

Sr[ReO₄]₂: The First Single Crystals of an Anhydrous Alkaline-Earth Metal *Meta*-Perrhenate

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Dedicated to Professor Hans-Jörg Deiseroth on the Occasion of his 75th Birthday

Abstract. Colorless single crystals of Sr[ReO₄]₂ were obtained from halide melts at 1123 K in open corundum crucibles. X-ray diffraction revealed that Sr[ReO₄]₂ crystallizes in the monoclinic space group *P*2₁/*n* with the lattice parameters *a* = 627.31(4) pm, *b* = 1004.56(7) pm, *c* = 1271.25(9) pm and β = 97.118(3)° for *Z* = 4. The crystal structure contains a unique Sr²⁺-cation site surrounded by eight crystallographically different oxygen atoms forming distorted bicapped trigonal prisms. All corners of these [SrO₈]¹⁴⁻ polyhedra (*d*(Sr–O) = 259–

268 pm) are shared with tetrahedral *meta*-perrhenate units [ReO₄]⁻ (*d*(Re–O) = 166–173 pm) formed from two crystallographically different Re⁷⁺ cations surrounded by four O²⁻ anions each, building up the three-dimensional mosaic-like structure of Sr[ReO₄]₂. Single-crystal Raman data confirm the presence of two different kinds of symmetry-free *meta*-perrhenate units [ReO₄]⁻ and match well with results known from literature.

Introduction

During our ongoing investigations in possible host lattices for lanthanoid(II)-cation doping we became interested in strontium *meta*-perrhenate Sr[ReO₄]₂ and its crystalline hydrates Sr[ReO₄]₂·H₂O^[1] and Sr[ReO₄]₂·2 H₂O^[2] (previously described erroneously as Sr[ReO₄]₂·1.5 H₂O^[3]) as Sr²⁺ sites are known to be perfectly sized for doping with Eu²⁺.^[4] However, even though the high chemical and thermal stability of perrhenates lead to easy handling compared to the other alkaline-earth metal oxometalates(VII),^[5] there is a surprising lack of structure data in some areas. Even though there are recent reports on anhydrous alkali metal *meta*-perrhenates A[ReO₄]₂ (A = Na – Cs),^[6] no structural data on anhydrous alkaline-earth metal *meta*-perrhenates have been reported up to now with the exception of some mixed cationic ones, like for example CaNa[ReO₄]₃.^[7] However, *Jeitschko* et al. did excellent work on *ortho*-perrhenates (e.g. Sr₃[ReO₆]₂^[8]) and mixed anionic *meso*-perrhenates, such as Sr₃X[ReO₅]₃ (X = Cl, Br and I)^[9] in the past.

We now share the progress on our current investigations with a new *meta*-perrhenate Sr[ReO₄]₂ as rhenium with the atomic number of 75 is the element best suited for a dedicated publication on the occasion of a 75th birthday.

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Results and Discussion

Crystal Structure

Sr[ReO₄]₂, the first anhydrous alkaline-earth metal *meta*-perrhenate investigated by means of single-crystal X-ray diffraction, crystallizes in the monoclinic space group *P*2₁/*n* with the lattice parameters *a* = 627.31(4) pm, *b* = 1004.56(7) pm, *c* = 1271.25(9) pm and β = 97.118(3)° for *Z* = 4 (Table 1 and Table 2) matching well, when compared to the unit-cell dimensions obtained from powder X-ray diffraction data in 1992 (*a* = 628.8(2) pm, *b* = 1006.4(3) pm, *c* = 1272.9(3) pm and β = 97.06(2)°)^[10]. Unique Sr²⁺ cations on 4*e* sites are surrounded by eight crystallographically different O²⁻ anions forming distorted bicapped trigonal prisms (*d*(Sr–O_{body}) = 253–260 pm, *d*(Sr–O_{cap}) = 260–268 pm, Figure 1). Two Re⁷⁺-cation sites each surrounded by four oxygen atoms build two sets of *meta*-perrhenate tetrahedra [ReO₄]⁻ (*d*(Re–O) = 166–174 pm, χ (O–Re–O) = 106–113°, Figure 1) connecting the [SrO₈]¹⁴⁻ polyhedra via all corners (χ (Sr–O–Re) = 129–175°) thus creating the three-dimensional structure of Sr[ReO₄]₂ with a mosaic-like arrangement (Figure 2). The Re–O bond lengths (Table 3) compare well with those in CaNa[ReO₄]₃ (*d*(Re–O) = 171–173 pm), despite the inferior data quality and high mosaicity for Sr[ReO₄]₂ caused by a competing high-temperature form and degradation due to hygroscopicity.

A view at the **Madelung Part of the Lattice Energy (MAPLE)**^[11–13] shows just a small difference between Sr[ReO₄]₂ (MAPLE = 70.096 kJ·mol⁻¹) and the sum of the binary oxides (MAPLE(SrO) + MAPLE(Re₂O₇) = (3.762 + 65.798) kJ·mol⁻¹ = 69.560 kJ·mol⁻¹). This can easily be explained by looking at the differences in the coordination spheres of the cations present within the monoclinic Sr[ReO₄]₂ (Table 3) compared to those of the binary oxides SrO (*d*(Sr–O) =

Table 1. Crystallographic data for Sr[ReO₄]₂ and their determination.

Structured formula	Sr[ReO ₄] ₂
Crystal system	monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i> (no. 14)
<i>a</i> /pm	627.31(4)
<i>b</i> /pm	1004.56(7)
<i>c</i> /pm	1271.25(9)
β / °	97.118(3)
Number of formula units, <i>Z</i>	4
Molar volume, <i>V_m</i> /cm ³ ·mol ⁻¹	119.68(3)
Calculated density, <i>D_x</i> /g·cm ⁻³	4.913(1)
Temperature, <i>T</i> /K	293(2)
Crystal color	colorless, transparent
Crystal shape	needle-shaped
Ranges, 2θ /°	5.2–48.9
<i>h</i> , <i>k</i> , <i>l</i> range	±7, ±11, ±14
Diffractometer	Bruker-Nonius κ -CCD
Radiation	Mo- <i>K</i> _α (λ = 71.07 pm)
Monochromator	graphite
Absorption coefficient, μ /mm ⁻¹	37.07
Measured reflections	9417
Unique reflections	1314
<i>R_{int}</i> / <i>R_σ</i>	0.117 / 0.071
<i>R</i> ₁ ^a / <i>wR</i> ₂ ^b / GooF ^c (all reflections)	0.076 / 0.098 / 1.055
Residual electron density / 10 ⁶ ·pm ⁻³ (max. /min.)	1.52 / -1.39

a) $R_1 = \sum \|F_o\| - \|F_c\| / \sum \|F_o\|$, b) $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum (wF_o^2)^2]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (xP)^2 + yP]$ with $P = [(F_o^2) + 2F_c^2]/3$. c) GooF: $S = [\sum w(F_o^2 - F_c^2)^2 / (n-p)]^{1/2}$, with *n* being the number of reflections and *p* being the number of parameters.

Table 2. Fractional atomic coordinates and equivalent isotropic displacement parameters for Sr[ReO₄]₂ with all atoms on general Wyck-off sites 4e.

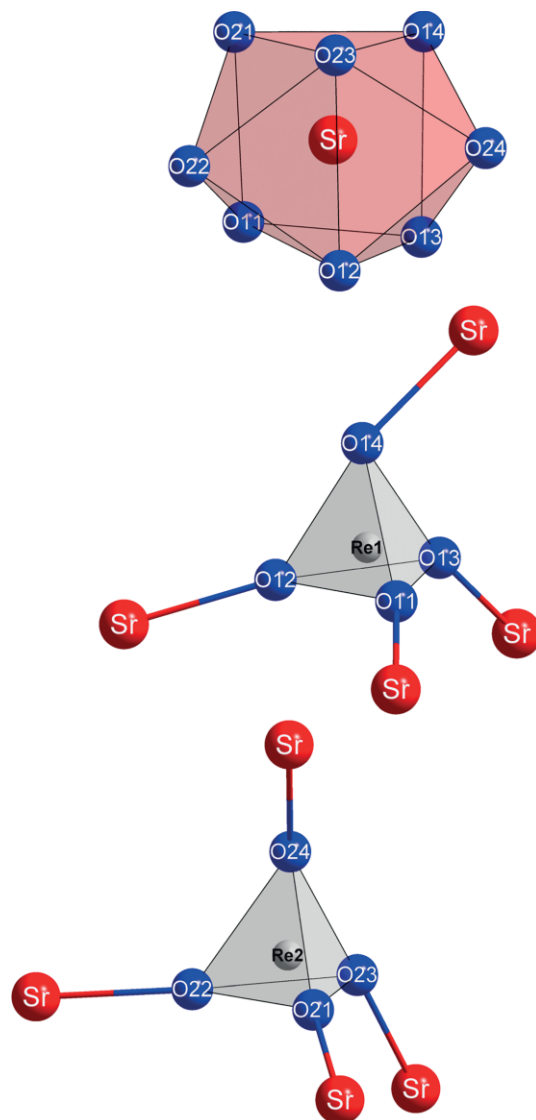
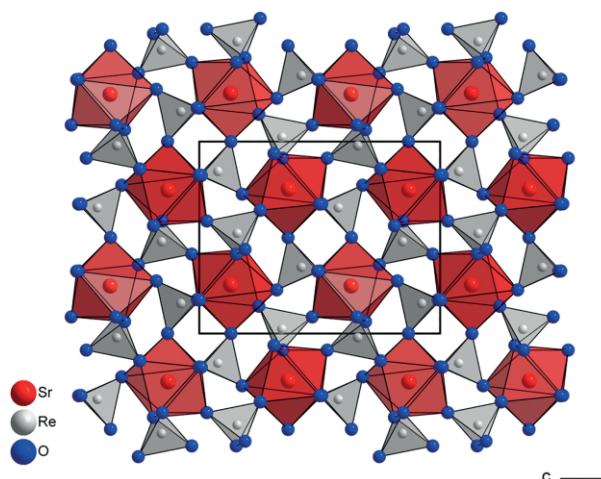
Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U_{eq}</i> / pm ²
Sr	0.3035(3)	0.74730(19)	0.13008(15)	333(5)
Re1	0.24900(16)	0.15560(9)	0.07690(7)	359(3)
Re2	0.78515(16)	0.47791(9)	0.15717(7)	366(3)
O11	0.009(3)	0.1759(17)	0.0087(14)	750(57)
O12	0.559(3)	0.8254(18)	0.0005(13)	807(65)
O13	0.266(3)	0.0004(14)	0.1316(12)	533(46)
O14	0.274(3)	0.2734(14)	0.1783(11)	430(38)
O21	0.989(3)	0.5861(16)	0.1534(12)	549(44)
O22	0.730(3)	0.4135(17)	0.0312(11)	555(46)
O23	0.564(3)	0.5620(15)	0.1900(13)	543(44)
O24	0.643(3)	0.8577(15)	0.2472(12)	476(41)

a) The anisotropic displacement factor takes the form $U_{ij} = \exp[-2\pi^2(h^2a^2U_{11} + k^2b^2U_{22} + l^2c^2U_{33} + 2klb^*c^*U_{23} + 2hla^*c^*U_{13} + 2hka^*b^*U_{12})]$.^[16]

258.1 pm (6 ×), NaCl type)^[14] and orthorhombic Re₂O₇ (*d*(Re–O) = 168–181 pm for C.N. = 4 and 165–216 pm for C.N. = 6).^[15]

Raman Spectroscopy

The Raman spectrum of Sr[ReO₄]₂ (Figure 3) shows four bands of deformation vibrations (δ ([ReO₄]⁻) = 314–348 cm⁻¹) and seven higher energetic bands belonging to stretching vibrations (ν ([ReO₄]⁻) = 896–1008 cm⁻¹), all of them belonging to two different kinds of *meta*-perrhenate units

**Figure 1.** Biccapped trigonal prism [SrO₈]¹⁴⁻ (top) and the two different [ReO₄]⁻ tetrahedra (mid and bottom) including their Sr²⁺-cationic connectivity in the crystal structure of Sr[ReO₄]₂.**Figure 2.** View at the crystal structure of Sr[ReO₄]₂ along [100].

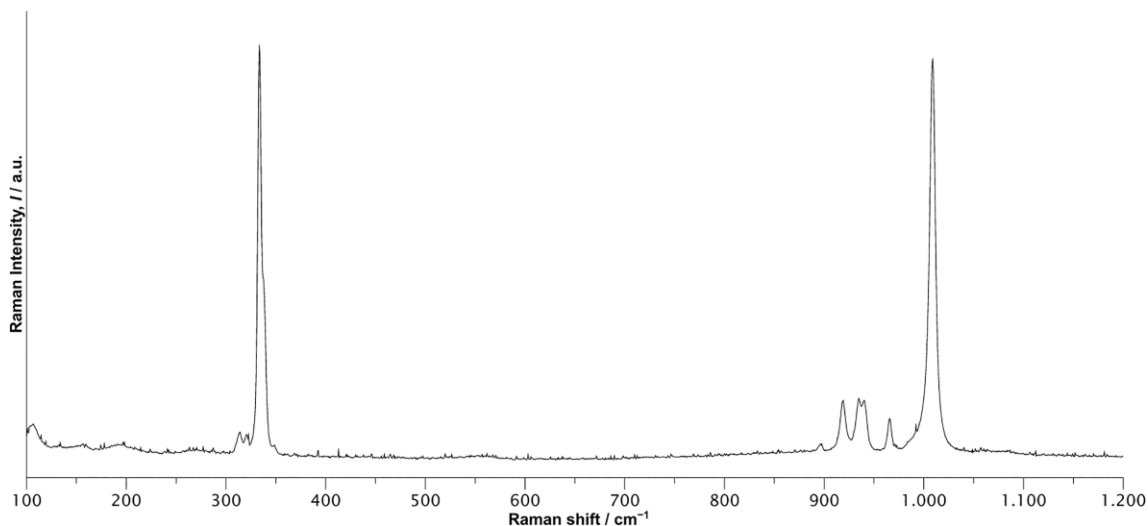


Figure 3. Single-crystal Raman spectrum of Sr[ReO₄]₂ recorded with an excitation wavelength of $\lambda = 532$ nm.

Table 3. Interatomic distances (d/pm) in Sr[ReO₄]₂ with estimated standard deviations in parentheses.

Sr–O11	259(2)	Re1–O11	166(2)
Sr–O12	256(2)	Re1–O12	166(2)
Sr–O13	255(1)	Re1–O13	170(1)
Sr–O14	256(1)	Re1–O14	174(1)
Sr–O21	260(2)	Re2–O21	168(2)
Sr–O22	260(2)	Re2–O22	172(1)
Sr–O23	253(2)	Re2–O23	172(2)
Sr–O24	268(1)	Re2–O24	173(1)

(Table 4). The minor shifts observed between our recorded data and the literature Raman spectrum by *Ulbricht et al.*^[17] result from different instruments and sample preparation.

Table 4. Single-crystal Raman data for Sr[ReO₄]₂ compared with the Raman shifts $\tilde{\nu}/\text{cm}^{-1}$ reported in the literature^a.

Mode	Sr[ReO ₄] ₂ (powder) [17]	Sr[ReO ₄] ₂ (single crystal) this work
$\delta([\text{ReO}_4]^-)$	315 (vw)	314 (w)
	335 (m)	321 (w)
	339 (m)	334 (vs)
	343 (m)	348 (vw)
	354 (w)	
$\nu([\text{ReO}_4]^-)$	904 (m)	896 (vw)
	914 (m)	919 (m)
	932 (w)	934 (m)
		940 (m)
	960 (w)	966 (w)
	986 (m)	992 (vw)
	997 (s)	1008 (vs)

a) (vw) very weak, (w) weak, (m) medium, (s) strong, (vs) very strong.

Conclusions

Sr[ReO₄]₂ is to the best of our knowledge the first alkaline-earth metal *meta*-perrhenate characterized by means of single-crystal X-ray diffraction and its successful structure determination is a first step towards doping experiments with Eu²⁺.

Investigations in the various phases of strontium *meta*-perrhenate Sr[ReO₄]₂ at different temperatures, in its hydration or dehydration process, as well as in halide-containing mixed anionic phases with compositions like SrX[ReO₄] and Sr₅X[ReO₅]₃ ($X = \text{Cl}$ and Br)^[9] are currently ongoing and have already shown promising results for the analogous barium *meta*-perrhenates.^[18]

Experimental Section

Synthesis: Strontium *meta*-perrhenate monohydrate Sr[ReO₄]₂·H₂O was prepared under atmospheric conditions from commercially available potassium *meta*-perrhenate K[ReO₄] (Alpha Aesar, Kandel, Germany, 99%) via cation exchange as described in^[5] using Amberlite® IR-120 (Fluka, Buchs, Switzerland) as resin and strontium chloride hexahydrate (Merck, Darmstadt, Germany, 99%) as source of Sr²⁺ cations. Afterwards, equimolar amounts of Sr[ReO₄]₂·H₂O and SrCl₂·6H₂O were homogenized and heated to 1123 K with a rate of 10 K·min⁻¹ in an open corundum crucible. Upon reaching the reaction temperature, the furnace was turned off, slowly cooling the sample to room temperature. Colorless, transparent, hygroscopic needles of Sr[ReO₄]₂ were observed, but only in a poor yield due to the formation of chloride-containing by-products such as Sr₃Cl[ReO₅]₃^[9] and Sr₄OCl₆.^[19] Phase pure, microcrystalline samples of monoclinic Sr[ReO₄]₂ can be obtained by dehydration of its hydrates.^[10] To avoid degradation by moisture the sample was stored under paraffin oil (Honeywell, Seelze, Germany, extra pure) before further manipulations were conducted.

Crystallographic Studies: To conduct the single-crystal X-ray diffraction experiments, a suitable single crystal of the title compound was sealed into a thin-walled glass capillary and subsequently mounted on a Bruker-Nonius κ -CCD diffractometer equipped with a Mo- K_{α} radiation source ($\lambda = 71.07$ pm), a graphite monochromator and a CCD detector. The program DENZO^[20] was used to process the collected intensity data and to apply a numerical absorption correction with the HABITUS program.^[21] After the analysis of systematic absences lead to the space group $P2_1/n$ (no. 14), the crystal structure was solved and refined using the SHELX-97 program package.^[22–24] In addition to the crystallographic data provided in Table 1 and Table 2, further details

of the crystal structure investigations may be obtained from the ICSD, Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (Fax: +49-7247-808-666; E-Mail: crysdata@fiz-karlsruhe.de, <http://www.fiz-karlsruhe.de/request> for deposited data.html) on quoting the depository number CSD-2024123.

Raman Spectroscopy: After the crystallographic studies Raman spectroscopic measurements were conducted on the same sample using an XploRA microscope LASER Raman spectrometer (Horiba Jobin, Yvon, Bensheim, Germany) equipped with a green LASER (excitation line at $\lambda = 532$ nm with a maximum power output of 25 mW and 4×15 s accumulation time). It was safe to assume that the experiment was performed on an anhydrous area of the sample, as no $\nu(\text{O-H})$ vibrations were observed at $3200\text{--}3600\text{ cm}^{-1}$.

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Keywords: Perrhenate; Strontium; Structure elucidation; X-ray diffraction; Raman spectroscopy

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