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Preparation and Crystal Structure of the Isotypic Orthorhombic Strontium Perrhenate Halides $Sr_5(ReO_5)_3X$ (X = Cl, Br, I) and Structure Refinement of the Related Hexagonal Apatite-like Compound $Ba_5(ReO_5)_3Cl$

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The title compounds were obtained by annealing powders of the alkaline-earth metaperrhenates $M(ReO_4)_2 \cdot H_2O$ with an excess of the corresponding alkaline-earth halides in open alumina crucibles. The strontium compounds are new. They crystallize with an orthorhombic cell (*Pnma*, $Z = 4$). Their structure was determined from single-crystal X-ray data of $Sr_5(ReO_5)_3Cl$: $a = 743.80(9)$ pm, $b = 1843.4(2)$ pm, $c = 1056.3(1)$ pm, $V = 1.4483$ nm^3, $R = 0.021$ for 1850 structure factors and 78 variable parameters. The positions of the heavy atoms correspond to those of the hexagonal apatite structure. This is also the case for the known hexagonal compound $Ba_5(ReO_5)_3Cl$ whose structure was essentially confirmed by a refinement from single-crystal data: $R = 0.024$ for 696 F's and 30 variables. The differences and similarities of these structures are discussed considering group–subgroup relationships and near-neighbor environments. Differential scanning calorimetry and high-temperature Simon–Guinier data did not reveal displacive phase transformations of the three strontium compounds to a hexagonal structure up to 650°C.

1. Introduction

Apatites and related compounds have been the subject of numerous investigations. Especially, the well known hydroxyapatites (*1–3*) and the related phosphate halides $M_5(PO_4)_3X$ (M = Ca, Sr, Ba, Cd; X = F, Cl, Br) are structurally well characterized (4–9). Later investigations have shown that VO_4, CrO_4, and MnO_4 groups can be substituted for the phosphate group in the apatite structure. Examples are $Pb_5(VO_4)_3Cl$ (*10*), $Cd_5(VO_4)_3X$ (X = Br, I) (*11*), $Ca_5(CrO_4)_3OH$ (*12*), and $Ba_5(MnO_4)_3Cl$ (*13*). Numerous structures $M_5(ReO_5)_3X$, closely related to the apatite structure, were found in the systems MO–Re_2O_7–MX_2 (M = Ca, Sr, Ba; X = F, Cl, Br, I, OH, O_2, NO_3, CO_3) (*14–20*). In these structures the PO_4 tetrahedra are replaced by square pyramidal ReO_5 groups.

Here we report the crystal structure of the isotypic compounds $Sr_5(ReO_5)_3X$ (X = Cl, Br, I) which crystallize in a new orthorhombic structure type. They seem to be new compounds, although the related compound $Ba_3Sr_2(ReO_5)_3Cl$ has been characterized and was found to crystallize with a different monoclinic structure (*20*). We also confirm the crystal structure of $Ba_5(ReO_5)_3Cl$ (*14*), with the exception of a minor difference concerning the positions of the chlorine atoms.

2. Sample Preparation and Lattice Constants

Starting materials were rhenium powder (>99%, Starck), the alkaline-earth oxides

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TABLE I

LATTICE CONSTANTS OF $Sr_5(ReO_5)_3X$ (X = Cl, Br, I) AND $Ba_5(ReO_5)_3Cl$

Compound	a (pm)	b (pm)	c (pm)	V (nm^3)	Reference
$Sr_5(ReO_5)_3Cl$	743.80(9)[a]	1843.4(2)	1056.3(2)	1.4483	this work
$Sr_5(ReO_5)_3Cl$[b]	742.6(1)	1840.1(2)	1054.5(1)	1.4409	this work
$Sr_5(ReO_5)_3Br$	743.41(9)	1847.8(3)	1057.6(2)	1.4528	this work
$Sr_5(ReO_5)_3I$	747.3(2)	1864.6(5)	1070.0(3)	1.491	this work
$Ba_5(ReO_5)_3Cl$	1092.6(1)	1092.6(1)	778.16(8)	0.8046	this work
$Ba_5(ReO_5)_3Cl$[b]	1090.6(4)	1091.1(3)	778.3(1)	0.8021	this work
$Ba_5(ReO_5)_3Cl$	1093.5(7)	1093.5(7)	779.5(5)	0.8072	(*14*)

[a] Standard deviations in the least significant digits are given in parentheses throughout the paper.

[b] These data were obtained on the four-circle diffractometer; they are affected by systematic errors due to absorption effects.

(Ventron, >99.5%), $SrCl_2 \cdot 6H_2O$ (Merck, p.a.), $SrBr_2 \cdot 6H_2O$ (Riedel-de Haën, "chem. rein"), $BaCl_2 \cdot 2H_2O$ (Merck, p.a.), and SrI_2 (Alfa Products), which had a nominal purity of only 95%. However, our energy dispersive X-ray analysis of this starting material revealed no other alkaline-earth or halide component. The alkaline-earth metaperrhenates $M(ReO_4)_2 \cdot H_2O$ were prepared by dissolving rhenium powder in a 30% hydrogen peroxide solution, which was neutralized with the alkaline-earth oxides as described previously (*21*). Then the powders of the alkaline-earth metaperrhenates and the corresponding alkaline-earth halides were mixed in molar ratio 1 : 4 and annealed in open alumina crucibles for 4 days at 800°C, 600°C, and 500°C for the chlorine, bromine, and iodine compounds, respectively. After the reaction mixture was cooled in the furnace, the excess halide matrix was dissolved in methanole in an ultrasonic bath. In all cases the reactions resulted in transparent yellow needles. Energy dispersive analyses of the samples using a scanning electron microscope did not reveal any impurity elements heavier than sodium.

The lattice constants (Table I) were obtained by least-squares fits of the Guinier powder data. Cu $K\alpha_1$ radiation was used with α-quartz (a = 491.30 pm, c = 540.46 pm) as an internal standard. The identification of the diffraction lines was facilitated by intensity calculations (*22*) using the positional parameters of the refined structures. As examples the evaluations of the patterns of $Sr_5(ReO_5)_3Br$ and $Sr_5(ReO_5)_3I$ are shown in Table II.

3. Structure Determinations

Single crystals of $Sr_5(ReO_5)_3Cl$ and $Ba_5(ReO_5)_3Cl$ were examined by the Buerger precession and the Weissenberg methods to establish their symmetry and suitability for intensity data collection. The single crystals of $Sr_5(ReO_5)_3Cl$ were found to be orthorhombic. The systematic extinctions ($hk0$ observed only with $h = 2n$ and $0kl$ only with $k + l = 2n$) led to the space groups $Pn2_1a$ and $Pnma$, of which the centrosymmetric group $Pnma$ (No. 62) was found to be correct during the structure refinements. The precession photographs of $Ba_5(ReO_5)_3Cl$ confirmed the previously reported hexagonal Laue symmetry $6/mmm$. The space group extinctions ($h0l$ only with $l = 2n$) are typical for the space groups $P6_3cm$, $P\bar{6}c2$, and $P6_3/mcm$, of which the group $P6_3cm$ (No. 185) was established to be correct during the structure refinements in agreement with the earlier investigation (*14*).

Intensity data for the structure determina-

TABLE II

GUINIER POWDER PATTERNS OF $Sr_5(ReO_5)_3Br$ AND $Sr_5(ReO_5)_3I$[a]

		$Sr_5(ReO_5)_3Br$					$Sr_5(ReO_5)_3I$				
HKL	*hkl*	$2\theta_0$	Q_0	Q_c	I_0	I_c	$2\theta_0$	Q_0	Q_c	I_0	I_c
100	020	9.519	116	117	w	7	—	—	115	—	<1
	011	9.609	118	119	w	13	9.446	114	116	vw	2
	101	14.565	271	270	vw	2	14.456	267	266	vw	2
110	031	16.623	352	353	w	14	16.506	347	346	vw	5
	002	16.753	358	358	vw	4	16.536	349	349	vvw	<1
	121	17.432	387	388	w	17	17.306	382	381	w	15
200	040	19.201	469	469	vw	4	19.027	460	460	vw	7
	022	19.321	475	475	w	12	19.067	462	464	w	18
111	131	20.500	534	534	s	41	20.307	524	525	s	36
	102	20.600	539	539	m	25	20.397	528	528	m	22
	112	21.179	569	568	vw	1	—	—	557	—	1
002	200	23.907	723	724	s	48	23.807	717	716	s	42
	210	24.396	752	753	w	12	24.287	746	745	w	16
	201	25.355	812	813	vw	3	25.227	804	804	vw	5
210	013	25.615	828	834	vw	3	25.367	813	815	vw	1
	103	28.003	987	986	vw	1	27.627	961	965	vw	1
	230			987		1	—	—	975	—	<1
	151	28.213	1001	1003	s	41	27.958	984	985	s	36
211	142	28.293	1007	1007	s	43	28.058	990	989	s	38
	113	28.403	1014	1015	s	47	28.128	995	994	s	43
300	060	28.962	1054	1054	s	59	28.688	1035	1035	s	58
	033	29.142	1067	1068	vs	100	28.788	1042	1045	vs	100
112	231	29.272	1076	1077	vs	84	29.058	1061	1062	vs	74
	202	29.342	1081	1081	m	33	29.128	1066	1066	m	29
	212	29.742	1110	1111	vw	2	29.528	1095	1094	vw	5
202	240	30.841	1192	1192	w	12	30.638	1176	1176	w	10
	222	30.921	1198	1199	m	26	30.698	1181	1181	m	23
	152	31.860	1270	1271	vw	4	31.608	1250	1248	vw	3
	241	32.000	1281	1282	vw	1	—	—	1264	—	3
	232	32.799	1344	1345	w	17	32.568	1325	1324	m	21
	250	34.178	1455	1456	w	10	33.918	1434	1435	w	12
212	213	35.387	1557	1558	vw	1	35.098	1532	1531	vw	1
221	162	35.787	1591	1593	w	9	35.498	1566	1564	w	8
	104	36.006	1610	1611	w	6	35.638	1578	1577	vw	5
	223	36.406	1645	1646	w	10	36.098	1618	1617	w	13
	171	37.086	1705	1706	s	20	36.778	1677	1676	w	18
311	153	37.225	1717	1718	s	27	36.889	1687	1684	m	24
	124	37.355	1729	1729	w	19	36.939	1692	1692	w	16
302	260	37.885	1776	1778	w	7	—	—	1752	—	6
	233	38.055	1792	1792	w	9	—	—	1761	—	8
	252	—	—	1814	—	<1	—	—	1785	—	1
	321	38.514	1833	1835	w	11	38.289	1813	1814	w	10
	261	38.834	1863	1868	vw	1	38.579	1839	1839	vw	3
	172	40.033	1975	1974	vw	2	39.629	1937	1938	vw	2
	243	—	—	1997	—	<1	39.859	1958	1962	vw	1
	312	40.433	2013	2015	vw	2	40.209	1991	1990	vw	2
222	262	41.692	2134	2136	m	21	41.319	2098	2101	w	19
	181	—	—	2145	—	1	41.399	2106	2107	vw	1
	204	41.891	2154	2154	w	14	41.489	2115	2114	w	12

[a] The diagrams were recorded with Cu $K\alpha_1$ radiation. The Q values are defined by $Q = 100/d^2$ (nm^{-2}). For the intensity calculations the positional parameters of $Sr_5(ReO_5)_3Cl$ were used. Only reflections up to $2\theta = 42°$ are listed. Very weak reflections ($I_c \leq 1$) are listed only when they are observed. The first column contains the indices *HKL* of the corresponding (undistorted) hexagonal subcell.

TABLE III

CRYSTALLOGRAPHIC DATA FOR $Sr_5(ReO_5)_3Cl$ AND $Ba_5(ReO_5)_3Cl$

	$Sr_5(ReO_5)_3Cl$	$Ba_5(ReO_5)_3Cl$
Lattice constants	see Table I	
Formula units per cell	$Z = 4$	$Z = 2$
Space group	*Pnma*	$P6_3cm$
Formula weight	1272.1	1520.7
Calculated density [g/cm³]	$\rho_c = 5.834$	$\rho_c = 6.277$
Observed density [g/cm³]	—	$\rho_o = 5.79^a$
Absorption coefficient [cm⁻¹]	μ(Mo $K\alpha$) = 433	μ(Mo $K\alpha$) = 351
Cryst. dimensions [μm^3]	220 · 40 · 40	20 · 40 · 40
$\theta/2\theta$ scans up to	$2\theta = 70°$	$2\theta = 80°$
Range in h, k, l	±11, ±29, 0 + 16	±16, ±16, 0 − 14
Total number of reflections	13408	10449
Unique reflections	3584	1032
Transm. coeff. (highest/lowest)	1.63	1.43
Internal residual	$R_i = 0.042$	$R_i = 0.041$
Reflections with $I_0 > 3\sigma(I_0)$	1850	696
Number of variables	78	30
Conventional residual	$R = 0.021$	$R = 0.024$
Weighted residual	$R_w = 0.024$	$R_w = 0.032$

[a] Taken from (*14*).

tions were recorded on a four-circle diffractometer with graphite–monochromated Mo $K\alpha$ radiation, a scintillation counter, and a pulse-height discriminator. The background was determined on both sides of each $\theta/2\theta$ scan. Empirical absorption corrections were made on the basis of psi-scan data. The crystallographic data and some results are summarized in Table III.

The structure of $Sr_5(ReO_5)_3Cl$ was determined by interpretation of the Patterson map, which resulted in the positions of the metal atoms. The chlorine and oxygen positions were located in difference Fourier syntheses. The structure was refined by full-matrix least-squares cycles using atomic scattering factors (*23*), corrected for anomalous dispersion (*24*). A parameter accounting for secondary isotropic extinction was refined and applied to the calculated structure factors. A refinement of occupancy parameters together with the thermal parameters did not suggest any deviations from the ideal values. In the final least-squares cycles the ideal occupancies were assumed with anisotropic thermal parameters for the metal and chlorine atoms and isotropic thermal parameters for the oxygen ones. The final conventional and weighted residuals were found to be $R = 0.021$ and $R_w = 0.024$ for 1850 structure factors and 78 variable parameters.

For the structure refinement of $Ba_5(ReO_5)_3Cl$ the starting parameters for the metal positions were taken from the previous investigation (*14*). After least-squares refinements as described above, the positions of the oxygen and chlorine atoms were found by a difference Fourier synthesis. Somewhat in contrast to the previous inves-

TABLE IV

ATOMIC PARAMETERS OF $Sr_5(ReO_5)_3Cl$ AND $Ba_5(ReO_5)_3Cl$[a]

$Sr_5(ReO_5)_3Cl$					
Atom	Pnma	x	y	z	B
Sr1	8d	0.00039(8)	0.08524(3)	0.25318(6)	0.709(8)
Sr2	8d	0.26026(9)	0.61045(3)	0.38569(6)	1.05(1)
Sr3	4c	0.2780(1)	1/4	0.49014(9)	1.16(1)
Re1	8d	0.20681(3)	0.05713(1)	0.55871(2)	0.602(3)
Re2	4c	0.22011(5)	1/4	0.14672(3)	0.663(5)
O1	8d	0.0404(7)	0.1162(3)	0.4890(5)	1.49(8)
O2	8d	0.0545(7)	0.0517(3)	0.6942(5)	1.08(7)
O3	8d	0.0778(7)	0.1825(3)	0.0714(5)	1.10(7)
O4	8d	0.1266(7)	0.6160(3)	0.1106(5)	1.22(8)
O5	8d	0.2248(7)	0.0351(3)	0.0995(5)	1.18(7)
O6	8d	0.2503(7)	0.1828(3)	0.2733(4)	1.04(7)
O7	8d	0.2644(7)	0.0314(3)	0.3970(5)	1.05(7)
O8	4c	0.418(1)	1/4	0.0604(8)	2.0(1)
Cℓ	4c	0.1219(4)	1/4	0.7565(3)	1.62(4)
$Ba_5(ReO_5)_3Cl$					
Atom	$P6_3cm$	x	y	z	B
Ba1	4b	2/3	1/3	0.4887(2)	0.647(8)
Ba2	6c	0.26164(7)	0	0.7279(1)	0.82(1)
Re	6c	0.39192(4)	0	0.287	0.538(6)
O1	6c	0.295(1)	0	0.103(2)	1.6(2)
O2	12d	0.5765(7)	0.1311(6)	0.242(1)	0.91(9)
O3	12d	0.3885(7)	0.1302(7)	0.4162(8)	0.8(1)
Cℓ	2a	0	0	0.948(1)	1.8(1)

[a] The atomic parameters of $Sr_5(ReO_5)_3Cl$ were standardized by the program STRUCTURE TIDY (*25*); the parameters of $Ba_5(ReO_5)_3Cl$ correspond to those of Ref. (*14*). The origin of the hexagonal cell was held constant by fixing the z parameter of the Re atoms. The last column contains the equivalent isotropic B values (×100 in units of nm^2) of the anisotropic thermal parameters of the metal and chlorine atoms and the isotropic B values of the oxygen atoms.

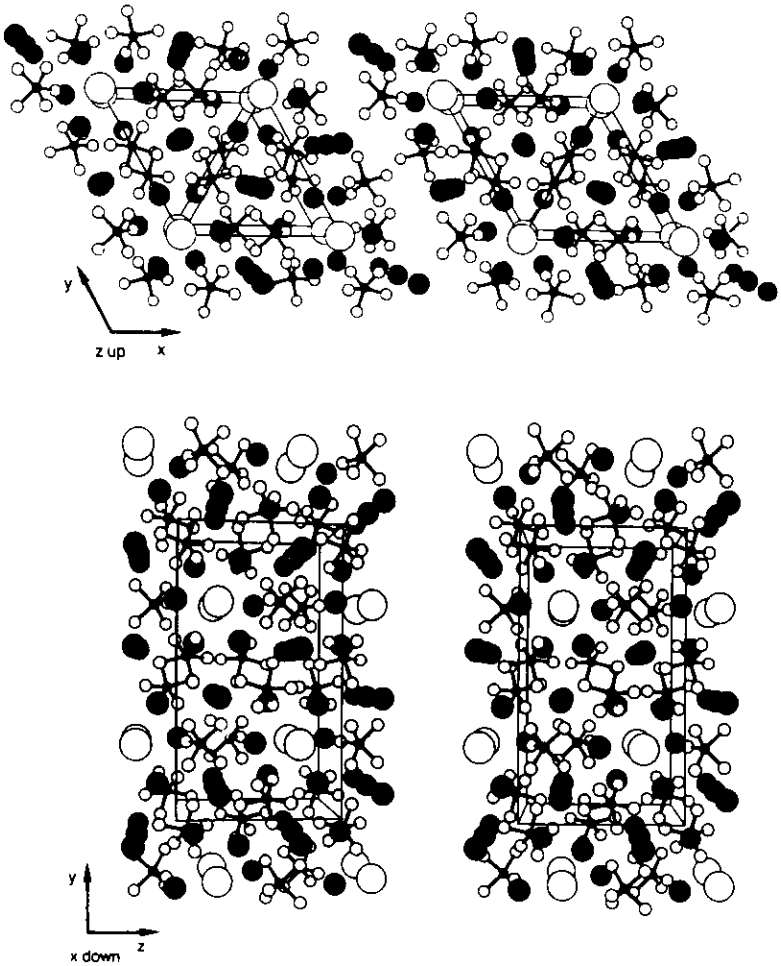

FIG. 1. Stereoplots of the structures of hexagonal $Ba_5(ReO_5)_3Cl$ and orthorhombic $Sr_5(ReO_5)_3Cl$. Large and small black spheres represent the alkaline-earth and the rhenium atoms, respectively. The oxygen and chlorine atoms are shown as small and large light spheres.

tigation, only one position (instead of a split position) was found for the chlorine atoms. The chlorine atoms in the barium compound have six neighbors forming an octahedron. They are situated on a threefold axis with mirror planes parallel to this axis (site symmetry $3m$). Apparently, this octahedral site is somewhat too large for the chlorine atoms. This can be seen from the large thermal parameters not only along the threefold axis (B_{33} = 0.022(3) nm^2 = 2.2 Å^2) but also perpendicular to it (B_{11} = 0.015(1) nm^2). Besse *et al.* (*14*) have refined the structure with the chlorine atoms with equal (50%) occupancy in the two adjacent positions 0, 0, 0.076(6) and 0, 0, 0.943(6), which are 104(10) pm apart. Actually, there is no reason to expect an equal occupation of the two sites, since they are not related by symmetry. (Thus, the situation has little in common with the frequently encountered problem of an atom being either on or off a mirror plane.) Nevertheless, we have removed the chlorine atoms and calculated a difference Fourier synthesis. The highest peaks were at 0, 0, 0.957 and 0, 0, 0.125 with $34 \cdot 10^3$

e/nm^3 and $11 \cdot 10^3$ e/nm^3. The least-squares refinement with 100% occupancy of that chlorine position with the higher electron density resulted again in the positional parameters of Table IV. The final difference Fourier synthesis gave no indication for the occupancy of another position on the threefold axis (the highest peak at 0, 0, 0.291 had an electron density of only $2.5 \cdot 10^3$ e/nm^3). The final residuals are $R = 0.024$ and $R_w = 0.032$ for 696 F values and 30 variables. The residual of the previous refinement (*14*) was 0.068 for 730 structure factors. Stereoplots of both structures are shown in Fig. 1. The interatomic distances are given in Table V. Listings of the anisotropic thermal parameters and of the structure factors may be obtained from the authors.

TABLE V

INTERATOMIC DISTANCES (pm) IN THE STRUCTURES OF $Sr_5(ReO_5)_3Cl$ AND $Ba_5(ReO_5)_3Cl$[a]

$Sr_5(ReO_5)_3Cl$

Sr1:	1 O5	250.5(5)	O1:	1 Re1	180.6(5)
	1 O7	256.6(5)		1 Sr1	257.2(5)
	1 O1	257.2(5)		1 Sr2	260.1(5)
	1 O6	259.5(5)		1 Sr3	303.4(5)
	1 O6	260.3(5)			
	1 O2	261.7(5)	O2:	1 Re1	182.8(5)
	1 O7	267.4(5)		1 Sr1	261.7(5)
	1 O3	269.0(5)		1 Sr2	267.7(5)
	1 O5	273.4(5)		1 Sr2	271.4(5)
Sr2:	1 O1	260.1(5)	O3:	1 Re2	181.6(5)
	1 O7	261.7(5)		1 Sr3	263.5(5)
	1 O5	265.4(5)		1 Sr2	265.8(5)
	1 O3	265.8(5)		1 Sr1	269.0(5)
	1 O2	267.7(5)			
	1 O2	271.4(5)	O4:	1 Re1	173.7(5)
	1 O4	272.7(5)		1 Sr2	272.7(5)
	1 O4	307.3(5)		1 Sr3	286.7(5)
	1 O8	343.3(6)		1 Sr2	307.3(5)
	1 Cl	304.1(2)			
	1 Cl	411.7(2)	O5:	1 Re1	182.6(5)
				1 Sr1	250.5(5)
Sr3:	2 O6	261.2(5)		1 Sr2	265.4(5)
	2 O3	263.5(5)		1 Sr1	273.4(5)
	1 O8	272.8(9)			
	2 O4	286.7(5)	O6:	1 Re2	183.6(5)
	2 O1	303.4(5)		1 Sr1	259.5(5)
	1 Cl	304.3(3)		1 Sr1	260.3(5)
	1 Cl	370.2(3)		1 Sr3	261.2(5)
Re1:	1 O4	173.7(5)	O7:	1 Re1	182.4(5)
	1 O1	180.6(5)		1 Sr1	256.6(5)
	1 O7	182.4(5)		1 Sr2	261.7(5)
	1 O5	182.6(5)		1 Sr1	267.4(5)
	1 O2	182.8(5)			
			O8:	1 Re2	173.3(9)
Re2:	1 O8	173.3(9)		1 Sr3	272.8(9)
	2 O3	181.6(5)		2 Sr2	343.3(6)
	2 O6	183.6(5)			
			Cl:	2 Sr2	304.1(2)
				1 Sr3	304.3(3)
				1 Sr3	370.2(3)
				2 Sr2	411.7(2)

$Ba_5(ReO_5)_3Cl$

Ba1:	3 O2	271.1(7)	O1:	1 Re1	178(1)
	3 O2	275.2(7)		1 Ba2	295(1)
	3 O3	278.1(7)		2 Ba2	320.9(8)
Ba2:	2 O2	277.9(4)	O2:	1 Re1	183.1(5)
	2 O3	280.3(6)		1 Ba1	271.1(7)
	2 O3	285.0(7)		1 Ba1	275.2(7)
	1 O1	295(1)		1 Ba2	277.9(4)
	2 O1	320.9(7)			
	1 Cl	333.4(5)	O3:	1 Re1	175.5(6)
	1 Cl	359.3(6)		1 Ba1	278.1(6)
				1 Ba2	280.3(6)
Re1:	2 O3	175.5(6)		1 Ba2	285.0(5)
	1 O1	178(1)			
	2 O2	183.1(5)	Cl:	3 Ba2	333.4(5)
				3 Ba2	359.3(6)

[a] All metal–oxygen distances shorter than 367 pm are listed. The shortest metal–rhenium distances are 359 pm (Sr–Re) and 371 pm (Ba–Re).

4. Discussion

The three strontium compounds $Sr_5(ReO_5)_3X$ (X = Cl, Br, I) crystallize with a new structure type, which can be derived from the structure of $Ba_5(ReO_5)_3Cl$. The structure of this latter compound was first determined by Besse *et al.* (*14*). Our present structure refinement essentially confirms the earlier work. The only difference with regard to the previous structure refinement lies in the position of the chlorine atoms. Previously the chlorine atoms were found in two positions (both with 50% occupancy) which are 104 pm apart: Cl1 with six barium neighbors, three at 313 pm and three at 389 pm, and Cl2 again with six barium neighbors, three at 328 pm and three at 367 pm. In our investigation the Cl atoms were found to be well localized in one position with full occupancy and with three barium neighbors at 333 pm and with three at 359 pm.

Besse *et al.* have already pointed out that the structure of $Ba_5(ReO_5)_3Cl$ is closely related to that of the classical apatite structure $Ca_5(PO_4)_3Cl$, which crystallizes in the space group $P6_3/m$. The metal and the chlorine positions of $Ba_5(ReO_5)_3Cl$ approximately correspond to the positions of the corresponding atoms in apatite, whereas the positions of the oxygen atoms are different. This is not a trivial consequence of the different composition (PO_4 vs ReO_5). Rather, it results from the fact that the square pyramids of the ReO_5 groups have the apex oxygen atoms all pointing approximately down the z axis. Thus, the mirror plane of the apatite

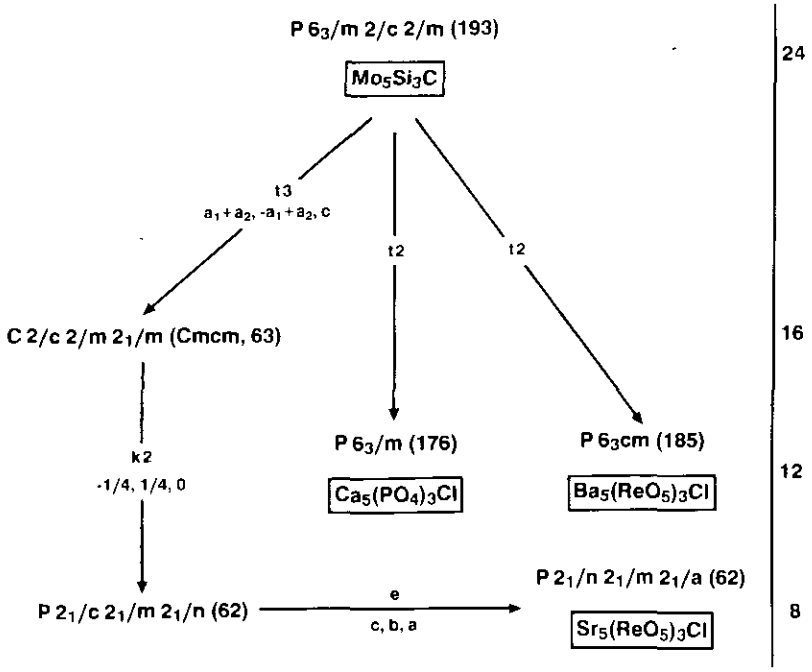

FIG. 2. Group–subgroup relationships of various apatite related structures. The multiplicities of the general positions of the space groups are given at the right-hand side.

structure perpendicular to the z axis is lost in $Ba_5(ReO_5)_3Cl$. As a quasi compensation this structure has mirror and glide planes parallel to the z axis, which are not present in the apatite structure. Thus, both structures crystalize in space groups which are subgroups of $P6_3/mcm$.

These group–subgroup relationships are shown in Fig. 2 in the manner formalized by Bärnighausen (*26*). In this scheme the *translationengleiche* (*t*) and *klassengleiche* (*k*) subgroups (*27*) are indicated as well as the *equivalent* (*e*) settings of a space group together with the index of the symmetry reduction and the vectors for the cell transformation. The metal and chlorine positions of the complex oxide halides correspond to the atomic positions of the Nowotny phase Mo_5Si_3C (*28*). The additional oxygen atoms of the phosphate and perrhenate groups lower the symmetry to the indicated subgroups.

The relation between the structure of the orthorhombic compounds $Sr_5(ReO_5)_3X$ (X = Cl, Br, I) and that of the hexagonal

TABLE VI

CORRESPONDENCE BETWEEN THE ATOMIC SITES OF THE $Sr_5(ReO_5)_3Cl$ AND $Ba_5(ReO_5)_3Cl$ STRUCTURES

$Ba_5(ReO_5)_3Cl$ $P6_3cm$ $Z = 2$		$Sr_5(ReO_5)_3Cl$ $Pnma$ $Z = 4$	
Ba1	(4*b*)	Sr1	(8*d*)
Ba2	(6*c*)	Sr2	(8*d*)
		Sr3	(4*c*)
Re1	(6*c*)	Re1	(8*d*)
		Re2	(4*c*)
O1	(6*c*)	O4	(8*d*)
		O8	(4*c*)
O2	(12*d*)	O5	(8*d*)
		O6	(8*d*)
		O7	(8*d*)
O3	(12*d*)	O1	(8*d*)
		O2	(8*d*)
		O3	(8*d*)
Cl	(2*a*)	Cl	(4*c*)

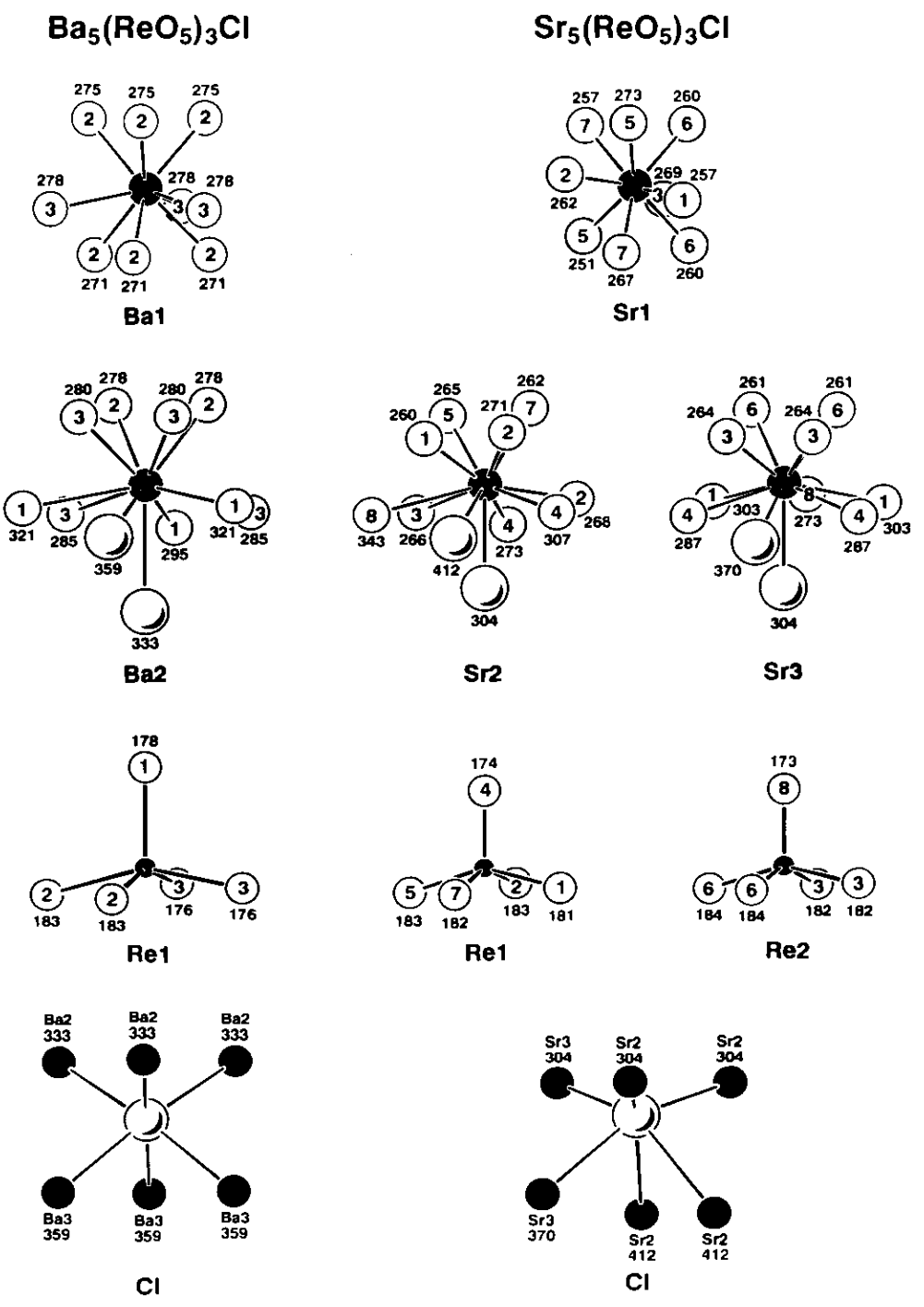

FIG. 3. Near-neighbor coordinations in the structure of $Ba_5(ReO_5)_3Cl$ as compared to the coordinations of the corresponding atoms in $Sr_5(ReO_5)_3Cl$. The atoms are represented in the same way as in Fig. 1. The single digit numbers correspond to the oxygen designations. Interatomic distances are indicated in pm units.

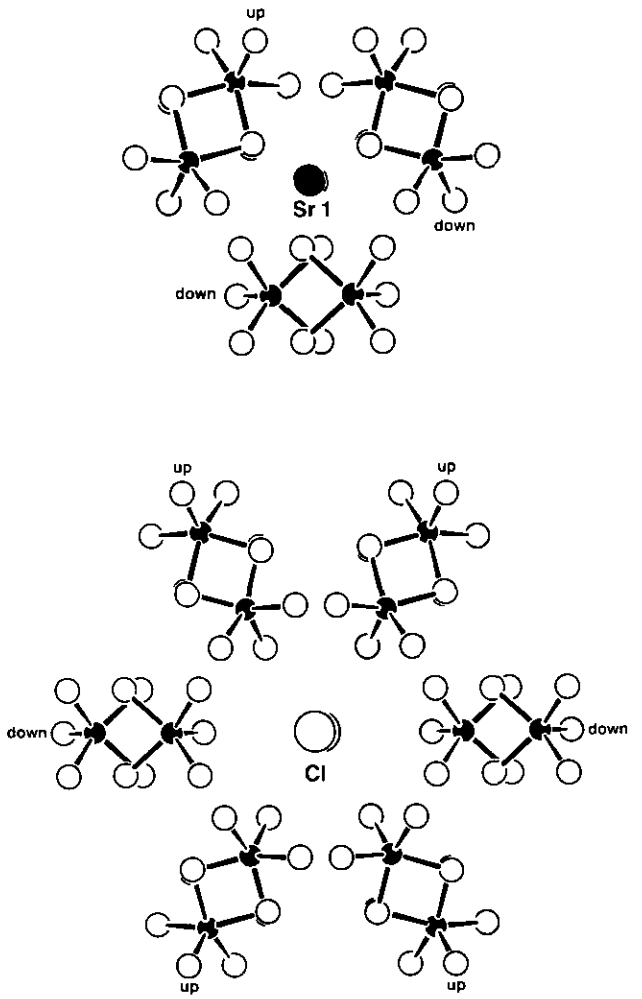

FIG. 4. The arrangements of the ReO_5 groups around the pseudotrigonal and pseudohexagonal axes in the orthorhombic $Sr_5(ReO_5)_3Cl$ structure. The trigonal and hexagonal symmetries are destroyed by the orientation of the square–pyramidal ReO_5 groups. This is most easily seen by looking at the apical oxygen atoms pointing upward or downward.

compound $Ba_5(ReO_5)_3Cl$ is more subtle. The correspondence of the atoms in the two structures is shown in Table VI and Fig. 3. The lower symmetry of the strontium compounds result from the differences in the orientations of the square-pyramidal ReO_5 groups as can be seen in Fig. 4: The near-neighbor environments of the Sr1 and Cl atoms in the structure of $Sr_5(ReO_5)_3Cl$ clearly violate the trigonal and hexagonal symmetry of the Ba and Cl atoms observed in $Ba_5(ReO_5)_3Cl$. The distortions of the hexagonal lattices, however, are minor: The values $c\sqrt{3}$ are only smaller than the corresponding lattice constant b by 0.76%, 0.87%, and 0.61% for the chlorine, bromine, and iodine compounds, respectively.

We considered the possibility that the orthorhombic structure of $Sr_5(ReO_5)_3Cl$ transforms on heating to a hexagonal structure. We therefore investigated the compounds $Sr_5(ReO_5)_3X$ (X = Cl, Br, I) by differential scanning calorimetry. Up to 500°C no indications for such phase transitions were

found. Similarly, high-temperature X-ray powder patterns of these compounds recorded with a Simon–Guinier camera (*29*) up to 650°C did not reveal a phase transformation. The resolution of our high temperature patterns was not high enough to show the orthorhombic splitting of the hexagonal subcell already at room temperature; however, several superstructure reflections of the orthorhombic compounds $Sr_5(ReO_5)_3X$ (those with $k + l \neq 2n$, e.g., the relatively strong reflection 232 of all three compounds) were clearly visible at 650°C. The energy required for a reorientation of the ReO_5 groups may be too high for a rapid phase transformation; however, it is also questionable whether the strontium compounds become thermodynamically stable at all in the hexagonal form at higher temperature.

This leads us to the differences in near-neighbor coordinations of the structures of $Ba_5(ReO_5)_3Cl$ and $Sr_5(ReO_5)_3X$. They can be understood best as resulting from the different sizes of the strontium and barium atoms. The Ba1 and Sr1 atoms have similar coordination with nine oxygen neighbors (Fig. 3). However, the coordination of the Ba2 atom is different from those of the corresponding (Table VI) Sr2 and Sr3 atoms. The Ba2 atom has coordination number (CN) 11 with two chlorine atoms at 333 pm and 359 pm and nine oxygen neighbors in the 278–321 pm range. Of the two corresponding strontium atoms the Sr2 atom has a smaller effective CN with only one chlorine and eight close oxygen neighbors. One chlorine atom and one oxygen atom, which could be considered to be bonding to the Ba2 atom with distances of 359 pm and 321 pm, respectively, are further away from the Sr2 atoms (412 pm and 343 pm) even though strontium is smaller than barium. Similarly, the Sr3 atom has a smaller effective CN because the chlorine atom at 359 pm from the Ba2 atom is 370 pm away from the corresponding Sr3 atom. These differences in the coordinations of the Ba2 atoms on the one hand and the Sr2 and Sr3 atoms on the other, necessarily result in differences in the oxygen and chlorine coordinations. Thus, the great asymmetry in the coordination of the chlorine atoms of $Sr_5(ReO_5)_3Cl$ (Fig. 3) can be rationalized as a consequence of the smaller space requirements of the strontium atoms.

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