

**N. Mercier et al.**

“A Hybrid Perovskite Resulting from the Solid State Reaction between the Organic Cations and the Perovskite Layers of  $\alpha$ 1-(Br-(CH<sub>2</sub>)<sub>2</sub>-NH<sub>3</sub>)<sub>2</sub>PbI<sub>4</sub>”

## Supporting informations

### Table of contents

1 – Single crystal X-Ray data of (Br-(CH <sub>2</sub> ) <sub>2</sub> -NH <sub>3</sub> ) <sub>2-x</sub> (I-(CH <sub>2</sub> ) <sub>2</sub> -NH <sub>3</sub> ) <sub>x</sub> PbBr <sub>x</sub> I <sub>4-x</sub> (x $\square$ 1) (phase A)	2
2 – DSC-TGA experiments	3
3 – Powder X-ray diffraction	5
4 – CPMAS <sup>1</sup> H- <sup>13</sup> C solid state NMR experiments	9
5 – Mass Spectroscopy	15

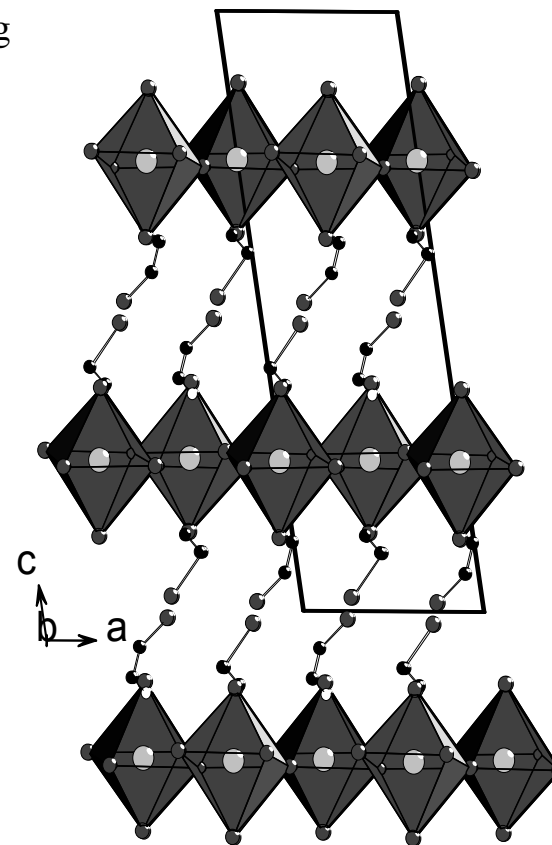
## 1– Single crystal X-Ray data of $(\text{Br}-(\text{CH}_2)_2\text{-NH}_3)_{2-x}(\text{I}-(\text{CH}_2)_2\text{-NH}_3)_x\text{PbBr}_x\text{I}_{4-x}$ ( $x \leq 1$ ) (sample A)

The heating (50°C, 40 hours) of red crystals of  $\alpha\text{-}1\text{-(Br}-(\text{CH}_2)_2\text{-NH}_3)_2\text{PbI}_4$  involves a bursting into many fragments of orange crystals. Several attempts of crystal structure determination of compound **A** (orange crystals) were then performed. The overall structure was found to be close to the structure of  $(\text{I}-(\text{CH}_2)_2\text{-NH}_3)_2\text{PbI}_4$ . Nevertheless, the poor data quality could not allow to unambiguously define the nature of halide belonging both to perovskite layers and cations, and one nitrogen atom was not located. The better result gives a reliability factor of 8.5% (given below), the Pb-X (X= I, Br) distances being in the range of 3.068 Å–3.193 Å: 3.068(3) Å, 3.121(2) Å, 3.125(3) Å, 3.154(2) Å, 3.155(2) Å, 3.193(3) Å.

### Summary of crystallographic data,

### and view of the structure along

Empirical formula	C4 H14 Br2 I4 N2 Pb
Formula weight	964.78
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	monoclinic, P21/n
Unit cell dimensions	a = 8.5239(8) Å    alpha = 90 deg. b = 8.6846(3) Å    beta = 99.710(10) deg. c = 25.583(5) Å    gamma = 90 deg.
Volume	1844.8(4) Å <sup>3</sup>
Z, Calculated density	4, 3.474 Mg/m <sup>3</sup>
Absorption coefficient	20.146 mm <sup>-1</sup>
F(000)	1664
Crystal size	0.1 x 0.04 x 0.02 mm
Theta range for data collection	2.42 to 25.66 deg.
Limiting indices	-9 ≤ h ≤ 10, -9 ≤ k ≤ 10, -28 ≤ l ≤ 30
Reflections collected / unique	21116 / 3240 [R(int) = 0.1035]
Completeness to theta = 25.66	92.5 %
Absorption correction	gaussian
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	3240 / 0 / 84
Goodness-of-fit on F <sup>2</sup>	1.045
Final R indices [I > 2sigma(I)]	R1 = 0.0864, wR2 = 0.2038
R indices (all data)	R1 = 0.1657, wR2 = 0.2341
Largest diff. peak and hole	1.708 and -2.047 e.Å <sup>-3</sup>



## 2 – DSC-TGA experiments

Differential scanning calorimetry (DSC) measurements were performed on a DSC-2010 TA Instruments system. All the DSC analysis were carried out by loading sample (approximately 5 mg) in a nearly hermetic aluminum capsule which was then located in the system unit (nitrogen atmosphere) and heated from room temperature up to 450°C with a ramp rate in the range of 2-10°C/min. Thermogravimetric analysis measurements (TGA-2050 Instruments System) consist of a 10°C/min ramp from 25°C to 900°C under a flowing nitrogen atmosphere

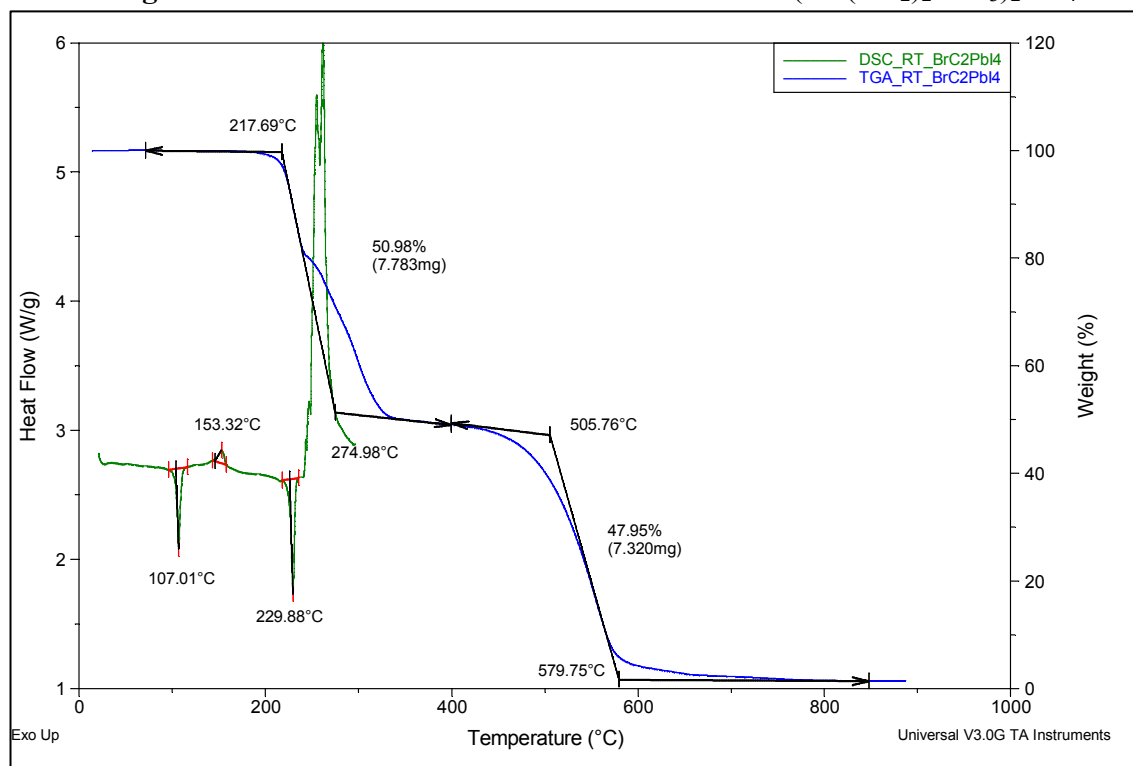
Results of TGA and DSC measurements of a mixture of  $\alpha 1$ - and  $\alpha 2$ -(Br-(CH<sub>2</sub>)<sub>2</sub>-NH<sub>3</sub>)<sub>2</sub>PbI<sub>4</sub> salts (**Figure 2a**) were recently reported (Sourisseau, S. ; Louvain, N. ; Bi, W. ; Mercier, N. ; Rondeau, D. ; Boucher, F. ; Buzaré, J.Y. ; Legein, C. *Chem. Mater.* **2007**, 19, 600).

We report here the DSC experiment of a mixture of  $\alpha 1$ - and  $\alpha 2$ -(Br-(CH<sub>2</sub>)<sub>2</sub>-NH<sub>3</sub>)<sub>2</sub>PbI<sub>4</sub> ( $\alpha 1$ , main phase) in the range of 30°C-120°C (heating at 10°C/mn, cooling at 5°C/mn) (**Figure 2b**).

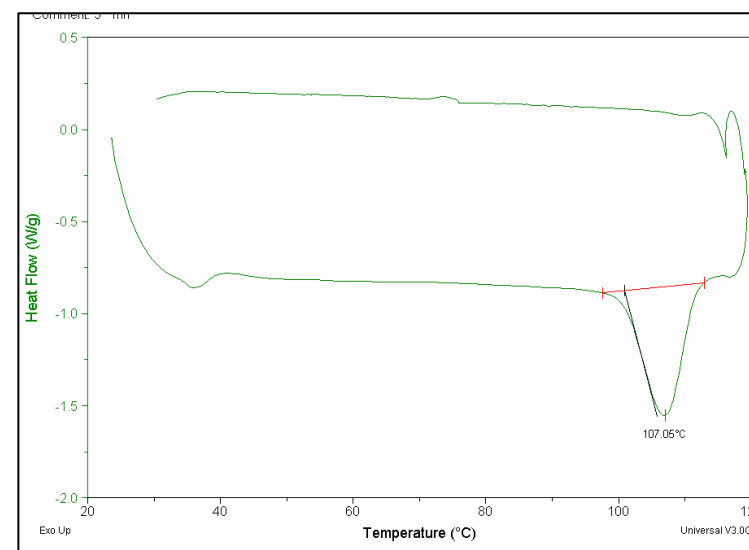
On **Figure 2c** are reported the TGA/DSC experiments of the sample **B**: which is the initial sample of  $\alpha 1/\alpha 2$ -(Br-(CH<sub>2</sub>)<sub>2</sub>-NH<sub>3</sub>)<sub>2</sub>PbI<sub>4</sub> previously heated at 150 °C for 1 hour ().

On **Figure 2d** are displayed the DSC curves (80-240°C range) of the initial sample (“a” curve), of the initial sample previously heated at 50 °C for 24 hours (“b” curve, **A** sample), and of the initial sample previously heated at 150 °C for 1 hour (“c” curve, **B** sample).

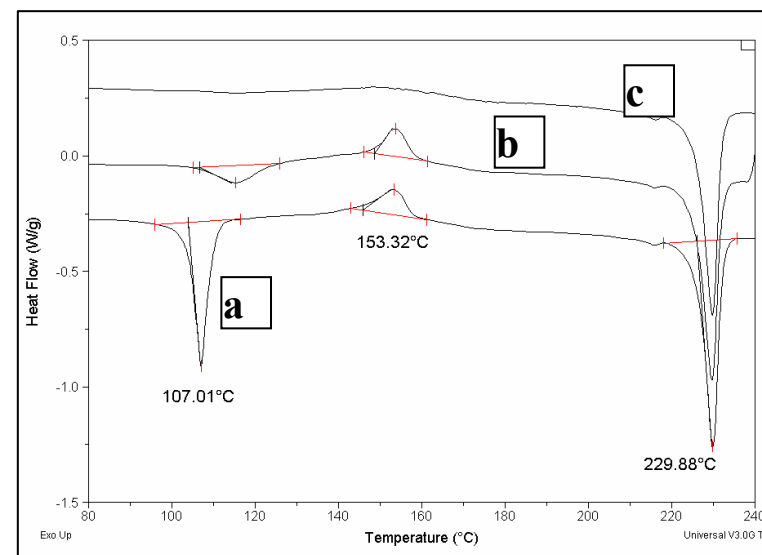
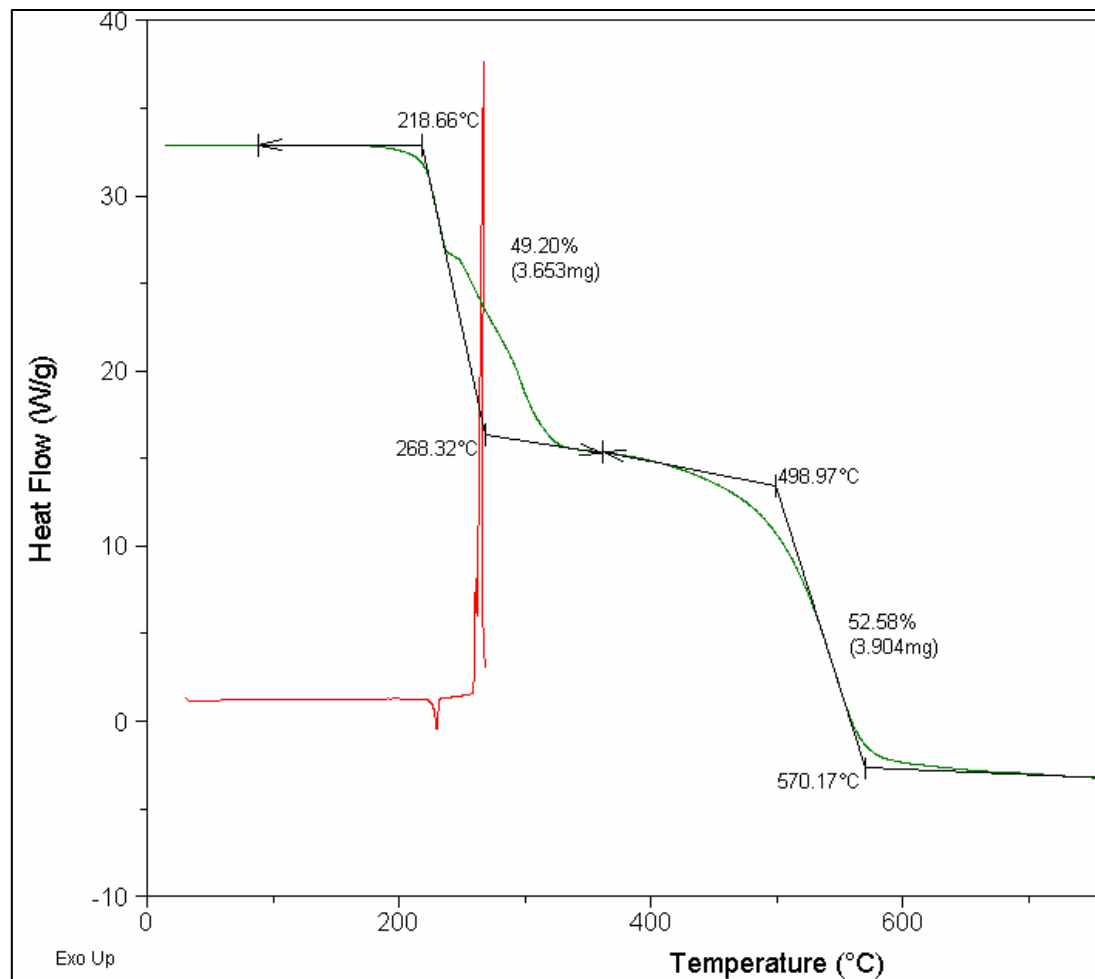
**Figure 2a** : TGA – DSC of a mixture of  $\alpha 1$ - and  $\alpha 2$ -(Br-(CH<sub>2</sub>)<sub>2</sub>-NH<sub>3</sub>)<sub>2</sub>PbI<sub>4</sub>



**Figure 2b** : DSC of  $\alpha 1$ - /  $\alpha 2$ -(Br-(CH<sub>2</sub>)<sub>2</sub>-NH<sub>3</sub>)<sub>2</sub>PbI<sub>4</sub> ( $\alpha 1$ , main phase) in the range of 30°C-120°C (heating at 10°C/mn, cooling at 5°C/mn)



**Figure 2c-** TGA-DSC curves of  $(\text{Br}-(\text{CH}_2)_2\text{-NH}_3)_{2-x}(\text{I}-(\text{CH}_2)_2\text{-NH}_3)_x\text{PbBr}_x\text{I}_{4-x}$  ( $x=1.85$ )  
(sample **B**: initial sample previously heated at 150 °C for 1 hour)



**Figure 2d-** DSC curve (80-240°C range) of the initial sample, (“a” curve), A sample (“b” curve), and B sample (“c” curve).

### 3 – Powder X-ray diffraction

**3a** – Cell refinements of the sample **A** (t= 24h, 50°C, see main text and Figure 2 of the article) and related phases (obtained during the solid state reaction) using the Profile Fitting tool of TOPAS.

[illegible][illegible]

**1°) T = 50 °C - t = 28.6h (data collection of 15 mn)**



Rexp : 6.20      Rwp : 7.87      Rp : 6.18      GOF : 1.27

## Background

One on X 34100(1200)  
Chebychev polynomial, 6 order

## Instrument

Primary radius (mm)	217.5
Secondary radius (mm)	217.5
VDS sample length (mm)	6
VDS Intensity correction applied	
Full Axial Convolution	
Filament Length (mm)	12
Sample Length (mm)	15
Receiving Slit Length (mm)	12
Primary Sollers (°)	2.5
Secondary Sollers (°)	2.5

## Corrections

Zero Error	0.2311 (28)
LP Factor	0

## Miscellaneous

Start X	6.5
Finish X	45

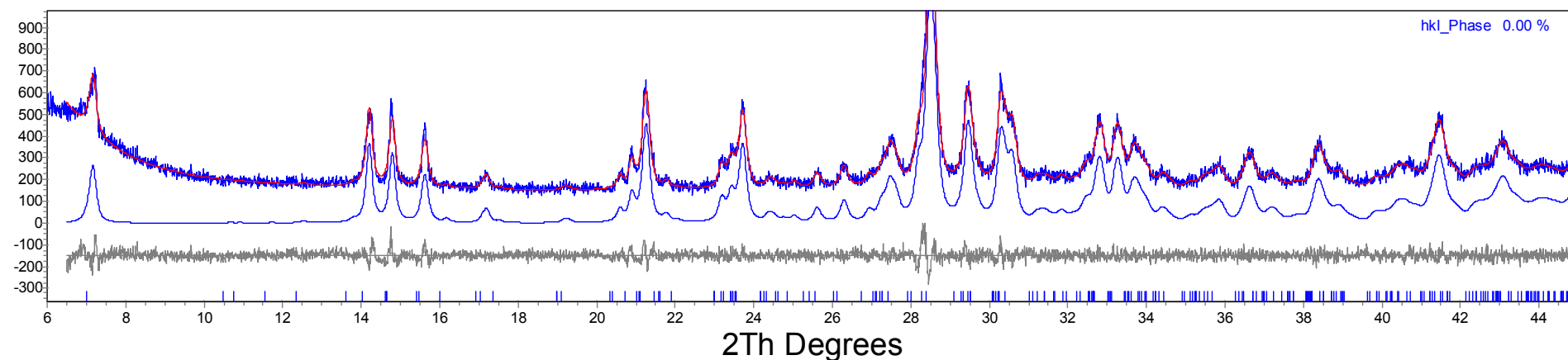
## hkl Phase - 1 Lebail method

Phase name	hkl_Phase
R-Bragg	0.364
Spacegroup	P21/n
Cell Mass	0.000
Cell Volume (Å^3)	1892.75 (41)
Wt% - Rietveld	0.000
Crystallite Size	
Cry Size Lorentzian (nm)	41.44 (39)
PV_TCHZ peak type	
U	0.6
V	-0.18
W	0.014
Z	0
X	0.01
Y	0

## Lattice parameters

a (Å)	8.6463 (12)
b (Å)	8.7634 (11)
c (Å)	25.3143 (29)
beta (°)	99.3267 (88)

2°) T =50°C - t = 65.4 h (data collection of 15mn)



#### R-Values

Rexp : 6.18 Rwp : 7.30 Rp : 5.58 GOF : 1.15

#### Background

One on X 34400 (1100)  
Chebychev polynomial, 6 order

#### Instrument

Primary radius (mm) 217.5  
Secondary radius (mm) 217.5  
VDS sample length (mm) 6  
VDS Intensity correction applied  
Full Axial Convolution  
Filament Length (mm) 12  
Sample Length (mm) 15  
Receiving Slit Length (mm) 12  
Primary Sollers (°) 2.5  
Secondary Sollers (°) 2.5

#### Corrections

Zero Error 0.1850 (19)  
LP Factor 0

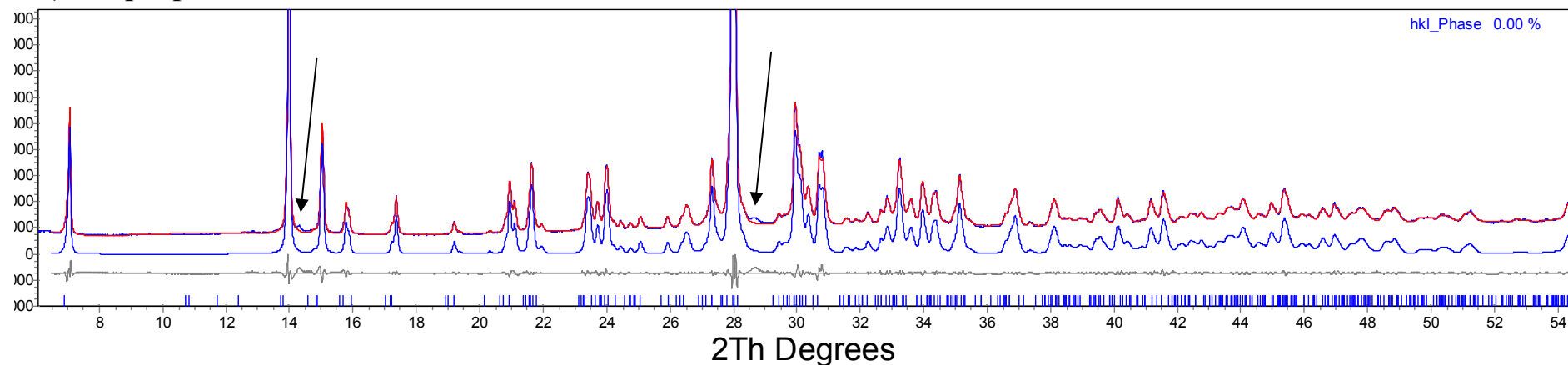
#### Miscellaneous

Start X 6.5  
Finish X 45

#### hkl Phase - 1 Le Bail method

Phase name	hkl_Phase
R-Bragg	0.301
Spacegroup	P21/n
Cell Mass	0.000
Cell Volume (Å <sup>3</sup> )	1881.87 (36)
Wt% - Rietveld	0.000
Crystallite Size	
Cry Size Lorentzian (nm)	59.12 (50)
PV_TCHZ peak type	
U	0.6
V	-0.18
W	0.014
Z	0
X	0.01
Y	0
Lattice parameters	
a (Å)	8.58008 (92)
b (Å)	8.69405 (85)
c (Å)	25.5610 (28)
beta (°)	99.2635 (73)

### 3°) sample post 150°C (X-ray pattern recorded at 25°C, data collection of 120 mn))



(Note the presence of two broad weak peaks (arrows) close to the (004) and (008) strong peaks which are not explained using the refined monoclinic cell)

#### R-Values

R<sub>exp</sub> : 0.59      R<sub>wp</sub> : 2.77      R<sub>p</sub> : 1.83      GOF : 4.70

#### Background

One on X  
Chebychev polynomial, 6 order

#### Instrument

Primary radius (mm)      217.5  
Secondary radius (mm)    217.5  
VDS sample length (mm)    6  
VDS Intensity correction applied  
Full Axial Convolution  
Filament Length (mm)      12  
Sample Length (mm)        15  
Receiving Slit Length (mm) 12  
Primary Sollers (°)        2.5  
Secondary Sollers (°)       2.5

#### Corrections

Zero Error      0.19182 (20)  
LP Factor        0

#### Miscellaneous

Start X      6.5  
Finish X     70  
Excluded Regions  
Start/Finish      0      0

#### hkl Phase - 1 Leball method

Phase name	hkl_Phase
R-Bragg	0.142
Spacegroup	P21/n
Cell Mass	0.000
Cell Volume (Å <sup>3</sup> )	1848.486 (43)
Wt% - Rietveld	0.000
Crystallite Size	
Cry Size Lorentzian (nm)	398.6 (32)
PV_TCHZ peak type	
U	0.09209977
V	-1.928398e-030
W	1.777927e-031
Z	-0.0003321673
X	0.07953515
Y	0.006475956
Lattice parameters	
a (Å)	8.37063 (13)
b (Å)	8.60656 (13)
c (Å)	25.94611 (25)
beta (°)	98.5413 (12)



## 4 –solid state $^{13}\text{C}$ NMR

Figure 4A displays the CPMAS solid state  $^1\text{H}$ - $^{13}\text{C}$  NMR spectrum of  $(\text{Br}-(\text{CH}_2)_2-\text{NH}_3)\text{Br}$  showing two resonances at 30.5 and 45.6 ppm assigned to C(Br) and C(NH<sub>3</sub>) respectively (Table 4A).

The CPMAS solid state  $^1\text{H}$ - $^{13}\text{C}$  NMR spectrum of  $(\text{I}-(\text{CH}_2)_2-\text{NH}_3)_2\text{PbI}_4$  (Figure 4B) exhibits two peaks at 4 and 45 ppm assigned to C(I) and C(NH<sub>3</sub>) respectively. Each peak is reconstructed with three contributions (Table 4B) with slightly different isotropic chemical shift values indicating carbon atom environments slightly different in this salt.

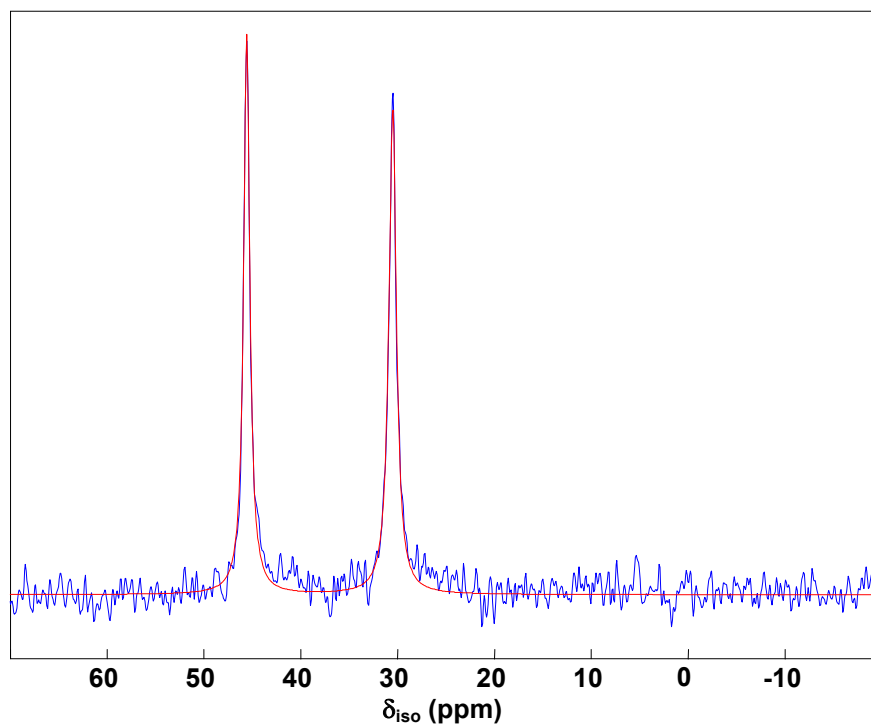
Figure 4C shows the CPMAS solid state  $^1\text{H}$ - $^{13}\text{C}$  NMR spectrum of  $\alpha 1/\alpha 2-(\text{Br}-(\text{CH}_2)_2-\text{NH}_3)_2\text{PbI}_4$  showing two resonances at 38.9 and 45.4 ppm assigned to C(Br) and C(NH<sub>3</sub>) respectively (Table 4C).

In these three compounds both C atoms are bonded to two hydrogen atoms. In these conditions, the CPMAS technique is quantitative since relative intensities of the two signals are similar (Tables 4A, 4B and 4C).

The CPMAS solid state  $^1\text{H}$ - $^{13}\text{C}$  NMR spectrum of  $\alpha 1/\alpha 2-(\text{Br}-(\text{CH}_2)_2-\text{NH}_3)_2\text{PbI}_4$  heated 24 hours at 50°C (Figure 4D) exhibits three resonances at 4, 31 and 45 ppm assigned to C(I), C(Br) and C(NH<sub>3</sub>) respectively (Table 4D). This results demonstrates unambiguously that both  $\text{I}-(\text{CH}_2)_2-\text{NH}_3^+$  and  $\text{Br}-(\text{CH}_2)_2-\text{NH}_3^+$  cations exist in the sample. The relative line intensities of the two resonances assigned to C(I) and C(Br) are nearly equal. So, the two cation quantities are close.

The CPMAS solid state  $^1\text{H}$ - $^{13}\text{C}$  NMR spectrum of  $\alpha 1/\alpha 2-(\text{Br}-(\text{CH}_2)_2-\text{NH}_3)_2\text{PbI}_4$  heated at 150°C (Figure 4E) exhibits also three peaks at 4, 31 and 45 ppm assigned to C(I), C(Br) and C(NH<sub>3</sub>) respectively (Table 4E). Nevertheless, the relative intensities of the resonances of both C(I) and C(Br) change compared to the previous sample heated at 50°C. The first one increases and the second one decreases. According to relative intensities, the ratio of C(I) and C(Br) can be estimated: 92% of C(I) and 8% of C(Br). Both C(I) and C(NH<sub>3</sub>) peaks are reconstructed with two contributions with slightly different isotropic chemical shift values (Table 4E) indicating carbon atom environments slightly different in this compound.

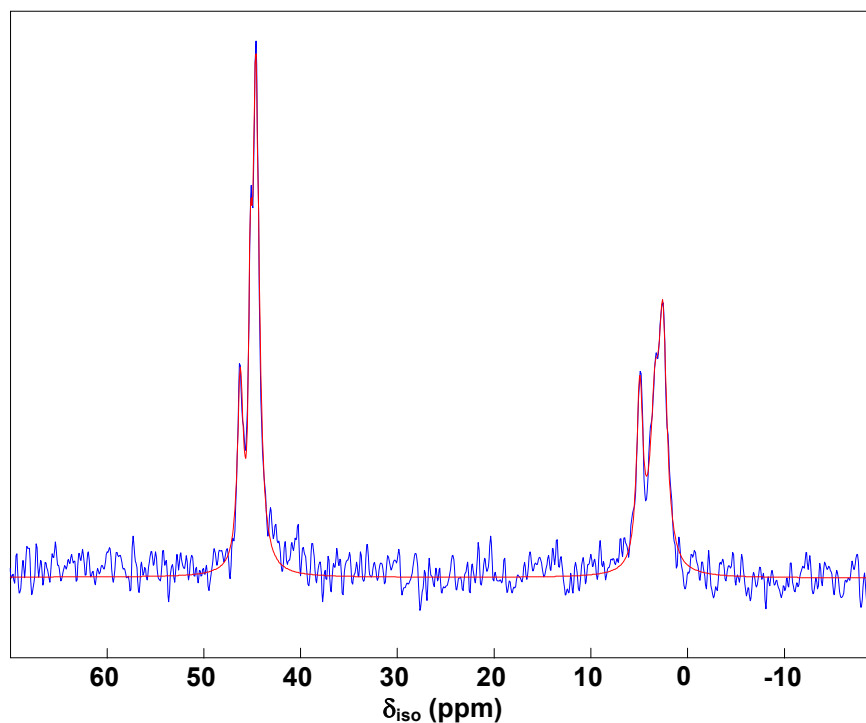
**Figure 4A.** Experimental (in blue) and reconstructed (in red) CPMAS solid state  $^1\text{H}$ - $^{13}\text{C}$  NMR spectrum of  $(\text{Br}-(\text{CH}_2)_2-\text{NH}_3)\text{Br}$ .



**Table 4A.** Isotropic Chemical Shifts,  $\delta_{\text{iso}}$  (ppm), Line Widths (ppm) and Relative Intensities (%) As Deduced from Spectrum Reconstruction of  $(\text{Br}-(\text{CH}_2)_2-\text{NH}_3)\text{Br}$  and Line Assignments.

$\delta_{\text{iso}}$	Line width	Relative intensity	Line Assignment
30.5	0.90	50.8	C(Br)
45.6	0.76	49.2	C(NH <sub>3</sub> )

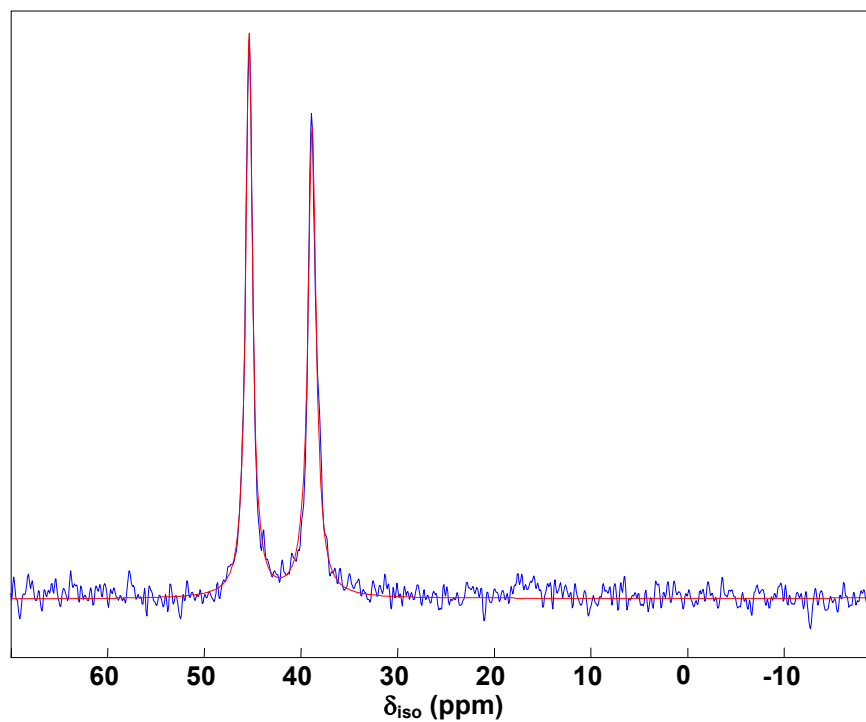
**Figure 4B.** Experimental (in blue) and reconstructed (in red) CPMAS solid state  $^1\text{H}$ - $^{13}\text{C}$  NMR spectrum of  $(\text{I}-(\text{CH}_2)_2\text{-NH}_3)_2\text{PbI}_4$ .



**Table 4B.** Isotropic Chemical Shifts,  $\delta_{\text{iso}}$  (ppm), Line Widths (ppm) and Relative Intensities (%) As Deduced from Spectrum Reconstruction of  $(\text{I}-(\text{CH}_2)_2\text{-NH}_3)_2\text{PbI}_4$  and Line Assignments.

$\delta_{\text{iso}}$	Line width	Relative intensity	Line Assignment
2.6	1.01	21.2	C(I)
3.4	1.04	13.1	
4.9	0.79	12.8	
44.6	0.80	37.3	C(NH <sub>3</sub> )
45.2	0.37	4.1	
46.2	0.71	11.6	

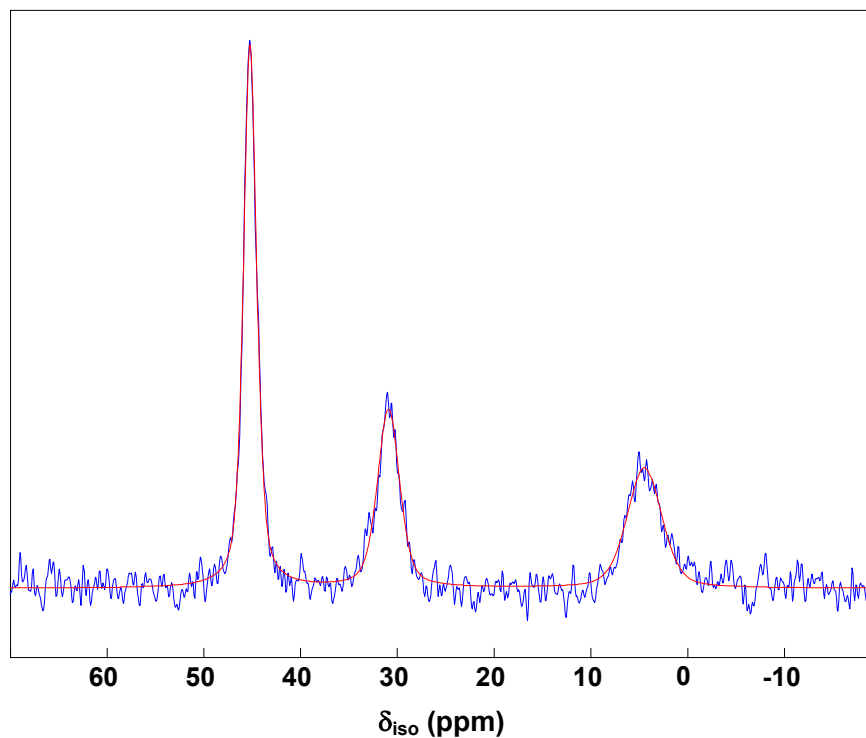
**Figure 4C.** Experimental (in blue) and reconstructed (in red) CPMAS solid state  $^1\text{H}$ - $^{13}\text{C}$  NMR spectrum of  $\alpha 1/\alpha 2\text{-(Br-(CH}_2)_2\text{-NH}_3)_2\text{PbI}_4$ .



**Table 4C.** Isotropic Chemical Shifts,  $\delta_{\text{iso}}$  (ppm), Line Widths (ppm) and Relative Intensities (%) As Deduced from Spectrum Reconstruction of  $\alpha 1/\alpha 2\text{-(Br-(CH}_2)_2\text{-NH}_3)_2\text{PbI}_4$  and Line Assignments.

$\delta_{\text{iso}}$	Line width	Relative intensity	Line Assignment
38.9	1.03	50.0	C(Br)
45.4	0.85	50.0	C(NH <sub>3</sub> )

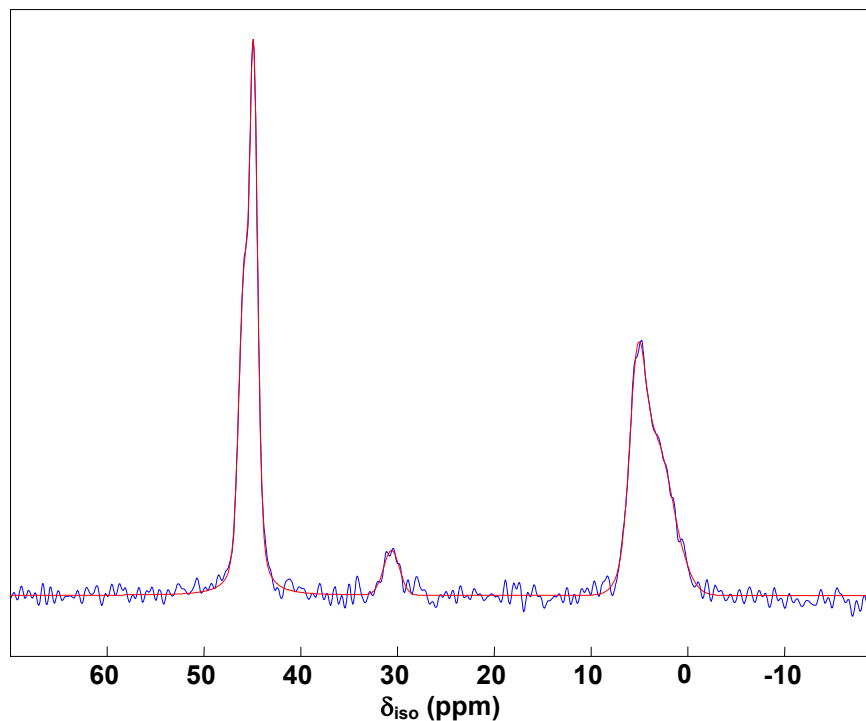
**Figure 4D.** Experimental (in blue) and reconstructed (in red) CPMAS solid state  $^1\text{H}$ - $^{13}\text{C}$  NMR spectrum of  $\alpha 1/\alpha 2\text{-(Br-(CH}_2)_2\text{-NH}_3)_2\text{PbI}_4$  heated 24 hours at  $50^\circ\text{C}$  (Sample A).



**Table 4D.** Isotropic Chemical Shifts,  $\delta_{\text{iso}}$  (ppm), Line Widths (ppm) and Relative Intensities (%) As Deduced from Spectrum Reconstruction of  $\alpha 1/\alpha 2\text{-(Br-(CH}_2)_2\text{-NH}_3)_2\text{PbI}_4$  heated 24 hours at  $50^\circ\text{C}$  (Sample A) and Line Assignments.

$\delta_{\text{iso}}$	Line width	Relative intensity	Line Assignment
4.5	4.24	26.0	C(I)
30.9	2.69	25.5	C(Br)
45.2	1.61	48.5	C(NH <sub>3</sub> )

**Figure 4E.** Experimental (in blue) and reconstructed (in red) CPMAS solid state  $^1\text{H}$ - $^{13}\text{C}$  NMR spectrum of  $\alpha 1/\alpha 2\text{-(Br-(CH}_2)_2\text{-NH}_3)_2\text{PbI}_4$  heated at  $150^\circ\text{C}$  (sample B).



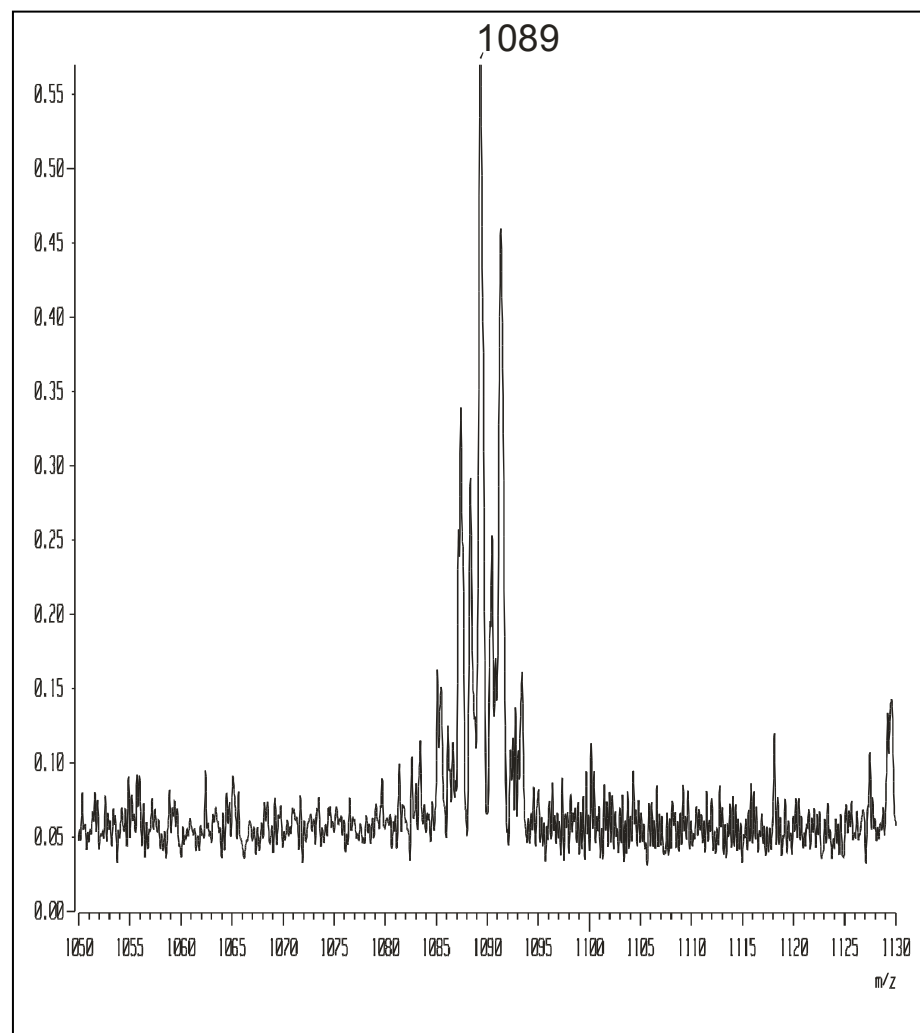
**Table 4E.** Isotropic Chemical Shifts,  $\delta_{\text{iso}}$  (ppm), Line Widths (ppm) and Relative Intensities (%) As Deduced from Spectrum Reconstruction of  $\alpha 1/\alpha 2\text{-(Br-(CH}_2)_2\text{-NH}_3)_2\text{PbI}_4$  heated at  $150^\circ\text{C}$  (Sample B) and Line Assignments.

$\delta_{\text{iso}}$	Line width	Relative intensity	Line Assignment
3.4	4.42	33.6	C(I)
5.2	1.82	13.3	
30.6	1.96	4.3	C(Br)
44.9	1.03	30.3	C(NH <sub>3</sub> )
45.9	1.22	18.5	

## 5 – Mass Spectroscopy

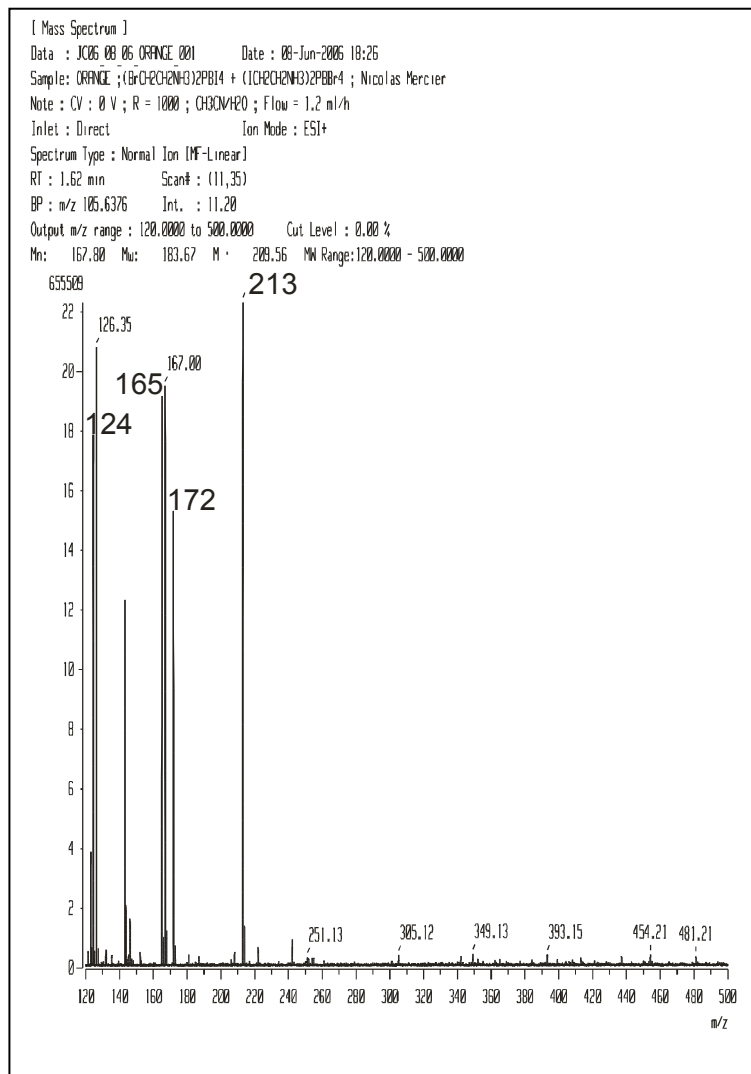
**Figure 5a.** SEI/MS mass spectrum of  $\alpha 1/\alpha 2\text{-(Br(CH}_2)_2\text{NH}_3)_2\text{PbI}_4$ .

Isotopic pattern centred on the  $m/z$  1089



**Figure 5b.** ESI/MS spectra of  $\alpha 1/\alpha 2$ -(Br(CH<sub>2</sub>)<sub>2</sub>NH<sub>3</sub>)<sub>2</sub>PbI<sub>4</sub> heated at 50°C 24 hours (**a**, sample **A**); and heated at 150°C (**b**, sample **B**).

-a-



-b-

