

Sodium hydrogencarbonate (NaHCO₃): coincidence-site lattice twinning and structure refinement

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Abstract. Sodium hydrogencarbonate (NaHCO₃) has been recrystallised hydrothermally using a cooling ramp from 250 °C to 190 °C at 0.069 GPa, and investigated by single crystal X-ray diffraction at room temperature and pressure. Representative crystal data are: monoclinic, space group $P2_1/n$, $Z = 4$, $a = 7.4688(4)$, $b = 9.6842(6)$, $c = 3.4791(2)$ Å, $\beta = 93.321(2)^\circ$, $R = 0.026$, and $D_x = 2.221$ g/cm³. The crystals investigated are complexly twinned by reticular pseudomerohedry, but give two coincidence-site lattices with pseudocell parameters: $a = 3.4791(2)$, $b = 9.6842(6)$, $c = 29.875(2)$ Å, $\beta = 93.321(2)^\circ$, twin axis $[001]$, twin index (Σ) = 4; and, $a = 8.4360(6)$, $b = 9.6811(7)$, $c = 24.941(2)$ Å, $\beta = 99.109(5)^\circ$, twin axis $[10\bar{1}]$, $\Sigma = 8$. The $\Sigma = 4$ and $\Sigma = 8$ twins occur in separate twinned crystals but in similar twin proportions (5.5 : 1), and are most likely secondary in origin. The two coincidence-site lattices are permitted in NaHCO₃ because β corresponds closely to the theoretical value given by the positive root of $[\sin^2(\beta - \pi/2) = 3/912]$.

Introduction

The hydrogencarbonate (bicarbonate) anion (HCO₃⁻) has a physiologically important role in the transport of carbon dioxide and the regulation of blood pH [1] and its naturally occurring sodium salt nahcolite (NaHCO₃) is an essential constituent of ore deposits for the industrial commodity soda ash [2]. The hydrogencarbonate anion is also of theoretical interest due to variation in hydrogen-bonded configurations and asymmetry of C–O distances and O–C–O angles induced by the strong O–H bond [3, 4]. In the structure of NaHCO₃, HCO₃⁻ anions are linked by hydrogen bonds into chains parallel to (101) (Fig. 1) [3, 5, 6]. The most recent refinement of the structure [6] was based on the film intensities and unit-cell parameters of Sass and Scheuerman [3]. Both of these studies used space group $P2_1/c$, but the equivalent space group $P2_1/n$

was used by Zachariassen [5] and is adopted in this study. The recent discovery of the HCO₃⁻ anion in the structural channel of Na-carbonate-bearing hydroxylapatite synthesized at high pressure and temperature [7] suggested an intracrystalline role for the hydroxylapatite nanocrystals of bone in the neutralization of acidity in the body [8]. In the present study, recrystallisation and annealing of NaHCO₃

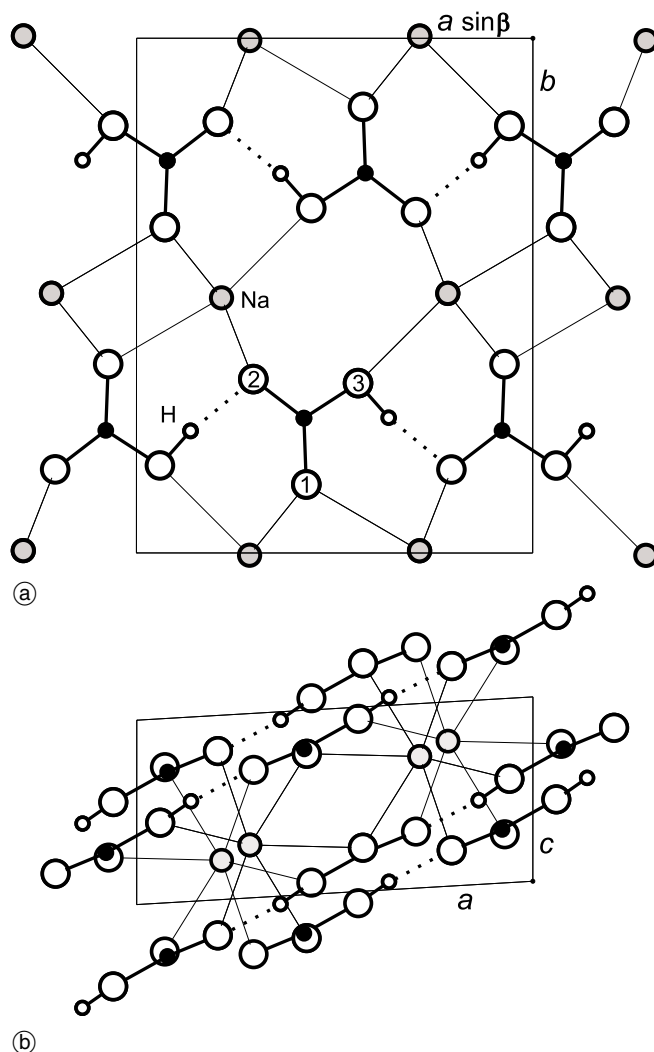


Fig. 1. Structure of sodium hydrogencarbonate (NaHCO₃), highlighting hydrogen-bonded chains of HCO₃⁻ anions: (a) [001] projection; (b) [010] projection; drawn with *ATOMS* [24].

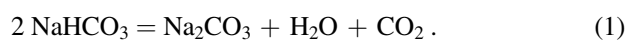
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has resulted in crystals twinned by reticular pseudomorphology, but giving two different three-dimensional coincidence-site lattices in the monoclinic system. We first report on this novel twin feature for crystals of low symmetry, and then discuss refinement of the NaHCO_3 structure.

The study of twinned crystals remains of active interest in crystal chemistry and materials science due to interference from overlap of reciprocal lattice points in structure analysis [9] and the control of grain boundary features of alloys by Σ lattice rotations (where Σ is the twin index, defined as the reciprocal of the fraction of coinciding lattice points) [10–12]. Growth twinning is commonly encountered in nahcolite with (101) as the twin and composition plane [13]: the twin habits are contact, penetration and reticulated.

Experimental

The synthesis experiment was conducted in a standard cold-seal hydrothermal bomb using reagent grade NaHCO_3 (Fisher Scientific Company) as starting material. The NaHCO_3 reagent was further characterized by powder X-ray diffraction and FTIR spectroscopy. No attempt was made to dry it because NaHCO_3 starts to break down at temperatures well below $\sim 100^\circ\text{C}$ in open air (1 atm.) [14], through the reaction:



The starting material was packed into a 38 mm long cylindrical capsule of pure gold welded tight at one end, and sealed by welding immediately after filling. To prevent the breakdown of NaHCO_3 during welding, the capsule was wrapped in a water-wetted tissue. The capsule was oriented along the vertical axis of the cold-seal bomb. Two-stage heating separated by a cooling ramp was employed to promote crystal growth. Pressure was applied first, and then temperature was raised to the target value of 250°C for a dwell time of 24 h, followed by a cooling ramp of $0.02^\circ\text{C}/\text{min}$ to 190°C , with pressure carefully maintained at 0.069 GPa. After annealing at 190°C for 48 h, the experiment was terminated by quenching the bomb in cold water. The uncertainty in pressure is estimated to be ± 0.002 GPa, and that of temperature, measured by a Chromel/Alumel thermocouple, is $\pm 10^\circ\text{C}$ over the length of the capsule.

The experimental products were characterized by optical petrography and powder X-ray diffraction. The synthesis experiment was conducted wholly within the stability field of NaHCO_3 + fluid [15], and the experimental products were accordingly crystals of NaHCO_3 and a trace amount of quenched aqueous fluid. Relatively large (up to $500\ \mu\text{m}$), colourless and clear crystals of NaHCO_3 were present at the top of the capsule and had evidently grown in the fluid space. Crystal A (Table 1) was selected from this assemblage. The remainder of the charge was a plug of coarse-grained, compacted recrystallised starting material: crystal B (Table 1) was selected from this assemblage, at the bottom of the capsule.

Table 1. Experimental details.

	NaHCO_3	NaHCO_3
apparatus	cold-seal hydrothermal bomb	
pressure (GPa)	0.069	
temperature ($^\circ\text{C}$)	190	
time (hour)	48	
crystal I.D.	A (xt394)	B (xt397)
crystal size ($\text{mm}^3 \times 10^3$)	3.75	0.94
crystal habit	prismatic	prismatic
	Twinned pseudocell	
a (\AA)	3.4791(2)	8.4360(6)
b (\AA)	9.6842(6)	9.6811(7)
c (\AA)	29.875(2)	24.941(2)
α ($^\circ$)	90.0	90.0
β ($^\circ$)	93.321(2)	99.109(5)
γ ($^\circ$)	90.0	90.0
V (\AA^3)	1004.9(1)	2011.2(3)
space group	$P2/m$	$P2/m$
	Zachariasen (1933) unit cell	
a (\AA)	7.4688(4)	7.4830(5)
b (\AA)	9.6842(6)	9.6811(7)
c (\AA)	3.4791(2)	3.4764(3)
α ($^\circ$)	90.0	90.0
β ($^\circ$)	93.321(2)	93.399(5)
γ ($^\circ$)	90.0	90.0
V (\AA^3)	251.22(3)	251.40(4)
space group	$P2_1/n$	$P2_1/n$
formula weight	84.01	84.01
D_x (g/cm^3)	2.221	2.220
reflections – unique	463	707
– number, with ($I < 3\sigma(I)$)	64	254
– R_{int}	0.014	0.018
– limits ($h; k; l$)	0,9; 0,12; –3,3	0,10; 0,13; –4,4
refined parameters	51	51
μ (cm^{-1})	3.6	3.6
R	0.026	0.032
wR	0.041	0.032
S	1.204	1.032
extinction ($\times 10^4$)	1.5(6)	0.5(1)
$\Delta\rho$ ($\text{e}\text{\AA}^{-3}$) (+)	0.19	0.24
(–)	0.22	0.24

Single-crystal measurements were made at room temperature and pressure with a Bruker Kappa CCD diffractometer and graphite-monochromatized $\text{MoK}\alpha$ X-radiation (50 kV, 32 mA, $\lambda = 0.71073\ \text{\AA}$). The COLLECT Bruker software was used for unit-cell refinement and data collection. The reflection data were processed with SORTAV-COLLECT, using an empirical procedure for absorption correction. Structure refinements were made with LINEX77 (State University of New York at Buffalo), using the ideal NaHCO_3 composition, and scattering factors for neutral atomic species and values of f' and f'' taken, respectively, from Tables 2.2A and 2.3.1 of the *International Tables for X-ray Crystallography* [16]. Rele-

Table 2. Atomic coordinates and isotropic displacement parameters (\AA^2). $U_{\text{eq}} = (1/3) \sum_i \sum_j U^{ij} a^i a^j$.

LM129, crystal A				
Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> , <i>U</i> _{eq}
Na	0.28551(9)	0.00439(6)	0.7133(2)	0.0218(4)
C	0.0775(2)	0.2381(2)	0.2903(4)	0.0153(4)
O(1)	0.0714(1)	0.3669(1)	0.2636(3)	0.0197(4)
O(2)	0.2052(2)	0.1623(1)	0.1931(3)	0.0203(4)
O(3)	0.9409(2)	0.1700(1)	0.4367(3)	0.0224(4)
H	0.364(3)	0.263(2)	0.043(6)	0.014(5)
LM129, crystal B				
Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> , <i>U</i> _{eq}
Na	0.28564(9)	0.00420(5)	0.7130(1)	0.0229(2)
C	0.0772(2)	0.2380(1)	0.2898(4)	0.0169(4)
O(1)	0.0710(2)	0.3670(1)	0.2636(2)	0.0205(3)
O(2)	0.2050(2)	0.1623(1)	0.1934(3)	0.0215(3)
O(3)	0.9408(2)	0.1704(1)	0.4368(3)	0.0238(3)
H	0.360(3)	0.263(1)	0.040(5)	0.007(5)

Table 3. Selected geometric parameters (\AA , $^\circ$)^a.

Experiment	LM129		Sharma [6]
	crystal A	crystal B	
Na–O(1 ⁱ)	2.470(1)	2.470(1)	2.477(5)
Na–O(1 ⁱⁱ)	2.423(1)	2.423(1)	2.441(6)
Na–O(1 ⁱⁱⁱ)	2.450(1)	2.448(1)	2.463(7)
Na–O(2)	2.367(1)	2.370(1)	2.385(7)
Na–O(2 ^{iv})	2.418(1)	2.417(1)	2.426(7)
Na–O(3 ^v)	2.425(1)	2.428(1)	2.432(5)
Mean	2.425	2.426	2.437
C–O(1)	1.252(2)	1.253(2)	1.249(7)
C–O(2)	1.265(2)	1.266(2)	1.274(6)
C–O(3 ^{vi})	1.340(2)	1.339(2)	1.346(7)
Mean	1.285	1.286	1.290
O(1)–O(2)	2.239(2)	2.241(1)	2.243(6)
O(1)–O(3 ^{vi})	2.240(2)	2.237(1)	2.247(6)
O(2 ^{vii})–O(3 ^{vi})	2.194(2)	2.198(2)	2.206(6)
Mean	2.224	2.225	2.232
O(1)–C–O(2)	125.7(1)	125.6(1)	125.5(5)
O(1)–C–O(3 ^{vi})	119.6(1)	119.3(1)	119.9(4)
O(2)–C–O(3 ^{vi})	114.8(2)	115.1(1)	114.6(5)
O(3)–H ⁱ	0.96(2)	0.97(2)	1.1(1)
O(3) ... O(2 ⁱ)	2.591(2)	2.592(2)	2.610(6)
H ... O(2)	1.64(2)	1.63(2)	1.6(1)
H ⁱ –O(3)–C ^{vii}	108(1)	109(1)	112(4)
O(3 ^{viii})–H ... O(2)	171(2)	173(2)	165(9)

a: Symmetry codes: (i) $1/2 + x, 1/2 - y, 1/2 + z$; (ii) $1/2 - x, -1/2 + y, 1/2 - z$; (iii) $1/2 - x, -1/2 + y, 1/2 - z$; (iv) $x, y, 1 + z$; (v) $1 - x, -y, 1 - z$; (vi) $-1 + x, y, z$; (vii) $1 + x, y, z$; (viii) $-1/2 + x, 1/2 - y, -1/2 + z$.

vant experimental details are given in Table 1, final parameters in Table 2, and selected bond distances and angles in Table 3.

Results and discussion

The single-crystal X-ray diffractometry resulted in new unit cells for the two crystals investigated, with volumes greater than that of the Zachariassen [5] structure for sodium hydrogencarbonate by $4 \times$ for crystal A and $8 \times$ for crystal B (Table 1). Their diffraction patterns (Figs. 2 and 3) were superficially consistent with integral superstructures, but closer inspection revealed that they both represented the Zachariassen structure twinned by reticular pseudomerohedry [17, 18], but giving two different three-dimensional coincidence-site lattices. Only reflections of two twin orientations (one dominant and one subordinate) related by rotation were consistently present for both crystals. There were a few very weak reflections visible which do not belong to any of the twin lattices and probably represent a minor crystal fragment in another orientation. Also, a few strong reflections were dropped by the COLLECT software (Fig. 2).

The twin law for crystal A is twin axis [001]. Comparison of intensities for 38 twin reflection pairs resulted in a twin proportion of 5.5(2):1. The twinned lattice is coincidence site within the resolution of the diffractometer: there is no doubling of common reflections and lattice rows of the two twin orientations are not misaligned. These observations are consistent with the twin plane $(\bar{1}08)$, a twin index (Σ) of 4 and twin obliquity of 0° . Thus, crystal A is twinned by reticular pseudomerohedry but the twinned lattice is coincidence site because of the accidental values of the unit-cell parameters a , c and β . For the major twin

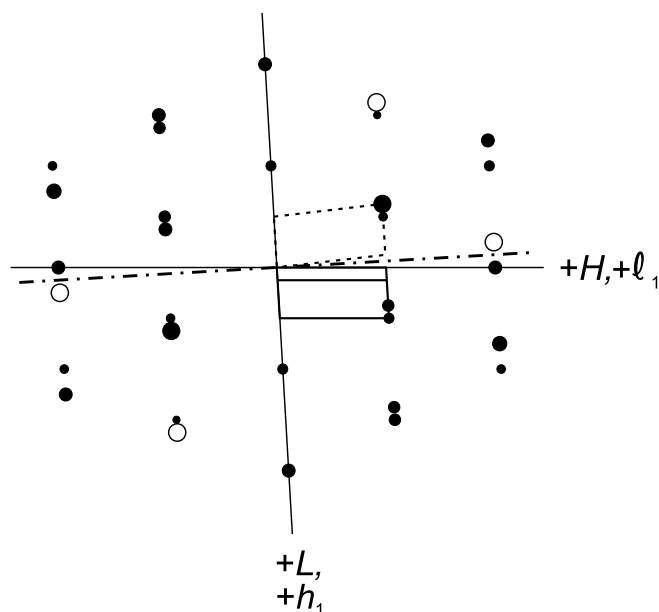


Fig. 2. *HOL* weighted reciprocal lattice level of twinned synthetic NaHCO_3 , crystal A; showing outlines of unit cell of twinned crystal and of true unit cell in the reference (solid lines) and twinned (dashed lines) orientation, and [001] twin axis (dot-dashed line); H and L refer to the twinned lattice and h and l to the true unit cell; open circles are strong reflections missing in the list; drawn with SHELXTL PC [25].

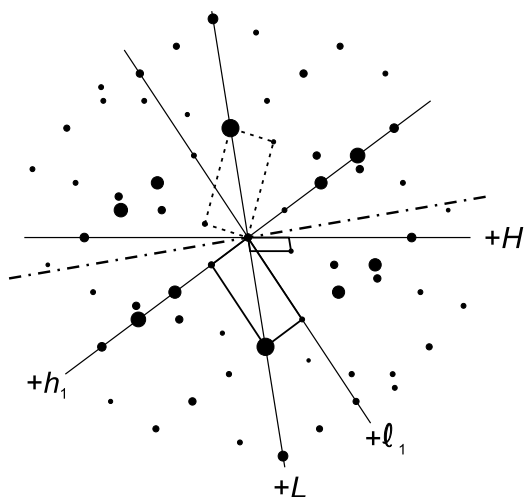


Fig. 3. $H2L$ weighted reciprocal lattice level of twinned synthetic NaHCO_3 , crystal B; dot-dashed line is trace of $[10\bar{1}]$ twin axis, and other symbols are as in Fig. 2; drawn with SHELXTL PC [25].

component the matrix for transformation to the Zachariasen [5] unit cell is:

$$\left(\frac{1}{4}\right) [\bar{1}, 0, \bar{1}; 0, 4, 0; 4, 0, 0],$$

and the corresponding matrix for the minor twin component is:

$$\left(\frac{1}{4}\right) [0, 0, 1; 0, \bar{4}, 0; 4, 0, 0].$$

The choice of (001) as twin plane does give a smaller twinned lattice ($\Sigma = 1$), but the obliquity of 3.32° would result in doubled reflections and misaligned reciprocal lattice rows.

The twin law for crystal B is twin axis $[10\bar{1}]$. Comparison of intensities for 24 twin reflection pairs resulted in a twin proportion of 5.5(9):1. The diffraction pattern (*e.g.*, Fig. 3) is consistent with a (101) twin plane and $\Sigma = 8$ (Fig. 5).

For the major twin component the matrix for transformation to the Zachariasen unit cell is:

$$\left(\frac{1}{8}\right) [\bar{6}, 0, 1; 0, \bar{8}, 0; 2, 0, 1],$$

and the corresponding matrix for the minor twin component is:

$$\left(\frac{1}{8}\right) [\bar{7}, 0, \bar{1}; 0, 8, 0; 1, 0, \bar{1}].$$

However, rotation of the major component on $[10\bar{1}]$, or reflection on (101), does not yield the coincidence-site lattice expected from the appearance of the diffraction pattern. Instead there is an obliquity of about 0.45° . Reflections that are seemingly twin related have slightly different interplanar spacings: *e.g.*, the d_{hkl} values for 224 of the major twin component and $2\bar{2}\bar{6}$ of the minor component are 2.682 and 2.662 Å, respectively. These discrepancies are related to the small strain in the minor component necessary to achieve coincidence of the twinned lattices (as detailed below). In summary, crystal B is twinned by reticular pseudomerohedry, and strained to lattice coherence.

Figures 4 and 5 show the real space lattice relationships between the coincidence-site lattices and the Zachariasen unit cell, in the orientation of the minor twin compo-

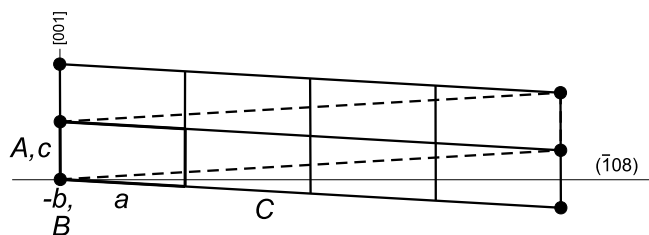


Fig. 4. Geometrical relationship of true unit cell (a, b, c) of NaHCO_3 to the unit cell of the twinned lattice (A, B, C) of crystal A, consistent with a twin index (Σ) of 4.

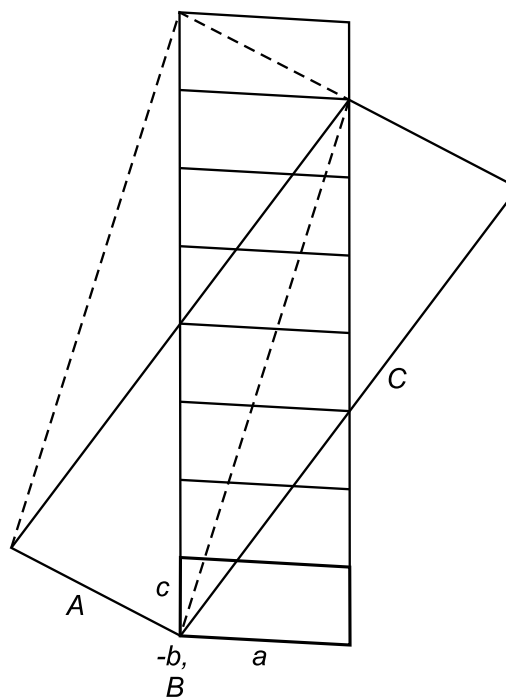


Fig. 5. Geometrical relationship of true unit cell (a, b, c) of NaHCO_3 to the unit cell of the twinned lattice (A, B, C) of crystal B, consistent with $\Sigma = 8$.

nent for crystal A and major component for crystal B, respectively. The reflections superimposed by twinning have indices HKL , $H = 0, \pm 4$ in crystal A and HKL , $H = 0$ in crystal B (where, H, K, L refer to the twinned lattices; *e.g.*, Figs. 2 and 3). Both crystals appeared to be singly twinned: there was no evidence of a contribution from the $[10\bar{1}]$ twin law in crystal A and, correspondingly, no evidence of a contribution from the $[001]$ twin law in crystal B.

For monoclinic twinned lattices which are in near coincidence, complete coincidence may be achieved by applying small strains to the unit-cell parameters. Such distortion seems quite feasible in the present case because the hydrogencarbonate anions in the NaHCO_3 structure are held together by only weak hydrogen bonds and relatively weak Na–O bonds (Fig. 1). The condition for coincidence of twin A in the a, c plane ($[001]$ twin axis) is:

$$\sin(\beta_A - \pi/2) = \left(\frac{1}{8}\right) (c/a) \quad (2)$$

(Fig. 4), and that of twin B in the (101) plane ($[10\bar{1}]$ twin axis) is:

$$\cos(\pi - \beta_B) = \left(\frac{3}{10}\right) (a/c) - \left(\frac{13}{10}\right) (c/a) \quad (3)$$

Table 4. Unit-cell dimensions for NaHCO₃^a.

		crystal A	crystal B	PDS 15–700
<i>a</i> (Å)	1 ^b	7.4688(4)	7.4830(5)	7.4756(7)
	2	7.4690(1)	7.4830(1)	—
	3	7.4689(1)	7.5445(1)	—
<i>b</i> (Å)	1	9.6842(6)	9.6811(7)	9.6863(9)
	2	9.6842(1)	9.6811(1)	—
	3	9.6842(1)	9.6810(1)	—
<i>c</i> (Å)	1	3.4791(2)	3.4764(3)	3.4808(3)
	2	3.4791(1)	3.4765(1)	—
	3	3.4791(1)	3.4456(1)	—
β (°)	1	93.321(2)	93.399(5)	93.388(6)
	2	93.355(1)	93.399(1)	—
	3	93.320(1)	92.617(1)	—
<i>V</i> (Å ³)	1	251.22	251.40	251.61
	2	251.22	251.40	—
	3	251.22	251.40	—
β_A (°) ^c	1	93.34	—	93.34
	2	93.34	—	—
	3	93.34	—	—
β_B (°) ^c	1	—	92.40	92.23
	2	—	92.39	—
	3	—	93.62	—
[10 $\bar{1}$]	1	—	8.4360	8.4307
	2	—	8.4360	—
	3	—	8.4360	—

a: Zachariasen [5] unit cell (*P*2₁/*n*).

b: 1 is twinned crystal; 2 is major twin component; 3 is minor component.

c: β_A for coincidence by rotation on [001]; β_B for coincidence by rotation on [10 $\bar{1}$].

(Fig. 5). Unit-cell parameters have been calculated for the separate major and minor twin components using only resolved reflections of the twinned lattices (*i.e.*, *HKL*, *H* = 1, 2, 3 for crystal A and *HKL*, *H* ≠ 0 for crystal B) and program LCREP [19], and used to derive values of β_A and β_B for coincidence of the respective twin laws in crystals A and B (Table 4). We have also included data for NaHCO₃ calculated from 38 reflections in the powder diffraction file PDS 15-700, since the values in the literature [3, 5, 6] were insufficiently accurate for comparison purposes.

The close agreement of β and β_A in Table 4 shows that the unit-cell dimensions for crystal A are consistent with lattice coincidence in the *a*, *c* plane through rotation on the twin axis [001]. Also, the values for the *b* unit-cell edges are essentially identical. Thus it appears that lattice coincidence in three dimensions was achieved in crystal A during the recrystallisation experiment. The marginally higher value of β for the major twin component suggests that the COLLECT software used predominantly reflections of the minor component in calculating the unit-cell parameters for this crystal.

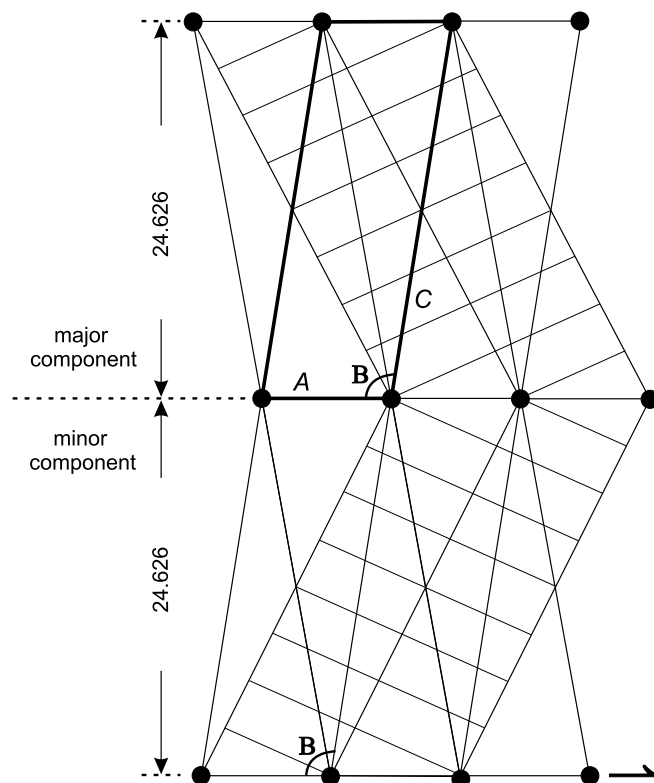


Fig. 6. Detailed geometrical relationship in the vicinity of a (101) twin boundary of crystal B of NaHCO₃, showing that the minor twin component must be strained homogeneously by simple shear (arrow; not drawn to scale) in the (101) plane, to give a coincidence-site twin lattice (A, C and beta).

In contrast to crystal A, there are significant discrepancies in the unit-cell parameters for crystal B. Although the parameters for the major twin component are in good agreement with the overall values derived for the twinned crystal, the unit-cell parameters *a* and *c* of the minor component are respectively stretched and shortened by about 1%. However, unit-cell volume and the magnitude of the [10 $\bar{1}$] vector remain essentially constant. This distortion is consistent with a simple shear strain of about 0.067 Å applied to each unit cell in the (101) plane and direction of $-A$. The shear strain accumulates to about 0.54 Å over a distance of eight unit cells of the minor component, and is required to achieve coincidence of the twinned lattices (Fig. 6).

The presence of two apparently unrelated twin laws for coincidence-site twinning in a crystalline substance of monoclinic symmetry is unusual and, for the present twin laws, occurs only for a unique value of β (93.29°) given by the positive root of:

$$\sin^2(\beta - \pi/2) = \sqrt[3]{9/12} \quad (4)$$

The experimental values of β for crystal A in Table 4 are in good agreement with this ideal value, further confirming that the twinning in this crystal results in a coincidence-site lattice. The marginal discrepancy in the β values for crystal B reflects the strain required for coherence of the twinned lattices.

To our knowledge, the [001] twin law of crystal A has not been reported previously for NaHCO₃. The [10 $\bar{1}$] twin law of crystal B probably corresponds to the (101) growth

twin commonly encountered in nahcolite [13], although the twinned natural crystals are unlikely to have coincidence-site lattices. Fragments of the present NaHCO_3 crystals studied by petrographic microscopy revealed no evidence of twinning, even though the crystals cleaved readily to yield thin $\{101\}$ crystal plates. However, these plates were terminated by fine ledges at the limit of optical resolution, which could indicate (101) twin domains associated with the $[10\bar{1}]$ twin of the matrix grains.

The real space twin relationships developed in Figs. 4–6 are consistent with low energy twin boundaries, lamellar twin domains and narrow, possibly nanoscale, domain widths. In particular, the twin relationship for crystal B is a strong indication that the minor twin component is strained homogeneously to twin coherence with the major component. Although we recognize that lamellar twinning may be caused by the generation of stacking faults during crystal growth [17], or even nucleated during recrystallisation, the characteristics of the present twins are more consistent with a secondary origin. Because the extended structure of NaHCO_3 is fragile and deforms readily, the present twinning could represent relief of nonhydrostatic stress resulting from either depressurisation or thermal contraction. Phase transition is another possible origin here. However, phase transition normally results in equal proportions of twin components. Moreover, a phase transition has not been reported for NaHCO_3 in the pressure-temperature range of experiment LM129 [14, 20, 21]. No phase transition was observed in room temperature measurements up to 11 GPa [20] and electrical and thermal measurements pointing to a phase transition at 92 °C and 1 atm. [21] probably reflected damage at the grain surface [14]. Nevertheless, the thermal stability of NaHCO_3 has not been investigated at confining pressure, and a structural phase transition has been reported for the related compound potassium hydrogencarbonate (KHCO_3) and attributed to order-disorder of the hydrogen-bonded $(\text{HCO}_3)_2$ dimer above 45 °C [22]. We note that the structural complications encountered in the latter study on KHCO_3 could be related to twinning below the phase transition.

The significance of the exclusive presence of the $[001]$ twin in crystal A from the fluid space at the top of the capsule and of the $[101]$ twin in crystal B from the NaHCO_3 nutrient at the bottom of the capsule is unclear. This restricted occurrence could have a genetic implication, related to the local conditions of recrystallisation, the thermal gradient along the length of the capsule, or the greater grain impingement on crystals in the matrix. There is also the possibility of a compositional control, because the a parameter and unit-cell volume are somewhat larger in crystal B than in crystal A (Table 4). Alternatively, the present observations on twin occurrences may simply reflect limited sampling, since grain orientation within the capsule will be a factor in relief of nonhydrostatic stress through twinning. The presence of one twin law to the exclusion of the other in the two grains presently investigated is more readily understood, since, once the threshold for twinning on one twin law is exceeded, twinning is likely to proceed to completion.

The present structure refinement for crystal A (Tables 2 and 3) was made using only reflections characteristic of

the major twin component with $H \neq 0, \pm 4$ (where, H, K, L refer to the twinned lattice). However, all non-equivalent reflections were used in the refinement for crystal B, with OKL reflection intensities corrected for twin proportion. The results for crystal B, with the superimposed OKL reflections included in the reflection list, are virtually identical to those for crystal A (Table 2). All refined parameters and bond distances and angles (Table 3) are better defined than in previous studies [3, 5, 6], but the essential features of the structure of NaHCO_3 are unchanged from Ref. [6].

The distortion of bond lengths and angles in the CO_3 group of hydrogencarbonate anions is controlled largely by the strength of the O–H bond [3]. These distortions are reduced slightly to give a more symmetrical CO_3 group in large cation structures, but the C–O(3) distance remains long and nearly single bonded: *e.g.*, C–O(3) = 1.334(2) Å in monoclinic KHCO_3 [21] and 1.340(2) Å in NaHCO_3 (Table 3). In comparison, distortion in the CO_3^{2-} anion resulting from different cation sizes and lower crystal symmetry is minor in inorganic carbonate structures: *e.g.*, in the orthorhombic structure of aragonite (CaCO_3) the divergence in C–O bond distances is only 0.0075 Å [23]. In NaHCO_3 , the HCO_3^- anions are tilted out of the (101) plane by about 5° to accommodate the Na^+ cations, but the carbon atom remains essentially in the plane of the three oxygen atoms. The aplanarity (perpendicular distance of the carbon atom to the plane of the oxygens) is only 0.005 Å in NaHCO_3 , compared with 0.018 Å in dolomite [$\text{CaMg}(\text{CO}_3)_2$] and 0.028 Å in aragonite [23].

Conclusions

Crystals of sodium hydrogencarbonate (NaHCO_3) recrystallised hydrothermally exhibit three-dimensional coincidence-site lattice twinning on two twin laws: twin axis $[001]$, $\Sigma = 4$, and twin axis $[10\bar{1}]$, $\Sigma = 8$. The coincidence-site lattice twins occur in separate grains but with similar proportions of major and minor twin components. These unusual twin systems for crystals of low symmetry are permitted because the experimental value of the β unit-cell parameter is very close to the theoretical value, given by the positive root of $[\sin^2(\beta - \pi/2) = 3/912]$. Complete coincidence of the twinned lattices requires only minor strain of this interesting hydrogen-bonded structure.

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