

thermal activation energies of reactions 1, 6 and 7 can be assumed to be very small or zero.

Geib and Steacie<sup>16</sup> report a lower limit of about 6 kcal./mole for reaction 4 obtained from measurements of the rate of exchange of D-atoms with water vapor in a flow system at vapor pressures of 0.05 mm. These authors attribute part of the exchange yield at this low pressure to wall reaction and estimate a more probable higher value (10.5 to 12 kcal.) for the homogeneous reaction. Farkas and Melville<sup>18</sup> obtained an apparent activation energy of 7 kcal./mole for reaction 4 from measurements of the mercury-sensitized exchange between deuterium and water vapor exposed to 2537 Å. light. Water vapor pressures were limited to 11–12 mm. Their value is probably low, because, as they suggest, their water may have been decomposed by excited mercury atoms. Both cited investigations suggest that the activation energy for the homogeneous exchange of D-atoms with water must be greater than 7 kcal./mole and at least as great as 12 kcal./mole. It is, therefore, reasonable and consistent to assign the apparent activation energy of  $18 \pm 1$  kcal./mole to reaction 4. The large pressures of water vapor employed in this work give strong support to the conclusion that reaction 4 is homogeneous.

Chain termination appears to be predominantly first order. Absence of a change in yield with five-fold variation in dosage rate in the chain region (samples 11, 12, 13, 14) indicates that reaction 7 cannot play a major role.

It is interesting to compare the value obtained in this work for  $G(-H_2O)$  in water vapor ( $11.7 \pm 0.6$  molecules/100 e.v.) with Hart's value of 3.8, measured in liquid tritium-water using formic acid and oxygen as free radical scavengers.<sup>20</sup> One may conclude from this comparison that about 70% of those water molecules which dissociate in the vapor would fail to do so in the liquid, or, that having dissociated, the resulting intermediates merely react to re-form water. In the gas phase one would expect reaction of the intermediates with an efficient scavenger to be favored over recombination, as indicated by the results of this investigation.

**Acknowledgment.**—The author is indebted to Dr. E. J. Hart for suggesting this work and to both Dr. Hart and Dr. S. Gordon for much helpful discussion. He is also grateful to L. Pobo and H. Rest for the mass spectrometer analyses and to Mrs. Lorraine Rolih for performing the tritium-water assays.

(20) E. J. Hart, *J. Phys. Chem.*, **56**, 594 (1952).  
LEMONT, ILL.

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

## Ion-deficient Phases in Titanium and Vanadium Compounds of the Perovskite Type<sup>1,2</sup>

BY MICHAEL KESTIGIAN, JOHN G. DICKINSON AND ROLAND WARD

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Cation deficiency, represented by  $M_{1-x}BO_3$ , has been observed in lanthanum vanadium oxide. Anion deficiency, represented by  $MBO_{3-x}$ , has been investigated in strontium titanium oxide, lanthanum titanium oxide, lanthanum zirconium oxide, lanthanum vanadium oxide and strontium vanadium oxide.

Departures from stoichiometry in compounds with the perovskite structure have been demonstrated in many instances. Cation deficiency, represented by  $M_{1-x}BO_3$ , appears to have the widest range in the sodium tungsten bronzes, where  $x$  may vary from 0.05 to 0.7.<sup>3</sup> The range narrows considerably in the strontium niobium oxide to 0.05 to 0.3,<sup>4</sup> and in the lanthanum titanium oxide to 0 to 0.3.<sup>5</sup> Part of the work described here is an extension of this phenomenon to lanthanum vanadium oxide.

Anion deficiency, represented by  $MBO_{3-x}$ , has been reported for several compounds with structures closely related to the perovskite type. In barium iron oxide,  $x$  is about 0.28<sup>6</sup> while for barium cobalt oxide three phases were reported with values of  $x = 0.28, 0.69$  and  $0.77$ .<sup>7</sup> Other oxygen deficient

phases such as  $SrFeO_{3-x}$ ,<sup>8-10</sup>  $BaNiO_{2.75}$  and  $BaNiO_2$ <sup>11</sup> also have been described. All of these phases were produced by heating under oxidizing conditions at various temperatures and there was no strict control over the composition of the final phase. With similar systems involving titanium and vanadium, however, precise control of the composition of mixtures is possible because of the availability of thermally stable higher oxides of these elements. This paper describes some oxygen deficient phases of titanium and vanadium.

### Experimental

The general technique used for the preparation of samples was to mix intimately finely divided powders of the reactants by grinding in an agate mortar. The samples were pelleted in a hydraulic press and placed in clear silica glass tubes which were sealed under vacuum at elevated temperatures. The sample was heated at an appropriate temperature for a specified period (usually about 24 hours). The sample was then reground and the process repeated until a homogeneous product was obtained. Because of the inevitable losses on handling and the tendency of strontium oxide to volatilize under conditions used, the composition of the final products was checked by chemical analysis. X-Ray diffraction pow-

(1) This research 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) The part of this work dealing with vanadium was abstracted from the Master's Thesis of John G. Dickinson, University of Connecticut, 1957.

(3) Hübregtse, Barker and Danielson, *Phys. Rev.*, **82**, 770 (1951).

(4) D. Ridgley and R. Ward, *THIS JOURNAL*, **77**, 6132 (1955).

(5) M. Kestigian and R. Ward, *ibid.*, **77**, 6199 (1955).

(6) M. Erchak, Jr., I. Fankuchen and R. Ward, *ibid.*, **68**, 2085 (1946).

(7) S. W. Strauss, I. Fankuchen and R. Ward, *ibid.*, **73**, 5084 (1951).

(8) G. H. Jonker, *Physica*, **20**, 1118 (1954).

(9) H. L. Yakel, *Acta Cryst.*, **3**, 394 (1955).

(10) C. Brisi, *Ricerca Sci.*, **24**, 1858 (1954).

(11) J. J. Lander and L. A. Wooten, *THIS JOURNAL*, **73**, 2452 (1951); J. J. Lander, *Acta Cryst.*, **4**, 148 (1951).

der photographs were taken for all of the products using a Philips X-ray diffraction unit with copper  $K\alpha$  radiation ( $\lambda$  1.5418 Å.) using a Philips camera of radius 57.3 mm. Exposure times were 10 hours.

**Preparation of  $\text{SrTiO}_{2.5}$ .**—Strontium oxide and titanium sesquioxide, prepared by methods previously described<sup>4,5</sup> were heated at 1200° for 24 hours. Mixtures with Sr/Ti = 1 gave a blue-violet product which appeared homogeneous under the microscope and gave an X-ray pattern corresponding to the cubic perovskite structure. No extraneous lines were observed. The lattice constant ( $3.902 \pm 0.002$  Å.) is identical with that of  $\text{SrTiO}_3$ . The density was found to be 4.77 g./ccm. compared with the calculated density 4.90 g./ccm. The analytical data are listed in Table I. Thus it appears likely that  $\text{SrTiO}_{2.5}$  can be described as having the cubic perovskite structure with one sixth of the oxygen positions vacant.

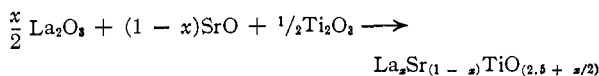
TABLE I

COMPOSITIONS AND LATTICE CONSTANTS OF SYSTEM  $\text{SrTiO}_{2.5}$ - $\text{LaTiO}_3$ 

Compn. of phase	% La	% Sr	% Ti(III)	$a_0^a$ (Å.)
$\text{SrTiO}_{2.5}$		48.5 (49.9)	26.7 (27.3)	3.902
$\text{La}_{0.25}\text{Sr}_{0.75}\text{TiO}_{2.5}$	18.2 (18.2)	35.5 (34.5)	25.7 (25.2)	3.912
$\text{La}_{0.50}\text{Sr}_{0.50}\text{TiO}_{2.5}$	33.5 (33.9)	20.9 (21.4)	23.5 (23.4)	3.917
$\text{La}_{0.75}\text{Sr}_{0.25}\text{TiO}_{2.5}$	47.1 (47.3)	9.8 (10.0)	21.0 (21.8)	3.923
$\text{LaTiO}_3$	59.0 (59.2)		19.9 (20.4)	3.926

<sup>a</sup> Lattice constants determined to  $\pm 0.002$  Å. Numbers in parentheses correspond to starting compositions of phases.

**The System  $\text{SrTiO}_{2.5}$ - $\text{LaTiO}_3$ .**—Mixtures of the component oxides were prepared in proportions indicated by the equation



Three mixtures ( $x = 0.25, 0.50$  and  $0.75$ ) were heated for two 24-hour periods at 1260°. The products appeared homogeneous by microscopic examination and gave X-ray powder patterns corresponding to the cubic perovskite. There were no extraneous lines in the patterns. The analyses and lattice constants of the products are given in Table I. The precision of the lattice constant ( $a_0$ ) determinations was  $\pm 0.002$  Å. In the chemical analyses, lanthanum was determined gravimetrically as the oxide, strontium by titration with ethylenediaminetetraacetic acid, and the titanium by the formation of  $\text{TiF}_6^{3-}$  and titration with permanganate in presence of boric acid. The precision of the analytical procedures was about  $\pm 0.31\%$  for La,  $\pm 0.6\%$  for high strontium products to  $\pm 3.6\%$  for the lowest strontium products and about  $\pm 2\%$  for Ti (III). The plot of  $a_0$  vs.  $x$  given in Fig. 1 indicates a Vegard's law dependence within experimental error.

The system  $\text{SrTiO}_{2.5}$ - $\text{SrTiO}_3$  was studied to see if any appreciable changes in lattice parameters occurred as the vacant anion sites were filled. The mixtures were prepared from appropriate amounts of  $\text{TiO}_2$ ,  $\text{Ti}_2\text{O}_3$  and SrO according to the general formula  $\text{SrTi}_{(1-x)}^{(III)}\text{Ti}_x^{(IV)}\text{O}_{(2.5+x/2)}$ . The values of  $x$  as determined by analyses of the final product were approximately 0.25, 0.50 and 0.75. No variations in lattice constant were found nor did any of the X-ray diffraction patterns contain additional lines.

It was hoped that a ternary oxide containing zirconium in an oxidation state lower than plus four could be prepared. Two methods of approach to the problem were attempted. The first of these methods involved experiments that were performed in trying to prepare a lower oxide of zirconium which was to be used as a starting material while in the second method of preparation, reducing conditions were used that would favor ternary oxide formation involving zirconium in a lower oxidation state.

It had been reported by Weiss and Neumann<sup>12</sup> that zirconium sesquioxide could be prepared by the combustion of zirconium hydride in insufficient oxygen. These results have not been duplicated by other investigators.

In an attempt to prepare a lower oxide of zirconium, zirconium metal, zirconium hydride, lanthanum metal and dry hydrogen gas were used in an attempt to reduce zirco-

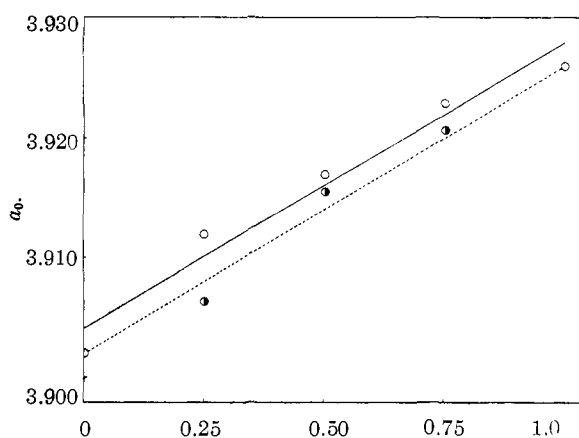
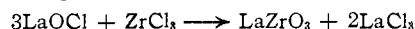


Fig. 1.—○,  $\text{La}_x\text{Sr}_{(1-x)}\text{TiO}_{(2.5+x/2)}$ ; ●,  $\text{La}_x\text{Sr}_{(1-x)}\text{Ti}_{(x)}^{\text{III}}\text{Ti}_{(1-x)}^{\text{IV}}\text{O}_3$ .

nium dioxide. X-Ray powder diffraction photographs of these products showed only lines corresponding to zirconium dioxide and zirconium metal.

The ternary system that was investigated was the lanthanum-zirconium-oxygen system. It was found that mixtures of lanthanum oxide and zirconium dioxide, when heated with lanthanum or zirconium metals or with lanthanum hydride always gave the face centered cubic  $\text{La}_2\text{Zr}_2\text{O}_7$ . Attempts to bring about the reaction



in fused lanthanum chloride also were fruitless.

**Preparation of  $\text{SrVO}_{2.5}$ .**—Vanadium sesquioxide was prepared by heating the pentoxide in hydrogen at 800° for 14 hours. Mixtures of this with strontium oxide corresponding to the ratio Sr/V = 1 gave a deep blue homogeneous product on heating for 24 hours at 1100°. All of the lines in the X-ray powder diffraction pattern of this product could be indexed on the basis of a cubic cell  $a_0 = 3.848 \pm 0.005$  Å. as shown in Table II.

TABLE II

OBSERVED AND CALCULATED INTERPLANAR SPACINGS AND INTENSITIES FOR PRODUCT  $\text{SrVO}_{2.5}$ 

$hkl$	$d/n(\text{obsd.})$	$d/n(\text{calcd.})$	$I(\text{obsd.})$	$I(\text{calcd.})$
100	3.864	3.845	W+	3
110	2.719	2.719	S	100
111	2.220	2.220	M	16
200	1.924	1.922	M+	38
210	1.721	1.720	W+	3
211	1.572	1.567	M+	58
220	1.360	1.359	M	21
300, 221	1.284	1.282	W	2
310	1.217	1.216	M	17
311	1.160	1.159	W+	6
222	1.110	1.110	W+	7
320	1.064	1.064	W--	1
321	1.028	1.028	M	23
400	0.9609	0.9611	W	4
410, 322	.9330	.9325	W-	3
411, 330	.9062	.9062	M+	30
331	.8825	.8820	W-	2
420	.8597	.8597	M	19
421	.8390	.8390	W-	3
332	.8198	.8197	M	16
422	.7848	.7848	M+	43

**$\text{LaVO}_3$ .**—Equimolar mixtures of  $\text{La}_2\text{O}_3$  and  $\text{V}_2\text{O}_5$  when heated at 1200° for two 24-hour periods gave a black homogeneous product. The X-ray powder diffraction pattern of this product, indexed on the basis of a tetragonal cell ( $a_0 = 5.546 \pm 0.005$  Å.,  $c_0 = 7.827 \pm 0.005$  Å.), is given in Table III.

(12) L. Weiss and E. Neumann, *Z. anorg. Chem.*, **65**, 2481 (1910).

TABLE III

OBSERVED AND CALCULATED INTERPLANAR SPACINGS AND INTENSITIES FOR PRODUCT  $\text{LaVO}_3$ 

<i>hkl</i>	<i>d</i> / <i>n</i> <sub>(obsd.)</sub>	<i>d</i> / <i>n</i> <sub>(calcd.)</sub>	<i>I</i> <sub>(obsd.)</sub>	<i>I</i> <sub>(calcd.)</sub> <sup>a</sup>
110	3.919	3.919	M	18.1
111	3.515	3.504	W	0
200	2.771	2.771	S	100
201	2.613	2.612	W	0
211	2.362	2.364	W	0
202	2.263	2.261	M	27.2
113	2.175	2.171	W---	0
220	1.960	1.960	M+	36.2
221	1.903	1.901	W	0
310	1.751	1.752	W+	9.3
311	1.710	1.710	W	0
312	1.600	1.599	M+	39.5
313	1.456	1.455	W-	0
400	1.388	1.386	M	21.4
401	1.364	1.364	W--	0
330	1.307	1.307	W	5.45
331	1.289	1.289	W--	0
420	1.248	1.248	M	17.0
421	1.225	1.224	W	0
422	1.182	1.181	W+	8.72
333	1.169	1.168	W-	0
404	1.132	1.131	W	6.74
424	1.047	1.048	M	20.4
513	1.004	1.004	W--	0
440	0.9805	0.9805	W-	3.73
441	.9728	.9728	W-	0
514	.9508	.9507	W-	4.46
531	.9443	.9442	W-	0
600	.9242	.9243	M-	14.1
602	.8995	.8996	W--	0
533	.8937	.8937	W--	0
620	.8768	.8768	M-	0
621	.8715	.8714	W	0
534	.8553	.8555	M-	16.3
604	.8359	.8358	W	0
623	.8311	.8312	M-	13.2
535	.8128	.8128	W	0
624	.8005	.8003	M	27.4
605	.7958	.7960	W--	0
710, 550	.7843	.7844	W-	8.80
711, 551	.7804	.7805	M-	0

<sup>a</sup> Calculated intensities based on idealized perovskite type structure.

The System  $\text{SrVO}_{2.5}$ - $\text{LaVO}_3$ .—Mixtures of strontium and lanthanum oxide and vanadium sesquioxide corresponding to  $\text{Sr}_{(1-x)}\text{La}_x\text{VO}_{(2.5+x/2)}$  were made where *x* was 0.2, 0.5 and 0.8. After heating for two 24 hour periods at 1150°, none of the products appeared to be homogeneous upon X-ray analysis. The addition of a small amount of strontium oxide and an additional heating gave homogeneous products with the two mixtures having the higher proportions of lanthanum. The X-ray powder diffraction patterns of these products also could be indexed on the bases of tetragonal cells. The lattice constants and analytical data for the pure phases obtained in this system are given in Table IV.

The mixture containing the least lanthanum could not be made to yield a pure product by prolonged heating or by the addition of excess strontium oxide. The lines in the diffraction patterns corresponding to the cubic phase showed a definite shift indicating an increase in lattice constant but additional lines which could not be indexed appeared in all the patterns. The intensities of these lines increased with mixtures in which *x* was 0.3 and 0.33 indicating the appearance of a new phase. The analyses of the product obtained with a mixture corresponding to *x* equal 0.2 were 41.68% Sr, 8.98% La, 27.38% V(III) indicating a final composition

TABLE IV

COMPOSITIONS AND LATTICE CONSTANTS OF SYSTEM  $\text{SrVO}_{2.5}$ - $\text{LaVO}_3$ 

	$\text{LaVO}_3$			
	$\text{SrVO}_{2.5}$	$\text{Sr}_{0.55}\text{La}_{0.45}\text{VO}_{2.71}$	$\text{Sr}_{0.35}\text{La}_{0.65}\text{VO}_{2.80}$	$\text{LaVO}_3$
Sr, %	48.8 (49.1)	25.4 (25.5)	8.0 (7.8)	
La, %		28.1 (28.1)	49.9 (49.2)	57.6 (58.4)
V (III), %	28.6 (28.6)	25.0 (25.1)	22.7 (22.5)	21.0 (21.4)
<i>a</i> <sub>0</sub> <sup>a</sup>	3.848	5.477	5.520	5.546
<i>c</i> <sub>0</sub> <sup>a</sup>		7.767	7.852	7.827

<sup>a</sup> Lattice constants determined to  $\pm 0.005$  Å. Numbers in parentheses correspond to theoretical compositions of phases.

$\text{Sr}_{0.88}\text{La}_{0.12}\text{VO}_{2.56}$ . These data are interpreted as an indication that the extent of solid solution of lanthanum in the cubic phase is less than 12 mole %.

The System  $\text{SrVO}_{2.5}$ - $\text{SrVO}_3$ .—By using appropriate mixtures of strontium oxide with vanadium sesquioxide and vanadium pentoxide or vanadium dioxide, homogeneous products were obtained from  $\text{SrV}^{(III)}\text{O}_{2.5}$  to  $\text{SrV}^{(III)}\text{V}^{(IV)}\text{O}_{2.75}$ . These phases give precisely the same diffraction pattern with no change in the lattice constant. Mixtures with higher vanadium(IV) content, however, give rise to products which appear heterogeneous under the microscope.

Cation Deficiency in Lanthanum Vanadium Oxide.—Mixtures of lanthanum oxide with vanadium sesquioxide and pentoxide were prepared to correspond to the formula  $\text{La}_{(2-x)}\text{V}_{(3-2x)}\text{O}_3$  where *x* was 0.23, 0.18, 0.13 and 0. Upon heating these mixtures at 1200° for two 24-hour periods, the product with the highest lanthanum content gave a diffraction pattern corresponding to the tetragonal cell (*a*<sub>0</sub> = 5.499 ± 0.005 Å.) while those with lower lanthanum content gave complex patterns which included the lines of the tetragonal phase. The latter decreased in intensity with decreasing lanthanum content but did not indicate any further change in lattice dimensions. The pure phase was analyzed for lanthanum and vanadium(III) and vanadium(IV). The procedure followed for the vanadium analyses depended on dissolving the sample in an HF-H<sub>2</sub>SO<sub>4</sub> mixture, with subsequent titration with permanganate. Another sample was dissolved in the same way but was titrated after reduction in a Jones reductor. The analyses gave 54.0% La, 6.6% V(IV), 15.4% V(III). Calculated for  $\text{La}_{0.9}\text{V}_{0.66}\text{V}_{0.34}\text{O}_3$ , 55.8% La, 7.1% V(IV), 15.7% V(III). This appears to represent the limiting composition of the tetragonal phase.

### Discussion

The systems  $\text{SrVO}_{2.5}$ - $\text{LaVO}_3$  and  $\text{SrTiO}_{2.5}$ - $\text{LaTiO}_3$  present some interesting differences. In the titanium system, both end constituents are cubic and no discontinuities in the structure occur over the entire range of composition. With the vanadium system, on the other hand,  $\text{SrVO}_{2.5}$  is cubic while  $\text{LaVO}_3$  is tetragonal. The tetragonal structure persists over 60% of the range from  $\text{LaVO}_3$  but the cubic structure apparently can accommodate only a small proportion of lanthanum. This discontinuity in the vanadium system and absence of a discontinuity in the titanium system lend some support to the suggestion of Geller and Bala<sup>15</sup> that transitions do not occur directly from the orthorhombic structures to the cubic perovskite (It is quite possible that  $\text{LaVO}_3$  is really orthorhombic although the diffraction patterns obtained in this study could be indexed satisfactorily as tetragonal.) The additional lines in the diffraction patterns of the products obtained on the low lanthanum side of the diagram correspond to spacings 3.08, 2.80, 2.08, 1.849 and 1.668. Attempts to prepare a lanthanum-rich phase which might correspond to this impurity have been made by heating mixtures such as  $2\text{La}_2\text{O}_3 + \text{V}_2\text{O}_5$ ,  $3\text{La}_2\text{O}_3 +$

(13) S. Geller and V. B. Bala, *Acta Cryst.*, **9**, 1019 (1956).

$V_2O_3$ . 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  $SrVO_{2.76}$ . An oxygen deficient phase,  $SrV_2O_4$ , has been reported by Rudorff and Reuter<sup>14</sup> 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 re-examine 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).

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

STORRS, CONNECTICUT

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

## The Preparation of a Barium Cobalt Oxide and other Phases with Similar Structures<sup>1,2</sup>

BY BEATRICE E. GUSHEE, LEWIS KATZ AND ROLAND WARD

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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.<sup>3</sup> 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 ( $a = 4.83 \text{ \AA}$ ). The barium-nickel-oxygen system also has been shown to yield several distinct phases.<sup>4,5</sup> The formula for the phase obtained at temperatures below 730° was  $BaNiO_3$  and the compound was assigned a hexagonal unit cell ( $a = 5.58 \text{ \AA}$ ,  $c = 4.832 \text{ \AA}$ ), determined on the basis of X-ray powder diffraction data.<sup>6</sup>

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 prep-

aration 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.<sup>4</sup> By the method of Blattner, Matthias and Merz,<sup>7</sup> 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 large-

(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.

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