|---|
| $A_g$ | $A$ | $A_1$ | $A_1$ | $A_1$ | $Ag$ | $A_g$ | $A_g$ |
| $B_{1g}$ | $B_1$ | $A_2$ | $B_2$ | $B_1$ | $A_g$ | $B_g$ | $B_g$ |
| $B_{2g}$ | $B_2$ | $B_1$ | $A_2$ | $B_2$ | $B_g$ | $A_g$ | $B_g$ |
| $B_{3g}$ | $B_3$ | $B_2$ | $B_1$ | $A_2$ | $B_g$ | $B_g$ | $A_g$ |
| $A_u$ | $A$ | $A_2$ | $A_2$ | $A_2$ | $A_u$ | $A_u$ | $A_u$ |
| $B_{1u}$ | $B_1$ | $A_1$ | $B_1$ | $B_2$ | $A_u$ | $B_u$ | $B_u$ |
| $B_{2u}$ | $B_2$ | $B_2$ | $A_1$ | $B_1$ | $B_u$ | $A_u$ | $B_u$ |
| $B_{3u}$ | $B_3$ | $B_1$ | $B_2$ | $A_1$ | $B_u$ | $B_u$ | $A_u$ |

| $D_{2h}^{16}$ (cont.) | $C_i$ | $C_2(z)$ $C_2$ | $C_2(y)$ $C_2$ | $C_2(x)$ $C_2$ | $\sigma(xy)$ $C_s$ | $\sigma(zx)$ $C_s$ | $\sigma(yz)$ $C_s$ |
|---|---|---|---|---|---|---|---|
| $A_g$ | $A_g$ | $A$ | $A$ | $A$ | $A'$ | $A'$ | $A_g$ |
| $B_{1g}$ | $A_g$ | $A$ | $B$ | $B$ | $A'$ | $A''$ | $A_g$ |
| $B_{2g}$ | $A_g$ | $B$ | $A$ | $B$ | $A''$ | $A'$ | $A_g$ |
| $B_{3g}$ | $A_g$ | $B$ | $B$ | $A$ | $A''$ | $A''$ | $A_g$ |
| $A_u$ | $A_u$ | $A$ | $A$ | $A$ | $A''$ | $A''$ | $A_u$ |
| $B_{1u}$ | $A_u$ | $A$ | $B$ | $B$ | $A''$ | $A'$ | $A_u$ |
| $B_{2u}$ | $A_u$ | $B$ | $A$ | $B$ | $A'$ | $A''$ | $A_u$ |
| $B_{3u}$ | $A_u$ | $B$ | $B$ | $A$ | $A'$ | $A'$ | $A_u$ |

| $T_d$ | $T$ | $D_{2d}$ | $C_{3v}$ | $S_4$ | $D_2$ | $C_{2v}$ |
|---|---|---|---|---|---|---|
| $A_1$ | $A$ | $A_1$ | $A_1$ | $A$ | $A$ | $A_1$ |
| $A_2$ | $A$ | $B_1$ | $A_2$ | $B$ | $A$ | $A_2$ |
| $E$ | $E$ | $A_1 + B_1$ | $E$ | $A + B$ | $2A$ | $A_1 + A_2$ |
| $F_1$ | $F$ | $A_2 + E$ | $A_2 + E$ | $A + E$ | $B_1 + B_2 + B_3$ | $A_2 + B_1 + B_2$ |
| $F_2$ | $F$ | $B_2 + E$ | $A_1 + E$ | $B + E$ | $B_1 + B_2 + B_3$ | $B_1 + B_2 + B_3$ |

| $T_d$ (cont.) | $C_3$ | $C_2$ | $C_s$ |
|---|---|---|---|
| $A_1$ | $A$ | $A$ | $A'$ |
| $A_2$ | $A$ | $A$ | $A''$ |
| $E$ | $E$ | $2A$ | $A' + A''$ |
| $F_1$ | $A + E$ | $A + 2B$ | $A' + 2A''$ |
| $F_2$ | $A + E$ | $A + 2B$ | $2A' + A''$ |

**Space Groups and Site Symmetries**

| Space group | | | Site symmetries |
|---|---|---|---|
| Pnma | or | $D_{2h}^{16}$ | $2C_i(4); C_1(8); C_s(4)$ |
| $P2_1$ | or | $C_{2h}$ | $4C_i(2); C_2(2); C_1(4)$ |

**Primitive and Centered Lattices** [63]

| Unit Cell | Symbol | Number of Repeat Units in Cell |
|---|---|---|
| Primitive | *P* | 1 |
| Rhobohedral* | *R* | 3 or 1† |
| Body centered | *I* | 2 |
| Side centered | *A*, *B* or *C* | 2 |
| Face centered | *F* | 4 |

* Also called trigonal.

† There are cases in which the number of repeat units in the crystallographic cell may be three or one. For the cases where it is three, Z will be devisable by three. For example, for TiS, $D_{3d}^{5}$-R3$_1$m , $Z = 9$, and therefore $Z' = 9/3 = 3$. However, for $Cr_2O_3$ , $D_{3d}^{6}$-R3c $Z = 2$, $Z' = 2/1 = 2$. Thus in the latter crystal the cell can be considered to be primitive.

$$Z' = \text{number of molecules in the Bravais of primitive cell}$$

$$= \frac{Z\,(\text{number of molecules in crystallographic cell})}{\text{repeat units in cell}}$$

If $Z = 4$ for an $F$-type lattice, then

$$Z' = 4/4 = 1$$

# Appendix C

- **Vibrational and Librational Modes of a Water Molecule**
- **Normal Modes of Vibration of Tetrahedral $XY_4$-$T_d$ Molecule**

**Vibrational and Librational Modes of Water Molecule**

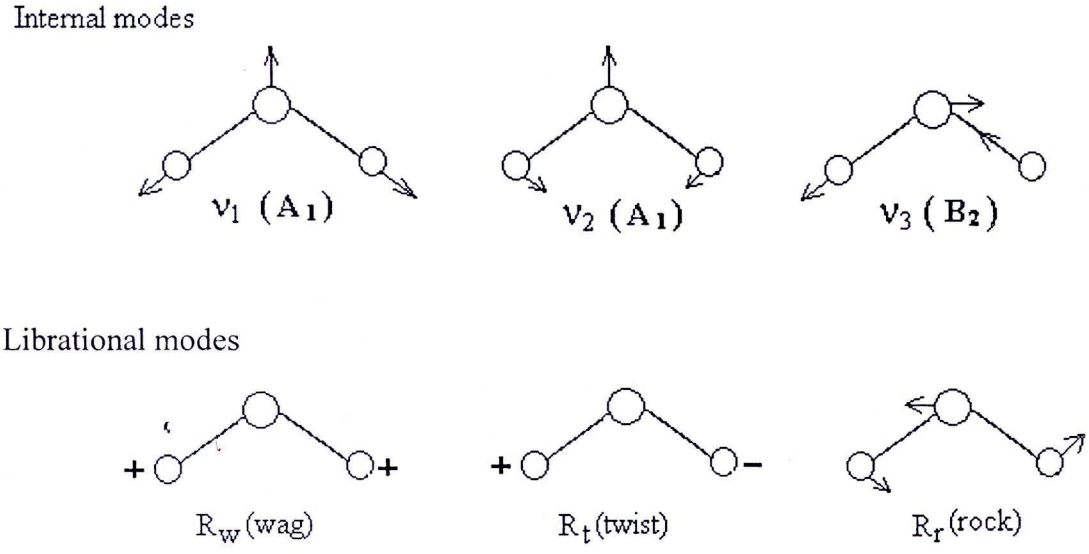


**Figure A.8** Vibrational and librational modes of a water molecule

**Table A.3** Vibrational frequencies of $H_2O$, HOD and $D_2O$ ($cm^{-1}$) in vapor state [19]

| Assignment | $H_2O$ | HOD | $D_2O$ |
|---|---|---|---|
| Symmetric stretching. | 3657<br>$\nu_1(A_1)$ | 2727<br>$\nu_{OD}(A')$ | 2671<br>$\nu_1(A_1)$ |
| Bending | 1595<br>$\nu_2(A_1)$ | 1402<br>$\nu_2(A')$ | 1178<br>$\nu_2(A_1)$ |
| Asymmetric stretching | 3756<br>$\nu_3(B_2)$ | 3707<br>$\nu_{OH}(A'')$ | 2788<br>$\nu_3(B_2)$ |

**Table A.4** Observed water bands ($cm^{-1}$) in hydrates [16]

| Type | $H_2O$ | HOD | $D_2O$ |
|---|---|---|---|
| Stretching modes (ν) | 3600-3000 | 2600-2300[a] | 2650-2300 |
| Bending modes (δ) | 1660-1590 | 1460-1400 | 1225-1175 |
| Library (R)* | 900-350 | 900-260[b] | 680-260 |
| Translatory modes (T') | 350-100 | | 330-95 |

* hindered rotation

[a] Uncoupled $\overline{\nu}_{OD}$ of isotopically dilute HDO. [b] Relatively large energy range due to the possibility of H and D out-of - plane motions

**Normal Modes of Vibration of Tetrahedral $XY_4$ Molecule ($T_d$)** [63]

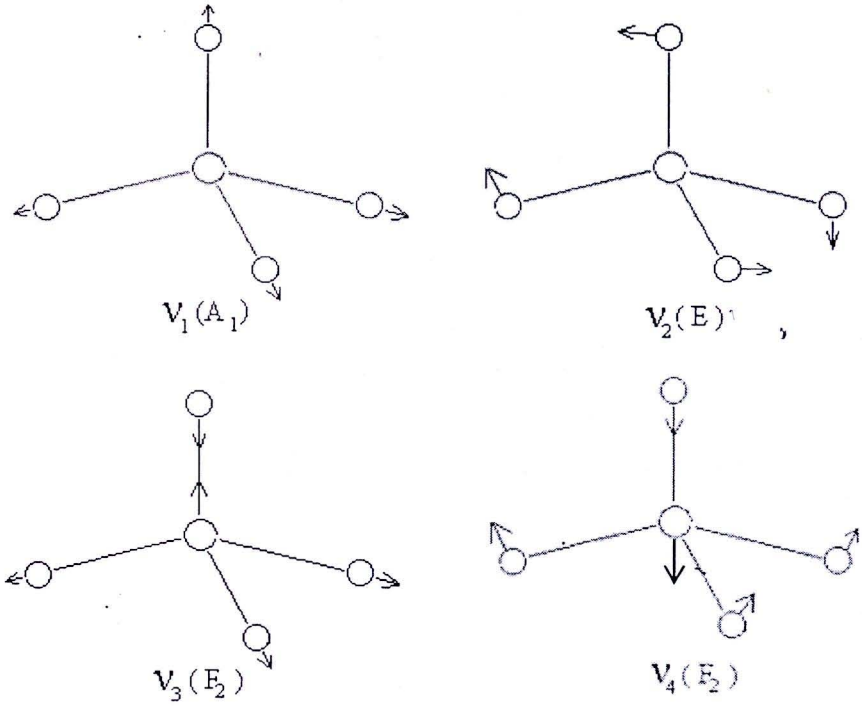


**Figure A.9** Vibrational modes of $PO_4^{3-}$ with $T_d$ point group[63]

**Table A.5** Vibrational frequencies ($cm^{-1}$) of $PO_4^{3-}$ [114]

| Ions | $\nu_1(A_1)$ | $\nu_2(E)$ | $\nu_3(F_2)$ | $\nu_4(F_2)$ |
|---|---|---|---|---|
| $PO_4^{3-}$ | 970 | 358 | 1080 | 500 |

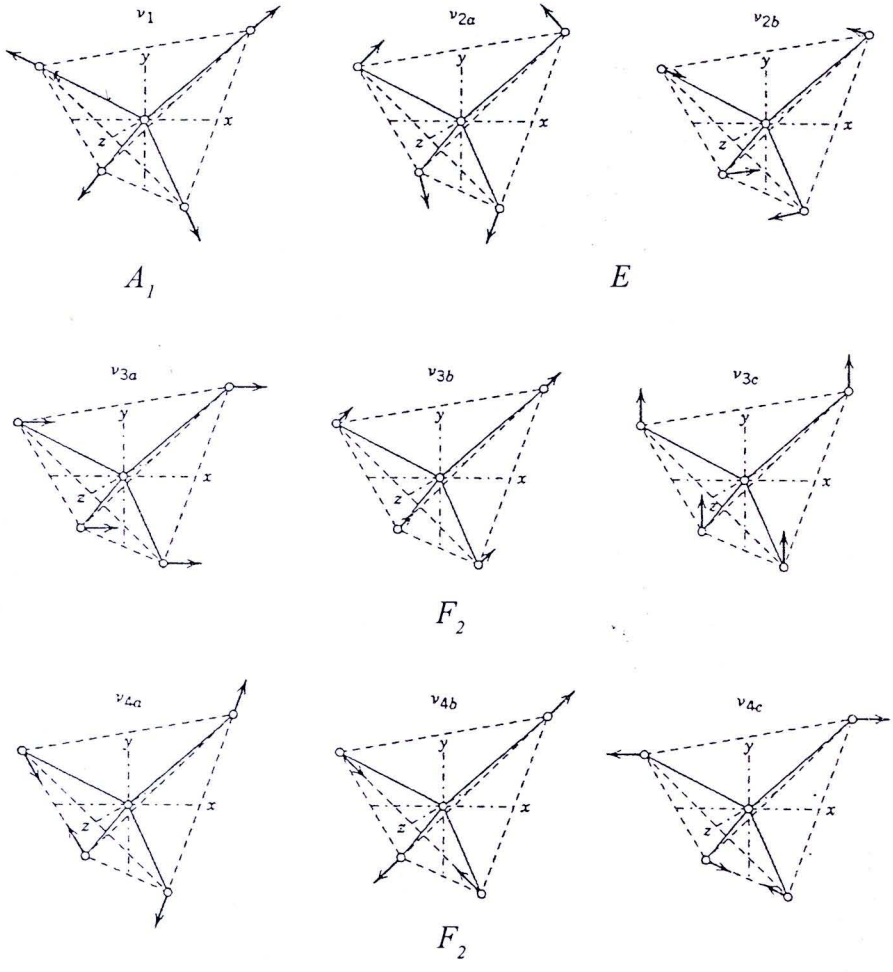


**Figure A.10** Normal modes of vibration for an $XY_4$ ($T_d$) symmetry

# Appendix D

## FTIR Spectrum of KBr

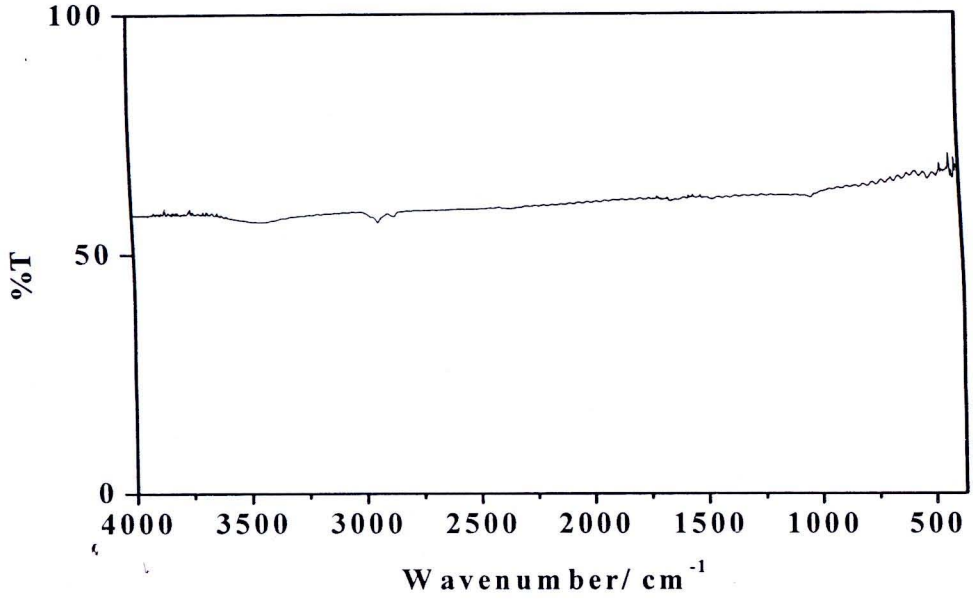


**Figure A.11** FTIR spectrum of KBr pellet in the region of 4000-370 $cm^{-1}$ recorded on a Perkin Elmer FTIR spectrum GX spectrophotometer

# Appendix E

## Instruments

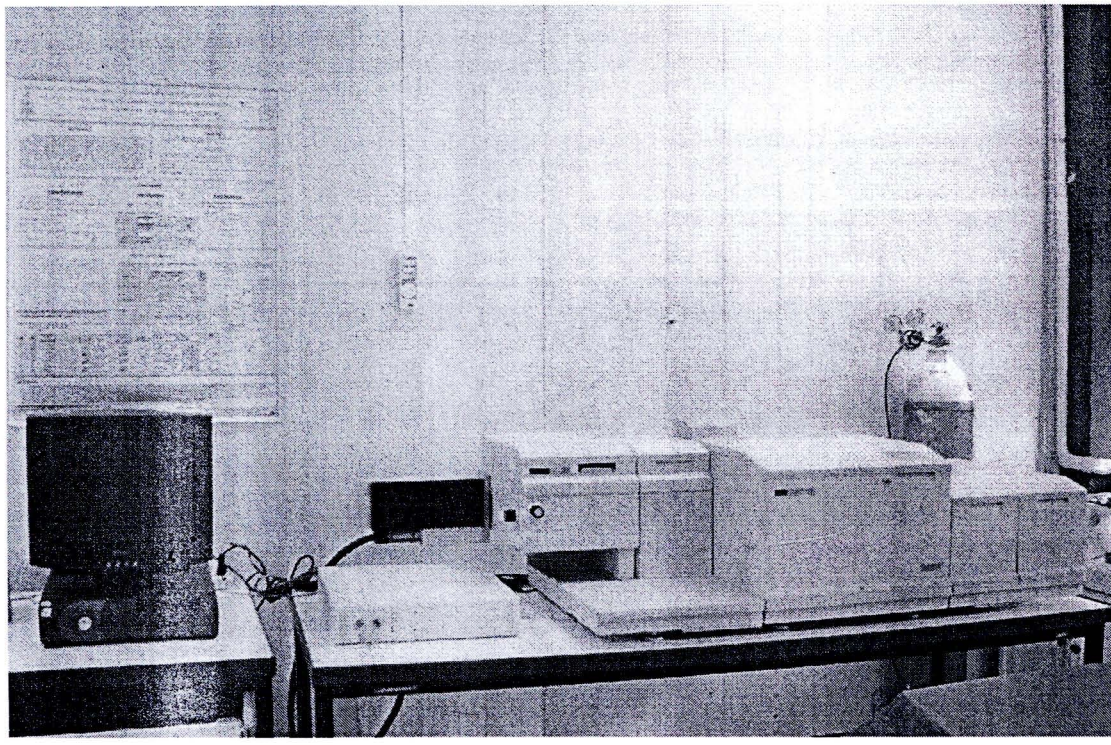

**Figure A.12** FTIR/ FT Raman Spectrophotometer, Perkin Elmer Spectrum GX

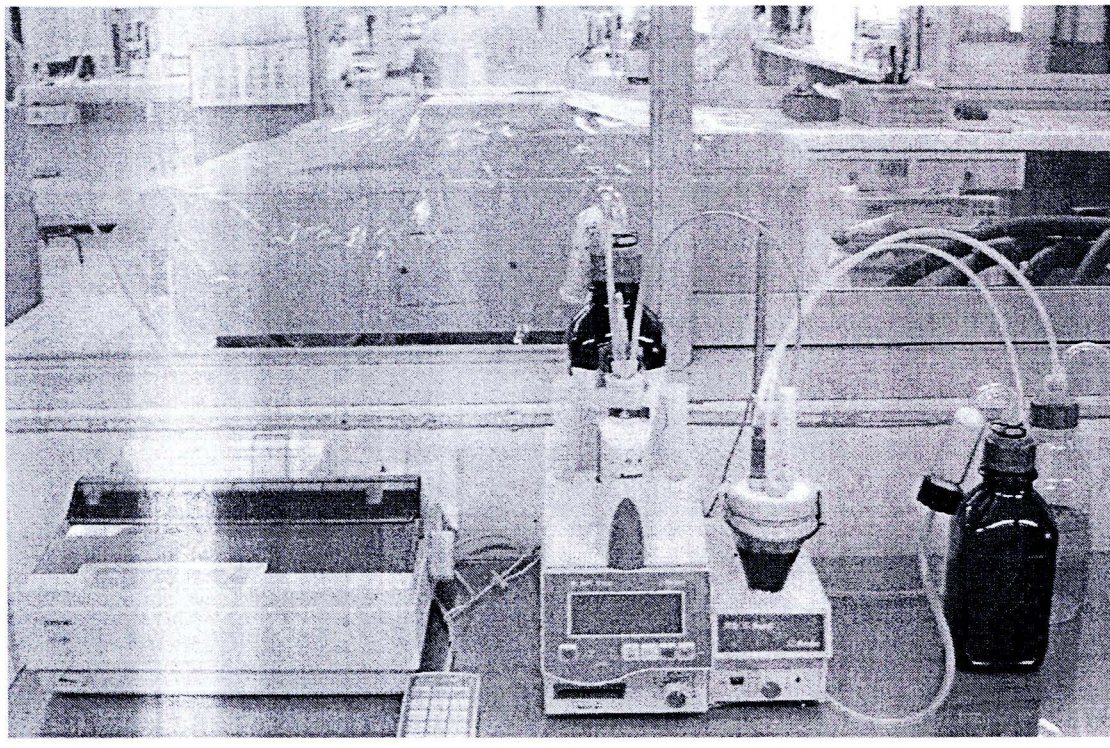

**Figure A.13** Karl Fischer Automatic Titrator (Metrohm 798 MPT Titrino)

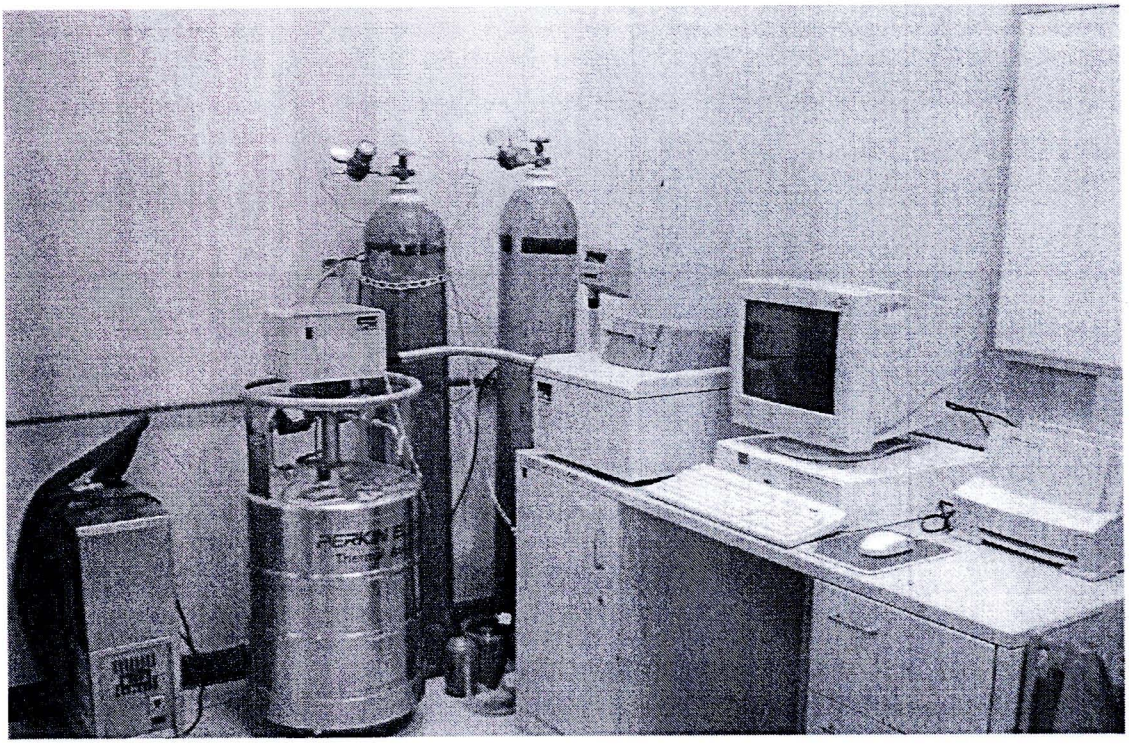

**Figure A.14** Differential Scanning Calorimeter (DSC), Perkin Elmer Pyris One

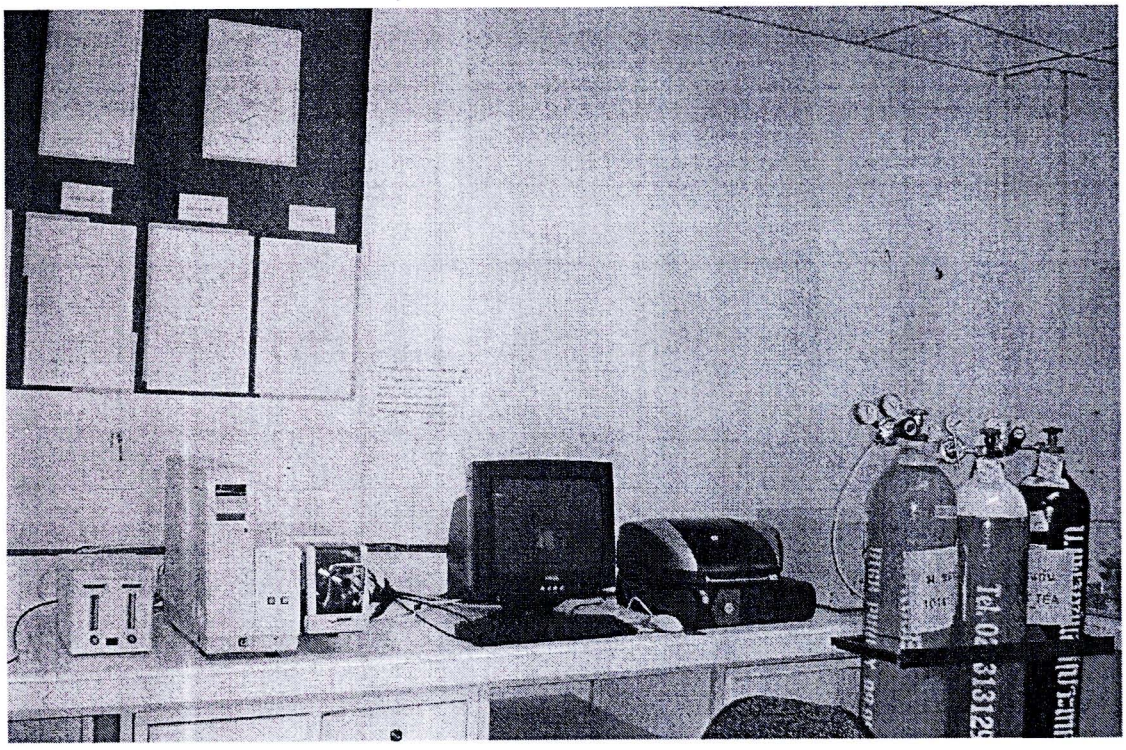

**Figure A.15** Thermal Gravimetric Analyzer, Differential Thermal Gravimetric, and Differential Thermal Analyzer (TGA/DTG/DTA), Perkin Elmer Pyris Diamond

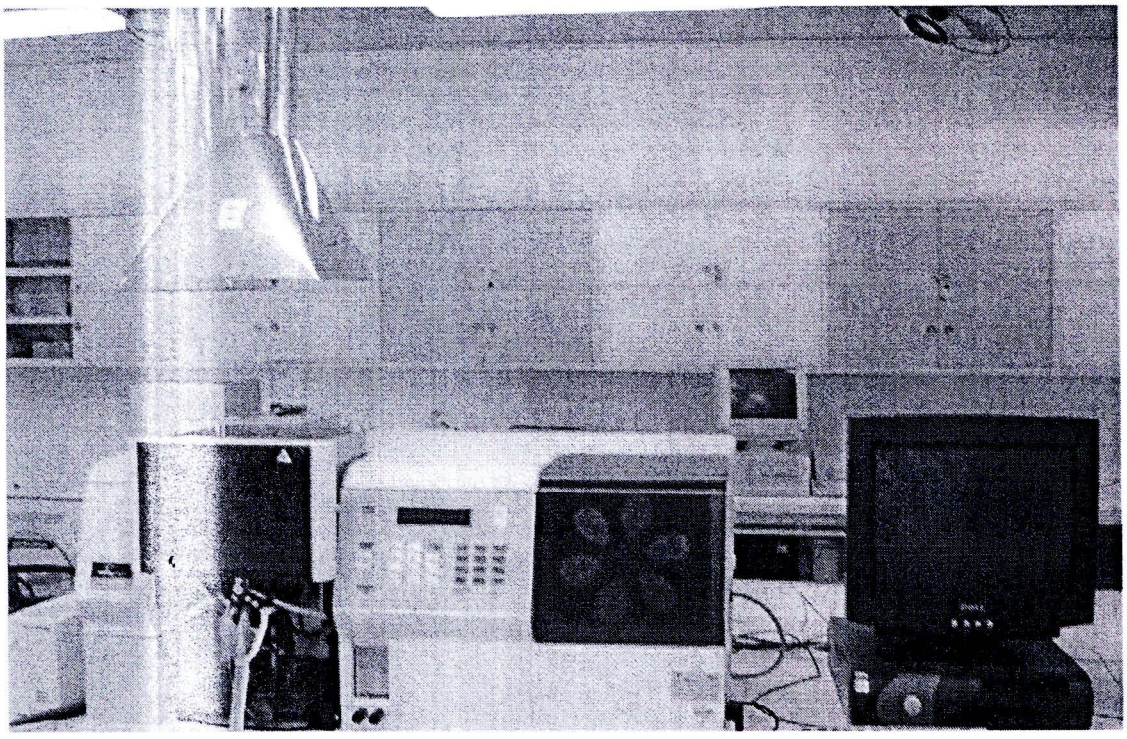

**Figure A.16** Atomic Absorption Spectrophotometer (AAS)/ Atomic Emission Spectrophotometer (AES), Perkin Elmer Analyst 100

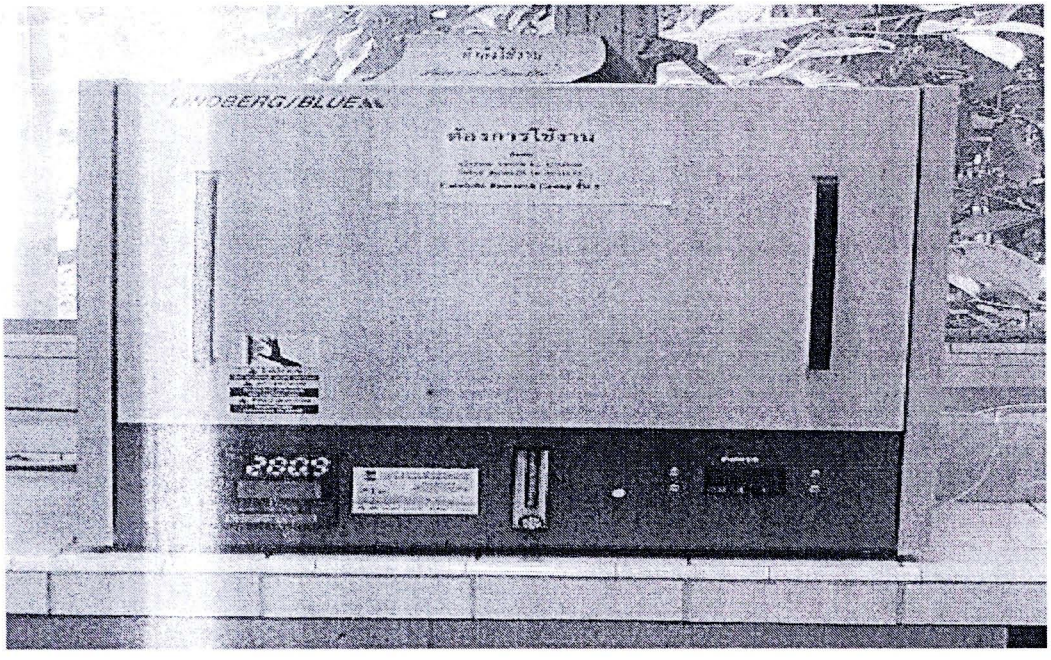


**Figure A.17** Oven (Lindberg 0-1200 $^{O}$C)

# Appendix F

## Publications

12th National Graduate Research Conference
CGAU and Khon Kaen University
February 12-13, 2009

PMP7

# Synthesis, Thermal Properties and Vibrational Spectroscopic Study of Dilithium Zinc Hydrogenphosphates Monohydrate ($Li_2Zn(HPO_4)_2.H_2O$)

# การสังเคราะห์ สมบัติทางความร้อนและการศึกษาสเปกโทรสโกปีการสั่นของไดลิเทียมซิงค์ไฮโดรเจนฟอสเฟตโมโนไฮเดรต

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Tipaporn Srithanratana (ทิพาภรณ์ ศรีธัญรัตน์) **

## ABSTRACT

Dilithium zinc hydrogenphosphates monohydrate ($Li_2Zn(HPO_4)_2.H_2O$) was synthesized from the reaction between zinc acetyl acetonate monohydrates ($Zn(C_5H_7O_2)_2.H_2O$) , phosphoric acid ($H_3PO_4$) and lithium hydroxide monohydrate ($LiOH.H_2O$) at room temperature. The synthesized samples were characterized by AES/AAS, XRD methods, and FTIR/FT Raman spectroscopy. The results confirm the structures of $Li_2Zn(HPO_4)_2.H_2O$ and its three calcined products, which two of them are heterogeneous catalysts. The selected solid sample undergoes two endothermic thermal transformations according to DSC curves. The first transformation is due to the release of water molecule of crystallization at 187.23 °C. The second one is at 286.25 °C, which is due to the release of water of constituent from $HPO_4^{2-}$ and transforms to $P_2O_7^{4-}$.

## บทคัดย่อ

ได้เตรียมไดลิเทียมซิงค์ไฮโดรเจนฟอสเฟตโมโนไฮเดรต ($Li_2Zn(HPO_4)_2.H_2O$) จากปฏิกิริยาระหว่าง ซิงค์อะซิติล อะซิโตเนต โมโนไฮเดรต ($Zn(C_5H_7O_2)_2.H_2O$) กรดฟอสฟอริก ($H_3PO_4$) และ ลิเทียมไฮดรอกไซด์ โมโนไฮเดรต ($LiOH.H_2O$) ที่อุณหภูมิห้อง การพิสูจน์เอกลักษณ์ของสารที่เตรียมได้อาศัยวิธี AES/AAS, XRD และสเปก โทรสโกปี FTIR/FT Raman ผลการทดลองยืนยันว่าเป็นโครงสร้างของ $Li_2Zn(HPO_4)_2.H_2O$ และผลิตผลสามตัวจากการแคลไซน์ ซึ่งสองตัวเป็นตัวเร่งปฏิกิริยาแบบวิวิธภัณฑ์ สารตัวอย่างแสดงการเปลี่ยนแปลงทางความร้อนแบบดูดความร้อนมีสองตำแหน่งตามกราฟ DSC ตำแหน่งการเปลี่ยนแปลงแรกคือที่ 187.23 °C เนื่องมาจากการปลดปล่อยโมเลกุลของน้ำผลึก ตำแหน่งที่สองที่ 286.25 °C เกิดจากการปลดปล่อยน้ำที่เป็นองค์ประกอบใน $HPO_4^{2-}$ แล้วเปลี่ยนไปเป็น $P_2O_7^{4-}$

**Key Words :** Thermal properties, FTIR/FT Raman spectra, $Li_2Zn(HPO_4)_2.H_2O$
**คำสำคัญ :** สมบัติทางความร้อน เอฟทีไออาร์/เอฟทีรามาน สเปกตรัม $Li_2Zn(HPO_4)_2.H_2O$

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12 National Graduate Research Conference
CGAU and Khon Kaen University
February 12-13, 2009



## Introduction

Layered acid phosphate are of continuing academic and industrial interest because of their extensive applications as heterogeneous catalysts (J.M. Thomas. et al, 1990,1992). Some of them can undergo ion exchange and reversible hydration in the same way as zeolites. Open-framework materials of aluminosilicates (zeolites) and aluminiphosphates with varying dimensions are of great interest for their chemical and physical properties and plethora of other applications (L. Flem. et al, 1991 and J.M. Thomas et al, 1994,1997). It is now established the amongst the non-zeolitic solid, the phosphate based open-framework materials display considerable structural diversity (A.K. Cheetham. et al, 1999). Of these, the metal phosphates, especially those of zinc, are interesting as they form structures similar to zeolites (T.E. Gier. et al, 1991 and X. Bu. et al, 1997) . The structure of lithium zinc hydrogenphosphate hydrate consists of lithium, zinc and phosphorus atoms tetrahedrally coordinated to oxygen atoms. The three-dimensional framework structure can be described as belonging to the family of stuffed cristobalite structure with zinc and phosphorus atoms as framework tetrahedral atoms (X. Bu et al, 1998). The extra-framework comprizers of lithium and water molecule, which are located in the cavity of the system (W.T.A. Harrision. et al, 1995). The water layers in lithium zinc hydrogenphosphate monohydrate can undergo reversible dehydration and rehydration provided it is not heated beyond 200 °C.

Recently, Harrison and co-workers (W.T.A. Harrision. et al, 1994) reported the low-temperature (~0°C) synthesis of a new layered two-dimensional zincophosphate material, $Na_2Zn(HPO_4)_2.4H_2O$, containing a network of layers of bifurcated tretrahedral 12-rings connected by sodium cations and hydrogen bonds. This work reports the preparation of $Li_2Zn(HPO_4)_2.H_2O$ by the ambient condition route.

The aim of this work was to synthesize $Li_2Zn(HPO_4)_2.H_2O$, and to study the vibrational spectra as well as the thermal transformation by using differential scanning calorimetry (DSC). Then the sample were characterized by standard methods.

## Materials and methods

### *Preparation*

The dilithium zinc hydrogenphosphate monohydrate, $Li_2Zn(HPO_4)_2.H_2O$, powder samples were prepared in three replications at room temperature 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) in de-iornized water. The molar ratio of the Li:Zn:P was 2:1:2 (A. Bensalem. et al, 2001). The reaction mixture led to the formation of a gelatinous white precipitate (~20 min). The precipitate was recovered by filtration, washed with de-ionized water several times and dried at 110 °C in air for 2 h.

### *Characterization*

The lithium and zinc content of the synthesized sample was determined by dissolving in 0.15 molar of nitric acid using atomic emission and atomic absorption spectrophotometry (AES and AAS, Perkin-Elmer, analyst100). The water content was analyzed by using the Karl-Fischer method. Thermal property of prepared sample was investigated on a differential scanning calorimeter by using about 5-10 mg of sample in an aluminium crucibles. The

thermogram was recorded over the temperature range of 60-600 °C using differential scanning calorimeter (DSC), Perkin-Elmer Pyris One. The heating rate employed was 10 °C $min^{-1}$. The structure of synthesized compound and the calcined products were studies by X-ray powder diffraction using D8 Advanced Powder Diffractometer (Bruker AXS, Karlsruhe, Germany) with Cu $K_\alpha$ radiation ($\lambda$ = 0.15406 Å). The diffraction patterns were taken in the range of $5° < 2\theta < 70°$ and the $2\theta$ step size was 0.02°. The FTIR and FT Raman spectra of synthesized compound and the calcined samples were recorded using KBr pellets on a Perkin-Elmer spectrum GX FTIR/FT Raman spectrophotometer in the range of 4000-370 $cm^{-1}$ with the resolution of 4 $cm^{-1}$ and 32 scans.

## Results and discussion

***Determination of metal (Li and Zn) and water content.***

The lithium and zinc content of prepared sample were determined by AES and AAS method and the mole ratio of Li:Zn was found to be 2.09:1.07. The water content of synthesized sample was confirmed by the Karl-Fischer method and the mole ratio of salt:$H_2O$ was found to be 1.00:1.13 Therefore, the formula of as-prepared compound can be $Li_2Zn(HPO_4)_2.H_2O$.

***Differential scanning calorimetry (DSC)***

The DSC curve of as-prepared sample (Figure 1) shows two endothermic peaks at 187.23 and 286.25 °C (onset peak at 179.04, 270.76 °C). The first one can be attributed to the removal of water of crystallization molecules in the structure. In fact, IR spectrum of the sample heated at 200 °C for 2 hr shows the lowing of the intensities of O-H stretching and bending vibrations attributed to water molecules (Figure 3b). The second step, observed at 286.25 °C can be assigned to the loss of water due to the additional dehydration from $HPO_4^{2-}$ anion and transform into $P_2O_7^{4-}$ ions [A. Bensalem. Et al, 1997, 2001 and 2007). The XRD data of the sample calcined at 450 °C for 2 hr shows transformation from $HPO_4^{2-}$ to $P_2O_7^{4-}$, which leads to a mixed phased of $Zn_2P_2O_7$ and $Li_4P_2O_7$ (A. Bensalem. et al, 2001 and 2007). This can be also confirmed by the FTIR spectrum of the sample calcined at 450 °C (Figure 3c). According to the DSC curve, the heat of dehydration and decomposition can be calculated and found to be 443.635 and 269.264 J/g for the first and second step, respectively.

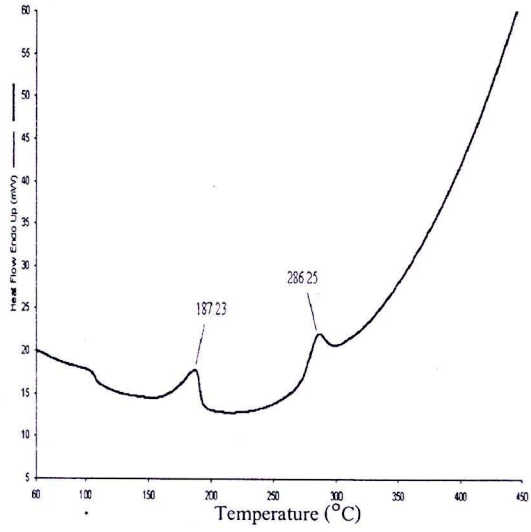


**Figure 1** DSC curve of the synthesized $Li_2Zn(HPO_4)_2.H_2O$ at the heating rate of 10 °C in $N_2$ atmosphere.

The structural changes due to two consecutive losses of water as the following equations:

$$Li_2Zn(HPO_4)_2.H_2O \xrightarrow{187\ ^\circ C} Li_2Zn(HPO_4)_2 + H_2O$$

$$Li_2Zn(HPO_4)_2 \xrightarrow{286\ ^\circ C} \tfrac{1}{2}(Zn_2P_2O_7) + \tfrac{1}{2}(Li_4P_2O_7) + H_2O$$

***X-ray powder diffraction***

The XRD patterns of the prepared $Li_2Zn(HPO_4)_2.H_2O$ and the calcined $Li_2Zn(HPO_4)_2.H_2O$ at 200 and 450 °C are illustrated in Figures 2(a), 2(b) and 2(c), respectively. All detectable peaks of the sample and the calcined products at 200 and 450 °C indexed as synthesized $Li_2Zn(HPO_4)_2.H_2O$ (Figure 2a) (A. Bensalem, 2001), $Li_2Zn(HPO_4)_2$ (Figure 2b) and the mixed phase of $Zn_2P_2O_7$ - $Li_4P_2O_7$ (Figure 2c) (PDF # 870409 and JCPDF 08-0038: Private Communication, 1998), respectively.

***FTIR and FT Raman spectroscopy***

The FTIR spectra of $Li_2Zn(HPO_4)_2.H_2O$ and its calcined products at 200 and 450 °C are presented in Figure 3. The bands assignment for the FTIR spectra of the studied compound are summarized in Table 1 and the corresponding FTIR spectra is reported in Figure 3.

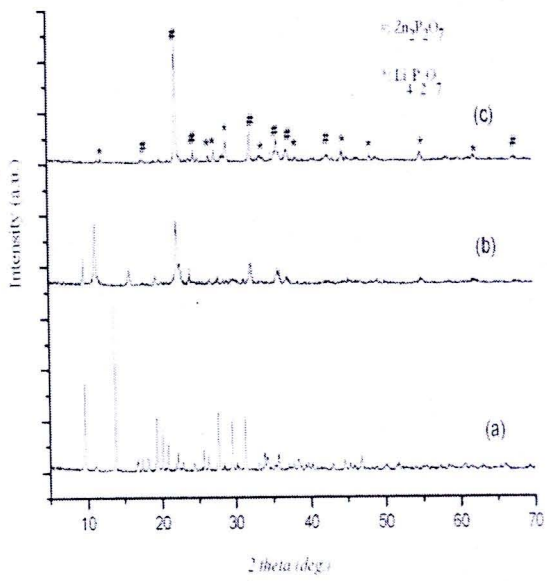


**Figure 2** X-ray diffraction patterns of : (a) the as-prepared sample, (b) the as- prepared sample calcined at 200 °C and (c) the as-prepared sample calcined at 450 °C.

**Table 1** the FTIR and FT Raman bands positions ($cm^{-1}$) at room temperature of $Li_2Zn(HPO_4)_2.H_2O$

| Wavenumber ($cm^{-1}$) | | Assignment |
|---|---|---|
| FTIR | FT Raman | |
| 3536 w | - | $\nu_{as}$(H-OP) |
| 3480 m | 3492 m | $\nu_s$(H-OP) |
| - | 3350 m | $\nu_3(B_2)$ $H_2O$ |
| 3275 w | 3237 w | $\nu_1(A_1)$ $H_2O$ |
| 1609 s | 1658 m | $\nu_2(A_1)$ $H_2O$ |
| 1121 m, 1066 s, | 1116 m, 1054 s, | |
| 1007 s, | 1001m | $\nu_3(F_2)$ $PO_4^{3-}$ |
| 948 s | - | $\nu_1(A_1)$ $PO_4^{3-}$ |
| 631 s, 613 m, | 658 m | |
| 574 m | | $\nu_4(F_2)$ $PO_4^{3-}$ |
| 563 w, 507 m | 564 m | $\rho(H_2O)$ |
| 470 m, 414 m | 443 m, 417.m | $\nu_2(E)$ $PO_4^{3-}$ |
| 399 w, 375 s | - | $\nu$(M-O) |

The free $H_2O$ molecule processes $C_{2v}$ symmetry. There are three normal modes of vibration namely the symmetric ($\nu_1$; $A_1$), antisymmetric stretching $\nu_3(B_2)$ and bending ($\nu_2$; $A_1$) vibrations. The bands at 3275 and 1609 $cm^{-1}$ are assigned to the O-H stretching and bending vibrational modes of water, respectively. The band observed at 563 and 507 $cm^{-1}$ are assigned to the librational modes of water, which were confirmed by their disappearances in the anhydrous compound as shown in Figure 3(b).

The vibrational bands of phosphate anion for $Li_2Zn(HPO_4)_2.H_2O$ are observed in 1100-400 $cm^{-1}$ region, while the phosphate ion vibrations are found at 1121, 1066 and 1007 $cm^{-1}$, those are attributed to asymmetric stretching $\nu_3(F_2)$ vibrations (removal of degeneracey). The band observed at 948 $cm^{-1}$ is assigned to symmetric stretching $\nu_1(A_1)$ vibration of phosphate group. The bands at 631, 613 and 574 $cm^{-1}$ are attributed to removal of triply degenerate asymmetric bending $\nu_4(F_2)$ vibrations and the bands at 470 and 414 $cm^{-1}$ are assigned to the removal of doubly degenerate symmetric bending $\nu_2(E)$ vibrations (K. Nakamoto, 1963 and B. Boonchom. Et al, 2008).

The FTIR spectrum of the calcined $Li_2Zn(HPO_4)_2.H_2O$ at 200 °C (Figure 3b) illustrates the same characteristic as that of $Li_2Zn(HPO_4)_2$ showed the disappearance of the O-H vibration, while the calcined product at 450 °C (Figure 3c) exhibits the same FTIR characteristic bands as that of $Li_4P_2O_7$ and $Zn_2P_2O_7$, which are based on the fundamental vibrating unit $P_2O_7^{4-}$ anion.

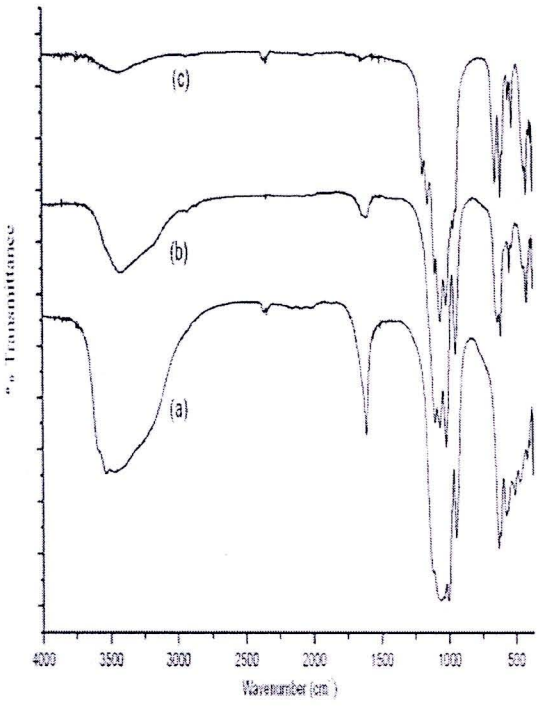


**Figure 3** The FTIR spectra of: (a) the as-prepared sample, (b) the as-prepared sample heated at 200 °C and (c) the as-prepared sample calcined at 450 °C

The FT Raman spectra of $Li_2Zn(HPO_4)_2.H_2O$ is shown in Figure 4. The bands assignment for the FT Raman of the studied compound are summarized in Table 1. In all spectra, the vibrational bands appear in the 1200-500 $cm^{-1}$ region corresponding to the stretching of phosphate, exhibit mostly the same feature as FTIR spectra. However, some vibrational bands are not observed in the FT Raman spectrum, which may be due to the selection rule or the asymmetric character. One very weak band near 3350 $cm^{-1}$ is observed in the FT Raman spectra of $Li_2Zn(HPO_4)_2.H_2O$, which is assigned to $\nu_3(B_2)$ $H_2O$ (A.A. Salah. et al, 2005).

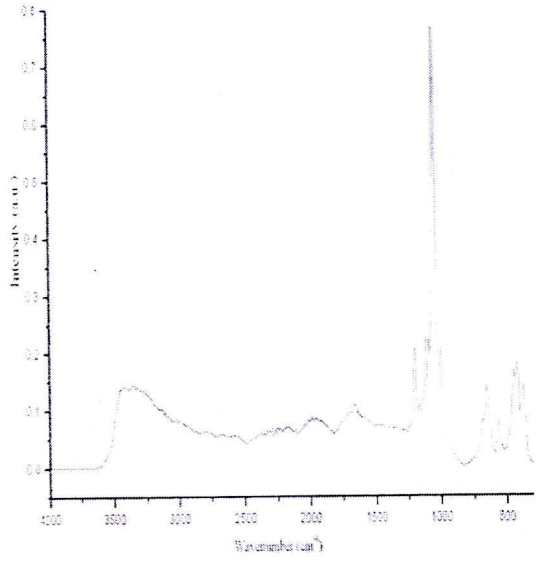

**Figure 4** FT Raman spectra of $Li_2Zn(HPO_4)_2.H_2O$ in the region of 4000-370 $cm^{-1}$

Finally, a study of the dehydration and rehydration processes in this compound, shown that the water molecules can be removed and rehydrated without disrupting the structure of the material, provided that the temperature is lower than 200 °C. The dehydration is performed by heating the sample at 200 °C for 2 hr, and the rehydration is performed by exposing the dehydrated sample to water for 2 hr under stirring for about 5000 r/min at ambient temperature. Then the surface water was then removed from the rehydrated sample by drying at 110 °C for 2 hr. This dehydration and rehydration processes were confirmed by the FT-IR spectra and the DSC curve. Indeed the DSC curve of the calcined sample at 200 °C (Figure 5a) does not show any endothermic peak at 187 °C which is the characteristic of the removal of water molecule as shown in Figure 6a, FTIR spectra showing the disappearance of O-H vibrations of water. The FTIR spectra (Figure 6b) and DSC curve (Figure 5b) of rehydration sample exhibit similar feature as those of the as-prepared sample.

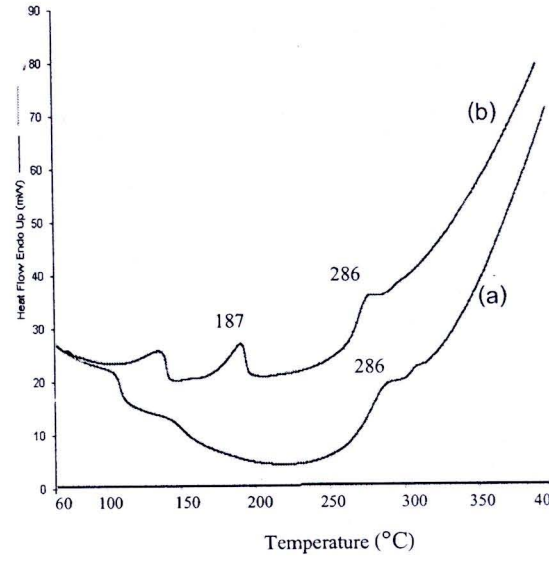


**Figure 5** The DSC curves of: (a) the dehydration of sample and (b) the rehydration of sample

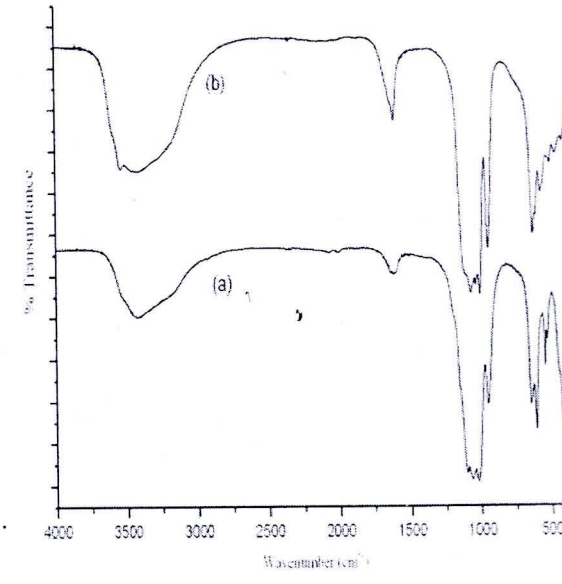


**Figure 6** The FTIR spectra of: (a) the as-prepared sample calcined at 200 °C and (b) the dehydrated sample exposed to moisture at room temperature for 2 hr.

## Conclusions

$Li_2Zn(HPO_4)_2.H_2O$ was synthesized and the thermal transformation occurs in two steps and the products are $Li_2Zn(HPO_4)_2$ and the mixed phases of $Li_4P_2O_7$-$Zn_2P_2O_7$, respectively. The synthesized $Li_2Zn(HPO_4)_2.H_2O$ and its thermal transformation products were confirmed by XRD, DSC, FTIR and FT Raman measurements. The heats of dehydration and decomposition are found to be 443.635 and 269.264 J/g for the first and second step, respectively. The water molecules in $Li_2Zn(HPO_4)_2.H_2O$, can be removed and rehydrated without destruction of the structure under the temperature of lower than 200 °C, which is similar to the case of zeolites. The synthesized $Li_2Zn(HPO_4)_2.H_2O$ and its decomposition products ($Li_4P_2O_7$ and $Zn_2P_2O_7$) powder can be useful for potential heterogeneous catalysts.

## Acknowledgements

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# Thermal decomposition kinetics and reversible hydration study of the $Li_2Zn(HPO_4)_2 \cdot H_2O$

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ABSTRACT

The dilithium zinc hydrogen phosphate monohydrate ($Li_2Zn(HPO_4)_2 \cdot H_2O$) was synthesized at the ambient temperature by using zinc acetyl acetonate monohydrate, phosphoric acid and lithium hydroxide monohydrate. The thermal stability of the $Li_2Zn(HPO_4)_2 \cdot H_2O$ was studied by non-isothermal kinetic method (Ozawa and Kissinger) from the differential scanning calorimetric (DSC) data. The studied hydrate undergoes two endothermic thermal transformations, which the first transformation is due to the release of water molecule of crystallization and the second one is due to the release of water of constituent from $HPO_4^{2-}$ anions and transforms to $P_2O_7^{4-}$. The activation energies ($E_a$) calculated for the dehydration step and decomposition step of the $Li_2Zn(HPO_4)_2 \cdot H_2O$ from different methods were found to be consistent. The dehydration and rehydration processes of the synthesized compound were investigated and found that the water of crystallization can be removed and rehydrated without the disrupting the structure of the material, provided it is not heated beyond 200 °C. The dehydration and rehydration processes of the synthesized $Li_2Zn(HPO_4)_2 \cdot H_2O$ exhibits similar property to the zeolite.



## 1. Introduction

Many metal hydrogen phosphates are used as heterogeneous catalysts for a variety of organic synthesis processes [1–3]. Because of their acidity and porosity, as layered materials they represent a vast class of intercalating compounds with useful chemical and thermal properties. There is a continuing academic and industrial interest in preparing new solid acid catalysts with different structures and acidities [4]. Thermal treatment of metal hydrogen phosphates is a great synthetic potential as they may turn simple compounds into advanced materials, such as ceramics, catalysts, and glasses. Open-framework materials of aluminosilicates and aluminophosphates with varying dimensions are of great interest [5–7]. It is now established that among the non-zeolite solid, the phosphate based open-framework material displays considerable structural diversity [8]. Among those metal phosphates, zincophosphate constitutes a large family. So far, zincophosphates with monomeric phases, chain, layers and three-dimension open-framework have been synthesized in the presence of different amines, alkali metal cations or metal complexes as structure directing agents [9]. Of these, the metal phosphates, especially those of zinc, are interesting as they form structures similar to zeolites.

The structure of lithium zinc hydrogen phosphate monohydrate consists of lithium, zinc and phosphorus atoms tetrahedrally coordinated to oxygen atoms. The three-dimensional framework structure can be described as belonging to the family of stuffed cristobalite structure with zinc and phosphorus atoms as framework tetrahedral atoms [10]. Some of them can undergo ion exchange and reversible hydration in the same way as zeolite. The interlayer species are water [11], ethanol and ethylene glycol [12]. The extra-framework comprises of lithium and water molecule, which are located in the layers of the system. The water layers in lithium zinc hydrogen phosphate monohydrate can undergo reversible dehydration and rehydration provided it is not heated beyond 200 °C [13]. A general objective of the analysis and prediction of thermally activated reactions is the derivation of a complete description of the progress of a reaction that is valid for any thermal treatment, such as isothermal, by linear heating or any other non-isothermal treatment [14–16]. The kinetic parameters, in many cases, also provide important information on thermal stability, rate of decomposition and life time prediction of materials and systems under different experimental and environmental conditions. The thermal analysis methods, particularly differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA), are the widely used methods for the evaluation of kinetic parameters of various reactions. The most widely used DSC method is the variable program rate method, which was originally developed by Kissinger for DSC. Later, Ozawa developed a simpler method which

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is popularly used for the calculation of kinetic parameters using TG and DSC data [17]. The method described in this paper is used to determine the activation energy $E_a$, for the thermal decomposition of the title compound from DSC data.

## 2. Experimental

The $Li_2Zn(HPO_4)_2 \cdot H_2O$ samples were prepared by the direct mixing of zinc acetyl acetonate monohydrate ($Zn(C_5H_7O_2)_2 \cdot H_2O$, 99% Fluka), phosphoric acid ($H_3PO_4$, 85 wt.% solution, Carlo Erba), and lithium hydroxide monohydrate ($LiOH \cdot H_2O$, 99% Fluka) in de-ionized water at ambient temperature. The molar ratio of the Li: Zn:P was 2:1:2. The reaction mixture led to the formation of a gelatinous white precipitate (~20 min). The precipitate was recovered by filtration, washed with de-ionized water several times and dried at 110 °C in air for 2 h [18]. The metal contents in synthesized samples were determined by atomic emission and atomic absorption spectrophotometry (AES and AAS, Perkin–Elmer, analyst100) for $Li^+$ and $Zn^{2+}$, respectively. The water content was analyzed by using the Karl Fischer method (Metrohm 798 MPT Titrino). Thermal property of the prepared sample was investigated on a DSC (Perkin–Elmer Pyris One) by using about 5–10 mg of sample in an aluminium pan. The thermogram was recorded over the temperature range of 60–600 °C and the heating rate of 10 °C $min^{-1}$. The structure of the synthesized compound and the calcined products were characterized by X-ray powder diffraction using D8 Advanced Powder Diffractometer (Bruker AXS, Karlsruhe, Germany) with Cu $K_\alpha$ radiation ($\lambda$ = 0.15406 Å). The diffraction patterns were taken in the range of $5° < 2\theta < 70°$ and the $2\theta$ step size was 0.02°. The FTIR spectra of the synthesized compound and the calcined samples were recorded using KBr pellets on an FTIR/FT Raman spectrophotometer (Perkin–Elmer spectrum GX) in the range of 4000–370 $cm^{-1}$ with the resolution of 4 $cm^{-1}$ and 32 scans.

## 3. Results and discussion

### 3.1. Characterization

The lithium, zinc and water content of the synthesized sample were found to be 2.09, 1.07 and 1.04 mol per formula, respectively. Therefore the structure of the as-prepared compound can be $Li_2Zn(HPO_4)_2 \cdot H_2O$.

The DSC curve of an as-prepared sample (Fig. 1) shows two endothermic peaks at 187 and 286 °C (onset at 179, 270 °C).

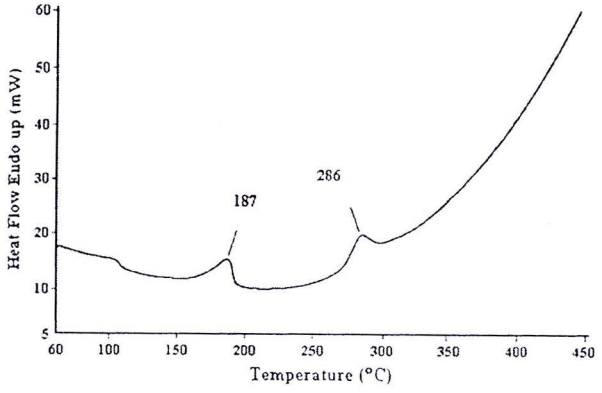


**Fig. 1.** DSC curve of the synthesized $Li_2Zn(HPO_4)_2 \cdot H_2O$ at the heating rate of 10 °C $min^{-1}$ in $N_2$ atmosphere.

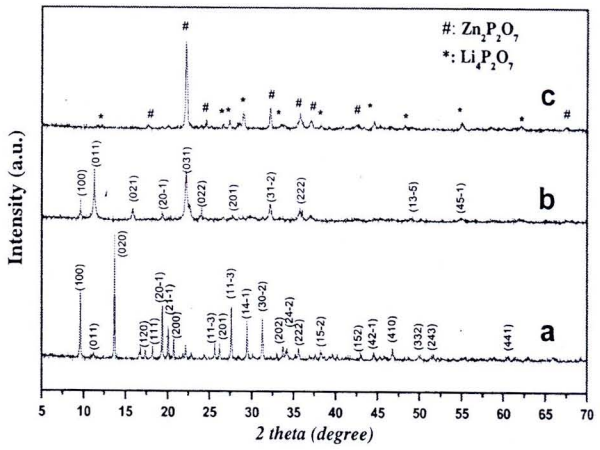


**Fig. 2.** X-ray diffraction patterns of: (a) the synthesized $Li_2Zn(HPO_4)_2 \cdot H_2O$, (b) the calcined sample at 200 °C and (c) the calcined sample at 450 °C.

The DSC curve in Fig. 1 illustrates a small endothermic peak at about 100 °C corresponding to the elimination of moisture or adsorbed water. The first step corresponds to the removal of water of crystallization molecules from the structure. The elimination of water molecules from the calcined sample at 200 °C (2 h) was confirmed by the disappearance of O–H stretching and bending vibrations attributed to water molecules in the FTIR spectrum (Fig. 3b). The second peak can be described to be due to the additional loss of water as the dehydration from the $HPO_4^{2-}$ anions and transforms into $P_2O_7^{4-}$ ions. The XRD pattern of the calcined sample at 450 °C (2 h) shows the transformation from $HPO_4^{2-}$ to $P_2O_7^{4-}$, which leads to a mixed phases of $Zn_2P_2O_7$ and $Li_4P_2O_7$. This can also be confirmed by the FTIR spectrum of the calcined sample at 450 °C (Fig. 3c). The structural changes due to two consecutive losses of water are suggested to be as the following equations:

$$Li_2Zn(HPO_4)_2 \cdot H_2O \xrightarrow{180°C} Li_2Zn(HPO_4)_2 + H_2O \quad (1)$$

$$Li_2Zn(HPO_4)_2 \xrightarrow{286°C} \frac{1}{2}(Zn_2P_2O_7) + \frac{1}{2}(Li_4P_2O_7) + H_2O \quad (2)$$

The XRD patterns of the synthesized $Li_2Zn(HPO_4)_2 \cdot H_2O$ and the calcined products at 200 and 450 °C are illustrated in Fig. 2a–c, respectively. All detectable peaks of the synthesized hydrate and

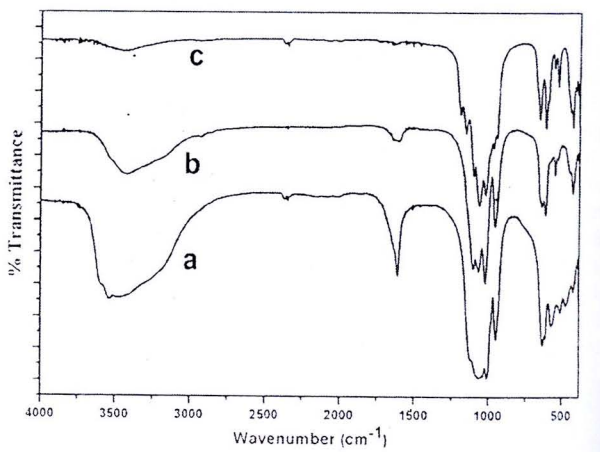


**Fig. 3.** The FTIR spectra of: (a) the as-prepared sample, (b) the calcined sample at 200 °C and (c) the calcined sample at 450 °C.

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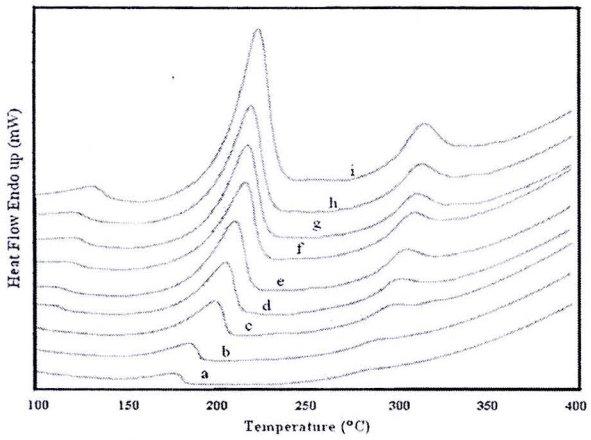


**Fig. 4.** DSC curves of the synthesized $Li_2Zn(HPO_4)_2 \cdot H_2O$ at different heating rates: $a = 5$, $b = 10$, $c = 20$, $d = 30$, $e = 40$, $f = 50$, $g = 60$, $h = 70$ and $i = 80$ °C $min^{-1}$ in $N_2$ atmosphere.

the calcined products at 200 and 450 °C are indexed as synthesized $Li_2Zn(HPO_4)_2 \cdot H_2O$ (Fig. 2a), $Li_2Zn(HPO_4)_2$ [13] (Fig. 2b) and the mixed phase of $Zn_2P_2O_7$–$Li_4P_2O_7$ (Fig. 2c) [19,20].

The FTIR spectra of $Li_2Zn(HPO_4)_2 \cdot H_2O$ and its calcined products at 200 and 450 °C are presented in Fig. 3a–c, respectively. The free $H_2O$ molecule possesses $C_{2v}$ symmetry. There are three normal modes of vibration namely the symmetric ($\nu_1$; $A_1$), antisymmetric stretching $\nu_3(B_2)$ and bending ($\nu_2$; $A_1$) vibrations. The bands at 3275 and 1609 $cm^{-1}$ are assigned to the O–H stretching and bending vibrational modes of water, respectively. The band observed at 507 $cm^{-1}$ is assigned to the librational mode of water, which was confirmed by its significantly decrease in the calcined product as shown in Fig. 3b. The vibrational bands of phosphate anion for $Li_2Zn(HPO_4)_2 \cdot H_2O$ are observed in 1100–400 $cm^{-1}$ region. The vibrational band at 1121, 1066 and 1007 $cm^{-1}$ are attributed to asymmetric stretching $\nu_3(F_2)$ vibrations (removal of degeneracy). The band observed at 948 $cm^{-1}$ is assigned to symmetric stretching $\nu_1(A_1)$ vibration of phosphate group. The bands at 631, 613 and 574 $cm^{-1}$ are attributed to removal of triply degenerate asymmetric bending $\nu_4(F_2)$ vibrations and the bands at 470 and 414 $cm^{-1}$ are assigned to the removal of doubly degenerate symmetric bending $\nu_2(E)$ vibrations [1,15,21,22]. The FTIR spectrum of the calcined $Li_2Zn(HPO_4)_2 \cdot H_2O$ at 200 °C (Fig. 3b) illustrates the same characteristic as that of $Li_2Zn(HPO_4)_2$ and shows the significantly decrease of the $\nu_{OH}$ ($H_2O$) and $\nu_2$ ($H_2O$), while the calcined product at 450 °C (Fig. 3c) exhibits the same FTIR characteristic bands as that of $Li_4P_2O_7$ and $Zn_2P_2O_7$, which are based on the fundamental vibrating unit $P_2O_7^{4-}$ anion. The P–O stretching modes of the $P_2O_7^{4-}$ anion are known to appear in the 1191–942 $cm^{-1}$ region. The symmetric $PO_2$ stretching vibration ($\nu_{sym}$, $PO_2$) is observed at 964 and 942 $cm^{-1}$, while the asymmetric stretching vibration ($\nu_{asym}$, $PO_2$) at 1191–1020 $cm^{-1}$ region. The $PO_3$ deformation and rocking modes, the POP deformations, the torsional and external modes are found in the 650–420 $cm^{-1}$ region.

### 3.2. Kinetics study

Dehydration and transformation of crystalline hydrates is a solid-state process of the type: A (solid) → B (solid) + C (gas) [23]. The kinetics of such reactions is described by various equations taking into account the special features of their mechanisms. The activation energy can be calculated by using the Ozawa [24] and Kissinger [25] methods. The Ozawa and Kissinger equations given below were used to calculate the activation energy, $E_a$.

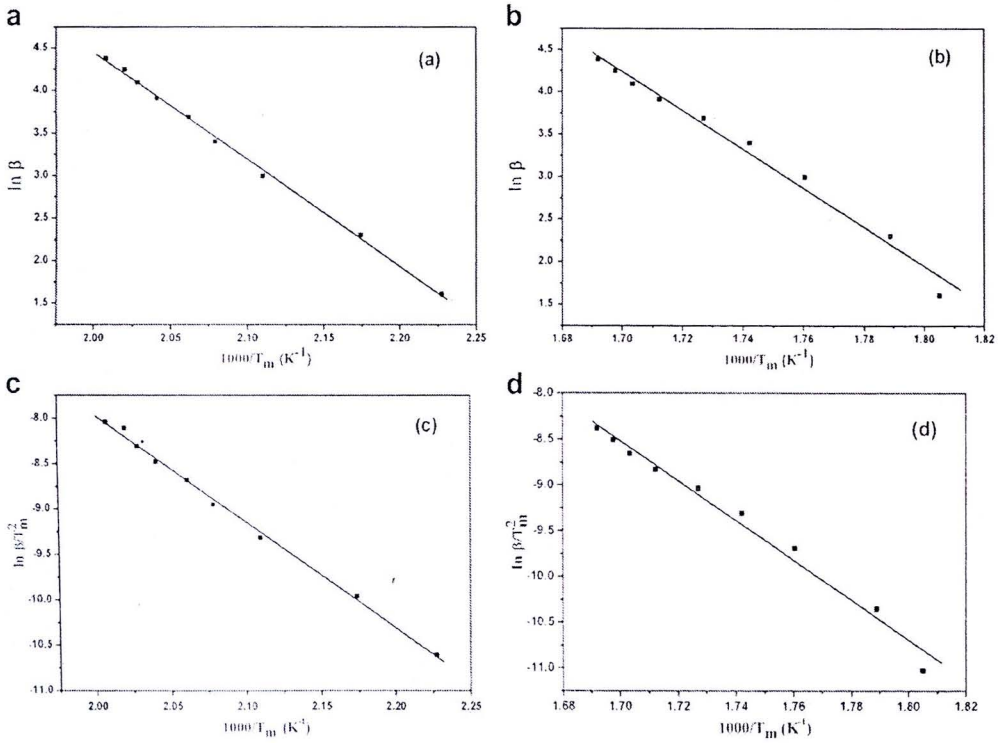


**Fig. 5.** Ozawa and Kissinger plot for the $E_a$ determination: (a) and (b) are the Ozawa plots for the first step and second step, respectively. (c) and (d) are the Kissinger plots for the first step and second step, respectively.

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**Table 1**
Activation energy and correlation coefficient of the linear regression ($r^2$) calculated by the Ozawa and Kissinger methods.

| Method | $E_a$ (kJ mol$^{-1}$) | | $r^2$ | |
|---|---|---|---|---|
| | First step | Second step | First step | Second step |
| Ozawa | 100.55 | 186.38 | 0.9989 | 0.9921 |
| Kissinger | 96.84 | 180.93 | 0.9985 | 0.9912 |

Ozawa equation:

$$\ln\beta = -\frac{E_a}{RT_m} + \text{const} \quad (3)$$

Kissinger equation:

$$\ln\left(\frac{\beta}{T_m^2}\right) = -\frac{E_a}{RT_m} + \text{const} \quad (4)$$

where $\beta$ is the heating rate (5, 10, 20, 30, 40, 50, 60, 70 and 80 °C min$^{-1}$), $T_m$ is absolute maximum temperature on DSC curve (K), $E_a$ is the activation energy of the process (kJ mol$^{-1}$), const are integration constants and $R$ is the universal gas constant, 8.314 JK$^{-1}$ mol$^{-1}$. Either the plot of $\ln\beta$ versus $1000/T_m$ for Ozawa method (Fig. 5a and b) or the plot of $\ln(\beta/T_m^2)$ versus $1000/T_m$ for Kissinger method (Fig. 5c and d) give a straight line from which the activation energy values for the processes are calculated from the slope and presented in Table 1.

### 3.2.1. Calculation of activation energy

(a) *Ozawa method*: $\ln\beta$ versus the reciprocal of the absolute temperature $1000/T_m$ is plotted. The slope of the straight line plot is used for the calculation of approximate value of $E_a$. The corresponding plot is shown in Fig. 5a and b for the first step and second steps, respectively.

(b) *Kissinger method*: This is an alternate method for calculating activation energies. Plot of $\ln(\beta/T_m^2)$versus $1000/T_m$. The slope of the straight line plot, is used for the calculation of approximate value of $E_a$. The corresponding plot is shown in Fig. 5c and d for the first step and second steps, respectively.

### 3.3. Reversible hydration study

The study of the dehydration and rehydration processes in this compound illustrated that the water molecules can be removed and rehydrated without disrupting the structure of the material,

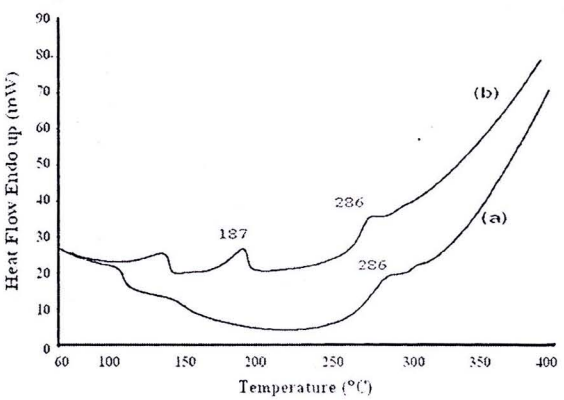


**Fig. 6.** The DSC curves of: (a) the dehydration of sample and (b) the rehydration of sample at the heating rate of 10 °C min$^{-1}$.

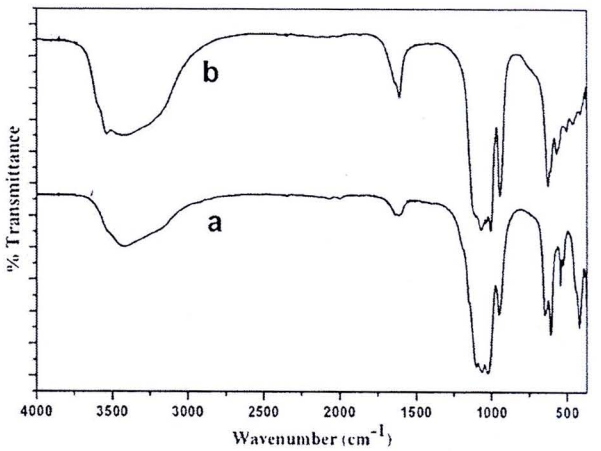


**Fig. 7.** The FTIR spectra of: (a) the calcined product at 200 °C and (b) the dehydrated sample exposed to moisture at room temperature for 2 h.

provided that the temperature is lower than 200 °C. The dehydration was investigated by heating the sample at 200 °C for 2 h, and the rehydration was carried out by exposing the dehydrated sample to water for 2 h at ambient temperature. Then the surface water was removed from the rehydrated sample by drying at 110 °C for 2 h. The dehydration and rehydration processes of the studied hydrate were confirmed by the FTIR spectra and the DSC curves. Indeed the DSC curve of the calcined hydrated sample at 200 °C (Fig. 6a) does not show any endothermic peak at 187 °C which is the characteristic of the removal of water molecule as shown in Fig. 7a, while the FTIR spectra show the significant decrease of $\nu_{OH}$ ($H_2O$) and $\nu_2(H_2O)$. The FTIR spectra (Fig. 7b) and DSC curve (Fig. 6b) of rehydration sample exhibit similar feature as those of the as-prepared sample. The small endothermic peak at about 130 °C is suggested to be due to the adsorbed water or moisture similar to that appear in Fig. 4. The endothermic peaks at 187 and 286 °C are interpreted to be involved the hydrogen bonded water and the coordinated one, respectively.

The water content of the rehydration sample was confirmed by using the Karl Fischer method and the mole ratio of salt: $H_2O$ was found to be 1.00:1.13. The dehydration and rehydration processes of the synthesized sample, showed that the water of crystallization can be removed and incorporated back to the structure without the destruction of the structure under the condition of lower than 200 °C. The dehydration and rehydration processes of the synthesized compound are similar to zeolite. Therefore, the synthesized sample can be an alternative material to replace zeolite in case of the acidity of material is required.

## 4. Conclusion

The $Li_2Zn(HPO_4)_2\cdot H_2O$ and its decomposition products ($Li_2Zn(HPO_4)_2$ and the mixed phase of $Zn_2P_2O_7$ and $Li_4P_2O_7$) were successfully synthesized at ambient temperature. The $Li_2Zn(HPO_4)_2\cdot H_2O$ decomposes in two steps at 187 °C and 286 °C due to the dehydration and decomposition.. The activation energy values calculated using Ozawa and Kissinger methods are in good agreement. The activation energy values are not considerably influenced by the range of heating rates employed in the present study. The water molecule in $Li_2Zn(HPO_4)_2\cdot H_2O$ can be removed and rehydrated without destruction of the structure under the temperature of not higher than 200 °C, which is similar to the case of zeolites. The rehydration process study of this compound and the activation energies are reported for the first time.

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# VITAE

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