Ag_2HgO_2: the first silver mercurate

Stephan Deibele, Jan Curda, Eva-Maria Peters and Martin Jansen*

Max-Planck Institut für Festkörperforschung, Heisenbergstrasse 1, D-70569 Stuttgart, Germany.
E-mail: martin@jansen.mpi-stuttgart.mpg.de

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The silver mercurate Ag_2HgO_2 is accessible by oxygen high pressure synthesis; the compound crystallizes in a novel structure type with three interpenetrating Ag–O–Hg (10, 3) nets.

Following research into high-T_c superconductivity the Hg-based copper oxides have been found to represent a remarkable group among the cuprate HTSCs: the highest transition temperature so far has been found in the system $HgBa_2Ca_{n-1}Cu_nO_{2n+2+\delta}$ at *ca*. 133.5 K. Within a short period it has been possible to synthesize series of Hg-based homologues, which differ in the number of CuO_2 layers per unit cell.[1–4] Compared to the related group of superconducting Tl-based copper oxides[5,6] the differences in the oxidation states and coordination chemistry of Tl and Hg are significant. Whereas Tl^{3+} cations prefer a distorted octahedral oxygen environment, Hg^{2+} cations are usually coordinated by two oxygen ions in a linear 'dumb-bell' like arrangement. The higher T_c of $HgBa_2CuO_{4+\delta}$ relative to $TlBa_2CuO_{5-\delta}$ could be a result of this difference in the coordination chemistry, which influences the oxygen stoichiometry in the HgO_δ and $TlO_{1-\delta}$ layers. Oxygen depletion in the mercury compound is possible, whereas the coordination of Tl^{3+} in the thallium compound only allows a small amount of oxygen depletion.

As a consequence of the presence of toxic heavy metal cations in the above mentioned superconducting phases, many attempts have been made to replace them by non-toxic cations. A promising candidate for the substitution of mercury in these layered oxides is silver, owing to its preference to linear coordination in silver oxides. However, all attemps to synthesize superconducting layered oxides containing silver instead of mercury have so far failed. As a first step towards Ag-based superconductors we have investigated the synthesis of ternary silver mercurates that might allow a partial substitution of silver for mercury by proceeding *via* solid state reactions of oxide mixtures, *e.g.* $Ag_xHgO_y/BaO/CuO$. The novel material Ag_2HgO_2 represents such a precursor, containing Ag^+ and Hg^{2+} cations in the characteristic oxygen 'dumb-bell' coordination mode.

Black crystals of Ag_2HgO_2 were prepared by solid state reaction of Ag_2O (precipitated from an aqueous $AgNO_3$ solution by adding 3 M NaOH solution) and HgO (Aldrich, 99%) under oxygen pressure. The binary oxides were mixed in a molar ratio of 1:1 and then annealed for 3–5 days in gold crucibles placed in stainless steel autoclaves. The optimized reaction temperature and oxygen pressure were 310 °C and 150 MPa, respectively. As an accelerator 3 ml water or 1 ml 1 M KOH solution for single crystalline products were added.

According to the structure determination using single-crystal diffractometer data, Ag_2HgO_2 shows a novel structure type.† Both cations are in d^{10} configuration exhibiting characteristic linear oxygen coordination (Table 1). The O–Ag–O units (Ag–O distances: 211.7 and 212.1 pm; O–Ag–O angle: 178.5°) form zigzag chains along [100] and [010]. These chains are connected *via* O–Hg–O units (Hg–O distance: 202.6 pm; O–Hg–O angle: 165.6°) to a three-dimensional net, consisting of decagons with oxygen atoms forming the knots (Fig. 1). As a consequence of these connectivities oxygen attains a threefold coordination (2 × Ag, 1 × Hg). The (10, 3) net is topologically identical to the net formed by silicon in $ThSi_2$ or by boron in α-B_2O_3.[7] In this respect, Ag_2HgO_2 can be regarded as antitypic to boronoxide. The crystal structure consists of three such identical (10, 3) nets, interpenetrating each other.

The silver partial structure in Ag_2HgO_2 shows a structural feature which is very common to silver-rich oxides: in spite of their positive charges, the silver cations form cluster-like agglomerates[8,9] with Ag–Ag distances ranging in general from *ca*. 280 to 330 pm, some may even be shorter than the distance in silver metal (289 pm). In Ag_2HgO_2 the presence of two different cations in d^{10} configuration yields an unprecedented situation. The shortest Ag–Hg distances of *ca*. 333.4 pm are somewhat larger than the Ag–Ag contacts, which range between 297.4 and 308.7 pm, however, they are still less than the van der Waals distance. This suggests the presence of weak bonding interactions between all d^{10} configurated cations in Ag_2HgO_2. Considering all Ag–Ag contacts up to the van der Waals distance for silver of *ca*. 340 pm, the silver atoms form a three dimensional network of corner-sharing tetrahedra. Includ-

Table 1 Selected bond lengths (pm) and angles (°) for Ag_2HgO_2

Hg–O^{i}	202.6(9)	Ag–Ag^{vii}	305.6(1)
Hg–O^{ii}	202.6(9)	Ag–Ag^{viii}	305.6(1)
Ag–O^{iii}	211.7(10)	Ag–Ag^{ix}	308.7(1)
Ag–O^{iv}	212.1(10)	Ag–Ag^{x}	308.7(1)
Ag–Ag^{v}	297.4(2)	Ag–Hg	333.4(2)
Ag–Ag^{vi}	304.6(2)		
O–Hg–O	165.6(6)	O–Ag–O	178.5(1)

Symmetry codes: (i) $0.5 + x, 1.5 - y, 0.25 - z$; (ii) $1.5 - y, 0.5 + x, -0.25 + z$; (iii) $-1 + y, x, -z$; (iv) $-0.5 + y, 0.5 - x, 0.25 + z$; (v) $y, x, -z$; (vi) $-y, -x, 0.5 - z$; (vii) $-0.5 + y, 0.5 - x, 0.25 + z$; (viii) $0.5 - y, 0.5 + x, -0.25 + z$; (ix) $-0.5 + x, 0.5 - y, 0.25 - z$; (x) $0.5 + x, 0.5 - y, 0.25 - z$.

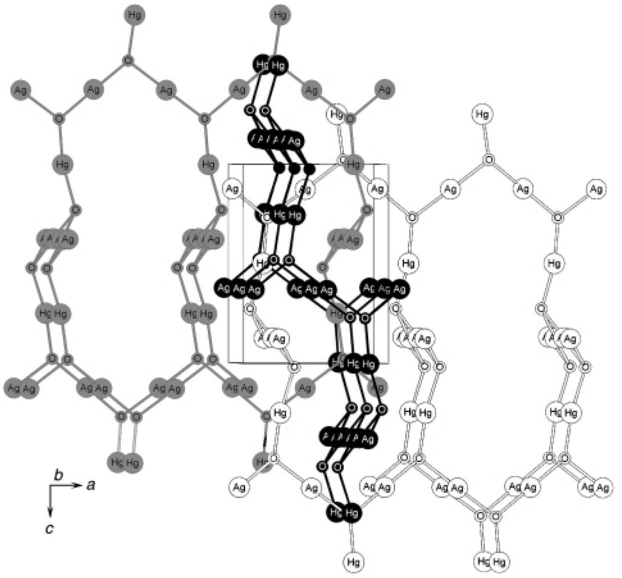

Fig. 1 Perspective view of the crystal structure of Ag_2HgO_2: the three identical interpenetrating Ag–O–Hg (10, 3) nets are colored white, gray and black.

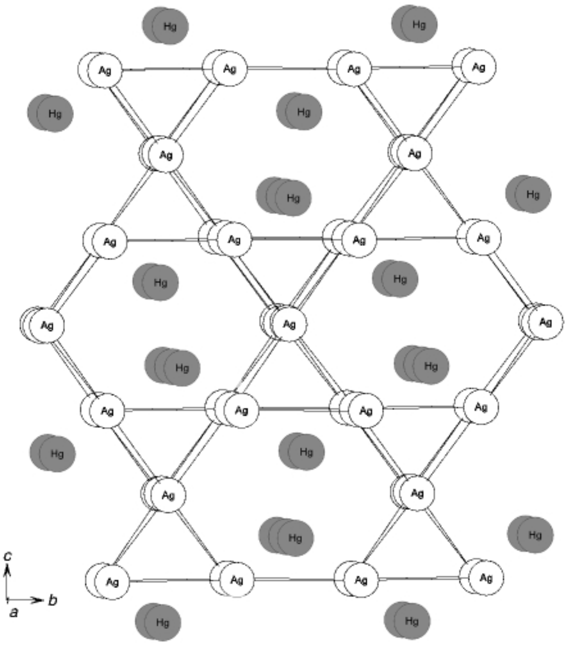

Fig. 2 The cation partial structure of Ag_2HgO_2.

ing mercury the resulting arrangement closely corresponds to Laves phase $MgCu_2$. In this description the silver cations occupy the Cu positions, whereas the mercury cations are located on the Mg positions in $MgCu_2$ (Fig. 2). Thus, the approach of describing crystal structures of extended non-metallic solids starting with the partial structures of the constituting metals applies well to Ag_2HgO_2.[10, 11]

The title compound decomposes at 340 °C in one step into its elements. According to EDX analyses (average of 20 spots), the Ag/Hg ratio is 1.95:1 and the samples are free of potassium. Measurements of the magnetic susceptibility show temperature independent diamagnetic behavior ($\chi_{obs} = -127 \times 10^6$ cm^3 mol^{-1}; $\chi_{cal} = -109 \times 10^6$ cm^3 mol^{-1}). In the temperature range investigated, 50–300 K, Ag_2HgO_2 is semiconducting ($\Delta E_{gap} = 0.24$ eV).

In our view the novel silver mercurate Ag_2HgO_2 might be of significant importance in the field of superconductivity either after doping or for use as a starting material for the synthesis of Ag/Hg/Ca/Ba/Cu/O phases.

Notes and references

† *Crystal data* for Ag_2HgO_2: $M = 448.33$, tetragonal, space group $P4_32_12$ (no. 96), $a = 617.4(1)$, $c = 842.2(1)$ pm, $U = 321.1(1) \times 10^6$ pm^3, $Z = 4$, $\mu = 59.54$ mm^{-1}, 2006 reflections measured, 388 unique ($R_{int} = 0.075$), no. of parameters 25. Final R-values for all data: $R1 = 0.032$ and $wR2 = 0.083$.

X-Ray data were collected on a single-crystal diffractometer with a CCD area detector and graphite monochromated Mo-Kα radiation at room temperature. The structure was solved using the Patterson technique and refined by full-matrix least squares on F^2. An absorption correction with the program HABITUS[12] was applied. Atomic parameters are listed in Table 2.

Table 2 Positional and isotropic displacement (U_{eq})[a] parameters for Ag_2HgO_2

Atom	x	y	z	$U_{eq}/10^{-1}$ pm^2
Hg	0.7825(1)	0.7825(1)	0	23(1)
Ag	0.0023(2)	0.2464(2)	0.1232(1)	28(1)
O	0.3756(16)	0.7525(16)	0.0207(11)	24(2)

[a] $U_{eq} = 1/3(U_{11} + U_{22} + U_{33})$.

CCDC 182/1572. See http://www.rsc.org/suppdata/cc/b0/b000400f/ for crystallographic files in .cif format.

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