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The Modification of Structures of Ternary Oxides by Cation Substitution. I. Substitution of Strontium for Barium in Barium Ruthenium Oxide and in Barium Iridium Oxide

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The effect of variation of the depth of close-packed AO_3 layers on the structures of compounds of the type AMO_3 is studied using the systems $Ba_{1-x}Sr_xRuO_3$ and $Ba_{1-x}Sr_xIrO_3$. It is found that with increasing values of x the nine-layer structure with stacking sequence chh gives way to the four-layer structure (ch,ch) and finally to the three-layer perovskite-type structure (c,c,c). With ruthenium, the successive changes occur when x is about $1/6$ and $1/3$. The iridium case is more complex. Barium iridium oxide has a structure which is based on a superlattice of that of the ruthenium compound. It is probably oxygen deficient. The transformations to the four-layer structure and to the perovskite-type structure occur at somewhat higher strontium content. Some barium is necessary to stabilize the perovskite-type phase.

Introduction

A correlation of the structures of a number of ternary oxides containing a large cation A and a smaller cation M can be made on the basis of cubic and hexagonal close packing of layers of composition AO_3, the M cations occupying the octahedral interstices among the oxide ions.[1] In the case where all of the octahedral sites are occupied, the formula is AMO_3. Hexagonal close packing leads to face sharing of the oxygen octahedra. It has been suggested that hexagonal close packing is promoted by interactions between adjacent M cations either by direct metal–metal bonds involving d electrons or d orbitals and polarizable anions.[1,2] It has been observed that, for most of the compounds of this type, the A cation is the largest of its species—Cs^+ or Ba^{2+} [1,2]—while smaller A cation analogs are cubic close packed.

The structure of $BaRuO_3$ has been shown to have the stacking sequence chh. The three face-sharing oxygen octahedra contain ruthenium ions.[3] The analogous strontium compound, $SrRuO_3$, was characterized as an orthorhombic perovskite-type compound.[4] The AO_3 stacking sequence in this compound is entirely cubic. It was of some interest to study the effect of A cation substitution on these structures.

(1) L. Katz and R. Ward, *Inorg. Chem.*, **3**, 205 (1964).
(2) G. Blasse, *J. Inorg. Nucl. Chem.*, **27**, 993 (1965).
(3) P. C. Donohue, L. Katz, and R. Ward, *Inorg. Chem.*, **4**, 306 (1965).
(4) J. J. Randall and R. Ward, *J. Am. Chem. Soc.*, **81**, 2629 (1959).

Experimental Section

The System $Ba_{1-x}Sr_xRuO_3$. Preparation.—The preparation of phases in the system $Ba_{1-x}Sr_xRuO_3$ was effected by heating appropriate mixtures of barium and strontium carbonates with finely divided elemental ruthenium in air at temperatures from 1000 to 1200°. Repeated regrinding between heat treatments served to give homogeneous products. The stoichiometry is represented by the equation

$$(1 - x)BaCO_3 + xSrCO_3 + Ru + O_2 \longrightarrow Ba_{1-x}Sr_xRuO_3 + CO_2$$

The carbonates were used in preference to the oxides merely because they are easier to handle. Five values of x from $1/12$ to $2/3$ were used. With $x \geq 1/2$, the products of these reactions gave diffraction patterns corresponding to the orthorhombic perovskite structure only. The product at 1000° from the mixture with composition $x = 1/12$ gave a powder diffraction pattern corresponding to the nine-layer structure of $BaRuO_3$ with an appreciably smaller unit cell. The product of the same mixture at 1100° gave, in addition, lines of a new phase (X) and, at 1200°, only the pattern of X. It is apparent that the tolerance of the barium ruthenium oxide structure for strontium substitution is quite low. The phase X appeared along with the nine-layer phase at 1000° when $x = 1/6$. At 1100 and 1200° this mixture gave only phase X. At 1000° when $x = 1/3$, phase X appeared along with the perovskite-like phase. It seemed reasonable to suppose that phase X would have a close-packed structure since its composition was intermediate between those of two other close-packed structures. This indeed was found. The pattern corresponding to the composition $Ba_{5/6}Sr_{1/6}RuO_3$ appeared to be entirely due to phase X.

Structure of $Ba_{5/6}Sr_{1/6}RuO_3$.—The powder pattern was indexed on the basis of a hexagonal cell $a = 5.712 \pm 0.005$ A and $c = 9.488 \pm 0.005$ A. The a axis is thus of the proper di-

mension for the AO_3 layer where A is mostly Ba^{2+}, and the c axis is about 4 times the thickness of such an AO_3 layer. The only structure of this kind so far described is that of the high-temperature form of $BaMnO_3$.[5]

Some small single crystals were obtained by the slow cooling from 1100° of a mixture using excess of barium chloride as a flux. The crystals appeared to be cracked, and the spot quality of the precession photographs was rather poor, but sufficient data were obtained to confirm the cell dimensions derived from powder data. The structure determination and refinement were based on powder data.

Intensities were measured by weighing cutout tracings of the powder pattern peaks. Intensities were calculated for the composition $Ba_{5/6}Sr_{1/6}RuO_3$ in space group $P6_3/mmc$. The positions used are listed in Table I. Using the ideal parameters $z = 0.875$ for Ru and $x = 5/6$ for O, the R factor based on intensities was 21.3%. With $z = 0.890$ for Ru, the value which corresponds to the separation in $BaRuO_3$, the R factor dropped to 16.7%. The four-layer arrangement similar to that of high-temperature $BaMnO_3$ is thus well established for $Ba_{5/6}Sr_{1/6}RuO_3$. The indexing and intensity data are shown in Table II.

TABLE I

ATOMIC POSITIONS FOR $Ba_{5/6}Sr_{1/6}RuO_3$ SPACE GROUP 194, $P6_3/mmc$

2 ($Ba_{5/6}Sr_{1/6}$)	a	0, 0, 0; 0, 0, 1/2
2 ($Ba_{5/6}Sr_{1/6}$)	c	1/3, 2/3, 1/4; 2/3, 1/3, 3/4
4 Ru	f	1/3, 2/3, z; 2/3, 1/3, $\bar{z}$; 2/3, 1/3, 1/2 + z; 1/3, 2/3, 1/2 − z
6 O	g	1/2, 0, 0; 0, 1/, 0; 1/2, 1/2, 0; 1/2, 0, 1/2; 0, 1/2, 1/2; 1/2, 1/2, 1/2
6 O	h	x, 2x, 1/4; 2$\bar{x}$, $\bar{x}$, 1/4; x, $\bar{x}$, 1/4; $\bar{x}$, 2$\bar{x}$, 3/4; 2x, x, 3/4; $\bar{x}$, x, 3/4

TABLE II

X-RAY POWDER DATA FOR $Ba_{5/6}Sr_{1/6}RuO_3$

H	K	L	DOBS	DCAL	IOBS	ICAL	H	K	L	DOBS	DCAL	IOBS	ICAL
1	0	0	4.954	4.948	7.0	5.1	3	1	2	1.318	1.318	5.9	5.9
1	0	1	4.390	4.387	6.0	2.3	3	1	3	1.259	1.259	8.6	10.7
1	0	2	3.430	3.425	57.4	43.8	2	1	6	1.207	1.207	5.5	6.6
1	1	0	2.859	2.857	100.0	104.0	4	0	2	1.196	1.197	2.5	3.8
1	0	3	2.667	2.665	63.0	53.7	3	1	4	1.187	1.188	7.4	3.8
2	0	1	2.392	2.394	.6	.6	0	0	8		1.186		3.0
0	0	4	2.370	2.372	4.0	2.3	4	0	3	1.151	1.152	5.0	5.1
2	0	2	2.192	2.194	35.3	32.3	3	1	5	1.112	1.112	4.3	5.0
1	0	4	2.138	2.139	15.5	12.9	3	2	2	1.104	1.104	3.0	3.6
2	0	3	1.949	1.949	32.1	30.2	1	1	8	1.095	1.095	11.3	11.2
2	1	0	1.868	1.870	.7	.7	4	1	0	1.079	1.079	7.2	11.7
1	1	4	1.826	1.825	.3	.3	3	2	3	1.071	1.068	4.6	6.9
1	0	5	1.771	1.772	11.4	11.0	3	1	6	1.036	1.036	5.9	4.4
2	1	2	1.739	1.740	10.8	14.8	4	0	5		1.036		2.7
2	0	4	1.712	1.712	8.9	8.2	4	0	6	.9741	.9735	4.0	3.1
3	0	0	1.650	1.649	21.0	21.9	3	2	5		.9742		3.9
2	1	3	1.609	1.610	21.7	24.4	3	0	8	.9627	.9630	7.4	9.6
1	0	6	1.505	1.507	17.5	6.5	3	3	0	.9519	.9523	3.5	5.1
2	0	5		1.506		8.3	5	0	3	.9440	.9445	.2	3.0
2	1	4	1.468	1.469	9.9	7.8	2	3	6	.9217	.9222	2.5	4.4
2	2	0	1.428	1.428	14.3	18.0	2	2	8	.9122	.9126	12.0	13.3
2	0	6	1.332	1.332	16.0	6.3	4	2	3	.8961	.8968	4.8	7.9
2	1	5		1.332		8.3							

In order to refine parameters further, the resolved reflections from the powder data were converted to structure factors by taking square roots after dividing out the Lorentz and polarization corrections and the multiplicities. These reflections, 31 in all, were used in the Busing, Martin, and Levy least-squares program.[6] An over-all temperature factor and the two position parameters were refined. After three cycles the R factor (based on structure factors) dropped to 6.8%. The final parameters were 0.8807 ± 0.0021 for Ru and 0.829 ± 0.012 for O. The observed and calculated structure factors are listed in Table III. Bond distances and angles are shown in Table IV. Figure 1 shows the four-layer structure, with the atoms numbered as in Table IV.

The System $Ba_{1-x}Sr_xIrO_3$. Preparation and X-Ray Analysis.— $BaIrO_3$, prepared by the reaction of BaO_2 and Ir metal heated at 1000° in air, was previously reported to have a powder diffraction similar to that of $BaRuO_3$.[3] The main reflections could be indexed on the basis of a hexagonal unit cell ($a = 5.76 \pm 0.01$ A, $c = 22.2 \pm 0.1$ A), but there were a number of reflections which could not be so indexed.

Single crystals were obtained as before from a barium chloride flux. The $h0l$ net obtained using a Buerger precession camera was very similar to that of $BaRuO_3$ but contained a number of weaker reflections which required a c axis of 44.4 A. The $hk0$ net showed sixfold symmetry in the positions of reflections but not quite sixfold in their intensities. The true symmetry is therefore lower than hexagonal, and the pseudo-hexagonal cell has a c axis twice as long as that of $BaRuO_3$.

In order to determine the extent to which $BaIrO_3$ resembles $BaRuO_3$, about 50 $h0l$ superlattice reflections were ignored, and a least-squares refinement was carried out with the remaining

TABLE III

OBSERVED AND CALCULATED FACTORS FOR RESOLVED POWDER REFLECTIONS OF $Ba_{5/6}Sr_{1/6}RuO_3$

H	K	L	FOBS	FCAL*	H	K	L	FOBS	FCAL*
1	0	0	12.1	10.9	2	1	3	37.7	39.0
1	0	1	9.0	5.4	2	1	4	28.4	24.7
1	0	2	36.0	35.2	2	2	0	80.5	78.8
1	1	0	82.2	89.1	3	1	2	24.9	25.3
1	0	3	48.9	47.7	3	1	3	31.6	32.7
2	0	1	5.5	6.7	2	1	6	26.4	27.3
0	0	4	35.1	30.2	4	0	2	25.3	30.5
2	0	2	46.6	48.5	4	0	3	37.1	34.0
1	0	4	32.2	29.5	3	1	5	25.0	25.1
2	0	3	51.1	51.4	3	2	2	20.9	22.7
2	1	0	10.4	6.9	1	1	8	57.6	53.1
1	1	4	10.7	6.5	4	1	0	53.5	53.4
1	0	5	34.2	34.4	3	2	3	26.2	28.2
2	1	2	24.0	28.7	3	0	8	46.3	46.8
2	0	4	31.5	30.9	3	3	0	45.2	47.2
3	0	0	78.5	72.5					

* Overall isotropic temperature factor with B = 0.8 A^{-2} applied.

TABLE IV

BOND DISTANCES AND ANGLES FOR $Ba_{5/6}Sr_{1/6}RuO_3$[a]

Atoms	Distances, A	Angle, deg
Ru_1–Ru_2	2.473	
O_1–Ru_2–O_2	2.01 2.01	86
O_3–Ru_2–O_2	2.00 2.01	91
O_3–Ru_2–O_4	2.00 2.00	91
O_2–Ba^b–O_5	2.85	58
O_3–$Ba_2{}^b$–O_6	2.85	60
Ru_2–O_2–Ru_1	2.00	76

[a] The standard error in the Ru–Ru distance is about 0.03 A. The standard errors in the cation-oxygen distances are in the range 0.03–0.05 A. Estimated standard errors in the angles are about 2°. [b] Ba = $Ba_{5/6}$, $Sr_{1/6}$.

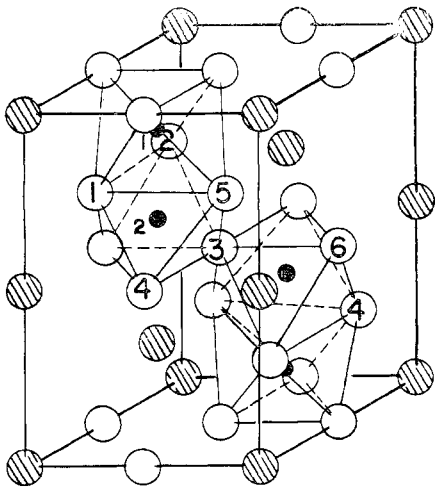

Figure 1.—Four-layer structure. This structure, previously reported for high-temperature $BaMnO_3$, is adopted by $Ba_{5/6}Sr_{1/6}RuO_3$: ●, Ru; O, O; ∅, Ba, Sr.

(5) A. Hardy, *Bull. Soc. Chim. France*, 1329 (1961).

(6) W. R. Busing, K. O. Martin, and H. A. Levy, Oak Ridge National Laboratory Report ORNL-TM-305 (1962).

h0l data (91 reflections). The *R* factor dropped to 14.1%, showing the basic similarity between the two structures. However, the detailed structure of $BaIrO_3$ is not yet known.

Values of x from $^1/_6$ to $^5/_6$ in the system $Ba_{1-x}Sr_xIrO_3$ were tried. The phase with the four-layer structure was obtained pure at $x = {}^1/_3$; its powder pattern could be indexed completely on the basis of a hexagonal unit cell with $a = 5.707 \pm 0.005$ A and $c = 9.767 \pm 0.005$ A. A refinement for this four-layer structure was carried out on the powder data. For this purpose, the Busing, Martin, and Levy least-squares program was adapted by Norman Morrow of our laboratory for the refinement of powder data including unresolved reflections. The *R* factor based on intensities dropped to 15.4% after four cycles. The final position parameters were: iridium $z = 0.8866 \pm 0.001$ and oxygen $x = 0.759 \pm 0.015$. The value of the oxygen parameter leads to an unreasonably close oxygen–oxygen distance for the three oxygen ions sharing the common face. This result and the experience with $BaIrO_3$ emphasize the need for further investigation of the oxygen positions (an investigation which is planned); however, the Ir–Ir distance is not likely to be affected very much and may be tentatively reported as 2.67 ± 0.03 A in the four-layer structure. Table V lists the powder data.

TABLE V

X-RAY POWDER DATA FOR $Ba_{2/3}Sr_{1/3}IrO_3$

H	K	L	DOBS	DCAL	IOBS	ICAL	H	K	L	DOBS	DCAL	IOBS	ICAL
1	0	0	4.960	4.942	26.6	42.9	2	0	5	1.427	1.427	8.5	6.5
1	0	1	4.425	4.410	27.8	50.7	2	1	4	1.482	1.484	9.3	11.8
1	0	2	3.479	3.474	26.8	31.4	2	2	0	1.427	1.427	16.6	17.4
1	1	0	2.856	2.853	164.0	151.0	1	1	6	1.412	1.414	8.9	2.6
1	0	3	2.719	2.719	83.6	85.6	2	2	1		1.412		
2	0	0	2.465	2.471	7.0	2.6	3	0	4		1.366		
0	0	4		2.442			2	0	6	1.359	1.359		
2	0	1	2.398	2.396	6.5	5.1	3	1	1		1.357	22.3	17.7
2	0	2	2.202	2.205	39.4	34.0	2	1	5	1.350	1.350		
1	0	4		2.189			1	0	7	1.344	1.343		
2	0	3	1.968	1.968	42.9	39.8	3	1	2	1.320	1.320	5.7	2.7
2	1	0	1.867	1.868	2.5	3.5	3	1	3	1.261	1.263	16.3	15.9
1	1	4	1.853	1.855	5.3	3.7	2	1	6	1.226	1.227		
2	1	1	1.835	1.835	5.2	5.0	4	0	1		1.226	16.3	17.9
1	0	5	1.817	1.817	9.5	9.2	0	0	8	1.219	1.221		
2	1	2	1.744	1.745	17.3	17.4	2	0	7		1.215		
2	0	4	1.734	1.737			4	0	3	1.153	1.155	7.0	5.7
3	0	0	1.647	1.647	26.9	25.2	3	2	1		1.126		
2	1	3	1.620	1.620	42.7	39.9	1	1	8	1.121	1.122	15.2	15.3
1	0	6	1.544	1.546	6.84	7.5	3	1	5		1.122		

The distorted perovskite phase similar to the corresponding ruthenium compound was obtained at $x = {}^2/_3$. At $x = {}^5/_6$ the perovskite phase was present along with another unidentified phase, the pattern of which resembled that of Sr_2IrO_4.

Discussion

If we assume that the oxygen octahedra formed by the close-packed AO_3 layers are regular, the distance between centers of the face-sharing octahedra is 2.37 A in the phase of composition $Ba_{5/6}Sr_{1/6}RuO_3$. The Ru–Ru distance of 2.47 A shows the effect of repulsive forces between the Ru^{4+} cations. For the high-temperature form of $BaMnO_3$, the distance between centers of face-shared octahedra is 2.34 A while the Mn–Mn distance is reported as 2.62 A. One might conclude that there are stronger bonds between the Ru^{4+} ions than the Mn^{4+} ions. However, the large error possible in the Mn–Mn distance makes any such conclusion highly tentative.

In the nine-layer structure of $BaRuO_3$, the Ru–Ru distance is 2.55 A while the distance between centers of face-sharing octahedra is 2.40 A. The larger Ru–Ru distance might be due to a weaker metal–metal interaction when the central ion has to form two bonds.

The range of x in the different phases of the system $Ba_{1-x}Sr_xRuO_3$ could not be determined since it was obvious that equilibrium was not reached. Cell volumes were found to change with changing strontium content in products containing the same two phases. Even repeated grinding and heating failed to give concordant results. Higher temperatures appeared to favor the conversion from the nine-layer to the four-layer structure. Thus, with $x = 0.05$, only the nine-layer structure was found at 1000°, but at 1100°, both the nine-layer and four-layer structures were found. With $x = 0.1$, only the nine-layer structure was present in the product at 1000°, and only the four-layer structure was in the product at 1100°. Upon increasing x to 0.15, none of the products at any temperature gave the nine-layer structure. We might place the upper limit at $x = 0.1$ for the nine-layer structure, but this value might be increased considerably if low-temperature methods of synthesis such as hydrothermal methods could be employed. The four-layer structure is clearly the stable phase in the temperature range 1100–1200° with $x = 0.10$ and in the temperature range 1000–1200° when $0.15 \leq x \leq 0.2$. The lattice dimensions are $a = 5.717 \pm 0.005$ A, $c = 9.49 \pm 0.01$ A when $x = 0.1$ and $a = 5.706 \pm 0.005$ A, $c = 9.485 \pm 0.01$ A when $x = 0.20$. The perovskite phase makes its appearance in the products when $0.25 \leq x \leq 0.35$. The lattice dimensions for the four-layer structure vary in these products from $a = 5.700 \pm 0.005$ A, $c = 9.481 \pm 0.01$ A, $x = 0.25$ at 1000° to $a = 5.692 \pm 0.005$ A, $c = 9.473 \pm 0.01$ A, $x = 0.35$ at 1200°. Only the perovskite phase was found in mixtures with $x \geq 0.5$.

It should be noted that, over the range of composition of the four-layer structure, the a axis decreases more sharply than the c axis with increasing strontium content. This could be due to the repulsive forces between the pairs of Ru^{4+} ions in the face-shared octahedra. The system $Ba_{1-x}Sr_xIrO_3$ is different in some important respects from the ruthenium system in that the end members are different. The larger unit cell required at $x = 0$ and the indications obtained from the variations of the temperature factors for the oxygens suggest that the structure contains ordered oxygen vacancies. The structure, however, is closely related to that of the nine-layer ruthenium compound. It takes appreciably more strontium ($x \geq 0.33$) to give the four-layer structure, and the transformation does not appear to be so sensitive to temperature changes in the range studied. No evidence of a superlattice was obtained with the four-layer structure. With larger proportions of strontium, an orthorhombic perovskite phase is formed. Thus, in general, the two systems behave in a similar manner.

The end member in the iridium system ($x = 1$) has not been made. Randall[4] found that all attempts to prepare $SrIrO_3$ led invariably to Sr_2IrO_4, with the K_2NiF_4 structure. The perovskite-type phase could be obtained in the system $SrRu_{1-x}Ir_xO_3$ up to $x = 0.5$. It is interesting that substitution of Ba for one-third of the Sr will stabilize the perovskite phase.

There is an inherent difficulty in studying these systems by solid-state reactions. Because of the topo-

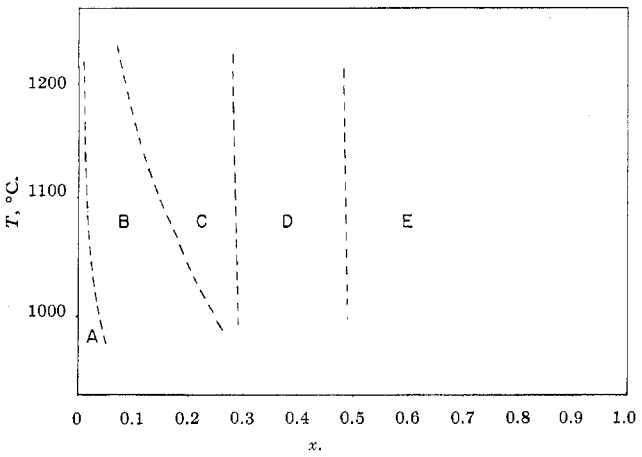

Figure 2.—The system $Ba_{1-x}Sr_xRuO_3$: A, nine-layer-structure-type region; B, two-phase region, nine-layer and four-layer types; C, four-layer-structure-type region; D, two-phase region, four-layer and perovskite types; E, perovskite-structure-type region.

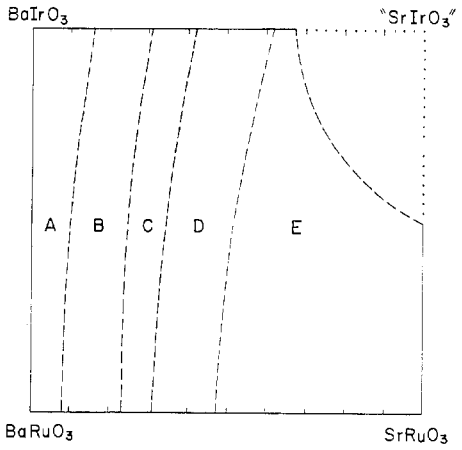

Figure 3.—Tentative description of the system $Ba_{1-x}Sr_x$-$Ru_{1-y}Ir_yO_3$ at about 1000°: A, nine-layer-structure-type region; B, two-phase region, nine-layer and four-layer types; C, four-layer-structure-type region; D, two-phase region, four-layer and perovskite types; E, perovskite-type region. The area near the "$SrIrO_3$" corner is the unrealized portion of the perovskite-type region.

chemical nature of the reactions, local concentration of reactants inevitably must vary. Conditions are far from equilibrium. The products are phases of high lattice energy in which diffusion of ions is slow at the temperatures used in these experiments. This is probably the reason for the observed variability in the cell dimensions of phases in two-phase regions. Structure data for the system $Ba_{1-x}Sr_xRuO_3$ are summarized in Figure 2.

Figure 3 is a highly tentative description of the system $Ba_{1-x}Sr_xRu_{1-y}Ir_yO_3$ based on the data for about 1000°. For the purpose of this description the upper right-hand corner of the figure has been labeled "$SrIrO_3$." This section of the diagram is indicated by dotted lines. $SrIrO_3$, as mentioned earlier, is still hypothetical; previous attempts to make it produced Sr_2IrO_4.

The thickness of the AO_3 layer is shown to be an important factor in the stacking sequence of the layers. If metal–metal bonding plays a part in bringing about hexagonal close packing of the layers, the repulsive forces also seem to be significant. When the decrease in layer thickness would bring the M cations too close together, the stacking sequence tends to become cubic and the M cations are separated by an oxide ion; *i.e.*, the coordination polyhedra share corners rather than faces.

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