

Rietveld microstructural study of BaCO₃ from natural carbonation of Ba(OH)₂•8(H₂O)

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Abstract : It is shown that barium hydroxide octahydrate, frequently used in various syntheses including supraconductors, is highly sensitive to natural carbonation. A “fresh” product as received from chemical companies could contain already more than 30% of BaCO₃. The microstructures of the resulting BaCO₃ are examined by transmission electron microscopy and from X-ray line broadening by whole powder pattern fitting technique.

Keywords : Carbonation, Rietveld method, barium carbonate, barium hydroxide octahydrate

Introduction

By checking the quality of a commercial barium hydroxide octahydrate Ba(OH)₂•8H₂O product (Aldrich), it was found to be in fact pure BaCO₃, apparently. Carbonation occurs naturally as the process of atmospheric CO₂ sequestration in minerals, forming carbonates. This is a relatively slow process and some studies report that, though the mortar hardening process usually takes weeks to complete, significant carbonation depths in concrete, at ambient temperature, can take up to 20 years [1] (partial pressure of CO₂ is typically 0.03% to 0.04% by volume of air). The degradation of superconducting ceramics like YBa₂Cu₃O_{7-δ} obtained by solid state sintering is known to be due to carbonation processes [2]. The presence of a carbonate layer at the solid/gas interface contributes to decrease the critical current density after several months ageing in air conditions. On the other hand, carbonation has beneficial effects on the prevention of climate change by reducing the level of greenhouse gas emission, and therefore, research is made in order to optimize CO₂ sequestration (using Mg(OH)₂ for instance [3]). Because the powder diffraction pattern of the BaCO₃ ex-Ba(OH)₂•8H₂O (Aldrich) exhibited strong anisotropic line-broadening, it was decided to characterize it by applying the Rietveld method including a microstructure approach. A second, and older, commercial sample (from Prolabo) of barium hydroxide octahydrate was also found completely transformed into BaCO₃ and analyzed for comparison.

Experimental

The X-ray powder patterns were recorded on a Bruker D8 Advance diffractometer (Bragg-Brentano, Cu-Kα, operating at 40KV, 40mA, equipped with variable slits : V6-V6) using a ‘zero background’ monocrystalline silicon sample holder. The diffractograms revealed that the Aldrich and then the Prolabo samples of barium hydroxide octahydrate were pure BaCO₃, and more (Prolabo) or less (Aldrich) well crystallized. The starting Aldrich sample is said to contain already up to 2% BaCO₃. By optical microscopy, both Aldrich and Prolabo samples appear as millimeter sized white pellets (almost transparent if thin). These pellets are much bigger in the Prolabo sample. They seem to have kept the single crystal shapes from the

original barium hydroxide octahydrate in the Aldrich sample (fig. 1). For transmission electron microscopy observations, the samples are prepared as follows : in order to avoid decrease of size by grinding, the powders are ultrasonically dispersed in methanol. A few droplets are deposited on a Cu grid covered with a carbon coated holey film. Electron microscopy was performed with a JEOL-2010 electron microscope operating at 200 kV fitted with a side-entry $\pm 30^\circ$ double tilt specimen holder and equipped with a KEVEX energy dispersive X-ray (EDX) analyzer (Fig. 2). We cannot give exactly the ageing conditions but the Aldrich product container was first open 5 years ago, and the Prolabo one was open since more than 15 years. Closing the containers was apparently insufficient for preventing carbonation to occur. TGA was performed on the two BaCO_3 samples. An important weight loss occurred in the range 40-170°C : 9.29% (Prolabo sample) and 44.34% (Aldrich). This can be interpreted as due to adsorbed water in very large quantity : 1.16 and 8.65 water molecules respectively for one BaCO_3 molecule in the Prolabo and Aldrich samples. It appears that the main part of the crystal water in the $\text{Ba(OH)}_2 \cdot 8\text{H}_2\text{O}$ formula stayed adsorbed on the Aldrich sample after carbonation. This suggests a quite higher specific surface for the Aldrich sample than for the Prolabo sample, as already obvious from differences in X-ray line broadening. Powder patterns made on both samples after heating up to 600°C or 400°C (before any CO_2 weight loss), and then cooling to room temperature, show BaCO_3 again. However, this dried barium carbonate is rather unstable since 2-3% of $\text{Ba(OH)}_2 \cdot \text{H}_2\text{O}$ is formed after a few hours in air, from the Prolabo sample (heated at 600°C). After one day in air, the Aldrich sample heated at 400°C leads approximately to a 1/3,1/3,1/3 mixture of $\text{Ba(OH)}_2 \cdot \text{H}_2\text{O}$, $\text{Ba(OH)}_2 \cdot 3\text{H}_2\text{O}$ and BaCO_3 . This extreme reactivity is certainly uncommon for BaCO_3 , and may be due to the quite high specific surface of the samples and also to some imperfections revealed after the departure of the adsorbed water. It may be suggested that such highly reactive samples could have some interest in catalysis.

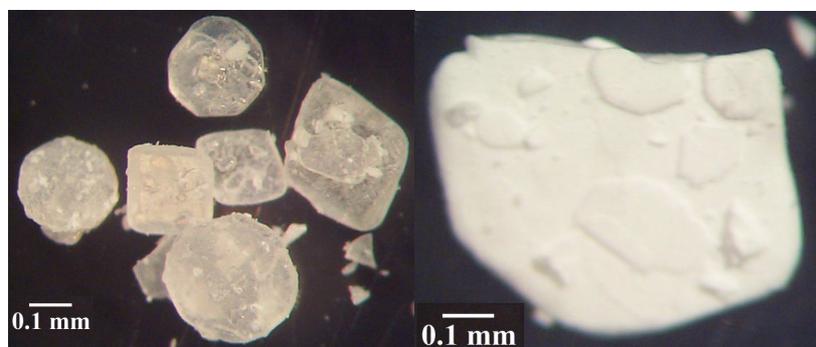


Fig. 1. Aldrich (left) and Prolabo (right) samples by optical microscopy .

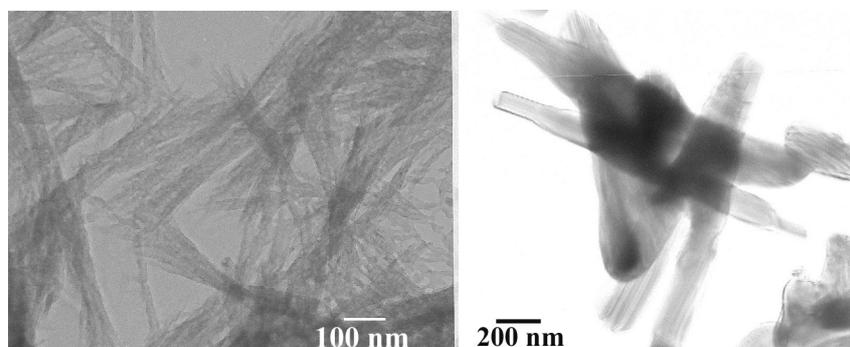


Fig. 2. Aldrich (left) and Prolabo (right) samples by TEM.

Rietveld method

Microstructure investigation from diffraction data is usually performed by the Warren-Averbach method [4] (using Fourier transformation of profile shape), by the variance or integral breadth methods or by Williamson & Hall plot [5]. In the present case it is not possible to isolate two harmonics for any family of reflections for applying the Warren Averbach method. Isolating one reflection appears even impossible in the Aldrich sample case, due to strong overlapping and huge line broadening (there are close to 350 reflections in the 16-150°2θ range). Those methods requiring individual line profiles for extracting microstructural parameters are thus disqualified, as they are usually for structurally complex compounds. There is no really another choice than to apply a whole powder pattern fitting approach, overcoming the problem of overlapping peaks. A method allowing for anisotropic size/microstrain modelling in the Rietveld method was applied through the ARIT software [6]. Though an approach without the structure constraint would be feasible (Le Bail method [7]) and even recommended if no overlapping occurs, on the contrary it is important to make here simultaneously the microstructure and crystal structure approach, fixing the relative intensities of overlapping calculated peaks close to what they should be.

Profile shapes are described in the ARIT program [6] by Fourier series, allowing the replace the $h = f * g$ convolution by a simple product in Fourier space : $H = F \times G$. The calculated G part is obtained from the fit of the pattern of a well crystallized sample representing g , and recorded in exactly the same conditions (CeO₂ “sharp” from the Size-Strain Round Robin [8], in this case). The experimental pattern h for an ill-crystallized material is fitted by reusing the previously determined G part, multiplied by the F sample contribution, where $F_n = A_n^S A_n^D$ is the traditional product of the size and microstrain Fourier coefficients. Currently, ARIT applies a flexible model for the microstrain part and only one model for the size-broadening part which was found to give relative satisfaction (but other size models could be introduced as well). In the following, we use the B. E. Warren formalism [4].

For modelling a microstrain effect in ARIT, a hypothetical Gaussian strain distribution is considered (see Warren, p. 270 [4]) such as :

$$A_n^D = \langle \cos 2\pi l Z_n \rangle = \exp(-2\pi^2 l^2 \langle Z_n^2 \rangle)$$

In that equation, $\langle Z_n^2 \rangle$ is modelled in ARIT by a flexible variation law of the distortion versus the distance according to the following equation :

$$\langle Z_n^2 \rangle = |n|^K \langle Z_1^2 \rangle$$

The ARIT program refines two microstrain parameters : K and $\langle Z_1^2 \rangle$ (i.e. $\langle Z_n^2 \rangle$ for $n = 1$). It is to be noted that if K is refined to $K = 2$, the calculated microstrain profile shape will be Gaussian, and if K is refined to $K = 1$, it will be Lorentzian. Other shapes being possible, depending on the final refined value of K .

The size effect is modelled in ARIT through the size Fourier coefficient A_n^S which is described in terms of $p(i)$, the fraction of the columns of length i cells by the expression [4]:

$$A_n^S = \frac{1}{N_3} \sum_{i=|n|}^{\infty} (i-|n|) p(i)$$

where N_3 is the mean column length number. Modelling $p(i)$ allows to define A_n^S . It would not be really difficult to introduce several models in ARIT, however, there is currently only one model proposed which is a continuously decreasing size distribution function defined by :

$$p(n) = \gamma^2 \exp(-\gamma|n|)$$

The size Fourier coefficients corresponding to this arbitrary size distribution function are :

$$A_n^S = \exp(-\gamma|n|),$$

And the average number of unit cells is $N_3 = 1/\gamma$. Practically, fictitious quantities have to be defined like in the Warren book ([4] p. 273). The real distance along the columns of cells perpendicular to the reflecting planes is defined by :

$$L = n a'_3$$

Where a'_3 depends on the interval of definition of the reflections $[\theta_2\theta_1]$ according to :

$$a'_3 = \lambda / 2 (\sin \theta_2 - \sin \theta_1)$$

Details about how anisotropic size and microstrain effects are undertaken in ARIT (ellipsoids describing the $\langle Z^2 \rangle_{(hkl)}$ and $N_{3(hkl)}$ values) may be found in [6].

Results

Fitting the powder diffraction data of the BaCO₃ samples was realized by using a $[2\theta_2-2\theta_1]$ profile definition range of 20°, leading to $a'_3 = 4.419 \text{ \AA}$.

- Aldrich sample

Without size/microstrain effect, the conventional Rietveld R factors (background subtracted, peak only) were : $R_P = 11.6$ and $R_{WP} = 14.8\%$. They dropped to $R_P = 9.7$ and $R_{WP} = 12.8\%$ after application of the anisotropic microstructure model, with a Bragg R factor $R_B = 4.7$ (fig. 3). The parameters proposed by ARIT are the mean size as obtained from : $\bar{M} = N_3 a'_3$, the K parameter defining the variation law of the distortion versus the distance and the strain parameter defined as $\langle Z^2 \rangle$ from which one can easily estimate values like $\langle \epsilon^2 \rangle = \langle Z^2 \rangle / n^2$, by using the K parameter and L as defined above. The mean size \bar{M} is related to the usually called “surface” size distribution, while another definition \bar{M}_1 is obtained for a so-called “volume” distribution (which may be similar to the size distribution observed by electron microscopy if the grain size is analogous to the coherently diffracting domain size). According to the model of size distribution retained in these calculations, we have approximately $\bar{M}_1 \sim 2\bar{M}$. The final results \bar{M}_1 and $\langle \epsilon^2 \rangle = \langle Z^2 \rangle$ ($\langle \epsilon^2 \rangle$ for $L = a'_3$) are given in Table I for a selection of $[hkl]$ directions. It is seen from these results that the mean crystal shape from the size/microstrain Rietveld analysis correspond to ribbons elongated in the $[100]$ direction. The \bar{M}_1 values correspond well to what is observed by electron microscopy, showing that the ribbons seen on the fig. 2 correspond to the coherently diffracting domain shapes (quite smaller than the pseudo crystals seen on fig. 1).

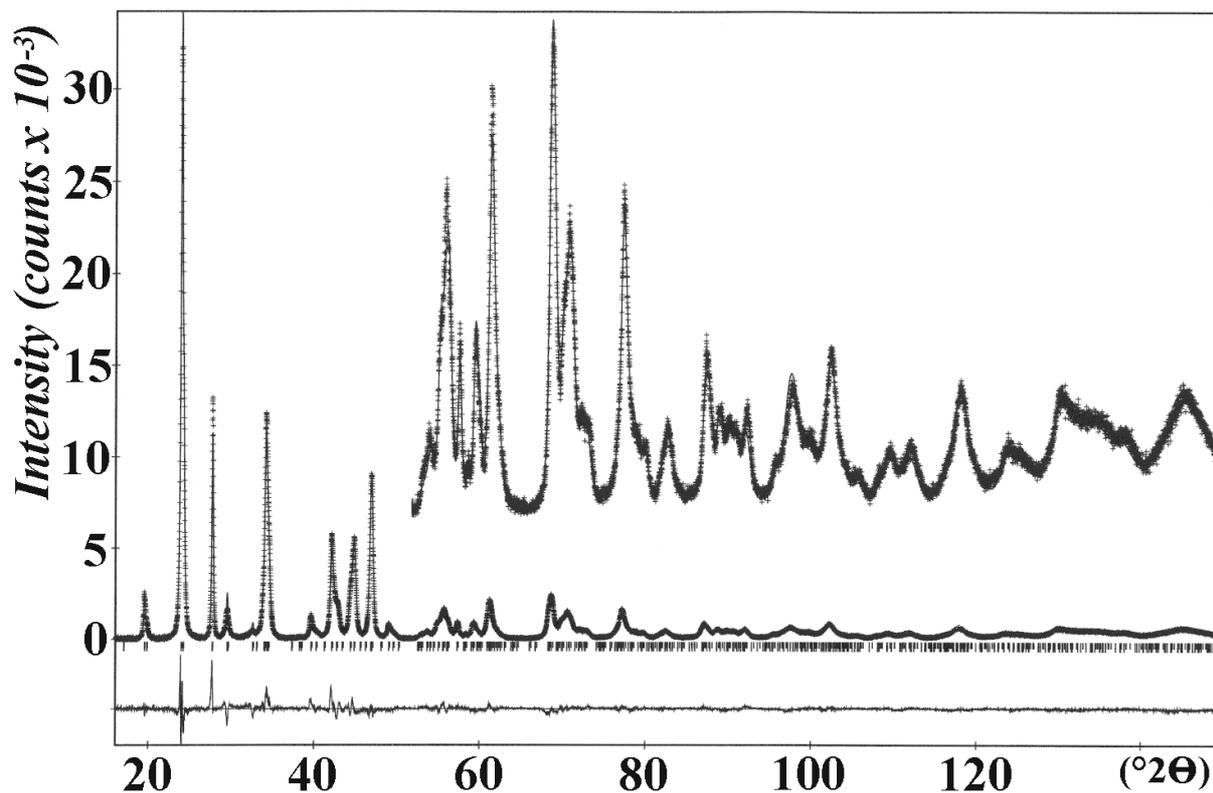


Fig. 3. Rietveld plot for the BaCO_3 Aldrich sample, including anisotropic microstructure model

$[hkl]$	\overline{M}_1 (nm) (A)	\overline{M}_1 (nm) (P)	$\langle \varepsilon^2 \rangle \times 10^4$ (A)	$\langle \varepsilon^2 \rangle \times 10^4$ (P)
100	659	544	3.28	0.101
201	231	589	1.67	0.084
101	144	706	1.09	0.067
001	93	> 2000	0.72	0.050
111	65	627	1.04	0.071
110	60	512	2.01	0.102
011	47	759	0.77	0.058
010	30	444	1.20	0.108

Table I. Mean volume-weighted size \overline{M}_1 (nm) and distortion $\langle \varepsilon^2 \rangle$ for the Aldrich (A) ($K = 1.38(1)$) and Prolabo (P) ($K = 1.51(3)$) BaCO_3 samples as a function of the orientation.

- Prolabo sample

The powder pattern shows narrower reflections, but the initial Rietveld fit with size/microstrain contribution was not very satisfying with $R_P = 14.8$ and $R_{WP} = 18.6\%$. The cell parameters were found meaningfully different from those of the Aldrich sample. The main problem limiting a better fit was obviously bridges occurring between some neighbouring reflections at various places on the powder pattern. By a matter of facts, this occurs exactly at the places where some couples of reflections are narrower in the Aldrich sample, due to the different cell parameters. It was thus suspected that the Prolabo sample could be at a different reacting stage (posterior) than the Aldrich sample, and that the reaction was uncomplete leading to an inhomogeneous compound. The Prolabo sample could contain a significant proportion of smaller coherently diffracting domains, similar to those of the Aldrich sample and with analogous cell parameters. This hypothesis was tested by a two-phase Rietveld modelling, adding a second constrained contribution, refining only the scale factor for that hypothetical small grain part. The R factors were lowered by more than 3 %. This approach allowed to fit the bumps between the pairs of reflections (fig. 4). The proportion of that small grain size part was estimated to be close to 36%. Extracting size/microstrain values will certainly lead to meaningless results in the Prolabo sample case, due to that problem, but it was however attempted, leading to $R_P = 11.5$ and $R_{WP} = 14.5\%$, with a Bragg R factor $R_B = 6.4\%$ (fig. 5). The final results \overline{M}_1 and $\langle \epsilon^2 \rangle$ are gathered in Table I.

Sample	a (nm)	b (nm)	c (nm)
Aldrich	0.52794(5)	0.89521(9)	0.64285(4)
Prolabo	0.53088(1)	0.89169(2)	0.64339(2)
Ref. 9	0.5313(1)	0.8896(1)	0.6428(1)

Table II. Cell parameters for the Aldrich and Prolabo BaCO_3 samples.

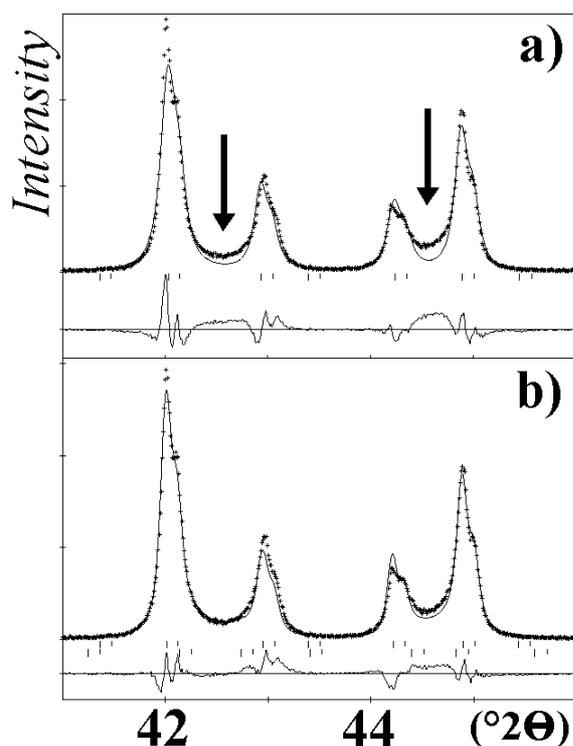


Fig. 4. Fits with one (a) and two phases (b) on the Prolabo sample showing the bridges between neighbouring reflections (arrows in a) and a better fit in (b). Vertical bars correspond to reflection positions ($K\alpha_{1,2}$).

Discussion

We do not give here the Rietveld-refined atomic coordinates because they are quite similar to those published in the single crystal study [9], for both the Aldrich and Prolabo samples. The discrepancy between the cell parameters of the two BaCO_3 samples could be due to differences in remaining OH^- and/or

H₂O molecules in the crystal structure. We don't know exactly. The discrepancy is seen mainly for the *a* and *b* cell parameters, but it is less than 1% (Table II). An obvious difference is in the grain size and distortion parameter values, respectively ten times larger and smaller in the Prolabo sample than in the Aldrich sample. However, looking more in details shows that if the same [010] direction is observed for the shorter crystallite size, the larger size is quite not in the same direction.

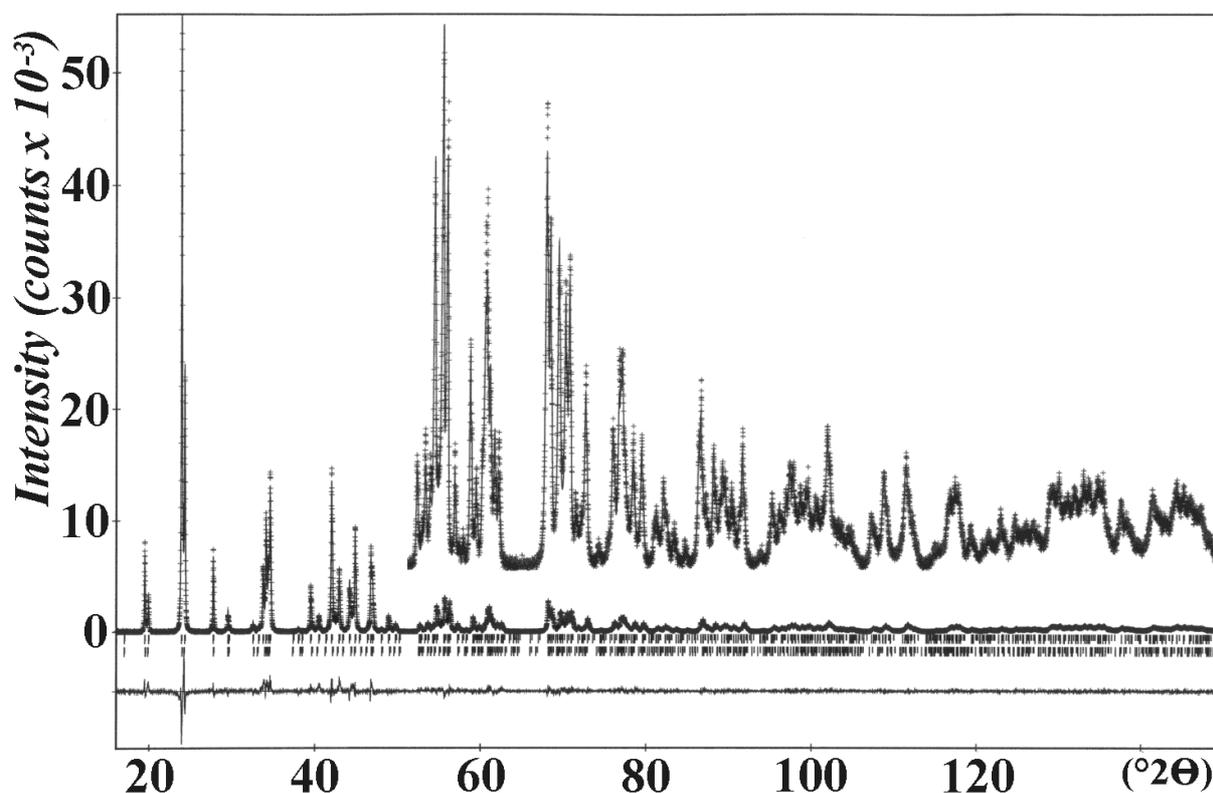


Fig. 5. Rietveld plot for the BaCO₃ Prolabo sample, including the anisotropic microstructure model.

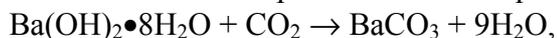
For microstructure analysis by a Bragg-Brentano goniometer, one has to produce a good sample surface from a compact sample, otherwise, additional broadening effects due to imperfect conditions can occur. Some problems due to compaction can result, however, namely preferred orientation. This is the case for both samples, and the preferred orientation directions are also curiously different in both samples. The Aldrich sample presents an important preferred orientation in the [001] direction (disclosed by testing various directions, and concluding from a clear improvement in the R factors). Multiple preferred orientation in directions all included in the (hk0) plane were found ([100], [010], [110], [230]) for the Prolabo sample, suggesting needle-like mean microcrystal shapes, elongated along the [001] direction.

Conclusion

A previous study under different climatic factors has shown that the natural carbonation of Mg(OH)₂ or MgO is never complete even after a prolonged exposure [3]. In the case of the barium hydroxide octahydrate, the carbonation appears to be complete, leading to the

witherite variety of BaCO₃. It seems that the crystallite size may continue to evolve after the complete carbonation. Though informative about the crystal shape of the reaction products, this study leaves many unanswered questions :

- Why this ribbon shape for the Aldrich sample smaller than for the Prolabo one ? Is this due to differences in the starting barium hydroxide octahydrate or due to differences in ageing ?
- Where has gone the water in that oversimplified chemical equation :



since the final Prolabo product is apparently almost dry ? Can we suppose that the crystal water is first involved in the carbonation reaction and stays adsorbed almost entirely (Aldrich sample). That adsorbed water would be further evacuated slowly in vapor phase during the continuing ageing process, while the crystallites grow by face adhesion with other crystallites ? If this is true, then the crystallites would grow by sharing preferably their (001) and (010) faces, but apparently not their (100) faces (Table I).

- The role of water is unknown. Is this reaction a truly solid-gas reaction or is H₂CO₃ involved, produced by dissolving CO₂ into H₂O, coming from the water in the solid ? Are there any non-obvious structural relationships between BaCO₃ and Ba(OH)₂•8H₂O or some hypothetically intermediate compound formed during the reaction (the mono- or three-hydrate), which could explain the ribbon growing ? Or is the ribbon form a further effect after the carbonation ? Studying the carbonation of a single crystal would possibly reveal structure relationship, if any, as suggested by the final shape of the BaCO₃ pellets very similar to the original octahydrate crystal shape for the Aldrich sample.

Understanding more the natural carbonation process of Ba(OH)₂•8H₂O would need additional work. The fact that the reaction can be complete in soft (ambient temperature, in air) conditions suggest that it could be made quite faster in more appropriate conditions, for instance under a pressured flow of hot CO₂ gas.

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