$Ag_2Cu_2O_3$: The First Silver Copper Oxide[**]

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Among cuprate superconductors the highest critical temperatures T_c are shown by mercury-containing derivatives.[1–3] These complex oxides are superior to thallium-based superconductors, which in turn were an improvement over the family of bismuth superconductors. This heavy metal trend shows an undesired but tenacious presence of toxic metals in superconducting materials,[4] and continuing efforts to design and prepare more benign high-T_c superconductors have been made.

One of the most promising strategies in this sense was the substitution of silver for mercury. The ions Ag^I and Hg^{II} show similar crystal chemistry, have comparable ionic radii, and tend to occupy linear coordination environments such as that found in the new mercury-based superconductors. Many attempts have been made in laboratories around the world to prepare layered oxides related to those in the mercury family, but containing silver. For this purpose, solid-state reactions under high pressures of oxygen have generally been used owing to the low thermal stability of silver oxides.[5] This approach has not led to the isolation of a silver copper oxide, although a new series of copper/carbonate superconductors prepared under high pressure was discovered.[6, 7]

As a first step into the investigation of the crystal chemistry of complex silver copper oxides, we considered the synthesis and study of simple ternary oxides. Several database searches failed to show any precedent of such an oxide, natural nor synthetic.[8] Consequently we decided to tackle this problem as a basic aspect of fundamental chemical interest as well as of potential application in the chemistry of cuprate superconductors.

As an alternative to methods with high oxygen pressures, we concentrated on the use of low temperatures for the synthesis of the new oxide in order to avoid the anticipated decomposition problems. In addition to the common Ag_2O and CuO, several silver oxides[9–11] and copper oxides[12–14] have been obtained by electrochemical deposition from aqueous solutions or molten hydroxides fluxes. The electrochemical potential is a tool for controlling the oxidation state.[11, 13] We have used basic aqueous media or molten hydroxide fluxes to precipitate the precursor to the new oxide $Ag_2Cu_2O_3$ (see the Experimental Section); the application of electrochemical potential was not necessary for the isolation of this particular oxide.

Chemical and thermogravimetric analyses (TGA) indicated a formula of $Ag_2Cu_2O_3$ for the new compound (53.4 % Ag, 33.0 % Cu by atomic absorption; 12.3 % O by TGA; expected values for $Ag_2Cu_2O_3$: 55.2 % Ag, 32.5 % Cu, 12.3 % O). Furthermore, energy dispersive X-ray analyses (EDX) carried out in the analytical electron microscope (TEM) showed a constant ratio for Ag and Cu in all 20 microcrystals analyzed, which confirmed the isolation of a pure homogeneous phase. The thermal stability of this new oxide is enhanced with respect to that of Ag_2O or even CuO. Thus, TGA shows the decomposition of $Ag_2Cu_2O_3$ at 260 °C (inflection point of the weight loss), whereas a mixture of Ag_2O and CuO under the same experimental conditions presents the two corresponding decomposition processes at 100 and 225 °C, respectively. The reasons for this can be found in the structural features described below.

X-ray powder diffraction patterns were indexed in the tetragonal system ($a = 5.89$ Å, $c = 10.7$ Å), whereas electron diffraction studies allowed the reconstruction of the reciprocal lattice and the spotting of systematic absences which were unambiguously consistent with space group $I4_1/amd$. The structure of $Ag_2Cu_2O_3$ was refined by the Rietveld method (Figure 1) with the structure of the mineral paramelaconite (Cu_4O_3) as a starting model.[15] The structure of $Ag_2Cu_2O_3$ consists of alternating chains of edge-sharing square-planar CuO_4 units and zigzag chains of AgO_2 units with linearly coordinated silver ions. These chains run parallel to *a* and *b* consecutively as we move along the *c* direction (Figure 2). This structure is related to that of PdO, although in $Ag_2Cu_2O_3$ silver is linearly coordinated and the alternation of Cu and Ag leads to a doubling of the unit cell in all three directions of space. The coordination of the metals is typical of Cu^{II} and Ag^I, but there are several unique features. There are two nonequivalent oxygen atoms (O1, bonded to two Cu and two Ag atoms, and O2, bonded to four Cu atoms). The square-planar coordination of Cu^{II} suffers a concurrent rhombic distortion with a short Cu–O1 bond and a longer Cu–O2 bond. The Ag–O1 bond (2.13(1) Å) is correspondingly longer than those found in silver oxides with analogous linear

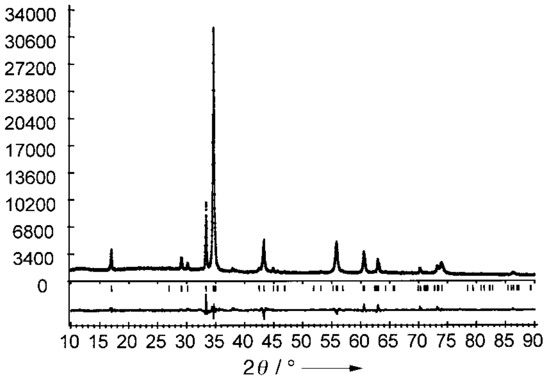

Figure 1. Powder X-ray diffraction pattern and Rietveld analysis for $Ag_2Cu_2O_3$. The dots correspond to experimental data, the continuous line is the calculated profile, and the bottom line represents the difference between the two. The small vertical lines mark the positions of allowed Bragg reflections.

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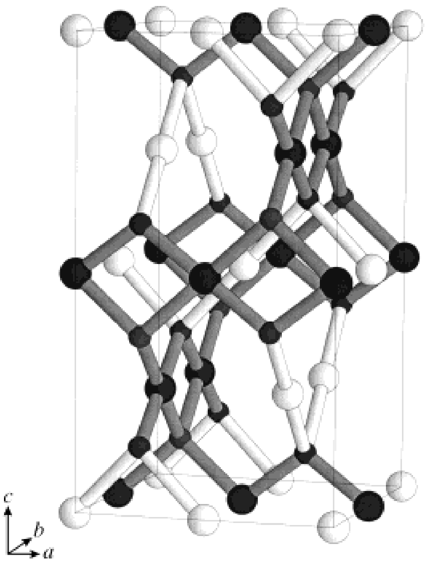

Figure 2. Crystal structure of $Ag_2Cu_2O_3$ (Ag^I: white spheres, Cu^{II}: large black spheres, O: small black spheres). Hexagonal tunnels running parallel to *a* and *b* are interconnected through tetrahedral vacant oxygen sites at (0,3/4,1/8). Bond distances [Å] and angles [°] (O1 is bonded to two Cu and two Ag atoms, and O2 to four Cu atoms): Ag–O1 2.13(1), Cu–O1 1.858(8), Cu–O2 1.9874(1), M···M = M···M′ 2.9429(2), 3.3865(1); O1-Cu-O2 100.1(3), 79.9(6), Ag-O1-Ag 87.5(4), Cu-O1-Cu 104.7(4), Cu-O2-Cu 116.860(8), 95.530(8), Ag-O1-Cu 116.2(4).

coordination (2.02–2.04 Å). The displacement of O1 towards Cu^{II} and away from Ag^I is easy to understand from a simple ionic point of view and explains the thermal stabilization of $Ag_2Cu_2O_3$ mentioned above.

The remarkable structure of $Ag_2Cu_2O_3$ presents a three-dimensional array of tunnels (parallel to *a* and *b*) with a minimum dimension corresponding to the Ag···Cu separation of 2.9429(2) Å (*a*/2). As in $YBa_2Cu_3O_6$, these metal-constrained tunnels could be most adequate for the diffusion of oxygen species. The tunnels lead directly to vacant oxygen sites, which could possibly be occupied with concomitant oxidation of Ag^I (linear) to Ag^{III} (square planar). Similarly, the structure could easily stand the elimination of one oxygen atom (O2) with the simultaneous reduction of Cu^{II} (square planar) to Cu^I (linear). This rich solid-state redox crystal chemistry should lead to a very interesting electroactive phase. Indeed, preliminary cyclic voltammograms of this novel phase confirm this potential.

On the other hand, the efficient low-temperature route to $Ag_2Cu_2O_3$ shows the way for preparing many other silver-containing cuprates of increasing complexity. In combination with the electrochemical control of oxidation states, the low-temperature synthesis and crystallization approach represents a serious alternative to the high-temperature, high-pressure search for silver-based superconductors.

Experimental Section

$Ag_2Cu_2O_3$: $Cu(NO_3)_2 \cdot 3H_2O$ (0.77 g, 3.2 mmol; Merck, p.a. 99.5%) and $AgNO_3$ (0.52 g, 3.1 mmol; Panreac, p.a. 99.98%) were dissolved in deionized water (2 mL). An aqueous solution of 3 M NaOH (4 mL) was added with stirring. The very dark green precipitate formed was isolated by filtration under vacuum and washed with water until the pH value of the filtrate was neutral. This solid precursor of unknown structure was heated in air at 90 °C for 24 hours to yield the black oxide $Ag_2Cu_2O_3$ quantitatively. Collection of powder X-ray data: $10 < 2\theta < 90°$, step 0.02°, $Cu_{K\alpha}$ radiation ($\lambda = 1.5418$ Å). Refined profile parameters: scale factor $1.155(7) \times 10^{-5}$, zero point $-0.185(2)$, $U = 0.87(4)$, $V = -0.20(3)$, $W = 0.037(5)$; η (pseudo-Voigt peak shape parameter) = 0.64(1). Crystal structure analysis of $Ag_2Cu_2O_3$: tetragonal, $a = 5.8857(3)$, $c = 10.6868(7)$ Å, space group $I4_1/amd$, origin choice 2, $Z = 4$; atom (site; fractional coordinates; B_{iso}; occupancy): Ag (*8c*; 0,0,0; 3.01(7); 2), Cu (*8d* ; 0,0,0.5; 2.7(1); 2), O1 (*8e*; 0,0.25,0.144(1); 2.2(6); 2), O2 (*4b*; 0,0.25,0.375; 1.0(8); 1). $R = 0.0391$, $R_{wp} = 0.0561$, $R_{expected} = 0.0267$, $\chi^2 = 4.41$.

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A Self-Assembled Calix[4]arene Dimer Linked through Hydrogen-Bonded 2-Ureidopyrimidin-4(1*H*)-one Groups[**]

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The self-assembly of simple fragments to form structures with designed cavities and networks mediated by noncovalent, complementary interactions such as hydrogen bonding, hydrophobic interactions, and metal–ligand bonding is a

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