

High- and low-temperature La_2RuO_5 by powder neutron diffraction

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The structure of dilanthanum ruthenium pentoxide was solved by powder neutron diffraction at room temperature and 1.5 K. High-temperature La_2RuO_5 crystallizes in the monoclinic space group $P2_1/c$. Upon cooling, the sample undergoes a phase transition to the triclinic low-temperature form (space group $P\bar{1}$). This transition leads to pronounced changes in the Ru—O—Ru bond distances, resulting in a dimerization of the ruthenium ions.

Comment

Among the various modifications of the perovskite structure, compounds belonging to the so-called [110]-phases are quite special. In these oxides, the three-dimensional perovskite framework can be considered to be cut along the [110] direction, resulting in blocks of different possible thicknesses. Many of the [110]-phases have the general composition $A_nB_nO_{3n+2}$, in which n represents the number of BO_6 octahedra within the blocks (Lichtenberg *et al.*, 2001). The thinnest possible blocks correspond to zigzag chains of single BO_6 octahedra, which are isolated by the A -type cations. This arrangement is found, for example, in LaTaO_4 ($n = 2$, corresponding to $\text{La}_2\text{Ta}_2\text{O}_8$; Cava & Roth, 1981).

The title compound is closely related to the $A_nB_nO_{3n+2}$ family of oxides. It can be described formally as an $n = 2$ member, in which the perovskite slabs are separated by one additional AO unit. Fig. 1 shows the structural relationship between the cubic perovskite archetype structure, La_2RuO_5 , and the [110]-phases. La_2RuO_5 was discovered independently by two groups. Boullay *et al.* (2003) published an *ab initio* structural determination based on powder X-ray diffraction data, while Khalifah *et al.* (2002) reported electrical and magnetic properties. In the latter paper, a structural phase transition at 160 K was also described. This transition is accompanied by strong changes in the magnetic susceptibility and electrical resistivity. Khalifah *et al.* (2002) used powder neutron diffraction for their investigations, but unfortunately no structural details were given and to the best of our knowledge this information has not been published so far. In

the course of our own research on the physical properties of ruthenates, we came across the need for structural data for both the high-temperature (ht) and the low-temperature (lt) modification of La_2RuO_5 . As a starting model for ht- La_2RuO_5 , the atomic coordinates given by Boullay *et al.* (2003) were used. For the triclinic lt-phase, possible new positions were generated using the program *PowderCell* (Kraus & Nolze, 1996). Figs. 2 and 3 show the results of the refinements. A graphical presentation of the crystal structures at 293 and 1.5 K is given in Fig. 4.

In the high-temperature modification, atom La1 is coordinated by nine O atoms, with bond distances ranging from

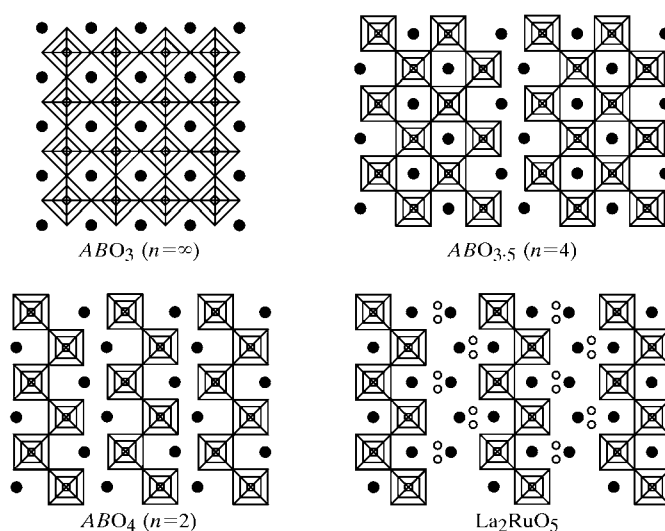


Figure 1

Structural similarities between the [110]-phases and La_2RuO_5 . The cubic perovskite (top left) can be considered the ∞ member of the $A_nB_nO_{3n+2}$ series. The representatives for the $n = 4$ and $n = 2$ compounds are $\text{SrTaO}_{3.5}$ and LaTaO_4 , respectively.

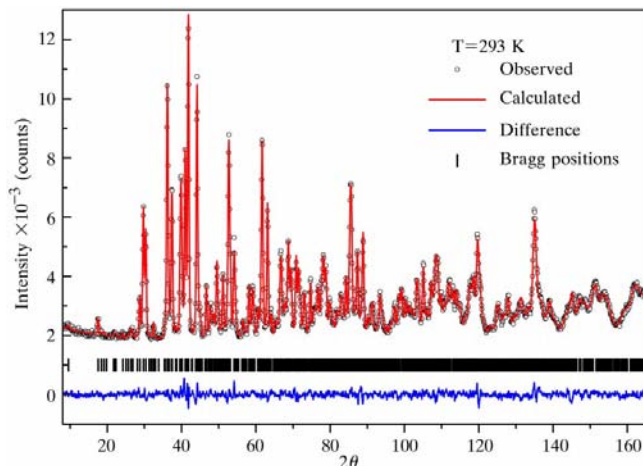


Figure 2

Rietveld refinement plot of La_2RuO_5 at 293 K.

2.325 (6) to 2.968 (6) Å. The coordination geometry is rather irregular and cannot be described in terms of a simple polyhedron. For atom La2, an irregular ninefold O-atom coordination is observed, with bond distances ranging from 2.342 (7) to 2.836 (6) Å. It is noteworthy that the shortest La–O distances are found for atom O5, *i.e.* the O atom in between the perovskite blocks. The RuO₆ moieties can be described as slightly distorted octahedra. The difference between the longest and shortest bonds is 0.13 (1) Å. The O–Ru–O bond angles range from 82.5 (4) to 95.2 (4)°. The Ru–Ru distances in the zigzag chains are, within experimental error, identical to the Ru···Ru distances along the crystallographic *c* axis. Additionally, the Ru^{iv}–O3–Ru^v (zigzag chain) and Ru^v–O4–Ruⁱⁱⁱ (along *c*) bond angles are very similar [155.4 (5) and 152.8 (4)°, respectively; symmetry codes as in Table 1].

For the low-temperature modification, the coordination geometries change significantly, although the dimensions of the unit cell remain very similar. For atoms La1 and La1A, the bond lengths lie in the ranges 2.320 (7)–3.054 (6) and 2.352 (6)–3.000 (6) Å, respectively. Interestingly, the La1–

O1A bond becomes rather short [2.381 (7) Å]. The interatomic distances for atoms La2 and La2A are 2.332 (6)–2.820 (7) and 2.346 (7)–2.834 (7) Å, respectively. The most interesting changes concern the ruthenium–oxygen coordination. Within the zigzag chains, the Ruⁱ–O3A–Ru^{ix} distance is 0.23 (2) Å shorter than the Ruⁱ–O3–Ru^{ix} distance. A similar, although less pronounced, effect was found for the distances parallel to the *c* direction; here, the Ru^{vii}–O4–Ru^{ix} distance is 0.12 (2) Å shorter than the Ruⁱ–O4A–Ru^{ix} distance. These changes in the interatomic distances can be described as a dimerization of the ruthenium ions, which apparently occurs both within the zigzag chains and along *c*. In addition, the bond angles differ significantly in the ht- and lt-modifications. The Ru–O–Ru angles within the zigzag chains are 153.2 (5)° for Ruⁱ–O3–Ru^{ix} and 160.2 (6)° for Ruⁱ–O3A–Ru^{ix}. The corresponding angles along the *c* axis (Ru^{vii}–O4–Ru^{ix} and Ruⁱ–O4A–Ru^{ix}), on the other hand, are almost identical (151°; symmetry codes as in Table 2). It is worth noting that within the zigzag chains the shorter Ru···Ru distance is accompanied by a bond angle closer to 180°. Both effects are expected to increase the superexchange interaction between these neighbouring ruthenium ions. Calculations of the electronic band structure based on our Rietveld results are currently in progress and the results will be reported elsewhere.

Experimental

Polycrystalline La₂RuO₅ was prepared from La₂O₃ and RuO₂. La₂O₃ was dried at 1173 K for 6 h prior to use. The thoroughly ground stoichiometric mixture was heated in an alumina crucible at 1423 K for 48 h with one intermediate grinding. Phase purity was checked by preliminary X-ray diffraction measurements.

High-temperature phase

Crystal data

La₂RuO₅
M_r = 458.89
 Monoclinic, *P*2₁/*c*
a = 9.1850 (4) Å
b = 5.8294 (2) Å
c = 7.9552 (3) Å
 β = 100.79 (2)°
V = 418.42 (4) Å³
Z = 4

D_x = 7.285 Mg m⁻³
 Neutron radiation
 λ = 1.4935 Å
 μ = 0.29 mm⁻¹
T = 293 K
 Specimen shape: cylinder
 35 × 8 mm
 Particle morphology: irregular
 powder, black

Data collection

SINQ HRPT diffractometer
 Specimen mounting: vanadium can
 Specimen mounted in transmission
 mode
 Scan method: fixed

Absorption correction: for a
 cylinder mounted on the φ axis
 $2\theta_{\min}$ = 4.6, $2\theta_{\max}$ = 164.9°
 Increment in 2θ = 0.05°

Refinement

Refinement on *I*_{net}
R_p = 0.023
R_{wp} = 0.029
R_{exp} = 0.018
S = 1.61
 Wavelength of incident radiation:
 1.4935 Å

Profile function: Thompson–Cox–
 Hastings pseudo-Voigt
 46 parameters
 Weighting scheme based on
 measured s.u.'s
 $(\Delta/\sigma)_{\max}$ < 0.001
 Preferred orientation correction:
 none

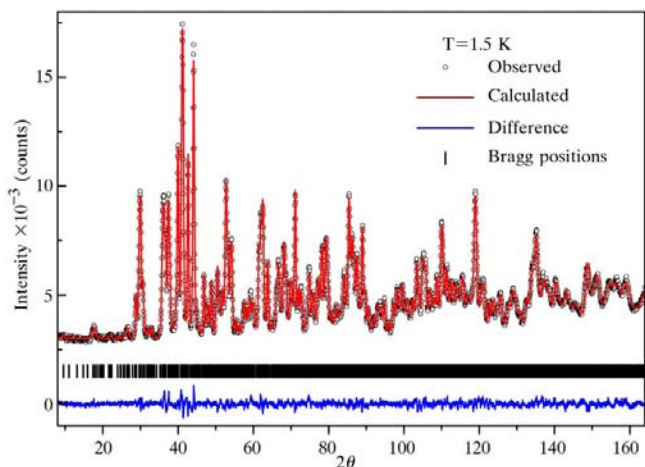


Figure 3
 Rietveld refinement plot of La₂RuO₅ at 1.5 K.

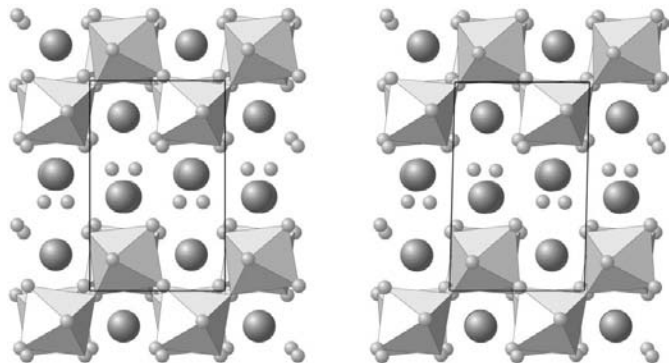


Figure 4
 The structure of ht- (left) and lt-La₂RuO₅ (right), viewed along [001].

Table 1

Selected geometric parameters (Å, °) for the high-temperature phase.

Ru1—O1	1.939 (7)	Ru1—O4 ⁱⁱ	2.048 (8)
Ru1—O2 ⁱ	1.954 (7)	Ru1—O4 ⁱⁱⁱ	2.044 (8)
Ru1—O3 ⁱ	2.065 (8)	Ru1—Ru1 ⁱⁱ	3.975 (8)
Ru1—O3 ⁱⁱ	2.004 (7)	Ru1—Ru1 ^{xii}	3.978 (7)
O1—Ru1—O2 ⁱ	95.2 (4)	O3 ⁱ —Ru1—O3 ⁱⁱ	95.1 (5)
O1—Ru1—O3 ⁱ	177.2 (5)	O3 ⁱ —Ru1—O4 ⁱⁱ	86.0 (4)
O1—Ru1—O3 ⁱⁱ	87.2 (4)	O3 ⁱ —Ru1—O4 ⁱⁱⁱ	94.2 (4)
O1—Ru1—O4 ⁱⁱ	92.6 (4)	O3 ⁱⁱ —Ru1—O4 ⁱⁱ	88.1 (4)
O1—Ru1—O4 ⁱⁱⁱ	87.2 (4)	O3 ⁱⁱ —Ru1—O4 ⁱⁱⁱ	90.8 (5)
O2 ⁱ —Ru1—O3 ⁱ	82.5 (4)	O4 ⁱⁱ —Ru1—O4 ⁱⁱⁱ	178.9 (6)
O2 ⁱ —Ru1—O3 ⁱⁱ	177.3 (5)	Ru1 ^{iv} —O3—Ru1 ^v	155.4 (5)
O2 ⁱ —Ru1—O4 ⁱⁱ	93.0 (4)	Ru1 ^v —O4—Ru1 ⁱⁱⁱ	152.8 (4)
O2 ⁱ —Ru1—O4 ⁱⁱⁱ	88.1 (4)		

Symmetry codes: (i) $x, y + 1, z$; (ii) $-x, y + \frac{1}{2}, -z + \frac{1}{2}$; (iii) $-x, -y + 1, -z + 1$; (iv) $x, y - 1, z$; (v) $-x, y - \frac{1}{2}, -z + \frac{1}{2}$; (xii) $x, \frac{3}{2} - y, \frac{1}{2} - z$.

Low-temperature phase

Crystal data

La₄Ru₂O₁₀
M_r = 917.78
 Triclinic, P1̄
a = 9.1614 (8) Å
b = 5.8075 (5) Å
c = 7.9584 (8) Å
 α = 89.78 (8)°
 β = 101.00 (8)°
 γ = 91.76 (8)°
V = 415.45 (13) Å³

Z = 2
D_x = 7.337 Mg m⁻³
 Neutron radiation
 λ = 1.4935 Å
 μ = 0.30 mm⁻¹
T = 1.5 (1) K
 Specimen shape: cylinder
 35 × 8 mm
 Particle morphology: irregular
 powder, black

Data collection

SINQ HRPT diffractometer
 Specimen mounting: vanadium can
 Specimen mounted in transmission
 mode
 Scan method: fixed

Absorption correction: for a
 cylinder mounted on the φ axis
 $2\theta_{\min}$ = 4.6, $2\theta_{\max}$ = 165.0°
 Increment in 2θ = 0.1°

Refinement

Refinement on *I*_{net}
R_p = 0.019
R_{wp} = 0.023
R_{exp} = 0.014
S = 1.62
 Wavelength of incident radiation:
 1.4935 Å

Profile function: Thompson–Cox–
 Hastings pseudo-Voigt
 68 parameters
 Weighting scheme based on
 measured s.u.'s
 $(\Delta\sigma)_{\max}$ < 0.001
 Preferred orientation correction:
 none

To reduce the number of free parameters, isotropic displacement parameters were used for all atoms. Attempts to refine the displacement parameters for the various O-atom positions independently led to unreasonable values for some of the atoms (especially for the It phase) and only slightly reduced the residual parameters. We therefore decided to use one common displacement parameter for all O atoms. Because there was a strong correlation between refinement

Table 2

Selected geometric parameters (Å, °) for the low-temperature phase.

Ru1—O1	1.888 (8)	Ru1A—O3 ^{ix}	2.097 (8)
Ru1—O2A ^{vi}	2.042 (8)	Ru1A—O3A ^{ix}	1.969 (8)
Ru1—O3	2.062 (8)	Ru1A—O4 ^{ix}	2.049 (8)
Ru1—O3A ^{vi}	1.957 (8)	Ru1A—O4A ^x	2.050 (8)
Ru1—O4 ^{vii}	2.007 (8)	Ru1—Ru1A ^{ix}	4.045 (8)
Ru1—O4A ^{vi}	2.118 (8)	Ru1 ⁱ —Ru1A ^{ix}	3.868 (8)
Ru1A—O1A	1.979 (8)	Ru1 ^{vii} —Ru1A ^{ix}	3.923 (8)
Ru1A—O2 ^{viii}	1.873 (8)	Ru1 ⁱ —Ru1A ^{xi}	4.036 (8)
Ru1—O3—Ru1A ^{ix}	153.2 (5)	Ru1 ^{vii} —O4—Ru1A ^{ix}	150.6 (5)
Ru1 ⁱ —O3A—Ru1A ^{ix}	160.2 (6)	Ru1 ⁱ —O4A—Ru1A ^{xi}	151.0 (5)

Symmetry codes: (i) $x, y + 1, z$; (vi) $x, y - 1, z$; (vii) $-x, -y, -z + 2$; (viii) $x, y + 1, z + 1$; (ix) $-x, -y + 1, -z + 2$; (x) $x, y, z + 1$; (xi) $x, y, z - 1$.

parameters, it was furthermore necessary to use a common displacement parameter for the La atoms in the It phase.

For both compounds, data collection: *SINQ Instrument Control System (SICS)* (Fischer *et al.*, 2000); cell refinement: *FULLPROF2000* (Rodríguez-Carvajal, 1990); data reduction: *SINQ Instrument Control System (SICS)*; structure refinement: *FULLPROF2000*; molecular graphics: *ATOMS for Windows* (Dowty, 1995); publication software: *PLATON* (Spek, 2003) and *FULPROF2000*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TY1006). Services for accessing these data are described at the back of the journal.

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