Crystal Structure of the Double Carbonate $K_2Ca_2(CO_3)_3$

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The crystal structure of $K_2Ca_2(CO_3)_3$ was determined from single-crystal X-ray diffraction data. This double carbonate crystallises in the space group $R\overline{3}$ (No. 146), with unit-cell dimensions $a = 13.010(4)$, $c = 8.615(3)$ Å, $V = 1262.9(9)$ Å^3 and $Z = 6$. Anisotropic refinements gave $R_w = 0.018$ for 816 unique reflections. The two crystallographically different carbonate ions are located in columns around the three-fold axes at which 1/4 of the cations are situated (one Ca^{2+} and one K^+), the remainder being located in general positions between the carbonate columns. The carbonate ions are more or less inclined relative to the (001)-plane and do not form an unequivocally layered structure. Experimental and calculated powder X-ray diffraction data for $K_2Ca_2(CO_3)_3$ are presented.

The first published investigation of the K_2CO_3–$CaCO_3$ system was performed by Niggli[1] in 1916. Niggli studied the K_2CO_3-rich side of the system, in 1 atm of CO_2 and in the temperature range 700–900 °C, and found one intermediate phase; $K_2Ca(CO_3)_2$, melting at 813 °C. Kröger et al.[2] investigated the phase relations and presented a phase diagram for the binary system K_2CO_3–$CaCO_3$ in the temperature range 500–1400 °C, at approximately 50 bar. They found two intermediate phases, the double carbonates $K_2Ca(CO_3)_2$ and $K_2Ca_2(CO_3)_3$. Walenta[3] describes the occurrence of a new carbonate mineral containing calcium and potassium as main cation components. From optical crystallography, Walenta concluded that this new mineral belongs to the 'rhombohedral system'. Cooper et al.[4] determined the phase relations in the ternary system Na_2CO_3–K_2CO_3–$CaCO_3$ at 1 kbar. In the binary sub-system K_2CO_3–$CaCO_3$ they describe three intermediate phases, two $K_2Ca(CO_3)_2$ phases, fairchildite and bütschliite (which is a low temperature modification of the former) and an unnamed phase, $K_2Ca_2(CO_3)_3$, referred to as phase A. $K_2Ca_2(CO_3)_3$ is an incongruently melting phase (810 °C) which decomposes at 512 °C to calcite and bütschliite. The crystals of phase A are described as pale yellow–green granules, with grains that always exhibit polysynthetic twin lamellae parallel and perpendicular to the c-axis.

Although this double carbonate $K_2Ca_2(CO_3)_3$ has been known since 1943, the crystal structure has not been determined; in fact not even an unambiguous powder diffraction pattern is available. The two other

double carbonates in the system K_2CO_3–$CaCO_3$ have been found in wood ash in partly burned fir, hemlock and other trees in the western United States.[5,6] Fairchildite has also been identified in ash from the combustion of biomass fuels.[7]

The aim of the present work is to determine the structure of the double carbonate $K_2Ca_2(CO_3)_3$ by single-crystal X-ray diffraction, and to present an accurate powder X-ray diffraction pattern that can serve as a reliable identification tool for this phase.

Experimental

Synthesis. The growth of single crystals of $K_2Ca_2(CO_3)_3$ of sufficient size for single-crystal X-ray diffraction investigations cannot easily be carried out under normal pressure conditions. On the one hand, the material decomposes at higher temperatures before melting, and on the other, solution growth may fail due to the poor solubility of the compounds. A high-pressure technique using a sealed container seemed to present a more promising approach. As long as the piston-cylinder technique[8] was available for the single-crystal growth experiment, a minimum pressure of 10 kbar had to be chosen. The melting point of 810 °C at 1 kbar for $K_2Ca_2(CO_3)_3$ shifts to a higher temperature at 10 kbar if the compound remains a stable phase. Therefore a temperature of 950 °C at 10 kbar was assumed to be still in the sub-solidus region. A stoichiometric mixture of dried K_2CO_3 (Baker) and $CaCO_3$ (Riedel-deHaën) was prepared as a starting material for $K_2Ca_2(CO_3)_3$. This mixture was heated in a CO_2 atmosphere at 750 °C for 11 d. The new phase was assumed to be pure since, according to an X-ray

O K(1)
● K(2)
○ Ca(1)
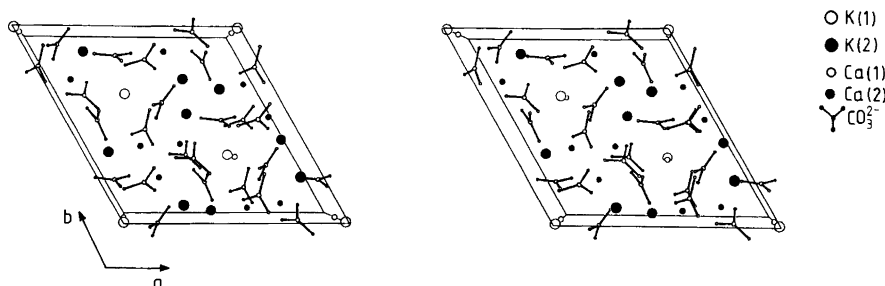● Ca(2)
$\curlyvee$ CO$_3^{2-}$

Fig. 1. A stereoscopic view of the structure perpendicular to the (001)-plane. Ca(1) and K(1) are located on the three-fold axes (special position a) and Ca(2) and K(2) in general positions between the axes.

powder diffractogram, no traces of the starting components or fairchildite and bütschliite could be seen.

This material was then placed in a sealed gold capsule that was heated at 950 °C for 2 h. The cooling was made by slowly decreasing the temperature by 10 °C h^{-1} to 750 °C. After reaching 750 °C the experiment was quenched simply by switching off the heater and releasing the pressure. The resulting crystals were checked with powder X-ray diffraction, and were found to be identical to the starting material.

P–T calibrations of the piston-cylinder equipment were made by DTA determinations of pressure temperature effects on the melting point of LiCl. At any given pressure the probable temperature uncertainty may be at most ±8 °C; at any temperature set point the pressure uncertainty (always running the experiment in the piston-out mode) may be considered to be ±0.5 kbar.

X-Ray measurements. The material from the high-pressure experiments could be described as pale yellow–green granules, usually consisting of several intergrown crystals. Preliminary investigations were performed on a number of crystals, in the search for a suitable single crystal. The impressions of intergrown crystals from optical examination and of the twin lamellae reported by Cooper *et al.*[4] were confirmed in Weissenberg and precession photographs. A small fragment finally turned out to be a single crystal suitable for an X-ray diffraction investigation.

X-Ray intensity data were collected with a SYNTEX R3 automated four-circle diffractometer using graphite-monochromated Mo$K\alpha$ radiation at 293 K. The background was measured on each side of every reflection for a time equal to the peak measurement. Cell parameters were determined by 25 reflections with 5.97 < 2θ < 21.92°. A psi-scan was carried out at 10 reflections selected from intensity measurement in the range 5.94 < 2θ < 52.20°. Experimental details are listed in Table 1.

Calculations were carried out using the Xtal3.2 program package.[9] Of a total of 8581 reflections measured, 816 unique reflections were used in the calculations. The structure was solved using direct methods. Scattering factors used (Ca^{2+}, K$^+$, O$^-$, C^0) were taken from Ref. 10. A Lorenz polarisation correction and an empirical absorption correction based on the psi-scan were

Table 1. Crystal and experimental data for K$_2$Ca$_2$(CO$_3$)$_3$.

Formula	K$_2$Ca$_2$(CO$_3$)$_3$
M_r	338.38
Crystal system	Trigonal
Space group	*R3* (No. 146)
a/Å	13.010(4)
c/Å	8.615(3)
V/Å^3	1262.9(9)
Z	6
D_c/g cm^{-3}	2.67
Radiation	Mo$K\alpha$
Wavelength, λ/Å	0.710 73
F(000)	1025.62
Crystal description	Pale yellow–green
Crystal size/mm	0.12 × 0.15 × 0.08
Diffractometer:	Nicolet R3 upgraded by Siemens
Temperature/K	293
No. of reflns for cell determination (2θ range/°)	25 (5.97 < 2θ < 21.92)
Scan mode	θ–2θ
2θ range/°	5.96 < 2θ < 60.2
hkl range	$-18 \leqslant h \leqslant 18$ $-18 \leqslant k \leqslant 19$ $0 \leqslant l \leqslant 13$
2θ scan speed/° min^{-1}	1.01–3.08
Total no. of reflns measured	8581
Test reflns (deviation %)	1 −4 2 (1.3) 1 2 2 (1.3) 1 1 3 (1.2)
No. of independent reflns	816
R (R_w)	0.018 (0.018)
S	1.002
No. parameters refined	96
Weights calcd according to	$w = 1/(\sigma^2 + 2.84 - 0.003\,85F - 3.53 \sin \theta)$
Corrections	Decay, Lorenz polarization and absorption
Max. resid. electron density/e Å^{-3}	0.314

applied. All atoms found were refined anisotropically. The full-matrix least-square refinements of 96 parameters gave a final *R*-value of 0.018 ($R_w = 0.018$). Details of the calculations are also listed in Table 1.

Results and discussion

Description of the structure. Figure 1 shows a stereoscopic view of the structure perpendicular to the (001)-plane.

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There are two structually different types of each cation, the cations labelled Ca(1) and K(1) lie on a three-fold axis, in the special position a, whereas Ca(2) and K(2) are found in general positions between the three-fold axes. The two carbonate ions are located in columns around K(1) and Ca(1).

The cation–oxygen coordination of the four different cations is illustrated in Fig. 2, which shows a small fraction of the structure, perpendicular to the (110)-plane. For clarity only one of each type of carbonate ion is depicted. The various bond distances and angles are given in Table 2. C(1) coordinates the oxygens O(4), O(5) and O(6), C(2) coordinates O(1), O(2) and O(3). Ca(1) coordinates nine oxygens in a form that could be described as a tricapped trigonal prism. The Ca(1)–O distances vary between 2.409(6) and 2.562(6) Å for the oxygens O(2), O(3) and O(6). K(1) coordinates six oxygens in a slightly irregular trigonal prism, with rather consistent distances; K(1)–O(2) is 2.735(3) Å and
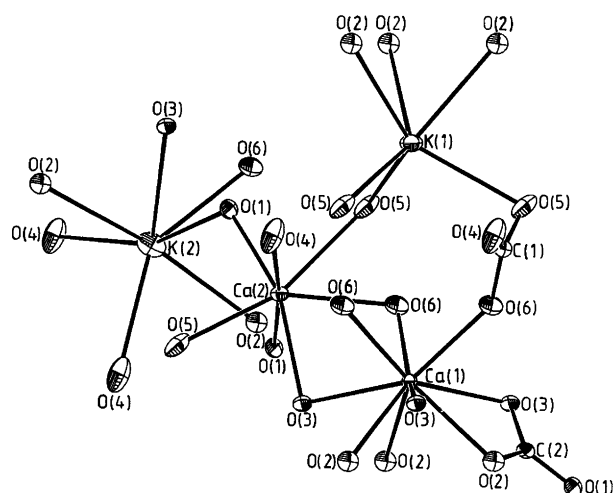
Table 3. Fractional atomic coordinates and equivalent isotropic displacement parameters with e. s. d.s in parentheses.

Atom	x/a	y/b	z/c	$U_{eq}/Å^2$
Ca(1)	1/3	2/3	0.1122(1)	0.0106(2)
Ca(2)	0.26829(4)	0.39207(4)	0.90183(7)	0.0135(2)
K(1)	1/3	2/3	0.5389(1)	0.0206(3)
K(2)	0.25005(6)	0.89606(6)	0.45037(9)	0.0286(2)
O(1)	0.0602(2)	0.6677(2)	0.3646(2)	0.0178(7)
O(2)	0.0828(2)	0.1628(2)	0.6367(2)	0.0175(7)
O(3)	0.2631(2)	0.4476(2)	0.1652(2)	0.0169(7)
O(4)	0.2959(2)	0.8702(2)	0.7623(3)	0.033(1)
O(5)	0.1231(2)	0.5865(2)	0.6915(2)	0.0261(8)
O(6)	0.0962(2)	0.9354(2)	0.2628(2)	0.0264(8)
C(1)	0.1409(2)	0.5254(2)	0.7937(2)	0.0120(7)
C(2)	0.1378(2)	0.6625(2)	0.2777(6)	0.0117(7)

$$U_{eq} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j.$$

K(1)–O(5) is 2.729(7) Å. Ca(1) and K(1) share three oxygens, O(2), in a common polyhedron face. Both K(2) and Ca(2) are seven-coordinated, the former rather irregularly while the latter can be described as a distorted pentagonal bipyramid. The Ca(2)–O distances show small variations, 2.367(3)–2.392(2) Å, except for Ca(2)–O(6), that is 2.488(5) Å. In general, each oxygen is shared by three or four cations besides the carbon atom.

The orientation of the structure in Fig. 3 is identical to that in Fig. 2. Ca(1), Ca(2) and K(2) each coordinate two oxygens within the same carbonate ion; Ca(1) and K(2) to O(2) and O(3) in the $(C(2)O_3)^{2-}$ ion and Ca(2) to O(5) and O(6) in the $(C(1)O_3)^{2-}$ ion. As also can be seen in Fig. 3, K(1) differs from the other cations and coordinates only oxygens from different carbonate ions.

Fig. 2. A fragment of the structure viewed along the [110]-direction showing the cation-oxygen coordination and the atom-labelling scheme. Only one of each type of carbonate ion is shown.

Table 2. Selected interatomic distances (in Å) and bond angles (in °).

Ca(1)–O(2)	2.465(3)	K(1)–O(2)	2.735(3)
Ca(1)–O(3)	2.562(6)	K(1)–O(5)	2.729(7)
Ca(1)–O(6)	2.409(6)	K(2)–O(1)	2.852(3)
Ca(2)–O(1)	2.367(3)	K(2)–O(2)	2.856(3)
Ca(2)–O(1)	2.385(3)	K(2)–O(2)	2.983(4)
Ca(2)–O(3)	2.392(2)	K(2)–O(3)	3.047(2)
Ca(2)–O(4)	2.381(2)	K(2)–O(4)	2.677(6)
Ca(2)–O(5)	2.388(5)	K(2)–O(4)	2.809(3)
Ca(2)–O(5)	2.614(4)	K(2)–O(6)	2.811(5)
Ca(2)–O(6)	2.488(5)		
C(1)–O(4)	1.260(6)	C(2)–O(1)	1.285(7)
C(1)–O(5)	1.282(5)	C(2)–O(2)	1.274(6)
C(1)–O(6)	1.281(4)	C(2)–O(3)	1.287(5)
O(4)–C(1)–O(6)	120.8(5)	O(1)–C(2)–O(2)	121.0(4)
O(4)–C(1)–O(5)	121.9(4)	O(1)–C(2)–O(3)	119.1(4)
O(6)–C(1)–O(5)	117.3(6)	O(3)–C(2)–O(2)	119.8(5)

Discussion

The crystal structure of $K_2Ca_2(CO_3)_3$ does not resemble the common rhombohedral and orthorhombic carbonates,[11] where the carbonate groups are oriented parallel
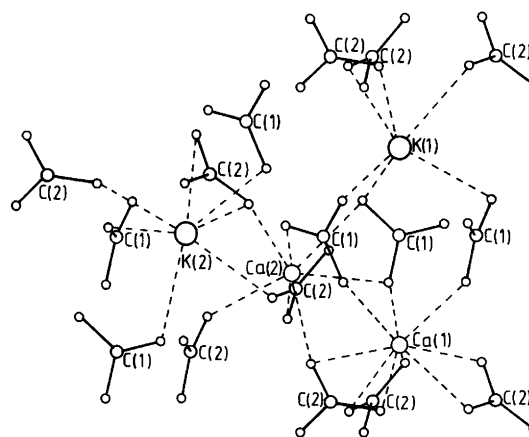

Fig. 3. The same view of the structure as in Fig. 2, complemented with all the carbonate ions. The cation–oxygen coordinations are indicated by dashed lines.

Table 4. Powder diffraction data for the different double carbonates in the K_2CO_3-$CaCO_3$ system compared to the data given by Walenta[3].

K₂Ca₂(CO₃)₃[a]			K₂Ca₂(CO₃)₃ calc[b]			Bütschliite[c]			Fairchildite[d]			Walenta[e]	
d	*I*	*hkl*	*d*	*I*	*hkl*	*d*	*I*	*hkl*	*d*	*I*	*hkl*	*d*	*I*
6.87	9	101	6.84	8	101	4.51	2	101	6.67	14	002	6.11	90
6.54	9	110	6.51	9	110	4.14	2	102	4.59	12	100	4.00	5
3.83	13	12−1	3.82	13	12−1	3.25	4	102	4.34	10	101	3.86	10
3.43	8	202	3.42	7	202	3.02	35	006	3.19	100	103	3.62	10
3.04	76	21−2	3.03	77	21−2	2.86	100	105	3.34	8	004	3.20	100
2.95	100	31−1	2.94	100	31−1	2.69	13	110	2.7	30	104	3.04	5
2.63	30	113	2.63	32	113	2.31	1	201	2.65	70	110	2.9	80
2.54	42	312	2.53	46	312	2.26	6	202	2.31	2	105	2.49	40
2.48	18	23−1	2.48	15	23−1	2.07	14	204	2.29	6	200	2.37	50
2.47	33	140	2.46	43	140	2.01	5	009	2.26	6	201	2.31	50
2.29	15	303	2.28	17	303	1.96	7	205	2.23	16	006	2.26	10
2.22	14	32−2	2.22	15	32−2	1.75	5	211	2.17	20	202	2.07	5
2.16	10	223	2.17	5	330	1.69	20	1010	2.07	2	114	2.04	5
2.02	7	024	2.15	10	223	1.64	20	$2\overline{1}4$	2.04	14	203	1.92	50
1.98	7	15−1	2.01	7	024	1.61	6	119	1.89	14	204	1.6	5
1.91	33	422	1.97	8	15−1	1.58	3	215	1.76	2	107	1.53	5
1.87	28	41−3	1.92	12	214	1.55	2	1011	1.72	4	211	1.51	5
1.84	10	51−2	1.91	20	422	1.35	3	$20\overline{1}1$	1.7	10	166	1.19	5
1.81	14	250	1.88	10	600	1.26	4	$3\overline{1}3$	1.68	2	212		
1.78	10	134	1.87	33	41−3	1.25	6	$10\overline{1}4$	1.67	2	008		
1.71	6	105	1.83	12	51−2	1.23	4	$30\overline{9}$	1.62	2	213		
1.53	6	253	1.81	10	34−1	1.22	2	315	1.6	2	206		
1.51	8	13−5	1.80	17	250	1.1	1	1115	1.54	2	214		
1.47	6	62−2	1.77	12	134	1.04	20	$11\overline{1}6$	1.53	2	300		
			1.70	6	015	1.03	1	$32\overline{5}$	1.47	2	207		
			1.57	10	603	0.93	20	$221\overline{4}$	1.41	2	118		
			1.53	10	253				1.32	2	220		
			1.51	9	13−5				1.28	2	217		
			1.47	7	62−2				1.26	2	306		

[a]Experimental powder diffraction data using CuKα radiation, corrected for apparatus-error by the usage of internal standard (Si), treated with PIRUM.[13] [b]Powder diffraction data calculated from the single crystal structure data with LAZY PULVERIX.[14] Relative peak intensities less than 5 have been excluded. [c]Powder diffraction data from Balascio *et al.*[15] [d]Powder diffraction data from Swanson *et al.*[16] [e]Powder diffraction data from Walenta.[3] There are no *hkl* available.

in planes resulting in layered structures. In $K_2Ca_2(CO_3)_3$ the carbonate groups are more or less inclined relative to the (001)-plane (Fig. 1). In the structure of fairchildite,[12] $K_2Ca(CO_3)_2$, the other known high-temperature phase in the K_2CO_3-$CaCO_3$ system, half of the carbonate groups are parallel to the (001)-plane whereas the other half are inclined and disordered.

Owing to the similar scattering power of K^+ and Ca^{2+}, it is not possible to distinguish between these ions in least-squares refinement. For stoichiometric reasons, however, and considering the number of molecules in the unit cell, it is natural to assume that the cations should occupy one general and one special position each. Furthermore, taking into account the cation–oxygen distances of the four available sites; 2.409(6)–2.562(6), 2.367(3)–2.488(5), 2.729(7)–2.735(3) and 2.677(6)–3.047(2) Å, respectively and the smaller radius of Ca^{2+}, the latter is assigned the two smaller sites and K^+ the two larger sites. Then all the Ca–O bonds become shorter than the shortest K–O bonds (Table 2). Furthermore, introduction of Ca^{2+} in the K^+ sites and vice versa gave a poorer least-squares fit.

The C–O distances vary between 1.260(6) and 1.287(5) Å, which are within the normal range for carbonates; 1.25–1.31 Å.[11] The O–C–O angles are all close to 120°, except for O(6)–C(1)–O(5) and O(4)–C(1)–O(5) where the angles are 117.3 and 121.9°, respectively. Both C(1) and C(2) are slightly displaced from the plane formed by the three oxygens, O(4), O(5), O(6) and O(1), O(2), O(3), respectively, in the carbonate group. C(1) is displaced 0.009 Å and C(2) 0.007 Å from the plane formed by the oxygens.

In Table 4 powder diffraction data of fairchildite, bütschliite, the Ca–K carbonate described by Walenta[3] and the present phase, $K_2Ca_2(CO_3)_3$, are given together with a calculated data set from the investigated single crystal. It is obvious that the powder diffraction data published by Walenta[3] do not match unequivocally with any of the powder diffractograms of bütschliite, fairchildite or $K_2Ca_2(CO_3)_3$. The carbonate found by Walenta[3] may then represent a fourth phase in the system, although it seems more likely that this phase does not belong to the present system at all, but rather to an adjacent system due to the presence of the minor components

Fe and Mg. Kröger *et al.*[2] present a Debyeogram of $K_2Ca_2(CO_3)_3$ that, however, can not be used as a reliable identification tool. Furthermore, the present calculated powder pattern based on data from the single crystal determination agrees unambiguously with the experimental powder X-ray pattern of $K_2Ca_2(CO_3)_3$ synthesised at 1 bar CO_2, thus confirming that the high-pressure crystals are identical with $K_2Ca_2(CO_3)_3$ synthesised at 1 bar.

Since bütschliite and fairchildite have been found in the ashes of fir, hemlock and biomass,[5-7] it is plausible that $K_2Ca_2(CO_3)_3$ also should occur in combustion products. The identification, however, has probably been obstructed by the absence of a powder diffraction characterisation of the phase. Studies are in progress to establish whether $K_2Ca_2(CO_3)_3$ can be found in ashes from combustion of biomass fuels, or not.

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