High-Pressure Synthesis and Structure of a New Aurate, $CaAu_2O_4$

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High-pressure techniques provide a versatile route for the synthesis of new materials unstable under ambient conditions.[1−4] Exploratory aurate chemistry is a case in point: since gold has the highest electron affinity of all the metals,[5] the stability of gold oxide is expected to be low. Indeed Au_2O_3 entirely decomposes to metallic gold below 250 °C at the atmospheric pressure. Although high pressure may prevent the reduction of Au(III) ions until sufficient activation of the reaction is achieved, this strategy has been only sparingly applied. In a few examples, it was successful in producing Au(III) compounds under relatively low-pressure (5 GPa) conditions.[6−8] The possibility of gold as a substitute for copper in high-T_c oxide superconductor has added further incentives to research under high-pressure conditions.[9−11] Recently, $LnCu_2O_4$ (Ln = rare earth metals) has been described as a new spinel-related class of cuprates.[12,13] We report here the synthesis of an analogous composition, $CaAu_2O_4$, using a uniaxial split-sphere high-pressure apparatus (USSA 2000) and its structural characterization.[14]

A mechanical mixture of reagent grade CaO and Au_2O_3 in a 1:1 molar ratio was placed in a sealed Au capsule with an inside diameter of 3.2 mm and a wall thickness of 0.1 mm. A yellowish green powder with a unique X-ray diffraction pattern was obtained from a high-pressure run held at 12 GPa and 1000 °C for 3 h. The run was terminated by shutting the power off and slowly releasing the pressure. After recovery, the electron probe microanalysis indicated an oxide ratio of 0.96(6) CaO:1.01(2) Au_2O_3, referred to four oxygens. Details of the cell assembly along with the temperature and the pressure calibrations[15] are described in the literature.[16]

Following its initial characterization, crystal growth experiments were carried out using hydroxide rather than the oxide starting materials in runs held at 15 GPa and 1200 °C for 3 h. Water, introduced via $Ca(OH)_2$, was believed to act as a mineralizer and to aid in the growth of crystals. Single crystals, with approximately trigonal-prismatic shapes and 50 μm on edge, were examined using optical microscopy, precession photography and diffractometry.[17] There was no evidence of twinning.

Synchrotron X-ray powder diffraction data were collected in capillary mode[18,19] and using a position-sensitive detector[20] at the X-7A beamline at the National Synchrotron Light Source, Brookhaven National Laboratory. The wavelength ($\lambda = 1.1485(1)$ Å) was calibrated using a CeO_2 standard ($a = 5.4113(1)$ Å). To account for sample absorption, the material was weighed, the capillary size (0.20 mm diameter) was carefully measured and the correction to the Debye−Waller factor ($\Delta B = 6.2$ Å^2)[21,22] was estimated.

A starting model for the structure was determined by noting the limited possibilities for fitting the $CaAu_2$ stoichiometry in the observed unit cell volume[17] and space group $I4_1/a$. Calculation of powder diffraction patterns based on these models indicated Ca and Au are located at positions 4b and 8c, respectively. Subsequently, the oxygen position was added to fit the intensity of peaks contributed to largely by oxygens (Figure 1). Rietveld refinement using the GSAS package[23] was then carried out.

The structure model derived from the powder study (Table 1) was also refined using single-crystal data.[17] The final refinement employed an anisotropic and isotropic model for the displacement parameters of the metal and oxygen atoms, respectively. This confirmed the bulk powder and single-crystal structure determinations were equivalent.

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(17) $CaAu_2O_4$: fw 498.016, space group $I4_1/a$ (No. 88), $a = 5.99114(1)$, $c = 10.04983(3)$ Å, $V = 360.7262$ Å^3 at 20 °C, $Z = 4$, D_{calc} (g/cm^3) 9.170. Radiation (graphite monochromator) Mo Kα, μ(Mo) = 823.7 cm^{-1}. Diffractometer Enraf-Nonius CAD4, data collected 2680, $2\theta_{min}$ 4.7°, $2\theta_{max}$ 60.0°, $(hkl)_{max}$ 8, 8, 16; data octants ALL, scan method ω. Absorption Method DIFABS, number of unique data ($I > 3.0\sigma(I)$) 221, $R_{merge} = 2.21$. Refinement method full-matrix least-squares on F, anomalous dispersion: Au, Ca; weighting scheme $[\sigma^2(I) + 0.0008I^2]^{-1/2}$, atoms refined anisotropic: Au, Ca; isotropic: O. Parameters varied 14, data/parameter ratio 15.8, $R = 0.043$, $R_{wp} = 0.042$, error of fit = 1.65, sec. extinction coefficient = $0.021(6) \times 10^{-4}$ mm, Z package written and maintained by J. C. Calabrese, Du Pont Co.

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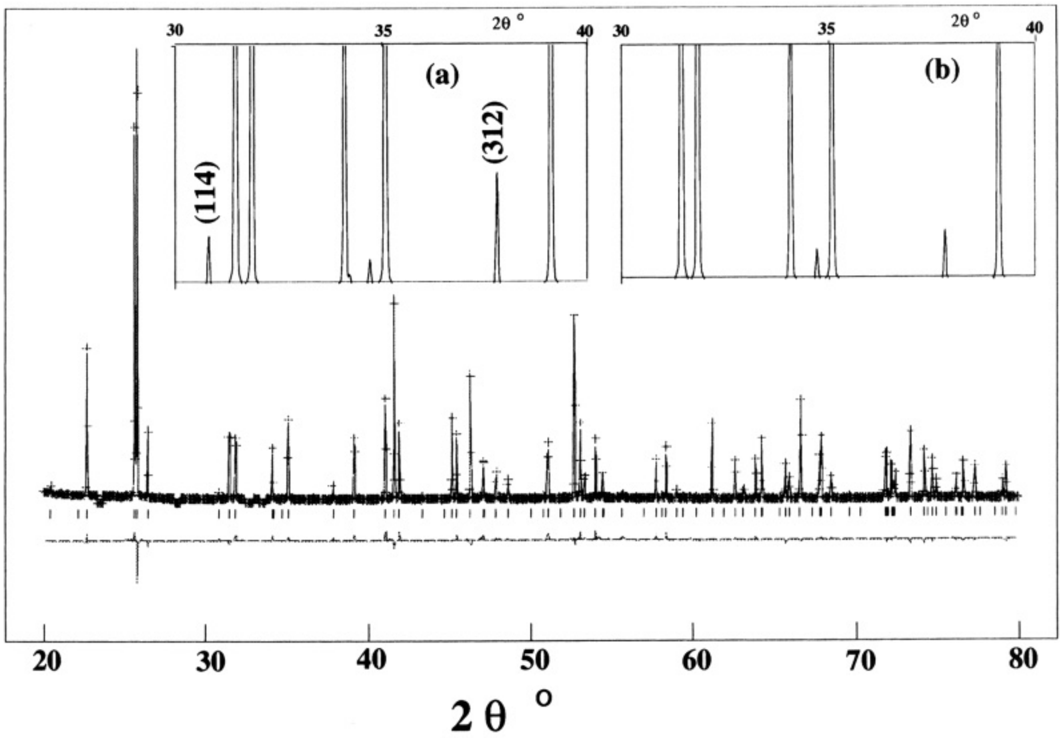

Figure 1. Final fit of observed (+) and calculated (solid line) powder diffraction patterns for $CaAu_2O_4$. The vertical marks indicate positions of all possible reflections; fit parameters, $R_{wp} = 0.082$ and $\chi^2 = 1.90$. The calculated patterns (a) with oxygen in the refined position and (b) without oxygen are compared between 30° and 40°.

Table 1. Fractional Coordinates[a] (×10^4) and Isotropic Thermal[b] Parameters for $CaAu_2O_4$

atom	*x*	*y*	*z*	$B_{iso}{}^{I}$	$B_{iso}{}^{II}$
Au(8c)	0	0	0	0.4(0)′	0.8(1)
Ca(4b)	$^1/_2$	$^1/_4$	$-^1/_8$	0.5(1)′	0.8(1)
O(16f)^{I}	1543(17)	447(17)	8249(11)	0.2(1)	
O(16f)^{II}	1477(8)	405(9)	8246(5)		0.8(1)

[a] Space group $I4_1/a$, $a = 5.99114(1)$ and $c = 10.04983(3)$ Å from powder data. [b] I and II indicate single crystal and powder, respectively. Metal atom sites (′) were refined with anisotropic thermal parameters; B_{equiv} is given for these atoms. $B_{eq} = (8\pi^2/3)\sum_i\sum_j U_{ij}a^*_i a^*_j \mathbf{a}_i \cdot \mathbf{a}_j$.

Following our solution of the structure of $CaAu_2O_4$ we became aware of its isostructural relationship to the recently reported $LaPd_2O_4$.[24] The structure consists of two building elements, AuO_4 square planes and distorted CaO_8 dodecahedra. The AuO_4 unit has O−Au−O angles close to 90° ($\angle_{min} = 83.4(3)°$, $\angle_{max} = 96.6(3)°$) and the average Au−O bond length, 2.004(7) Å is comparable to the value in Au_2O_3 (2.013 Å),[25] consistent with the presence of Au(III) ions. The planes are stacked in a staggered fashion in columns along [100] and [010] producing a square-antiprismatic arrangement of oxygens between them (Figure 2). Each AuO_4 plane is linked by four others in adjacent perpendicular columns. The Ca ions are located in the cavities at the intersection of these columns. They are bonded to eight oxygens on twelve planes with two Ca−O bond distances, 2.53(1) and 2.46(1) Å. The CaO_8 unit is connected to four neighbors by edge-sharing.

The three-dimensional connectivity in $CaAu_2O_4$ is unique for aurates but is similar to that in monoclinic $LnCu_2O_4$. In that material ordering of Cu^{2+} and Cu^{3+} ions reduces the symmetry from the ideal tetragonal found in $CaAu_2O_4$.[12,13]

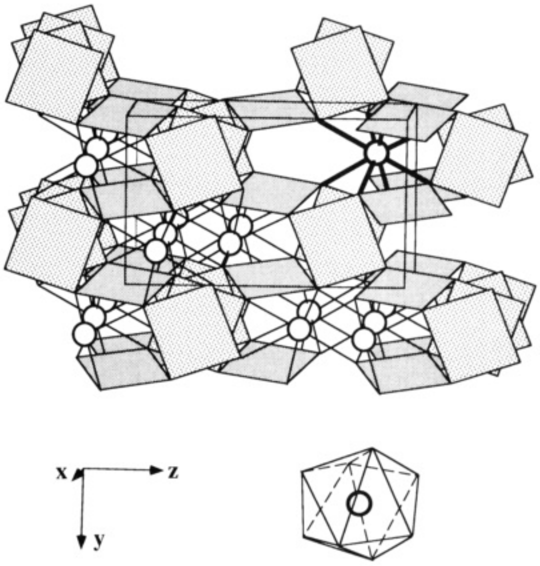

Figure 2. View of the structure of $CaAu_2O_4$ projected along [100]. The AuO_4 units and Ca ions are represented by the planes and circles, respectively. Ca−O bonds are emphasized by the thick solid line on the right top of the unit cell, and its dodecahedral coordination is shown below the projection. Some AuO_4 units and Ca ions are removed for the sake of clarity.

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Supplementary Material Available: Tables of anisotropic thermal parameters, selected bond distances and angles, and structural factors from single-crystal refinement (1 page). Ordering information is given on any current masthead page.

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