

instance reported where there is a lack of correlation between factors which are expected to govern the acid strength and the stability constants.<sup>19,20</sup>

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CONNECTICUT, STORRS, CONNECTICUT]

## Compounds with the Hexagonal Barium Titanate Structure<sup>1,2</sup>

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A number of compounds of the type  $Ba(M,Ti)_3O_3$  where  $M = Ti^{3+}, V, Cr, Mn, Fe, Co, Ru, Rh, Ir, Pt$  have been prepared and are shown to have the hexagonal barium titanate structure. The phases probably have a composition close to  $Ba(M_{1/3}Ti_{2/3})_3O_3$  and are in some cases oxygen-deficient. Evidence from X-ray and magnetic studies indicates that the M cation is concentrated mainly in the 4-fold position in the hexagonal cell and is bonded directly to a titanium ion in the neighboring position. The adoption of the structure appears to be dependent upon the formation of a metal-metal bond through overlapping d-orbitals.

### Introduction

A high temperature form of barium titanate was first observed by Megaw<sup>3</sup> who suggested that it was rhombohedral. Single crystals were grown from alkali carbonate fluxes<sup>4</sup> and Matthias,<sup>5</sup> using a modification of this procedure, obtained amber colored flat hexagonal plates of the compound which were used by Burbank and Evans<sup>6</sup> to determine the structure. The amber color of the crystals, which was attributed to dissolved platinum acquired from the reaction vessel, could be removed by heating in air at 200° for a few hours.<sup>5</sup>

The transition from cubic to hexagonal  $BaTiO_3$  occurs with the formation of an intermediate phase at 1450°, according to Statton,<sup>7</sup> but Race and Roy<sup>8</sup> have reported a reversible transition at 1460°. The same authors have found that the transition temperature is raised by the addition of  $Ca^{2+}$ ,  $TiO_2$ ,  $SiO_2$  and  $BaCl_2$  but is lowered by  $K^+$ .<sup>9,10</sup> Wood has noted that the hexagonal form may be obtained at 1200° by using barium chloride, potassium and sodium carbonates as fluxes with appropriate quantities of barium carbonate and titanium dioxide.<sup>11</sup>

In a previous communication from this Laboratory, it was suggested that the platinum was instrumental in bringing about the formation of the hexagonal phase, and it was shown that the presence of many ions other than platinum led to this structure.<sup>12</sup> This paper describes the characterization of some of these phases.

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(2) Abstracted from the Doctoral Thesis of John Guy Dickinson submitted to the University of Connecticut 1960.

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### Experimental

An intimate mixture of the reactants in stoichiometric proportions was prepared by grinding in an agate mortar. Ordinarily the powders were pelleted to minimize reaction with the containers. Those samples which had to be protected from oxidation were sealed in evacuated silica capsules, the others were heated in open zirconium silicate boats in a muffle furnace. With the vacuum preparations, the samples were given a preliminary heating of about 0.5 hr. and were again mixed by grinding and heated under controlled conditions usually for 24 hr. periods. Examination of the products for homogeneity was made microscopically and by X-rays. Most of the products were microcrystalline powders. The presence of the hexagonal barium titanate phase could be detected readily by examining the forward reflections obtained with a General Electric XRD-5 diffractometer. If the tracing revealed the presence of other phases, the grinding and heating cycle was repeated until no change was observed.

From the nature of the ions which appeared to favor the incidence of the hexagonal phase, it was assumed that they were being substituted for part of the titanium in the  $BaTiO_3$  crystal.<sup>12</sup> Several systems were examined on this basis.

1.  $Ba(Pt_xTi_{1-x})_3O_3$ .—Crystals prepared by the procedure of Matthias<sup>5</sup> were a deep amber color. No change was observed in the color upon heating the crystals for extended periods of time from 500 to 1300° in zirconium silicate boats in air. At 1500° melting or reaction with the boat occurred with the separation of metallic platinum. The residue contained tetragonal barium titanate. The amber crystals when ground to a fine powder gave a diffraction pattern which could be completely indexed using the lattice parameters given by Burbank and Evans.<sup>6</sup>

Mixtures of barium carbonate, titanium dioxide and platinum dioxide hydrate corresponding to the formula where  $x$  ranged from 0.005 to 0.5 were heated in air and also *in vacuo* at temperatures from 400 to 1250°. The purest phase appeared to be formed at  $x = 0.1$ . Above this value, platinum lines and below this value tetragonal barium titanate lines were found in the diffraction pattern. Attempts to extend the proportion of platinum in the crystal were made by heating the samples in oxygen, *in vacuo* and by incorporating various amounts of potassium carbonate in the mixtures. None of these attempts was successful.

2.  $Ba(M_xTi_{1-x})_3O_3$  where  $M = Ru, Rh, Pd, Os, Ir$ .—The hexagonal barium titanate structure was not obtained by use of either palladium or osmium. All of the others, however, gave the hexagonal phase upon heating in air appropriate mixtures composed of the platinum metal, barium carbonate and titanium dioxide. The metals (99.9+%) were in powder form (325 mesh).

At first it seemed that a wide homogeneity range existed in the case of the iridium system,<sup>12</sup> and it was decided on this basis to give it a more exhaustive examination.

Comparison of the diffractometer tracings of three carefully prepared samples of the preparations  $Ba(Ir_xTi_{1-x})_3O_3$

in which  $x$  was 0.25, 0.33 and 0.50 showed the presence of the lines of tetragonal barium titanate in the first of these and the lines of the compound  $\text{BaIrO}_3$  in the last. Figure 1 gives a comparison of the tracings at  $31^\circ < \theta < 33.5^\circ$ . The pattern of the preparation  $\text{Ba}(\text{Ir}_{1/3}\text{Ti}_{2/3})\text{O}_3$  could be indexed completely on the basis of the hexagonal barium titanate structure. The corresponding preparations using ruthenium and rhodium also gave clean diffraction patterns of the hexagonal phase. The ruthenium and iridium compounds were made by heating at  $1100^\circ$ , the rhodium compound at  $1250^\circ$ .

It has been found that the composition of preparations of this kind may vary due to losses of metal oxides by evaporation or by reaction with containers. Chemical analysis of the iridium compound gave Ba 48.5%, Ti 11.4%, Ir 22.7%. The sample was dissolved in boiling hydrochloric acid. The barium was determined as sulfate and the titanium by precipitation with cupferron and ignition to  $\text{TiO}_2$ . No good procedure was found for the determination of iridium. The method of Gilchrist<sup>13</sup> was not successful due to coprecipitation of titanium and difficulty was experienced in carrying out colorimetric determinations for lack of a suitable standard. The procedure employed consisted of evaporation to dryness of the solution remaining after the removal of the barium and titanium. The residue was ignited under hydrogen at red heat and the iridium was weighed as the metal.

3.  $\text{BaM}_2\text{Ti}_{1-x}\text{O}_3$  where  $M = \text{Ti, V, Cr, Mn, Fe, Co}$ .—Mixtures of barium carbonate and titanium dioxide with iron(III) oxide or cobalt(II) carbonate when heated in air at  $1100^\circ$  yielded products which gave diffraction patterns corresponding to that of the hexagonal barium titanate when  $x$  was 0.33. Products obtained using other proportions of reactants contained other phases.

The pure hexagonal phase was also obtained by heating a mixture of barium oxide, manganese dioxide and titanium dioxide *in vacuo*. The composition of the mixture corresponded to the formula  $\text{Ba}(\text{Mn}_{1/3}\text{Ti}_{2/3})\text{O}_3$ . With different proportions of manganese dioxide, impurities were detectable in the products. Mixtures of barium oxide, titanium(III) oxide and titanium dioxide when heated *in vacuo* gave mixtures of the tetragonal barium titanate and the cubic  $\text{BaTiO}_{2.5}$ . A mixture of these oxides, however, with finely powdered titanium metal to give the proportion Ba:Ti:Ti(III):Ti(IV) = 1:0.05:0.28:0.67 (corresponding to the formula  $\text{Ba}(\text{Ti}_{0.48}\text{Ti}_{0.52})\text{O}_{2.76}$ ) was found to yield the pure hexagonal phase as a black microcrystalline powder when heated *in vacuo*.

Chemical analysis of this product gave Ba 59.6%, Ti (total) 20.4%, Ti(III) 8.3%, compared with Ba 59.9%, Ti (total) 20.9%, Ti(III) 10.0% calculated from the formula  $\text{Ba}(\text{Ti}_{0.48}^{\text{III}}\text{Ti}_{0.52}^{\text{IV}})\text{O}_{2.76}$ . The value for Ti(III) was derived from the gain in weight upon heating the product in air. The chromium and vanadium systems both gave the hexagonal barium titanate structure but the products were never obtained as single phases. The vanadium compound always was contaminated by vanadium dioxide. Subjecting these products to various inert or reducing conditions did not remove this impurity. The persistence of this phase suggests that it was formed by precipitation upon cooling the sample.

4. **Miscellaneous Systems.**—The other fourth period elements scandium, nickel, copper, zinc and gallium failed to produce the hexagonal phase nor was it obtained with the fifth period elements from yttrium to molybdenum or with silver. Iridium gave rise to a cubic phase with  $\text{Ba}(\text{Ir}_x\text{Ti}_{1-x})\text{O}_{3-0.5x}$  in which the approximate range of  $x$  is 0.4 to 0.6. Tantalum, tungsten and rhenium gave no recognizable products.

Attempts to form the hexagonal phase with zirconium instead of titanium were unsuccessful when iridium and ruthenium were used as the stabilizing cations. On the other hand, it was found that the product formed at  $1100^\circ$  *in vacuo* from a mixture of barium oxide with iridium(IV) oxide and iron(III) oxide gave a diffraction pattern corresponding to the hexagonal barium titanate structure. The composition of this phase appears to be  $\text{Ba}(\text{Fe}_{1/3}\text{Ir}_{2/3})\text{O}_{2.84}$ .

**X-Ray Diffraction Data.**—The hexagonal barium titanate structure can be regarded as composed of close packed  $\text{BaO}_3$  layers. The layer repetition is ABCACB, and the

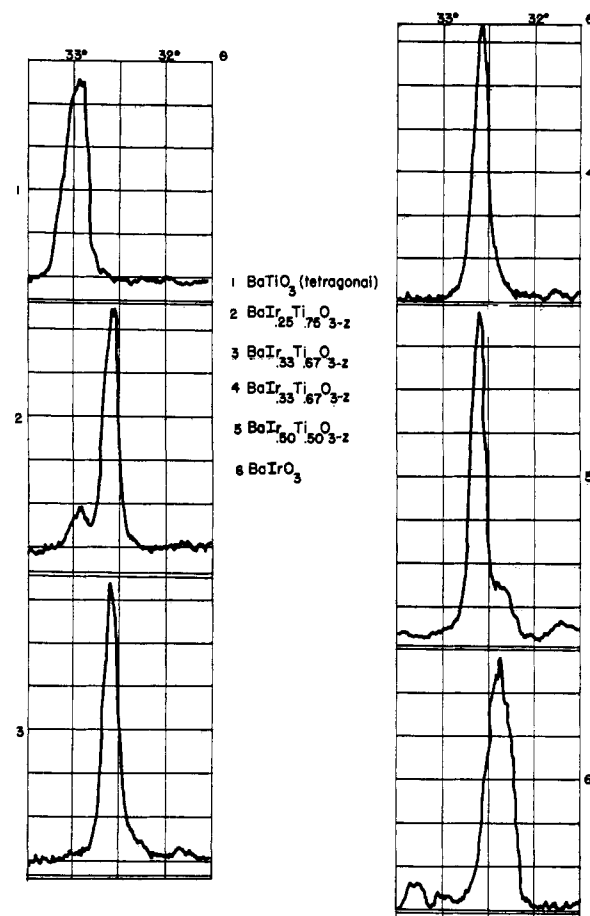


Fig. 1.—Diffractometer tracing of products in the system  $\text{BaTiO}_3\text{-BaIrO}_3$  showing the occurrence of a unique phase at composition  $\text{Ba}(\text{Ir}_{0.33}\text{Ti}_{0.67})\text{O}_3$ .

unit cell contains six formula units of  $\text{BaTiO}_3$ . The six titanium atoms occupy two crystallographically different positions, one fourfold and the other twofold. The titaniums in both positions are in octahedral coordination with oxygen. The  $\text{TiO}_6$  octahedra of the fourfold titaniums, however, are arranged in face-sharing pairs (forming  $\text{Ti}_2\text{O}_9$  groups) whereas the  $\text{TiO}_6$  octahedra of the twofold titaniums share only corners.

Many attempts were made to prepare crystals of the compound  $\text{Ba}(\text{Ir}_{0.33}\text{Ti}_{0.67})\text{O}_3$  sufficiently large for single crystal X-ray analysis. Various fluxes, reaction times, temperatures and containers were used with no success. Since single crystals were not available, the intensities needed were obtained from powder data using a General Electric XRD-5 Diffractometer. The comparisons of calculated and observed intensities are given in Table I. The position parameters used were the same as those determined by Burbank and Evans.<sup>6</sup> No attempt was made to use the powder data to refine the one  $z$  parameter for titanium or iridium, nor the three oxygen parameters. "Reliability factors" were calculated by summing the absolute differences of the square roots of the observed and calculated intensities and dividing the difference by the sum of the square roots of the observed intensities.

Calculations were made by assuming various amounts of iridium entered the hexagonal structure. Data for substitution into the fourfold position are given in Table I.

The variation in reliability factor with the proportion of iridium placed in the fourfold and in the twofold positions is shown in Fig. 2. It can be seen that the best agreement is obtained with the substitution of one third of the titanium the substitution being made all in the fourfold position. With random substitution, the agreement is less satisfactory.

X-Ray powder intensity data also were taken for the hexagonal phase  $\text{Ba}(\text{Ti}_{0.48}^{\text{III}}\text{Ti}_{0.52}^{\text{IV}})\text{O}_{2.76}$ . Since it was not pos-

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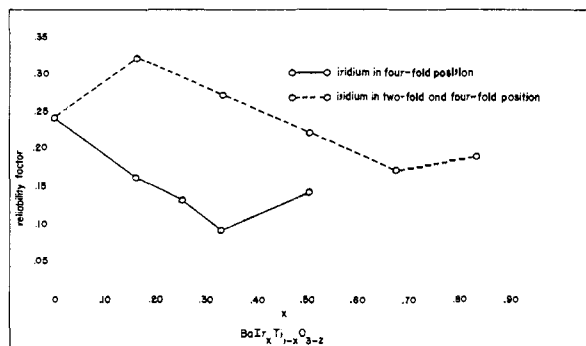


Fig. 2.—The variation of reliability factor with iridium content in the system  $\text{Ba}(\text{Ir}_x\text{Ti}_{1-x})\text{O}_3$ . The solid line represents intensity calculations based on placing all the iridium in the 4-fold position; the dotted line is for a random distribution.

sible to distinguish  $\text{Ti}^{\text{III}}$  and  $\text{Ti}^{\text{IV}}$  from X-ray scattering, no preferred position for the titanium(III) could be ascertained. A "reliability factor" of 0.12 was obtained for this compound. The intensity data are listed in Table II.

TABLE I  
X-RAY DATA FOR  $\text{BaIr}_{0.33}\text{Ti}_{0.67}\text{O}_3$   
 $a = 5.74, c = 14.2 \text{ \AA}$ .

<i>hkl</i>	$d_{\text{obsd}}$	$d_{\text{calcd}}$	$I_{\text{obsd}}$	$I_{\text{calcd}}$
002	7.12	7.10	1.5	2.2
100	4.99	4.97	0.9	1.8
101	4.69	4.68	6.4	3.7
102	4.06	4.07	6.9	2.6
004	3.54	3.55	1.9	2.8
103	3.43	3.42	9.8	13.1
110, 104	2.87	2.87	100.0	100.0
112	2.66	2.66	1.6	2.0
105, 201, 200	2.46	2.46	9.7	8.5
006, 202	2.34	2.34	6.7	6.8
114	2.23	2.23	5.8	6.3
203	2.20	2.20	10.4	10.1
204	2.03	2.04	22.7	21.0
107, 205	1.87	1.87	16.5	15.0
213	1.74	1.75	2.5	2.9
300, 214, 108, 301	1.66	1.66	29.2	34.2
215, 303, 207	1.57	1.57	11.0	8.6
304, 118	1.499	1.500	6.7	4.6
220, 208, 305	1.432	1.430	14.1	12.9
310, 311, 217	1.374	1.371	6.1	7.8
209, 313	1.324	1.323	5.9	9.4
314, 218	1.282	1.282	7.2	7.6
401; 315; 1, 0, 11	1.237	1.237	4.0	4.3
403, 219	1.203	1.201	4.7	4.1
404; 0, 0, 12	1.170	1.170	3.5	4.0
321; 405; 317; 309; 2, 0, 11	1.136	1.136	4.8	5.4

**Magnetic Data.**—Magnetic susceptibility measurements were made on those samples which were available in sufficiently large quantity and which appeared to be pure by X-ray examination. The data obtained are listed in Table III. The Gouy balance used for these measurements could detect weight changes of the order of 0.00003 g. The measurements were taken over the temperature range from  $-20$  to  $50^\circ$ . Correction was made for the diamagnetism of the ions present. The samples containing trivalent titanium and iron were contaminated with a small quantity of a ferromagnetic impurity for which adjustment had to be made.

TABLE II  
X-RAY DATA FOR  $\text{Ba}(\text{Ti}_{0.48}^{\text{III}}\text{Ti}_{0.52}^{\text{IV}})\text{O}_{2.76}$   
 $a = 5.74, c = 14.1 \text{ \AA}$ .

<i>hkl</i>	$d_{\text{obsd}}$	$d_{\text{calcd}}$	$I_{\text{obsd}}$	$I_{\text{calcd}}$
102	4.06	4.06	12.4	8.1
103	3.41	3.41	22.4	26.7
104, 110	2.88	2.87	100.0	100.0
105, 201	2.45	2.45	7.5	5.1
006, 202	2.34	2.34	17.9	16.8
203	2.20	2.19	18.8	18.7
204	2.03	2.03	29.2	23.8
211, 107, 205	1.86	1.86	9.9	11.8
116, 212	1.81	1.81	6.7	8.2
213	1.74	1.74	5.8	6.4
108, 214, 300	1.66	1.66	28.5	22.4
207, 215, 303	1.56	1.56	5.6	6.5
304, 118	1.494	1.498	2.6	4.2
109	1.488	1.489	2.6	2.5
220, 208	1.438	1.434	13.5	13.5
311, 217	1.367	1.371	4.6	6.6
312; 306; 1, 0, 10	1.350	1.352	3.5	5.0
313, 209	1.318	1.322	5.8	8.4
314, 218	1.282	1.283	6.8	7.3
401; 315; 1, 0, 11	1.235	1.237	0.2	1.9
402; 226; 2, 0, 10	1.222	1.223	5.0	3.7
403, 219	1.201	1.200	5.2	4.4
404; 0, 0, 12	1.172	1.171	2.2	4.2
321; 405; 317; 309; 2, 0, 11	1.134	1.136	2.3	5.3
322; 2, 1, 10	1.125	1.125	0.7	3.1
323	1.108	1.107	1.6	2.4

TABLE III  
MAGNETIC DATA FOR SOME PHASES WITH THE HEXAGONAL BARIUM TITANATE STRUCTURE

Compound	$\theta, ^\circ\text{K}$ .	$\mu$ (eff)	Unpaired electrons per paramagnetic ion
$\text{Ba}(\text{Ir}_{0.33}\text{Ti}_{0.67})\text{O}_3$	$-470$	2.1	1.3
$\text{Ba}(\text{Ru}_{0.33}\text{Ti}_{0.67})\text{O}_3$	$-240$	2.7	1.9
$\text{Ba}(\text{Co}_{0.33}\text{Ti}_{0.67})\text{O}_{2.67}$	$-197$	3.9	3.0
$\text{Ba}(\text{Fe}_{0.33}\text{Ti}_{0.67})\text{O}_{2.67}$	$-100$	4.6	3.7
$\text{Ba}(\text{Mn}_{0.33}\text{Ti}_{0.67})\text{O}_{2.84}$	$-180$	4.5	3.6
$\text{Ba}(\text{Ti}_{0.48}^{\text{III}}\text{Ti}_{0.52}^{\text{IV}})\text{O}_{2.76}$	$-350$	1.72	1.0

### Discussion

It has been demonstrated that the hexagonal barium titanate structure is adopted most readily when foreign ions are introduced. In the certain absence of impurities, we have not been able to obtain this form except by making sure that part of the titanium was in the trivalent state. The possibility exists that the conversion to the hexagonal form at about  $1450^\circ$  occurs with the loss of some oxygen.

That a deficiency of oxygen is not the only factor involved in the stabilization of the hexagonal form seems to be indicated by the failure to induce the structure by use of such trivalent cations as aluminum, scandium, yttrium and indium. The latter gives rise to a cubic perovskite phase which has about the same oxygen-deficiency as the hexagonal barium titanate we prepared. The phase  $\text{Ba}(\text{In}_{0.4}\text{Ti}_{0.6})\text{O}_{2.8}$  is a quite good conductor at  $1000^\circ$ . The presumption is that the conductivity is due to the mobility of the oxide ions made possible by the anion vacancies. No amount of

annealing of this phase produced the hexagonal form.

All of the ions which we have found to bring about the formation of the hexagonal phase are transition metal cations having one or more d electrons. The proportion of this cation required in the case of iridium seems to be close to one half the proportion of titanium and the preferred site of the iridium is in the fourfold position. The intensity data seem to establish this beyond reasonable doubt. We are assuming that the  $\text{IrO}_6$  octahedron shared a face with the  $\text{TiO}_6$  octahedron.

The close proximity of the metal ions in this position, assuming a distance close to that in hexagonal barium titanate, suggests the strong possibility of metal-metal bonding. The hypothesis is advanced that it is interaction of the impurity metal with the titanium which is responsible for the adoption of the hexagonal structure. The d electrons supplied by the foreign ion are necessary to form this bond.

The widespread occurrence of the perovskite structure is due to the high lattice energy achieved in the close packing of the  $\text{AO}_3$  layers with the cations carrying the larger charge being accommodated in oxygen octahedra between these layers. The close approach of the B cations in the hexagonal  $\text{ABO}_3$  structure would be expected to result in a reduction of stability. Our suggestion is that the formation of metal-metal bonds may furnish enough additional energy to stabilize the structure.

The composition of the phase  $\text{Ba}(\text{Ir}_x\text{Ti}_{(1-x)})\text{O}_3$  seems to be well within the limits  $0.25 < x < 0.50$  and is probably close to  $x = 0.33$ . Of the other phases it can only be said that in most instances the cleanest diffraction patterns of the hexagonal phase were obtained when the proportions of the cations used in the preparation corresponded to the formula  $\text{Ba}(\text{M}_{0.33}\text{Ti}_{0.67})\text{O}_3$ . M could be Mn, Fe, Co, Ru, Rh. It is not known from analysis that these phases are oxygen-deficient, but it seems reasonably certain that some of them are.

The formula seems reasonable in view of the suggestion of the importance of forming a metal-metal bond since it corresponds to one of each pair of cations in the face-shared octahedra being an M cation. This explanation does not agree with our experiments with platinum as the stabilizing cation which we could introduce only to the extent of  $x = 0.1$ . It is interesting to note that calculation of reliability factors using the data of Burbank and Evans,<sup>8</sup> but with the supposition that platinum is present in the fourfold position gives an over-all improvement from 0.22 to 0.18. There is a broad minimum at  $x = 0.1$ . The reliability factor is 0.12 if only the forward reflections are considered. There remain other problems concerning the platinum system which we were not able to resolve. The amber crystals were not decolorized by any heat treatment we employed short of melting, nor could we obtain by direct synthesis the hexagonal phase  $\text{Ba}(\text{Pt}_{0.25}\text{Ti}_{0.75})\text{O}_3$  reported by Blattner.<sup>4</sup>

Topochemical factors in the reactions of mixtures of this type are difficult to understand and control.

The magnetic data in Table III are not in conflict with the existence of metal-metal bonding between the cations in the fourfold positions. The typical d orbital splitting for ions in octahedral coordination is assumed to occur, the separation of the two higher  $e_g$  levels from the three  $t_{2g}$  lower levels being greater in the case of iridium and ruthenium than with the 4th period transition metals. Since the oxygen octahedra surrounding the cations in the fourfold positions share a face, the  $d_{xy}$ ,  $d_{xz}$ , and  $d_{yz}$  orbitals of the two cations are directed toward each other so that molecular orbitals could be formed between the two cations. It seems plausible to assume that the three bonding orbitals thus formed are substantially lower in energy than the atomic orbitals and that the antibonding orbitals lie at a much higher level than the two  $e_g$  atomic orbitals. The following electronic distribution would then be expected to occur. The d electrons of iridium and ruthenium should occupy the three  $t_{2g}$  orbitals giving one unpaired electron for the  $5d^5$  iridium(IV) ion and two unpaired electrons for the  $4d^4$  ruthenium(IV) ion. On the other hand, the d electrons of the 4th period elements should be distributed over the  $t_{2g}$  and the  $e_g$  orbitals. Hence the  $3d^7$  cobalt(II) ion should have three unpaired electrons, the  $3d^6$  iron(II) ion four unpaired electrons and the  $3d^4$  manganese(III) ion four unpaired electrons. The oxidation states are chosen rather arbitrarily to fit the data. They are not incompatible with the chemistry of these elements, in this type of compound. The agreement of these estimates of paramagnetism with the data in Table III is about as good as could be expected in view of the possibility of mixed oxidation states in some of the cations and the difficulty of working with dense microcrystalline powders. The high negative values of  $\theta$  may be ascribed to the possible increase in number of unpaired electrons by thermal promotion giving the  $1/\chi$  vs.  $T$  curve a smaller slope.

The failure to obtain this phase with the nickel(II) as the stabilizing cation may be due to the preferred formation of  $\text{BaNiO}_3$  which consists of a hexagonal close packed arrangement of  $\text{BaO}_3$  layers held together by nickel in face-shared octahedra. It seems likely that each nickel atom in this structure is bonded to two other nickel atoms along the  $c$ -axis of the crystal.<sup>14</sup>

Recently in this Laboratory we have encountered other examples of systems with structures resembling the hexagonal barium titanate structure which contain no titanium. These compounds seem to be of the type  $\text{Ba}(\text{Os}_{0.5}\text{M}_{0.5})\text{O}_3$  where M is a transition metal. These systems now are being studied.

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