V_2O_3. Corresponding lines have not been obtained.

The system $LaTiO_3$–$LaVO_3$ is now being studied to see whether solid solution can be effected between the tetragonal vanadium and the cubic titanium compounds.

The lattice constant–composition diagram for the titanium system given in Fig. 1 is taken as a linear relationship between the lattice constant and the amount of lanthanum substituted for strontium. The experimental points appear to lie somewhat above the straight line but the apparent deviation is within experimental error. The determination of the lattice constants for corresponding samples in the system $LaTiO_3$–$SrTiO_3$ gave points which conform more closely to the expected values represented by the dashed line in the diagram.

The strontium titanium oxide system represents the widest homogeneity range in the oxygen-deficient ternary oxides of the perovskite type since the cubic phase extends from $SrTiO_{2.5}$ to $SrTiO_3$. In all other cases, structural changes occur as the oxygen content is varied over a wide range.

The preliminary data obtained for the system $SrVO_{2.5}$–$SrVO_3$ indicate that the limit of the cubic phase is not far beyond $SrVO_{2.75}$. An oxygen deficient phase, SrV_2O_4, has been reported by Rudorff and Reuter[14] who express the formula as $(Sr_{0.66}V_{0.33})VO_{2.66}$ with part of the vanadium replacing strontium in the A-cation position. It was in the attempt to prepare a phase corresponding to this in the strontium–titanium(III) oxide system that we found the cubic $SrTiO_{2.5}$. With mixtures containing higher than equimolar proportions in titanium sesquioxide, the latter always was found in the product. In view of this finding, we intend to reexamine the strontium oxide–vanadium sesquioxide system.

Acknowledgment.—We are grateful to Dr. Lewis Katz for assistance in interpretation of the X-ray data and to Dr. W. C. Purdy for suggesting the analytical procedure for titanium(III), vanadium(III) and (IV).

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(14) W. Rudorff and B. Reuter, *Z. anorg. Chem.*, **253**, 177 (1947).

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

The Preparation of a Barium Cobalt Oxide and other Phases with Similar Structures[1,2]

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The preparation of anion deficient ternary oxides of barium and the transition metals iron, cobalt and nickel having the approximate formulas $BaFeO_{2.72}$, $BaCoO_{2.85}$ and $BaNiO_{2.5}$ is described. Single crystals of the cobalt compound grown from a potassium carbonate flux were found to contain a small amount of potassium but were structurally similar to the product obtained without a flux. The crystal structure was found to be similar to that of $BaNiO_3$ reported by Lander as determined from X-ray powder diffraction data. Some evidence was found for similar phases in ternary oxides of barium with manganese and vanadium. The suggestion is made that the adoption of this structure may depend upon the formation of metal–metal bonds. Phases of this type have not been obtained with strontium.

The existence of several phases in the barium–cobalt–oxygen system has been noted.[3] Among these, a phase of approximate composition $BaCoO_{2.72}$ was obtained at temperatures below 760°. The X-ray powder diffraction pattern of this product was interpreted on the basis of a cubic perovskite structure (a = 4.83 Å.). The barium–nickel–oxygen system also has been shown to yield several distinct phases.[4,5] The formula for the phase obtained at temperatures below 730° was $BaNiO_3$ and the compound was assigned a hexagonal unit cell (a = 5.58 Å., c = 4.832 Å.), determined on the basis of X-ray powder diffraction data.[6]

A marked similarity between the diffraction pattern of the cobalt and nickel compounds was noted and because of the difference in reported formulas, it seemed advisable to study the barium cobalt oxide in more detail. This paper describes the preparation and structure determination of the compound, and also points to some similar phases obtained with other transition metals of the 4th period.

Experimental

Barium cobalt oxide was prepared by heating finely ground, intimate mixtures of barium nitrate with either cobaltous carbonate or nitrate in air at 680° using a Leco boat as the container. The heating was for a period of 24 hours with occasional removal for grinding. The crystals were too small for single crystal X-ray analysis, but the powder pattern corresponded to the data given by Strauss.[4] By the method of Blattner, Matthias and Merz,[7] however, acicular crystals were grown using a 1:1 sodium carbonate–potassium carbonate flux. The samples that yielded single crystals were prepared by grinding and mixing the reactants together with an approximately equal amount of flux in an agate mortar. The reaction mixtures were placed in a furnace at room temperature, together with a control sample without flux. The temperature was raised to 400° over a period of two hours, then raised to 680 by 25° increments over a period of 12 hours, maintained at 680° for 24 hours, and cooled to 250° over a period of four days. The furnace was then turned off and allowed to cool to room temperature.

The product consisted of a mass of fine black needles imbedded in a crust composed of the flux. The crystals were washed quickly with water and dried at about 90°. In spite of the use of the flux, the crystals were small, the larg-

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(1) This work was supported by the Office of Naval Research. Reproduction in whole or in part is permitted for any purpose of the United States Government.

(2) Taken in part from the doctorate thesis submitted by Beatrice Gushee to The University of Connecticut, 1956.

(3) S. W. Strauss, I. Fankuchen and R. Ward, THIS JOURNAL, **73**, 5084 (1951).

(4) J. J. Lander, *ibid.*, **73**, 2450 (1951).

(5) J. J. Lander and L. A. Wooten, *ibid.*, **73**, 2452 (1951).

(6) J. J. Lander, *Acta Cryst.*, **4**, 148 (1951).

(7) H. Blattner, B. Matthias and W. Merz, *Helv. Phys. Acta*, **20**, 225 (1947)

est being about 0.05 mm. in diameter and 0.75 mm. in length.

The composition of the products was determined from the barium and cobalt analysis and from a determination of the average oxidation number of the cobalt. The barium was determined gravimetrically as the sulfate and the cobalt by the iodometric method of Laitinen and Burdett.[8] This method uses a peroxide oxidation to form a complex of cobalt(III) and then a reaction with iodide in acid solution to yield cobalt(II) and iodine. The iodine is then titrated with standard thiosulfate solution.

TABLE I

$BaCoO_{2.85}$, PREPARED AT 680° WITH FLUX

Hexagonal: $a = 5.59$ Å.; $c = 4.82$ Å.

$I_{obsd.}$	$d_{obsd.}$	$d_{calcd.}$	Plane	$I_{obsd.}$	$d_{obsd.}$	$d_{calcd.}$	Plane
w−	8.46 Å.		?			1.21	222
w	6.90		?			1.20	213
w−	5.59		?			1.20	004
w−−	4.87	4.83 Å.	100	m	1.17 Å.	1.17 Å.	401
s+	3.40	3.41	101			1.17	312
s+	2.80	2.79	110			1.17	104
w+	2.43	2.42	200	w−	1.13	1.14	303
m−	2.38	2.40	002	w	1.10	1.10	114
s	2.16	2.16	201	m−	1.08	1.08	321
		2.15	102			1.08	401
w+	1.82	1.83	210			1.08	204
		1.82	112	m−	1.06	1.05	410
m	1.71	1.71	211	w	1.03	1.03	411
		1.70	202			1.03	313
m−	1.62	1.61	300	w	1.01	1.01	322
w+	1.51	1.53	301			1.00	214
		1.52	103	w−	0.963	0.966	500
m	1.45	1.45	212			.966	412
m+	1.40	1.40	220			.964	403
w+	1.33	1.34	310			.963	304
		1.34	302	w−	.950	.947	501
		1.33	203	w	.940	.942	105
m	1.29	1.29	311	w+	.910	.911	323
m−	1.20	1.21	400			.909	224
				m−	.899	.897	421

To determine the average oxidation number of the cobalt an adaption of the method of Struthers[9] was used. As originally applied to the determination of iron, Fe(IV) is reduced to Fe(III) with excess hydrochloric acid. Hydrated ferric oxide precipitates in the reaction vessel. Chlorine, formed by the oxidation of the chloride ion, is led into a flask containing an excess of chilled potassium iodide solution, causing the liberation of an amount of iodine equivalent to the amount of Fe(IV) reduced to Fe(III). The iodine is then titrated with standard thiosulfate solution. The variation of this method used for Co(IV) and Ni(IV) was made possible by the fact that both Co(IV) and Ni(IV) are reduced by dilute hydrochloric acid to the divalent state, and, in this state, are soluble in dilute hydrochloric acid. This made possible the use of one ground-glass-stoppered round-bottomed flask for the entire reaction and the ensuing titration. Into the 250-ml. flask were pipetted 25 ml. of 0.4 *M* HCl and 25 ml. of 0.16 *M* KI solution, an excess in both cases. The sample (0.2 to 0.4 g.) was added and the flask and content warmed to about 60° until the sample dissolved. The flask was cooled and the contents titrated with standard thiosulfate solution. From four analyses of 2 different samples prepared without a flux, the following results were obtained. Average oxidation number of cobalt 3.69 ± 0.03; %Ba 55.7 ± 0.04; %Co 23.8 ± 0.52. The formula based on these data is taken as $BaCoO_{2.85}$. The analysis of the crystals prepared by use of the flux (four analyses of one sample) gave the average oxidation state of cobalt 3.75 ± 0.06; %Ba 46.7 ± 0.45; %Co 25.2 ± 0.85. Since the powder pattern of this material was the same as that of the product made without a flux, it is assumed that the low value obtained for the barium analysis is due to the replacement of part of the barium by potassium. This assumption gives the formula $Ba_{0.78}K_{0.22}CoO_{2.76}$ which corresponds to %Ba 49.0, %Co 25.8 and %K 3.9. The potassium was not determined quantitatively but its presence was established by qualitative test.

Zero and first level Weissenberg photographs about *c* were taken using Mo Kα radiation. The crystals are hexagonal ($a = 5.59 \pm 0.01$ Å., $c = 4.82 \pm 0.01$ Å.). The only systematic absences are *hhl* when *l* is odd. C_{6l} symmetry of both zero and first level photographs establish the Laue group as D_{6h}. Space group possibilities are therefore: $P6_3mc$, $P\bar{6}2c$, or $P6_3/mmc$.

Space group $P6_3/mmc$ proved satisfactory for the structure determination. Since twice the Ba^{+2} diameter is appreciably greater than 4.82 Å. (the length of *c*), the only possible twofold positions for barium in this space group are 2c and 2d. These differ only in choice of origin. Selecting 2c for barium: $^1/_3, ^2/_3, ^1/_4; ^2/_3, ^1/_3, ^3/_4$, cobalt would be expected from charge considerations, to be in 2a: 0, 0, 0; 0, 0, $^1/_2$. For this cation arrangement, the cobalt and barium contribution to the intensities of *hk*0 reflections would contain the factor $2f_{Co} + 2f_{Ba}$ if $h - k = 3n$ and $2f_{Co} - f_{Ba}$ if $h - k \neq 3n$. The intensities of reflections for which $h - k$ is a multiple of 3 are all strong and are indeed found to differ only as the angle-dependent part of the intensity expression. Since twice the atomic number of cobalt is nearly equal to the atomic number of barium, $2f_{Co} - f_{Ba}$ is nearly zero. Thus reflections for which $h - k$ is not a multiple of three could have only a slight contribution from the cations. The only reflection of this type to be observed was 200; this was so weak as to have been missed on a first inspection of the photographs.

For first level reflections, the Co contribution would always be zero, and barium would contribute only to reflections for which $h - k \neq 3n$. This contribution would always be the same function of the atomic scattering factor except for sign changes and therefore, apart from the contribution of oxygens, the *hkl* intensities should again change principally as a function of Bragg angle. The only first level reflections which are observed are those for which the Ba contribution is not zero, and the fall off in intensities is as expected Thus the observations confirm the postulated cation arrangement.

Although the intensities provide little evidence for the placement of oxygens, packing considerations would require that the oxygens and bariums be in an essentially close packed arrangement. This would at least approximate oxygens in 6*h* of $P6_3/mmc$ with the parameter $x = ^5/_6$: $^5/_6, ^2/_3, ^1/_4; ^1/_3, ^1/_6, ^1/_4; ^5/_6, ^1/_6, ^1/_4; ^1/_6, ^1/_3, ^1/_4; ^2/_3, ^5/_6, ^1/_4; ^1/_6, ^5/_6, ^3/_4$. The structure is then the same as that arrived at for $BaNiO_3$ from powder data.[10]

The density of samples prepared without flux was found to be 6.2 g./cm.^{3} which corresponds to 2 formula weights of $BaCoO_{2.85}$ per unit cell (theoretical density, 6.24 g./cm.^{3}).

Barium nickel oxide was obtained as a black crystalline product by heating mixtures of barium nitrate and nickel carbonate or nickel nitrate hexahydrate in air at 680°. X-Ray powder diffraction data and the density of these products confirmed those reported by Lander and Wooten[5,6] but chemical analysis gave contrary results. The percentage of nickel was determined by the method of Bickerdike and Willard[11] and the oxidation state of nickel by the method of Struthers.[9] The data obtained were: Ba, 55.6 ± 0.40%; Ni, 24.34%; oxidation state of nickel 2.96. These results give an approximate formula $BaNiO_{2.5}$ whereas Lander and Wooten report the stoichiometric formula $BaNiO_3$.

Barium iron oxide was obtained as a black sinter from the reaction between barium nitrate and ferric nitrate hexahydrate between 680 and 720°. Several determinations of the oxidation number of iron by the method of Struthers[9] led to an average value of 3.48 ± 0.01. Assuming a one to one barium to iron ratio, the formula would be $BaFeO_{2.74}$. The powder pattern obtained from this product resembles somewhat that of the $Ba_3Fe_8O_{21}$ reported by Erchak, Fankuchen and Ward,[12] but is sufficiently different to make one doubt that the two products are identical. The $BaFeO_{2.74}$ powder pattern appears to be indexed best with a hexagonal cell for which $a = 5.76$ Å. and $c = 13.9$ Å. These cell parameters are not unlike those reported by Malinofsky

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[8] H. A. Laitenen and L. W. Burdett, *Anal. Chem.*, **23**, 1268 (1951).

[9] R. Ward and J. D. Struthers, THIS JOURNAL, **59**, 1849 (1937).

[10] The drawing in Lander's paper would apply equally well to the barium cobalt oxide under discussion. However, the listed positions for barium, or oxygen, in Lander's paper are not consistent with his drawing.

[11] E. L. Bickerdike and H. H. Willard, *Ind. Eng. Chem., Anal. Ed.*, **24**, 6, 1026 (1952).

[12] M. Erchak, Jr., I. Fankuchen and R. Ward, THIS JOURNAL, **68**, 2085 (1946).

and Kedesdy[13] for a barium iron oxide (a = 5.68 Å., c = 13.86 Å.).

Barium manganese oxide was prepared by the reaction of barium carbonate with an 80% manganous nitrate solution. The most nearly homogeneous preparations were black powders prepared at 900 and 1000° in air. These products had nearly identical X-ray powder patterns which were indexed on the basis of a hexagonal unit cell, Table II, with a = 5.7 Å. and c = 4.8 Å., close to the cell sizes of the cobalt and nickel phases obtained at about 700°. Chemical analyses of the manganese phases have not been made.

TABLE II

BARIUM MANGANESE OXIDE PREPARED AT 900°

Hexagonal: $a \doteq 5.7$ Å.; $c \doteq 4.8$ Å.

$I_{\text{obsd.}}$	$d_{\text{obsd.}}$	$d_{\text{calcd.}}$	Plane
m	3.45 Å.	3.45	101
s	2.86	2.86	110
		2.47	200
w	2.41	2.40	002
s	2.20	2.22	201
w	2.17	2.15	102
w–	1.84	1.87	210
		1.84	112
s–	1.73	1.74	211
		1.72	202
m	1.64	1.65	300
m	1.53	1.55	301
		1.52	103
m–	1.48	1.48	212
m	1.43	1.43	220
w–	1.35	1.37	310
		1.36	302
		1.34	203
m–	1.32	1.32	311
w–	1.22	1.24	400
		1.23	222
		1.22	213
w	1.19	1.20	004
		1.20	401
		1.19	312
w	1.10	1.10	402
		1.11	114
		1.10	321
m–	1.08	1.08	204
		1.08	410

Barium vanadium oxide was not obtained in a form pure enough for chemical analysis. The most nearly homogeneous product resulted from heating a thoroughly ground mixture of barium nitrate and vanadium sesquioxide in hydrogen at 1000° for 30 hours. This was a black crystalline material containing some white flecks. The prominent lines of the X-ray powder photograph formed a pattern quite similar to those of the barium nickel oxide, barium cobalt oxide and barium manganese oxide. By analogy, the cell constants would be about a = 5.8 Å. or a multiple of 5.8 Å. and c = 4.9 Å. or a multiple of 4.9 Å.

Discussion

It has been pointed out by Lander[6] that the hexagonal structure of the barium nickel oxide may be related to the cubic perovskite structure by regarding these structures as being built up from the close packed layers of barium and oxide ions which are stacked in hexagonal close packing in the first and in cubic close packing in the second. The major difference lies in the consequent association of the NiO_6 octahedra which share faces in the hexagonal structure and corners in the cubic structure. The confirmation of this arrangement by the use of single crystals of the barium cobalt oxide is interesting in view of the oxygen deficiency of this phase. The analytical data on the barium nickel oxide reported here are at variance with those given by Lander and Wooten.[5] According to our data, the phase $BaNiO_{2.5}$ prepared at 680° has the same structure as the phase $BaNiO_3$ prepared by Lander and Wooten[5,6] who report a different structure for the phase $BaNiO_{2.5}$ prepared at 1000°. In these crystals, the interatomic distance of the transition metal atoms (Ni–Ni distance 2.42 Å., Co–Co 2.39 Å.) is near the distance of closest approach in the metals which suggests the possibility of metal–metal bonds. This may be indeed a requirement for the adoption of this structure.

It is perhaps significant that this structure has been found only in compounds involving a transition metal in an oxidation state below its maximum. The structure assigned to the hexagonal form of $BaTiO_3$[14] shows two thirds of the TiO_6 octahedra sharing faces with Ti–Ti distance 2.67 Å. It is remarkable that this phase has only been prepared using a mixture of barium carbonate and titanium dioxide and a barium chloride flux in a platinum container and that the single crystals used in the study were not white. It is conceivable that some reduction of the titanium is necessary or that some platinum may have been present in the crystals.

Attempts to prepare similar phases with strontium as the A cation and any of the 4th period transition metals as the B cation have not been successful.

In summary it should be emphasized that the stoichiometry of crystals of this type of compound may be an important factor in determining the atomic arrangement. There are major difficulties in obtaining pure and homogeneous products which are worthy of chemical analysis. It may be possible that these phases could be obtained as stoichiometric ABO_3 compounds, but our results appear to indicate that they are more easily obtained with an oxygen deficiency.

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(13) W. W. Malinofsky and H. Kedesdy, THIS JOURNAL, **76**, 3090 (1954).

(14) R. O. Burbank and H. T. Evans, *Acta Cryst.*, **1**, 330 (1948).