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High Pressure Synthesis of (ABX_3) $(AX)_n$ Compounds*

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When ABX_3 compounds form the perovskite structure at atmospheric pressure (i.e., $SrTiO_3$, $SrZrO_3$, $CaTiO_3$), the other members of the $(ABX_3)(AX)_n$ series ($n = 0, 1/3, 1/2, 1$) can generally be formed also. However, if the relative size of the A cation is too large, then the ABX_3 end members form a hexagonal polytype that transforms to the perovskite structure only at elevated pressures. In such cases, pressure is often needed for the synthesis of the interlayer compounds (ABX_3) $(AX)_n$. In this paper we report the high pressure synthesis of several (ABX_3) $(AX)_n$ compounds having ABX_3 hexagonal polytype counterparts at atmospheric pressure with B = Ir, Ru, and Cr.

Compounds with the general formula $(ABX_3)(AX)_n$, where $n = 0$, 1/3, 1/2, 1, usually crystallize in a series of closely related structures, if the larger A cation has a radius $1.0 < r_A < 1.9$ Å and the smaller B cation has a radius $0.5 < r_B < 1.2$ Å. In the formula, X represents an anion such as oxygen, fluorine, or chlorine. The structure of the perovskite ($n = 0$) end member consists of a three-dimensional array of corner-shared BX_6 octahedra with the A cation occupying the large voids in this network (Fig. 1a). The other three members of this structural series consist of $1/n$ perovskite (ABX_3) units interleaved with a rock-salt layer. This generates a body-centered tetragonal unit cell. Figures 1b–d illustrate the unit cells for $n = 1/3$, 1/2, and 1, respectively.

If ABX_3 compounds form the perovskite structure at atmospheric pressure, as is the case for $SrTiO_3$, $SrZrO_3$, $CaMnO_3$, $CaTiO_3$, and $KFeF_3$, then the other members of the $(ABX_3)(AX)_n$ series can generally be formed also. However, if the relative size of the A cation is too large, then the ABX_3 end members do not take the perovskite structure at atmospheric pressure, but form a hexagonal polytype that only transforms to the perovskite structure at some higher pressure (*1*). In this case, pressure is needed for the synthesis of the interlayer compounds $(ABX_3)(AX)_n$. In this paper we report the high pressure synthesis of several $(ABX_3)(AX)_n$ compounds having ABX_3 hexagonal polytypes at atmospheric pressure.

Experimental

The samples prepared in this study were synthesized by tightly packing starting materials into cylindrical gold or platinum capsules and subjecting them to the desired pressure in a belt (*2*) apparatus capable of developing pressures to 90 kbar. The capsules consisted of 0.150 in. diam. × 0.005 in. thick tubing with 0.1 in. thick end plugs. In a typical run, the desired pressure was attained, and then the temperature was raised and held for 1/2 hr. The specimen was subsequently quenched to room temperature before the pressure was released. Structural analysis of the recovered specimen was then carried out at atmospheric pressure by conventional X-ray powder-diffraction studies using a Norelco goniometer with LiF monochromated Cu*Kα* radiation. All cell dimensions given are accurate to one unit in the last place quoted.

The choice of starting materials used to form the high-pressure phases depended on the system studied. In some cases, different combinations of starting materials could be used to prepare the same compound. For the two intermediate members of the systems $(SrBO_3)(SrO)_n$ with B = Ru, Ir, and Cr,

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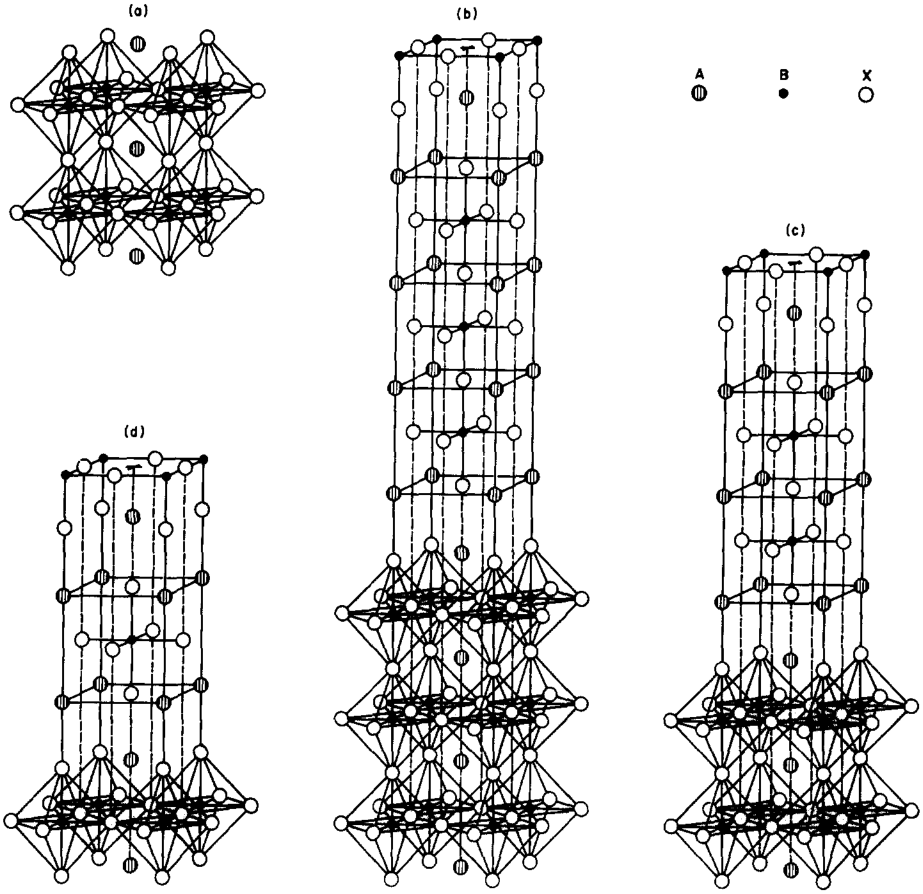

FIG. 1. Comparison of (a) the perovskite ABX_3 with the interlayer compounds $(AX)_nABX_3$, where (b) $n = 1/3$, (c) $n = 1/2$ and (d) $n = 1$.

the high-pressure phase could be prepared by reacting stoichiometric amounts of SrO and BO_2, SrO and $SrBO_3$, Sr_2BO_4 and BO_2, or $SrBO_3$ and Sr_2BO_4. The starting materials $SrBO_3$ and Sr_2BO_4 with B = Ru and Ir were prepared by the reaction of $SrCO_3$ and BO_2 or B metal powder in Alundum boats at 800°C in air. CrO_2 was prepared by the decomposition of CrO_3 at high pressure (*3*), $SrCrO_3$ was prepared by the high-pressure reaction of SrO and CrO_2 (*4*), and the atmospheric pressure form of Sr_2CrO_4 was prepared by the reaction of $Sr(OH)_2$, Cr_2O_3 and $SrCrO_4$ (*5*). Ba_2RuO_4 was prepared at high pressure by the reaction of BaO and $BaRuO_3$ while $(ANiF_3)(AF)_n$ with A = K and Rb were prepared by the reaction of AF and NiF_2. The use of SrO or BaO as prepared by heating the carbonate in flowing H_2–Ar at 1400°C always led to impurities because of the extreme reactivity of these oxides to moisture and CO_2 in the air. The stability of the alkaline-earth hydroxides or carbonates at high pressure prevented their participation in the reaction, thereby upsetting the stoichiometry and requiring some excess of "SrO" or "BaO" for complete reaction. The excess hydroxide or carbonate could then be removed from the product by washing. Where possible, reactions involving no alkaline earth oxides were used, such as $2Sr_2IrO_4 + IrO_2 = Sr_4Ir_3O_{10}$. Where use of alkaline-earth oxides were required, the reaction involving the least amount was chosen.

Results and Discussion

We have found two new compounds in the SrO–IrO_2 system at elevated pressures. At atmospheric pressure there is no compound formation between the compositions $SrIrO_3$ and Sr_2IrO_4. However, at high pressure and temperature, $Sr_4Ir_3O_{10}$ and $Sr_3Ir_2O_7$ are formed by the reaction of appropriate amounts of Sr_2IrO_4 and IrO_2. Both compounds have body-centered tetragonal unit cells and structures which are very closely related to that of Sr_2IrO_4. Sr_2Ir_3 $O_{10}$with $a = 3\ .93$ Å and $c = 28.4$ Å has three perovskite units alternating with one rock salt layer, $Sr_3Ir_2O_7$ with $a = 3.90$ Å and $c = 20.9$ Å has two perovskite units alternating with one rock salt layer while Sr_2IrO_4 (*6*) with $a = 3.89$ Å and $c = 12.92$ Å has one perovskite unit alternating with one rock salt layer. At atmospheric pressure the composition $SrIrO_3$ has the distorted hexagonal $BaTiO_3$ structure with cubic (*c*) and hexagonal (*h*) close-packed SrO_3 layers stacked in the sequence (*cch cch*) (*7*). At high pressure (45 kbar and 1000°C), the distorted 6*H* structure transforms (*7*) to the all cubic-close-packed perovskite structure. This result is consistent with earlier work (*8*, *1*, *9*), showing that the 6*H* forms of $RbNiF_3$, $CsFeF_3$, and $CsMnF_3$ all transform to the perovskite structure at elevated pressures. In general, the effect of pressure on perovskite-related layer compounds is to increase the proportion of cubic to hexagonal-close-packed-layers and thus to decrease the number of face-shared octahedra with their close B–B cation distances.

In the preparation of the two new compounds, $Sr_4Ir_3O_{10}$ and $Sr_3Ir_2O_7$, it was found that lower synthesis pressures are required as the proportion of perovskite units is reduced. For $Sr_4Ir_3O_{10}$ ($n = 1/3$), pressures greater than 35 kbar at 1000°C are needed, while $Sr_3Ir_2O_7$ ($n = 1/2$) is prepared at pressures greater than 10 kbar. The end member [Sr_2IrO_4 ($n = 1$)] can easily be prepared at atmosphere pressure (*6*). Apparently the matching requirements of alternate layers of SrO and $SrIrO_3$, in the compound Sr_2IrO_4, constrains the lattice parameters sufficiently to stabilize perovskite interlayers. As the proportion of SrO to $SrIrO_3$ decreases, these constraints are weakened, and high pressures are necessary to stabilize the structure. Table I summarizes the structural and synthesis data for $SrIrO_3(SrO)_n$, $n = 0$, 1/3, 1/2, 1. Table II lists the X-ray powder diffraction data we obtained for $Sr_4Ir_3O_{10}$ and $Sr_3Ir_2O_7$.

TABLE I

Compound	Synthesis pressure	Structural data (Å)
Sr_2IrO_4	1 atm.	$a = 3.89$, $c = 12.92$
$Sr_3Ir_2O_7$	>10 kbar	$a = 3.90$, $c = 20.9$
$Sr_4Ir_3O_{10}$	>35 kbar	$a = 3.93$, $c = 28.4$
$SrIrO_3$	>45 kbar	$a = 5.60$, $b = 5.58$ $c = 7.89$

TABLE IIa

CRYSTALLOGRAPHIC DATA FOR $Sr_4Ir_3O_{10}$
($a = 3.93$ Å, $c = 28.4$ Å)

h k l	d_{calcd}	d_{obsd}	I_{obsd}
0 0 6	4.733	4.741	5
1 0 1	3.893	3.906	28
1 0 3	3.630	3.652	4
0 0 8	3.550	3.594	3
1 0 7	2.823	2.816	100
1 1 0	2.779	2.778	100
0 0 14	2.029	2.026	18
2 0 0	1.965	1.963	45
2 0 6	1.815	1.809	4
1 1 12	1.802	1.802	3
2 1 1	1.754	1.759	7
1 1 14	1.639	1.638	21
2 0 10	1.616	1.612	51
2 1 7	1.613		
2 0 14	1.411	1.411	17
2 2 0	1.390	1.392	9
1 0 21	1.279	1.278	5
3 0 5	1.277		
3 0 7	1.247	1.244	14
3 1 0	1.243		
2 2 14	1.146	1.146	7
2 1 21	1.072	1.072	7
3 1 14	1.060	1.059	8
3 2 7	1.053	1.054	14

TABLE IIb

CRYSTALLOGRAPHIC DATA FOR $Sr_3Ir_2O_7$
($a = 3.90$ Å, $c = 20.9$ Å)

h k l	d_{calcd}	d_{obsd}	I_{obsd}
0 0 4	5.225	5.226	14
1 0 1	3.834	3.831	14
0 0 6	2.483	3.483	2
1 0 5	2.851	2.851	100
1 1 0	2.758	2.753	52
1 1 4	2.439	2.434	4
1 0 7	2.371	2.369	6
0 0 10	2.090	2.088	16
1 0 9	1.995	1.992	8
2 0 0	1.950	1.949	29
2 0 2	1.917	1.916	2
2 0 4	1.827	1.826	4
0 0 12	1.742	1.738	7
2 1 1	1.738		
2 0 6	1.702	1.703	2
1 1 10	1.666	1.664	21
2 1 5	1.610	1.608	36
2 1 7	1.506	1.507	2
1 1 12	1.473	1.470	2
2 0 10	1.426	1.424	15
2 1 9	1.395	1.394	5
2 2 0	1.379	1.378	7
2 2 4	1.333	1.335	2
1 1 14	1.313	1.310	9
1 0 15	1.312		
2 0 12	1.299	1.298	3
3 0 1	1.298		
2 2 6	1.282	1.281	3
3 0 5	1.241	1.239	8
3 1 0	1.233	1.233	10
2 2 10	1.151	1.1150	6
3 0 9	1.134	1.133	1
2 1 15	1.089	1.088	7
2 0 16	1.085	1.085	5
3 1 10	1.062	1.062	10
3 2 5	1.047	1.047	10

The high-pressure phases with perovskite-related structure show considerable stability when quenched to atmospheric pressure and room temperature (*10*). The high-pressure phases $Sr_4Ir_3O_{10}$ and $Sr_3Ir_2O_7$ only slowly disproportionate to Sr_2IrO_4 and the atmospheric pressure form of $SrIrO_3$ at temperatures greater than 800°C. The high-pressure perovskite form of $SrIrO_3$ only slowly retransforms to the distorted 6*H* form at 1200°C.

These results for the $SrIrO_3(SrO)_n$ compounds suggested the feasibility of high-pressure synthesis of analogous interlayer compounds where the ABO_3 ($n = 0$) end member has a perovskite-related hexagonal layer structure. At atmospheric pressure, $BaRuO_3$ has the 9R polytype structure with *hhchhchhc* stacking sequence. This structure transforms (*10*) at 15 kbar to the 4*H* structure (*hchc*) and further transforms to the 6*H* structure (*cchcch*) at 30 kbar. A study of the $BaRuO_3$–$SrRuO_3$ phase diagram as a function of pressure (*10*) indicated that $BaRuO_3$ would have the perovskite structure of $SrRuO_3$ at about 120 kbar. Since the perovskite form of $BaRuO_3$ requires higher pressures to stabilize than we had available, we decided to prepare Ba_2RuO_4. This end member has the lowest ratio of perovskite to rocksalt units and should therefore require the least pressure to prepare. We were in fact able to synthesize Ba_2RuO_4 with the K_2NiF_4 structure by the reaction of $BaRuO_3 +$ BaO at 65 kbar and 1200°C. The best results were obtained with a 10% excess of "BaO", which was subsequently washed away. The X-ray powder diffraction data (Table III) could be indexed on the basis of a body-centered tetragonal unit cell with $a = 3.99$ Å and $c = 13.4$ Å. Since such high pressure was needed for the synthesis of Ba_2RuO_4 and since we encountered difficulties in working with exact amounts of BaO, the intermediate members of the series ($n = 1/3$ and $1/2$) were not tried.

TABLE III

CRYSTALLOGRAPHIC DATE FOR Ba_2RuO_4

($a = 3.99$ Å, $c = 13.43$ Å)

$h\,k\,l$	d_{calcd}	d_{obsd}	I_{obsd}
0 0 4	3.358	3.349	4
1 0 3	2.979	2.976	100
1 1 0	2.821	2.825	59
1 1 2	2.601	2.598	3
1 0 5	2.228	2.231	18
1 1 4	2.160	2.159	13
2 0 0	1.995	1.998	29
1 1 6	1.754	1.751	17
1 0 7	1.729	1.723	3
2 0 4	1.715	1.711	3
0 0 8	1.679	1.674	5
2 0 6 2 1 5	1.489 1.486	1.488	15
1 1 8	1.443	1.439	5
2 2 0	1.411	1.412	7
2 1 7	1.307	1.304	2
2 0 8	1.285	1.283	4
3 0 3	1.275	1.277	6
2 2 6 3 0 5	1.193 1.192	1.193	6
2 1 9	1.145	1.412	2
3 1 6	1.099	1.099	5
3 2 3	1.074	1.075	8
3 1 8 2 1 1 1	1.009 1.008	1.006	8

In the system SrO–CrO_2, only Sr_2CrO_4 is known at atmospheric pressure, and it has a structure with chromium in tetrahedral coordination (*11*). Chamberland (*4*) has reported the high-pressure preparation of $SrCrO_3$ with the perovskite structure by the reaction of Sr_2CrO_4 and CrO_2 at 65 kbar and 1000°C. We report that at 65 kbar and 1000°C Sr_2CrO_4 transforms to the K_2NiF_4 structure with $a = 3.82$ Å and $c = 12.4$ Å. This transformation is accompanied by a 12% decrease in volume and a change of coordination for the chromium from four to six oxygens. The reaction of Sr_2CrO_4 and CrO_2 or $SrCrO_3 +$ SrO led to the preparation of $Sr_3Cr_2O_7$ with the body-centered tetragonal unit cell of Fig. 1b ($a = 3.82$ Å, $c = 20.1$ Å). There were small amounts of impurities present in the product due to impurity of the starting materials Sr_2CrO_4 and SrO. Since neither the Sr_2CrO_4 or SrO could be made sufficiently pure, the preparation of $Sr_4Cr_3O_{10}$, with its very exacting Sr:Cr ratio, was not successful. X-ray diffraction data for Sr_2CrO_4 and $Sr_3Cr_2O_7$ are given in Table IV.

Many solid state reactions are extremely slow or lead to poorly crystallized products if carried out at atmospheric pressure. Where the product is stabilized by pressure, as is the case for perovskites, high pressures may reduce reaction times to less than an hour and/or markedly increase the crystallinity of the product.

In the interlayer series $(SrO)_n(SrRuO_3)$, the end members $SrRuO_3$ and Sr_2RuO_4 are both thermodynamically stable at one atmosphere, in contrast to the series $(SrO)_n(SrIrO_3)$. Although this means that the two intermediary compounds $Sr_4Ru_3O_{10}$ and $Sr_3Ru_2O_7$ can be prepared at one atmosphere by reacting appropriate mixtures of $SrRuO_3$ and Sr_2RuO_4, we found that we could obtain single-phase $Sr_3Ru_2O_7$ only by repeated 1100°C firings

TABLE IVa

CRYSTALLOGRAPHIC DATA FOR $Sr_3Cr_2O_7$
($a = 3.82$ Å, $c = 20.1$ Å)

h k l	d_{calcd}	d_{obsd}	I_{obsd}	*h k l*	d_{calcd}	d_{obsd}	I_{obsd}
0 0 4	5.025	5.021	4	1 0 11	1.648	1.646	6
1 0 1	3.753	3.743	9	1 1 10	1.613	1.610	29
0 0 6	3.350	3.348	12	2 1 5	1.572	1.572	64
1 0 3	3.319	3.324	9	2 0 8	1.521	1.520	4
1 0 5	2.769	2.769	100	2 1 7	1.468	1.467	7
1 1 0	2.701	2.700	92	1 1 12	1.424	1.423	8
0 0 8	2.513	2.506	5	2 0 10	1.385	1.383	27
1 1 4	2.379	2.372	9	2 2 0	1.351	1.350	24
1 0 7	2.295	2.299	15	1 0 15	1.265	1.267	5
1 1 6	2.103	2.104	55	2 0 12 0 0 16	1.259 1.256	1.257	10
0 0 10	2.010	2.009	34				
1 0 9	1.928	1.924	9	2 1 11	1.248	1.248	8
2 0 0	1.910	1.909	82	3 0 5	1.214	1.214	12
1 1 8	1.840	1.836	5	3 1 0	1.208	1.208	18
2 1 1	1.702	1.701	2	3 0 7	1.164	1.163	5
0 0 12	1.675	1.674	8	3 1 6	1.136	1.136	13
2 0 6 2 1 3	1.659 1.655	1.657	10	1 0 17 2 2 10	1.130 1.121	1.129 1.121	8 12

and regrindings for periods up to 2 weeks. By contrast, 15 min at 20 kbar and 1000°C was sufficient to obtain a single-phase product of $Sr_3Ru_2O_7$ ($a = 3.89$ Å, $c = 20.7$ Å) by the same reaction. The compound $Sr_4Ru_3O_{10}$ could be made only as an impure phase using the same reaction condition.

We have also synthesized $K_3Ni_2F_7$ in 30 min by reacting mixed fluorides at 65 kbar and 800°C ($a = 3.99$ Å, $c = 21.3$ Å). Even though $KNiF_3$ is a perovskite and K_2NiF_4 is stable at 1 atmosphere, synthesis of $K_3Ni_2F_7$ at 1 atmosphere is very difficult, if not impossible, whereas at high pressures it is quite routine and rapid.

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TABLE IVb

CRYSTALLOGRAPHIC DATA FOR Sr_2CrO_4
($a = 3.82$ Å, $c = 12.40$ Å)

h k l	d_{calcd}	d_{obsd}	I_{obsd}
1 0 1	3.651	3.660	12
0 0 4	3.100	3.140	16
1 0 3	2.805	2.820	100
1 1 0	2.701	2.712	100
1 1 2	2.476	2.479	6
1 0 5	2.080	2.083	16
0 0 6	2.067	2.074	10
1 1 4	2.037	2.047	26
2 0 0	1.910	1.907	43
2 0 2	1.825	1.823	7
2 1 1	1.692	1.691	4
1 1 6	1.641	1.649	9
2 0 4	1.626	1.627	8
2 1 3	1.579	1.584	28
2 1 5 2 0 6	1.407 1.403	1.409	14
2 2 0	1.351	1.353	13
3 0 3	1.217	1.221	7
3 1 0	1.208	1.208	9
3 0 5	1.133	1.135	7
2 2 6 1 1 10	1.131 1.270	1.128	6

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