

Two Ti-doped distrontium ruthenium tetraoxides: $\text{Sr}_2\text{Ru}_{0.93}\text{Ti}_{0.07}\text{O}_4$ and $\text{Sr}_2\text{Ru}_{0.81}\text{Ti}_{0.19}\text{O}_4$

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Crystals of titanium-doped distrontium ruthenium tetraoxide, $\text{Sr}_2\text{Ru}_{1-x}\text{Ti}_x\text{O}_4$, with $x = 0.07$ and 0.19 , were grown by floating-zone melting, and their structures were solved using single-crystal X-ray diffraction. Increasing Ti content leads to a distinctive systematic variation of cell parameters and interatomic distances with respect to the undoped material.

Comment

The origin of superconductivity in Sr_2RuO_4 (Maeno *et al.*, 1994) remains an unsolved problem. In contrast to the isostructural compound $(\text{La,Sr})_2\text{CuO}_4$, superconductivity in Sr_2RuO_4 is easily suppressed, even by traces of impurities (Mackenzie *et al.*, 1998). Although this effect is rather undesired, it offers the unique opportunity to study the normal state of distrontium ruthenate and thus can help us to understand the mechanism of superconductivity in this unusual material.

Single crystals of undoped Sr_2RuO_4 have been examined in detail by Walz & Lichtenberg (1993) and Müller-Buschbaum & Wilkens (1990).

Titanium doping has been found to alter dramatically the physical characteristics of Sr_2RuO_4 (Minakata & Maeno, 2001; Braden *et al.*, 2002), and extensive investigations of electrical resistivity, magnetism, heat capacity and IR spectroscopy have been reported (Pucher *et al.*, 2002). It is therefore important to study the effect of doping on the crystallographic structure. In this paper, we present structure refinements for crystals of $\text{Sr}_2\text{Ru}_{1-x}\text{Ti}_x\text{O}_4$, with $x = 0.07$ and 0.19 , *viz.* compounds (I) and (II), respectively.

Sr_2RuO_4 and its Ti-substituted analogs crystallize in the so-called K_2NiF_4 -type structure. This structure consists of perovskite monolayers, stacked along the c axis and separated by rock-salt-type layers. The coordination of the Ru atoms is typical for perovskites, as it consists of an O-atom octahedron

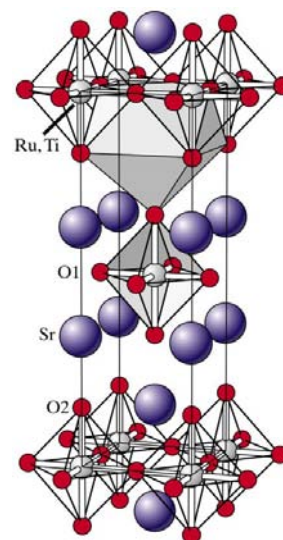


Figure 1

The crystal structure of $\text{Sr}_2\text{Ru}_{1-x}\text{Ti}_x\text{O}_4$, showing the Ru/TiO_6 octahedra and SrO_9 capped tetragonal antiprisms.

in the first coordination sphere, followed by a cube of eight Sr atoms. For the Sr atoms, the 12-fold cuboctahedral coordination geometry in perovskites is replaced by a ninefold coordination, which can be described as a capped tetragonal antiprism. The different structural elements are shown in Fig. 1.

The structure refinements converged smoothly and led to small s.u. values both for fractional coordinates and for anisotropic displacement parameters. The obtained titanium contents of 7.1 (2) and 19.0 (4)% are close to the expected values of x (0.10 and 0.20, respectively), indicating that there was no severe loss of titanium during the growth procedure.

Ti doping leads to a systematic modification of the crystal structure. With increasing Ti content, cell parameter a increases, while c decreases. At the same time, the Ru/Ti—O2 distance decreases (Tables 1 and 2) and, consequently, the elongation of the Ru/TiO_6 octahedra is reduced. This result agrees with the expected behavior. Ru^{4+} is a Jahn–Teller-active ion and therefore a significant distortion of the RuO_6 octahedra is expected. Ti^{4+} , on the other hand, is not a Jahn–Teller ion. Consequently, the substitution of titanium for ruthenium should reduce the elongation of the octahedra.

The SrO_9 unit shows only minor modifications. While the Sr—O1 distance decreases upon Ti doping, the distance of the equatorial O2 atoms ($\frac{1}{2}, \frac{1}{2}, \frac{1}{2} - z_{\text{O2}}$) increases. The interatomic distance to the capping O2 atom ($0, 0, z_{\text{O2}}$) also slightly increases. The deviations of the latter three values, on the other hand, are quite small (0.002–0.006 Å) and barely significant within a tolerance range of 3σ .

Experimental

Single crystals of $\text{Sr}_2\text{Ru}_{1-x}\text{Ti}_x\text{O}_4$ were grown by the floating-zone melting technique (Ikeda *et al.*, 2002; Mao *et al.*, 2000) in a CSI FZ-T-10000-H furnace equipped with four power lamps of 1500 W each. Polycrystalline starting materials with $x = 0.10$ and 0.20 were

synthesized by conventional solid-state reactions from SrCO₃, RuO₂ and TiO₂. To account for the evaporation of some RuO₂ during crystal growth, a 10% excess of ruthenium oxide was used. Rods of the polycrystalline compounds, approximately 7 mm in diameter and 100 mm in length, were pressed and sintered at 1623 K for 24 h. Crystal growth was performed in flowing air (1 l h⁻¹) with a growth rate of 5 mm h⁻¹. Seed- and feed-rods were counter-rotated at 35 r.p.m. The resulting boules could be easily cleaved and single crystals of appropriate sizes were selected for structure analysis.

Compound (I)

Crystal data

Sr ₂ Ru _{0.93} Ti _{0.07} O ₄	Mo K α radiation
$M_r = 334.99$	Cell parameters from 25 reflections
Tetragonal, <i>I4/mmm</i>	$\theta = 9.7\text{--}18.0^\circ$
$a = 3.8736$ (3) Å	$\mu = 31.43$ mm ⁻¹
$c = 12.720$ (7) Å	$T = 293$ K
$V = 190.87$ (10) Å ³	Triangular plate, black
$Z = 2$	$0.20 \times 0.09 \times 0.03$ mm
$D_x = 5.829$ Mg m ⁻³	

Data collection

Siemens Syntex <i>P2</i> ₁ diffractometer	$\theta_{\max} = 42.5^\circ$
$\omega/2\theta$ scans	$h = -7 \rightarrow 7$
Absorption correction: analytical (de Meulenaer & Tompa, 1965)	$k = -7 \rightarrow 7$
$T_{\min} = 0.077$, $T_{\max} = 0.453$	$l = -24 \rightarrow 24$
2882 measured reflections	3 standard reflections
247 independent reflections	every 100 reflections
247 reflections with $I > 2\sigma(I)$	intensity decay: <1%
$R_{\text{int}} = 0.031$	

Refinement

Refinement on F^2	$(\Delta/\sigma)_{\max} < 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.014$	$\Delta\rho_{\max} = 1.62$ e Å ⁻³
$wR(F^2) = 0.033$	$\Delta\rho_{\min} = -1.43$ e Å ⁻³
$S = 1.31$	Extinction correction: <i>SHELXL97</i>
247 reflections	Extinction coefficient: 0.064 (3)
14 parameters	
$w = 1/[\sigma^2(F_o^2) + (0.0158P)^2 + 0.1824P]$	
where $P = (F_o^2 + 2F_c^2)/3$	

Table 1

Selected bond lengths (Å) for (I).

Ru/Ti—O1	1.9368 (2)	Sr—O2	2.443 (3)
Ru/Ti—O2	2.052 (3)	Sr—O1 ⁱⁱ	2.6894 (7)
Ru/Ti—Sr ⁱ	3.3142 (6)	Sr—O2 ⁱ	2.7453 (3)

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

Compound (II)

Crystal data

Sr ₂ Ru _{0.81} Ti _{0.19} O ₄	Mo K α radiation
$M_r = 330.21$	Cell parameters from 25 reflections
Tetragonal, <i>I4/mmm</i>	$\theta = 7.1\text{--}18.0^\circ$
$a = 3.8767$ (5) Å	$\mu = 31.27$ mm ⁻¹
$c = 12.698$ (3) Å	$T = 293$ K
$V = 190.83$ (6) Å ³	Rectangular plate, black
$Z = 2$	$0.15 \times 0.09 \times 0.02$ mm
$D_x = 5.747$ Mg m ⁻³	

Table 2

Selected bond lengths (Å) for (II).

Ru/Ti—O1	1.9383 (2)	Sr—O2	2.448 (3)
Ru/Ti—O2	2.042 (3)	Sr—O1 ^{iv}	2.6855 (4)
Ru/Ti—Sr ⁱⁱⁱ	3.3120 (4)	Sr—O2 ⁱ	2.7474 (4)

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

Data collection

Siemens Syntex <i>P2</i> ₁ diffractometer	$R_{\text{int}} = 0.038$
$\omega/2\theta$ scans	$\theta_{\max} = 42.5^\circ$
Absorption correction: analytical (de Meulenaer & Tompa, 1965)	$h = -7 \rightarrow 7$
$T_{\min} = 0.074$, $T_{\max} = 0.529$	$k = -7 \rightarrow 7$
2882 measured reflections	$l = -24 \rightarrow 24$
247 independent reflections	3 standard reflections
246 reflections with $I > 2\sigma(I)$	every 100 reflections
	intensity decay: <1%

Refinement

Refinement on F^2	$(\Delta/\sigma)_{\max} = 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.019$	$\Delta\rho_{\max} = 1.40$ e Å ⁻³
$wR(F^2) = 0.045$	$\Delta\rho_{\min} = -2.97$ e Å ⁻³
$S = 1.41$	Extinction correction: <i>SHELXL97</i>
247 reflections	Extinction coefficient: 0.047 (3)
14 parameters	
$w = 1/[\sigma^2(F_o^2) + (0.0183P)^2 + 0.4584P]$	
where $P = (F_o^2 + 2F_c^2)/3$	

Because of the plate-like shape and high linear absorption coefficient of the crystals, an absorption correction was mandatory. The crystal faces and distances were thoroughly determined, and the analytical absorption correction procedure (Alcock, 1970) implemented in *PLATON* (Spek, 2003) was used. Equal displacement parameters were used for Ru and Ti, and the sum of their site-occupancy factors was fixed to yield a complete occupation of the corresponding site.

For both compounds, data collection: *P2*₁ *Software* (Kopf & Abeln, 1995); cell refinement: *P2*₁ *Software*; data reduction: *P2*₁ *Software*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ATOMS for Windows* (Dowty, 1995); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1623). Services for accessing these data are described at the back of the journal.

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