

STUDIES ON CLATHRASILS: VII. A NEW CLATHRATE COMPOUND OF SILICA: SYNTHESIS, CRYSTALLOGRAPHIC, AND THERMAL PROPERTIES.

H. Gies
Mineralogisches Institut der Universität Kiel
23 Kiel
FRG

ABSTRACT: Using 1-aminoadamantane a new type of silica host framework has been stabilized. The clathrasil is rhombohedral with $a = 13.887\text{\AA}$ and $c = 40.989\text{\AA}$ for the hexagonal unit cell. Heating the compound on a thermal analyser shows that from 500°C on the guest molecule evaporates. The silica framework only very slowly breaks down when heated at 1100°C for several hours yielding cristobalite. Since 1-aminoadamantane stabilizes, at higher temperatures of synthesis, dodecasil 1H the new clathrasil is regarded as low temperature form for this particular guest molecule.

INTRODUCTION:

In recent years, the structural relationship between ice and silica has been extended to include clathrate compounds. The new term clathrasils has been introduced for this group of host guest compounds /1/. Three different silica host frameworks have been synthesized so far: Melanophlogite, $46\text{SiO}_2 \cdot 2\text{M}^{12} \cdot 6\text{M}^{14}$, /2/ and dodecasil 3C (D3C), $132\text{SiO}_2 \cdot 16\text{M}^{12} \cdot 8\text{M}^{16}$, /3/ isostructural with the clathrate hydrates of type I and II respectively, and dodecasil 1H (D1H), $32\text{SiO}_2 \cdot 3\text{M}^{12} \cdot 2\text{M}^{12} \cdot 1\text{M}^{20}$ /4/. The silica frameworks have been stabilized using organic and/or inorganic guest molecules typical for each clathrasil framework. These guest molecules occupy cage like voids in the open framework; their size, shape, and chemical characteristics determine which host lattice may be formed. In this study we report on a new silica framework stabilized with 1-aminoadamantane as guest molecule.

1 EXPERIMENTAL

A 1 M aqueous solution of ethylenediamine(en) was used to hydrolyse $\text{Si}(\text{OCH}_3)_4$ in the molecular proportions $\text{len}:\text{O}:\text{SiO}_2$. Methanol formed through hydrolysis remained in the solution. 1-aminoadamantane was then added (0.1 mg/ml); samples of solution were sealed in silica tubes (\varnothing 0.5mm, 2mm wall thickness), and heated 165°C for 2-3 weeks in an oven. By then small rhombohedron shaped colourless crystals had appeared. After a further 4-6 weeks the estimated yield was about 30% of the starting silica. The crystals were analysed with energy

dispersive X-ray fluorescence. Only silicon was detected as part of the framework. Attempts to synthesize the rhombohedral phase at 170°C and above yielded D1H. No lower temperature limit was determined.

Thermogravimetric analyses were performed using a Dupont 1090 system; X-ray powder patterns were recorded with Hägg-Guinier camera. For electron diffraction a Philips 802 electron microscope and for X-ray fluorescence a Kratos CORA analytical microscope were used.

2 RESULTS AND DISCUSSION

2.1 Crystallographic properties

The colourless rhombohedron shaped crystals (0.01 mm size) were always intergrown so that no X-ray single crystal investigation could be made. Initial values for the unit cell constants were obtained by electron diffraction. On avoiding multiple diffraction by imaging only the 00ℓ row, no systematic extinctions for a c -glide plane could be observed (Fig. 1),

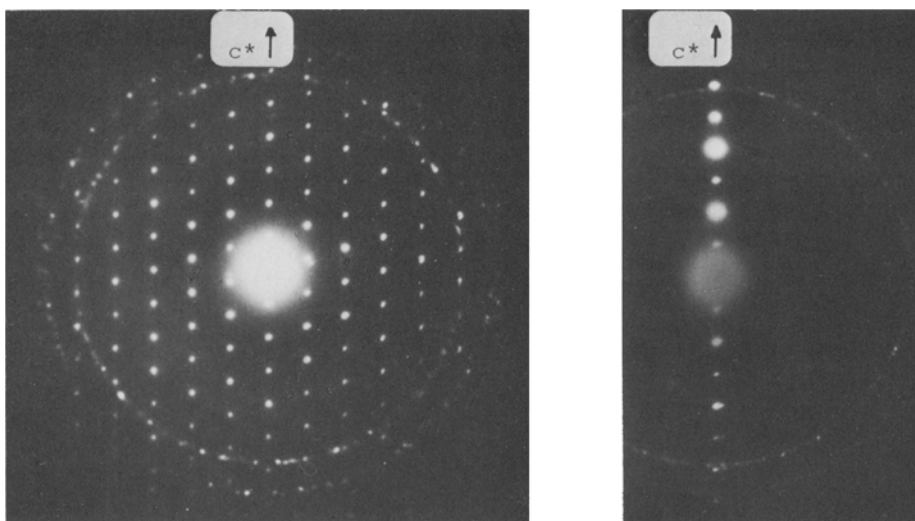


Fig. 1: Electron diffraction photographs of the $h0\ell$ zone and the 00ℓ row of the new clathrasil.

so that the only possible space groups are $R3$, $R\bar{3}$, $R32$, $R3m$ and $R\bar{3}m$. In Tab. 1 the indexed X-ray powder pattern is listed with intensities for the compound including the guest molecules. A least squares refinement of lattice parameters using this indexed pattern gives $a = 13.887(6)\text{\AA}$ and $c = 40.989(45)\text{\AA}$ for the hexagonal unit cell. The density of the compound including the guest molecules was found to be 2.01 g/cm^3 by the "sink-or-swim" technique. This is comparable with values for the other clathrasils: Melanophlogite $\sim 2.01\text{ g/cm}^3$, D3C $\sim 2.06\text{ g/cm}^3$, and D1H $\sim 2.03\text{ g/cm}^3$.


h k l	d _{obs.}	I/I _o	h k l	d _{obs.}	I/I _o
0 0 3	13.55	2	1 2 2	4.411	2
0 1 1	11.61	37	0 2 7	4.152	35
0 1 2	10.36	4	1 2 4		
0 1 4	7.814	15	0 3 0	3.996	15
1 1 0	6.901	24	1 2 5		
0 0 6			0 2 8		
1 1 3	6.180	6	0 1 10	3.844	25
0 2 2	5.767	64	0 3 3		
0 1 7	5.183	100	0 3 3	3.588	9
0 2 4					
1 1 6	4.860	28	2 2 0	3.460	7
0 2 5					
0 1 8	4.717	27	0 3 6	3.398	71
0 0 9	4.515	45	0 3 6		
1 2 1			1 2 8	0 0 12	3.368
			2 2 3		
			1 3 1	3.323	

Tab. 1 : X-ray powder data of the new clathrasil.

2.2 Thermal properties.

A 2.36 mg sample was heated in a thermal analyser at 25°C/min to a maximum of 975°C (Fig. 2). Only one region of weight loss was revealed. A large guest molecule as 1-aminoadamantane can only be expelled after decomposition of the organic skeleton. As with other clathrasils the material turns black at ~500°C indicating fragmentation of the organic guest species. This observation explains the weight loss occurring at 500°C (see Fig. 2). X-ray powder data proved that the silica framework remained unchanged. After 11 h at 1100°C the host lattice started to break down; after a further 12 h at that temperature only cristobalite was detected. The density measurement of the heated sample gave 1.91 g/cm³.

Considering all experimental results the new phase can clearly be identified as a new clathrasil type. Crystallographic data (rhombohedral with $a = 13.887\text{\AA}$ and $c = 40.989\text{\AA}$), chemical analysis (silica host framework) and density measurement ($\rho = 2.01\text{g/cm}^3$) showed that the material is a low density form of silica. The typical conditions for synthesis (guest molecule: 1-aminoadamantane) and the characteristic thermal behaviour (weight loss starting from 500°C) proved that the new phase is a host guest compound which has no zeolitic attributes but is comparable to the clathrasil family.

It is known from other clathrasils that different SiO₂ host frameworks can be stabilized with the same guest molecule at different temperatures of synthesis. The structure determining guest molecule fits the void of the cage of the low temperature modification very well, while a somewhat bigger cage houses the guest molecule in the high temperature modification. Thus piperidine  stabilizes the D3C

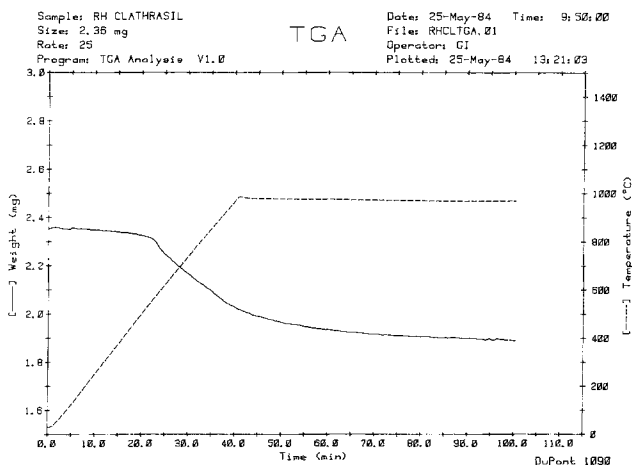


Fig. 2: Thermogravimetric diagram of the new clathrasil.

framework and is housed in a $[5^{12}6^4]$ cage ($V = 221\text{\AA}^3$) on synthesis at temperatures below 200°C , but the D1H framework with its larger $[5^{12}6^8]$ cage ($V = 348\text{\AA}^3$) is favoured at higher temperatures of synthesis. A similar relationship is found between the new clathrasil and the high temperature D1H framework for the 1-aminoadamantane guest molecule. Instead of the $[5^{12}6^8]$ cage in D1H a slightly smaller cage houses this molecule at temperatures below 170°C . The 3-D arrangement of this smaller cage to give a silica framework is not in accordance with a member of the dodecasil polytypic series but indicates a new independent clathrasil.

Acknowledgement

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