

STRUCTURAL REINVESTIGATION OF SYNTHETIC KILCHOANITE,
A $\text{Ca}_3\text{Si}_2\text{O}_7$ POLYMORPH

von

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Abstract

Single crystals of kilchoanite ($\text{Ca}_3\text{Si}_2\text{O}_7$) were obtained as transparent prismatic crystals during the hydrothermal treatment of a rubidium calcium silicate glass at 1kbar and 800°C. The crystal structure of kilchoanite was determined from single-crystal X-ray diffraction data (Mo- K_α radiation, $2\theta_{\text{max}}=25.34^\circ$, $R_{\text{int}}=2.58\%$) and refined in space group *Ima2* (no. 46) to $R(\text{IFl})=2.14\%$ using 1151 observed reflections with $I > 2\sigma(I)$. Unit-cell parameters are: $a = 21.9641(14)$, $b = 5.0841(3)$, $c=11.4403(7)$ Å, $V=1277.51(14)$ Å³, $Z=2$. The structure belongs to the group of mixed anion silicates consisting of insular tetrahedra and trimers in the ratio 1:1, i.e. the crystallochemical formula can be written as $\text{Ca}_6[\text{SiO}_4][\text{Si}_3\text{O}_{10}]$. Linkage between the anion groups is provided by Ca cations which are distributed among four crystallographically independent positions.

Introduction

Natural $\text{Ca}_3\text{Si}_2\text{O}_7$ occurs in two modifications: rankinite and kilchoanite. Both minerals are typically formed during the pyrometamorphism of siliceous limestones (GRAPES, 2011). From a structural point of view both polymorphs differ considerably. Whereas the sorosilicate rankinite contains $[\text{Si}_2\text{O}_7]$ -moieties, kilchoanite belongs to the group of mixed anion silicates and is build up from $[\text{SiO}_4]$ - and $[\text{Si}_3\text{O}_{10}]$ -units in the ratio 1:1. In the course of a study on the crystallization behaviour of rubidium calcium silicate glasses under hydrothermal conditions we obtained high quality single crystals of kilchoanite. An examination of the published structural parameters revealed that the crystallographic data of kilchoanite are of modest quality only ($R(\text{IFl}) = 0.089$). Therefore, we decided to reinvestigate the crystal structure of kilchoanite in more detail.

Experimental details

The single crystals for this study were synthesized from a glass of $\text{Rb}_2\text{Ca}_2\text{Si}_2\text{O}_7$ composition. The glass was prepared by fusing a stoichiometric mixture of dried Rb_2CO_3 (Alfa Aesar, 99.8%), CaCO_3 (Merck, p.a.) and SiO_2 (Alfa Aesar, 99.995%) in a covered platinum crucible at 1200°C

for 4h and quenching in air. The product was crushed and ground in an agate mortar. Approximately 0.05g of the glass and 0.038g of 1 M Rb_2CO_3 solution were loaded and sealed in a gold capsule (4mm inner diameter and 25mm in height). The hydrothermal experiment was performed in an externally heated Tuttle-type “cold seal” autoclave. The sample was taken at room temperature to a pressure of 1 kbar. Subsequently, the temperature was increased to 800°C. The run duration at the final temperature was 18 days. After quenching, the recovered sample was examined using a petrographic microscope. Based on the observed morphologies and optical properties it was obvious that it consisted of a mixture of three different crystalline phases, which were identified using single crystal diffractometry: wollastonite (needles, main phase), $\text{Rb}_2\text{CO}_3 \cdot 1.5\text{H}_2\text{O}$ (plates) and kilchoanite (prims).

A kilchoanite sample of good optical quality was selected for the single crystal diffraction studies and mounted on the tip of a glass fibre using nail hardener. Data collection at ambient temperature was performed on an Oxford Diffraction Gemini R Ultra single crystal diffractometer. Indexing indicated the presence of an orthorhombic unit cell. Intensity data corresponding to a complete hemisphere of reciprocal space were collected in 253 frames with ω -scans using 1.0° scan width per frame. For integration and data reduction the CrysAlisPro software package was employed. A semi-empirical absorption correction was applied. Intensity statistics suggested that the compound is non-centrosymmetric. Structure solution and consecutive least-square refinement calculations were carried out in space group *I m a 2* with the programs SIR92 (ALTOMARE et al., 1993) and SHELXL97 (SHELDRICK, 2008), respectively, both embedded in the WinGX program suite (FARRUGIA, 1999). Final full matrix least squares refinement cycles including fractional coordinates and anisotropic displacement parameters for all atoms converged to a residual of $R1 = 0.0214$ for 117 parameters and 1151 observed reflections. The largest shift/esd. in the final cycles was < 0.001 . The final difference electron density map was featureless, with highest peak and deepest hole of $+0.28$ and $-0.480 \text{ e} \cdot \text{Å}^{-3}$, respectively (see Table 1). Refined atomic coordinates, anisotropic displacement parameters as well as selected interatomic distances are given in Tables 2, 3, and 4 respectively. Crystallographic data for the structure reported here have been deposited with the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (crysdata@FIZ-Karlsruhe.de), and are available on quoting the deposition number 424472. Figures showing structural details were prepared using the program Atoms5.1 (DOWTY, 2000).

Results

The results of our structural investigations confirm the model given by TAYLOR (1971), although our refinements are of much higher quality concerning the obtained residual values as well as the standard uncertainties of the fractional atomic coordinates and the bond distances and angles. The structure can be characterized as a mixed anion silicate comprising individual $[\text{SiO}_4]$ tetrahedra and $[\text{Si}_3\text{O}_{10}]$ -trimers. The central $[\text{Si}(1)\text{O}_4]$ -tetrahedron of a trimer resides on a 2-fold axis running parallel to $[001]$ and shares two different O(2) with the adjacent two $\text{Si}(3)\text{O}_4$ -tetrahedra (see Figure 1). The insular tetrahedron around Si(2) occupies a special Wyckoff position as well (site symmetry *m.*). Individual Si-O bond distances show a considerable scatter. However, the observed values are in the normal range for tetraoxosilicates. For the central $\text{Si}(1)\text{O}_4$ tetrahedron, for example, two groups of Si-O bond distances can be distinguished. The two Si-O bonds to the bridging oxygen ligands O(2) (1.668 Å) are considerably longer than the two non-

bridging bonds (1.581 Å). The terminal Si(3)O₄-polyhedra is characterized by one long (1.705 Å) and three shorter (average 1.611 Å) Si-O bonds. A quantitative measure of tetrahedral distortion is given by the quadratic elongation λ and the angle variance σ^2 , respectively (ROBINSON et al., 1971). These parameters have values of $\lambda = 1.003$ and $\sigma^2 = 9.50$ for Si(1), $\lambda = 1.006$ and $\sigma^2 = 27.12$ for Si(2) and $\lambda = 1.011$ and $\sigma^2 = 45.54$ for Si(3). Due to constraints imposed by space group symmetry, the Si(3)-O(2)-Si(1) angles are identical and have values of 120.97°. The insular tetrahedra as well as the [Si₃O₁₀] groups are located in alternating layers perpendicular to [100] at $x = 0$ and $\frac{1}{2}$ (for the trimers) and $x = \frac{1}{4}$ and $\frac{3}{4}$ (for Si(2)O₄). Charge compensation in the structure is achieved by the incorporation of calcium cations distributed among four crystallographically independent sites. The coordination polyhedra around the Ca-positions Ca(1), Ca(2) and Ca(4) can be described as distorted octahedra. The coordination sphere of the remaining Ca(3) is more irregular. To an upper limit of 3.0 Å eight oxygen ligands can be found. The resulting polyhedron can be regarded as a distorted tetragonal antiprism.

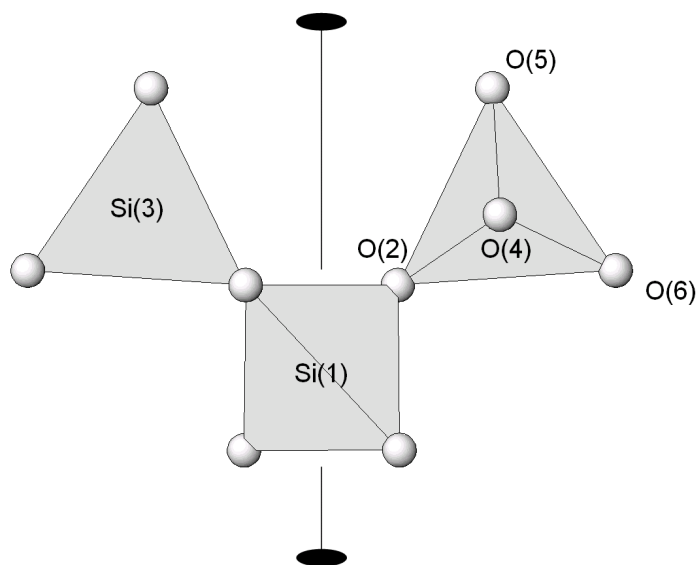


Figure 1
A single "horseshoe-like"
[Si₃O₁₀]-group in kilchoanite.

Bond valence sums (BVS) were calculated using the parameters for the Si-O and Ca-O bonds given by BRESE & O'KEEFFE (1991). The BVS-values for the different cation species are close to the expected values of 4.00 and 2.00 valence units (v.u.): Si(1): 4.022 v.u., Si(2): 3.901 v.u., Si(3): 3.909 v.u., Ca(1): 1.902 v.u., Ca(2): 1.966 v.u., Ca(3): 1.782 v.u. and Ca(4): 2.111 v.u..

Mixed anion compounds with horseshoe-shaped arrangements of the trimers as in kilchoanite can be found in a number of other phases including Na₂Ca₂Si₂O₇ (KAHLENBERG & HÖSCH, 2002), Ba₄Al₂O₇ (KAHLENBERG, 2001) or Sr₄Ga₂O₇ (KAHLENBERG et al., 2005). The comparison between the structures of kilchoanite (Fig. 2a) and Na₂Ca₂Si₂O₇ (Figure 2b), for example, reveals certain similarities. The insular tetrahedra and the trimer units in both compounds are concentrated in alternating layers. Major differences between both structures are due to the incorporation of additional Na cations in the structure of Na₂Ca₂Si₂O₇ as well as the different symmetries of the [Si₃O₁₀]-groups.

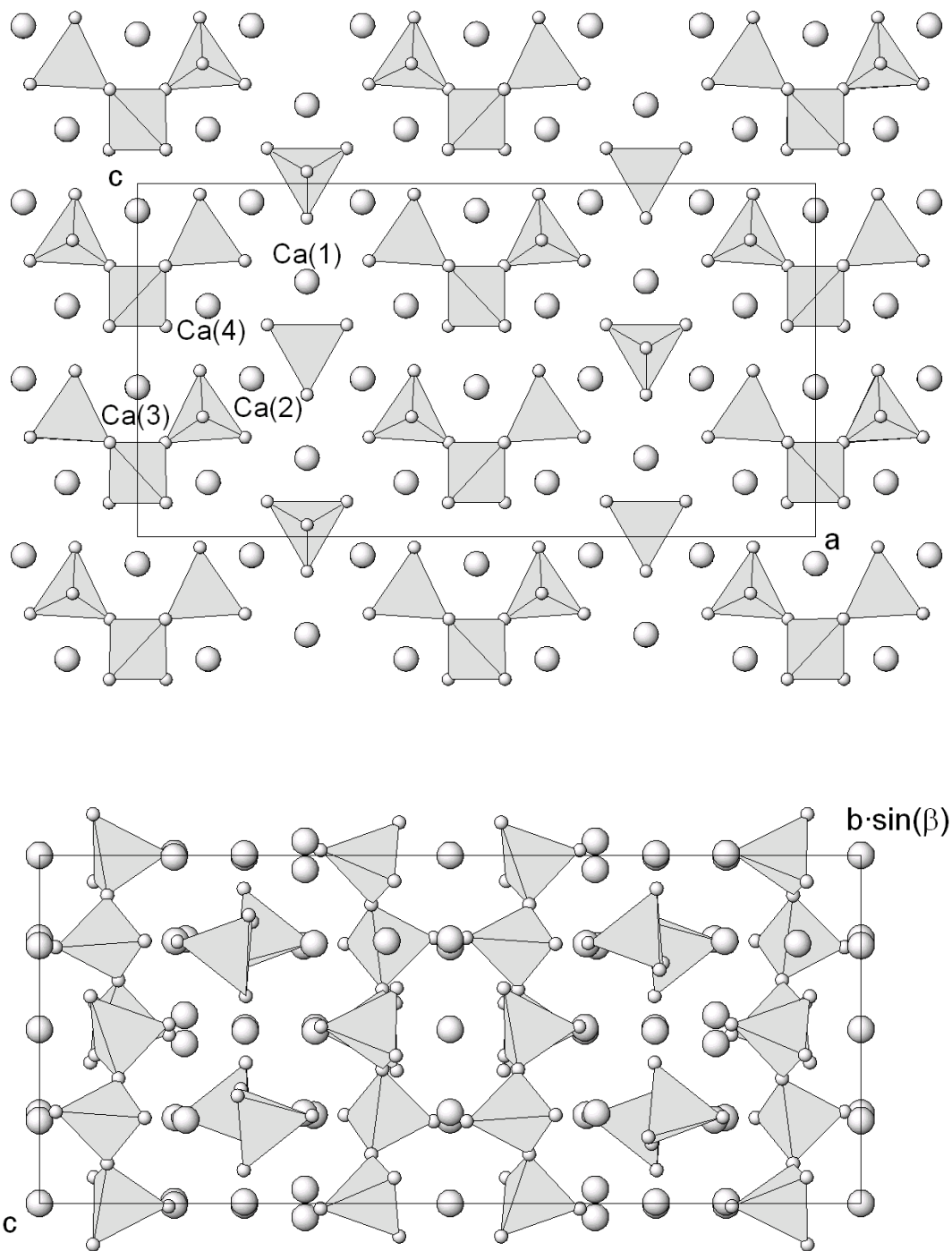


Figure 2
 Projections of the structures of (a) kilchoanite parallel to [010] and (b) Na₂Ca₂Si₂O₇ parallel to [100].
 Larger grey spheres correspond to Ca and/or Na atoms, respectively.

| | | |
|-----------------------------------|---|---------------------|
| Empirical formula | Ca ₈ Si ₈ O ₇ | |
| Temperature | 293(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | orthorhombic | |
| Space group | <i>I m a 2</i> | |
| Unit cell dimensions | <i>a</i> = 21.9641(14) Å | $\alpha = 90^\circ$ |
| | <i>b</i> = 5.0841(3) Å | $\beta = 90^\circ$ |
| | <i>c</i> = 11.4403(7) Å | $\gamma = 90^\circ$ |
| Volume | 1277.51(14) Å ³ | |
| Z | 8 | |
| Density (calculated) | 2.999 g/cm ³ | |
| Absorption coefficient | 2.954 mm ⁻¹ | |
| F(000) | 1152 | |
| Crystal size | 0.12 x 0.09 x 0.07 mm ³ | |
| Theta range for data collection | 3.56 to 25.34° | |
| Index ranges | -26 <= <i>h</i> <= 17, -6 <= <i>k</i> <= 6, -13 <= <i>l</i> <= 13 | |
| Reflections collected | 3686 | |
| Independent reflections | 1197 [R(int) = 0.0258] | |
| Completeness to theta = 25.34° | 99.8 % | |
| Max. and min. transmission | 0.8199 and 0.7182 | |
| Refinement method | Full-matrix least-squares on F ² | |
| Data / restraints / parameters | 1197 / 1 / 117 | |
| Goodness-of-fit on F ² | 1.110 | |
| Final R indices [I > 2sigma(I)] | R1 = 0.0214, wR2 = 0.0519 | |
| R indices (all data) | R1 = 0.0227, wR2 = 0.0527 | |
| Absolute structure parameter | 0.00(11) | |
| Largest diff. peak and hole | 0.277 and -0.481 e. Å ⁻³ | |

Table 1
Crystal data and structure refinement for kilchoanite.

| | x | y | z | U(eq) |
|-------|---------|----------|---------|-------|
| Ca(1) | 2500 | -6(2) | 7222(1) | 6(1) |
| Ca(2) | 1682(1) | 37(2) | 4471(1) | 8(1) |
| Ca(3) | 0 | 5000 | -769(1) | 8(1) |
| Ca(4) | 1040(1) | 25(1) | 1535(1) | 6(1) |
| Si(1) | 0 | 5000 | 1763(1) | 5(1) |
| Si(2) | 2500 | 4275(3) | 5332(1) | 5(1) |
| Si(3) | 1003(1) | 5582(2) | 3438(1) | 5(1) |
| O(1) | 2500 | -2536(6) | 5336(3) | 9(1) |
| O(2) | 410(1) | -3130(4) | 2665(2) | 6(1) |
| O(3) | 2500 | 2075(6) | 9021(3) | 9(1) |
| O(4) | 960(1) | 2429(4) | 3392(2) | 7(1) |
| O(5) | 920(1) | -3082(4) | 4698(2) | 8(1) |
| O(6) | 3416(1) | -1970(4) | 7816(2) | 7(1) |
| O(7) | 3086(1) | 2983(4) | 5995(2) | 7(1) |
| O(8) | -418(1) | -3230(4) | 960(2) | 9(1) |

Table 2
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for kilchoanite.
U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

| | | | |
|---------------|----------|--|------------|
| Ca(1)-O(3) | 2.315(3) | Si(3)-O(5)#7 | 1.604(3) |
| Ca(1)-O(6)#1 | 2.346(2) | Si(3)-O(4) | 1.607(2) |
| Ca(1)-O(6) | 2.346(2) | Si(3)-O(6)#5 | 1.623(2) |
| Ca(1)-O(7) | 2.436(2) | Si(3)-O(2)#7 | 1.705(2) |
| Ca(1)-O(7)#1 | 2.436(2) | | |
| Ca(1)-O(1) | 2.511(4) | | |
| | | O(8)#7-Si(1)-O(8)#8 | 108.94(19) |
| Ca(2)-O(5) | 2.320(2) | O(8)#7-Si(1)-O(2)#8 | 111.73(11) |
| Ca(2)-O(4) | 2.349(2) | O(8)#8-Si(1)-O(2)#8 | 110.43(10) |
| Ca(2)-O(7)#1 | 2.355(3) | O(8)#7-Si(1)-O(2)#7 | 110.43(10) |
| Ca(2)-O(3)#5 | 2.377(2) | O(8)#8-Si(1)-O(2)#7 | 111.73(11) |
| Ca(2)-O(1) | 2.434(2) | O(2)#8-Si(1)-O(2)#7 | 103.52(17) |
| Ca(2)-O(6)#6 | 2.462(2) | | |
| | | O(1)#7-Si(2)-O(7)#1 | 113.63(11) |
| Ca(3)-O(8)#7 | 2.360(2) | O(1)#7-Si(2)-O(7) | 113.63(12) |
| Ca(3)-O(8)#8 | 2.360(2) | O(7)#1-Si(2)-O(7) | 104.06(19) |
| Ca(3)-O(2)#9 | 2.560(2) | O(1)#7-Si(2)-O(3)#5 | 114.80(18) |
| Ca(3)-O(2)#10 | 2.560(2) | O(7)#1-Si(2)-O(3)#5 | 104.81(12) |
| Ca(3)-O(5)#9 | 2.612(2) | O(7)-Si(2)-O(3)#5 | 104.81(12) |
| Ca(3)-O(5)#10 | 2.612(2) | | |
| Ca(3)-O(4)#9 | 2.625(2) | O(5)#7-Si(3)-O(4) | 116.46(14) |
| Ca(3)-O(4)#10 | 2.625(2) | O(5)#7-Si(3)-O(6)#5 | 107.41(13) |
| | | O(4)-Si(3)-O(6)#5 | 117.77(13) |
| Ca(4)-O(8)#8 | 2.225(2) | O(5)#7-Si(3)-O(2)#7 | 102.49(12) |
| Ca(4)-O(7)#5 | 2.257(2) | O(4)-Si(3)-O(2)#7 | 108.72(12) |
| Ca(4)-O(5)#13 | 2.337(3) | O(6)#5-Si(3)-O(2)#7 | 101.92(13) |
| Ca(4)-O(6)#6 | 2.447(2) | | |
| Ca(4)-O(4) | 2.457(3) | Si(1)#4-O(2)-Si(3)#4 | 120.97(12) |
| Ca(4)-O(2) | 2.482(2) | | |
| Si(1)-O(8)#7 | 1.581(2) | Symmetry transformations used to generate equivalent atoms: | |
| Si(1)-O(8)#8 | 1.581(2) | #1 -x+1/2,y,z #2 -x+1/2,-y+1/2,z+1/2 #3 x+0,-y+1/2,z+1/2 | |
| Si(1)-O(2)#8 | 1.668(2) | #4 x,y-1,z #5 -x+1/2,-y+1/2,z-1/2 #6 -x+1/2,-y-1/2,z-1/2 | |
| Si(1)-O(2)#7 | 1.668(2) | #7 x,y+1,z #8 -x,-y,z #9 -x+0,y+1/2,z-1/2 | |
| Si(2)-O(1)#7 | 1.621(3) | #10 x+0,-y+1/2,z-1/2 #11 -x+0,y-1/2,z-1/2 #12 x+0,-y+3/2,z-1/2 | |
| Si(2)-O(7)#1 | 1.632(3) | #13 x+0,-y-1/2,z-1/2 #14 -x,-y+1,z #15 -x+1/2,y+1,z | |
| Si(2)-O(7) | 1.632(3) | #16 -x+0,y+1/2,z+1/2 #17 -x+0,y-1/2,z+1/2 #18 x+0,-y-1/2,z+1/2 | |
| Si(2)-O(3)#5 | 1.649(4) | #19 -x+1/2,-y-1/2,z+1/2 | |

Table 3
Selected bond lengths [\AA] and angles [$^\circ$] for kilchoanite.

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