Isabel Grosskreuz and Bernd Marler*

Rietveld structure analysis of keatite, a rare, metastable SiO_2 polymorph

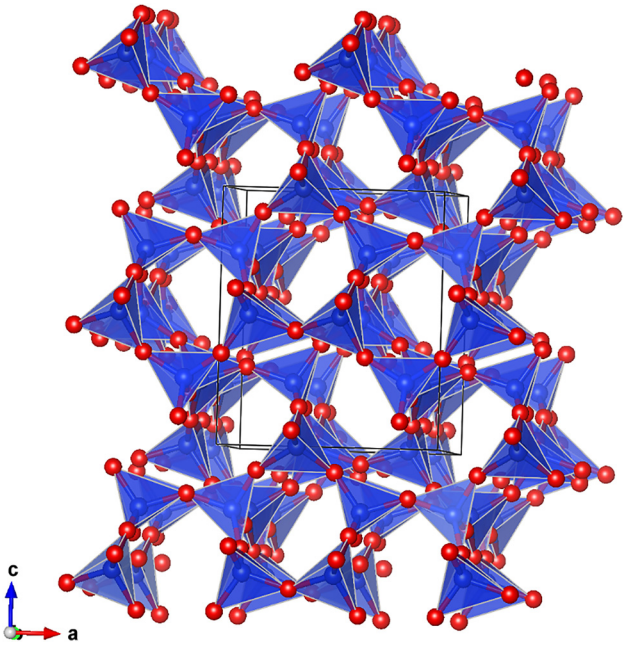

Figure 1: Structural representation of keatite (projection along b).

https://doi.org/10.1515/ncrs-2023-0135
Received March 21, 2023; accepted April 29, 2023;
published online May 10, 2023

Abstract

$O_{24}Si_{12}$, tetragonal, $P4_32_12$ (no. 96), a = 7.4462(1) Å, c = 8.5838(4) Å, V = 475.93(3) Å^3, Z = 1, $R(F)$ = 0.037, T = 293 K.

CCDC no.: 2259819

Tables 1 and 2 contain details of the measurement method and a list of the atom sites, respectively. Figures 1 and 2 present the crystal structure of keatite and the morphology of the crystals, respectively.

***Corresponding author: Bernd Marler**, Institute of Geology, Mineralogy und Geophysics, Ruhr–University Bochum, Universitaetsstrasse 150, 44801 Bochum Germany, E-mail: bernd.marler@rub.de. https://orcid.org/0000-0003-3769-3595

Isabel Grosskreuz, Institute of Geology, Mineralogy und Geophysics, Ruhr–University Bochum, Universitaetsstrasse 150, 44801 Bochum Germany. https://orcid.org/0000-0002-5609-4750

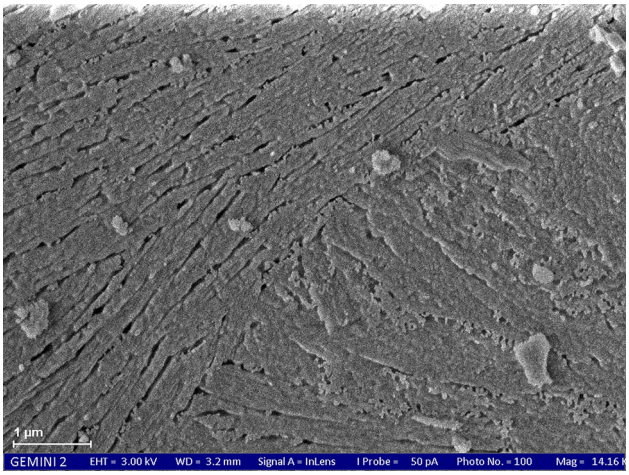

Figure 2: Scanning electron micrograph of keatite.

1 Source of material

Fine grained keatite crystals were synthesized according to Ferreira da Silva and Fernández Navarro [3] using a silicate gel prepared from tetraethyl orthosilicate, $LiNO_3$, $Cr(NO_3)_3$, water, and heated at 830 K. The reaction mixture consisted of 0.5 Cr_2O_3: 5 Li_2O: 94.5 SiO_2. This led to a sample with 94.4 % keatite and two impurity phases: dilithium phyllodisilicate (4.3 %) [4] and quartz (1.3 %). The sample has a light yellow color due to the small chromium content.

2 Experimental details

Scanning electron micrographs were taken using a Zeiss Merlin Gemini 2 electron microscope. The samples were gold coated prior to analysis. For a semi-quantitative chemical analysis, an OXFORD AZtec Energy X-ray microanalysis system attached to the electron microscope was used. The diffractometer used for collecting the powder diffraction data was equipped with a curved germanium (111) primary monochromator and a Braun linear position-sensitive detector (2θ coverage = 6°). The sample was sealed in a glass capillary (0.3 mm in diameter) to avoid a preferred orientation of the crystals. No absorption correction was necessary. Soft distance restraints were used for d(Si–O) = 1.61(1) Å, d(Si–Si) = 3.10(4) Å,

Table 1: Data collection and handling.

Crystal:	Light yellow plates; average size $3 \times 3 \times 0.1$ μm^3
Wavelength:	Cu *K*α radiation (1.54059 Å)
μ:	6.86 cm^{-1}
Diffractometer, scan mode:	Siemens D5000, Debye-Scherrer
$N(hkl)_{measured}$	4767
$N(param)_{refined}$:	16
Programs:	Fullprof 2K [1], VESTA [2]

Table 2: Fractional atomic coordinates and isotropic displacement parameters (Å^2).

Atom	*x*	*y*	*z*	U_{iso}
Si1	0.328230 (5)	0.11886 (9)	0.2490 (2)	0.0125 (2)*
Si2	0.4102 (2)	0.4102 (2)	0.00000	0.0125 (2)*
O1	0.4488 (3)	0.1266 (7)	0.4014 (3)	0.0195 (4)*
O2	0.1156 (4)	0.1222 (6)	0.30658 (19)	0.0195 (4)*
O3	0.3593 (5)	0.3017 (4)	0.1526 (2)	0.0195 (4)*

d(O–O) = 2.62(2) Å. Isotropic displacement parameters B(iso) for Si and O atoms, respectively, were constrained to be equal. The structures of the two impurity phases were included in the refinement with fixed structural parameters.

3 Comment

Synthetic keatite, also known as "silica K" and originally named "A New Crystalline Silica", was for the first time obtained in 1954 by hydrothermal treatment of silicic acid by P. P. Keat [5]. According to Keat (and, later, according to [3,6–10]) an alkaline compound like MOH or M_2CO_3 (M = Li, Na, K) of low concentration is necessary or at least favourable for a successful synthesis of keatite. Keatite is difficult to synthesize as a pure phase and crystallizes always as very fine-grained material. In 2013 Keatite was also discovered in nature "as a precipitate in the core of ultrahigh-pressure (UHP) clinopyroxene (Cpx) within garnet pyroxenite from the Kokchetav Massif, Kazakhstan" [11]. The structure of keatite was solved by Shropshire et al. in 1959 [12]. The authors had to use quite small single crystals, and only the intensities of (hh0) and (hhl) reflections could be determined. Relying, at that time, on film methods (Weissenberg photographs) the structure could not be refined well. The authors state: " … the intensity measurements are less reliable than in most structure determinations". No other structure analysis on keatite has been published, so far. Only powder data were available for the structure analysis presented here. The chemical analysis of 10 individual keatite crystals yielded an average value of Cr/Si = 0.025. Cr is slightly enriched compared to the very low value of the reaction mixture (Cr/Si = 0.005). Li is incorporated in the impurity phase dilithium phyllodisilicate. The X-ray powder data were indexed in the tetragonal crystal system proposing the space group symmetry $P4_32_12$. The Rietveld refinement not only confirmed the rough structure model published by Keat [5] but led to an improved precision concerning atomic coordinates, bond lengths and bond angles. Cr could not be located in the structure of keatite. Keatite is a metastable SiO_2 polymorph and does not appear in the phase diagram (p, T) of the silica polymorphs. Although the structure of keatite contains only two crystallographically independent Si sites, the framework structure is quite complex due to the high symmetry. While the framework structures of most dense silica polymorphs like quartz, tridymite and cristobalite are dominated by 6-rings of interconnected $[SiO_{4/2}]$ tetrahedra, the framework of keatite is predominantly constructed from 5- and 7-rings. The density of keatite calculated from the structure data is 2.516 g/cm^3, a value intermediate between the ones of the high-temperature polymorph cristobalite (2.318 g/cm^3) and the low temperature polymorph quartz (2.649 g/cm^3). The geometrical analysis of the structure gave interatomic distances and bond angles that are typical for dense silica polymorphs.

Acknowledgements: The authors thank Hermann Gies for helpful discussions. The keatite sample was kindly provided by Brigitte Martin, Bochum.
Author contributions: All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.
Research funding: Deutsche Forschungsgemeinschaft with grant number MA 6641/3–1.
Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

References

1. Rodriguez-Carvajal J. Fullprof: A Program for Rietveld Refinement and Profile Matching Analysis of Complex Powder Diffraction Patterns, Version 7.30; ILL: Grenoble, France, 2020. http://www.ill.eu/sites/fullprof/index.html.
2. Momma K., Izumi F. VESTA 3 for three-dimensional visualization of crystal, volumetric and morphology data. *Appl. Crystallogr.* 2011, *44*, 1272–1276.
3. Ferreira da Silva M. G., Fernández Navarro J. M. Formation of "keatite" from lithium oxide – silica gels in the presence of chromium oxide. *J. Non-Cryst. Solids* 1989, *109*, 191–197.

4. Liebau F. Untersuchungen an Schichtsilikaten des Formeltyps $Am(Si_2O_5)_n$. I. Die Kristallstruktur der Zimmertemperaturform des $Li_2Si_2O_5$. *Acta Crystallogr.* 1961, *14*, 389–395.
5. Keat P. P. A new crystalline silica. *Science* 1954, *120*, 328–330.
6. Bettermann P., Liebau F. The transformation of amorphous silica to crystalline silica under hydrothermal conditions. *Contrib. Mineral. Petrol.* 1975, *53*, 25–36.
7. Carr R. M., Fyfe W. S. Some observations on the crystallization of amorphous silica. *Am. Mineral.* 1958, *43*, 908–916.
8. White J., Corwin J. F. Synthesis and origin of chalcedony. *Am. Mineral.* 1961, *46*, 112–119.
9. Martin B., Röller K. Keatite – microstructure, growth fabric and crystal-structure. 1. Microstructure and texture. *Neues Jahrbuch Mineral. Monatsh.* 1990, *10*, 462–466.
10. Martin B. Keatite. II–Hydrothermal synthesis from silica-glass. *Eur. J. Mineral.* 1995, *7*, 1389–1397.
11. Hill T. R., Konish H., Huifang X. Natural occurrence of keatite precipitates in UHP clinopyroxene from the Kokchetav Massif: a TEM investigation. *Am. Mineral.* 2013, *98*, 187–196.
12. Shropshire J., Keat P., Vaughan P. A. The crystal structure of keatite, a new form of silica. *Z. Kristallogr. Cryst. Mater.* 1959, *112*, 409–413.