On the Intergrowth of the Silver Oxides Ag_2O_3 and Ag_3O_4

Peter Fischer and Martin Jansen*

Institut für Anorganische Chemie der Universität Bonn, Gerhard-Domagk-Strasse 1, D-5300 Bonn 1, Germany

Fischer, P. and Jansen, M., 1991. On the Intergrowth of the Silver Oxides Ag_2O_3 and Ag_3O_4. – Acta Chem. Scand. 45: 816–819.

A new silver oxide has been detected by cyclic voltammetry and X-ray powder techniques. It is formed during the anodic oxidation of aqueous silver (I) electrolytes $[c(Ag^+) = 0.3$ mol dm^{-3}, $c(F^-) = 0.3$ mol dm^{-3}, $c(ClO_4^-) = 1.4$ mol dm^{-3}, $i = 50$ mA $cm^{-2}]$. The new phase is shown to be an intergrowth of Ag_3O_4 and Ag_2O_3 with the hypothetical composition range Ag_xO_y; $3/4 > x/y > 2/3$.

Dedicated to Professor Sten Andersson on the occasion of his 60th birthday.

Recently, we have shown the anodic oxidation of aqueous silver(I) solutions to be a convenient and efficient route for the synthesis of highly oxidized binary silver oxides in an extremely pure, and at the same time well defined, crystalline state. The crystal structures and some of the properties of the previously unknown oxides Ag_2O_3[1,2] and Ag_3O_4[3,4] have been determined, and AgO[5] has been prepared for the first time with stoichiometric composition and as single crystals. The crystal structure of the latter, as previously derived from powder data, has been confirmed and refined by applying X-ray single-crystal techniques.

Ag_2O_3 contains silver in square planar coordination with oxygen, which was expected because of the d^8 electron configuration of Ag^{3+}. Ag_3O_4 is a mixed-valent compound of type (III) according to the classification of Robin and Day:[6] the surroundings of all silver atoms are virtually equivalent and square planar. This is indicative of Ag^{3+}/Ag^{2+} mixed valency (in contrast to $AgO \equiv Ag^+Ag^{3+}O_2$). Ag_3O_4 is the first and so far only paramagnetic silver oxide, the paramagnetic region ranging down to about 50 K. Thus Ag_3O_4 exhibits structural and electronic properties that are estimated to be important for superconductivity in ceramic copper oxides. As combinations of the square planar groups containing Ag^{2+} and Ag^{3+} seem topologically possible in almost arbitrary ratios, such oxides might be of interest as models for the copper systems mentioned. In order to being able to vary the Ag^{2+}/Ag^{3+} ratio purposely we have investigated the processes occurring at electro-crystallization of the silver oxides by cyclic voltammetry.[7] From these investigations we have concluded that the oxides deposited at the anode can be oxidized and reduced reversibly in the solid state. For the cathodic reactions in particular, the different silver oxide species corresponding to each particular peak in the cyclic voltammogram (CV) were identified by X-ray powder techniques.

In addition to the known phases AgO, Ag_3O_4 and Ag_2O_3, another oxide appeared (at 1.015 V) showing new reflections in the powder diagram. In addition, $Ag_7O_8ClO_4$ was identified unambiguously.

Experimental

Cyclic voltammetry. Potentiodynamic studies were carried out in a thermostatted cell which is normally used for polarography (Metrohm, Herisau). The platinum working electrode was a wire of diameter 0.3 mm and length 20 mm, while the counter-electrode consisted of a platinum wire of diameter 1 mm. All potentials were measured against an Ag^+/Ag reference electrode, with $c(Ag^+)$ for the reference being the same as within the electrolyte in the cell. The equivalent potentials vs. a normal hydrogen electrode (NHE) were calculated using Nernst's law. Before starting the potential scans, electrolyses were carried out with a total charge of 300 mA s using various anodic current densities at the working electrode to deposit silver oxide phases. Potential scan experiments involved the use of a potentiostat/galvanostat (PAR model 363) and a digital voltage programmer (Intelligent Control PRODIS 1/161) in conjunction with an $X-Y$ recorder (Linseis LY 1600). In all voltammetric studies a sweep rate of 20 mV s^{-1} was used. The temperature was held at $-2\,°C$ to avoid thermal decomposition of the silver oxides. The electrolyte was an aqueous silver perchlorate solution with the addition of a constant amount of 0.3 mol dm^{-3} sodium fluoride. The Ag^+ concentrations were varied between 0.1–1.0 mol dm^{-3}; the ionic strengths $I = \frac{1}{2}\Sigma c_i z_i^2$ were fixed at a value of 2.0 by adding appropriate amounts of sodium perchlorate to the solution.

X-ray powder diffraction. To identify and characterize the crystalline silver oxide phases which had formed at the working electrode, the platinum wire was cut off, washed
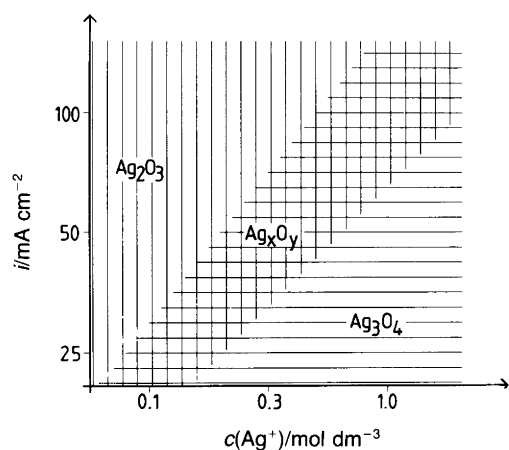
* To whom correspondence should be addressed.

Fig. 1. Dependence of the product composition on current density and Ag concentration.
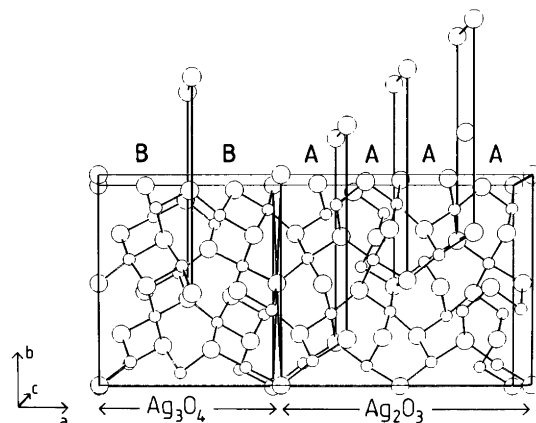

Fig. 2. One possible intergrowth Ag_xO_y consisting of complete cells of Ag_3O_4 (left part) and Ag_2O_3 (right part). The interconnecting planes bordering the subunits are marked with thick lines.

twice with bidestilled water (0 °C) and mounted on the goniometer head of a powder diffractometer (Stoe, STADI P). A range from $2\theta = 25$ to $55°$ was recorded using Cu $K_{\alpha 1}$ radiation (Ge monochromator) and a position-sensitive detector (PSD, aperture in $2\theta = 30°$) having an angular resolution of $0.04°$.

Results and discussion

With increasing current density and decreasing Ag^+-concentration higher oxides are formed, starting with Ag_3O_4, followed by the new phase 'Ag_xO_y' mentioned initially, and finally Ag_2O_3. Only when Ag^+ concentrations >0.6 mol dm^{-3} are applied is the new clathrate phase $Ag_7O_8ClO_4$ formed. This is verified by cyclic voltammetry as well as by X-ray powder investigations. The intensities in the powder diagrams are partly in error owing to the preferred orientation of the silver oxide crystals with respect to the platinum wire. In spite of this fact the phases Ag_3O_4, Ag_2O_3 and $Ag_7O_8ClO_4$ have been unambiguously identified because of the good agreement between the angular positions observed and those determined independently using powders with random distributions of crystallites. At 50 mA cm^{-2} [$c(Ag^+) = 0.30$ mol dm^{-3}] the new binary oxide appears, showing reflections that are mostly similar to those of

Ag_2O_3 and Ag_3O_4, together with a few additional ones, especially an intense broad line at $2\theta = 27.2°$. There are two possibilities of interpretation: either a new compound is being formed simultaneously with Ag_3O_4 and Ag_2O_3 which has a very simple crystal structure that yields only a few lines in the powder diagram, or the crystal structure of the new phase is very similar to that of Ag_2O_3 and/or Ag_3O_4.

The latter assumption is supported by three facts: firstly, the broad line at $2\theta = 27.2°$ is very close to intense lines of Ag_2O_3 (26.7°) and Ag_3O_4 (27.7°); secondly, the cathodic peak of Ag_xO_y in the cyclic voltammogram appears almost in the middle of those of Ag_2O_3 and Ag_3O_4, indicating that the free enthalpy of formation of Ag_xO_y might be an average of the free enthalpies of formation of Ag_2O_3 and Ag_3O_4; thirdly, Ag_xO_y is formed under electrolytic conditions when Ag_2O_3 and Ag_3O_4 are expected to grow together at the anode (Fig. 1).

This leads to the conclusion that Ag_xO_y might be an intergrowth of Ag_2O_3 and Ag_3O_4. As a topological precondition, this interpretation would demand metric compatibility of the Ag_2O_3 and Ag_3O_4 lattices along at least two directions. Indeed, it is possible to transform the monoclinic cell of Ag_3O_4 into a pseudo-orthorhombic that fulfils this condition rather well (Table 1). In addition, planes

Table 1. Relationships between the lattices of Ag_2O_3, Ag_3O_4 and Ag_xO_y.

Parameter	Ag_3O_4	Transformation matrix	Ag_3O_4 transformed unit cell	Ag_2O_3	Mismatch / %
a/Å	3.5787	$\begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 2 \\ 1 & 0 & 0 \end{bmatrix}$	9.208	12.869	–
b/Å	9.2079		10.915^a	10.490^a	4.0
c/Å	5.6771		3.576^a	3.664^a	2.5
α/°	90		88.89	90	1.2
β/°	106.14		90	90	0
γ/°	90		90	90	0

[a] Bold numbers indicate the lattice constants in the compatible directions.

Table 2. Subunits of the parent cells building up Ag_xO_y.

Subunit	Parent compound	Shifts of the interface layers	
		Δy	Δz
A	Ag_2O_3	0.1756	−0.2488
B	Ag_3O_4	−0.0744	0.0012

parallel to (100) containing atoms with the same first sphere of coordination both in Ag_3O_4 and Ag_2O_3, serving as interfaces to interconnect parts of these two oxides, are present. These planes are defined by oxygen atoms in Ag_3O_4 that do not belong to the Ag_2O_2 rings (position 4e in $P2_1/c$),[4] and all oxygen atoms in Ag_2O_3 with coordination number three (position 16b in $Fdd2$).[2] In Ag_2O_3 there are four symmetrically equivalent interfaces per unit cell, and two in Ag_3O_4 (Fig. 2).

Next to the planes as described and depicted in Fig. 2, within each of the structures there is another set of planes with identical topology that intersect the structures in the same manner and might serve as interfaces. The resulting subunits (four identical ones in Ag_2O_3, type A, and two in Ag_3O_4, type B) are compiled in Table 2. The bordering planes of each subunit are symmetrically equivalent. As can be seen from Fig. 2 and Table 2, they are shifted with

respect to each other within the *bc*-plane. The exact symmetry operation transforming one plane into the next is the *d*-type mirror glide plane perpendicular to the *b*-axis in Ag_2O_3, and a 2_1 screw axis parallel to the *a*-direction in the transformed cell of Ag_3O_4. The subunits may be combined to form oxides Ag_xO_y with $2/3 < x/y < 3/4$. In order to maintain translational symmetry, i.e. to be able to define a new unit cell, the orientations of both the interfaces that border the new unit cell and the first sphere of coordination of the oxygen atoms involved have to be equal. This condition is fulfilled exactly if the numbers of subunits A and B building up the new structure are both even. If the sum of shifts Δy and Δz is zero or $n/2$ the unit cell of the intergrowth remains pseudo-orthorhombic, with *b* and *c* lattice constants as given in Table 1. Otherwise the *a*-direction of the intergrowth is inclined with respect to that of the parent cells. Table 3 shows all distinguishable intergrowths Ag_xO_y consisting of up to six subcells of the respective parent structures.

Powder diagrams of selected intergrowth structures as described above have been calculated using the arithmetic averages of the *b* and *c* lattice constants of pure Ag_2O_3 and Ag_3O_4 (transformed unit cell), respectively. Fig. 3 shows an experimental powder diagram and calculated patterns for the combinations BAABAA and BABAAA. Both calculations simulate the observed diagram to a considerable extent; in particular the additional broad and intense line at
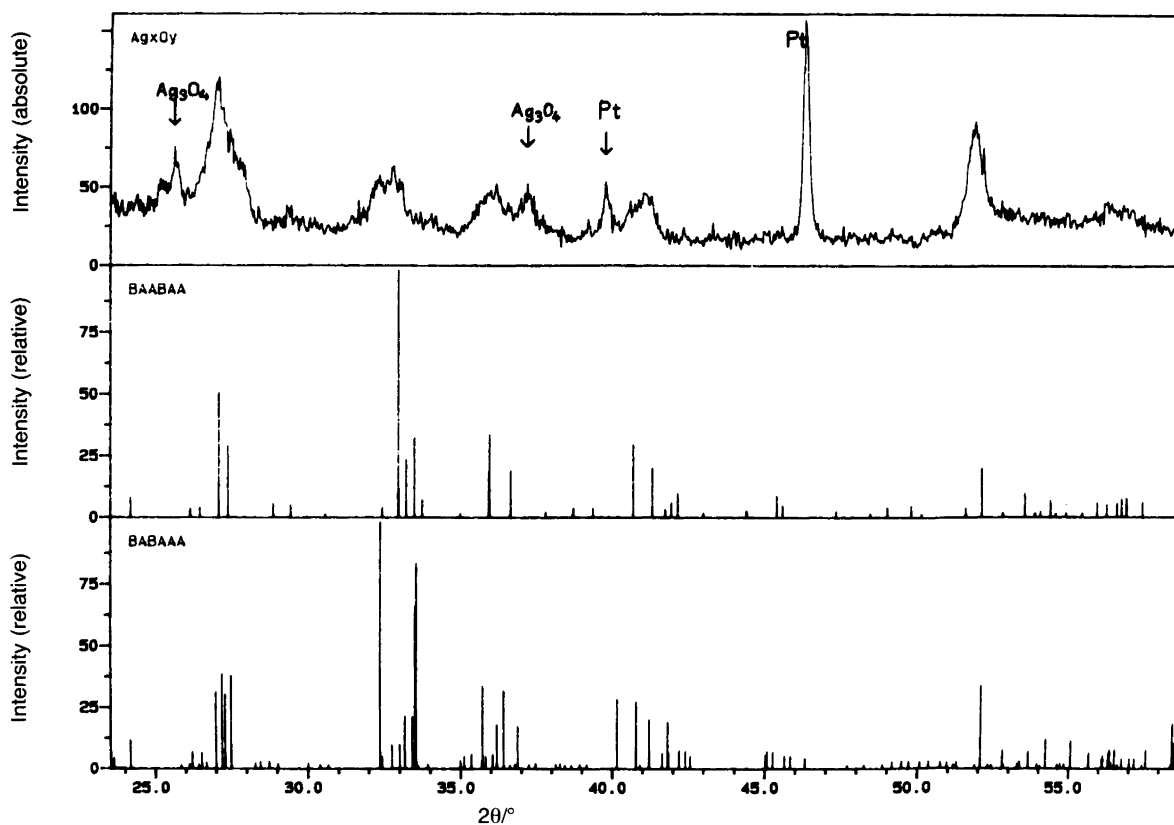

Fig. 3. Observed powder diagram of Ag_xO_y in comparison with calculated patterns of structure models for Ag_xO_y.

Table 3. Distinct combinations of up to six A- or B-subunits.

Combinations of subunits	Lattice constant of the resulting unit cell, $a/\text{Å}$		Stoichiometry
AA $(=\frac{1}{2} Ag_2O_3)$			
BB $(= Ag_3O_4)$			
AABB	16.532	t[a]	Ag_8O_{11}
ABAB	16.270	t	Ag_8O_{11}
AAAABB	22.077	o	Ag_5O_7
AAABAB	22.605	t	Ag_5O_7
AABAAB	22.077	o	Ag_5O_7
AABBBB	25.420	t	$Ag_{14}O_{19}$
ABABBB	25.250	t	$Ag_{14}O_{19}$
ABBABB	24.916	t	$Ag_{14}O_{19}$

[a] t, triclinic; o, pseudo-orthorhombic.

$27.2°$ (2θ) and the weak one at $29.4°$ are reproduced by most combinations of subunits.

The experimental data available seem to give sufficient support for the existence of intergrowths between Ag_2O_3 and Ag_3O_4. However, so far we are not able to differentiate between particular combinations of subunits. Unfortunately, the highly recommended analytical tool for the solution of this type of structural problem, high-resolution transmission electron microscopy, is not applicable because of the low thermal stability of the compounds under consideration.

A similar situation of intergrowth is reported for electrochemically deposited modifications of manganese dioxide.[8] Two modifications, ramsdellite and β-MnO_2, are found to grow epitaxially on each other. The intergrowth is named γ-MnO_2. The topological building principal is virtually the same as found for Ag_2O_3 and Ag_3O_4. Intergrowths consisting of Tl_2O_3 and PbO_2 as parent compounds have been described by Switzer et al.[9] In this case the compositions of the intergrowths were found to be dependent on the current density in a similar manner as in the silver oxide systems.

References

1. Standke, B. and Jansen, M. Angew. Chem. 97 (1985) 114; Angew. Chem., Int. Ed. Engl. 24 (1985) 118.
2. Standke, B. and Jansen, M. Z. Anorg. Allg. Chem. 535 (1986) 39.
3. Standke, B. and Jansen, M. Angew. Chem. 98 (1986) 78; Angew. Chem., Int. Ed. Engl. 25 (1986) 77.
4. Standke, B. and Jansen, M. J. Solid State Chem. 67 (1987) 278.
5. Jansen, M. and Fischer, P. J. Less-Common Metals 137 (1988) 123.
6. Robin, M. B. and Day, P. Adv. Inorg. Chem. Radiochem. 10 (1967) 247.
7. Fischer, P. and Jansen, M. Solid State Ionics. In press.
8. de Wolff, P. M. Acta Crystallogr. 12 (1959) 341.
9. Switzer, J. A., Shane, M. J. and Philipps, R. J. Science 247 (1990) 444.