Crystal structure of pentasilver chloride silicate, $\text{Ag}_5[\text{SiO}_4]\text{Cl}$

Wilhelm Klein^{I,II} and Martin Jansen^{*,II}

^I Technische Universität München, Forschungsneutronenquelle Heinz Maier-Leibnitz (FRM II), Lichtenbergstr. 1, 85747 Garching, Germany

^{II} Max-Planck-Institut für Festkörperforschung, Heisenbergstr. 1, 70569 Stuttgart, Germany

Received March 13, 2009; accepted and available on-line April 1, 2009; CSD no. 409992

Abstract

$\text{Ag}_{20}\text{Cl}_4\text{O}_{16}\text{Si}_4$, monoclinic, $P12_1/c1$ (no. 14), $a = 12.8931(8) \text{ \AA}$, $b = 19.092(1) \text{ \AA}$, $c = 12.7599(7) \text{ \AA}$, $\beta = 118.356(1)^\circ$, $V = 2764.0 \text{ \AA}^3$, $Z = 4$, $R_g(F) = 0.038$, $wR_{\text{ref}}(F^2) = 0.107$, $T = 293 \text{ K}$.

Source of material

Single crystals of $\text{Ag}_5\text{SiO}_4\text{Cl}$ have been prepared *via* reaction of AgCl and elemental Ag and Si under elevated oxygen pressure using 1 ml H_2O as an accelerator. The mixture was annealed for 60 h in gold crucibles placed in stainless steel autoclaves [1]. The reaction temperature and oxygen pressure were 823 K and 170 MPa, respectively.

Discussion

In the course of our systematic studies of ternary silver oxides, among others we have investigated the system Ag-Si-O . Some interesting results have been obtained e.g. the first tetrasilicate [2], the subvalent (with respect to the silver part) Ag_5SiO_4 [3], and recently the formally most simple orthosilicate, Ag_4SiO_4 [4]. At conditions suitable also for synthesis of the latter compound but in presence of a chlorine source [5] $\text{Ag}_5\text{SiO}_4\text{Cl}$ has been obtained. The crystal structure is constituted of Cl atoms and isolated, slightly distorted SiO_4 tetrahedra, all separated by Ag cations. The SiO_4 tetrahedra form rods along $[1\ 0\ \bar{1}]$, as shown in the figure. All tetrahedra of a rod are oriented with one apex in the same direction so one threefold axis of all tetrahedra is nearly parallel to the $[1\ 0\ \bar{1}]$ direction. The rods are packed in an almost hexagonal close manner, and every two rod layers perpendicular to the b axis the tetrahedral orientation changes by 180° . Although both the unit cell parameters as well as the tetrahedral packing are close to trigonal symmetry, it has to be noted that the pseudotrigonal axes, i.e. the b -axis and the rod axis, are not parallel but perpendicular. All O atoms are bound to one Si atom and two or three Ag atoms, while the Cl atoms are only coordinated to Ag with one or two short and four longer contacts. The Ag atoms are either in almost linear coordination by two O atoms or in trigonal planar by one Cl and two O atoms. The composition of the title compound resembles to the formerly obtained subvalent Ag_5SiO_4 , where discrete Ag_6^{4+} octahedra with Ag-Ag contacts shorter than distances in elemental silver are found, besides SiO_4 tetrahedra and isolated Ag cations in common coordination [3]. In the new compound, after formal addition of one Cl per formula to this composition, no short Ag-Ag contacts are observed. According to thermal analysis, $\text{Ag}_5\text{SiO}_4\text{Cl}$ starts to decompose at 460°C , slightly above Ag_4SiO_4 [4].

Table 1. Data collection and handling.

Crystal:	red block, size $0.1 \times 0.1 \times 0.1 \text{ mm}$
Wavelength:	$\text{Mo } K_\alpha$ radiation ($0.71073 \text{ \AA}$)
μ :	144.24 cm^{-1}
Diffractometer, scan mode:	SMART APEX, Bruker AXS, ω
$2\theta_{\text{max}}$:	70.02°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	42905, 6977
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 5654
$N(\text{param})_{\text{refined}}$:	398
Programs:	SHELXS-97 [6], Jana2006 [7], DIAMOND [8]

* Correspondence author (e-mail: M.Jansen@fkf.mpg.de)

Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Ag(1)	4e	0.07520(5)	0.24815(2)	0.41686(5)	0.0294(3)	0.0182(2)	0.0292(3)	−0.0034(2)	0.0070(2)	−0.0034(2)
Ag(2)	4e	0.70229(5)	0.10752(3)	0.04801(5)	0.0200(2)	0.0351(3)	0.0231(2)	−0.0012(2)	0.0039(2)	−0.0055(2)
Ag(3)	4e	0.69287(5)	0.03756(3)	0.80237(5)	0.0339(3)	0.0261(2)	0.0235(2)	0.0047(2)	0.0147(2)	0.0067(2)
Ag(4)	4e	0.56725(5)	0.24826(3)	0.42946(5)	0.0318(3)	0.0230(3)	0.0323(3)	0.0066(2)	0.0098(2)	0.0066(2)
Ag(5)	4e	0.19344(4)	0.10033(3)	0.55641(4)	0.0218(3)	0.0306(3)	0.0204(2)	0.0041(2)	0.0015(2)	0.0001(2)
Ag(6)	4e	0.44021(4)	0.10729(3)	0.29353(5)	0.0184(2)	0.0320(3)	0.0215(2)	0.0034(2)	0.0029(2)	−0.0001(2)
Ag(7)	4e	0.94141(4)	0.10012(3)	0.79519(5)	0.0219(3)	0.0303(3)	0.0233(2)	0.0006(2)	0.0037(2)	−0.0050(2)
Ag(8)	4e	0.94021(5)	0.03908(3)	0.05765(5)	0.0256(3)	0.0253(2)	0.0315(3)	−0.0051(2)	0.0150(2)	−0.0053(2)
Ag(9)	4e	0.94393(5)	0.04021(3)	0.55823(4)	0.0326(3)	0.0256(2)	0.0236(2)	0.0062(2)	0.0163(2)	0.0063(2)
Ag(10)	4e	0.19112(5)	0.04614(3)	0.81431(5)	0.0240(3)	0.0310(3)	0.0305(3)	−0.0100(2)	0.0133(2)	−0.0049(2)
Ag(11)	4e	0.43317(7)	0.03980(4)	0.06113(7)	0.0497(4)	0.0526(4)	0.0754(5)	0.0247(3)	0.0408(4)	0.0435(4)
Ag(12)	4e	0.19664(5)	0.05639(3)	0.32915(5)	0.0416(3)	0.0273(3)	0.0365(3)	0.0076(2)	0.0227(3)	0.0100(2)
Ag(13)	4e	0.54006(7)	0.19796(3)	0.68326(7)	0.0650(5)	0.0288(3)	0.0673(5)	−0.0029(3)	0.0512(4)	−0.0081(3)
Ag(14)	4e	0.79953(6)	0.24740(3)	0.72487(6)	0.0462(4)	0.0264(3)	0.0353(3)	−0.0084(2)	0.0168(3)	−0.0026(2)
Ag(15)	4e	0.33231(7)	0.20334(3)	0.99470(7)	0.0580(4)	0.0236(3)	0.0600(4)	0.0038(2)	0.0424(4)	0.0065(2)
Ag(16)	4e	0.26037(6)	0.24600(3)	0.70911(6)	0.0347(3)	0.0278(3)	0.0567(4)	0.0030(2)	0.0155(3)	0.0103(3)
Ag(17)	4e	0.82841(8)	0.19326(3)	0.46273(8)	0.0745(5)	0.0273(3)	0.0747(5)	0.0064(3)	0.0580(4)	0.0014(3)
Ag(18)	4e	0.99868(7)	0.19730(3)	0.14585(7)	0.0520(4)	0.0265(3)	0.0687(5)	−0.0024(2)	0.0404(4)	0.0029(3)
Ag(19)	4e	0.67068(6)	0.05271(3)	0.28340(6)	0.0399(3)	0.0266(3)	0.0505(4)	−0.0098(2)	0.0296(3)	−0.0068(2)
Ag(20)	4e	0.43063(8)	0.04573(4)	0.55860(7)	0.0751(5)	0.0543(4)	0.0725(5)	−0.0448(4)	0.0560(5)	−0.0338(4)
Si(1)	4e	0.6789(1)	0.10260(8)	0.5654(1)	0.0124(7)	0.0166(7)	0.0121(7)	0.0012(5)	0.0048(6)	0.0007(5)
O(11)	4e	0.6000(4)	0.0676(2)	0.4342(4)	0.022(2)	0.026(2)	0.015(2)	0.004(2)	0.006(2)	−0.001(2)
O(12)	4e	0.6070(4)	0.1000(2)	0.6412(4)	0.025(2)	0.022(2)	0.021(2)	0.002(2)	0.016(2)	0.002(2)
O(13)	4e	0.8015(4)	0.0587(2)	0.6360(4)	0.023(2)	0.017(2)	0.023(2)	0.006(2)	0.010(2)	0.002(2)
O(14)	4e	0.7082(4)	0.1843(2)	0.5519(4)	0.027(2)	0.015(2)	0.022(2)	−0.001(2)	0.010(2)	0.002(2)
Si(2)	4e	0.4250(1)	0.10725(8)	0.8229(1)	0.0131(7)	0.0139(7)	0.0161(7)	0.0001(5)	0.0057(6)	0.0012(5)
O(21)	4e	0.5525(4)	0.0698(2)	0.8934(4)	0.021(2)	0.026(2)	0.031(2)	0.004(2)	0.009(2)	−0.004(2)
O(22)	4e	0.3496(4)	0.0624(2)	0.6997(4)	0.022(2)	0.016(2)	0.017(2)	0.003(2)	0.002(2)	−0.001(2)
O(23)	4e	0.3543(4)	0.1062(2)	0.9005(4)	0.022(2)	0.024(2)	0.024(2)	0.000(2)	0.014(2)	0.001(2)
O(24)	4e	0.4393(4)	0.1882(2)	0.7917(4)	0.022(2)	0.016(2)	0.025(2)	−0.001(2)	0.009(2)	0.001(2)
Si(3)	4e	0.9332(1)	0.10047(8)	0.3138(1)	0.0125(7)	0.0125(7)	0.0130(7)	−0.0011(5)	0.0037(6)	−0.0004(5)
O(31)	4e	1.0606(4)	0.1385(2)	0.3915(4)	0.014(2)	0.020(2)	0.021(2)	−0.003(2)	0.002(2)	−0.000(2)
O(32)	4e	0.8620(4)	0.0957(2)	0.3898(4)	0.020(2)	0.022(2)	0.025(2)	0.001(2)	0.014(2)	0.002(2)
O(33)	4e	0.8604(4)	0.1466(2)	0.1937(4)	0.014(2)	0.022(2)	0.019(2)	−0.001(2)	0.004(2)	−0.001(2)
O(34)	4e	0.9582(4)	0.0220(2)	0.2791(4)	0.018(2)	0.020(2)	0.018(2)	0.002(2)	0.008(2)	−0.002(2)
Si(4)	4e	0.1739(1)	0.10460(8)	0.0656(1)	0.0165(8)	0.0133(7)	0.0150(7)	0.0005(5)	0.0066(6)	0.0011(5)
O(41)	4e	0.2934(3)	0.1509(2)	0.1403(4)	0.012(2)	0.027(2)	0.014(2)	−0.008(2)	−0.001(2)	−0.004(2)
O(42)	4e	0.0971(4)	0.1429(2)	−0.0630(4)	0.019(2)	0.018(2)	0.018(2)	−0.003(2)	0.002(2)	−0.003(2)
O(43)	4e	0.0990(4)	0.0998(2)	0.1395(4)	0.020(2)	0.027(2)	0.025(2)	−0.003(2)	0.014(2)	−0.006(2)
O(44)	4e	0.2100(4)	0.0262(2)	0.0418(4)	0.029(2)	0.019(2)	0.025(2)	0.001(2)	0.015(2)	−0.003(2)
Cl(1)	4e	0.3358(2)	0.17290(8)	0.4338(2)	0.0281(8)	0.0230(7)	0.0335(8)	−0.0032(6)	0.0149(7)	−0.0042(6)
Cl(2)	4e	0.0735(2)	0.18130(9)	0.6708(2)	0.0309(9)	0.0263(7)	0.0324(8)	0.0015(6)	0.0147(7)	0.0005(6)
Cl(3)	4e	0.5788(1)	0.17058(9)	0.1727(2)	0.0243(8)	0.0222(7)	0.0420(9)	−0.0003(6)	0.0148(7)	0.0009(6)
Cl(4)	4e	0.8077(2)	0.17905(9)	0.9026(2)	0.042(1)	0.0254(7)	0.0290(8)	−0.0028(7)	0.0168(7)	−0.0007(6)

Acknowledgments. We gratefully acknowledge E.-M. Peters for performing the EDX analyses and Dr. J. Nuss for recording the X-ray single crystal diffraction data.

References

- Linke, C.; Jansen, M.: Über Ag₂SnO₃, das erste Silberstannat. *Z. Anorg. Allg. Chem.* **623** (1997) 1441–1446.
- Jansen, M.; Keller, H.-L.: Ag₁₀Si₄O₁₃, das erste Tetrasilicat. *Angew. Chem.* **91** (1979) 500; *Angew. Chem. Int. Ed. Engl.* **18** (1979) 464.
- Linke, C.; Jansen, M.: Subvalent Ternary Silver Oxides: Synthesis, Structural Characterization, and Physical Properties of Pentasilver Orthosilicate, Ag₅SiO₄. *Inorg. Chem.* **33** (1994) 2614–2616.
- Klein, W.; Jansen, M.: Synthesis and Crystal Structure of Silver Nesosilicate, Ag₄SiO₄. *Z. Anorg. Allg. Chem.* **634** (2008) 1077–1081.
- Curda, J.; Peters, E.-M.; Klein, W.; Jansen, M.: Crystal structure of silver chloride chromate(VI), Ag₃ClCrO₄. *Z. Kristallogr. NCS* **216** (2001) 180.
- Sheldrick, G. M.: SHELXS-97. Program for the Solution of Crystal Structures. University of Göttingen, Germany 1997.
- Petricke, V.; Dusek, M.; Palatinus L.: Jana2006. Structure Determination Software Programs. Institute of Physics, Praha, Czech Republic.
- Brandenburg, K.: DIAMOND. Visual Crystal Structure Information System. Version 3.1e. Crystal Impact, Bonn, Germany 1998.