

First Refinement of the Sinoite Structure of a Natural Crystal from the Neuschwanstein (EL6) Meteorite

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Dedicated to Professor Gerhard Thiele on the occasion of his 70th birthday

A well-shaped sinoite crystal was milled out of a polished thin section of the Neuschwanstein (EL6) chondrite. The structure was refined on the basis of X-ray single crystal data: $Cmc2_1$, $a = 885.66(18)$, $b = 549.61(11)$, $c = 484.23(10)$ pm, $R1 = 0.0282$, 491 F^2 values, 26 variable parameters. The structure consists of a complex three-dimensional network of corner-sharing SiN_3O tetrahedra (Si–O 161.9, Si–N 171.9–172.8 pm). The crystal chemical peculiarities of Si_2N_2O are briefly discussed.

Key words: Sinoite, Enstatite Chondrites, X-Ray Diffraction

Introduction

Synthetic silicon oxynitride Si_2N_2O (sinoite) can be prepared by a gas-phase reaction between SiO and N_2 at 1723 K [1] or by nitriding silicon–silica mixtures (molar ratio $Si/SiO_2 = 3$) [2] in the temperature range 1623–1723 K. This oxynitride is an excellent refractory material with high chemical and oxidation resistance. It occurs also as a surface oxidation product of Si_3N_4 .

Sinoite is a technically important composite material in sinter-forged Si_3N_4 – Si_2N_2O composites with superplastic properties and it also forms during sintering processes of Si_3N_4 , when early transition metal oxides (TiO_2 , ZrO_2 , Y_2O_3) or Al_2O_3 are used as sintering additives. The relevance of sinoite to materials science is manifested through more than 800 entries in the SciFinder data base [3].

The structure of synthetic sinoite has been refined on the basis of Weissenberg film data [4, 5] and was confirmed later with a higher accuracy from diffractometer data [1]. The pressure-dependence of the lattice parameters, bond lengths, and bond angles of Si_2N_2O was studied up to 23 kbar by time-of-flight neutron diffraction [2]. The Si_2N_2O structure consists of a three-

dimensional network of all corner-sharing SiN_3O tetrahedra.

The natural occurrence of sinoite was first observed, but not identified in 1905 within two EL6 enstatite chondrites [6]. Many years later this phase was identified in several EL6 chondrites, mainly occurring as euhedral, lath-like grains, frequently associated with Fe,Ni metal and enstatite [7–9]. Sinoite is a rare phase in E chondrites and its formation has been discussed controversially [10, and refs. therein]. Condensation of sinoite within the solar nebula at high temperature and pressure from a gas of solar composition was suggested by [11] and [12]; however, thermodynamic calculations ruled out the nebular condensation model, e.g. [13, 14]. Other authors favored a metamorphic origin of sinoite, e.g. [15–18]. Sinoite formation over geologic time scales at metamorphic temperatures of ~ 1120 K was suggested [17, 18]. Rubin [10] found sinoite in impact-melted portions of the QUE94368 EL4 and concluded that sinoite crystallized from EL impact melts. He also suggested that sinoite-bearing EL6 could be annealed impact-melt breccias, but he did not rule out a metamorphic origin for the sinoite formation. Recently, Bischoff *et al.* [19] and Jord-

ing & Bischoff [20] studied 31 enstatite chondrites and stated that the occurrence of sinoite is restricted to EL chondrites of higher petrologic type, EL impact melt rocks, and EL chondrites having impact-melted areas. The finding of sinoite in the impact melt rock Ilafegh 009 and in impact melt areas of QUE 94368 supports the crystallization model of Rubin [10]. Many of the EL6 chondrites represent high-grade metamorphic rocks. Bischoff *et al.* [19] and Jording & Bischoff [20] suggested that if partial melting was involved during high-grade metamorphism, sinoite may also have crystallized from such melts. Also, these authors could not rule out formation of sinoite during metamorphism over geologic time scales at high temperatures.

Preliminary crystallographic data on natural sinoite were reported by Bischoff *et al.* [19]. Herein we report on the first single crystal study on natural sinoite.

Experimental Section

Selection of the single crystal

The two sinoite grains studied by X-ray diffraction were isolated from the Neuschwanstein (EL6) chondrite. The meteorite fell on April 6, 2002, 20:20 h (UT) and a first fragment of 1.75 kg was recovered July 14, 2002. Preliminary results on the mineralogy and chemistry of the Neuschwanstein chondrite were published [21, 22].

Several thin sections of Neuschwanstein were studied by optical and electron microscopy. The sinoites, used in this study, were identified by optical microscopy in transmitted and reflected light with a ZEISS polarizing microscope (AxioPhot). A JEOL (840A) scanning electron microscope attached with an EDS (Oxford Instruments) was used for phase identification and to resolve the fine-grained mineral assemblages.

The X-ray irradiated grains were isolated from thin sections by using the Medenbach microdrill attached at a conventional optical microscope with a rotating object stage. A diamond cutter was used for drilling. After the groove had been cut to the desired depth, the sample cylinder remained attached to the epoxy layer of the thin section. The samples were carefully removed with a preparation needle.

X-ray film data and structure refinement

Two separated sinoite crystals were roughly $30 \times 50 \times 90 \mu\text{m}$ (crystal A) and $50 \times 50 \times 30 \mu\text{m}$ (crystal B) in size. Crystal A is shown in Fig. 1 and is part of an aggregate of euhedral to subhedral sinoites. It contains some inclusions that could not be identified due to their small grain size. Crystal B does not show detectable inclusions.

Table 1. Crystal data and structure refinement for natural sinoite from Neuschwanstein (EL6), space group $Cmc2_1$; $Z = 4$.

| | |
|---|---|
| Empirical formula | $\text{Si}_2\text{N}_2\text{O}$ |
| Molar mass [g/mol] | 100.20 |
| Unit cell dimensions [pm] | $a = 885.66(18)$ $b = 549.61(11)$ $c = 484.23(10)$ $V = 0.2357 \text{ nm}^3$ |
| Calculated density [g/cm ³] | 2.82 |
| Crystal size [μm^3] | $10 \times 40 \times 70$ |
| Detector distance | 40 mm |
| Exposure time | 35 min |
| ω Range; increment | $0 - 180^\circ$; 1.0° |
| Integr. param. A, B, EMS | 13.0; 3.0; 0.014 |
| Transm. ratio (max/min) | 1.08 |
| Absorption coefficient [mm ⁻¹] | 1.17 |
| $F(000)$ | 200 |
| θ Range [$^\circ$] | 4 to 37 |
| Range in hkl | $\pm 14, \pm 9, \pm 7$ |
| Total no. reflections | 1592 |
| Independent reflections | 491 ($R_{\text{int}} = 0.0311$) |
| Reflections with $I > 2\sigma(I)$ | 478 ($R_{\text{sigma}} = 0.0216$) |
| Data/parameters | 491 / 26 |
| Goodness-of-fit on F^2 | 1.166 |
| Final R indices [$I > 2\sigma(I)$] | $R1 = 0.0272$; $wR2 = 0.0662$ |
| R Indices (all data) | $R1 = 0.0282$; $wR2 = 0.0665$ |
| Extinction coefficient | 0.01(1) |
| Flack parameter | 0.4(3) |
| Largest diff. peak and hole [$\text{e}/\text{\AA}^3$] | 0.38 / -0.40 |

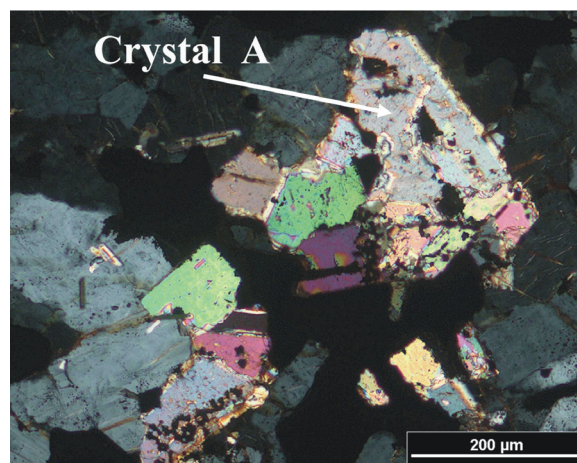


Fig. 1. Sinoites can be well detected in Neuschwanstein based on their high birefringence. They often form aggregates of euhedral to subhedral grains. The upper right sinoite crystal (crystal A) was used for X-ray diffraction studies. Photomicrographs in polarized light, crossed nicols.

The irregularly-shaped crystals, milled out of the polished thin section of Neuschwanstein (EL6) were glued to a quartz fibre and first examined on a Buerger precession camera (equipped with an imaging plate system Fujifilm BAS–

Table 2. Atomic coordinates and anisotropic displacement parameters (pm^2) for natural sinoite from Neuschwanstein (EL6). U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor. The exponent of the anisotropic displacement parameters is defined through $\exp\{-2\pi^2 \cdot (U_{11}h^2a^{*2} + \dots + U_{12}hka^*b^*)\}$.

| Atom | Wyckoff position | <i>x</i> | <i>y</i> | <i>z</i> | U_{11} | U_{22} | U_{33} | U_{23} | U_{13} | U_{12} | U_{eq} |
|------|------------------|------------|-------------|-------------|----------|----------|----------|----------|----------|----------|-----------------|
| Si | 8b | 0.82343(5) | 0.84841(6) | 0.72939(15) | 58(2) | 53(2) | 60(2) | 2(2) | -3(2) | -1(1) | 57(4) |
| N | 8b | 0.7826(2) | 0.87595(19) | 0.3838(3) | 78(6) | 60(4) | 38(6) | 4(3) | -10(6) | -20(4) | 58(6) |
| O | 4a | 0 | 0.7870(3) | 0.7809(4) | 52(6) | 121(6) | 108(10) | -2(5) | 0 | 0 | 94(3) |

1800) in order to establish suitability for intensity data collection. Intensity data were collected at room temperature on a Stoe IPDS-II diffractometer with graphite monochromatized Mo- K_{α} radiation. Numerical absorption corrections were applied to the data. Crystal A consisted of two domains. The larger domain was integrated simultaneously with the second one, omitting coincidentally overlapped reflections. Crystal B was of minor quality, especially due to an inclusion/appendage of kamazite ($bcc \text{ Fe}_{1-x}\text{Ni}_x$) with a lattice parameter of 283.5 pm. All relevant crystallographic data for the data collection and evaluation of the first crystal are listed in Table 1.

Careful analysis of the data set of the larger domain of crystal A revealed a *C* centered orthorhombic lattice, and the additional systematic extinctions ($h0l$ only observed for $h, l = 2n$) lead to space groups $Cmc2_1$ and $Cmcm$, of which the non-centrosymmetric group $Cmc2_1$ (No. 36) was found to be correct during structure refinement, in agreement with previous investigations on synthetic sinoite [5]. The atomic positions initially determined by these authors were then taken as starting values and the structure was refined using SHELXL-97 (full-matrix least-squares on F_o^2) [23] with anisotropic atomic displacement parameters for all sites. Refinement of the Flack parameter [24, 25] indicated the wrong absolute structure. The atomic parameters were then inverted and the structure was refined again with the Flack parameter listed in Table 1. A refinement as an inversion twin gave the same results. A final difference Fourier synthesis revealed no significant residual peaks (see Table 1). The refined positional parameters are listed in Table 2. Further details on the structure refinement are available.*

Discussion

The structure of sinoite, $\text{Si}_2\text{N}_2\text{O}$, has been refined for the first time from naturally grown crystals taken from a meteorite, *i. e.* Neuschwanstein (EL6). The precision of the present structure refinement is even better than for the synthetic crystals reported by Sjöberg *et al.* [1].

In Fig. 2 we present perspective views of the $\text{Si}_2\text{N}_2\text{O}$ structure along the *b* and the *c* axis. The sinoite structure

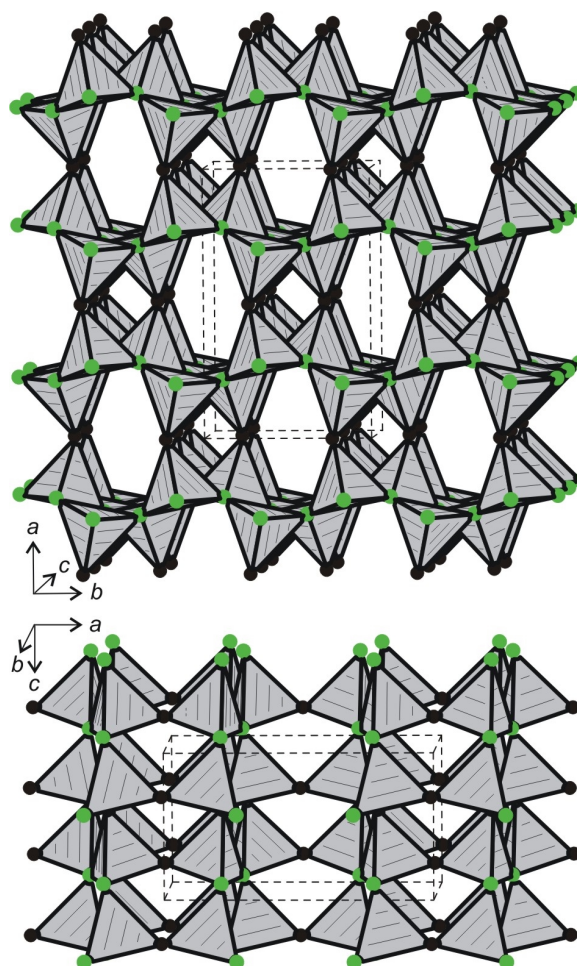


Fig. 2. Corner-sharing SiN_3O tetrahedra in the crystal structure of $\text{Si}_2\text{N}_2\text{O}$. The nitrogen and oxygen atoms are drawn as gray and black circles, respectively. For details see text.

is built up from all corner-sharing SiN_3O tetrahedra with a Si–O distance of 161.9(1) pm and three Si–N distances of 171.9(2), 172.1(2), and 172.8(1) pm, in good agreement with the data derived from the synthetic material [1]. Similar distances (159–162 pm Si–O and 168–178 pm Si–N) have recently been observed for the SiN_3O entities in the novel layer silicate $\text{Ca}[\text{Si}_2\text{N}_2\text{O}_2]$ [26].

*Details may be obtained from: Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), by quoting the Registry No. CSD-415575.

As is evident from the upper drawing of Fig. 2, the SiN_3O tetrahedra are condensed *via* the nitrogen atoms within the xz plane around $x \sim 1/4$ and $\sim 3/4$. These layers are condensed in the third direction exclusively *via* the oxygen atoms. The non-centrosymmetry of the $\text{Si}_2\text{N}_2\text{O}$ structure is readily evident from a view of the structure along the b axis. The SiN_3O tetrahedra point exclusively to the $-c$ direction.

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