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Key indicators

Powder X-ray study
 $T = 295\text{ K}$
Mean $\sigma(\text{O}-\text{C}) = 0.002\text{ \AA}$
 R factor = 0.080
 wR factor = 0.128
Data-to-parameter ratio = 0.0

For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

KCaF(CO₃) from X-ray powder data

Potassium calcium fluoride carbonate, KCaF(CO₃), has been synthesized and its structure solved from X-ray powder diffraction data. The K, Ca, F and C atoms lie at sites with $\bar{6}m2$ imposed symmetry and the unique O atom has imposed mm site symmetry. The compound consists of Ca–F–Ca chains parallel to the c axis and planar CO₃ groups perpendicular to the c axis, the corners of the hexagonal cell being occupied by K⁺ ions. The compound is not a solid solution, since the structure differs from those of both KF and CaCO₃.

Comment

The title compound was first discovered by West & Fletcher (1992), but its crystal structure was not determined because the decomposition of CaCO₃ made it difficult to grow single crystals. In the present study, the structure has been determined by the Rietveld refinement from powder diffraction data.

Fig. 1 shows the result of the Rietveld refinement and Fig. 2 shows the crystal structure. The K atoms are coordinated by six O atoms [K–Oⁱ = 2.779 (1) Å; symmetry code: (i) $x - 1, y, z$] and three F atoms [K–F = 2.9450 (1) Å], and the Ca atoms are coordinated by six O atoms [Ca–O = 2.557 (1) Å] and two F atoms [Ca–F = 2.2275 (1) Å]. The C and O atoms form CO₃²⁻ ions, with a C–O distance of 1.284 (2) Å and an O–C–O angle of 120°; these values are typical for carbonates. The title compound is not a solid solution formed from CaCO₃ and KF because the structure differs from those of both compounds. Although CaCO₃ can be regarded as having an NaCl-type structure (with $a = 6.4265\text{ \AA}$ and $\alpha = 101.91^\circ$), the

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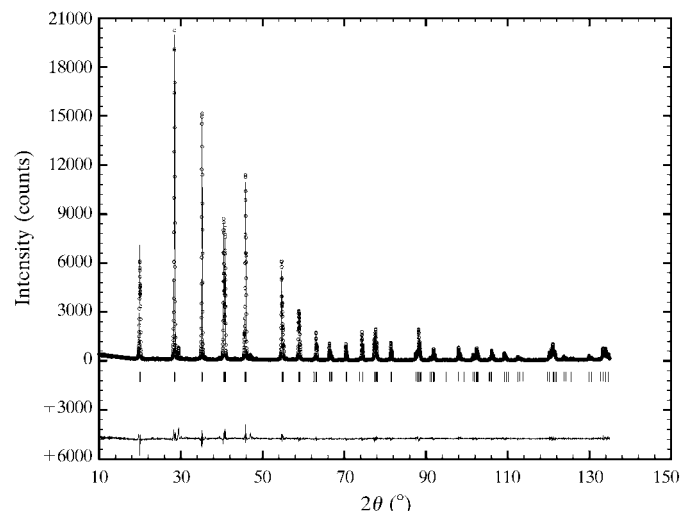


Figure 1

A comparison of observed (circles) and calculated (solid line) intensities for KCaF(CO₃). The difference pattern is also shown.

large lattice mismatch between CaCO_3 and KF ($a = 5.367 \text{ \AA}$ and $\alpha = 90^\circ$) might be one of the reasons why these compounds cannot form a solid solution.

Experimental

Appropriate amounts of analytically pure CaCO_3 and KF were mixed, thoroughly ground and fired at 873–893 K in air for 24 h, as described by West & Fletcher (1992). However, a CaO impurity was always found in the product, probably as a result of the decomposition of CaCO_3 . We therefore synthesized the title compound by firing the mixture at the same temperature in a stream of CO_2 for 24 h, and a white powder containing only a small amount of CaO (1–3 mol%) was obtained.

Crystal data

$\text{KCaF}(\text{CO}_3)$	$D_x = 2.615 \text{ Mg m}^{-3}$
$M_r = 158.17$	Cu $K\alpha$ radiation
Hexagonal, $P\bar{6}m2$	$T = 295 \text{ K}$
$a = 5.10093 (7) \text{ \AA}$	Plate, white
$c = 4.45510 (7) \text{ \AA}$	$15 \times 35 \times 1 \text{ mm}$
$V = 100.389 (5) \text{ \AA}^3$	Specimen prepared at 873 K
$Z = 1$	

Data collection

Rigaku RINT-2400 diffractometer	Specimen mounted in reflection mode
Specimen mounting: packed powder pellet	$2\theta_{\min} = 10$, $2\theta_{\max} = 135^\circ$
	Increment in $2\theta = 0.02^\circ$

Refinement

Refinement on I_{net}	Profile function: pseudo-Voigt
$R_p = 0.080$	26 parameters
$R_{\text{wp}} = 0.128$	$w = 1/Y_i$
$R_{\text{exp}} = 0.056$	$(\Delta/\sigma)_{\max} = 0.01$
$S = 2.26$	Preferred orientation correction:
Wavelength of incident radiation:	$I_{\text{corr}} = I_{\text{obs}}[G_2 + (1 - G_2) - \exp(-G_1 a^2)]$
$K\alpha_1 = 1.540562$,	fibre axis [001] (March, 1932;
$K\alpha_2 = 1.544390 \text{ \AA}$	Toraya, 1986)
Excluded region(s): none	

The powder pattern can be indexed on the basis of a hexagonal cell, with cell parameters [$a = 5.1023 (3) \text{ \AA}$ and $c = 4.4590 (4) \text{ \AA}$] in good agreement with previously reported values (West & Fletcher, 1992). No systematic extinctions are found for any diffraction peak. The possible space groups belong to the Laue classes $\bar{3}$, $\bar{3}m$, $6/m$ and $6/mmm$. *FULLPROF* (Rodríguez-Carvajal, 2003) was applied to the pattern and a total of 135 independent $|F_{\text{obs}}|$ were extracted on the basis of the Le Bail *et al.* (1988) method, using space group $P\bar{6}m2$. Direct methods and difference Fourier synthesis (*SHELXS97*; Sheldrick, 1997) were then applied to these extracted $|F_{\text{obs}}|$. The CO_3 group, the F atom and the heavy cations (K or Ca atoms) could be detected on the basis of the interatomic distances and angles in the E

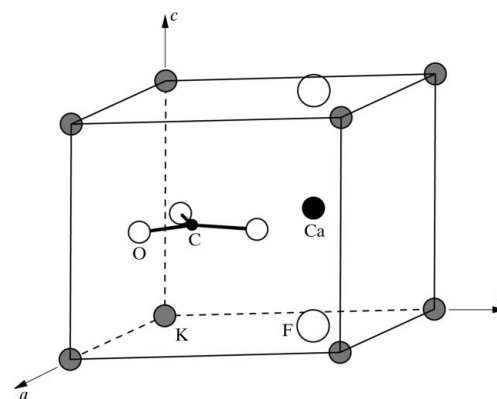


Figure 2

The contents of the unit cell of $\text{KCaF}(\text{CO}_3)$. Large black circles denote Ca atoms, small black circles denote C atoms, grey circles denote K atoms, large open circles denote F atoms and small open circles denote O atoms.

map. The heavy cations were distinguished by the bond-valence method (Brown, 1977), since their atomic scattering factors were close to one another. The final structure was obtained by performing a Rietveld refinement.

Data collection: *RINT2400* (Rigaku, 1993); cell refinement: *HIGHSCORE* (Philips Electronics, 2002); data reduction: *HIGHSCORE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *FULLPROF* (Rodríguez-Carvajal, 2003); molecular graphics: *Balls & Sticks* (Kang & Ozawa, 2003); software used to prepare material for publication: *enCIFer* (CCDC, 2003).

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