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Subvalent Ternary Silver Oxides: Synthesis, Structural Characterization, and Physical Properties of Pentasilver Orthosilicate, Ag_5SiO_4

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Single crystals of Ag_5SiO_4 have been obtained by hydrothermal reaction of Ag powder with amorphous SiO_2 under high oxygen pressure. The crystal structure was explored by single-crystal X-ray diffraction. Ag_5SiO_4 crystallizes with orthorhombic symmetry in space group *Pnnm* (No. 58) with $a = 9.856(1)$ Å, $b = 9.108(1)$ Å, $c = 6.271(1)$ Å and 4 formula units per cell. The crystal structure of Ag_5SiO_4 consists of Ag_6 clusters along with isolated Ag^+ and tetrahedral SiO_4^{4-} ions. The physical and structural properties suggest a formulation as $[Ag_6]^{4+}(Ag^+)_4(SiO_4^{4-})_2$.

Introduction

As a general structural feature of ternary silver-rich oxides the cationic part tend to segregate.[1] In spite of their positive charge the cations form clusterlike agglomerates, which, quite independent of the type of chemical bond between oxygen and silver or of the anionic matrix present, display impressive uniform topological features. The Ag–Ag distances are similar to and sometimes even shorter than those in the metal, and the arrangements generally represent sections of the fcc structure. These observations have led us to suggest the existence of weak attractive Ag^+–Ag^+ interactions.[2] Admittedly, this interpretation contradicts the generally accepted rule that closed-shell configurations, such as d^{10}, do not undergo conventional bonding interactions. Although, from some physical properties, there is further support for that interpretation, the discussion on the amount and the nature of the Ag^+–Ag^+ interactions still continues. However, regardless of the question whether bonding between the d^{10}-configurated cations is present or not, there should exist low-lying empty bands originating from silver 5s or 5p orbitals within the clusterlike ensembles of silver ions. These bands are expected to accommodate additional electrons, thus producing subvalency with respect to silver.[3] As a consequence silver should be liable to the formation of subvalent compounds, much more pronounced than indicated by the only very few examples, such as Ag_3O[4] or Ag_2F,[5] known so far. The reason for this obvious lack of a broader chemistry of subvalent silver might be that the synthesis of, e.g., subvalent multinary silver oxides seems to afford conflicting requirements. On one hand a sufficient thermal activation is necessary to achieve reaction of the solid-state components, while on the other hand silver oxide decomposes to give the metal at elevated temperatures. Usually we avoid the latter by applying high oxygen pressure during the reaction.[6] However, when aiming at subvalent silver oxides, this measure does not seem to be appropriate.

Surprisingly, recently we have been able to obtain Ag_5GeO_4[7] by a solid-state reaction which applies elevated oxygen pressures as a first subvalent ternary silver oxide, taking advantage of the oxygen buffering capability of metallic silver. Of course, the system in that somewhat paradox situation is not in equilibrium and the silver metal will be oxidized throughout in the course of a long-term experiment. Although the balance between reaction time, temperature and oxygen pressure seems to be rather crucial, quantitative yields with respect to the educts Ag, Ag_2O, and GeO_2 could be achieved. In order to work out whether this synthetic route has some general applicability we have started investigating the system $Ag/Ag_2O/SiO_2$.

Experimental Section

Synthesis of Ag_5SiO_4. Starting materials were silver powder and silicon dioxide. Silver powder was obtained from an aqueous solution of $AgNO_3$ (>99.8%, Merck) by adding $N_2H_4{\cdot}H_2O$ as a reducing agent. Amorphous SiO_2 was derived via sol–gel methods by hydrolysis of $Si(OEt)_4$ (>98%, Janssen). The finely divided silicon dioxide was subsequently dried at 200 °C under reduced pressure ($p \sim 500$ Pa).

Ag powder and SiO_2 were mixed in a 6:1 molar ratio ($Ag:SiO_2$) (1 g Ag, 9.271 mmol, 0.0929 g SiO_2, 1.545 mmol) and then were annealed for 6 days in silver crucibles (0.8 cm diameter, 4 cm height) which were placed in stainless steel autoclaves (ATS 351, modified Bridgman seal, $V = 20$ cm^3) adding 4 cm^3 of bidistilled water as an accelerator. The optimized reaction temperature and oxygen pressure are 350 °C and 50 MPa, respectively. Without an excess of silver, small amounts of $Ag_{10}Si_4O_{13}$[8] or $Ag_6Si_2O_7$[6] form as by products. The estimated yield of Ag_5SiO_4 in this case is about 80%.

Structure Determination. Powder diffraction patterns were obtained from thoroughly grounded samples mounted between pieces of cellophane tape. A Stadi P powder diffractometer (Cu Kα_1 radiation, Ge monochromator) equipped with a PSD (Position Sensitive Detector, open square 4–6° in 2θ, Stoe & Cie) was employed for this purpose.

A single crystal shaped like a prism with the approximate dimensions $0.04 \times 0.05 \times 0.07$ mm was chosen for the X-ray structure determination. Diffraction data were collected on a CAD4 single-crystal diffractometer (Mo Kα_1 radiation, graphite monochromator, Enraf Nonius) at room temperature up to $\theta = 35°$.

Weissenberg photographs suggested orthorhombic symmetry with two possible point groups, *mmm* or *2mm*. The systematic extinctions indicated the diffraction symbol *P-nn* with two possible space groups *P2nn* and *Pnnm*.

Structure determination and refinements were carried out with the SHELXS 86 and SHELXL 93 program packages.[9] The centrosymmetric space group *Pnnm*, No. 58 was found to be correct in course of structure refinements. Silver sites were found by direct methods; silicon and oxygen

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Table 1. Selected Data Collection and Structure Refinement Parameters for Ag_5SiO_4

$a = 9.856(1)$ Å[a]	$T = 20$ °C
$b = 9.108(1)$ Å	$\lambda = 0.710\,70$ Å
$c = 6.271(1)$ Å	$\rho_{obsd} = 7.450$ g cm^{-3}
$V = 563.0(1)$ Å^3	$\mu = 172.24$ cm^{-1}
$Z = 4$	R (F_o, $I > 2\sigma(I)$) = 4.95%
fw = 631.44 gmol^{-1}	R_w (F_o^2, $I > 2\sigma(I)$)[b] = 12.08%
space group: P nnm, No. 58	

[a] Room-temperature powder data, Si as external standard, Cu Kα_1 radiation. [b] $w = 1/\sigma^2F_o^2 + (0.0626P)^2 + 12.6718P$ with $P = (F_o^2 + 2F_c^2)/3$).

Table 2. Atomic Coordinates and Equivalent Isotropic Displacement Parameters for Ag_5SiO_4[a]

atom	x/a	y/b	z/c	U_{eq}
Ag(1)	0.1228(1)	0.5662(1)	0.2227(1)	0.012(1)
Ag(2)	0.0975(1)	0.2981(1)	0	0.014(1)
Ag(3)	0.1227(1)	0.8931(1)	0.2449(1)	0.031(1)
Si(1)	0.3837(2)	0.7393(3)	0	0.006(1)
O(1)	0.0488(7)	0.7278(7)	0.5000	0.011(2)
O(2)	0.2024(7)	0.3939(7)	0.5000	0.010(3)
O(3)	0.3498(5)	0.6466(5)	0.2175(8)	0.012(2)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

sites were derived from difference Fourier syntheses. The structure was refined by full-matrix, least-squares methods (based on F_o^2) with anisotropic thermal parameters. Because of the small size of the investigated crystal no absorption correction was performed. Final conventional and weighted R values along with additional crystallographic data are given in Table 1. Scattering factors were taken from ref 18.

Physical Measurements. All measurements were carried out using freshly prepared and purified samples. The crystals of Ag_5SiO_4 formed during the reaction were considerably bigger than those of Ag_2O, so that the excess Ag_2O could be removed mechanically by passing the crude sample through a sieve (140 mesh). Afterwards its purity was checked by XRD.

Magnetization data were taken with an applied field of 2 T from 2 to 295 K on a Quantum Design SQUID magnetometer with a 397.8-mg sample, the purity of which was checked previously and subsequently by XRD. Coupled SEM/EDX measurements were carried out using single crystals of Ag_5SiO_4 on a DSM 940 REM (Zeiss) with an attached PV 9800 EDX analyzer (EDAX) at an accelerating voltage of 25 kV. The AgL edge and SiK edge have been analyzed and corrections for atom number, X-ray absorption, and fluorescence were applied.

Thermal behavior was estimated by DTA/TG and temperature dependent Guinier photographs. DTA/TG investigations were carried out simultaneously with a Netzsch STA 429 thermoanalyzer in the range of 20 to 1000 °C at a heating rate of 10° min^{-1}. Temperature-dependent Guinier photographs were taken on an Enraf Nonius FR 553 Guinier camera in nine temperature steps, 50 °C each from 200 to 600 °C. XANES measurements were carried out with the EXAFS II spectrometer at the DESY (Deutsches Elektronen Synchrotron, Hamburg, Germany) analyzing the AgL_3 edge.[10]

Structure Description. The composition, determined by X-ray structure analysis, was found to be Ag_5SiO_4 and confirmed with respect to the Ag:Si ratio by SEM/EDX using single crystals. The Ag:Si ratio averaged over 15 point analyzes was found to be 4.92:1.

Silver-silver contacts in systems for which we assume bonding d^{10}–d^{10} interactions[1] usually range from 289 pm (distance in silver metal) to 340 pm (van der Waals distance[11]). The silver partial structure in Ag_5SiO_4, similar to Ag_5GeO_4[7], exhibits some silver–silver distances that are shortened significantly (up to 19 pm) compared to those mentioned above. The crystallographically independent silver atoms, Ag(1) and Ag(2) (cf. Table 2), virtually from octahedral Ag_6-clusters. The silver–silver distances within these clusters are between 270.4(1) and 286.2(1) pm (Figure 1). The remaining silver-silver contacts are in the range of 297.0(1) to 330.4(1) pm as expected for weak Ag–Ag interactions (cf. Table 3). Each silver atom of the Ag_6^{4+} cluster is surrounded by oxygen atoms in a particular one sided coordination (Figure 1). Ag(1) exhibits a distorted trigonal pyramidal coordination with bond angles varying slightly around 90°, while Ag(2) forms a heavily bent 2-fold coordination with bond angles of approximately 90°, again (cf. Table 3). The Ag_6 groups are separated by SiO_4^{4-} tetrahedra, the dimensions of which are in good agreement with those of orthosilicates reported in the literature (cf. Table 4). Each of these SiO_4^{4-} ions protrudes with one edge into the space between two Ag_6 clusters (Figure 2). Ag(3) completes both the coordination of the oxygen atoms as well as the silver coordination of the cluster atoms Ag(1) and Ag(2), thus forming a three-dimensional network of silver.

Physical Properties. Thermal decomposition occurs in two steps at 461.8 and 502.8 °C, accompanied by an overall weight loss of 5.4% (5.1% calculated based on the reaction $Ag_5SiO_4 = 5Ag + SiO_2 + O_2$). The

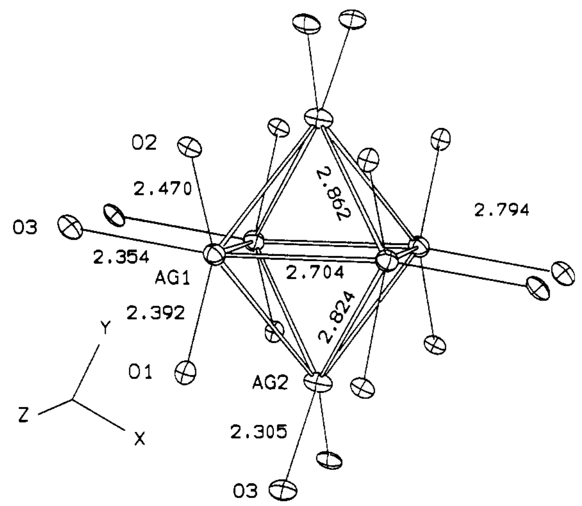

Figure 1. Depiction of an Ag_6^{4+} cluster and its oxygen coordination. Distances are given in Å.

Table 3. Bond Lengths (Å) and Angles (deg) for Ag_5SiO_4

	Bond Lengths		
Ag(1)–O(1)	2.392(4)	Ag(1)–Ag(3)[4]	2.970(1)
Ag(1)–O(2)	2.470(4)	Ag(1)–Ag(3)	2.981(1)
Ag(1)–O(3)	2.354(5)	Ag(2)–Ag(3)[1,3]	3.178(1)
Ag(2)–O(3)[4,5]	2.305(5)	Ag(2)–Ag(3)[4,5]	3.304(1)
Ag(3)–O(1)	2.314(5)	Ag(3)–Ag(3)[2]	3.071(2)
Ag(3)–O(2)[6]	2.309(5)	Ag(3)–Ag(3)[8]	3.105(2)
Ag(3)–O(3)[7]	2.337(5)	Ag(3)–Ag(3)[10]	3.200(2)
Ag(1)–Ag(1)[1]	2.704(1)	Si(1)–O(3)[2]	1.638(5)
Ag(1)–Ag(1)[2]	2.794(1)	Si(1)–O(2)[6]	1.644(7)
Ag(1)–Ag(2)	2.824(1)	Si(1)–O(1)[10]	1.655(7)
Ag(1)–Ag(2)[3]	2.862(1)		
	Bond Angles		
O(3)–Ag(1)–O(1)	96.2(2)	Ag(1)–Ag(1)–Ag(2)	60.79(1)
O(3)–Ag(1)–O(2)	84.6(2)	Ag(2)–Ag(1)–Ag(2)	93.72(2)
O(1)–Ag(1)–O(2)	88.6(2)	Ag(1)–Ag(2)–Ag(1)	59.29(3)
O(3)–Ag(2)–O(3)	100.5(2)	Ag(1)–Ag(2)–Ag(1)	56.79(2)
O(2)–Ag(3)–O(1)	134.2(2)	Ag(1)–Ag(2)–Ag(1)	86.28(2)
O(2)–Ag(3)–O(3)	88.7(2)	Ag(1)–Ag(2)–Ag(1)	56.80(2)
O(1)–Ag(3)–O(3)	127.5(2)	Ag(1)–Ag(2)–Ag(1)	58.42(2)
Ag(1)–Ag(1)–Ag(1)	90.0	O(1)–Si(1)–O(2)	110.7(3)
Ag(1)–Ag(1)–Ag(2)	62.31(2)	O(1)–Si(1)–O(3)	107.1(2)
Ag(1)–Ag(1)–Ag(2)	60.36(1)	O(2)–Si(1)–O(3)	109.6(2)
Ag(1)–Ag(1)–Ag(2)	60.89(2)	O(3)–Si(1)–O(3)	112.7(4)

[a] Symmetry transformations used to generate equivalent atoms: (1) $-x, -y + 1, z$; (2) $x, y, -z$; (3) $-x, -y + 1, -z$; (4) $-x + 0.5, y - 0.5, -z + 1$; (5) $-x + 0.5, y - 0.5, z - 0.5$; (6) $-x + 0.5, y + 0.5, z - 0.5$; (7) $-x + 0.5, y + 0.5, -z + 1$; (8) $-x, -y + 2, z$; (9) $x, y, -z + 1$; (10) $x + 0.5, -y + 1.5, -z + 1$.

Table 4. Comparison of the Si–O Distances and Angles in Silicates of the Alkaline Metals and in Ag_5SiO_4

substance	Si–O dist, (Å)	Si–O square, deg
Ag_5SiO_4	1.638(5)–1.655(7)	107.1(2)–112.7(4)
Li_4SiO_4[a]	1.634(1)–1.642(1)	109.1(1)–110.4(1)
Na_4SiO_4[b]	1.630(1)–1.651(1)	106.9(2)–112.7(2)
K_4SiO_4[c]	1.629(1)–1.641(1)	108.1(2)–111.6(3)

[a] Reference 15. [b] Reference 16. [c] Reference 17.

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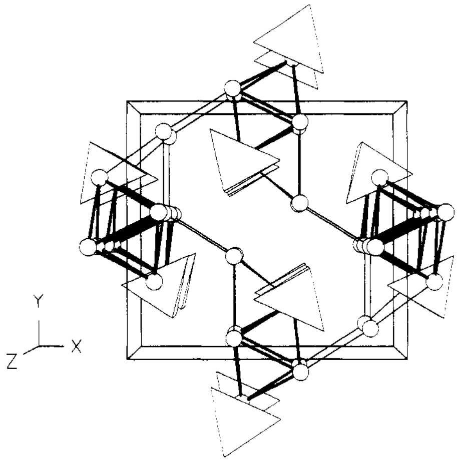

Figure 2. Unit cell in the crystal structure of Ag_5SiO_4 and its nearest coordination, SiO_4^{4-} as opaque tetrahedra with projection along [100].

products formed during thermal decomposition were found by X-ray powder diffraction to be silver and silicon dioxide. Temperature-dependent Guinier photographs gave no indication on the formation of an intermediate phase during decomposition. Exposure to daylight causes slow decomposition (4–6 days) of the crystals which appear black with a greenish metallic luster when freshly prepared. Magnetic measurements showed Ag_5SiO_4 to be diamagnetic with a molar susceptibility of -177×10^{-6} cm^3 mol^{-1}, corresponding pretty well to the value of -169×10^{-6} cm^3 mol^{-1} calculated from the atomic increments.[12]

Discussion

The surprising composition Ag_5SiO_4 cannot be understood in terms of regular oxidation states of the composing elements, Ag^+, Si^{4+}, and O^{2-}. Therefore, one excess electron per formula unit must be present. Taking this into account, three different formulations are possible: $Ag_{10}Si^{2+}Si^{4+}O_8$ with mixed-valent silicon, $(Ag_5)^{4+}(SiO_4)^{4-}$ containing localized electrons within the silver partial structure, and $(Ag_5)^{5+}(SiO_4)^{4-}(e^-)$ exhibiting metallic conductivity due to the delocalized electrons.

The only anions present in the structure of Ag_5SiO_4 are SiO_4^{4-} tetrahedra with a geometry as expected for Si^{4+}; thus, the presence of Si^{2+} clearly can be excluded (cf. Table 4). Therefore, the excess electron per formula unit must be accommodated by the silver partial structure which would lead to an average oxidation state of +0.8 with respect to silver. The rather pronounced differences in the silver–silver distances within the crystal structure may be assigned to different valence states. The silver atoms which exhibit shorter Ag–Ag contacts to each other form an almost octahedral Ag_6 cluster. The contraction seems to be a consequence of the localization of the excess electrons in this part of the structure. A better description of this compound would thus be given by $[Ag_6]^{4+}(Ag^+)_4(SiO_4^{4-})_2$. Because of the diamagnetism, we suggest that the cluster contains two paired electrons within its A_1 skeleton orbital (total symmetry of an $Ag_6O_{16}^{12-}$ group is nearly C_{2v}, with 2 along [001]). This interpretation based on crystal chemical considerations and on physical properties gains further support by XANES (Figure 3). In general the preedge peak in AgL_3 spectra (~3.350 keV) corresponds to an excitation into empty states rooting from 4d-orbitals of silver, and the peak area is indicative for the density of unoccupied states. It is thus expected that the preedge features should be sensitive to the valence state of silver.[13] This becomes obvious by comparing the spectra of e.g. Ag_2O_3 and Ag_2O. The unusual electron richness in the silver partial structure of Ag_5SiO_4 leads to completely filled 4d states (cf. Figure 3).

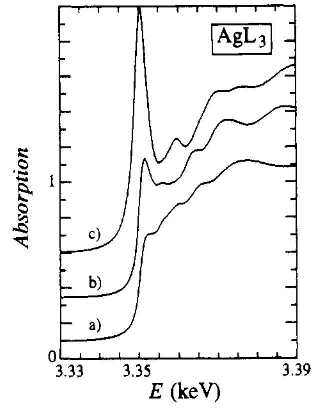

Figure 3. XANES of (a) Ag_5SiO_4, (b) Ag_2O, and (c) Ag_2O_3.

Following these interpretations Ag_5SiO_4 would contain an octahedral cluster formed by six metal atoms with the lowest number of cluster centred electrons (two) known, so far. However, this 2-electron–6-center bond seems to be too weak to explain the spontaneous formation of Ag_5SiO_4 (instead of Ag_4SiO_4 and $^1/_2Ag_2O$). So again the attractive interactions between d^{10} configurated coin metal ions come into play as an strengthening component of the silver–silver bonding.

The same type of Ag_6^{4+} cluster has been found in Ag_3O[4], in $Ag_6Ge_{10}P_{12}$[14] (admittedly with prevalent metallic bonding), and in Ag_5GeO_4[7]. This might be taken as an indication for a particular tendency of silver to form such units, and we feel encouraged to try the synthesis of further solids containing silver clusters.

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Supplementary Material Available: Tables of crystallographic details (Table S1) and thermal displacement parameters (Table S2) (2 pages). Ordering information is given on any current masthead page.

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