

# Reversible CO<sub>2</sub> absorption by the 6H perovskite Ba<sub>4</sub>Sb<sub>2</sub>O<sub>9</sub>

Matthew T. Dunstan,<sup>1</sup> Wen Liu,<sup>2</sup> Adriano F. Pavan,<sup>3</sup> Justin A. Kimpton,<sup>4</sup>

Chris D. Ling,<sup>3</sup> Stuart A. Scott,<sup>5</sup> John S. Dennis,<sup>2</sup> and Clare P. Grey<sup>1</sup>



<sup>1</sup>Department of Chemistry, University of Cambridge, Lensfield Road, CB2 1EW, UK

<sup>2</sup>Department of Chemical Engineering and Biotechnology, University of Cambridge, Pembroke Street, CB2 3RA, UK

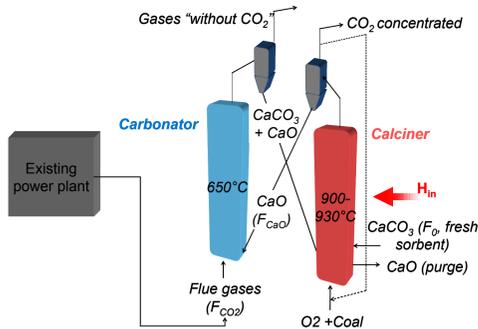
<sup>3</sup>School of Chemistry, The University of Sydney, Sydney NSW 2006, Australia

<sup>4</sup>Australian Synchrotron, 800 Blackburn Road, Clayton VIC 3168, Australia

<sup>5</sup>Department of Engineering, University of Cambridge, Trumpington Street, Cambridge CB2 1PZ, UK

Email: mtd33@cam.ac.uk

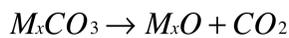
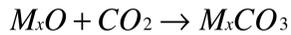
## What is CO<sub>2</sub> Chemical Looping?



Rodriguez-Gomez, N., PhD Thesis, Instituto Nacional del Carbón (INCAR) (2010)

Allows for the separation of CO<sub>2</sub> from flue gases for the purposes of CO<sub>2</sub> sequestration.

Use a solid carrier to chemically absorb CO<sub>2</sub>:



## Current Materials of Interest

### Desirable Properties

- High absorption capacity at high temperatures (400-900°C) to allow for heat recovery
- Fast reaction kinetics
- Retention of capacity upon many carbonation-regeneration cycles

### Amines (MEA, DEA):

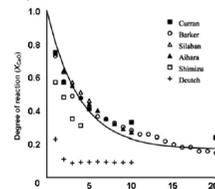
- Most developed technology
- React at low temperatures (~40°C)
- Inefficient; consumes ~30% of power output

### Alkali Oxides (Li<sub>2</sub>ZrO<sub>3</sub>, Li<sub>4</sub>SiO<sub>4</sub>):

- Good stability at high temperatures (400°C-700°C)
- Retains capacity over many cycles
- Many different compounds allow tuning of absorption temperature
- Carbonation of pure compounds is slow

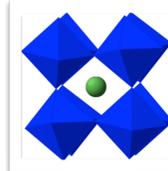
### CaO and derivatives:

- Cheap and abundant material
- Excellent reaction kinetics
- Sintering over many cycles leads to a loss in capacity



Pfeiffer, H. in *Advances in CO<sub>2</sub> Conversion and Utilization*, ACS Symposium Series; American Chemical Society: Washington, DC, (2010).

## Why Perovskites?



Perovskite ABO<sub>3</sub>:  
12 coordinate A site  
6 coordinate B site

### Perovskites

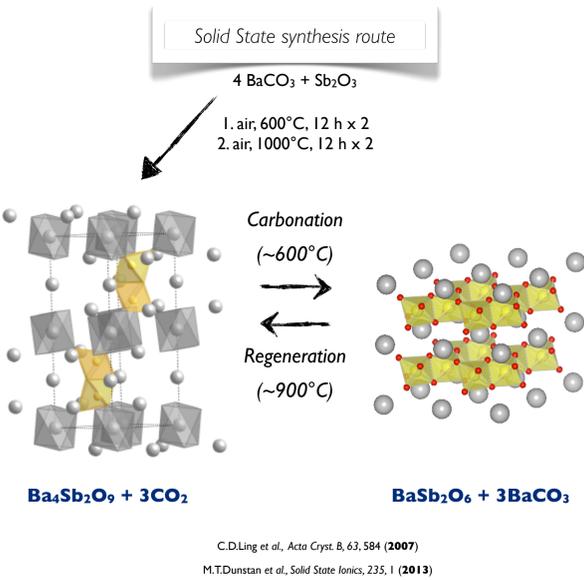
- Excellent thermal and mechanical stability
- Can be made from abundant elements
- Stable framework even after the formation of carbonate
- Doping of different elements gives a great deal of control over physical properties
- **No studies to show whether they are able to be regenerated after carbonation**

### Aims

- Observe carbonation reactions *in-situ*
- Determine if regeneration after carbonation is possible
- Monitor the structural and morphological changes upon cycling

J.C. Abanades et al., *Energy & Fuels*, 17, 308 (2003) K. Nakagawa et al., *J. Electrochem. Soc.*, 145, 1344 (1998)  
G.T. Rochelle, *Science*, 325, 1652 (2009) M. Kato et al., *J. Mater. Sci. Lett.*, 21, 465 (2002)

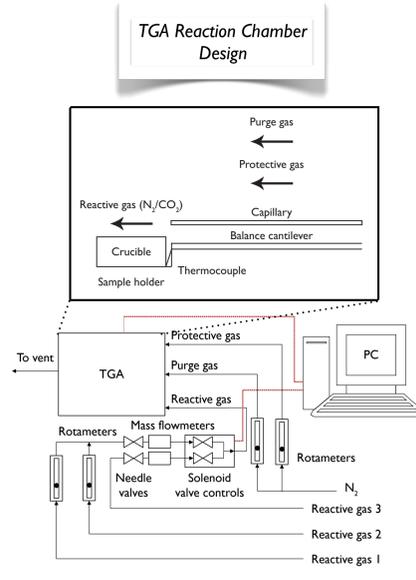
## Synthesis and Carbonation of Ba<sub>4</sub>Sb<sub>2</sub>O<sub>9</sub>



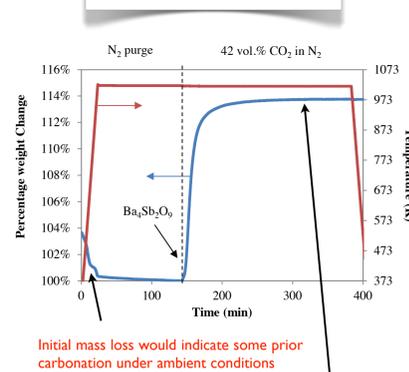
C.D.Ling et al., *Acta Cryst. B*, 63, 584 (2007)

M.T.Dunstan et al., *Solid State Ionics*, 235, 1 (2013)

## Thermogravimetric studies of carbonation



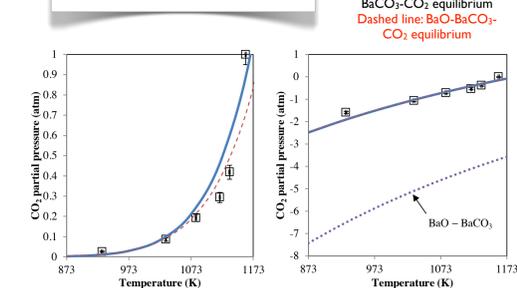
### Initial Carbonation Experiment



Initial mass loss would indicate some prior carbonation under ambient conditions  
13.75% mass increase after carbonation indicates the carbonation products must have stoichiometry BaCO<sub>3</sub> and ~BaSb<sub>1.89</sub>O<sub>5.72</sub> (BaSb<sub>2</sub>O<sub>6</sub>)

M.T.Dunstan et al., submitted

### Carbonation Equilibrium Curves

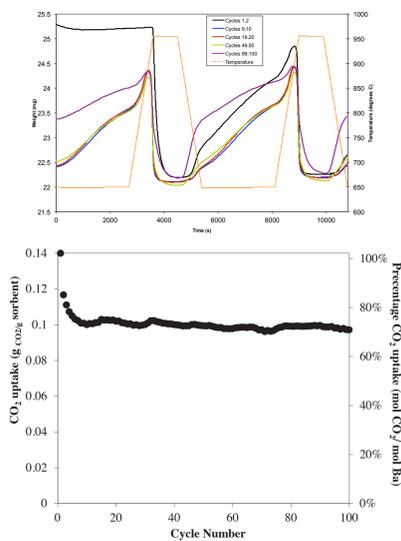


Unlike the BaO-BaCO<sub>3</sub> system, which requires unfeasibly high temperatures to regenerate, Ba<sub>4</sub>Sb<sub>2</sub>O<sub>9</sub> is able to regenerate at much lower temperatures, mimicking the thermodynamic properties of CaO.

Ba<sub>4</sub>Sb<sub>2</sub>O<sub>9</sub>-BaCO<sub>3</sub> equilibrium fit:

$$K_p = p_{CO_2} = 8.5 \times 10^6 \cdot \exp\left(-\frac{1.8 \times 10^4}{T}\right)$$

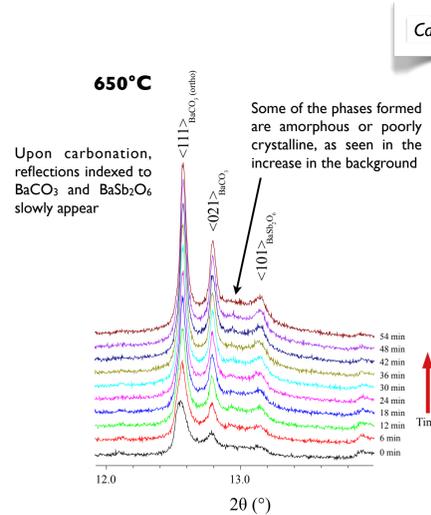
## TGA cycling studies



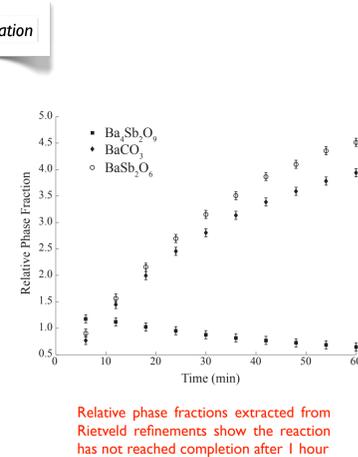
We tested the cycling capacity of Ba<sub>4</sub>Sb<sub>2</sub>O<sub>9</sub> over 100 cycles of carbonation at 600°C and desorption at 950°C in 100% CO<sub>2</sub>. In later cycles it appeared that the material was more reactive towards absorption, indicating that changes in morphology or structure may activate the material for better absorption.

Importantly, we found that Ba<sub>4</sub>Sb<sub>2</sub>O<sub>9</sub> retains its absorption capacity even after 100 cycles, making it suitable for chemical looping applications.

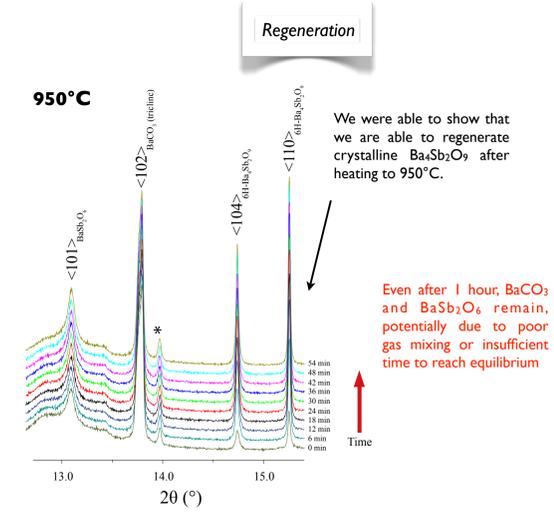
## In-situ synchrotron XRD of carbonation and regeneration reactions



Upon carbonation, reflections indexed to BaCO<sub>3</sub> and BaSb<sub>2</sub>O<sub>6</sub> slowly appear  
Some of the phases formed are amorphous or poorly crystalline, as seen in the increase in the background



Relative phase fractions extracted from Rietveld refinements show the reaction has not reached completion after 1 hour



We were able to show that we are able to regenerate crystalline Ba<sub>4</sub>Sb<sub>2</sub>O<sub>9</sub> after heating to 950°C.

Even after 1 hour, BaCO<sub>3</sub> and BaSb<sub>2</sub>O<sub>6</sub> remain, potentially due to poor gas mixing or insufficient time to reach equilibrium

The carbonation and regeneration reactions were observed with *in-situ* synchrotron XRD carried out on the PD beamline at the Australian Synchrotron, performed under flowing CO<sub>2</sub> using a capillary gas-flow cell.

## Conclusions

Ba<sub>4</sub>Sb<sub>2</sub>O<sub>9</sub>, a perovskite-type material, is able to absorb CO<sub>2</sub> at ~600°C forming BaCO<sub>3</sub> and BaSb<sub>2</sub>O<sub>6</sub>, and is able to be regenerated upon heating to 950°C.

S-XRD and TGA make it possible to monitor the carbonation and regeneration reactions *in-situ*, identifying the phases present at each stage and the relative rates and capacities of absorption.

Importantly, Ba<sub>4</sub>Sb<sub>2</sub>O<sub>9</sub> is able to be cycled between 600-950°C to reversibly absorb CO<sub>2</sub>, and retains its capacity over 100 cycles.

It appears that the stability of Ba<sub>4</sub>Sb<sub>2</sub>O<sub>9</sub> upon cycling comes in part from its ability to regenerate its original particle morphology, recreating a porous structure from a dense shell of BaCO<sub>3</sub> in each cycle.

This study demonstrates the potential to employ a whole new class of inorganic oxide materials with stable and flexible chemical compositions and structures for applications in carbon capture and storage.

## Acknowledgements

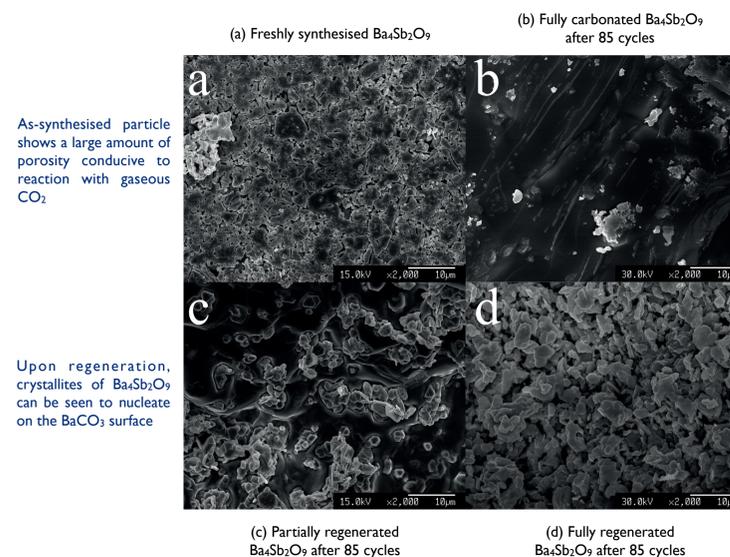
M.T.D thanks the Cambridge Commonwealth Trusts for the award of a PhD scholarship, and Trinity College, University of Cambridge, UK for the award of an External Research Studentship. We would also like to thank the Australian Synchrotron for the award of beamtime.

Cambridge Commonwealth Trust

Cambridge Overseas Trust

TrinityCollegeCambridge

## Structural changes of Ba<sub>4</sub>Sb<sub>2</sub>O<sub>9</sub> monitored by Scanning Electron Microscopy (SEM)



As-synthesised particle shows a large amount of porosity conducive to reaction with gaseous CO<sub>2</sub>

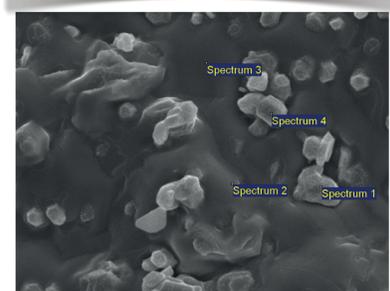
Upon regeneration, crystallites of Ba<sub>4</sub>Sb<sub>2</sub>O<sub>9</sub> can be seen to nucleate on the BaCO<sub>3</sub> surface

Loss of porosity on forming surface layer of BaCO<sub>3</sub>

Evidence of surface cracking associated with particle strain - possible route to further carbonation

Significant porosity recreated upon full regeneration - an explanation for the stable cycling capacity of Ba<sub>4</sub>Sb<sub>2</sub>O<sub>9</sub>

### SEM-EDX elemental analysis: Partially regenerated Ba<sub>4</sub>Sb<sub>2</sub>O<sub>9</sub>



Spectra	C	O	Sb	Ba	Phase
1	20.58	47.62	9.58	22.21	Ba <sub>4</sub> Sb <sub>2</sub> O <sub>9</sub>
2	34.25	43.96	0.58	21.21	BaCO <sub>3</sub>
3	34.29	47.24	-	18.47	BaCO <sub>3</sub>
4	17.93	45.00	10.83	26.24	Ba <sub>4</sub> Sb <sub>2</sub> O <sub>9</sub>