

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF CONNECTICUT, STORRS, CONNECTICUT**The Modification of Structures of Ternary Oxides by Cation Substitution.****II. Substitution of Various Cations for Ruthenium in Barium Ruthenium Oxide**

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Several systems represented by the formula BaRu_{1-x}M_xO₃ were studied to find some correlation between the nature of the substituent M and the crystal structure. The incidence of hexagonal close packing in the BaO₃ layers has been attributed to metal-metal interaction leading to the face sharing of oxygen octahedra. When M = Ir or Mn, the structure remains essentially that of the nine-layer type characteristic of BaRuO₃. The substitution is apparently random at all compositions. When M = Ni, oxidation of ruthenium occurs to give Ba₃Ru₂NiO₉ with the hexagonal barium titanate structure in which the ruthenium atoms are found in the face-sharing octahedra. The ruthenium appears to be in the pentavalent state. An isostructural compound Ba₃Ru₂MgO₉ is also described. No evidence for the substitution of nickel in the nine-layer structure or for the substitution of ruthenium in the Ba₃Ni₂O₉ structure was found. Zirconium could not be introduced into the nine-layer structure, but substantial substitution of ruthenium for zirconium occurred in the perovskite-type phase causing distortion from the cubic structure of BaZrO₃.

Introduction

The structures of AMO₃ compounds have been shown to be sensitive not only to the size of the A and M cations but also to the nature of the M cation. Partial substitution for Ti in BaTiO₃ by a variety of transition metals produced many phases with the hexagonal barium titanate structure.¹ Iridium and ruthenium were among the substituent atoms which were effective in this way. It seemed that the proportion most favorable to the hexagonal BaTiO₃ structure was 1/3 Ir or Ru to 2/3 Ti.

This paper is concerned with the substitution represented by the formula BaRu_{1-x}M_xO₃. In the choice of M cations first consideration was given to tetravalent transition metal cations with and without d electrons. Another consideration was that the compound BaMO₃ should have a structure based on the close packing of BaO₃ layers. Zirconium(IV), manganese(IV), and nickel(IV) furnished suitable examples. Titanium(IV) is not considered here. In the previous work in which iridium was substituted for titanium in the hexagonal BaTiO₃ structure,¹ no phases other than the perovskite-type BaTiO₃, the hexagonal BaTiO₃ type, and the BaIrO₃ type were observed. One might assume similar behavior for ruthenium with titanium. (BaTi_{2/3}Ru_{1/3}O₃ has been shown to have the hexagonal BaTiO₃ structure.¹) The structures of BaRuO₃² and BaIrO₃³ are closely related, and it was found at the outset that iridium could be substituted completely for ruthenium. The superlattice lines in the diffraction patterns are absent in the products in which $x \geq 0.5$. As might be expected, the structure remains essentially the nine-layer type characteristic of BaRuO₃ over the entire range of composition. The other M cations chosen, however, would seem to require a change in structure with increasing values of x .

BaZrO₃ has the perovskite structure; BaMnO₃ in its

high-temperature form, according to Hardy,⁴ has a four-layer structure, while the usual modification is the two-layer BaNiO₃ structure.^{4,5} BaNiO₃ changes readily upon heating above 800° to Ba₃Ni₂O₉ according to Lander.⁶ There is some question about the oxidation state of nickel in the compound obtained at lower temperature. Substitution of manganese for ruthenium was previously reported.² A more detailed study is described here.

Experimental Section

The reagents used were CP or reagent grade for all the preparations.

(1) **The System BaRu_{1-x}Zr_xO₃.**—Mixtures of barium peroxide, zirconium dioxide, and finely powdered ruthenium metal were heated at temperatures from 1000 to 1200°. At $x = 1/3$, the X-ray powder diffraction pattern of the product showed the presence of BaRuO₃ and a perovskite-like phase. The lattice parameters of the nine-layer structure did not differ noticeably from those of pure BaRuO₃ indicating that little or no zirconium is taken up. With $x \geq 1/2$, only the perovskite-type phase appeared in the products. Line splitting in the diffraction patterns indicated some distortion from the cubic structure of BaZrO₃, but the nature of the distortion was not determined.

(2) **The System BaRu_{1-x}Mn_xO₃.**—Barium carbonate or barium peroxide when heated at 1000 to 1100° with mixtures of manganese dioxide and ruthenium powder gave products with a nine-layer structure like that of BaRuO₃. At 1100°, the product of a mixture corresponding to $x = 0.75$ gave a phase with the nine-layer structure, but additional lines in the diffraction pattern indicated the presence of another phase. This seemed at first to indicate an upper limit to the solubility of manganese(IV) as was previously suggested.² The product appeared to have melted, and the diffraction pattern was rather poor. Further preparations made at 1000°, however, gave a single sharp pattern characteristic of the nine-layer structure. This structure was found consistently in preparations where x was as high as 0.95.

The unit cell dimensions of all products were measured and were found to decrease with increasing manganese content as shown in Figure 1. The decrease of both the a and c axes is essentially linear from $x = 0$ to $x = 2/3$. Thereafter, there is

(1) J. G. Dickinson, L. Katz, and R. Ward, *J. Am. Chem. Soc.*, **83**, 3026 (1961).

(2) P. C. Donohue, L. Katz, and R. Ward, *Inorg. Chem.*, **4**, 306 (1965).

(3) See preceding paper.

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

(5) B. E. Gushue, L. Katz, and R. Ward, *J. Am. Chem. Soc.*, **79**, 5601 (1957).

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

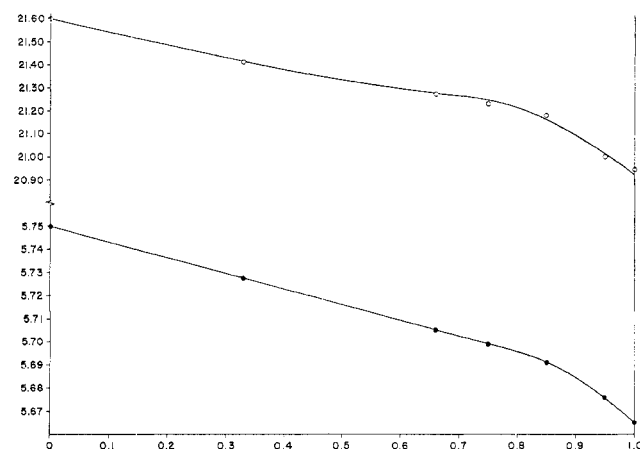


Figure 1.—Cell dimensions vs. composition for $\text{BaRu}_{1-x}\text{Mn}_x\text{O}_3$. Open circles are for the c axis; dots are for the a axis.

a sharper drop. It will be noted that the figure gives values for the a and c axes of BaMnO_3 . These values were obtained from a product of a reaction between barium peroxide and manganese dioxide at 1000° . This product was found to be in the form of acicular crystals instead of the usual microcrystalline powder. The needlelike crystals appeared to have a fibrous character and did not give a good single crystal diffraction pattern. The sample when powdered, however, gave a diffraction pattern which was entirely that of the nine-layer structure. Efforts to repeat this preparation proved futile in spite of many attempts to simulate the original conditions.

To determine whether there was any site preference for the manganese in the nine-layer structure, intensity calculations were carried out for the compositions $\text{BaRu}_{2/3}\text{Mn}_{1/3}\text{O}_3$ and $\text{BaRu}_{1/3}\text{Mn}_{2/3}\text{O}_3$. The atoms in proportion $2/3$ were placed in the outer face-shared octahedra and the atoms in proportion $1/3$ in the central position, i.e., sites 6c and 3b, respectively, of space group $R\bar{3}m$.² Intensities corresponding to completely random distribution of ruthenium and manganese in these sites were also calculated. The observed intensities were estimated by cutting out and weighing tracings of the diffractometer peaks. The results are given in Tables I and II along with the R factors based on intensities. The results clearly show that Mn(IV) substitutes completely randomly for Ru(IV) .

TABLE I

COMPARISON OF OBSERVED AND CALCULATED X-RAY INTENSITIES FOR ORDERED AND RANDOM MODELS FOR $\text{BaRu}_{2/3}\text{Mn}_{1/3}\text{O}_3$. $\text{Cu K}\alpha$ RADIATION. CALCULATED INTENSITIES ARE CORRECTED FOR LORENTZ AND POLARIZATION EFFECTS

H	K	L	IOBS	ORDERED ICAL	RANDOM ICAL	H	K	L	IOBS	ORDERED ICAL	RANDOM ICAL
1	0	1	6.5	2.6	2.5	0	2	10	13.7	8.9	9.7
1	0	4	17.2	8.5	18.7	2	1	7	7.1	7.1	8.0
0	1	5	55.7	71.9	54.0	1	0	13	2.9	6.4	4.9
1	1	0	100.0	100.0	100.0	1	2	8	10.0	10.8	10.9
1	0	7	14.0	14.2	16.2	0	1	14	3.2	3.1	4.3
0	0	9	21.0	18.5	4.5	2	2	0	21.2	18.6	18.5
0	1	8	15.1	18.5	18.2	2	1	10	9.7	7.2	10.1
0	2	4	19.1	11.7	17.4	0	2	13	3.7	7.2	5.5
1	1	6	31.0	4.4	1.8	3	1	5	5.7	10.1	7.6
2	0	5	20.0	41.0	33.0	1	3	7	1.8	3.0	3.4
1	0	10	20.0	12.2	13.5	3	1	8	5.0	4.7	4.7
0	2	7	19.2	8.3	9.2	0	4	5	7.4	5.4	4.3
1	1	9	13.2	1.8	1.7	0	0	18	3.9	2.6	2.6
2	0	8	16.5	13.5	13.7	1	3	10	4.5	5.0	5.0
2	1	4	3.5	2.2	4.9	1	1	18	5.2	8.5	8.7
1	2	5	14.3	22.7	16.9	4	1	0	5.5	5.5	5.5
3	0	0	16.5	20.2	20.2						

R FACTOR ORDERED=20.6

R FACTOR RANDOM=13.0

(3) The Systems $\text{BaRu}_{1-x}\text{Ni}_x\text{O}_3$ and $\text{BaRu}_{1-x}\text{Mg}_x\text{O}_3$.—Barium peroxide or barium carbonate was heated in air at 1100° in intimate mixture with nickel carbonate and ruthenium metal powder in order to prepare $\text{BaRu}_{1-x}\text{Ni}_x\text{O}_3$. The proportions of reactants were chosen for values of x from 0.05 to 0.75.

The X-ray powder diffraction patterns of the products at $x = 0.05$ and 0.1 showed the presence of two phases. The dominant one had the nine-layer structure of BaRuO_3 showing no change

TABLE II
COMPARISON OF OBSERVED AND CALCULATED X-RAY INTENSITIES FOR ORDERED AND RANDOM MODELS FOR $\text{BaRu}_{1/3}\text{Mn}_{2/3}\text{O}_3$. $\text{Cu K}\alpha$ RADIATION. CALCULATED INTENSITIES ARE CORRECTED FOR LORENTZ AND POLARIZATION EFFECTS

H	K	L	IOBS	ORDERED ICAL	RANDOM ICAL	H	K	L	IOBS	ORDERED ICAL	RANDOM ICAL
1	0	1	2.5	1.0	.5	3	0	0	18.2	20.2	20.2
1	0	4	23.6	43.4	25.6	0	2	10	15.7	10.7	9.8
0	1	5	71.7	42.3	59.8	2	1	7	7.1	8.5	7.5
1	1	0	100.0	100.0	100.0	1	0	13	4.7	3.0	4.7
1	0	7	10.7	17.2	15.1	1	2	8	9.1	9.9	9.7
0	0	9	19.2	7.0	7.0	0	1	14	3.0	6.6	5.1
0	1	8	17.6	16.2	15.9	2	2	0	15.1	19.1	19.1
2	0	5	33.3	20.5	22.2	2	1	10	7.0	11.1	10.1
1	0	10	11.7	29.1	37.2	0	2	13	5.5	4.3	6.0
0	2	4	14.7	14.8	13.4	1	3	4	3.0	5.2	3.7
0	2	7	8.6	9.9	8.8	3	1	5	5.2	6.0	8.6
1	1	9	15.0	3.9	4.1	2	0	14	6.7	6.7	5.5
2	0	8	16.7	13.0	12.8						
2	1	4	5.1	11.5	6.7						
1	2	5	16.7	13.1	18.7						

R FACTOR ORDERED=29.7

R FACTOR RANDOM=14.9

in lattice parameters; the other was of the hexagonal barium titanate type. The latter phase was the only one observed at $x = 0.25$ and 0.33. With higher proportions of nickel, this phase was obtained mixed with $\text{Ba}_3\text{Ni}_2\text{O}_8$, a compound characterized by Lander.⁶

The X-ray powder pattern of the phase at $x = 0.33$ with the hexagonal barium titanate structure was completely indexed on the basis of a hexagonal unit cell of dimensions $a = 5.75$ Å, $c = 14.12$ Å. It seemed possible in view of the difficulty of maintaining nickel in a high oxidation state at high temperatures that the compound contained nickel(II) and ruthenium(V). The compound readily dissolved in dilute hydrochloric acid liberating chlorine.

It was found possible to substitute magnesium for nickel. The compound $\text{BaRu}_{2/3}\text{Mg}_{1/3}\text{O}_3$ was prepared by heating an appropriate mixture of barium carbonate, magnesium oxide, and ruthenium metal in air at 1200° . The diffraction pattern could be indexed completely on the basis of a hexagonal cell $a = 5.76$ Å, $c = 14.14$ Å.

In the hexagonal barium titanate structure, there are pairs of face-shared octahedra which are joined to other face-shared octahedra through a completely corner-sharing octahedron. In order to determine if there is any site preference in these compounds, the R factors based on intensities were calculated for the three possible configurations of Ru and Ni or Mg. The first possibility (case I) is Ru in the face-shared octahedra and Mg or Ni in the corner-sharing octahedron. The second type of ordering (case II) would place the nickel or magnesium and half of the ruthenium in the face-shared octahedra. The remainder of the ruthenium would be in the corner-shared octahedron. Finally, we could have a completely random distribution of the ruthenium and the nickel or magnesium (case III).

The observed intensities were obtained as previously described. They were corrected for Lorentz and polarization effects. The calculation and refinement of each possible configuration were done using the Busing, Martin, and Levy least-squares program which was adapted to refine unresolved powder data by Norman Morrow of this laboratory.

The observed and calculated intensities and R factors are shown in Tables III and IV. The results show that the ruthenium atoms lie in the face-shared octahedra. The magnesium or nickel atoms occupy the corner-shared octahedron. The Ru—Ru distance is about 2.63 Å, within the limits of error for both cases.

An estimation of the average oxidation state of the ruthenium in the magnesium compound was made by measuring the chlorine liberated by the reaction of a weighed sample with excess hydrochloric acid.⁷ Ru(IV) is stable under these conditions. The results were variable and apparently depended upon the previous history of the sample. By heating the compound in air at 600° , a sample was obtained which contained 80% of the ruthenium in the pentavalent state.

(7) J. D. Struthers and R. Ward, *J. Am. Chem. Soc.*, **59**, 1849 (1937).

TABLE III

COMPARISON OF OBSERVED AND CALCULATED X-RAY INTENSITIES FOR THREE MODELS FOR BaRu_{2/3}Ni_{1/3}O₃: CASE I, Ni IN CORNER-SHARING OCTAHEDRA; CASE II, Ru IN CORNER-SHARING OCTAHEDRA; CASE III, RANDOM. OBSERVED INTENSITIES ARE CORRECTED FOR LORENTZ AND POLARIZATION EFFECTS

H	K	L	CASE1 CASE2 CASE3				H	K	L	CASE1 CASE2 CASE3			
			IOBS	ICAL	ICAL	ICAL				IOBS	ICAL	ICAL	ICAL
1	0	0	.7	1.3	.4	.0	2	0	7	184.0	158.9	120.3	136.3
1	0	1	5.3	3.9	.7	1.5	2	1	5				
1	0	2	7.4	8.2	2.9	4.4	1	1	8				
0	0	4	4.6	1.9	.0	.2	3	0	4	104.0	100.4	87.2	89.2
1	0	3	41.6	48.9	47.7	48.4	1	0	9				
1	0	4	400.0	406.6	409.8	409.0	2	2	0	274.0	270.6	276.1	275.3
1	1	0					2	0	8				
2	0	0					2	1	7	82.4	85.0	44.9	55.2
1	0	5	68.2	76.0	62.8	67.7	3	1	3				
2	0	1					2	0	9	159.0	152.9	132.5	138.3
0	0	6	52.8	56.6	43.0	47.5	2	2	4				
2	0	2					2	1	8	195.0	199.0	238.1	225.5
1	1	4	15.7	14.4	.6	2.8	3	1	4				
2	0	3	86.0	89.5	86.2	87.7	1	0	11	80.7	83.3	57.9	65.8
2	0	4	189.0	188.8	181.2	176.6	3	1	5				
2	0	5					4	0	2				
1	0	7	148.0	155.2	110.2	123.5	2	0	10	70.8	53.0	46.2	47.8
2	1	0					2	2	6				
1	1	6	24.2	34.5	24.7	27.6	4	0	3				
2	1	2					3	0	8	135.0	151.0	138.3	142.3
2	1	3	40.7	51.4	49.7	50.5	2	1	6				
2	1	4					4	0	4	105.0	112.2	112.3	112.1
1	0	8	405.0	401.3	428.2	419.4	0	0	12				
1	0	9											
3	0	0											
3	0	1											

R FACTORS 9.8 13.4 10.7

TABLE IV

COMPARISON OF OBSERVED AND CALCULATED X-RAY INTENSITIES FOR THREE MODELS FOR BaRu_{2/3}Mg_{1/3}O₃: CASE I, Mg IN CORNER-SHARING OCTAHEDRA; CASE II, Ru IN CORNER-SHARING OCTAHEDRA; CASE III, RANDOM. OBSERVED INTENSITIES ARE CORRECTED FOR LORENTZ AND POLARIZATION EFFECTS

H	K	L	CASE1 CASE2 CASE3				H	K	L	CASE1 CASE2 CASE3			
			IOBS	ICAL	ICAL	ICAL				IOBS	ICAL	ICAL	ICAL
0	0	2	1.2	2.0	.3	.0	2	0	8	349.6	313.9	314.9	314.9
1	0	0	3.8	3.6	3.3	.4	2	2	0				
1	0	1	5.2	6.1	.0	.4	2	1	7	129.6	123.9	94.0	110.1
1	0	2	10.0	19.9	2.0	5.6	1	0	10				
0	0	4	8.2	7.7	.3	1.7	3	0	6	42.3	69.5	33.1	42.9
1	0	3	50.9	81.0	83.8	83.5	3	1	2				
1	0	4	496.0	493.9	502.5	506.1	2	2	4				
1	1	0					3	1	3	232.7	226.3	167.8	183.5
1	1	2	5.1	8.7	1.4	.1	3	3	4				
2	0	0					2	1	8	247.3	240.1	316.3	292.8
1	0	5	83.5	106.1	51.4	60.3	3	1	4				
2	0	1					4	0	0				
0	0	6	81.5	92.5	50.9	62.2	1	0	11	122.8	119.8	51.9	69.5
2	0	2					3	1	5				
1	1	4	138.1	153.0	122.9	129.3	2	1	10				
2	0	3					2	2	6	79.2	97.3	65.3	75.5
2	0	4	218.4	208.5	244.7	237.7	4	0	2				
2	1	0					3	0	8				
1	0	7	202.1	203.7	116.0	138.0	2	1	9	142.8	178.6	144.6	154.5
2	1	1					4	0	3				
1	1	6	40.1	31.1	39.2	49.2	0	0	12	165.0	137.5	148.8	147.2
2	1	2					4	0	4				
2	1	3	58.2	61.4	65.3	64.6	2	0	11				
1	0	8					3	1	7				
2	1	4	499.3	495.5	535.0	541.0	4	0	5	167.2	191.7	112.0	139.5
3	0	0					2	1	10				
2	0	7	248.0	254.0	147.3	178.6	3	2	2				
2	1	5					1	1	12				
1	1	8					3	1	8	612.4	619.9	621.6	630.9
3	0	4	147.0	137.4	100.2	108.9	4	1	0				
1	0	9											

R FACTORS 8.1 18.7 14.2

Discussion

It is interesting to note that in the system BaRuO₃-BaZrO₃ none of the zirconium could be incorporated in the nine-layer structure of BaRuO₃. Ruthenium is evidently taken up readily in the perovskite-like phase, causing a distortion from cubic symmetry, but no intermediate phases with face-sharing octahedra are formed under the conditions used in these experiments. This is in sharp contrast to the behavior of titanium, which gives a phase with the hexagonal barium titanate structure at composition BaTi_{2/3}-Ru_{1/3}O₃. In this compound (or its iridium analog) the

titanium was thought to share the face-shared octahedra with the ruthenium atom. The apparent reluctance of zirconium to adopt this position may be because of the difficulty of accommodating a larger Zr(IV) cation in this position. On the other hand, it might be simply due to the fact that the perovskite-type structure is the more stable one. Metal-metal bond formation must represent a very small contribution to the total energy of the crystal.

Manganese(IV) is small enough and the oxidation state is sufficiently stable to give complete and random substitution in the nine-layer structure. It is surprising, though, that the ruthenium does not substitute in the two-layer structure of the low-temperature form of BaMnO₃, which contains manganese(IV) in a continuous string of face-shared octahedra, or in the four-layer structure of the high-temperature form in which there are pairs of face-shared octahedra occupied by manganese(IV). Phases with these structures were not formed in the system BaRuO₃-BaMnO₃. As little as 5 mole % of ruthenium stabilizes the nine-layer structure for manganese. One suspects that the preparation of supposedly pure BaMnO₃ with this structure was due to the inadvertent presence of some impurity. It is conceivable that the atmosphere of the furnace in which the crystals of this compound were formed contained some strontium oxide or some ruthenium oxide. However, the deliberate addition of trace amounts of these substances did not yield the desired product. The fibrous nature of the crystals suggests that a nucleation phenomenon is involved. Accidents of this kind are occasionally difficult to duplicate.

The system BaRuO₃-BaNiO₃ was not realized under the conditions used in this study. The temperatures were too high to favor the tetravalent state for nickel. The formation of a phase with the hexagonal barium titanate structure at the composition BaRu_{2/3}Ni_{1/3}O₃ and of an analogous magnesium compound is interesting for several reasons. First, it suggests the existence of pentavalent ruthenium—a very unusual oxidation state for this element. The analytical data on different preparations of the magnesium compound indicate that most of the ruthenium is present as Ru(V) and that more sophisticated methods of preparation could lead to the stoichiometric compound. The assumption is made that the nickel is reduced to Ni(II) in this structure. The second point of interest is that the ruthenium atoms are in the face-shared octahedral sites. Ru(V) like Cr(III) is a d³ ion. Most AM'_{2/3}M''_{1/3}O₃ compounds in which A is barium and M' is chromium(III) have the hexagonal barium titanate structure. It seems reasonable to ascribe this to the ready formation of a metal-metal bond between the two d³ ions. The complete substitution of Mn(IV) in the BaRuO₃ may be due to the fact that it is also a d³ ion.

Finally, the existence of ordered compounds of the type BaRu_{2/3}M_{1/3}O₃ offers an additional example of structures with ruthenium in adjacent face-shared octahedra. A number of other compounds with the

hexagonal BaTiO_3 structure are reported by Blasse.⁸ In this publication an explanation for the adoption of this structure in terms of anion polarization is presented.

A study of the magnetic properties of a series of these compounds is contemplated in the hope that the function of the d electrons may be revealed.

(8) G. Blasse, *J. Inorg. Nucl. Chem.*, **27**, 993 (1965).

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The Preparation and Some Properties of Yttrium, Dysprosium, and Ytterbium Alkoxides

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Isopropoxides of yttrium, dysprosium, and ytterbium have been prepared by treating the metals with isopropyl alcohol using mercuric chloride as a catalyst. The reactants were refluxed for 24 hr at 82°, and the isopropoxides were recrystallized from isopropyl alcohol. The use of stoichiometric amounts of mercuric chloride resulted in chloride contamination and alkene alkoxide formation. High-purity isopropoxides of these metals could not be made by the metal chloride-ammonia method commonly employed to make group IV-B transition metal alkoxides. Heavier alkoxides were made by an alcoholysis reaction of the isopropoxides with the appropriate higher boiling alcohol in benzene. Compounds prepared by alcoholysis methods included the 2-pentoxides of yttrium, dysprosium, and ytterbium and yttrium *t*-butoxide, 3-methyl-2-butoxide, 2-hexoxide, 3-ethyl-3-pentoxide, 3-hexoxide, 2-ethyl-1-hexoxide, and phenoxide. All the alkoxides were solids which sublimed or decomposed on melting at 200° or higher. The alkoxides with heavier and branched-chain alkoxy groups were the most stable, but all differences were small and the chemistry was virtually identical for the three metals with the same alkoxy group attached. Thermal and hydrolytic decomposition was quantitative to the oxides.

Introduction

Only during the past 15 years have major efforts been directed toward a systematic investigation of metal alkoxides. Particularly important has been the work of Bradley.^{1,2} Most metal alkoxides can be readily prepared and afford an opportunity for fundamental investigations of the metal-oxygen bond as influenced by adjacent organic groups. It was found, however, that classical methods of alkoxide synthesis failed to produce high-purity compounds of yttrium, dysprosium, and ytterbium. Preliminary work with other lanthanides indicates that the reactions are general to the series.

Metal alkoxides provide a direct route to ultra-high-purity, fine-particulate oxides by thermal and hydrolytic decomposition.³ Transition metal alkoxides have previously been investigated for vapor deposition of oxides on refractory substrates.⁴

Owing to the lanthanide contraction there is little difference in the atomic size of these three elements. Yttrium, dysprosium, and ytterbium have covalent

radii⁵ of 1.62, 1.59, and 1.70 Å and electronegativities⁶ of 1.11, 1.10, and 1.06, respectively. Therefore, the reactions they undergo and the properties of the alkoxides formed are expected to be quite similar. For more electronegative elements such as titanium, zirconium, and aluminum, many of the alkoxides are liquids. In this instance the nature of the alkoxide group determines whether the compound is a solid or a liquid. For the electropositive elements such as lithium, sodium, and potassium, the alkoxides are always solids regardless of the alkoxide group. The alkoxides of yttrium, dysprosium, and ytterbium fall intermediate between these extremes, and, thus far, the alkoxides prepared by us have been solids. Volatility has been found to vary appreciably with the length and branching of the alkoxide group, however.

The rates of reactions for preparation of the alkoxides are faster for the compounds which have smaller covalent radii. The covalent radii⁵ of aluminum, lithium, and titanium are 1.25, 1.23, and 1.32 Å, and the reactions are relatively rapid. The covalent radii⁵ of zirconium and hafnium are 1.45 and 1.44 Å, and the reactions are considerably slower. For yttrium, dysprosium, and ytterbium, the reactions are much

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