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Synthesis and Crystal Structure of Silver Nesosilicate, Ag_4SiO_4

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Abstract. The new silver silicate Ag_4SiO_4 has been obtained by solid state reactions starting from stoichiometric amounts of the binary oxides at elevated temperatures and oxygen pressures. Ag_4SiO_4 crystallizes in space group $P4_2/n$ (No. 86) with a = 7.3169(3), c = 4.9595(4) Å, V = 265.52(3) Å^3, Z = 2; the structure refinement was based on 343 independent reflections and resulted in R_1 = 2.70 %, wR_2 = 5.85 %. The crystal structure consists of isolated SiO_4 tetrahedra which are linked by Ag cations. The Ag atoms are almost linearly coordinated by two oxygen atoms. The AgO_2 dumbbells form chains, and every two of these chains are wound around each other forming double helices running along [001]. This arrangement of Ag and O atoms corresponds to a section of the Ag_2O structure. Ag_4SiO_4 is photosensitive and decomposes within a few weeks into silver, SiO_2 and oxygen.

Keywords: Silver; Silicon; Silver silicate; High oxygen pressure; Crystal structure

Introduction

Among the naturally occurring minerals, silicates represent the largest group with respect to occurrence and number, showing an unique structural wealth. Surprisingly, our knowledge about the crystal structures [1−7] of the supposedly simplest of these compounds, the nesosilicates of monovalent cations of the composition A_4SiO_4, is limited owing to problems concerning synthesis or structure solution. Li_4SiO_4 for example crystallizes in different modifications [1−4], which partially show ionic conductivity and therefore include disordered Li atoms. The crystal structure of K_4SiO_4 was solved considering the systematic twinning, resulting from a phase transition which occurs while cooling the samples from reaction temperature to RT [7]. The synthesis of Rb_4SiO_4 and Cs_4SiO_4 has not yet been achieved at all [4].

The composition "Ag_4SiO_4" was reported for the first time in 1958 by *Thilo* and *Wodtcke* [8]. This silver silicate was obtained by ion exchange from Ca_2SiO_4 in fused $AgNO_3$ and was described to have a deep red or vermilion colour [8−10]. Besides the triclinic lattice parameters no further structural information was provided at that time. However, a more recent structure determination proved the described compound to be a mixed silicate nitrate, $Ag_9(SiO_4)_2(NO_3)$ [11], a composition that well complies with the method of synthesis.

When aiming at the synthesis of higher silver oxides problems commonly result from the low thermal stability of Ag_2O, and conventional solid state reactions at elevated temperatures cannot be applied. The first silver silicates were obtained at rather mild conditions from topochemical reactions by exchange of cations from alkali and alkaline earth silicates in melts of $AgNO_3$ [8, 10]. The possibility to perform syntheses at elevated oxygen pressures has extended the number of accessible compounds enormously [12−17], with Ag/Si ratios varying between 2 and 5, and lead to crystals suitable for structure determinations. The results obtained were, in part, rather surprising, as there were found the first tetrasilicates [13, 14] and Ag_5SiO_4, a subvalent compound with respect to the Ag part of structure [16]. The colours of silver silicates correlate roughly with the Ag/Si ratio and range from yellow (Ag_2SiO_3) to red ($Ag_{10}Si_4O_{13}$, $Ag_{18}(SiO_4)_2(Si_4O_{13})$, $Ag_6Si_2O_7$) to greenish black metallic (Ag_5SiO_4). Furthermore, all silver silicates are photosensitive.

Although meanwhile isolated SiO_4 tetrahedra have been found in some ternary and quaternary silver oxides [11, 14, 16, 18], surprisingly the simple nesosilicate of this row, Ag_4SiO_4, was still missing. The first crystals of Ag_4SiO_4 were obtained as a by-product when performing syntheses which were originally aiming at ternary silver oxides of different compositions. Here we present a method to reproducibly prepare pure samples, and report on the crystal structure of Ag_4SiO_4.

Experimental Section

Synthesis

Ag_4SiO_4 was prepared applying elevated oxygen pressures in stainless steel autoclaves [19] by reaction of silver(I) oxide and silicon

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dioxide. In a typical experiment 60 mg of SiO_2 (1 mmol; 99 %, Sigma-Aldrich) and 480 mg Ag_2O (2.1 mmol; freshly precipitated from $AgNO_3$ and KOH solutions, washed with water and dried at 75 °C) were intimately ground in an agate mortar and filled into a gold crucible. The crucibles were sealed at one end and crimped at the other and placed in an autoclave. Pure, light yellow samples were obtained by reacting the educt mixture at a temperature of 200 °C in an oxygen pressure above 240 MPa for 6 d. By adding 1 ml of diluted CsOH solution into the crucible, single crystals, up to an edge length of about 1 mm, were grown within three weeks at 280 °C. Samples have to be stored in the dark in order to avoid decomposition and formation of elemental silver at the surface.

Energy Dispersive Microanalysis

EDX analyses were carried out on large crystals of different samples of Ag_4SiO_4 with a Philips XL 30 TMP, equipped with an energy dispersive unit for microanalysis (Phoenix, EDAX). The Ag/Si ratios of the yellow crystals were in average found to be slightly below 4.

X-ray Powder Diffraction

X-Ray diffraction powder data were taken on a Stoe Stadi-P diffractometer (Cu Kα_1, Ge monochromator, linear PSD) in steps of 0.1° over a 2θ range from 5° to 100° with the samples sealed in glass capillaries of 0.2 mm diameter. The observed reflections are listed in Table 1.

Table 1 Experimental X-ray powder data for Ag_4SiO_4 with $d > 1.35$ Å.

d_{obs} [Å]	I / I_0	h	k	l
5.1730	6.8	1	1	0
3.6578	4.7	2	0	0
2.9442	4.0	2	0	1
2.7309	100.0	2	1	1
2.5902	2.0	2	2	0
2.4802	11.3	0	0	2
2.3512	4.3	1	0	2
2.3139	18.1	3	1	0
2.2937	3.6	2	2	1
2.2357	3.1	1	1	2
2.0516	1.9	2	0	2
1.9756	1.8	2	1	2
1.8782	4.0	3	2	1
1.8294	2.0	4	0	0
1.7385	3.5	3	0	2
1.7244	3.4	3	3	0
1.6914	20.3	3	1	2
1.6703	2.1	4	1	1
1.6360	10.6	4	2	0
1.5746	2.0	1	1	3
1.5704	1.3	3	2	2
1.4753	8.1	2	1	3
1.4434	1.6	4	1	2
1.4157	1.7	3	3	2
1.4038	17.9	5	0	1
1.3658	6.1	4	2	2

X-ray Single Crystal Diffraction

Single crystals suitable for X-ray diffraction were selected and glued onto the tip of a glass capillary. Single crystal data were collected on an IPDS-II diffractometer (Stoe & Cie, Darmstadt, Mo Kα, graphite monochromator, absorption correction by the integration method). The structure was solved by direct methods [20a], all atoms were found at this stage, refinement by full-matrix, least-squares calculations based on F^2 [20b]. A summary of the data collection and processing, the crystallographic parameters, as well as details on structure solution and refinement is given in Table 2. The atomic coordinates and displacement parameters are shown in Tables 3 and 4. Further details of the crystal structure investigation are available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository number CSD-418314, the name of the authors and the citation of the paper.

Table 2 Crystallographic data and details of the structure determination of Ag_4SiO_4 (lattice parameters from powder data).

space group	$P4_2/n$ (No. 86)
a	7.3169(3) Å
c	4.9595(4) Å
cell volume V	265.52(3) Å^3
formula units Z	2
molar mass	523.57 g/mol
density (calculated)	6.567 g/cm^3
absorption coefficient μ	14.713 mm^{-1}
absorption correction	integration method
2θ range	7.88° − 57.58°
hkl region	$-10 \le h \le 10$ $-10 \le k \le 10$ $0 \le l \le 7$
measured reflections	1289
R_{int}	2.81 %
independent reflections	343
independent reflections ($I > 2\sigma$)	252
parameters	22
$R(F)$ ($I > 2\sigma(I)$ / all data)	2.70 % / 3.81 %
$R_w(F^2)$ ($I > 2\sigma(I)$ / all data)	5.85 % / 5.99 %
max. / min. difference electron density	0.64 / −1.87 e$^-$Å^{-3}
depository no.	CSD-418314

Table 3 Atomic coordinates and isotropic displacement parameters[a] in Å^2 for Ag_4SiO_4.

Atom	Wyckoff pos.	x	y	z	U_{eq}
Ag	8g	0.56178(7)	0.36246(6)	0.28515(11)	0.0221(2)
Si	2b	3/4	3/4	1/4	0.0129(7)
O	8g	0.6916(6)	0.5764(6)	0.0621(8)	0.0172(9)

[a] U_{eq} is defined as $\exp[-8\pi^2 U(\sin^2\theta/\lambda^2)]$.

Table 4 Anisotropic displacement parameters[a] in Å for Ag_4SiO_4.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ag	0.0221(4)	0.0217(3)	0.0225(3)	0.0053(2)	0.0019(2)	−0.0032(2)
Si	0.0121(9)	0.0121(9)	0.014(2)	0	0	0
O	0.019(2)	0.017(2)	0.016(2)	−0.002(2)	0.004(2)	−0.002(2)

[a] U_{ij} are defined as $\exp[-2\pi^2 (U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + U_{12}hka^*b^* + U_{13}hla^*c^* + U_{23}klb^*c^*)]$.

Thermal Analysis

Thermal decomposition experiments were performed with a STA 409 (Netzsch, Selb, Germany) with a heating rate of 10 °C/min in argon atmosphere. The decomposition of Ag_4SiO_4 occurs with an onset at 440 °C in a more-step mechanism, possibly including intermediate formation of Ag_2SiO_3 or other silver silicates. After the first clearly defined step with a weight loss of 2.5 % (2.3 % calc. for $4\ Ag_4SiO_4 => Ag_{10}Si_4O_{13} + 6\ Ag + 3/2\ O_2(\uparrow)$) at 500 °C, a continuous weight loss takes place.

Results and Discussion

Synthesis and Thermal Behaviour

The first crystals of Ag_4SiO_4 have been obtained from experiments at elevated oxygen pressures and relatively mild temperatures below 300 °C, aiming at ternary silver oxides of other compositions, with small amounts of water added to accelerate the crystal growth. Silicon, which is contained in the autoclave steel in a small amount, is dissolved from autoclaves at these conditions. Via EDX analyses, the Ag/Si ratio was found to deviate considerably and repeatedly from the only known yellow silver silicate, Ag_2SiO_3, and after identifying the true composition by single crystal structure determination, reproducible synthesis of single phase Ag_4SiO_4 was achieved following the prescription given above. To avoid formation of the closely related compound Ag_5SiO_4 as an impurity, higher oxygen pressures and addition of small amounts of an alkaline accelerator are necessary.

Thermal decomposition starts at about 440 °C, with a well defined weight loss at this temperature followed by a more continuous one. This implies a decomposition in multiple steps, possibly *via* formation of higher condensed silicates like the tetrasilicate $Ag_{10}Si_4O_{13}$ which would comply with the weight loss after the first step. After heating to 600 °C in an argon atmosphere only silver and SiO_2 were detected as solid residues.

Although the thermal stability of Ag_4SiO_4 is almost as usual for silver-rich oxides, and its synthesis does not make any specific problems, the time gap is surprisingly large between the begin of systematic experimental exploration of this field, applying the necessary high oxygen pressures [12], and the discovery of the new compound. As one possible reason we have identified that Ag_4SiO_4 is highly photosensitive. The samples rapidly seggregate a coating of elemental silver within a few hours exposed to daylight and, as a special pitfall, are hard to distinguish from Ag_5SiO_4 with respect to colour. After having Ag_4SiO_4 stored for weeks, it has decomposed completely, showing broad reflections of Ag and sharp ones of SiO_2 in the X-ray powder pattern.

Crystal Structure

As expected, Ag_4SiO_4 contains isolated SiO_4 tetrahedra (site $\bar{4}$) which show only slight deviations from ideal T_d symmetry with respect to the angles (Table 5, Fig. 1). The surrounding Ag cations have two close O atoms at 2.114 and 2.139 Å in almost linear coordination, with the Ag atom deviating from exact linearity in direction of another O atom at the larger distance of 2.57 Å (see Tab. 5). The AgO_2 dumbbells are linked to form HgO-like chains, and each two of them are twisted around the fourfold axis (Fig. 2) forming a ${}^1_\infty[(AgO)_n]_2^{2n-}$ double helix running along [001]. Due to an inversion centre both senses of rotation are realized in the Ag_4SiO_4 structure. The double helices are also part of the Ag_2O crystal structure, each chain belongs to one of the two interpenetrating, but independent networks of the cuprite structure type, as shown in Figure 3. The SiO_4 tetrahedron causes an elongation of the Ag−O bonds compared to those in Ag_2O (2.05 Å), and a decrease

Table 5 Selected bond lengths and angles for Ag_4SiO_4.

Atoms	Distances	Atoms	Distances
$Ag-O^{i}$	2.114(4) Å	$Si-O$	1.632(4) Å [4x]
$Ag-O$	2.139(4) Å	$Ag-Ag^{vi}$	3.0676(10) Å
$Ag-O^{ii}$	2.570(4) Å	$Ag-Ag^{vii}$	3.2086(9) Å
Atoms	Angles	Atoms	Angles
$O^{i}-Ag-O$	168.7(2)°	$O-Si-O^{iii}$	109.0(1)° [4x]
$O^{i}-Ag-O^{ii}$	101.1(2)°	$O-Si-O^{iv}$	110.4(3)° [2x]
$O-Ag-O^{ii}$	81.2(2)°	$Ag-O-Ag^{v}$	104.4(2)°

Symmetry operations: (i) = $1-y$, $-1/2+x$, $1/2+z$; (ii) = $1-x$, $1-y$, $-z$; (iii) = y, $3/2-x$, $1/2-z$; (iv) = $3/2-x$, $3/2-y$, z; (v) = $1/2+y$, $1-x$, $-1/2+z$; (vi) $1-x$, $1-y$, $1-z$; (vii) $3/2-x$, $1/2-y$, z.

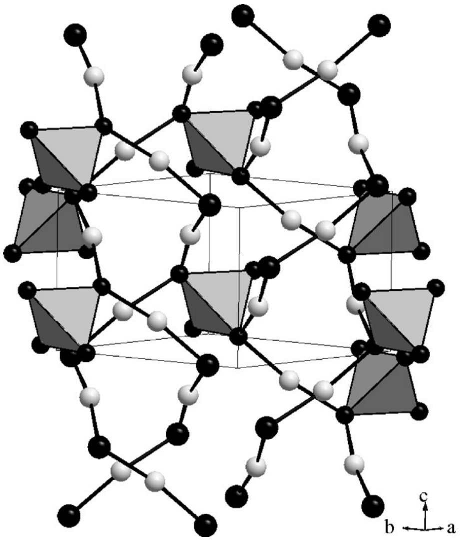

Figure 1 Crystal structure of Ag_4SiO_4, highlighted are SiO_4^{4-} tetrahedra and ${}^1_\infty[(AgO)_n]_2^{2n-}$ double helices.

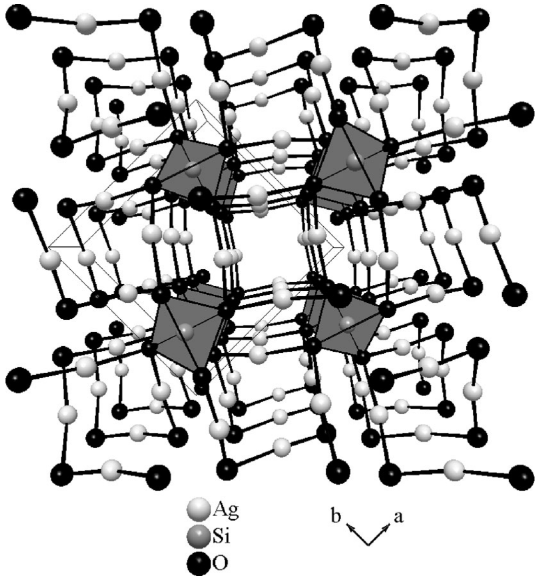

Figure 2 Crystal structure of Ag_4SiO_4, perspective view along [001], displaying the ${}^1_\infty[(AgO)_n]_2^{2n-}$ spirals around the fourfold axis of symmetry, and interconnecting SiO_4^{4-} tetrahedra.

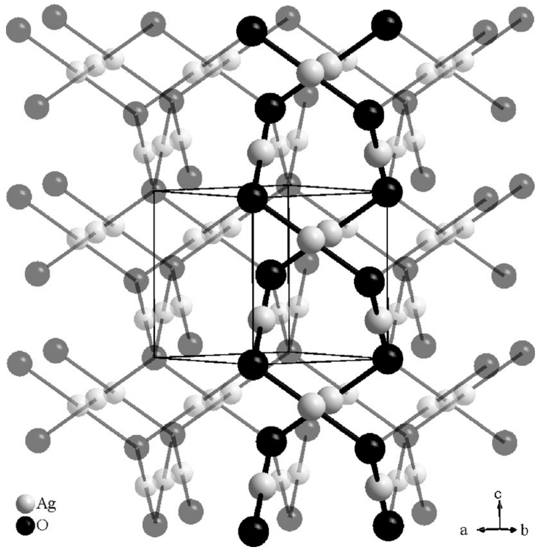

Figure 3 Crystal structure of Ag_2O, emphasising the relationship to the $^1_\infty[(AgO)_n]_2^{2n-}$ chains in Ag_4SiO_4.

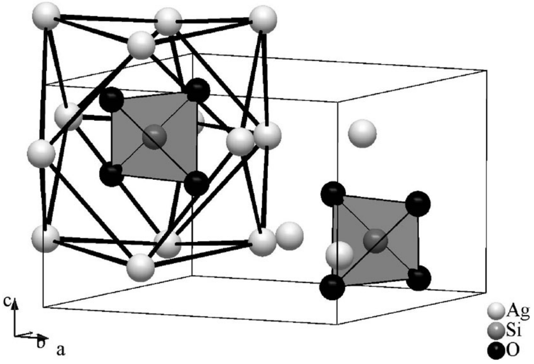

Figure 4 Cuboctahedral surrounding of SiO_4 tetrahedra by Ag cations in Ag_4SiO_4.

of the Ag−O−Ag angle within the chain(Ag_2O: 109.47°; Ag_4SiO_4: 104.4°). Consequently, the *c* axis of Ag_4SiO_4 is somewhat larger than the cubic lattice parameter of Ag_2O.

Again similar to the cuprite structure type, all the cations adopt a slightly disordered cubic close packing where the O anions are located in tetrahedral voids. In Ag_4SiO_4 both kinds of tetrahedral voids are partly occupied caused by the SiO_2-"impurity" as a perturbance with respect to Ag_2O. The Si atoms, resp. the SiO_4 tetrahedra, are surrounded by a cuboctahedron of Ag atoms (see Fig. 4), while the cuboctahedron around the Ag atoms includes three Si atoms, both such polyhedra are characteristic features of the cubic close packing.

With respect to the atomic packing, the structure of Ag_4SiO_4 is related to that of Ag_4GeO_4 [21] where similar but irregular cages of 12 Ag atoms around the GeO_4 tetrahedra are found. Obviously owing to the larger size of the GeO_4 tetrahedron its first coordination shell is more strongly deformed, and consequently, in Ag_4GeO_4 no $^1_\infty[AgO]_n$ chains are present, instead an irregular $^3_\infty[AgO]_n$ network results, and the symmetry is reduced to triclinic.

The crystal structure of Ag_4SiO_4 is considerably different from those of the corresponding alkali silicates. Such an observation has been quite commonly made for ternary silver oxides, and can be related to the presence of short Ag−Ag contacts, corresponding to attractive $d^{10}-d^{10}$ interactions between the Ag^I ions [22, 23]. However, in Ag_4SiO_4 the shortest Ag−Ag distances of 3.07 Å are quite large compared to those in silver metal (2.89 Å) and in related compounds, *e.g.* in Ag_5SiO_4 (2.70 Å), and are hardly responsible for the structural difference. Obviously, the Ag cations, all adopting the rather rigid linear coordination by oxygen, seem to have the largest structure directing influence in Ag_4SiO_4, which is also reflected by the close similarity to the crystal structure of Ag_2O. The d^{10}-d^{10} interactions, causing a bathochrome shift of the UV/VIS absorption edge [24], seem to depend on the relative number of silver ions presence and on the Ag-Ag separations. The unexpected bright yellow colour of Ag_4SiO_4 can thus be understood in terms of the relatively long Ag-Ag distances.

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