

Synthesis and Crystal Structure Determination of LaAuO₃

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A new ternary oxide of gold and lanthanum, LaAuO₃, has been prepared from Au₂O₃ · 2H₂O and La(OH)₃ by applying high oxygen pressure and adding aqueous KOH (55%) as a mineralizer. The bright yellow and diamagnetic LaAuO₃ crystallizes in the orthorhombic crystal system, *Pbcm*, $a = 403.35(7)$, $b = 1307.3(2)$, $c = 569.52(8)$ pm, $Z = 4$. The crystal structure (determined from 980 unique reflections with a final R value of 5.7% ($R_w = 4.7\%$)) consists of a grid of cubes formed by the oxygens which are either centered by lanthanum ions or face centered by gold ions. Thus, lanthanum is coordinated eightfold, and gold fourfold, by oxygen. LaAuO₃ may be described as a CaF₂ structure sheared within the (110) plane by half a translational period along [0 0 1]. © 1993 Academic Press, Inc.

Introduction

Among the plethora of approaches to syntheses of multinary oxides, the three chosen most frequently are (i) solid state reactions of the binary components, (ii) vapor deposition, and (iii) precipitation from liquid systems. Though seeming most versatile, the application of solid state reactions meets its limitations when thermally labile components are involved, e.g., oxides of noble metals or those in high oxidation states. As a rule, with this class of oxides, decomposition occurs prior to sufficient activation of the solid state reaction. These circumstances limit the access to multinary oxides of noble metals and thus explain the poor state of knowledge about them.

Taking remedial measures requires either developing routes for oxide syntheses at low temperatures or applying high oxygen pressures during the high temperature reactions in order to overcompensate for the equilibrium pressure of oxygen. In singular situations electrocrystallization at room

temperature has proven to be a very strong tool, as might be documented by the successful syntheses of binary Ag₂O₃, Ag₃O₄ (1, 2), or multinary HgAg₆O₈ClO₄ (3) silver oxides which by no means would be accessible via other routes. A technique of more universal applicability is to react the solid components in a steel autoclave with high oxygen pressure. By this means we have been able to react silver(I)-oxide with no further additives in the solid state with oxides of silicon, germanium, or boron (4-7). A drawback of this approach is the fact that the oxygen decomposition pressure of an oxide increases exponentially while raising temperature linearly. As a consequence, in many systems, like those involving gold oxides, the oxygen pressures required significantly exceed those available using autoclaves. For this reason all our attempts to synthesize ternary gold oxides other than alkali metal aurates failed unless we added species like water or alkali metal hydroxides which are known to promote the mobility of oxide systems and thus allow for lower reaction temperatures.

In this paper we report on preparation, crystal growth, and crystal structure deter-

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mination of LaAuO₃, the first ternary gold oxide of this type realized as a bulk material and in a pure state.

With the exception of a number of alkali metal and alkaline-earth metal aurates, respectively, that have been characterized structurally by X-ray powder techniques (e.g., KAuO₂, CsAuO₂, Li₅AuO₄) (8, 9) or by single crystal diffraction (Na₃AuO₃, Na₃AuO₂, Ba₉Au₂O₁₂, Sr₅Au₂O₈) (10–13), all ternary gold oxides (14) reported so far are of dubious identity.

Experimental Section

Synthesis: Starting materials. As starting materials for the synthesis of LaAuO₃ · *x*H₂O (*x* = 2–3) and reactive La(OH)₃ have been used. Au₂O₃ · *x*H₂O (*x* = 2–3) was prepared as described in (15) from elemental gold (Degussa, 99.99%). To assure its identity the samples have been converted via hydrothermal dehydration in a steel autoclave within 2 weeks at 300°C and an oxygen pressure of 3 kbars to polycrystalline Au₂O₃ (16) as confirmed by X-ray powder diffraction (STOE-Stadi P diffractometer with a position sensitive detector, germanium monochromator, and CuK α -radiation (λ = 154.056 pm)). The content of gold was determined by thermal decomposition to be 82.3% [Au] (assuming the formula Au₂O₃ · 2H₂O : 82.9% [Au]).

Reactive La(OH)₃ was prepared from reagent grade La₂O₃ (Aldrich, 99.99%) by conversion to the nitrate and subsequent decomposition at 450°C under vacuum within 2d to the oxide. Then this activated La₂O₃ was reacted in a humid atmosphere to La(OH)₃ at room temperature. The product was proven to be single-phased by X-ray powder diffraction (STOE-Stadi P diffractometer).

Appropriate amounts of La(OH)₃ (95 mg, 0.5 mmol) and Au₂O₃ · 2H₂O (120 mg, 0.25 mmol) were intimately mixed and placed into a gold tube (length : 3 cm, diameter : 0.9 cm) with 0.5 ml of aqueous KOH-solution (55%) as a mineralizer. The tube was closed permeable to gas with a gold lid,

transferred into a steel autoclave and heated to 600°C at a heating rate of 200°C/hr applying an oxygen pressure of 2 kbars (10 ml of liquid oxygen condensed into the autoclave ($V_{\text{eff}} = 0.021(1)$) by cooling with liquid nitrogen). After a reaction time of 3 days the autoclave was allowed to cool down to room temperature within 12 hr. To remove KOH the raw product was washed with water until neutrality of the filtrate.

Structure determination. A needle shaped crystal of LaAuO₃ (0.3 · 0.05 · 0.04 mm) was selected for X-ray investigations. Precession and Weissenberg photographs were taken of the 0 *k* *l*-, 1 *k* *l*-, *h* 0 *l*-, *h* *k* 0-, and *h* *k* 1-layers of the reciprocal lattice indicating *Pbcm* or *Pbc2*₁ being possible space groups.

Data collection was carried out on an Enraf-Nonius CAD4 automatic four circle diffractometer equipped with a graphite monochromator using MoK α radiation (λ = 71.069 pm). Essential crystal data and experimental details of the structure determination are listed in Table I.

TABLE I
EXPERIMENTAL DETAILS OF THE STRUCTURE
DETERMINATION FOR LaAuO₃

Molecular weight [g · mole ⁻¹]	383.97
Space group	<i>Pbcm</i> (No. 57)
Cell dimensions [pm]	<i>a</i> = 403.35 (7)
(from powder data)	<i>b</i> = 1307.3 (2)
	<i>c</i> = 569.52 (8)
<i>V</i> [10 ⁶ pm ³]	300.31 (4)
<i>Z</i>	4
<i>D</i> _{calc} [g · cm ⁻³]	8.49
θ range for data collection [°]	1 ≤ θ ≤ 40
<i>h</i> , <i>k</i> , <i>l</i> range for data collection	-7 ≤ <i>h</i> ≤ 7
	-18 ≤ <i>k</i> ≤ 23
	-10 ≤ <i>l</i> ≤ 10
Scan mode	ω/θ
Scan width [°]	0.90 + 0.35 tan θ
max. scan time [sec]	60
<i>F</i> (0 0 0)	640.0
Corrections	Lorentz polarization numerical absorption
$\mu_{\text{MoK}\alpha}$ (cm ⁻¹)	625.7
No. of reflections measured	5665
No. of unique reflections	980
No. of parameters	27
<i>R</i> value	0.057
<i>R</i> _w value	0.047
Weighting scheme	2.721 ($\sigma^2(F)$) + 0.0001 <i>F</i> ²
Maximum height in difference Fourier map [e · pm ⁻³]	9.91 · 10 ⁻⁶

TABLE II

X-RAY PATTERN OF LaAuO_3 : MILLER INDICES, RELATIVE INTENSITIES, OBSERVED d_o [pm], AND CALCULATED d_c [pm] SPACINGS

hkl	I/I_{max}	d_o	d_c
0 2 0	3.4	652.8	653.7
0 2 1	7.2	429.1	429.4
1 0 0	30.4	403.0	403.4
1 2 0	7.3	343.1	343.3
0 4 0	14.8	326.6	326.8
1 1 1	58.7	319.1	319.2
1 3 0	7.4	295.8	296.0
1 2 1	19.6	293.80	293.99
0 0 2	100.0	284.60	284.76
0 4 1	90.2	283.30	283.47
1 3 1	7.5	262.53	262.65
0 2 2	1.1	260.91	261.06
1 0 2	20.7	232.54	232.63
1 4 1	6.3	231.72	231.92
1 5 0	9.9	219.29	219.40
1 2 2		219.16	219.16
0 4 2	8.9	214.67	214.70
1 3 2	24.4	205.17	205.22
2 1 0	2.9	199.30	199.32
2 2 0	3.9	192.75	192.71
0 5 2		192.59	192.59
1 6 0	2.4	191.70	191.70
1 4 2	1.6	189.42	189.52
2 2 1	16.4	182.55	182.55
2 3 1	2.0	174.38	174.25
1 5 2	7.5	173.85	173.80
0 6 2	2.3	173.03	173.04
1 1 3	10.9	170.32	170.30
1 7 0	2.1	169.50	169.47
1 2 3	6.9	166.16	166.13
0 4 3	16.8	164.18	164.16
0 8 0	8.8	163.37	163.40
2 1 2		163.29	163.29
1 7 1	2.4	162.44	162.43
2 5 0	6.5	159.69	159.69
2 2 2		159.60	159.60
1 6 2	4.3	159.06	159.02
0 8 1	8.8	157.08	157.07
2 5 1	1.0	153.71	153.76
0 5 3		153.62	153.62
1 4 3	3.1	152.06	152.05
2 6 0	5.7	148.04	148.01
1 7 2	3.3	145.65	145.63
0 0 4	14.9	142.41	142.38
0 8 2	4.1	141.75	141.73

The cell parameters used in all calculations were determined from the X-ray powder pattern by indexing and least-squares refinement (c.f., Table II, STOE-Stadi P diffractometer and STOE-Stadi P software).

The program SHELXS-86 (17) was used for data reduction and structure solution which was achieved by interpretation of a Patterson map (La and Au positions) and Fourier techniques (O positions). Scattering factors for Au and La were taken from "International Tables for X-Ray Crystallography" (18); for oxygen those implemented in the programs SHELXS-86 and SHELX-76 have been used. Numerical absorption correction and final refinement by full matrix least-squares methods were performed using SHELX-76 (19).

Analyses. Differential thermal analysis (DTA) and thermogravimetry (TG) were

carried out simultaneously on a Netzsch STA 429 (heating rate: 5°/min, reference: high purity α - Al_2O_3). Energy dispersive X-ray analysis (EDX) was performed using an electron microscope (Zeiss DSM 940) equipped with EDX (EDAX PV9800). The amount of potassium was determined by atom absorption spectroscopy (Perkin Elmer 410). Magnetic measurements were performed using a SQUID magnetometer (Quantum Design MPMS; 3 T, 4–360 K).

Results

By solid state reaction of $\text{La}(\text{OH})_3$ and $\text{Au}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ and applying high oxygen pressure the novel ternary gold oxide LaAuO_3 has been obtained. The preparative procedure as described yields pure coarse crystalline samples. The needle shaped crystals are transparent and of bright yellow color. Magnetic measurements revealed diamagnetic behavior ($\chi_{\text{exp}} = -4.5 \cdot 10^{-5} \text{ cm}^3 \cdot \text{mole}^{-1}$, $\chi_{\text{calc}} = -8 \cdot 10^{-5} \text{ cm}^3 \cdot \text{mole}^{-1}$ (20)). LaAuO_3 is insensitive to atmospheric influences and to exposure to daylight. Its thermal stability (decomposition at 820.1°C to give La_2O_3 , Au, and O_2 , weight loss: 5.4% (obs) 6.0% (calc)) is surprisingly high as compared to binary gold oxides (21). The composition was ensured by EDX-analyses (La : Au = 1 : 0.96 ± 0.05 , calculated as the mean of eight different spot analyses) and X-ray structure determination. Absence of impurities was checked for by powder diffraction (La_2O_3 , Au), EDX analyses (K less than the limit of detectability of 0.3%) and atom absorption spectroscopy (the amount of K was determined to be $0.09\% \pm 0.05\%$). The results of the crystal structure determination (atomic parameters, equivalent thermal factors, and interatomic distances) are documented in Tables III and IV¹.

¹ Further details of the structure determination have been deposited as Supplementary Publication No. CSD-56819. Copies may be obtained through Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich technische Information mbH, W-7514 Eggenstein-Leopoldshafen, Germany.

TABLE III
FRACTIONAL COORDINATES AND EQUIVALENT
THERMAL PARAMETERS FOR LaAuO₃^a

Atom	Wykoff notation	Atomic parameters			Thermal parameters <i>U</i> _{eq} (pm ²)
		<i>x</i>	<i>y</i>	<i>z</i>	
Au	4 <i>d</i>	0.0715(1)	0.3293(1)	0.25	60(2)
La	4 <i>d</i>	0.2643(2)	0.5823(1)	0.25	62(3)
O(1)	8 <i>c</i>	0.2551(2)	0.4204(6)	0.0061(1)	86(25)
O(2)	4 <i>b</i>	0.8275(2)	0.25	0	96(38)

$$^a U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33}).$$

Discussion

The crystal structure contains one crystallographic independent position for Au with site symmetry *m*. The coordination by oxygen is approximately square planar (Fig. 1), thus, unambiguously indicating gold to be trivalent. The mirror plane is oriented perpendicular to the plane formed by the oxide ions of the AuO₄ group. For Au the maximal deviation from that plane is 14.3 pm. The Au–O bond length (mean : 199.6 pm) corresponds pretty well to the values determined for Au₂O₃ ((21); mean : 201.3 pm). The deviations from ideal geometry of a centered square are caused by different connectivities of the oxygen atoms to their next neighbors (see below).

Like gold, lanthanum is located on a crystallographically independent position with site symmetry *m*. It exhibits coordination number 8 with respect to oxygen. The polyhedron formed is approximately cubic (Fig. 2). Here, the mirror plane is oriented perpendicular to that edge of the cube connecting O(2)^{*i*} and O(2)^{*j*}. The mean bond length from lanthanum to oxygen (253.8

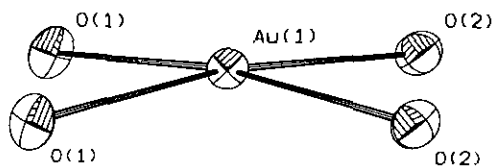


FIG. 1. The coordination of gold (deviation of gold from the "best plane" through oxygen is 14.3 pm).

TABLE IV
IMPORTANT DISTANCES [pm] AND ANGLES [°]
IN LaAuO₃

AuO ₄ - Square		
Au ^a - O(1) ^{a,b}	x2	197.4 (7)
Au ^a - O(2) ^{c,d}	x2	201.8 (4)
LaO ₈ - Cube		
La ^a - O(1) ^{a,b}	x2	253.2 (8)
La ^a - O(1) ^{e,f}	x2	255.3 (7)
La ^a - O(1) ^{g,h}	x2	242.6 (7)
La ^a - O(2) ^{i,j}	x2	264.0 (1)
O(1) ^g - O(1) ^h		277.8 (10)
O(1) ^g - O(1) ^f		292.7 (10)
O(1) ^g - O(1) ^b		287.0 (10)
O(1) ^f - O(1) ^e		291.3 (10)
O(1) ^f - O(2) ^j		281.7 (10)
O(1) ^b - O(1) ^a		291.7 (10)
O(1) ^b - O(2) ^j		319.8 (10)
O(2) ^j - O(2) ⁱ		284.8 (0)
O(1) ^e - O(1) ^b - O(1) ^a		91.4 (3)
O(1) ^e - O(1) ^b - O(1) ^g		88.2 (3)
O(1) ^g - O(1) ^b - O(1) ^a		91.4 (3)
O(1) ^f - O(1) ^e - O(2) ^j		89.3 (2)
O(1) ^b - O(1) ^e - O(2) ^j		97.6 (3)
O(1) ^b - O(1) ^e - O(1) ^f		88.7 (3)
O(1) ^b - O(1) ^g - O(2) ^j		88.6 (2)
O(1) ^b - O(1) ^g - O(2) ⁱ		90.7 (3)
O(1) ^g - O(1) ^g - O(2) ^j		89.3 (2)
O(1) ^g - O(2) ^j - O(1) ^f		83.8 (2)
O(1) ^g - O(2) ^j - O(2) ⁱ		90.7 (3)
O(1) ^f - O(2) ^j - O(2) ⁱ		90.8 (3)
Au ^a - Au ^{k,l}	x2	352.3 (4)
Au ^a - La ^m	x2	335.8 (2)
La ^a - La ⁿ	x2	403.4 (1)

^a *x*, *y*, *x*; ^b *x*, *y*, $-z + 0.5$; ^c $x - 1$, *y*, *z*; ^d $x - 1$, *y*, $z + 0.5$; ^e $-x$, $-y + 1$, $z + 0.5$; ^f $-x$, $-y + 1$, $-z$; ^g $-x + 1$, $-y + 1$, $z + 0.5$; ^h $-x + 1$, $-y + 1$, $-z$; ⁱ $-x + 1$, *y* + 0.5, $z + 0.5$; ^j $-x + 1$, *y* + 0.5, *z*; ^k *x*, $-y + 0.5$, $-z$; ^l *x*, $-y + 0.5$, $-z + 1$; ^m $-x$, $1 - y$, $-z$; ⁿ $x + 1$, *y*, *z*.

pm) seems to be quite normal as compared to other structures containing La in an eightfold, approximately cubic coordination. The mean La–O bond length of La₂Pd₂O₅ (22), for example, has been determined to be 254.8 pm. The O–O–O angles in the cube occupied by lanthanum are close to 90°. The maximal deviations are observed for O(1)^{*g*}–O(2)^{*i*}–O(1)^{*e*} (83.8°) and for O(1)^{*b*}–O(1)^{*e*}–O(2)^{*i*} (97.6°). They are obviously caused by the different bond lengths of La–O(2) (264.0 pm) and La–O(1) (242.6 pm), whereas this latter difference (in bond lengths) is caused by the different crystal chemical function of O(1) and O(2).

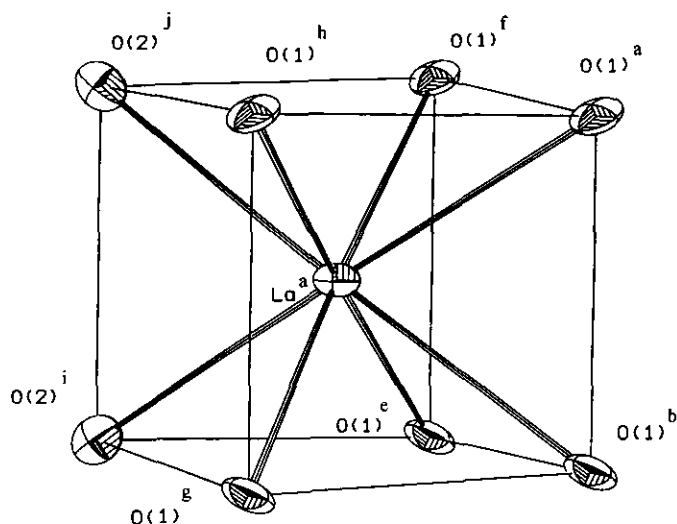


FIG. 2. The approximately cubic coordination of lanthanum. For the symmetry code, see Table IV.

Using a modified version of the notation of Niggli (23) the connectivities may be expressed as follows:

	O(1)	O(2)	C.N.
La	$\frac{6}{3}$	$\frac{2}{2}$	8
Au	$\frac{2}{1}$	$\frac{2}{2}$	4
C.N.	4	4	

Thus, the AuO_4 squares are connected to each other via half of their vertices (O(2)) while the LaO_8 polyhedra are connected via edges (O(1)) and vertices (O(2)). The longer distance of Au to O(2) as compared to O(1) is explicable by the higher bonding charge on O(2) which is connected to two gold atoms while O(1) is bonded only to one gold ion.

The three dimensional framework is dominated by a grid of cubes formed by the oxide ions (c.f. Fig. 3). This grid is topologically equivalent to the arrangement of chlorine ions in CsCl. Thus, the structure of LaAuO_3 may be discussed in a similar way as has been done for the structure of $\text{La}_2\text{Pd}_2\text{O}_5$ (22). It is possible to derive the three dimensional framework as follows from a two dimensional building unit (Figs. 4 and 5): In the x - y plane two thirds of the

cesium ions of the CsCl type of structure are removed and the remaining portion is replaced by lanthanum avoiding face sharing cubes being occupied by lanthanum, simultaneously. The empty cubes are arranged in a zigzag manner. Half of the common faces of the face sharing empty cubes are occupied by gold. For further details, see Fig. 4.

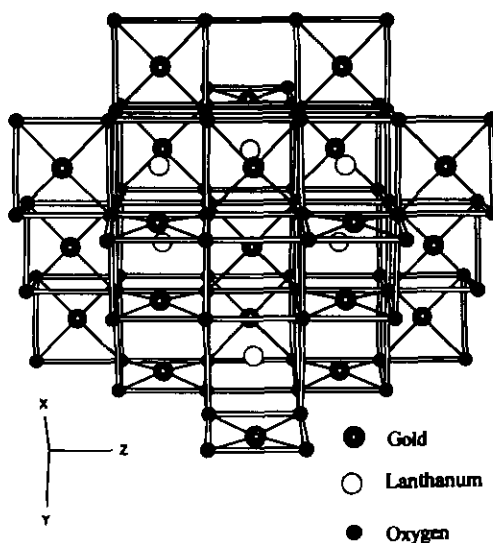


FIG. 3. Perspective drawing of the crystal structure of LaAuO_3 .

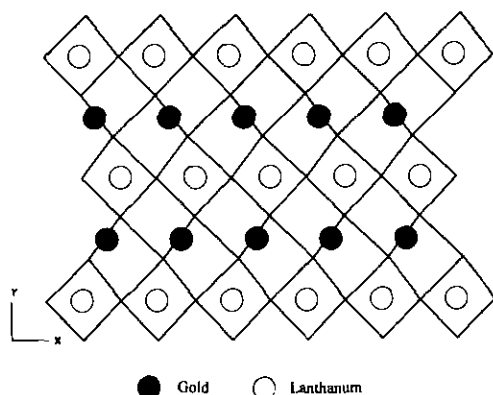


FIG. 4. Two dimensional building unit of LaAuO_3 as derived from the CsCl type of structure.

Identical two dimensional units of this type are stacked in the c -direction being shifted relatively to each other by the length of one face diagonal of the oxygen cubes along $[0\ 1\ 0]$. The real structure of LaAuO_3 formed by this procedure is depicted in Fig. 5.

Due to this building principle pairs of face sharing cubes are formed which are centered by Au on their common face. On closer examination of Fig. 5 it is visible that

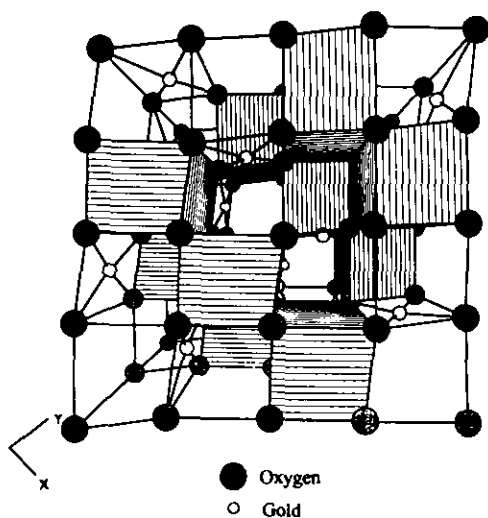


FIG. 5. A view of the three dimensional framework of LaAuO_3 along $[0\ 0\ 1]$.

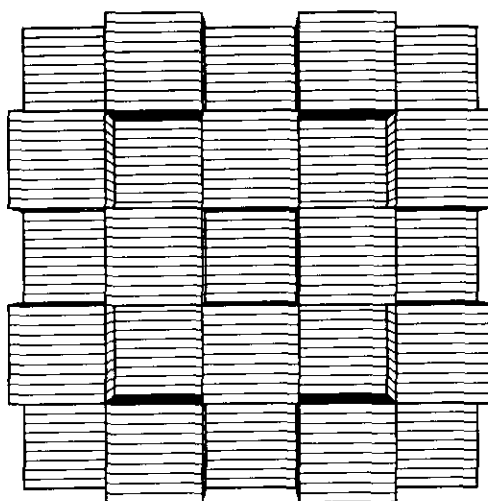


FIG. 6. The arrangement of the fluorine ions in CaF_2 (view direction : $[1\ 0\ 0]$).

viewing along $[0\ 0\ 1]$ the structure contains tunnels of cubes where no lanthanum is located. The gold ions are shifted towards these tunnels which explains the deviation of gold from the "best plane" through the neighboring oxygen atoms.

An alternative description of the structure of LaAuO_3 would start with the fluorite type of structure. The arrangement of the anions (F^-/O^{2-}) is equivalent (c.f., Fig. 6). Calcium is replaced by lanthanum and voids, gold is inserted into the faces of two adjacent cubes formed by oxygen.

Acknowledgments

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