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Synthesis and structure analysis of the potassium calcium silicate CAS-1. Application of a texture approach to structure solution using data collected in transmission mode

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Abstract

The crystal structure of the potassium calcium silicate material, CAS-1 ($(\text{Ca}_4\text{K}_4(\text{H}_2\text{O})_8)[\text{Si}_{16}\text{O}_{38}]$), has been determined from synchrotron powder diffraction data collected on a textured polycrystalline sample. It was not possible to solve the structure directly from normal high-resolution powder diffraction data, so the newly developed texture approach to structure solution using data collected in transmission mode was applied. Data analysis was performed using the computer program *Expol*, which has been developed to handle the large amount of data generated in transmission mode. The structure could then be solved by direct methods, and Rietveld refinement (using data collected on an untextured sample) converged with $R_F = 0.062$ and $R_{wp} = 0.175$ ($R_{exp} = 0.097$). This structure is the first novel structure to be solved using the texture method in this configuration. As suggested by ^{29}Si MAS NMR results (1 Q^4 and 3 Q^3 signals, all of equal intensity), CAS-1 ($C2$, $a = 24.158 \text{ \AA}$, $b = 7.016 \text{ \AA}$, $c = 6.482 \text{ \AA}$, $\beta = 95.19^\circ$) proved to be a layer silicate. The structure can be described as a series of silicate double layers connected via chains of edge-sharing $\text{CaO}_5(\text{H}_2\text{O})$ octahedra. There is a two-dimensional eight-ring channel system within the silicate layer, and K^+ ions, which balance the charge, are located in the eight-rings of the two 4.8^2 nets that form the double layer. One water molecule is located in the channel system and another bridges between K^+ and Ca^{2+} ions. The structure is related to that of the natural mineral rhodesite. **To cite this article:** J.L. Jordá et al., *C. R. Chimie 8 (2005)*.

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Résumé

La structure cristalline du silicate de potassium et de calcium, CAS-1 ($(\text{Ca}_4\text{K}_4(\text{H}_2\text{O})_8)[\text{Si}_{16}\text{O}_{38}]$), a été déterminée à partir de données de diffraction sur poudre obtenues par rayonnement synchrotron et collectées sur un échantillon polycristallin texturé. Il n'a pas été possible de résoudre la structure directement à partir de ces données et la méthode texturale, récemment développée pour la résolution de structures, a été appliquée en utilisant des données collectées en mode transmission. L'analyse

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des données a été réalisée à l'aide du programme *Expol*, qui a été développé pour traiter la grande quantité de données générée en mode transmission. La structure a pu alors être résolue par méthodes directes et l'affinement Rietveld (à partir des données collectées sur un échantillon non texturé) a convergé vers les valeurs de $R_f = 0,062$ et $R_{wp} = 0,175$ ($R_{exp} = 0,097$). Cette structure est la première à avoir été résolue grâce à l'utilisation de la méthode texturale dans cette configuration. Comme le suggéraient les résultats de RMN MAS du ^{29}Si (un signal Q^4 et trois signaux Q^3 , de même intensité), CAS-1 ($\text{C}2$, $a = 24,158 \text{ \AA}$, $b = 7,016 \text{ \AA}$, $c = 6,482 \text{ \AA}$, $\beta = 95,19^\circ$) s'est révélé être un silicate en feuillets. Sa structure peut être décrite comme une série de double feuillets silicate connectés par des chaînes d'octaèdres $\text{CaO}_5(\text{H}_2\text{O})$ partageant des arêtes. Les deux réseaux 4.8^2 formant ces feuillets silicate se caractérisent par la présence d'un système bidimensionnel de canaux, avec des ouvertures délimitées par huit côtés contenant les cations K^+ qui neutralisent la charge des feuillets silicate. Une molécule d'eau est située dans le système de canaux, l'autre relie les ions K^+ et Ca^{2+} . La structure est apparentée à celle du minéral naturel rhodésite. **Pour citer cet article : J.L. Jordá et al., C. R. Chimie 8 (2005).**

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Keywords: CAS-1; Layer silicate; Powder diffraction; ^{29}Si MAS NMR; Structure determination; Texture method

Mots clés : CAS-1 ; Silicate en feuillets ; Diffraction sur poudre ; RMN MAS du ^{29}Si ; Détermination structurale ; Méthode texturale

1. Introduction

During the course of an investigation involving the isomorphous substitution of divalent cations for Al and/or Si in host framework structures, a new potassium calcium silicate material, CAS-1 ($(\text{Ca}_4\text{K}_4(\text{H}_2\text{O})_8[\text{Si}_{16}\text{O}_{38}])$), was synthesized. Absorption, catalysis and ion-exchange measurements indicated that CAS-1 was microporous [1,2], and the X-ray powder diffraction pattern that the structure was novel.

Scanning electron micrographs (Fig. 1) showed that the crystallites had a needle-like morphology (ca. $100 \times 10 \times \sim 1 \mu\text{m}$), but none were of sufficient size and

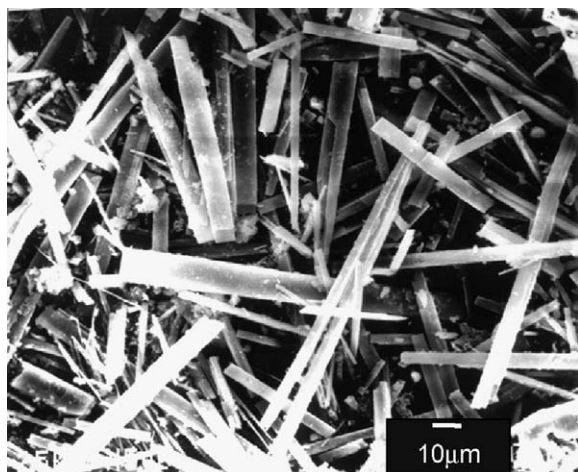


Fig. 1. Scanning electron micrograph of the CAS-1 sample.

quality for single crystal data collection. However, the sample appeared to be well-suited for the application of the texture approach to structure determination that we have been developing [3]. It proved to be possible to prepare a textured sample (with preferentially oriented crystallites), so the necessary X-ray diffraction data could be collected.

The texture method is an experimental approach to resolving reflections that overlap in a conventional powder diffraction pattern [4]. With the more single-crystal-like data that result, advantage can be taken of the very powerful structure solution programs that have been developed for single-crystal data. A description of the concept behind this approach to structure solution that has been written for non-crystallographers can be found in [5].

The method was first implemented in reflection mode [6], and such data were used to solve the structure of UTD-1F, with 117 atoms in the asymmetric unit [7]. In an attempt to make the experiment simpler, to obtain more complete data with fewer corrections, and to speed up the data collection, the method was recently adapted to work in transmission mode using a two-dimensional detector [8]. In view of the fact that a textured sample of CAS-1 could be prepared, and that attempts to determine its structure from standard high-resolution powder diffraction data had not been successful, CAS-1 was viewed as an ideal test case for the modified experimental setup and the new data analysis program.

2. Experimental

2.1. Synthesis

Two grams $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (≥ 96 wt.%, Beijing Hongxin Chemical Factory) were dissolved in 25 ml distilled water. Then 10.43 ml colloidal silica (6.05 mol/l aqueous solution, Qingdao Chemical Factory) were added to the solution. Finally, 2.41 g KOH (≥ 82 wt.%, Beijing Chemical Factory) were added at room temperature, and the mixture was stirred for a further 1/2 h. The resulting gel composition was 0.28 K_2O :0.13 CaO : SiO_2 :22 H_2O . This gel was transferred to a Teflon-lined stainless steel autoclave, and crystallization was carried out at 493 K under autogenous pressure without stirring for 6 days. The autoclave was then removed from the oven and cooled, and the product was separated by centrifuge, washed with distilled water six times and then dried in air at ca. 383 K.

2.2. Chemical analysis

Chemical analysis of as-synthesized CAS-1 yielded the molar ratios Si/Ca/K/Na of 4.86:1.00:1.085:0.136, respectively. Na was probably present as an impurity in the colloidal silica. Thermogravimetric analysis was performed on a PTC-10A instrument in air at a heating rate of 10 K/min, and showed a weight loss of 11.2 wt.% at 583 K.

2.3. ^{29}Si MAS NMR

^{29}Si MAS NMR data were collected using pulse widths of 2.2 μs and intervals of 5 μs on the InfinityPlus-400 spectrometer with a spinning rate of 5.0 kHz. The chemical shifts were referred to tetramethylsilane. The spectrum (Fig. 2) shows four signals of equal intensity. The chemical shifts of three signals fall into the Q^3 region and one into the Q^4 region.

2.4. High-resolution X-ray data collection

High-resolution X-ray powder diffraction data on an untextured sample of CAS-1 were collected on the powder diffractometer on Station B of the Swiss–Norwegian Beamlines (SNBL) at the European Synchrotron Radiation Facility (ESRF) in Grenoble, France. Details of the data collection are given in Table 1.

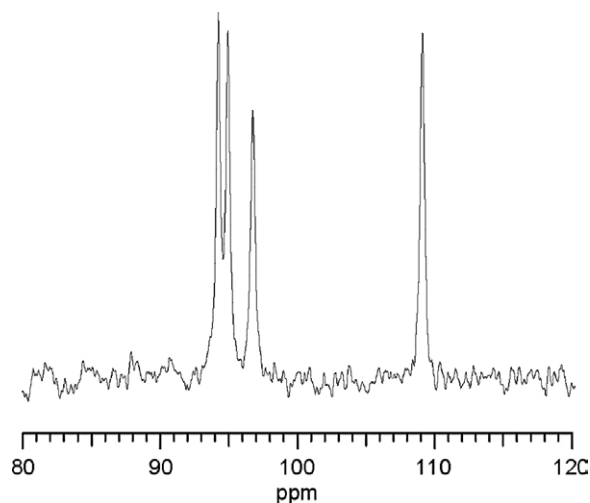


Fig. 2. ^{29}Si MAS NMR spectrum for CAS-1.

Table 1

X-ray data collection

High resolution		
Synchrotron facility		SNBL (Station B) at ESRF
Wavelength		0.79960(2) Å
Diffraction geometry		Debye–Scherrer
Analyzer crystal		Si 111
Sample		Rotating 1.0 mm capillary
2θ Range		3.5–52.0°
Step size		0.002° 2θ
Time per step	2.6–18.0° 2θ	1.0 s
	18.0–50.0° 2θ	6.0 s
Textured sample		
Synchrotron facility		SNBL (Station A) at ESRF
Wavelength		0.70056 Å
Standards		Si, zeolite A
Slit size		0.4 mm
Sample-detector distance	400 mm	240 mm
d_{\min}	1.77 Å	1.16 Å
Time per frame	120 s	220 s
Sample rotation per frame	5°	5°
Number of frames	72	72
Non-overlapping reflections used to calculate the ODF	102–3 1	0–1 1
	110–0 1	1–5 1
	12–7311	1 4 0
	1–3 1	

Initial attempts to index the diffraction pattern failed, and the presence of an impurity phase was suspected. Laboratory data collected on a second sample (different synthesis batch), in which the impurity phase proved to be dominant, allowed the impurity peaks in the original pattern to be identified, and then the main phase could be indexed on a monoclinic unit cell ($a = 24.158 \text{ \AA}$, $b = 7.016 \text{ \AA}$, $c = 6.482 \text{ \AA}$, $\beta = 95.19^\circ$) using the program N-TREOR [9]. A careful examination of the diffraction pattern indicated that the reflections hkl , $h + k = 2n + 1$ were systematically absent, so the two most probable space groups could be expected to be $C2/m$ or $C2$.

2.5. Preparation of a textured sample

To prepare a textured sample (one with a preferential orientation of the crystallites), a sample was mixed with water, disaggregated using ultrasound, and then allowed to settle. The lighter fraction, which remained suspended in water longest, was decanted off and filtered. It was then mixed with a polystyrene/THF solution (ca. two parts sample to one part polystyrene), and the resulting slurry was smeared (along a single direction) onto a glass slide. When the layer had dried, a second layer was applied in the same manner, and this procedure was continued until the sample was thick enough. Finally, a spherical sample with a diameter of ca. 0.3 mm was cut from the CAS-1/polystyrene preparation.

2.6. Collection of X-ray data on the textured sample

Three-dimensional diffraction data were collected on SNBL Station A at the ESRF using the imaging plate

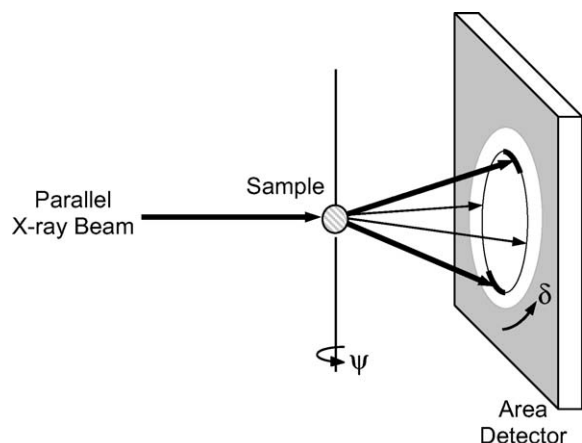


Fig. 3. Experimental setup for measurement of a textured sample in transmission mode.

setup illustrated in Fig. 3. An imaging plate frame was exposed as the sample was rotated 5° (ψ axis). In all, 72 frames, corresponding to a full 360° rotation of the sample, were exposed with the detector positioned 400 mm from the sample ($d_{\min} = 1.77 \text{ \AA}$), and then another 72 frames with the detector positioned 240 mm from the sample ($d_{\min} = 1.16 \text{ \AA}$). The latter were used to access the reflections at higher 2θ , but the resolution in peakwidth is significantly worse at this shorter sample-detector distance. To illustrate the effect of texture on the diffraction pattern, a typical imaging plate frame is shown in Fig. 4. Additional details of the data collection are given in Table 1.

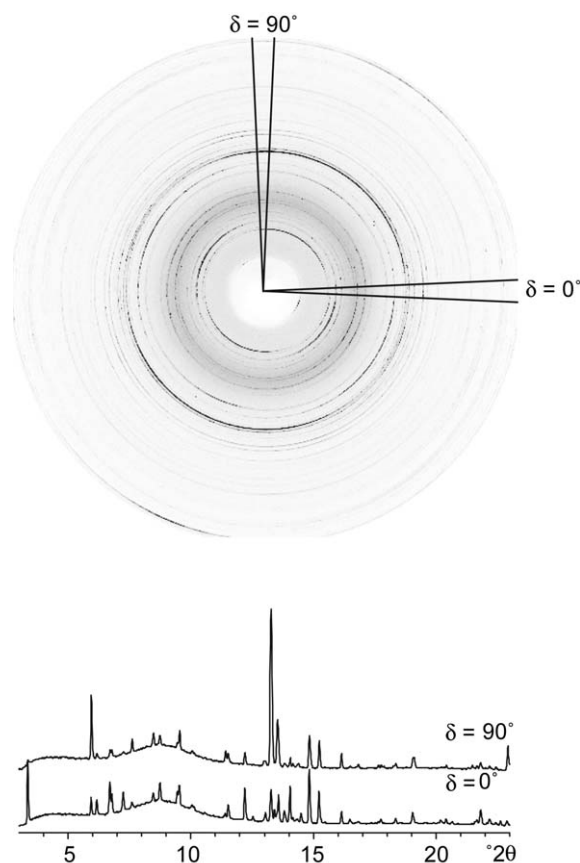


Fig. 4. One of the imaging plate frames ($\psi = 85^\circ$) collected on the textured sample of CAS-1. Note the significant intensity differences around the rings. The diffraction patterns extracted for two of the 72 radial wedges ($\delta = 0^\circ$ and 90°) are shown below.

3. Structure determination

3.1. The texture method

Each of the 72 imaging plate frames was divided into 72 radial wedges, corresponding to 5° tilts of the sample (δ), and these in turn were integrated into diffraction patterns using the program *Fit2d* [10] (see Fig. 4). Only one quadrant of each frame was used for data analysis (others are redundant), so diffraction patterns corresponding to a total of $72 \times 18 = 1296$ sample orientations $\{\psi, \delta\}$ were generated for each sample-detector distance.

Data analysis is based on the equation

$$y(2\theta, \psi, \delta) = \sum_{hkl} I_{hkl} P_{hkl}(\psi, \delta) G(2\theta - 2\theta_{hkl})$$

where $y(2\theta, \psi, \delta)$ is the intensity measured at step 2θ for the sample orientation (ψ, δ) , I_{hkl} is the single-crystal intensity for the reflection hkl , $P_{hkl}(\psi, \delta)$ its preferred orientation factor for the sample orientation (ψ, δ) , and $G(2\theta - 2\theta_{hkl})$ is the Rietveld-type peakshape function. First the orientations of the crystallites (orientation distribution function or ODF) were determined by evaluating how the intensities of (non-overlapping) reflections change as a function of sample orientation. This was done using the standard texture determination program BEARTEX [11]. Then this information was used to calculate how much of the total intensity of each reflection in the diffraction pattern would be observed for each sample orientation ($P_{hkl}(\psi, \delta)$ -values). In this way, reflections with similar 2θ or d -values but different orientations (e.g. the 333 and 511 reflections in a cubic system) can be distinguished from one another, because their intensities will be concentrated in different parts of space. Data analysis was performed using the computer program *Expol* [8].

3.2. Application of the texture method to CAS-1

The data collected on the textured CAS-1 sample were treated as described above. It was quickly apparent that the sedimentation treatment of the sample had removed the impurity phase and that the texture was quite pronounced, so data analysis was relatively straightforward. The ODF was determined using 10 non-overlapping reflections (see Fig. 5). Then a single set of intensities was extracted (using the ODF

and all patterns simultaneously) and used as input to SHELXS [12] assuming the space group $C2/m$.

A possible solution with four heavy atoms (multiplicities 4, 4, 4 and 8), and seven lighter ones was generated. In view of the chemical analysis and the positions of these atoms, the first heavy atom was assigned as Ca and the other three as Si. However, the ^{29}Si NMR spectrum showed the presence of four Si sites with approximately equal populations, so the symmetry was reduced to $C2$ and the Si in the site with multiplicity 8 was thereby split into two independent sites of multiplicity 4. The positions of the bridging O atoms were then calculated using the program KRIBER [13].

4. Structure completion and Rietveld refinement

The coordinates from KRIBER were optimized using the program DLS-76 [14], and then used as a starting point for structure completion and Rietveld refinement. For this, the program package XRS-82 [15] was used in conjunction with the high-resolution powder diffraction data collected on an untextured sample. Dif-

Table 2
Crystallographic data

Chemical composition	[(Ca ₄ K ₄ (H ₂ O) ₈] [Si ₁₆ O ₃₈]	
<i>Unit cell</i>		
<i>a</i>	24.158(2) Å	
<i>b</i>	7.0160(1) Å	
<i>c</i>	6.4816(4) Å	
β (°)	95.19(8)°	
Space Group	C2	
Standard peak for peak shape function (<i>hkl</i> , 2θ)	001, 7.10	
Peak range (number of FWHM)	20	
Number of observations	21,409	
Number of contributing reflections	918	
Number of geometric restraints ^a	47	
Si–O	1.61(1) Å	16
O–Si–O	109.5(2.0)°	24
Si–O–Si	145(8)°	7
Number of profile parameters	8	
Number of structural parameters	58	
Preferred orientation vector	[100]	
R_{exp}	0.097	
R_{wp}	0.175	
R_{F}	0.062	

^a The numbers given in parentheses are the esds assumed for each of the restraints. Each restraint was given a weight equivalent to the reciprocal of its esd.

ference Fourier maps revealed the location of a K^+ ion and two water molecules. Both water molecules are coordinated to the K^+ ion, and one is also coordinated to the Ca^{2+} ion. The model is in agreement with the ^{29}Si NMR results, which indicated the presence of three Q^3 and one Q^4 Si species. The discrepancies in the Si and Na content obtained from chemical analysis and the final structure probably result from the unidentified impurity phase.

A mismatch between the observed and calculated patterns was traced to the presence of some preferred orientation in the sample along the [100] direction (needles aligned along the capillary). Once this factor had been included, refinement proceeded smoothly and converged with the R -values $R_F = 0.062$, $R_{wp} = 0.175$, $R_{exp} = 0.097$ (Table 2). The final atomic parameters are given in Table 3 and selected distances and angles in Table 4. Estimated standard deviations were taken directly from the Rietveld refinement program and only take into account errors arising from counting statistics [16]. The fit of the profile calculated for this model to the experimental data is shown in Fig. 7. Geometric restraints were imposed on the bond distances and

angles of the atoms in the silicate layer. The H atoms of the water molecule were simulated by increasing the occupancy parameter of the associated O atoms from 1 to 1.25. Neutral scattering factors were used for all atoms.

5. Discussion

The structure of CAS-1 (Fig. 6a) can be described as a series of silicate double layers (Fig. 6b) connected via chains of edge-sharing $CaO_5(H_2O)$ octahedra (Fig. 6c). The silicate double layers consist of two 4.8^2 nets, which are linked to form a two-dimensional eight-ring channel system within the layer. The two nets are related to one another by a twofold axis along the [010]-direction (at O(1)). The negative charge is balanced by K^+ ions, which lie in the eight-rings of the 4.8^2 nets, where they coordinate to one terminal and five bridging oxygens of the silicate layer and to two H_2O molecules (Fig. 6d). One of the water molecules is located in the eight-ring channels along the [010] and [001] directions, while the other bridges to a Ca^{2+} ion in the octahedral chains between the sheets. Because the K^+

Table 3
Positional, thermal and occupancy parameters for CAS-1^a

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{iso} ($\times 100 \text{ \AA}^2$)	Occupancy ^b
Ca	0.2570(1)	0.0006(7)	0.9827(2)	0.88(4)	4.0
K	0.1165(1)	-0.0205(6)	0.2491(2)	2.62(8)	4.0
Si(1)	0.4335(1)	0 ^c	0.0100(2)	0.61(2) ^d	4.0
Si(2)	0.3656(1)	0.2802(5)	0.2368(3)	0.61(2) ^d	4.0
Si(3)	0.3558(1)	-0.0001(6)	0.5982(2)	0.61(2) ^d	4.0
Si(4)	0.3670(1)	0.7200(5)	0.2447(4)	0.61(2) ^d	4.0
O(1)	0.5	-0.0148(10)	0	0.61(2) ^e	2.0
O(2)	0.4039(1)	0.0334(6)	0.7816(4)	0.61(2) ^e	4.0
O(3)	0.3826(1)	0.4990(5)	0.2848(5)	0.61(2) ^e	4.0
O(4)	0.3137(2)	0.2700(8)	0.0647(5)	0.61(2) ^e	4.0
O(5)	0.3519(2)	0.1887(6)	0.4544(5)	0.61(2) ^e	4.0
O(6)	0.4193(2)	0.1741(4)	0.1583(5)	0.61(2) ^e	4.0
O(7)	0.2964(1)	-0.0493(7)	0.6764(5)	0.61(2) ^e	4.0
O(8)	0.3059(1)	0.7442(8)	0.1294(6)	0.61(2) ^e	4.0
O(9)	0.3766(2)	0.8206(6)	0.4689(5)	0.61(2) ^e	4.0
O(10)	0.4118(2)	0.8025(4)	0.0986(6)	0.61(2) ^e	4.0
Ow(1)	-0.0113(2)	0.0519(9)	0.7272(8)	8.16	5.0 ^f
Ow(2)	0.2248(2)	0.0691(7)	0.3333(7)	4.13	5.0 ^f

^a Numbers in parentheses are the esd's in the units of the least significant digit given. Values without an esd were not refined.

^b Occupancy parameters are given in terms of atoms per unit cell.

^c Fixed to define the zeropoint along the polar *b*-axis.

^{d-e} Thermal parameters with the same superscript were constrained to be equal.

^f Occupancy increased to approximate the electron density of the associated H atoms.

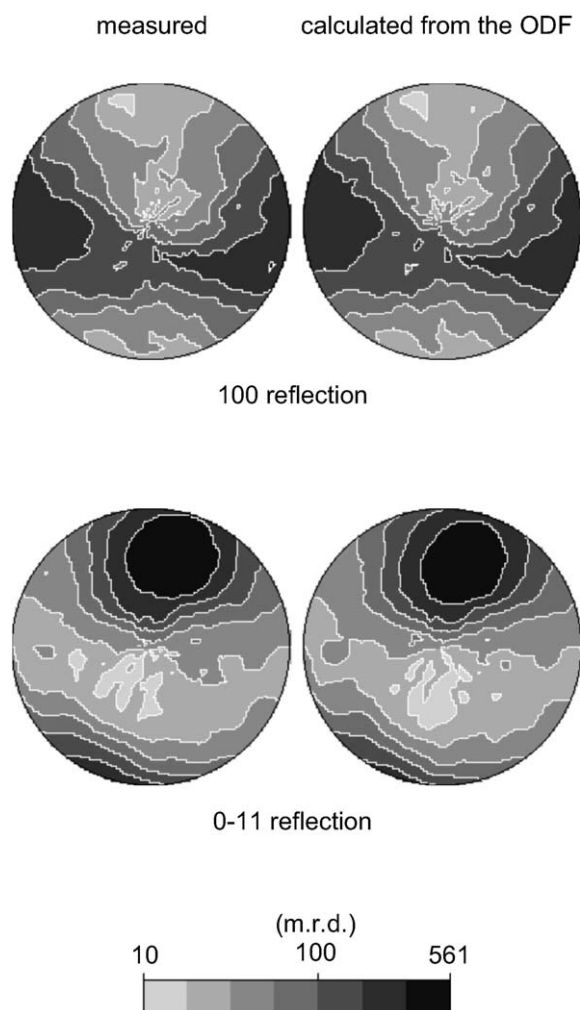


Fig. 5. Pole figures for two of the 10 non-overlapping reflections (1 0 0 and 0 $\bar{1}$ 1) that were used to calculate the crystallite orientation distribution function (ODF). On the left are the measured data and on the right the pole figure calculated from the ODF. Note that the intensity of each reflection is highly dependent upon the sample orientation (i.e. the position in the pole figure).

ions are near the surfaces of the double layer, the two-dimensional channel system contains only water molecules and is not blocked by cations.

The structure is related to that of the natural mineral rhodesite [17]. However, there are some important differences between the structures. First, the silicate layers in rhodesite are related by a mirror plane, while those in CAS-1 are related by a twofold axis. Second, the ratios of Si/Ca/K in rhodesite are 8:2:1, whereas those in CAS-1 are 8:2:2. Third, rhodesite is orthorhombic

Table 4
Selected interatomic distances (Å) and angles (°) for CAS-1

Si(1)–O(1)	1.62(1)	Ca–O(4)	2.37(3)
–O(2)	1.60(5)	–O(4')	2.36(2)
–O(6)	1.61(2)	–O(7)	2.33(7)
–O(10)	1.62(2)	–O(8)	2.34(4)
		–O(8')	2.36(4)
Si(2)–O(3)	1.61(1)	–Ow(2)	2.51(6)
–O(4)	1.60(7)		
–O(5)	1.61(2)	K–O(2)	3.19(1)
–O(6)	1.62(3)	–O(3)	3.02(1)
		–O(3')	3.47(1)
Si(3)–O(2)	1.60(7)	–O(4)	3.12(1)
–O(5)	1.62(1)	–O(5)	2.84(1)
–O(7)	1.60(4)	–O(6)	3.46(1)
–O(9)	1.62(2)	–O(9)	2.98(1)
		–O(10)	3.23(1)
Si(4)–O(3)	1.61(1)	–Ow(1)	2.61(1)
–O(8)	1.60(6)	–Ow(2)	2.69(1)
–O(9)	1.61(2)		
–O(10)	1.61(5)		
O–Si(1)–O	Min 108(1) Max 110(1)	O–Ca–O (eq)	Min 82(1) Max 105(1)
		O–Ca–O (ax)	Min 168(1) Max 173(1)
O–Si(2)–O	Min 106(1) Max 113(1)		
O–Si(3)–O	Min 105(1) Max 114(1)		
O–Si(4)–O	Min 105(1) Max 115(1)		
Si(1)–O(1)–Si(1)	173(1)	Ca–O(4)–Ca	97(1)
Si(1)–O(2)–Si(3)	154(1)	Si(2)–O(4)–Ca	126(1)
Si(2)–O(3)–Si(4)	146(1)	Si(2)–O(4)–Ca'	125(1)
Si(2)–O(5)–Si(3)	146(1)		
Si(1)–O(6)–Si(2)	139(1)	Ca–O(8)–Ca	98(1)
Si(3)–O(7)–Ca	134(1)	Si(4)–O(8)–Ca	134(1)
Si(3)–O(9)–Si(4)	141(1)	Si(4')–O(8)–Ca	127(1)
Si(1)–O(10)–Si(4)	141(1)		

(space group *Pnma*), while CAS-1 is monoclinic (space group *C2*). Fourth, the K⁺ ions in rhodesite are located in the middle of the silicate double layers, where they are coordinated to six bridging oxygens and four water molecules, while in CAS-1, the K⁺ ions are at the surfaces of the silicate double layers and are coordinated to one terminal and five bridging oxygens and to two water molecules. Finally, there are differences in the environments of the Ca²⁺ ions. In both structures, the Ca²⁺ ions are located between the silicate double layers and form chains of edge-sharing octahedra along

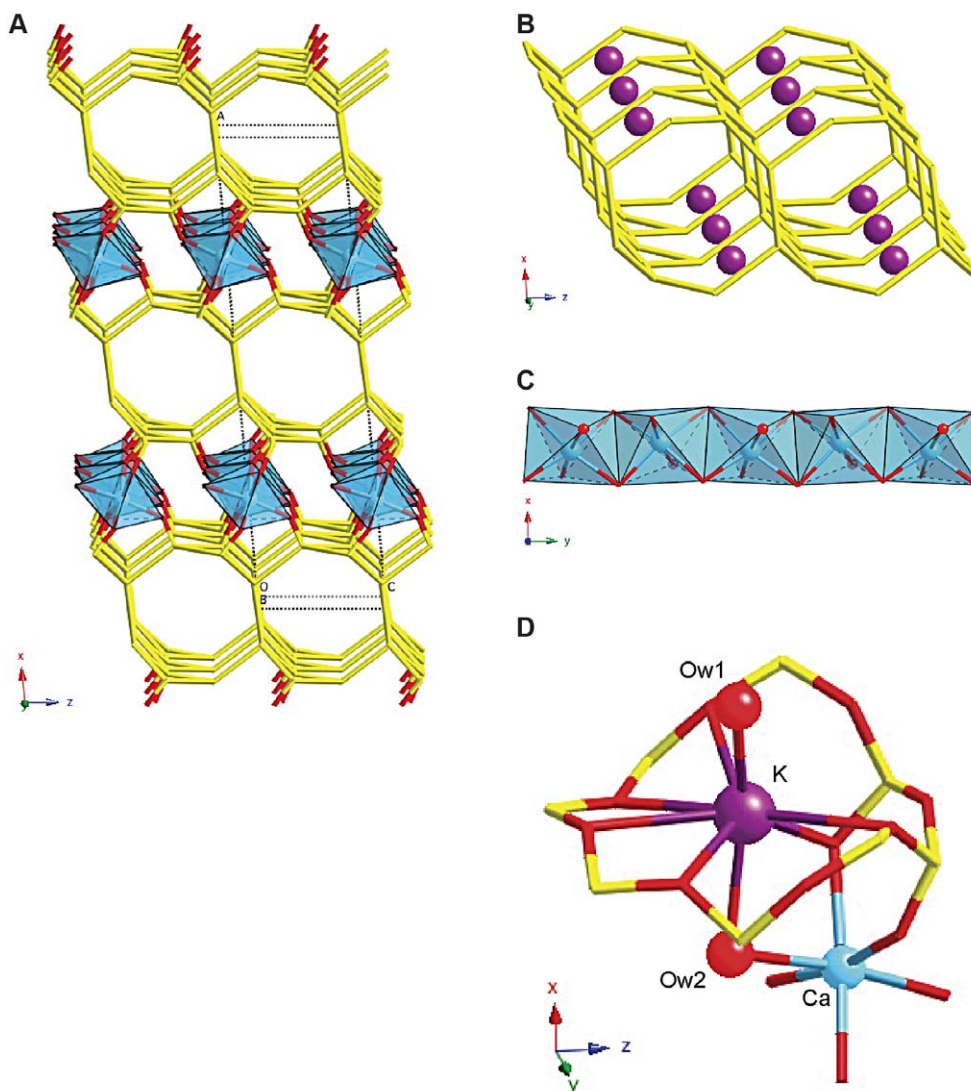


Fig. 6. The structure of CAS-1. (A) A simplified representation showing only the silicate double layers (stick representation) and the chains of edge-sharing $\text{CaO}_5(\text{H}_2\text{O})$ octahedra (polyhedra), (B) the silicate double layer showing the positions of the K^+ ions, (C) the chains of edge-sharing $\text{CaO}_5(\text{H}_2\text{O})$ octahedra in more detail, and (D) the coordination spheres of the Ca^{2+} and the K^+ ions.

[010], but in rhodesite, two kinds of Ca^{2+} ions are present. One is coordinated to six terminal oxygens of the silicate layers, while the other is coordinated to four terminal oxygens and two water molecules. In CAS-1, only one kind of Ca^{2+} ion is present, and it is coordinated to five terminal oxygens and one water molecule. The Ca^{2+} ions in the closely related aluminosilicate mineral hydrodelhayelite are similarly coordinated [18].

This structure determination represents the first true test of the texture method using data collected in trans-

mission mode. In particular it shows that the experimental setup is a viable one and that the data analysis software functions properly. Although the structure is not particularly complex, the presence of an impurity phase and the fact that some preferred orientation of the crystallites was present in the ‘untaxed’ sample would have complicated structure solution from the high-resolution powder diffraction data alone. With this result, the application of the method to more complex problems can be undertaken with confidence.

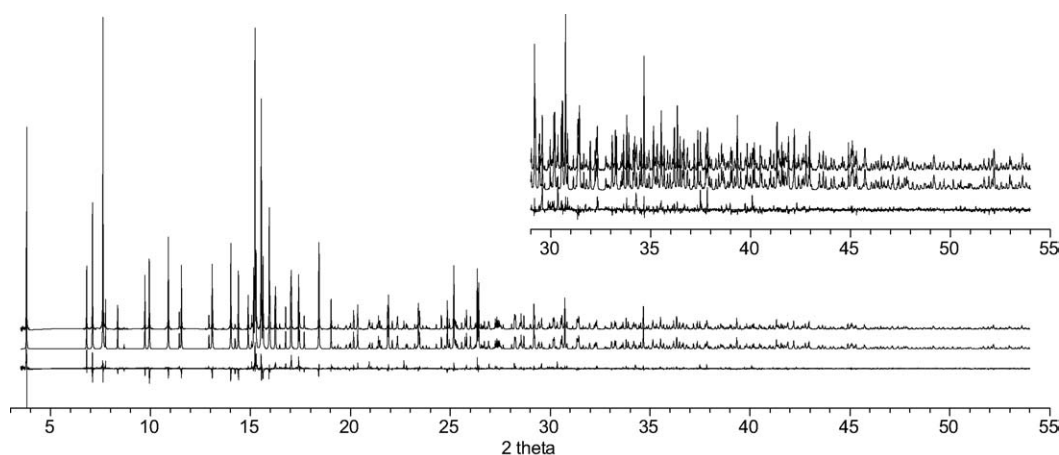


Fig. 7. The observed (top), calculated (middle) and difference (bottom) profiles for the Rietveld refinement of CAS-1. To show more detail, the scale for the second half of the pattern has been increased by a factor of 5 in the inset.

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