**Supporting Information**

# Nanoporous material based on heteroleptic bilayers built up from bis-phosphonium and *p*-sulfonato-calix[4]arene ions

Mohamed Makha,* Yatimah Alias, Colin L. Raston* and Alexandre N. Sobolev

## *1-Results of the combinatorial approach based on molar ratios of components: identification and characterisation of complexes 3-5*

| Code | $SO_3Na$-calix[4]arene | $(Ph_3P^+-CH_2PhCH_2-P^+Ph_3)$ $2Cl^-$ | $YbCl_3.6H_2O$ | pH | σ ($mS/cm^{-1}$) | Notes |
|---|---|---|---|---|---|---|
| Z32 | 1 | 1 | 2 | 6.05 | 4.60 | Structure complex **3** (**2D porous**) |
| Z42 | 1 | 1 | 3 | 6.08 | 4.70 | Z42j – isostructural Z32 |

| Code | $SO_3Na$-calix[4]arene | $(Ph_3P^+-CH_2PhCH_2-P^+Ph_3)$ $2Cl^-$ | $Er(NO_3)_3.5H_2O$ | pH | σ ($mS/cm^{-1}$) | Notes |
|---|---|---|---|---|---|---|
| Er42 | 1 | 1 | 3 | 6.18 | 4.06 | Structure complex **4** (**Expanded Bilayer**) |
| Er32 | 1 | 1 | 2 | 6.20 | | |

| Code | $SO_3Na$-calix[4]arene | $(Ph_3P^+-CH_2PhCH_2-P^+Ph_3)$ $2Cl^-$ | $Cs(NO_3)$ | pH | σ ($mS/cm^{-1}$) | Notes |
|---|---|---|---|---|---|---|
| Cs32 | 1 | 1 | 2 | 9.14 | 5.37 | Structure complex **5** (**compact structure**) Isostrustural to 4La3R |
| Cs42 | 1 | 1 | 3 | 9.57 | | |

| Code | $SO_3Na$-calix[4]arene | $(Ph_3P^+-CH_2PhCH_2-P^+Ph_3)$ $2Cl^-$ | $LaCl_3.7H_2O$ | pH | σ ($mS/cm^{-1}$) | Notes |
|---|---|---|---|---|---|---|
| 4La1 | 1 | 1 | 1 | 6.95 | 3.32 | |
| 4La2 | 1 | 1 | 2 | 6.59 | 4.31 | |
| 4La3 | 1 | 1 | 3 | 6.57 | 3.89 | isostructural to complex **5** |
| 4La4 | 1 | 2 | 1 | 6.72 | 4.20 | |

| Code | $SO_3Na$-calix[4]arene | $(Ph_3P^+-CH_2PhCH_2-P^+Ph_3)$ $2Cl^-$ | $GdCl_3.6H_2O$ | pH | σ ($mS/cm^{-1}$) | Notes |
|---|---|---|---|---|---|---|
| W1 | 1 | 0 | 1 | 6.36 | 2.13 | |
| W2 | 1 | 1 | 1 | 6.12 | 2.16 | |
| W4 | 1 | 3 | 1 | 6.22 | 3.74 | Too small unit cell |
| W6 | 1 | 5 | 1 | 6.37 | 4.45 | Too small unit cell |
| X1 | 1 | 1 | 0 | 8.25 | 1.39 | |
| X4 | 1 | 1 | 3 | 6.41 | 4.78 | |
| X6 | 1 | 1 | 5 | 6.34 | 6.68 | |

| Code | $SO_3Na$-calix[4]arene | $(Ph_3P^+-CH_2PhCH_2-P^+Ph_3)$ $2Cl^-$ | $YbCl_3.6H_2O$ | pH | σ ($mS/cm^{-1}$) | Notes |
|---|---|---|---|---|---|---|
| Y1 | 1 | 0 | 1 | 6.22 | 1.71 | |
| Y2 | 1 | 1 | 1 | 6.14 | 2.05 | |
| Y4 | 1 | 3 | 1 | 5.59 | 3.52 | Too small unit cell |
| Y6 | 1 | 5 | 1 | 6.17 | 4.52 | Too small unit cell |
| Z1 | 1 | 1 | 0 | 8.90 | 1.58 | |

| | | | | | | |
|---|---|---|---|---|---|---|
| Z4 | 1 | 1 | 3 | 6.10 | 4.87 | |
| Z6 | 1 | 1 | 5 | 6.18 | 6.43 | |

| Code | $SO_3Na$-calix[4]arene | $(Ph_3P^+-CH_2PhCH_2-P^+Ph_3)$ $2Cl^-$ | $GdCl_3.6H_2O$ | pH | σ ($mS/cm^{-1}$) | Notes |
|---|---|---|---|---|---|---|
| X32 | 1 | 1 | 2 | 6.14 | 2.25 | |
| X42 | 1 | 1 | 3 | 6.21 | 4.88 | |

## *Molar ratios of tectons (Sulfonato-calix[4]arene:* $(Ph_3P^+-CH_2PhCH_2-P^+Ph_3: Ln^{3+})$ *at different pH*

| Code | $SO_3Na$-calix[4]arene | $(Ph_3P^+-CH_2PhCH_2-P^+Ph_3)$ $2Cl^-$ | $GdCl_3.6H_2O$ | pH (a) | pH | σ ($mS/cm^{-1}$) | Notes |
|---|---|---|---|---|---|---|---|
| X32pH4 | 1 | 1 | 2 | 5.92 | 3.59 | 8.50 | |
| X42pH4 | 1 | 1 | 3 | 5.83 | 4.01 | 7.14 | |
| X32pH2 | 1 | 1 | 2 | 5.81 | 1.59 | 14.20 | |
| X42pH2 | 1 | 1 | 3 | 5.78 | 2.33 | 10.05 | |

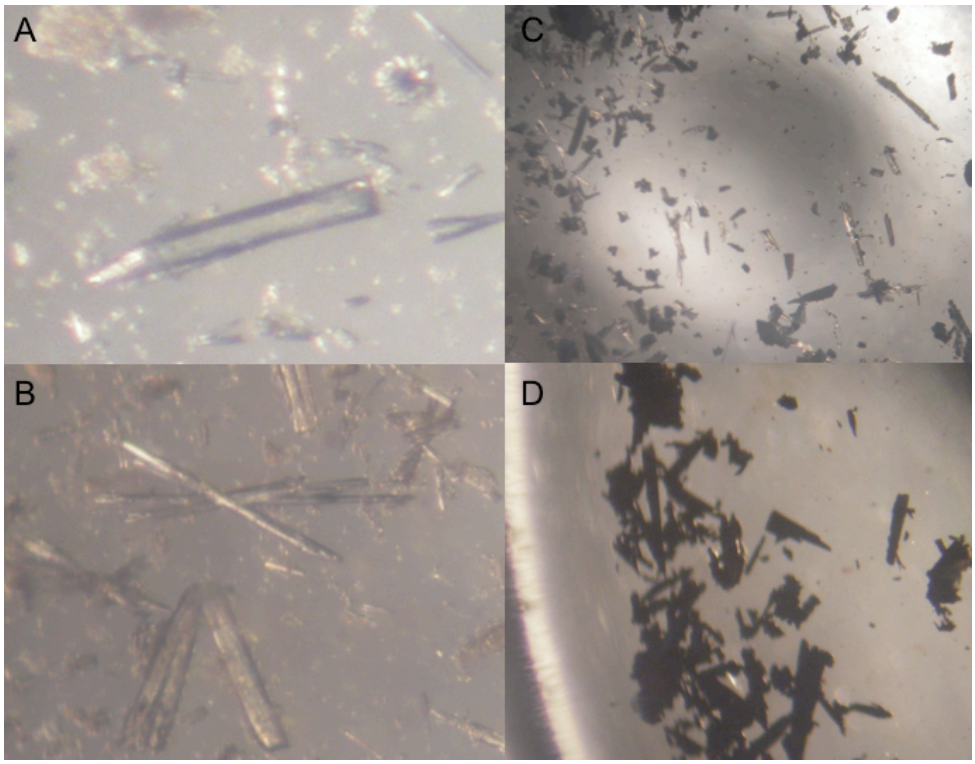
| Code | $SO_3Na$-calix[4]arene | $(Ph_3P^+-CH_2PhCH_2-P^+Ph_3)$ $2Cl^-$ | $YbCl_3.6H_2O$ | pH (a) | pH | σ ($mS/cm^{-1}$) | Notes |
|---|---|---|---|---|---|---|---|
| Z32pH4 | 1 | 1 | 2 | 5.72 | 3.57 | 7.21 | |
| Z42pH4 | 1 | 1 | 3 | 5.65 | 3.91 | 7.66 | |
| Z32pH2 | 1 | 1 | 2 | 5.91 | 2.15 | 10.11 | |
| Z42pH2 | 1 | 1 | 3 | 5.66 | 1.83 | 14.77 | |

| Code | $SO_3Na$-calix[4]arene | $(Ph_3P^+-CH_2PhCH_2-P^+Ph_3)$ $2Cl^-$ | $Er(NO_3)_3.5H_2O$ | pH (a) | pH | σ ($mS/cm^{-1}$) | Notes |
|---|---|---|---|---|---|---|---|
| Er32pH4 | 1 | 1 | 2 | 6.06 | 3.89 | 8.23 | |
| Er42pH4 | 1 | 1 | 3 | 5.87 | 3.74 | 7.39 | |
| Er32pH2 | 1 | 1 | 2 | 6.11 | 2.04 | 11.84 | |
| Er42pH2 | 1 | 1 | 3 | 5.98 | 2.28 | 9.79 | |

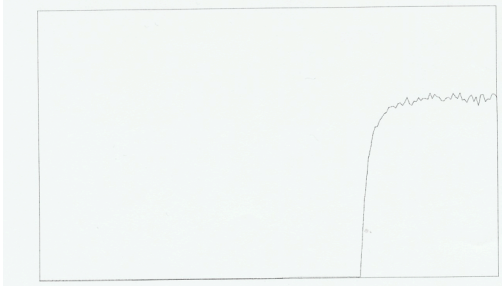
| Code | $SO_3Na$-calix[4]arene | $(Ph_3P^+-CH_2PhCH_2-P^+Ph_3)$ $2Cl^-$ | $Cs(NO_3)$ | pH (a) | pH | σ ($mS/cm^{-1}$) | Notes |
|---|---|---|---|---|---|---|---|
| Cs32pH4 | 1 | 1 | 2 | 9.60 | 3.94 | 7.46 | |
| Cs42pH4 | 1 | 1 | 3 | 9.58 | 3.27 | 9.69 | |
| Cs32pH2 | 1 | 1 | 2 | 9.54 | 2.22 | 11.52 | |
| Cs42pH2 | 1 | 1 | 3 | 9.57 | 2.12 | 13.55 | |

## *2- Assessment of porosity in complex 3*

(A) Crystal images of complex **3**, (B) crystals of complex **3** soaked in 2*M* HCl; (C) Isolated and dried crystals of complex **3** after HCl treatment and (D) crystals of complex **3** turned dark brown instantly after exposure to iodine (iodine is recovered from the crystals upon exposure to acetone).




## *3- ICP records on HCl leaching of Ytterbium*



Integration Time: 0.1000 sec
Sampling Period: 0.2000 sec
n: 200

| m/z | Range | Count | Mean | RSD% |
|---|---|---|---|---|
| 174 | 50,000,000 | 30068120.0 | 8496536.0 | 153.03 |
| 171 | 20,000,000 | 13227383.0 | 3744787.3 | 153.81 |

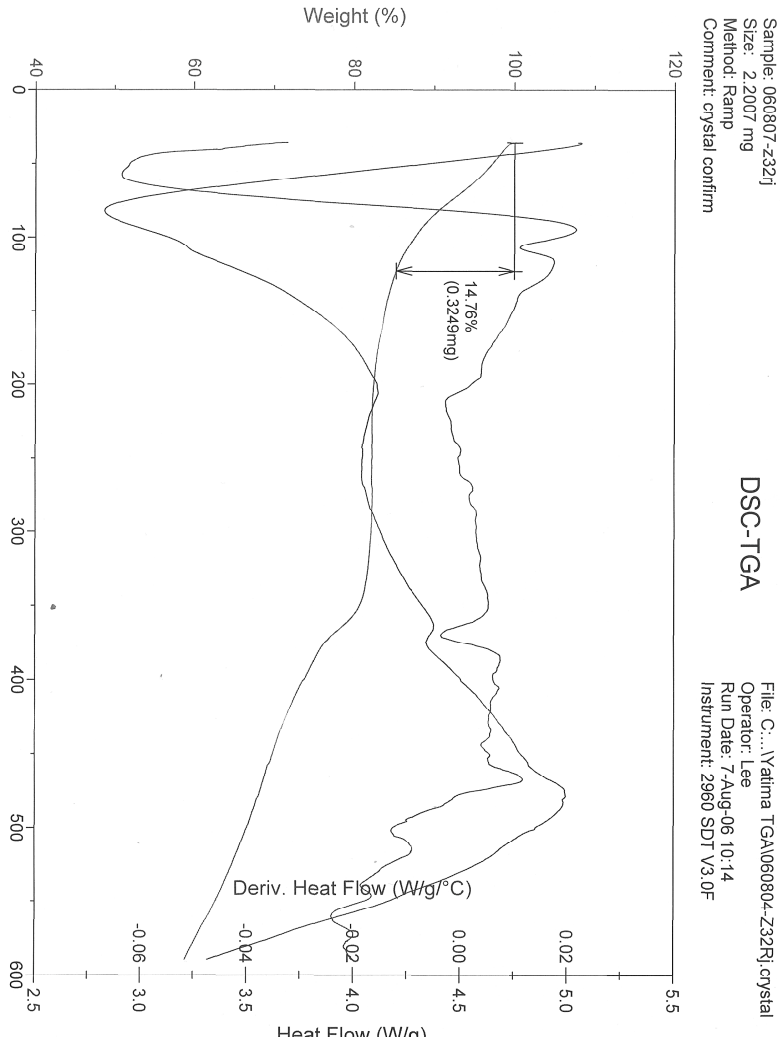
Tuning Parameters

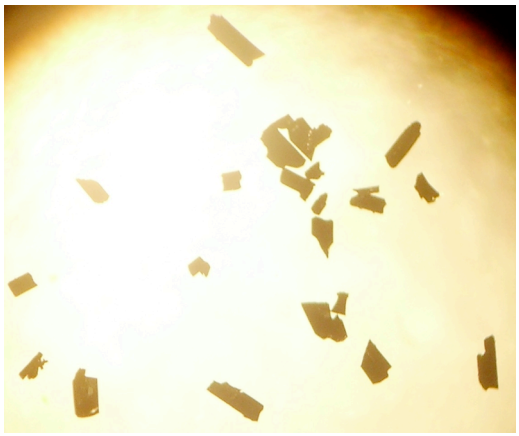
| ===Plasma Condition=== | | | ===Ion Lenses=== | | | ===Q-Pole Parameters=== | | |
|---|---|---|---|---|---|---|---|---|
| RF Power | : | 1500 W | Extract 1 | : | 4 V | AMU Gain | : | 130 |
| RF Matching | : | 1.8 V | Extract 2 | : | -100.5 V | AMU Offset | : | 124 |
| Smpl Depth | : | 6 mm | Omega Bias-cs | : | -32 V | Axis Gain | : | 1.0004 |
| Torch-H | : | -1.3 mm | Omega Lens-cs | : | 8 V | Axis Offset | : | -0.02 |
| Torch-V | : | 1.1 mm | Cell Entrance | : | -26 V | QP Bias | : | -3 V |
| Carrier Gas | : | 0.91 L/min | QP Focus | : | 2 V | | | |
| Makeup Gas | : | 0.2 L/min | Cell Exit | : | -42 V | ===Detector Parameters=== | | |
| Optional Gas | : | 0 % | | | | Discriminator | : | 8 mV |
| Nebulizer Pump | : | 0.15 rps | ===Octopole Parameters=== | | | Analog HV | : | 1940 V |
| Sample Pump | : | --- rps | OctP RF | : | 150 V | Pulse HV | : | 1520 V |
| S/C Temp | : | 2 degC | OctP Bias | : | -6 V | | | |

===Reaction Cell===

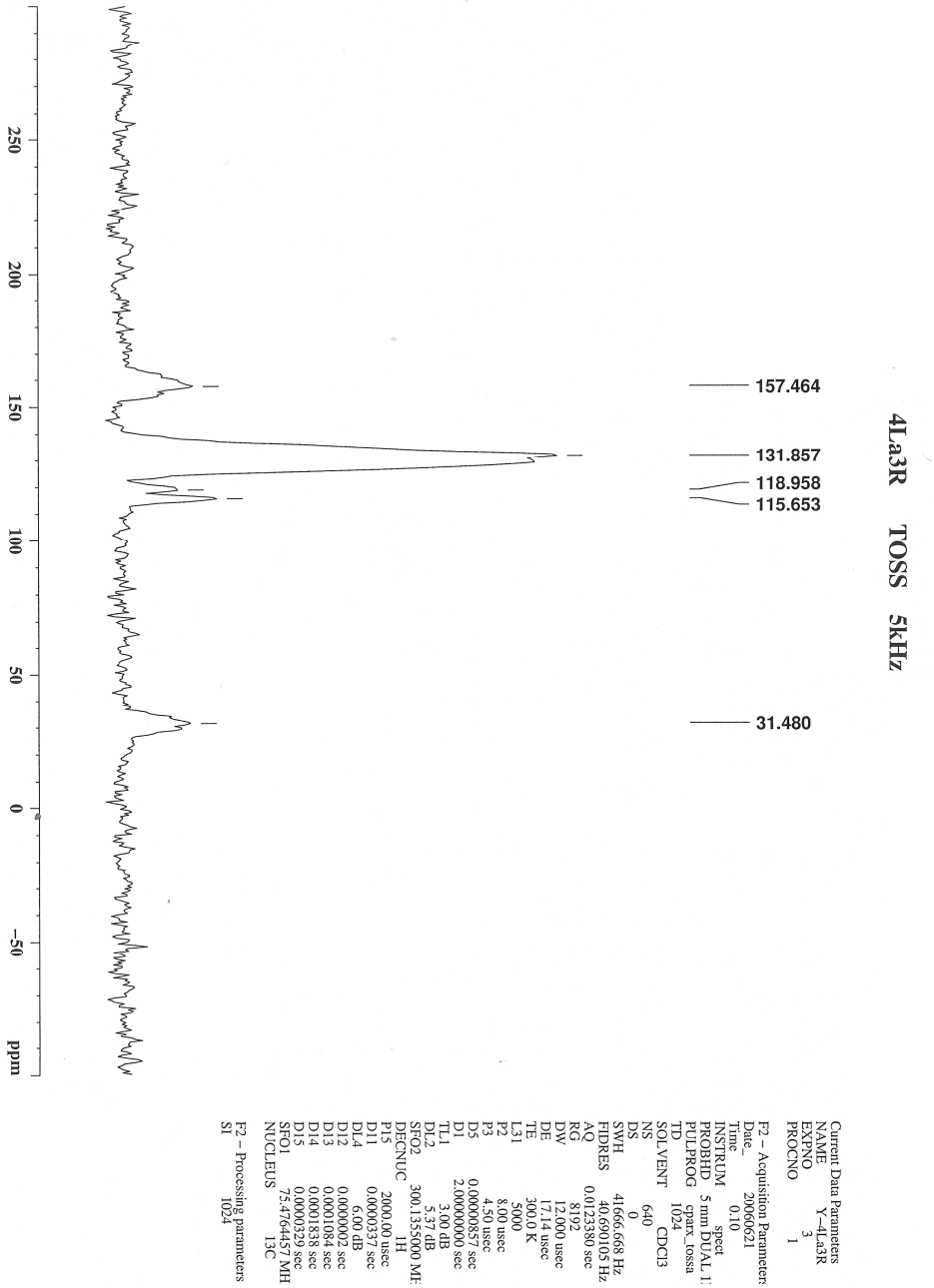
| Reaction Mode | : | OFF | | | | | | |
|---|---|---|---|---|---|---|---|---|
| H2 Gas | : | 0 mL/min | He Gas | : | 0 mL/min | Optional Gas | : | --- % |

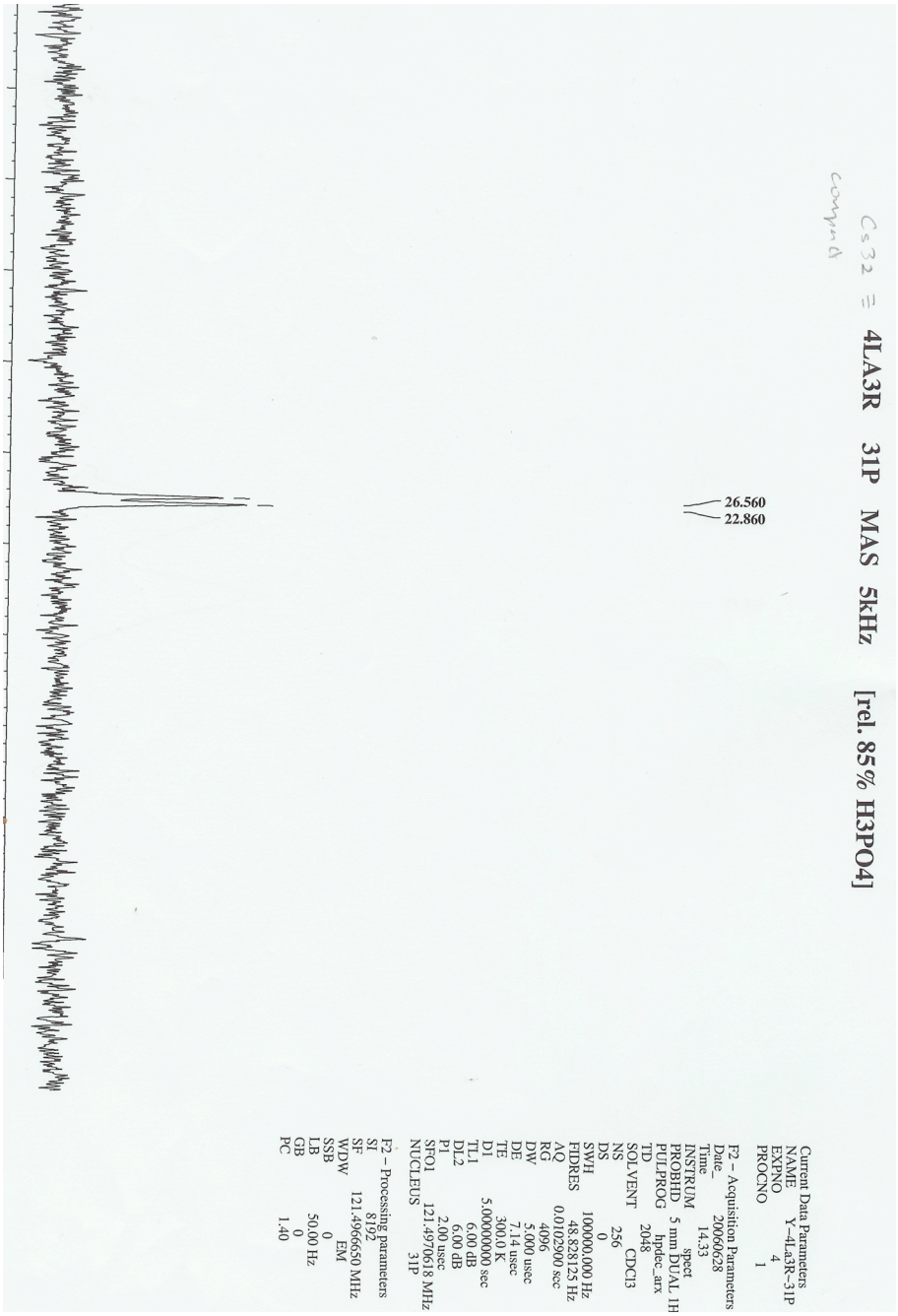
## *4- TGA analysis on complex 3 with crystals retained morpholgy at 600 °C*



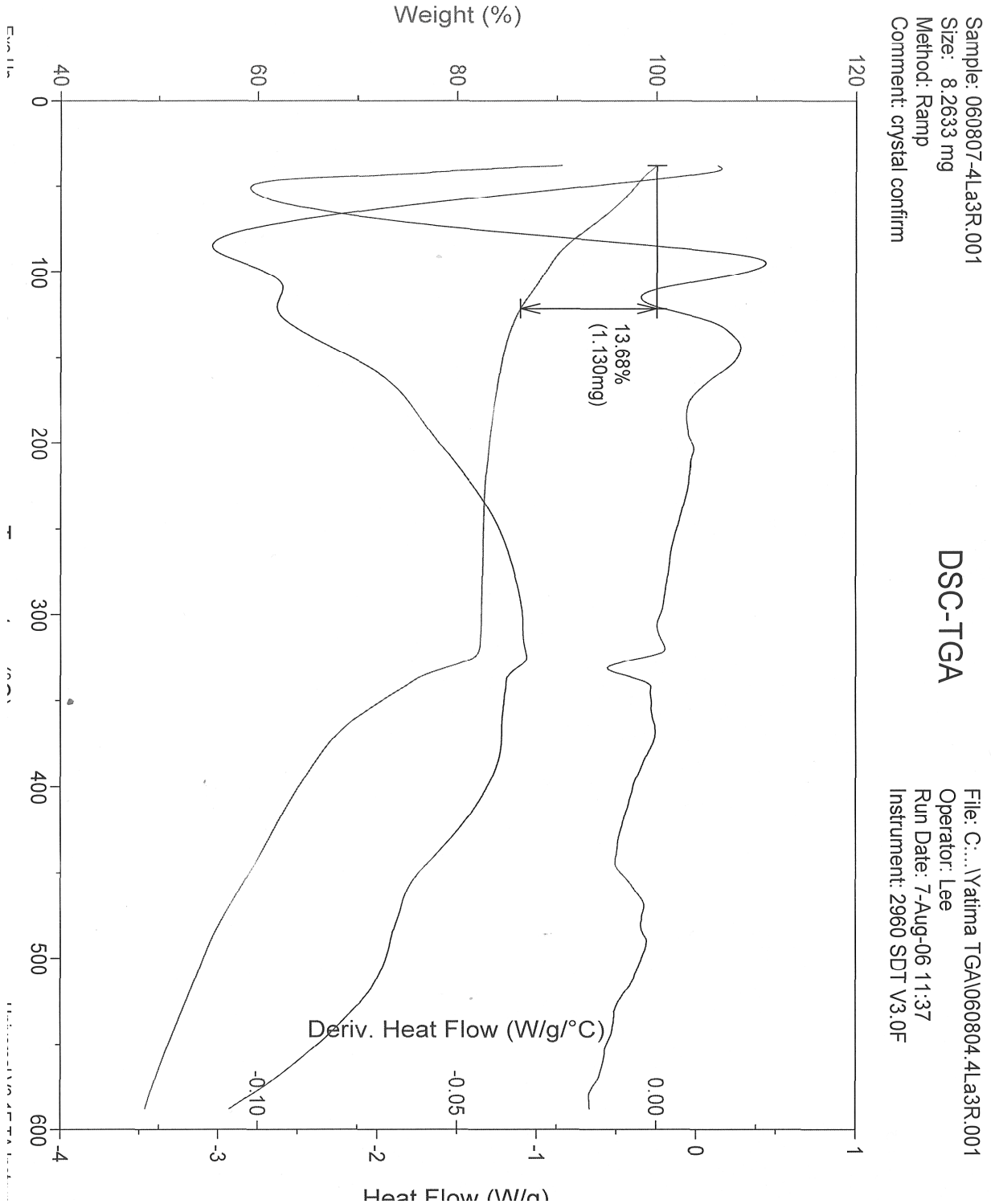



## *5- 13CMASS, 31PMASS NMR and TGA data on complex 5*






Sample: 060807-4La3R.001
Size: 8.2633 mg
Method: Ramp
Comment: crystal confirm
DSC-TGA
File: C:...\Yatima TGA\060804.4La3R.001
Operator: Lee
Run Date: 7-Aug-06 11:37
Instrument: 2960 SDT V3.0F
Weight (%)
Deriv. Heat Flow (W/g/°C)
Heat Flow (W/g)
13.68%
(1.130mg)