Structural investigations
of synthetic fairchildite, $K_2Ca(CO_3)_2$

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Abstract. X-ray investigations on single crystals of synthetic fairchildite, $K_2Ca(CO_3)_2$, confirmed the space group $P6_3/mmc$ with $a = 5.294(1)$ and $c = 13.355(2)$ Å. The structure was determined from three-dimensional Patterson and Fourier syntheses and refined by least-squares to $R_w = 0.046$. One of the two crystallographically different CO_3 groups exhibits an orientational disorder in the oxygens around the C atom. The two positions Me(1) [7] and Me(2) [8] are assumed to be statistically occupied by K and Ca atoms.

Introduction and synthesis

The $K_2CO_3 − CaCO_3$ system was investigated by Niggli (1916) up to $900°C$ and $0 − 45$ mol % $CaCO_3$. In the range of $20 − 45$ mol %, crystals, including the double carbonate $K_2Ca(CO_3)_2$, crystallize from the cooling melts below $755°C$. Niggli (1916) gave the approximate refractive indices for the crystals of this compound and described them as being optically uniaxial, negative. Eitel and Skaliks (1929) synthesized crystals of the double carbonate $K_2Ca(CO_3)_2$ under similar conditions and determined the optically negative character and the refraction indices $\varepsilon \sim 1.48$, $\omega = 1.530(3)$. Single crystal film data showed a hexagonal symmetry and lattice constants $a = 21$ Å, $c = 13.18$ Å. In addition these authors mentioned that the fourth order reflections in the a^* direction had on the average definitely larger intensities.

Analogous to the methods described above, Mrose et al. (1966) obtained crystals of $K_2Ca(CO_3)_2$ from an equimolar melt of K_2CO_3 and $CaCO_3$ at atmospheric pressure and temperatures in the range $704 − 970°C$. The crystals were hexagonal and had lattice constants, determined from single crystal data, of $a = 5.29$ and $c = 13.32$ Å. The observed extinctions indicated the possible space groups $P6_3/mmc$, $P\bar{6}2c$ and $P6_3mc$. According to Mrose

et al. (1966) the double carbonate is identical to the mineral fairchildite which was originally described by Milton and Axelrod (1947) as occurring in ashes formed by forest fires (compare Dawson and Sabina, 1957).

The $K_2Ca(CO_3)_2$ crystals for the present structure determination were synthesized according to Mrose et al. (1966). Weissenberg and precession film data confirmed the lattice constants given by these authors as well as the Laue symmetry and the extinction characteristics. The following lattice parameters were used for all calculations: $a = 5.294(1)$ and $c = 13.355(2)$Å. These parameters were determined by Swanson et al. (1970) from powder data (Ag internal standard: $a = 4.08641$ Å).

Determination of the crystal structure

The X-ray data for the structure determination were collected on an automatic two-circle diffractometer (Stoe-Stadi 2) using Mo$K\alpha$ radiation (graphite monochromator, ω-scan) for reflections with $\sin \theta/\lambda \leq 0.70 \text{Å}^{-1}$. 197 of 213 possible symmetry independent reflections with $I > 0$ were registered (rotation axis [001]). Absorption effects [$\mu(\text{Mo}K\alpha) = 20.9 \text{cm}^{-1}$] were taken into consideration as appropriate for the size and shape of the crystal ($0.3 \times 0.3 \times 0.15 \text{mm}^3$), and the Lorentz and polarization factors were applied in the usual manner.

The solution of the crystal structure followed from a 3-dimensional Patterson synthesis which gave the parameters for the metal atoms as well as those for the ordered carbonate group (with the carbon atom at $\frac{1}{3}, \frac{2}{3}, \frac{3}{4}$). In a subsequent Fourier synthesis, calculated in space group $P6_3/mmc$, the second carbonate group could be definitely located (center at $0, 0, 0$). The oxygens in this group occupy two 12-fold positions with different statistical occupancies.

In a subsequent full-matrix least-squares refinement, all atoms were assigned with anisotropic thermal parameters, except the atoms O(2) and O(3). The thermal parameters of these atoms could only be refined isotropically due to the low average scattering power. Taking anomalous dispersion and secondary extinctions into account, a conventional R value of 0.10 and an R_w of 0.046 (σ-weighting) were obtained for all reflections. The reduction of the R value through the introduction of σ-weighting is regarded as a consequence of unfavorable counting statistics from the weak reflections. Atomic scattering factors for K^+, Ca^{2+}, C^0 and O^0 (Int. Tabl. f. X-ray Cryst., 1968) and dispersion factors $\Delta f'$ and $\Delta f''$ (ibid., 1974) were used throughout in the structure calculations.

By splitting positions and generalizing special positional parameters, the structure can, in principle, also be described in the space groups $P6_3mc$ and $P\bar{6}2c$. However, no significantly different positional parameters, occupancies or thermal parameters were observed upon refinement in these space

Table 1. Atomic parameters and anisotropic temperature factors [O(2) and O(3) isotropic] for $K_2Ca(CO_3)_2$. Standard deviations are given in parentheses

Atom	Position	x	y	z	Occupancy	B_{equ}^*/ B_{iso}
Me(1)	4 f	$\frac{1}{3}$	$\frac{2}{3}$	0.0996(2)	1	1.12
Me(2)	2 b	0	0	$\frac{1}{4}$	1	1.33
C(1)	2 d	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{3}{4}$	1	1.41
C(2)	2 a	0	0	0	1	1.06
O(1)	6 h	0.52649(97)	1.05297(97)	$\frac{1}{4}$	1	1.85
O(2)	12 k	0.0865(32)	0.1730(32)	0.9224(25)	$\frac{1}{3}$	2.9(8)
O(3)	12 i	0.2380(30)	0	0	$\frac{1}{6}$	2.9(8)

Atom	β_{11}^{**}	$\beta_{22} = 2\beta_{12}$	β_{33}	$\beta_{13} = \beta_{23}$
Me(1)	0.0155(21)	0.0155(21)	0.0023(2)	0.0
Me(2)	0.0236(26)	0.0236(26)	0.0019(2)	0.0
C(1)	0.0137(67)	0.0137(67)	0.0038(11)	0.0
C(2)	0.026(11)	0.026(11)	0.0004(14)	0.0
O(1)	0.0248(48)	0.0129(61)	0.0039(5)	0.0

* $B_{equ} = (B_{11} + B_{22} + B_{33})/3$

** $ATF = \exp\left[-(h^2\beta_{11} + \ldots + 2hk\beta_{12} + \ldots)\right]$

groups. A quadrupling of the lattice constant a, as given in Eitel and Skaliks (1929), could not be confirmed even with long exposure times for Weissenberg films (up to 50 h, crystal size between 0.2 and 0.3 mm $\varnothing$).

The positional parameters and the temperature factors obtained are listed in Table 1. A list of the observed and the calculated structure factors has been deposited at the "Institut für Mineralogie und Kristallographie der Universität Wien", Vienna, Austria.

Discussion

The most important interatomic distances and bond angles are summarized in Table 2. Figure 1 shows part of the structure.

The structure generally agrees with that postulated by McKie and Frankis (1977) for the high temperature modification of the mineral nyererete, $Na_2Ca(CO_3)_2$. Of the two crystallographically different CO_3 groups, the $C(1)O_3$ group is oriented parallel to (001). The $C(2)O_3$ group exhibits an orientational disorder around a common C atom position (Fig. 2). The plane of the $C(2)O_3$ group includes an angle of 69° with (001) which is independent of the disorder of this group. This arrangement of the carbonate

Table 2. Interatomic distances (Å) for Me—O, O—O ≤ 3.5Å and bond angles (°) for the carbonate group in $K_2Ca(CO_3)_2$. Standard deviations, calculated from those of the atomic parameters, are given in parentheses

Me(1) polyhedron	Me(2) polyhedron
Me(1)—O(1) = 2.68(1) 3 × —O(2) = 2.76(2) 2 × —O(3) = 2.46(1) 1 × —O(2') = 3.27(2) 1 ×	Me(2)—O(1) = 2.66(1) 6 × —O(2) = 2.44(3) 2 ×
mean 2.76	mean 2.61
O(1)—O(1) = 3.07(2) 3 × —O(2) = 3.03(4) 1 ×	O(1)—O(1) = 2.23(1) 3 × —O(1) = 3.07(2) 3 × —O(2) = 3.03(4) 2 ×
C(1)O₃ group	C(2)O₃ group
C(1)—O(1) = 1.29(1) 3 ×	C(2)—O(2) = 1.31(3) 2 × —O(3) = 1.26(1) 1 ×
O(1)—O(1) = 2.23(1) 3 ×	
O(1)—C(1)—O(1) = 120(—) 3 ×	O(2)—O(2) = 2.22(5) 1 × —O(3) = 2.24(2) 2 ×
	O(2)—C(2)—O(2) = 116(2) 1 × —O(3) = 122(1) 2 ×

groups explains the weak double refractions observed for this compound. All C — O distances are in good agreement with crystal chemistry experience.

The average oxygen coordination of the 4-fold position with Me(1) — O ≤ 3.3 Å is seven; the coordination of Me(2) is always eight. In accordance with the chemical composition, it was expected that Me(1) be occupied by K and Me(2) by Ca, but a K — O distance in the Me(1) position with 2.46 Å seems to be very suspicious. On the other hand in the Me(2) position such short Me — O distances also occur and the Ca — O bonds are in both cases somewhat long (main source: Compilation of crystal structures by Cocco et al. (1972) and Hahn and Eysel (1970)]. Therefore an ordering of the metal atoms is not settled and a statistical distribution over the two positions seems to be possible. A local distortion of the atoms at this stage of refinement cannot be discussed.

The calculation of the bond strengths according to Brown and Wu (1976) upheld this interpretation. Assuming Me(1) to be occupied by K, a value of 1.60 results for this position. For Me(2), occupied by Ca, a value of 1.54 results, for C(1) 4.07 and for C(2) 3.97. For the reverse, Me(1) = Ca gives 1.08 and Me(2) = K gives 2.55. These bond strengths indicate mixed occupancy of Me(1) and Me(2) by both K and Ca atoms. Although a preference of Me(1) as K and Me(2) as Ca can be presumed from the average interatomic distances,
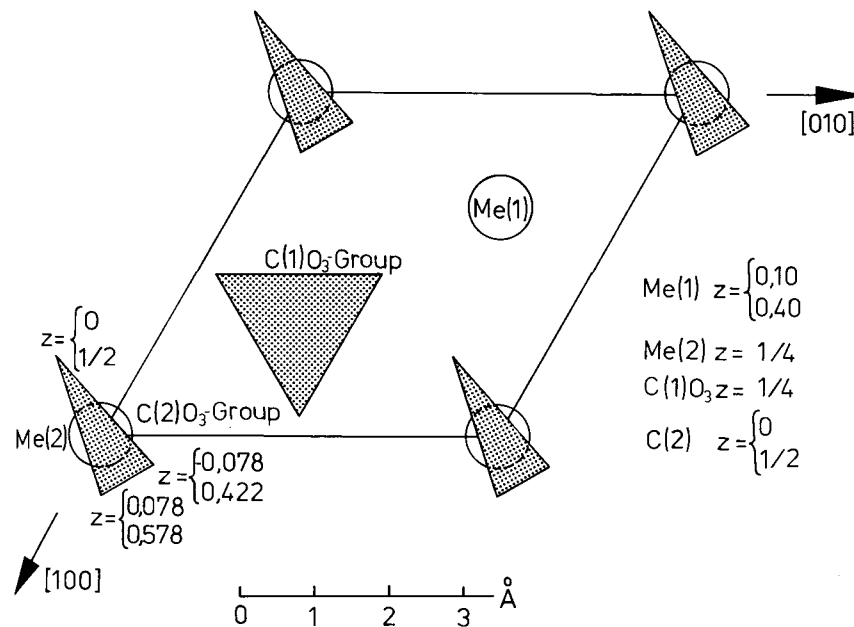
Fig. 1. Excerpt from the fairchildite structure. In this (001) projection only the atoms between $z \sim 0$ and $z \sim \frac{1}{2}$ are shown. Heights are in fractions of the lattice constant c. Of the six possible positions for the $C(2)O_3$ group only one has been shown
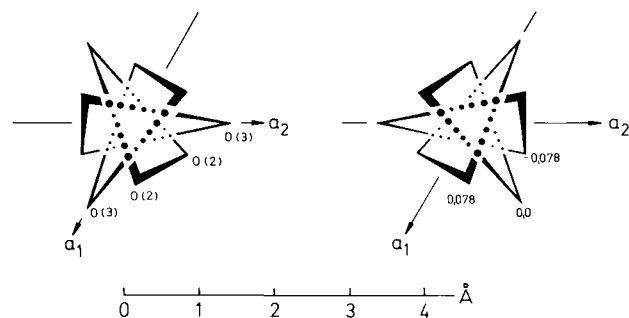

Fig. 2. Representation of the orientational disorder in the $C(2)O_3$ group centered at 0,0,0 [C(2) atom]. For clearness sake the carbon atom is not shown and the six possible positions are only partially shown. The heights of the oxygens are given in fractions of the lattice constant c

it cannot be proved by X-ray data due to the similar scattering power of these atoms.

Figure 3 shows the IR spectrum of fairchildite taken from a KBr pellet on a Perkin Elmer computer controlled IR Spectrograph 580B. The following
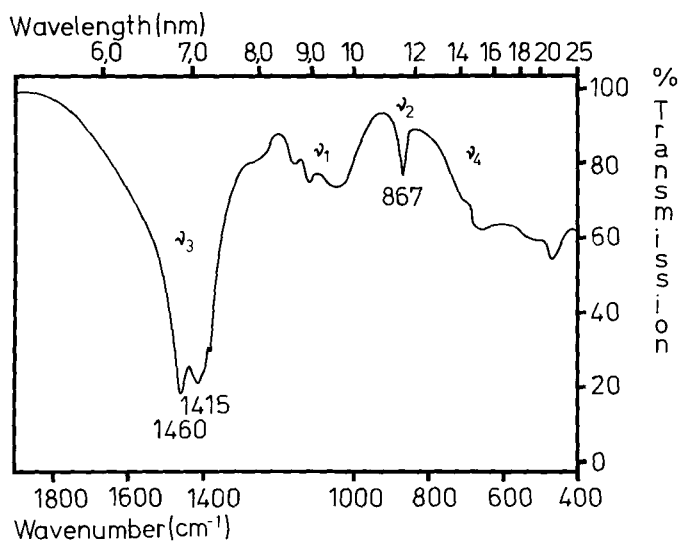
Fig. 3. IR absorption spectrum of fairchildite (KBr pellet) with probable assignments for the carbonate group vibrations

assignments for the carbonate group frequencies are assumed (e.g. see White, 1974):

> symmetric stretching vibrations (v_1),
> out-of-plane vibrations (v_2) $867\,\mathrm{cm}^{-1}$,
> asymmetric stretching vibrations (v_3) 1460 and $1415\,\mathrm{cm}^{-1}$,
> bending vibrations (v_4).

The splitting of the v_3 vibrations can be explained by the different bonding situations for the oxygens on the two carbonate groups. A quite plausible explanation for the broad absorption band of the v_1 vibrations, which originate entirely from the $C(2)O_3$ group, would be the orientational disorder of this group.

It should be mentioned that an ordering of the $C(2)O_3$ group would result in multiple lattice constants. Such an ordering could be possibly attained by slowly cooling the melt. However, as noted at the beginning, no such effects could be observed for any of the crystals investigated. It should also be mentioned that all crystals are uniaxial.

A calculated powder diffraction pattern based on the present structure agrees well with the experimental one (Swanson et al. 1970).

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