The crystal structure of alstonite, BaCa(CO$_3$)$_2$: an extraordinary example of ‘hidden’ complex twinning in large single crystals

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Abstract

Alstonite, BaCa(CO$_3$)$_2$, is a mineral described almost two centuries ago. It is widespread in Nature and forms magnificent cm-sized crystals. Notwithstanding, its crystal structure was still unknown. Here, we report the crystal-structure determination of the mineral and discuss it in relationship to other polymorphs of BaCa(CO$_3$)$_2$. Alstonite is trigonal, space group P31m, with unit-cell parameters $a = 17.4360(6)$ Å, $c = 6.1295(2)$ Å, $V = 1613.80(9)$ Å$^3$, and $Z = 12$. The crystal structure was solved and refined to $R_1 = 0.0727$ on the basis of 4515 reflections with $F_o > 4o(F_o)$ and 195 refined parameters. Alstonite is formed by the alternation, along c, of Ba-dominant and Ca-dominant layers, separated by CO$_3$ groups parallel to {0001}. The main take-home message is to show that not all structure determinations of minerals/compounds can be solved routinely. Some crystals, even large ones displaying excellent diffraction quality, can be twinned in complex ways, thus making their study a crystallographic challenge.

Keywords: alstonite, carbonate, barium, calcium, crystal structure, twinning

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Introduction

Alstonite, BaCa(CO$_3$)$_2$, is polymorphous with barytocalcite, paraalstonite and a recently published synthetic monoclinic phase (Spahr et al., 2019). It was first identified at the Brownley Hill mine near Alston Moor, Eden, Cumbria, UK (54.79639, −2.34833); and (4) A4119 roadcutting, Llantrasit, Rhondda Cynon Taf, Wales, UK

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In expectation of probable crystal twinning, a full diffraction sphere was collected. The diffraction pattern was apparently consistent with hexagonal symmetry [refined cell parameters are \(a = 17.4360(6)\ \text{Å}\) and \(c = 6.1295(2)\ \text{Å}\)]. The statistical tests on the distribution of \(|E|\) values ([\(|E^2-1| = 0.684\)]) suggested the structure to be non-centrosymmetric. Although the collected data exhibited very good merging factors according to \(\overline{3} (R_{\text{int}} = 0.077), 3\overline{m} (R_{\text{int}} = 0.081), 31m (R_{\text{int}} = 0.079), 6/m (R_{\text{int}} = 0.080)\), and \(6\overline{2}m\overline{m} (R_{\text{int}} = 0.081)\) Laue symmetries, the structure was solved initially through direct methods in the triclinic \(P1\) space group because the mineral was always reported as optically biaxial (although with a very low 2V angle). After several cycles, an ordered solution with full site occupations was finally determined \((R_{1} = 0.18)\) by carefully removing atoms with low site occupations and/or non-realistic distances with neighbouring atoms and adding significant positions found in the difference Fourier syntheses. Given the very common twinning reported for this mineral, we then took into account the twin law that makes the twin lattice hexagonal (i.e. twinning \(S9\)) and/or non-realistic distances with neighbouring atoms and added to the model.

Table 1 reports further details of the refinement. Atom coordinates and isotropic or equivalent isotropic displacement parameters are given in Table 2 and Table 3 lists the bond angles. The crystallographic information files have been deposited with the Principal Editor of *Mineralogical Magazine* and are available as Supplementary material (see below).

Although the structural model was optimised in the \(P31m\) space group, we decided to also have a look at the structure using the \(C\)-centred orthorhombic cell \((a \approx 3^{\text{h}}; b; i.e., a \approx 30\ \text{Å}, b \approx 17.4\ \text{Å} and c \approx 6.1\ \text{Å})\), as reported by previous authors (Gossner and Mussgnug, 1936; Dickens, 1971; Sartori, 1975). The reflection data set was transformed according to the transformation matrix \([210/010/001]\), again taking into account the twin law that makes the twin lattice hexagonal (i.e. twinning (Buckingham and Mussgnug, 1936; Klassen and Mussgnug, 1936). Here we report only the results from the first locality (that is the co-type locality of alstonite) because the tested crystal is of excellent diffraction quality with respect to the others.

The intensity data were collected using a Bruker D8 Venture diffractometer equipped with a Photon 100 CMOS and using graphite-monochromatised MoK\(\alpha\) radiation. The detector-to-crystal distance was 50 mm. Data were collected using \(\omega\) and \(\varphi\) scan modes, with a \(0.5^\circ\) frame-width and an exposure time of 20 s per frame. The data were corrected for Lorentz and polarisation factors and absorption using the software package APEX3 (Bruker AXS Inc., 2016).
by metric merohedry; Nespolo, 2004 and references therein). A structural model was obtained for both triclinal and monoclinic symmetry, space group C1 and Cm (both subgroups of P31m). Both the models showed higher R factors than the trigonal P31m model adopted here.

Crystal structure of alstonite

**Cation coordination**

Fourteen cation and fourteen anion sites occur in the crystal structure of alstonite. Among cation sites, three are occupied by Ba, three by Ca, and eight are C-centred positions. Barium is ten-fold coordinated, with average bond distances ranging between 2.808 and 2.822 Å, and Ba–O distances varying between 2.678 (Ba2–O3) and 2.877 Å (Ba3–O7). Bond-valence sums (BVS), calculated using the bond parameters of Brese and O’Keeffe (1991), show an overbonding of Ba atoms, with values ranging between 2.35 and 2.49 valence units (vu) (see Table S1 in the Supplementary materials). In the two other natural BaCa(CO3)2 polymorphs (Table 4), Ba is ten-fold coordinated in paralstonite, with an average <Ba–O> distance of 2.812 Å (Effenberger, 1980), and eleven-fold coordinated in barytocalcite, with an average <Ba–O> distance of 2.909 Å (Dickens and Bowen, 1971). Whereas in paralstonite an oversaturation of Ba atoms similar to that observed in alstonite can be calculated (2.44 vu, on the basis of the data of Effenberger, 1980), in barytocalcite such an overbonding is smaller, the BVS at the Ba site being 2.16 vu. Such an overbonding observed in alstonite could have different explanations: for instance, the bond character (covalent vs. ionic) may vary, and the relationship of Brese and O’Keeffe (1991), using a constant b value, does not account adequately for the different stiffness of the atoms. On the contrary, the observed overbonding can be only partially related to the replacement of Ba by smaller cations (e.g. Sr, as suggested by previous chemical analyses performed on samples from the type locality – Kreutz, 1969; Sartori, 1975). Recently, Spahr et al. (2019) described a new synthetic polymorph of BaCaCO3, with Ba and Ca atoms at a mixed occupied position; the Ba3Ca3(3)O polyhedron can be described as a strongly distorted trigonal prism. A six-fold coordination seems to be unusual; for instance in the other known anhydrous barium double carbonate mineral, norsethite, BaMg(CO3)2, Ba is twelve-fold coordinated with an average <Ba–O> distance of 2.947 Å (Effenberger and Zemann, 1985), although recent structural investigations suggested a [6+6] coordination for norsethite and its Mn-analogue BaMn(CO3)2 (e.g. Effenberger et al., 2014; Pippinger et al., 2014; Wen et al., 2019). In witherite, BaCO3, Ba is nine-fold coordinated (e.g. Ye et al., 2012).

Calcium is eight-fold coordinated, with <Ca–O> distances ranging between 2.500 and 2.544 Å; Ca–O distances vary between 2.184 (Ca1–O14) and 2.752 Å (Ca1–O2). This coordination is similar to that occurring in paralstonite, where <Ca–O> is 2.49 Å (Effenberger, 1980). On the contrary, barytocalcite has seven-fold coordinated Ca, with an average <Ca–O> distance of 2.388 Å (Dickens and Bowen, 1971).

The eight independent C sites show the typical flat triangular coordination, with <C–O> distances ranging between 1.235 (C4) and 1.340 Å (C1). Carbonate groups are parallel to [0001], in paralstonite (Effenberger, 1980). In barytocalcite, on the contrary, CO3 groups are parallel to [0101].

Table 4. Selected anhydrous Ba double carbonates discussed in the text.

| Mineral       | Chemical formula | a (Å) | b (Å) | c (Å) | β (°) | Space group | Reference            |
|---------------|------------------|-------|-------|-------|-------|-------------|----------------------|
| Alstonite     | BaCa(CO3)2       | 17.44 | 17.44 | 6.13  |       | P31m        | This work            |
| Barytocalcite | BaCa(CO3)2       | 8.09  | 5.23  | 6.54  | 106.1 | P21/m       | Dickens and Bowen (1971) |
| Norsethite    | BaMgCO3          | 5.02  | 5.02  | 18.77 |       | R3m         | Effenberger and Zemann (1985) |
| Paralstonite  | BaCa(CO3)2       | 8.69  | 8.69  | 6.15  |       | P321        | Effenberger (1980)    |
| Synthetic     | BaCa(CO3)2       | 6.68  | 5.10  | 4.19  | 109.3 | C2          | Spahr et al. (2019)    |
shifted. In addition, considering the O–Oe edge of the CO3 triangle perpendicular to the b direction, two CO3 configurations can be identified: the first one (hereafter called ‘up’) has the third oxygen in the +b direction, whereas the other (hereafter called ‘down’) has the third oxygen in the −b direction. Rows of CO3 groups with ‘up’ and ‘down’ configurations at y/b = 0 alternate, along b, with rows of CO3 groups in a ‘down’ configuration at y/b = ½. In this configuration, the C–O bonds always point towards the smaller Ca atoms. At y/b = ⅓, ⅔, and ⅖, staggered CO3 groups occur. These CO3 groups show C–O bonds pointing towards different atoms, i.e. three Ca atoms, two Ca atoms and one Ba atom, one Ca atom and two Ba atoms, and three Ba atoms. It is worth noting that these sequences are the result of the projection of two different layers, with the staggered CO3 groups having about the same z/c coordinates showing the same ‘up’ or ‘down’ configuration. Indeed, the crystal structure of alstonite can be described as a layered one, formed by the alternation of mixed (Ca/Ba) layers and CO3 groups parallel to [0001]. The Ba/Ca layer at z/c ≈ 0.10 is Barich and it is composed by Ba1, Ba3 and Ca1 sites; the other layer, at z/c ≈ 0.60, is Carich and it is composed of Ba2, Ca2 and Ca3 sites. This is one of the main differences of alstonite with respect to its dimorph paralstonite. Indeed, the latter is characterised by the alternation, along c, of Ca and Ba layers, separated by CO3 layers (Fig. 1). In addition, the projection along c shows the sequence ⋯Ca–Ba–CO3–Ca–Ba–CO3⋯ along a; CO3 groups have all the same ‘up’ configuration for y/b = 0, whereas they are staggered at y/b = ⅓ and ⅔. In paralstonite, staggered CO3 groups at about the same z/c coordinates display different ‘up’ and ‘down’ configurations in a 1:1 ratio. The different sequences ⋯CO3–(Ba/Ca)⋯ along a in alstonite and paralstonite are likely to be related to the doubling of the a axis in the former.

**Calculated versus observed powder-diffraction pattern**

To verify if the structural model obtained for alstonite matched its powder X-ray diffraction pattern, we also collected powder-diffraction data with a Bruker D8 Venture equipped with a Photon III CCD detector, with graphite-monochromatised CuKα radiation (λ = 1.54138 Å), and with 3 hours of exposure; the detector-to-sample distance was 6 cm. The program APEX3 (Bruker AXS Inc., 2016) was used to convert the measured diffraction rings to a conventional powder-diffraction pattern. The

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**Fig. 1.** Crystal structure of alstonite (a), as seen down c (above) and a (below). For the sake of comparison, the same projections for the crystal structure of paralstonite are shown in (b). Carbonate groups having ‘up’ and ‘down’ configurations are highlighted (when not staggered along c) with light yellow and light red boxes, respectively. Selected staggered CO3 groups are outlined with red lines, showing the different ‘up’ and ‘down’ configurations. Unit-cells are shown with blue solid lines. Symbols: circles represent Ba (violet), Ca (blue) and O (red) sites. CO3 is shown as black triangles.
excellent match between the calculated and observed X-ray powder-diffraction data is visually reported in Fig. 2 and testifies to the validity of the obtained structural model.

Summary and conclusion

The crystal structure of alstonite has been solved and refined in the space group P31m and its relationships with paralstonite and barytocalcite are discussed. It is worth noting that the solution of the crystal structure in a space group belonging to the trigonal symmetry, suggested by some morphological features, was initially discouraged by the biaxial optical behaviour of alstonite reported by previous authors. For this reason, these authors (e.g. Dickens, 1971; Sartori, 1975), continued to use a C-centred unit cell and persisted in using lower-symmetry models (monoclinic/triclinic) for their structure solutions. However, the present study strongly suggests that the symmetry is actually trigonal and the anomalous optical behaviour could be simulated by minor strain combined with the occurrence of widespread pervasive twinning. This phenomenon is quite common in uniaxial minerals having small 2V angles (e.g. calcite – Turner, 1975; quartz – Starkey, 2000).

Notwithstanding its finding in the first half of the 19th Century and its occurrence in well-developed crystals, some up to a cm in size, the crystal structure of alstonite remained unsolved up to this contribution. Indeed, alstonite is a good example that shows even large crystals having excellent diffraction quality can hide crystallographic pitfalls, such as widespread and complex twinning, thus making the structure solution puzzle a headache.

Supplementary material. To view supplementary material for this article, please visit https://doi.org/10.1180/mgm.2020.61

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Fig. 2. Calculated (red) vs. observed (black) X-ray powder diffraction data (CuKα radiation) for alstonite.
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