The Crystal Structures of the Isotypic Perrhenates $Ca_5Re_2O_{12}$ and $Sr_5Re_2O_{12}$

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Single crystals of the title compounds were obtained by annealing powders of the alkaline-earth oxides MO (M = Ca, Sr) with the metaperrhenates $M(ReO_4)_2 \cdot 2H_2O$ in open alumina crucibles. The crystal structures of these isotypic compounds are rhombohedral, space group $R\bar{3}c$. The lattice constants for the hexagonal setting are a = 955.36(8) pm, c = 5458.6(4) pm, and a = 995.30(7) pm, c = 5670.7(3) pm for the Ca and Sr compound, respectively, with Z = 18 formula units per cell. The structures were determined from single-crystal X-ray data: R = 0.024 (930 structure factors) and R = 0.042 (1228 F_o's) for 89 variable parameters each. Some portions of the structure can be derived from distorted perovskite subcells with vacancies for all atomic species. The alkaline-earth atoms occupy sites with six, eight, and nine oxygen neighbors. All rhenium atoms have octahedral oxygen coordination. Both compounds are yellow or dark green, depending on the oxygen partial pressure in the annealing atmosphere. © 1992 Academic Press, Inc.

Introduction

Many ternary alkine-earth rhenium oxides were investigated in the past (*1, 2*). Structurally well characterized are $Ca_{11}Re_4O_{24}$ (*3*), $Ca_{10}Re_6O_{29-x}$ (*3*), Sr_xReO_3 ($0.4 \leq x \leq 0.5$) (*4, 5*), $Sr_3Re_2O_9$ and $Ba_3Re_{2-x}O_9$ (*6, 7*), $Ba_5(ReO_5)_3O_2$ (*8*), and Ba_2ReO_5 (*9*). The results obtained from powder diffraction data of $Ca_5Re_2O_{12}$ and $Sr_5Re_2O_{12}$ were published earlier (*1, 2, 10*). A hexagonal subcell for these compounds was proposed on the basis of single-crystal data (*11, 12*). Longo, Katz, and Ward (*11*) suggested a large rhombohedral cell for the superstructure of these compounds, which we find to be correct in the present investigation. They also made a proposal for the

structure of the subcell, which is qualitatively correct for most of the metal and a majority of the oxygen positions. We have now determined the full crystal structures of these isotypic compounds. Preliminary reports of this work were given earlier (*13, 14*).

Sample Preparation

Starting materials were rhenium powder (> 99%, Starck) and the alkaline-earth oxides (Ventron, > 99.5%). For the preparation of the perrhenic acid $HReO_4$, 3 g of rhenium powder were dissolved in 10 ml of a hydrogen peroxide solution (30%, Merck) while cooling the reaction mixture in an ice bath (*15*). The perrhenic acid was subsequently neutralized by adding a stoichiometric amount of the corresponding alka-

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line-earth oxides. The solution was dried at 110°C, and the resulting alkaline-earth metaperrhenates $M(ReO_4)_2 \cdot 2H_2O$ (16–20) were mixed with the corresponding oxides MO in the ratio 1 : 4 and then annealed in alumina crucibles for 24 hr at 700°C in air and subsequently in an alumina boat at 1000°C for 2 weeks in a dynamic vacuum with a pressure of about 3 Pa. After the annealing processes the products were purified by dissolving the excess of metaperrhenate in methanol in an ultrasonic bath. The reactions resulted in small hexagonal platelets. Energy dispersive X-ray analyses of both samples did not reveal any contamination by elements heavier than sodium.

The Color of $Ca_5Re_2O_{12}$ and $Sr_5Re_2O_{12}$

It was already noted before (11) that the samples of $Ca_5Re_2O_{12}$ and $Sr_5Re_2O_{12}$ have different colors, depending on the annealing temperature. This we can confirm. Powders and single crystals of both compounds which have been annealed at 700°C are yellow at room temperature, while they have a dark-green color when they have been annealed at 1000°C. A high-temperature diffraction pattern recorded in a Simon–Guinier camera (21) from 20°C up to 960°C and a differential-thermal-analysis for $Ca_5Re_2O_{12}$ gave no indication for a phase transformation that could explain this behavior. It was assumed (11) that the change of the color is due to a reversible loss of a minor amount of oxygen, which results in a partial reduction of Re(VII). This was proved in an experiment by annealing a yellow powder of $Sr_5Re_2O_{12}$ in a dynamic atmosphere of high purity argon at 700°C for 5 days. Here we obtained the dark-green product. After cooling, the sample was heated again under an oxygen atmosphere at 1000°C for 3 days. This annealing process resulted in a powder of yellow color. Thus, the partial pressure of oxygen is the im-

portant factor and not the annealing temperature.

Crystal Structure

The single crystals of $Ca_5Re_2O_{12}$ and $Sr_5Re_2O_{12}$ were isolated from the samples purified in the ultrasonic bath. They were examined with Buerger precession cameras to establish their symmetry and suitability for data collection. The precession diagrams indicated trigonal symmetry with a pronounced subcell of dimensions $a' = a/\sqrt{3}$ and $c' = c/3$ as observed previously (11, 12). Most superstructure reflections are very weak and the superstructure can easily be missed (12). The lattice constants (Table I) were refined from the powder diagrams using α-quartz ($a = 491.30$ pm, $c = 540.46$ pm) as a standard. For identification purposes we list the $Sr_5Re_2O_{12}$ diagram in Table II. The systematic extinctions (hkl only with $-h + k + l = 3n$ and $h\bar{h}0l$ only with $l = 2n$) indicated a rhombohedral cell with $R3c$ and $R\bar{3}c$ as possible space groups, of which the centrosymmetric group $R\bar{3}c$ (No. 167) was found to be correct during the structure refinements.

Single-crystal intensity data were collected on an automated four-circle diffrac-

TABLE I

HEXAGONAL LATTICE CONSTANTS OF THE ISOTYPIC RHOMBOHEDRAL COMPOUNDS $Ca_5Re_2O_{12}$ AND $Sr_5Re_2O_{12}$[a]

	a (pm)	c (pm)	V (nm³)	Reference
$Ca_5Re_2O_{12}$	955.36(8)	5458.6(4)	4.3146	This work
$Ca_5Re_2O_{12}$[b]	955.07(11)	5458.3(5)	4.3124	This work
$Ca_5Re_2O_{12}$	956	5480	4.337	(11)
$Ca_5Re_2O_{12}$	553.2	1828	0.4845	(12)
$Sr_5Re_2O_{12}$	995.30(7)	5670.7(3)	4.8649	This work
$Sr_5Re_2O_{12}$[b]	994.6(3)	5672.7(7)	4.8570	This work
$Sr_5Re_2O_{12}$	996	5690	4.888	(11)
$Sr_5Re_2O_{12}$	575.6	1903	0.5460	(12)

[a] Standard deviations in the positions of the least significant digits are given in parentheses throughout the paper.
[b] These data were obtained on the four-circle diffractometer; they are less reliable.

TABLE II

GUINIER POWDER PATTERN OF Sr$_5$Re$_2$O$_{12}$[a]

H	K	L[b]	h	k	l	Q$_o$	Q$_c$	I$_o$	I$_c$	H	K	L[b]	h	k	l	Q$_o$	Q$_c$	I$_o$	I$_c$
—			0	1	8	333	334	w	9	0	0	10	0	0	30	2799	2799	vw	4
1	0	1	1	1	3	431	432	m	16	2	1	1	{4 1 3 / 1 4 3}			2855	2854	vw	{<1 / 2}
0	0	4	0	0	12	447	448	m	17										
1	0	2	1	1	6	515	516	s	40	2	1	2	{4 1 6 / 1 4 6}			2939	2938	w	{2 / 3}
—			0	2	4	588	588	vw	3										
1	0	3	1	1	9	655	656	w	6		—		4	0	16	2949	2950	m	2
—			2	0	8	736	737	vw	2	2	0	7	2	2	21	2990	2987	vw	1
1	0	4	1	1	12	851	852	s	21		—		3	1	20	2994	2994	vw	2
—			1	0	16	930	931	vw	2	1	1	8	{3 0 24 / 0 3 24}			3002	3003	w	{2 / 3}
—			2	1	1	944	945	vw	3										
1	0	5	1	1	15	1103	1103	vs	77	2	1	3	{1 4 9 / 4 1 9}			3080	3078	vw	{<1 / <1}
—			1	2	8	1140	1141	vw	3										
1	1	0	3	0	0	1211	1211	vs	100	1	0	10	1	1	30	3202	3203	m	16
—			0	1	20	1378	1378	vw	2		—		1	3	22	3253	3255	vw	2
1	0	6	1	1	18	1411	1411	m	19	2	1	4	{1 4 12 / 4 1 12}			3274	3274	w	{3 / 2}
—			1	2	14	1551	1552	vw	3										
2	0	1	2	2	3	1641	1643	vw	4	2	1	5	{4 1 15 / 1 4 15}			3526	3526	s	{14 / 14}
1	1	4	{3 0 12 / 0 3 12}			1659	1659	m	{6 / 11}	3	0	0	3	3	0	3634	3634	s	22
2	0	2	2	2	6	1726	1727	vw	2		—		1	0	34	3730	3729	vw	1
—			1	3	1	1752	1753	vw	3	1	0	11	1	1	33	—	3790	—	3
1	0	7	1	1	21	1775	1775	vw	2		—		2	3	20	—	3801	—	3
—			2	0	20	1784	1782	vw	2	2	1	6	{1 4 18 / 4 1 18}			3834	3834	m	{8 / 6}
—			3	1	8	1948	1949	vw	2										
2	0	4	2	2	12	2061	2063	w	6	1	1	10	{3 0 30 / 0 3 30}			4010	4010	w	{3 / 3}
—			3	1	11	2126	2126	vw	<1										
—			0	4	2	2166	2166	vw	<1	0	0	12	0	0	36	—	4030	—	2
—			1	2	20	2185	2186	m	8	3	0	4	3	3	12	4083	4082	w	8
2	0	5	2	2	15	2315	2315	vs	41		—		1	2	32	4127	4127	vw	<1
—			0	4	8	2353	2353	vw	1		—		5	1	1	4177	4176	vw	2
—			2	1	22	2446	2447	vw	2	2	0	10	2	2	30	4413	4414	m	12
—			1	3	16	2548	2546	vw	3	2	1	8	{1 4 24 / 4 1 24}			4618	4618	vw	{<1 / <1}
—			3	2	4	2606	2607	vw	2										
2	0	6	2	2	18	2622	2623	m	11		—		2	3	26	4659	4660	vw	2
—			2	0	26	2643	2641	vw	<1	2	2	0	6	0	0	4843	4845	m	17
—			0	4	14	2763	2763	vw	<1										

[a] The diagram was recorded with CuKα_1 radiation. The Q values are defined by $Q = 100/d^2$ (nm^{-2}). For the intensity calculations (22) the positional parameters of the refined structure were used.

[b] In the column HKL the indices of the hexagonal subcell are given. All observed reflections and all reflections with calculated intensities $I_c > 1$ are listed.

tometer with graphite monochromated MoKα radiation, a scintillation counter, and a pulse-height discriminator. Background counts were taken at both ends of each $\theta/2\theta$ scan and an empirical absorption correction was applied from psi-scan data. Further information on the data collections for Ca$_5$Re$_2$O$_{12}$ and Sr$_5$Re$_2$O$_{12}$ is given in Table III.

The structure of the Ca compound was solved first with a reduced ($F_o > 10\sigma$) data

TABLE III

CRYSTALLOGRAPHIC DATA FOR $Ca_5Re_2O_{12}$
AND $Sr_5Re_2O_{12}$

	$Ca_5Re_2O_{12}$	$Sr_5Re_2O_{12}$
Lattice constants	(see TABLE I)	
Formula units/hex. cell	18	18
Space group	$R\bar{3}c$	$R\bar{3}c$
Formula weight	764.80	1002.49
Calculated density [g/cm³]	$\rho_c = 5.30$	$\rho_c = 6.16$
Observed density [g/cm³]		$\rho_o = 6.14^a$
Absorption coefficient [cm⁻¹]	$\mu(MoK\alpha) = 283$	$\mu(MoK\alpha) = 464$
Cryst. dimensions [μm³]	$45 \times 45 \times 45$	$5 \times 50 \times 75$
$\theta/2\theta$ scans up to	$2\theta = 70°$	$2\theta = 90°$
Range in hkl	$\pm15, \pm15, +88$	$+19, \pm19, +113$
Total No. of reflections	12,778	10,472
Unique reflections	2443	3766
Transm. coeff. (highest/lowest)	1.66	4.13
Internal residual	$R_i = 0.051$	$R_i = 0.059$
Reflections with $I > 3\sigma(I)$	930	1228
Weights	$w = 1/\sigma^2$	$w = 1/\sigma^2$
No. of variables	89	89
Conventional residual	$R = 0.024$	$R = 0.042$
Weighted residual	$R_w = 0.019$	$R_w = 0.043$

^{a} Taken from (11).

set. Direct methods suggested positions for some rhenium atoms. The other atomic sites were obtained from difference Fourier syntheses and geometric considerations. This sounds simple, however, because of the large volume of the cell and weak scattering power of the oxygen positions, many trial structures were refined unsuccessfully before a satisfactory solution was obtained. Both structures were refined by full-matrix least-squares cycles. The atomic scattering factors (23) were corrected for anomalous dispersion (24). Weights were assigned according to the counting statistics. Parameters accounting for isotropic secondary extinction were refined and applied to the calculated structure factors. The final conventional and weighted residuals for the Ca compound (with the values for the Sr compound in parentheses) are $R = 0.024$ (0.042) and $R_w = 0.019$ (0.043) for 89 (89) variable parameters and 930 (1228) structure factors.

Final difference Fourier syntheses gave no indications for the occupancy of additional atomic sites. The atomic parameters and the interatomic distances are listed in Tables IV and V. The anisotropic thermal parameters and the structure factor tables are available from the authors. Projections of the structure are shown in Fig. 1.

Discussion

A description of the structure is somewhat difficult because of the large cell content (342 atoms for the hexagonal setting). Fortunately all metal atoms are situated at or close to the threefold screw and rotation axes. There are only two sequences for the metal atoms along these axes (Fig. 1), one

TABLE IV

ATOMIC PARAMETERS OF $Ca_5Re_2O_{12}$ AND $Sr_5Re_2O_{12}^a$

Atom	$R\bar{3}c$	x	y	z	B
$Ca_5Re_2O_{12}$					
Ca1	36f	0.0136(2)	0.3588(2)	0.18704(3)	0.83(4)
Ca2	36f	0.3723(2)	0.0422(2)	0.04918(3)	0.66(3)
Ca3	12c	0	0	0.10450(6)	0.79(3)
Ca4	6a	0	0	$\frac{1}{4}$	0.61(5)
Re1	18e	0.33560(7)	0	$\frac{1}{4}$	0.363(7)
Re2	12c	0	0	0.16150(1)	0.394(5)
Re3	6b	0	0	0	0.464(8)
O1	36f	0.0003(9)	0.1910(9)	0.2242(1)	0.8(1)
O2	36f	0.0033(9)	0.1632(9)	0.0193(1)	0.8(1)
O3	36f	0.1262(9)	0.1849(8)	0.1786(1)	0.8(1)
O4	36f	0.1824(9)	0.0670(8)	0.1401(1)	0.9(1)
O5	36f	0.1923(8)	0.3170(9)	0.1072(1)	0.8(1)
O6	36f	0.2507(9)	0.1124(9)	0.0828(1)	1.1(1)
$Sr_5Re_2O_{12}$					
Sr1	36f	0.0085(2)	0.3542(1)	0.18675(2)	0.93(2)
Sr2	36f	0.3670(2)	0.0401(1)	0.04930(2)	0.67(2)
Sr3	12c	0	0	0.10409(4)	0.66(2)
Sr4	6a	0	0	$\frac{1}{4}$	0.87(4)
Re1	18e	0.33302(9)	0	$\frac{1}{4}$	0.44(1)
Re2	12c	0	0	0.16235(2)	0.443(9)
Re3	6b	0	0	0	0.52(1)
O1	36f	0.000(1)	0.198(1)	0.2243(2)	1.1(2)
O2	36f	0.000(1)	0.156(1)	0.0186(2)	0.8(2)
O3	36f	0.129(1)	0.174(1)	0.1796(2)	1.0(2)
O4	36f	0.173(1)	0.050(1)	0.1420(2)	0.62(2)
O5	36f	0.197(1)	0.315(1)	0.1064(2)	1.0(2)
O6	36f	0.254(1)	0.118(1)	0.0828(2)	0.8(2)

Note. The atomic parameters were standardized by the program STRUCTURE TIDY (25).

^{a} The last column contains the equivalent isotropic B values ($\times 100$, in units of nm²) of the ellipsoidal thermal parameters.

TABLE V

INTERATOMIC DISTANCES (pm) IN THE STRUCTURES OF Ca$_5$Re$_2$O$_{12}$ AND Sr$_5$Re$_2$O$_{12}$[a]

			$M = $ Ca	$M = $ Sr
$M1$:	1	O4	234.1	252.8
	1	O5	240.8	254.3
	1	O3	243.3	260.0
	1	O3	246.8	263.7
	1	O2	252.1	269.4
	1	O1	254.8	261.7
	1	O2	261.2	273.2
	1	O2	267.6	280.5
$M2$:	1	O4	234.3	251.1
	1	O5	237.5	250.7
	1	O6	243.7	252.1
	1	O3	246.5	254.0
	1	O2	246.6	260.0
	1	O1	248.1	260.6
	1	O6	251.9	263.6
	1	O1	252.0	268.5
$M3$:	3	O6	239.2	250.0
	3	O4	246.9	264.0
	3	O5	264.7	274.6
$M4$:	6	O1	230.5	244.7
Re1:	2	O5	181.1	182.8
	2	O6	185.1	187.9
	2	O1	197.5	198.3
Re2:	3	O3	182.0	183.8
	3	O4	192.4	191.6
Re3:	6	O2	187.0	187.7
O1:	1	Re1	197.5	198.3
	1	$M4$	230.5	244.7
	1	$M2$	248.1	260.6
	1	$M2$	252.0	268.5
	1	$M1$	254.8	261.7
O2:	1	Re3	187.0	187.7
	1	$M2$	246.6	260.0
	1	$M1$	252.1	269.4
	1	$M1$	261.2	273.2
	1	$M1$	267.6	280.5
O3:	1	Re2	182.0	183.8
	1	$M1$	243.3	260.0
	1	$M2$	246.5	254.0
	1	$M1$	246.8	263.7
O4:	1	Re2	192.4	191.6
	1	$M1$	234.1	252.8
	1	$M2$	234.3	251.1
	1	$M3$	246.9	264.0
O5:	1	Re1	181.1	182.8
	1	$M2$	237.5	250.7
	1	$M1$	240.8	254.3
	1	$M3$	264.7	274.6

TABLE V—Continued

			$M = $ Ca	$M = $ Sr
O6:	1	Re1	185.1	187.9
	1	$M3$	239.2	250.0
	1	$M2$	243.7	252.1
	1	$M2$	251.9	263.6

[a] All metal–oxygen distances shorter than 320 pm are listed. The shortest metal–rhenium distances are 319.9 pm (Ca–Re) and 330.4 pm (Sr–Re). Standard deviations are all equal to or smaller than 0.8 pm and 1.2 pm for the Ca and Sr compound, respectively.

for the rotation axis (A) and the other for the screw axis (B) of space group $R\bar{3}c$. All oxygen atoms have one Re neighbor and their positions can be visualized best by showing the orientation of the ReO$_6$ octahedra.

In discussing near-neighbor coordinations we mostly refer to the Ca compound and give, where appropriate, the values for the isotypic Sr compound in parentheses. The Ca atoms occupy four atomic sites. The Ca1 and Ca2 atoms, being close to the screw axes in a general position, have eight oxygen neighbors in irregular arrangements. The Ca3 and Ca4 atoms are situated at the three-fold rotation axes with nine and six oxygen neighbors, respectively (Fig. 2). The three Re sites are all octahedrally coordinated to oxygen atoms. The six different oxygen atoms have, besides the one Re neighbor, four (O1, O2) or three Ca neighbors.

The interatomic distances are quite consistent for the two compounds. The average Re–O distances in the ReO$_6$ octahedra vary between 187.0 and 189.7 pm (Table VI). The larger values of 187.9 pm (189.7 pm in the Sr compound) correspond to those octahedra with the largest spread of individual distances as is usually observed (26). The shortest average M–O distances are found for the Ca4 (230.5 pm) and Sr4 (244.7 pm) atoms, which have the lowest CN (of six). The other average M–O distances are
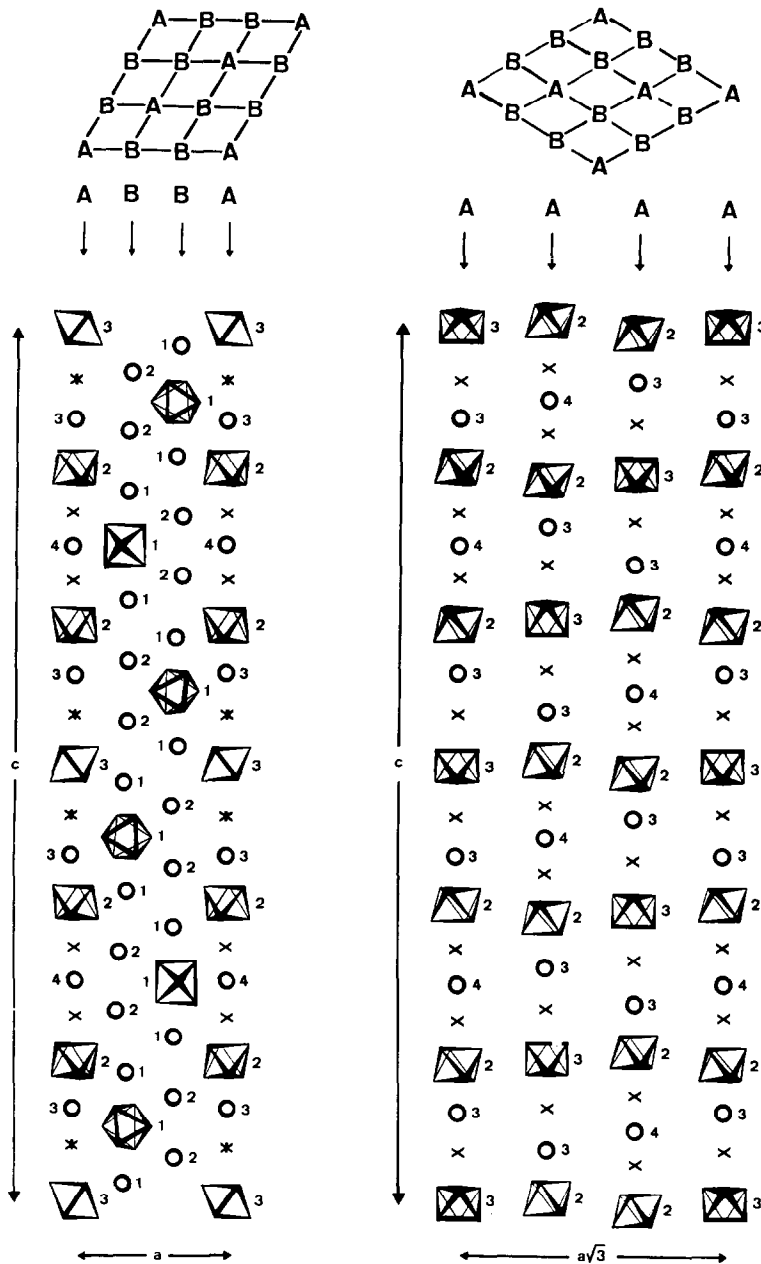
FIG. 1. Projections of the crystal structure of $Ca_5Re_2O_{12}$. In the upper part of the drawing, the trigonal cell (space group $R\bar{3}c$) is projected along the c axis. The positions of the trigonal rotation and screw axes are indicated by the letters A and B, respectively. In the lower part, two rows of these axes are projected perpendicular to the c direction. All oxygen atoms have one Re neighbor and the ReO_6 octahedra are outlined. Large circles represent Ca atoms. The numbers indicate the atom designations of the Re and Ca atoms. Stars and crosses indicate vacant metal sites with different oxygen coordinations.
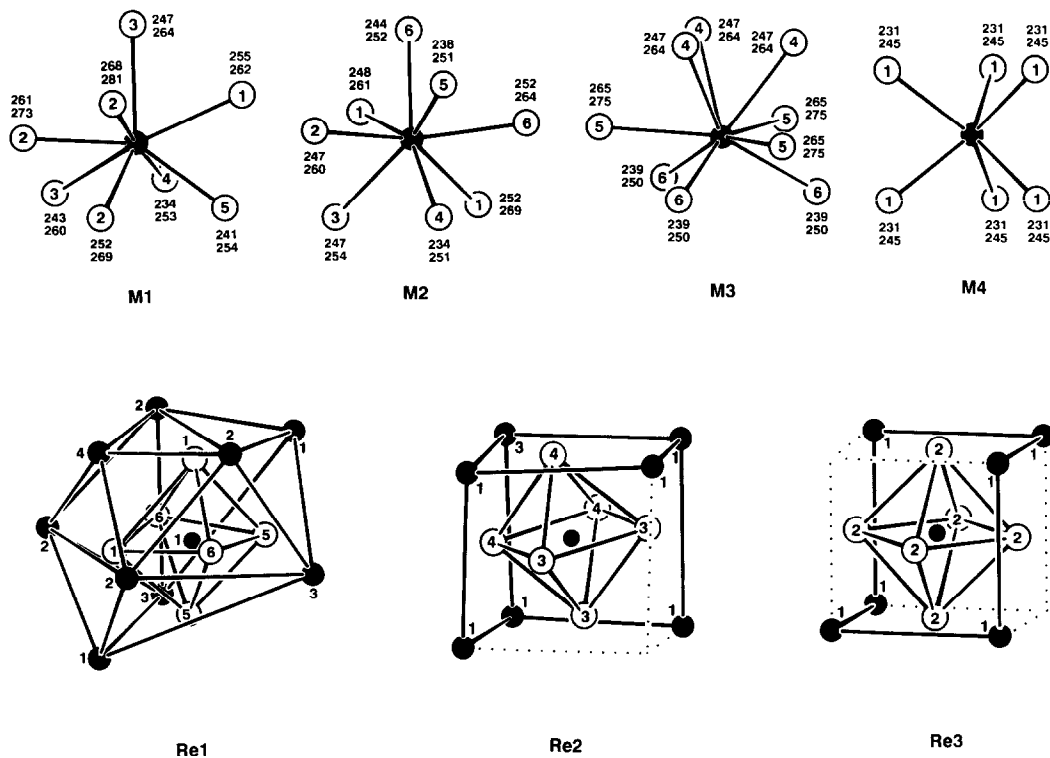
FIG. 2. Coordination of the metal atoms in the structures of M_5Re$_2$O$_{12}$ (M = Ca, Sr). In the upper row the oxygen coordination of the M atoms is shown. Single-digit numbers indicate the designations of the oxygen atoms. Interatomic distances are given in pm units; the larger number corresponds always to the Sr compound. The lower row shows the near-neighbor environments of the Re atoms. Besides the six oxygen neighbors, each Re atom has between six and nine M atoms in its vicinity. The seven and six M neighbors of the Re2 and Re3 atoms, respectively, may be thought of as forming the corners of a cube, which corresponds to the perovskite structure. The nine M neighbors of the Re1 atoms, however, make it difficult to visualize a perovskite-type building element with the Re1 atoms at the center.

larger, in agreement with the higher CN of these M atoms. However, the average M–O distances of the $M3$ atoms which have CN 9 are practically equal or even slightly shorter than the average M–O distances of the $M1$ atoms which have CN 8. This slight discrepancy is acceptable, because the Sr atoms have relatively low valency and thus the M–O interactions are weak.

In Table VI we have subtracted the appropriate oxygen radii of the average metal–oxygen distances and we compare the thus

obtained effective metal radii r_{eff} with the corresponding radii r_{IR} given by Shannon (26). It is remarkable that the Shannon radii are larger for the M atoms as well as for the Re atoms. For the Re atoms this difference is readily rationalized, because Shannon had obtained the radius for Re^{7+} CN 6 from only one compound, Re$_2$O$_7 \cdot 2$H$_2$O (27), with one highly distorted octahedral Re site, where the Re–O distances vary between 165 and 216 pm. Certainly the average value for this radius of 49.4 pm, obtained in the pres-

TABLE VI

COORDINATION NUMBERS (CN) AND AVERAGE
METAL–OXYGEN DISTANCES (d) IN $Ca_5Re_2O_{12}$
AND $Sr_5Re_2O_{12}$

Atom	CN	d (pm)	r_{eff} (pm)	r_{IR} (pm)
$Ca_5Re_2O_{12}$				
Re1	6	187.9	49.6	53
Re2	6	187.2	49.2	53
Re3	6	187.0	48.0	53
Ca1	8	250.1	111.6	112
Ca2	8	245.1	106.7	112
Ca3	9	250.3	112.3	118
Ca4	6	230.5	91.5	100
$Sr_5Re_2O_{12}$				
Re1	6	189.7	51.4	53
Re2	6	187.7	49.7	53
Re3	6	187.7	48.7	53
Sr1	8	264.4	125.9	126
Sr2	8	257.6	119.2	126
Sr3	9	262.9	124.9	131
Sr4	6	244.7	105.7	118

Note. The ionic radii obtained from these distances (assuming oxygen radii of 138 pm and 139 pm for CN IV and V, respectively) are listed under the heading "r_{eff}" and compared to the radii r_{IR} given by Shannon (26).

ent two structure determinations, is more reliable than the value of 53 pm given by Shannon.

Similarily the radii given by Shannon for Ca and Sr for various coordination numbers were obtained from various borates, carbonates, phosphates, arsenates, and similar compounds. In none of these do the M atoms share the oxygen atoms with such a (formally) highly charged cation as Re^{7+}. Chiari has recently compiled Ca–oxygen distances for a large number of compounds (28). The average Ca–O distances in $Ca_5Re_2O_{12}$ compare rather well with the range of average Ca–O distances observed in other compounds. Nevertheless, the average Ca–O distances for the Ca3 (CN 9) and Ca4 (CN 6) atoms of 250.3 pm and 230.5 pm are both slightly smaller than the small-

est previously observed values of 250.8 and 231.0 pm.

Longo, Katz, and Ward (*11*) have made a proposal for the hexagonal ("8-layer") subcell of the structure based on close packed Ca(Sr)–oxygen layers. This proposal is remarkably correct in as far as the metal positions are indeed located close to or on the threefold axes and there are several close packed M–oxygen layers discernible. The sequences of the metal atoms, however, show differences and some of the M–oxygen layers are highly distorted. Thus, a description of the structure as derived from close packed M–oxygen layers is not meaningful. Nevertheless, the structure contains building elements, which may be described as derived from the perovskite structure, $CaTiO_3$ (we remind the reader that this structure is sometimes described as a cubic close packed arrangement of CaO_3-layers with Ti atoms on those octahedral voids formed only by oxygen atoms). This is shown in the lower row of Fig. 2. It can be seen that the Re atoms have near-neighbor coordinations similar to those of the Ti atoms in $CaTiO_3$. They are all more or less distorted and one or two M positions are vacant in the environments of the Re2 and Re3 atoms, while the Re3 atoms have nine M atoms in their vicinity.

Acknowledgments

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