	Experiment title: Structural evolution of CO2 sorbents during cyclic operation	**Experiment number**: **HC-4790**
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Report:

1. Overview

The development of efficient and stable CO_2 sorbents is a crucial step towards carbon dioxide neutrality. Solid CaO- and MgO-based sorbents are highly promising materials for CO_2 capture, owning to their high theoretical CO_2 uptake (1.09 gCO2/gMgO; ~0.78 gCO2/gCaO) and intermediate operational temperatures (MgO: 300–450 °C; CaO: 600-700 °C) and natural abundance.

Bare MgO has a very low CO_2 uptake that can be accelerated appreciably through the addition of alkali metal salts (e.g., $NaNO_3$). Our research is focused on resolving the structural mechanism of CO_2 uptake by a combination of complementary in situ methods including *in situ* environmental SEM, *in situ* TEM and *in situ* XRD and GIXRD techniques. We are aiming to reveal the initial carbonation process and epitaxial formation of $MgCO_3$ as well as the sequential involvement of Na_2CO_3 and $Na_2Mg(CO_3)_2$ (double salt) phases using surface sensitive GIXRD. The same experimental strategy is followed for the calcination/carbonation behaviour of single crystalline $CaCO_3$.

2. Experimental part

In situ GIXRD experiments were performed on: (i) $CaCO_3$ (104) single crystals and (ii) MgO (100) single crystals coated with $NaNO_3$. A Kapton dome in situ cell (ESRF instrument pool) was used to perform cyclic calcination/carbonation under relevant conditions. The $CaCO_3$ samples were heated to 400° or 500° C in a flow of He (7 mL/min for 30-60 min). When complete calcination was achieved, the gas was switched to CO_2 (7 mL/min CO_2 for a few minutes). The MgO samples were treated at 500 °C in a flow of He (7 mL/min for 30

min) After cooling and stabilization at 315 °C for 15 min, the flow was switched to CO_2 (7 mL/min CO_2 for 15 min). The gas is then switched to He (7 mL/min for 15 min) to regenerate the material to the desired temperature (500 °C). GIXRD data were acquired using the Pilatus detector (1 fps) until the calcined or carbonated state was reached. The μ-scan (rocking curve) was then measured in the small angular range up to 2° to infer detailed orientation relationships and formation mechanisms.

Ex situ GIXRD experiments were performed on the two samples after carbonation in the tube furnace reactor:
1. MgO (100) single crystal coated with $NaNO_3$ powder after direct carbonation at 325° C for 4 hours.
2. MgO (100) single crystal coated with $NaNO_3$ powder after pre-treatment in CO_2 for 1 hour at 500°C, followed by carbonation at 325° C for 4 hours.

The two scans for each sample (θ and μ) were performed. The θ scan (around an axis, which is normal to the sample surface) was measured at the exact Bragg angle of the (200)-MgO reflection and in the angular range of -8° - 10° in order to have all the reflections of the <001> zone axis projected onto the detector. After this we performed rocking curve measurements of carbonate reflections that are co-aligned with the (200)-MgO diffraction maximum. We first find the θ value at which the (200)-MgO reflection is most intense and then perform the μ-scan in the angular range 0.5° - 4° (rocking curve).

Unfortunately, the in-situ experiments were not successful because the in-situ Kapton dome cell was leaking and it was not possible to replace it on site. However, the series of ex-situ GIXRD experiments on $NaNO_3$-promoted MgO(100) samples carbonated in the laboratory reactor under different carbonation conditions were a complete success and will be published soon.

3. Preliminary results

1. Ex-situ GRIXD results of the $NaNO_3$-promoted MgO (100) single crystal after direct carbonation at 325° C for 4 hours (Figure 1).

The design of the goniometer allows the sample to be moved vertically along the [001]-MgO direction (z-scan) with high precision, so we are able to measure GIXRD patterns on a sample surface and close to the MgO-$MgCO_3$ interphase. Figure 1 (A-B) shows the GIXRD θ-scan on the sample surface. While the bright single crystalline reflections correspond to the [001]-MgO zone axis, the ring diffraction pattern corresponds to both the $NaNO_3$ and $MgCO_3$ phases as is indexed in Figure 1B. Despite the polycrystalline nature of the GIXRD patterns of the phases formed, one can clearly see the enhanced arcs of both the $NaNO_3$ and $MgCO_3$ phases, which are co-aligned with the (200)-MgO. It indicates a textural state of these phases. In addition, we performed θ-scans close to the MgO-$MgCO_3$ interface. Figure 1 C, F shows GIXRD patterns at different θ positions. In contrast to the surface GIXRD pattern, only separated single crystalline diffraction maxima of the carbonate phase are present. What is more, the (105)-$Na_2Mg(CO_3)_2$ diffraction peak was detected (Figure 1C), although carbonation conditions used assumed a direct $MgO \rightarrow MgCO_3$ conversion rather than through the intermediate $Na_2Mg(CO_3)_2$ phase. Taking into account this finding, we assume that the diffraction maximum in Figure 1E, labelled "(104)-$MgCO_3$ or (006)-$Na_2Mg(CO_3)_2$" and located strictly below the (200)-MgO reflection, belongs to the double salt phase rather than to $MgCO_3$.* This is also supported by our HRTEM data of several FIB lamella sections along the $MgCO_3$/(001)MgO interface, which show that the (104)-$MgCO_3$ planes grow always at an angle to the (200)-MgO plane and not parallel to it, in contrast to the basal (006) plane of the double salt, which is always perfectly aligned with the (200)-MgO plane. To check the quality of the observed carbonate planes growing parallel to (200)-MgO, we performed rocking curve measurements at the Bragg position of the (200)-MgO diffraction maximum. Figure 1 D,E show the GIXRD rocking curve patterns on the sample surface. The only single crystalline reflections, (105)- Na2Mg(CO3)2 and the (104)-MgCO3 were revealed. This indicates that there are single crystalline blocks of these planes that do not grow parallel to the (100)MgO surface, but rather at an angle to it.

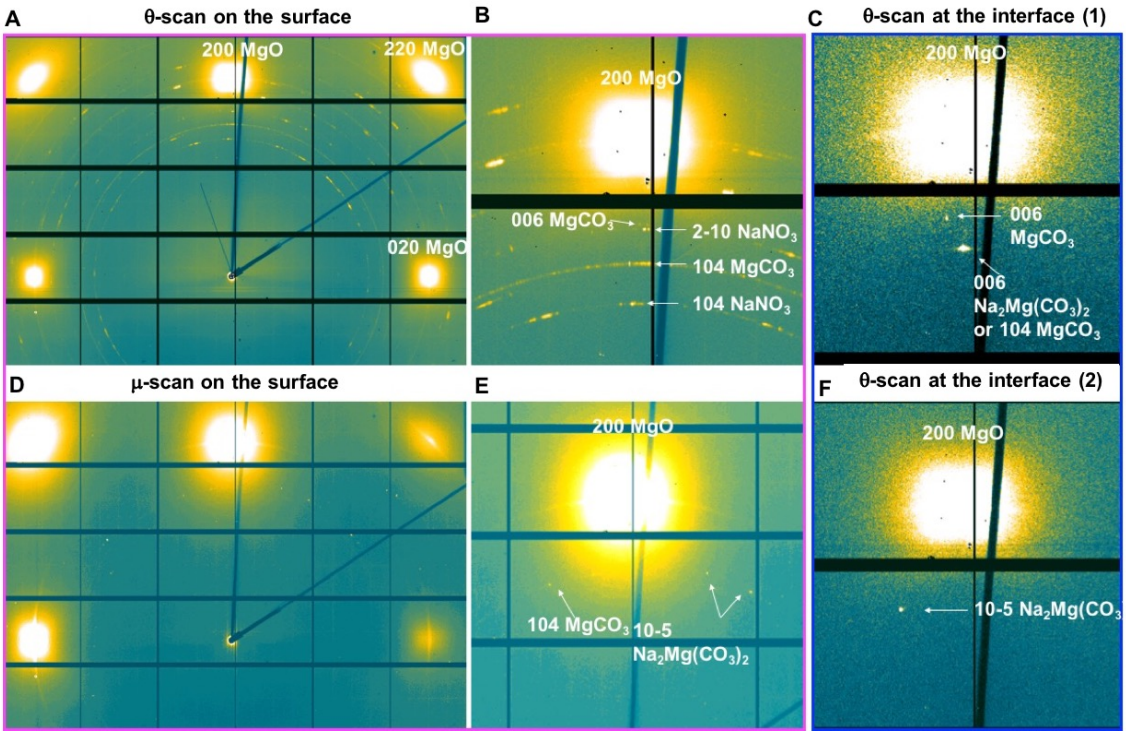

Figure 1. Ex-situ GIXRD data. A is the GIXRD pattern on the sample surface, and B is its magnified region around the (200)-MgO diffraction maximum. C,F - GIXRD patterns at the $MgCO_3$/MgO interphase at different positions of the θ – angle. D is the μ – scan (rocking curve) on the sample surface, and E is its magnified region around the (200)-MgO diffraction maximum.

2. *Ex situ GIXRD results of the $NaNO_3$-promoted MgO (100) single crystal after pre-treatment in CO_2 for 1 hour at 500°C, followed by carbonation at 325° C for 4 hours.*

The GIXRD pattern shows the θ–scan of the [001]-zone axis of the MgO (figure 2A). A magnified region just below the (200) MgO reflection reveals single crystalline spots labeled as the (006)-$MgCO_3$, the (006)-$Na_2Mg(CO_3)_2$ or the (104)$MgCO_3$ (difficult to distinguish) and the (104)-$Na_2Mg(CO_3)_2$ (Figure 2B). Based on the observation of only these single crystalline spots of the carbonate phases and their strong co-alignment with the (200)-MgO, we conclude that both carbonate phases grow oriented with respect to the MgO support. To show the quality of the double salt phase formed, the μ-scan (rocking curve) was performed (Figure 2C). The (006)-$Na_2Mg(CO_3)_2$ and (104)-$Na_2Mg(CO_3)_2$ reflections transforms into slightly elongated arcs. This indicates a good quality of the double salt crystals. In addition, the one-dimensional rocking curve measurements of the (006)-$Na_2Mg(CO_3)_2$ reflection carried out on our laboratory X-ray diffractometer reveal that the full width at half maximum of its rocking curve is even comparable to the instrumental one, indicating a high quality of the $Na_2Mg(CO_3)_2$ crystals growing along their basal plane on the MgO(100) surface. Furthermore, in agreement with the GIXRD data, the FIB-TEM lamella data of the (006)-$Na_2Mg(CO_3)_2$-MgO(001) interface reveal epitaxial growth of the double salt.

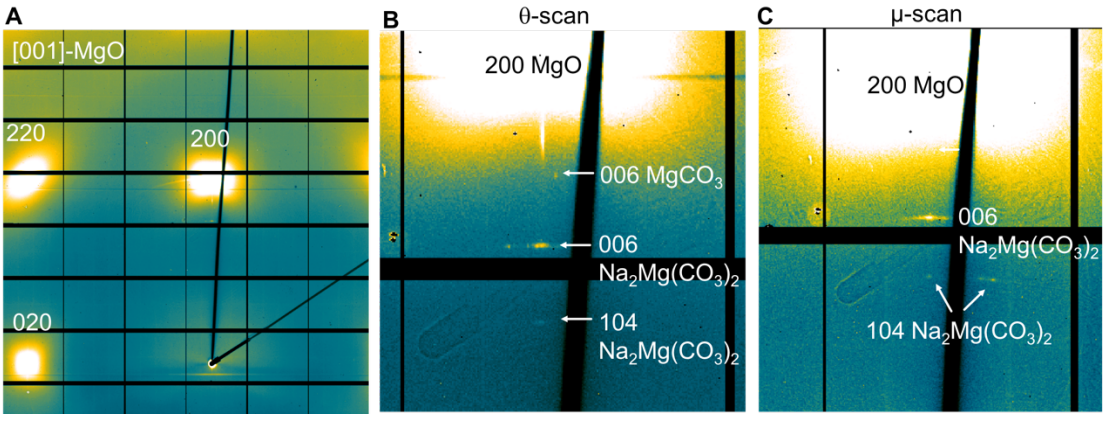

Figure 2. Ex-siut GIXRD data. A is the GIXRD pattern at the $MgCO_3$/MgO interphase, and B is its magnified region around the (200)-MgO diffraction maximum. C is the μ – scan (rocking curve).

* In our synchrotron experiment the wavelength was too small ($\lambda = 0.177$ Å) to distinguish between the (104)-$MgCO_3$ and the (006)- $Na_2Mg(CO_3)_2$ reflections.