

Static disorder of dodecasil 3C. A single-crystal study with synchrotron radiation

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Dedicated to Professor Dr. Friedrich Liebau to his 65th birthday

Received: July 1, 1991; in revised form: August 25, 1991

Static disorder / Dodecasil 3C / ZSM-49 / Synchrotron radiation

Abstract. A crystal of dodecasil 3C (ZSM-49, 136 SiO_2) was prepared and heat treated to expel the enclathrated guest species. The structure of this sample was refined [space group $Fd\bar{3}m$, $a = 19.369(6) \text{ \AA}$] to $R_w = 0.057$ from 1068 reflections collected at 573 K with synchrotron radiation at $\lambda = 0.593 \text{ \AA}$. Anisotropic refinement and subsequent Fourier analysis revealed split positions for three of the four oxygen atoms in the asymmetric unit. The split positions were refined using bond length constraints. The mean values of Si—O bond lengths and Si—O—Si angles changed from 1.546 to 1.581 $\text{\AA}$ and from 175.6 to 163.5° after this refinement. The refined structure of disordered dodecasil 3C is compared with distance least squares simulations in several subgroups of $Fd\bar{3}m$.

1. Introduction

In the past ten years a wide range of clathrate compounds of silica (Liebau, Gies, Gunarwadane and Marler, 1986; Gies, 1984, 1985) have been prepared and investigated. In all these structures corner-connected $[\text{SiO}_4]$ -tetrahedra form a three-dimensional framework with voids in the structure, large enough to host organic molecules such as pyrrolidine or smaller molecules such as N_2 , CO_2 etc. enclathrated during syntheses. One of these clathrate compounds of silica is dodecasil 3C (D3C), the structure of which has been solved by Gies (1984) with the guest species trimethylamine. In this structure $[\text{SiO}_4]$ -tetrahedra form pentagondodecahedral cages, so-

called $[5^{12}]$ -cages. These are interconnected to pseudo-hexagonal layers. By stacking these layers in an ABC sequence the cubic structure of D3C is formed. As a consequence of stacking a further cage is formed which consists of twelve 5-rings and four 6-rings, the $[5^{12}6^4]$ -cage. This unit may house larger molecules such as pyrrolidine, t-butanol, pyridine etc. Gies (1984) found in his study on D3C with trimethylamine large temperature factors for host lattice oxygen atoms and rather short Si–O bond length and high Si–O–Si angles. All these effects are an indication for a possible disorder in the structure. We therefore decided to reinvestigate the structure of D3C using the precise intensity data obtainable with synchrotron radiation. In order to avoid obstruction of the study of the host lattice by disordered guest molecules in the cages of D3C, a calcined sample of D3C was chosen.

2. Experimental and structure refinement

Single crystals of D3C were synthesized under hydrothermal conditions at 200°C within four weeks from a solution of 0.75 mol/l tetramethoxysilane as source for SiO₂ and 1.5 mol/l pyrrolidine as base and guest species. Some colourless crystals from this synthesis were treated for 48 h at 900°C in order to decompose and expel the guest species enclathrated. The crystals turned black during this process.

A crystal 180 · 110 · 150 µm in size was selected for single-crystal analysis. The crystal was carefully checked on a conventional 4-circle diffractometer for the absence of reflections, inconsistent with the extinction rules for $Fd\bar{3}m$. All reflections had sharp profiles and no sign of diffuse scattering was detected.

As a DSC-scan revealed a small displacive phase transition at 451 K, the single-crystal analysis was carried out at 523 ± 15 K. To obtain this temperature a gas flow furnace comparable to the one described by Tsukimura, Sato-Sorenson and Ghose (1989) was used. In contrast to Tsukimura et al. (1989), the sample was mounted within the furnace. The measurement was performed at the Stoe-type 5-circle diffractometer (Kupcik, Wendschuh-Josties, Wolf and Wulf, 1986) at Hasylab, DESY, Hamburg. A flat double-crystal [Si(111)] monochromator (+ n , – n) was used. The wavelength was $\lambda = 0.593$ Å. Conditions at Hasylab were: 5.3 GeV, single bunch with about one refill per hour. In two 1/16 spheres of the reciprocal asymmetric unit 1068 reflections were recorded in Ω scan mode up to $\theta_{\max} = 30^\circ$, of which 544 were unique. In order to avoid tackling of the furnace supplies with the diffractometer χ and ϕ had to be constrained. Due to the low absorption coefficient ($\mu = 6.24 \text{ cm}^{-1}$) no correction was carried out. Structure refinement was performed with the SHELX-System (Sheldrick, 1976).

Table 1. Positional and thermal parameters for the conventional anisotropic refinement of calcined D3C at 523 K.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	site symmetry		
Si(1)	0.06750(4)	0.06750(4)	0.37010(6)	.. <i>m</i>		
Si(2)	0.21641(6)	0.21641(6)	0.21641(6)	. 3 <i>m</i>		
Si(3)	0.125	0.125	0.125	43 <i>m</i>		
O(1)	0.0	0.3434(2)	−0.3434(2)	.. 2		
O(2)	0.2004(2)	0.2004(2)	0.2936(2)	.. <i>m</i>		
O(3)	0.3736(3)	0.125	0.125	2. <i>m</i>		
O(4)	0.1702(2)	0.1702(2)	0.1702(2)	. 3 <i>m</i>		
Atom	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₂₃	<i>U</i> ₁₃	<i>U</i> ₁₂
Si(1)	0.0331(4)	0.0331(4)	0.0323(6)	−0.0036(3)	−0.0036(3)	0.0029(4)
Si(2)	0.0274(4)	0.0274(4)	0.0274(4)	−0.0009(4)	−0.0009(4)	−0.0009(4)
Si(3)	0.0250(7)	0.0250(7)	0.0250(7)	0.0	0.0	0.0
O(1)	0.044(2)	0.101(2)	0.101(2)	−0.016(3)	−0.021(1)	−0.021(1)
O(2)	0.117(2)	0.117(2)	0.036(2)	0.023(2)	0.023(2)	−0.003(3)
O(3)	0.074(4)	0.059(2)	0.059(2)	−0.027(2)	0.0	0.0
O(4)	0.127(4)	0.127(4)	0.127(4)	−0.052(3)	−0.052(3)	−0.052(3)

U_{ij} from: $\exp(-2\pi^2(U_{11}h^2a^{*2} + \dots + 2U_{12}hka^*b^* + \dots))$.

Systematic absences lead to space groups $Fd\bar{3}$ and $Fd\bar{3}m$, as already reported by Gies (1984). In a preliminary single-crystal study on a CAD-4 diffractometer at 473 K [$a = 19.363(6)$ Å] and 623 K ($a = 19.364(12)$ Å) calcined D3C was refined in space groups $Fd\bar{3}$ and $Fd\bar{3}m$. Positional parameters and thermal displacement factors from refinements in $Fd\bar{3}$ and $Fd\bar{3}m$ agreed within two standard deviations. Averaging of the intensity data from HasyLab over two asymmetric units in reciprocal space in $Fd\bar{3}m$ led to an $R = \Sigma N(\Sigma F - \bar{F})^2 \cdot W / \Sigma(N-1) \cdot \Sigma W \cdot F^2 = 0.0258$ whereas the expected R -value from statistics was: $R_{\text{ex}} = \Sigma W(F^2) / \Sigma F^2 = 0.0299$. We therefore conclude, that $Fd\bar{3}m$ is the correct space group for the averaged structure of calcined D3C and refinement was performed in this space group. Conventional anisotropic refinement of the synchrotron data converged to $R = 0.0895$ and $R_w = \Sigma(|F_o| - |F_c|) \cdot \sqrt{w} / \Sigma(|F_o|) \cdot \sqrt{w} = 0.066$. In difference Fourier syntheses electron density was found in the $[5^{12}6^4]$ - and $[5^{12}]$ -cage. This electron density was included in the refinement as nitrogen (see also Results). The population parameters for these nitrogens refined to 0.06. Positional and anisotropic thermal parameters from this refinement are given in Table 1. Introducing split positions for statically disordered oxygen atoms as described later improved the R -values to $R = 0.071$ and $R_w = 0.0567$ and the effects in the difference Fourier syntheses disappeared as Figure 2b shows. Parameters for split positions are strongly correlated, so 10 bond length constraints on Si–O bonds and 9 on O–O bonds had to

Table 2. Positional and thermal parameters for the split position refinement of calcined D3C at 523 K.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	site symmetry
Si(1)	0.06742(4)	0.06742(4)	0.37000(6)	$\bar{1}$ <i>m</i>
Si(2)	0.21637(6)	0.21637(6)	0.21637(6)	$\bar{1}$ <i>3m</i>
Si(3)	0.125	0.125	0.125	$\bar{1}$ <i>3m</i>
O(1)	0.0	0.3433(2)	−0.3433(2)	$\bar{1}$ <i>2</i>
O(2a)	0.1887(5)	0.1887(5)	0.2889(5)	$\bar{1}$ <i>m</i>
O(2b)	0.2074(9)	0.2059(9)	0.2966(3)	
O(3a)	0.125	0.125	0.3791(16)	$\bar{1}$ <i>m</i>
O(3b)	0.125	0.125	0.3688(15)	$\bar{1}$ <i>m</i>
O(4)	0.1728(8)	0.1838(5)	0.1549(6)	$\bar{1}$

Atom	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₂₃	<i>U</i> ₁₃	<i>U</i> ₁₂
Si(1)	0.0313(4)	0.0313(4)	0.0322(7)	−0.0031(3)	−0.0031(3)	0.0036(4)
Si(2)	0.0276(4)	0.0276(4)	0.0276(4)	−0.0004(4)	−0.0004(4)	−0.0004(4)
Si(3)	0.0241(7)	0.0241(7)	0.0241(7)	0.0	0.0	0.0
O(1)	0.055(2)	0.113(2)	0.113(2)	−0.018(3)	0.025(2)	−0.025(2)
O(2a)	0.082(6)	0.082(6)	0.029(5)	0.012(3)	0.012(3)	−0.029(7)
O(2b)	0.116(15)	0.107(15)	0.063(5)	0.033(11)	0.000(11)	−0.039(5)
O(3a)	0.105(10)	0.105(10)	0.061(9)	0.0	0.0	−0.032(10)
O(3b)	0.043(6)	0.043(6)	0.107(14)	0.0	0.0	−0.023(6)
O(4)	0.095(15)	0.054(9)	0.032(6)	0.015(9)	−0.026(9)	−0.047(7)

U_{ij} from: $\exp(-2\pi^2(U_{11}h^2a^{*2} + \dots + 2U_{12}hka^*b^* + \dots))$

be incorporated into the refinement. The bond length constraints had no significant effect on *R*-values. Final results of this refinement are listed in Table 2, bond lengths and angles in Table 3. Careful inspection of difference Fourier syntheses and lists of observed and calculated structure factors revealed no systematic errors. Maximum residuals in difference Fourier maps were 0.5 e/Å³.¹

3. Results

Gies (1984) already pointed out, that the high temperature factors observed for oxygen atoms of the host lattice, the unusually short Si—O bonds and the high O—Si—O angles may be due to static or dynamic disorder of the host lattice. A comparison of thermal parameters from Gies' refinement for D3C with trimethylamine and our's for calcined D3C at 523 K (Synchrotron) and 623 K (CAD-4) (Fig. 1) (Könnecke, 1992) shows that

¹ Additional material to this paper can be ordered referring to CSD 54243, names of authors and citation of the paper at the Fachinformationszentrum Energie-Physik-Mathematik, D-7514 Eggenstein-Leopoldshafen 2, Federal Republic of Germany.

Table 3. Selected bond lengths for calcined D3C at 523 K.

a) for calcined D3C after conventional refinement

	Si(1)–O(2)	1.546	Si(1)–O(1)–Si(1)	169.38
2 ×	Si(1)–O(1)	1.563	Si(1)–O(2)–Si(2)	178.16
	Si(1)–O(3)	1.574	Si(1)–O(3)–Si(1)	174.94
	Si(2)–O(4)	1.538	Si(3)–O(4)–Si(2)	180.00
3 ×	Si(2)–O(2)	1.559		
4 ×	Si(3)–O(4)	1.522		
	mean value:	1.546	mean value:	175.6

O–Si–O Angles between 108.21–110.74°

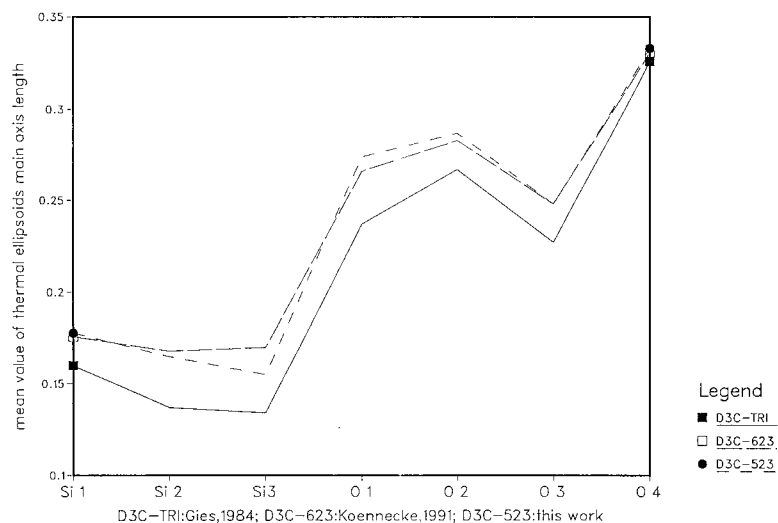
errors: distances: 0.005 Å, angles: 0.4°

b) for calcined D3C after split positions refinement

2 ×	Si(1)–O(1)	1.569	Si(1)–O(1)–Si(1)	169.18
	Si(1)–O(2a)	1.579	Si(1)–O(2a)–Si(2)	157.50
	Si(1)–O(2b)	1.579	Si(1)–O(2b)–Si(2)	163.98
	Si(1)–O(3a)	1.588	Si(1)–O(3a)–Si(1)	167.25
	Si(1)–O(3b)	1.578	Si(1)–O(3b)–Si(1)	175.78
	Si(2)–O(4)	1.588	Si(3)–O(4)–Si(2)	150.87
3 ×	Si(2)–O(2a)	1.598		
3 ×	Si(2)–O(2b)	1.572		
12 ×	Si(3)–O(4)	1.580		
	mean value:	1.581	mean value:	163.5

O–Si–O Angles between 104.31–114.39°

errors: distances: 0.02 Å, angles: 1.9°

**Fig. 1.** Comparison of thermal parameters from different measurements on D3C, errors: Si: 0.001, O: 0.004

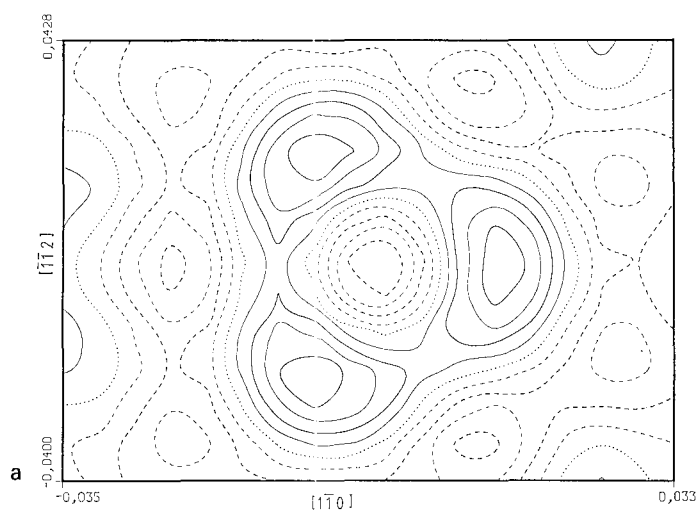


Fig. 2a. Difference electron density near oxygen 4, view $\parallel [111]$, layer: 0.174, contour steps: $0.1 \text{ el}/\text{\AA}^3$, negative contours dashed, positive solid.

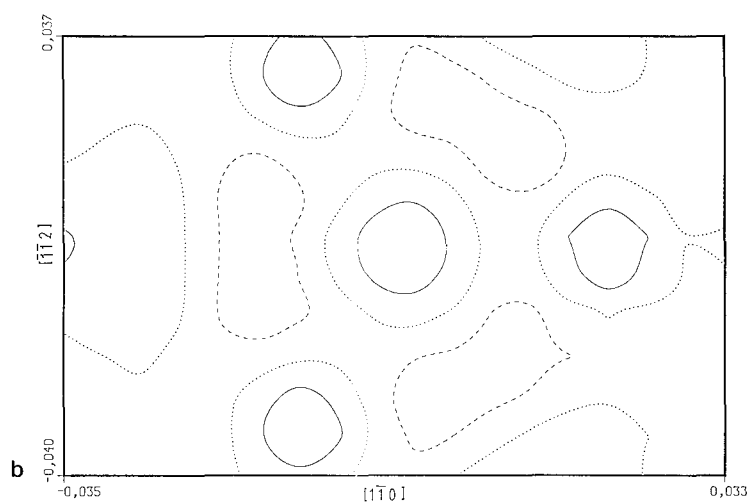


Fig. 2b. Difference electron density near oxygen 4 after split positions refinement, view $\parallel [111]$, layer: 0.174, counter steps: $0.1 \text{ el}/\text{\AA}^3$, negative contours dashed, positive solid.

the expellation of guest species has increased the thermal parameters of all host lattice atoms. The difference of the thermal parameters between 523 K and 623 K is comparatively small. A dynamic disorder should only depend on temperature (i. e. energy for thermal motion) and not on small structural changes such as the expellation of guest molecules. Therefore we conclude, that the disorder in D3C is static.

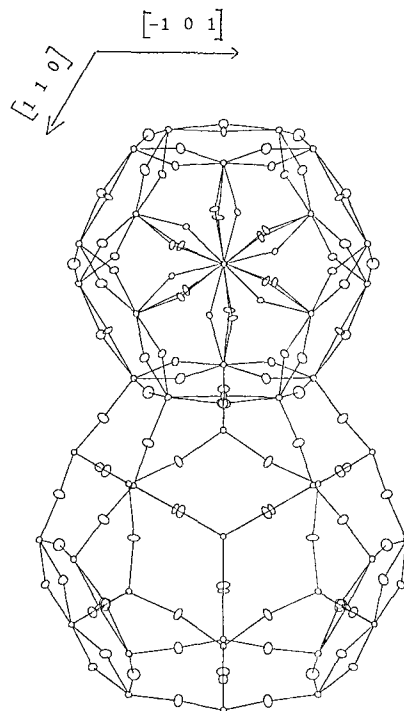


Fig. 3. Refined structure of calcined D3C at 523 K, view $\parallel [1 -1 1]$.

A careful inspection of difference Fourier syntheses after the conventional anisotropic refinement of the HasyLab data set revealed features as shown on Figure 2a for oxygen 2, 3, 4. These contour maps (negative peaks at the positions of oxygens, surrounded by three or two positive peaks) were interpreted as split positions for the oxygen atoms. They were refined subsequently. After this refinement the mean value of Si—O-bond lengths increased from 1.546 to 1.581 Å, the mean value of O—Si—O angles decreased from 175.6 to 163.5°. These values are much closer to the distances (1.608 Å) and angles (144°) postulated by Brown and Gibbs (1969) and Hill and Gibbs (1979) for silica polymorphs, without being identical (see Table 3). No indications for split positions were found for oxygen 1 and the silicon atoms in difference Fourier syntheses. Presumably the static disorder of oxygen 1 is well enough described by the anisotropic temperature factors. The thermal parameters for the silicon atoms are not significantly larger as those frequently observed for silicates. We conclude from this result, that there is no disorder of the silicon atoms.

These results indicate, that $Fd\bar{3}m$ is merely the space group for the average structure of calcined D3C. As no diffuse intensity or extra reflec-

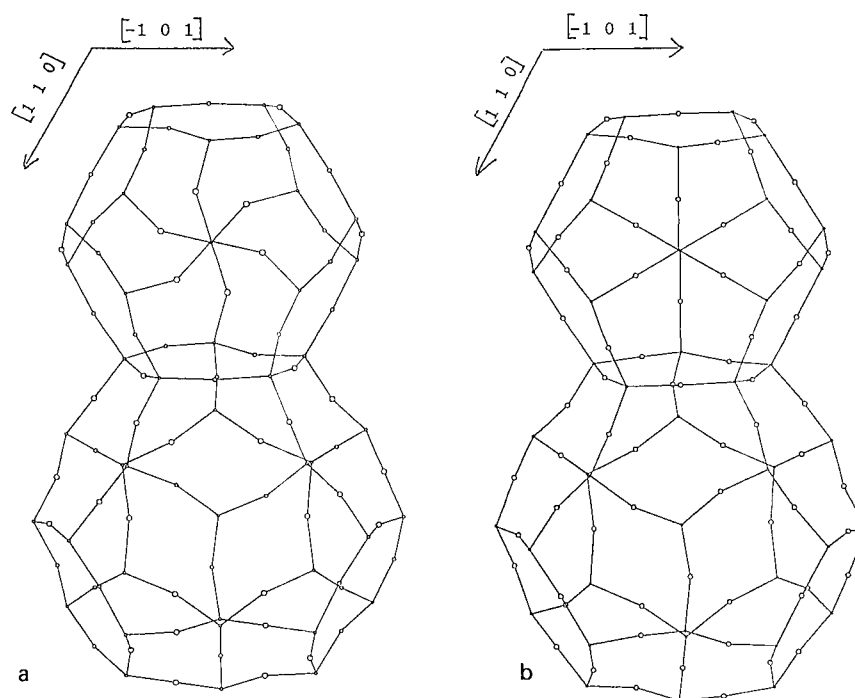


Fig. 4a. DSL-simulation for D3C in $R3$, view $\parallel [1 - 1]$. All directions referring to cubic axes.

Fig. 4b. DSL-simulation for D3C in $Fddd$, view $\parallel [1 - 1]$.

tions were found on the diffractometer and only sharp reflections were observed, we conclude that there is a long range order in calcined D3C. Similar observations are reported for dodecasil 1H, another polytype of the dodecasil family by Mieke, Vogt, Fuess and Müller (1992).

A possible model for the observed disorder is an incoherent superposition of intensities from twinning. As three positions are observed for oxygen 4, at least three individuals should be present. But Mieke et al. (1992) calculated for D1H a simulated set of structure factors by superposing three twin structures with equal weights. After conventional anisotropic refinement of this set, the pattern in the difference Fourier syntheses did not show any interpretable features in contrast to the one based on the observed structure factors. From this result we conclude that there is no superposition of intensities from twins in D1H and, because of the similarity of the structures and the effects observed, in D3C.

Presumably there is a long range order in calcined D3C, but a local disorder, similar to the observations of Burckhardt and Trömel (1983) for $\text{SrTe}_5\text{O}_{11}$.

In order to find local symmetries distance least squares simulations were performed in several subgroups of $Fd\bar{3}m$ for D3C with the DLS-76 program (Baerlocher et al., 1977) and compared with the results of the split positions structure refinement. A part of the refined structure is shown in Figure 3. The simulations in $F1$ and $F\bar{1}$ failed to converge because of the large number of parameters. Simulations in $I\bar{1}$ and $I4_1$ resulted in structures which could be described in $I4_1/a$. But the simulated structure in $I4_1/a$ fails to explain the observed disorder. Simulations in $I4_1/amd$ and $Fddd$ proved to be very similar, but did not fit the observed disorder. Only the simulation in $R\bar{3}$ explains part of the disorder in the structure D3C. However, certain features, especially in the $[5^{12}6^4]$ -cage are not interpreted by this model. We therefore conclude, that parts of the structure of calcined D3C may adopt rhombohedral symmetry locally.

In the $[5^{12}]$ - as well as in the $[5^{12}6^4]$ - cage of calcined D3C diffuse electron density ($0.5 \text{ e}/\text{\AA}^3$) in the middle of the cages was found. This intensity is either due to relicts of guest species not completely expelled or to gases which migrated into the cages after the heat treatment. As these peaks were smeared out no chemical information about the nature of these relicts could be obtained.

Acknowledgements. This work has been supported by the Bundesminister für Forschung und Technologie under grant No. 03-FU2DAR and by the Fonds der Chemischen Industrie.

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