STRUCTURAL RELATIONS AMONG DOUBLE OXIDES OF TRIVALENT ELEMENTS

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ABSTRACT

The crystal structures assumed by equimolar and 3:5 molar ratio compounds of the sesquioxides are reported, a number of them for the first time, and the effect of ionic radius ratio as the controlling variable is demonstrated. In addition, the effect of cation charge upon the cation-size-tolerance of a structure is demonstrated by comparison between $A^{3+}B^{3+}O_3$ compounds and known structures of $A^{2+}B^{4+}O_3$ compounds. Several ambiguities and discrepancies in the literature are corrected. Some properties of the compounds are recorded and consideration is given to the bearing of the results upon problems of the distribution of rare elements in natural minerals and upon the preparation of crystalline compounds with specific desired properties.

IONIC SUBSTITUTIONS

Crystal structure studies and investigations of the substitution of different elements in specific structures have developed into one of the important borderline fields between geochemistry and mineralogy on the one hand, and ceramic technology on the other hand. In the geological sciences, information on crystal structure substitutions is a guide to the distribution of elements in minerals and rocks; such investigations are becoming increasingly important as the rarer elements are being sought. This is particularly true in the case of elements which do not occur as major constituents of any known mineral but proxy for more abundant elements in common minerals. In ceramic technology, investigations of crystal structure substitutions combined with measurement of the properties of crystalline compounds and solid solutions, offer a basis for predicting the properties of crystals and crystalline aggregates and of guiding the preparation of materials with specific, desired properties, such as high melting point, low thermal expansion or high dielectric constant.

The present investigation deals primarily with the crystal structures obtained in various combinations of trivalent elements in double oxides

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and with analogies to similar structures of double-oxide combinations of cations of other valence. Most of the double-oxide combinations encountered are 1:1 molar ratio compounds or solid solutions. A smaller number of double-oxide combinations have a 3:5 ideal molecular proportion of the component oxides and show a garnet structure. Since ionic size is by far the most important consideration, it has been possible to make several types of substitutions in a particular structure. The simplest one is the introduction of an ion similar in size and charge to one of the original ions; others include the substitution of two ions of similar size but with different charges, one greater and the other less than those of the original ions.

PEROVSKITE STRUCTURES

$$La^{3+} Al^{3+} O_3$$

Perovskite $\boxed{Ca^{2+} Ti^{4+} O_3}$

$$K^+ Nb^{5+} O_3$$

$$Re^{6+} O_3$$

$$[ABO_3]$$

GARNET STRUCTURES

$\boxed{Mn_3^{2+} Al_2^{3+} (Si^{4+} O_4)_3}$ Spessartite

$Y_3^{3+} Al_2^{3+} (Al^{3+} O_4)_3$ $= 3 Y_2O_3 \cdot 5 Al_2O_3$

$Y_3 (\overline{YAl}) (Al O_4)_3$ $= Y_2O_3 \cdot Al_2O_3$

$Sm_3^{3+} Ga_2^{3+} (Ga^{3+} O_4)_3$ $= 3 Sm_2O_3 \cdot 5 Ga_2O_3$

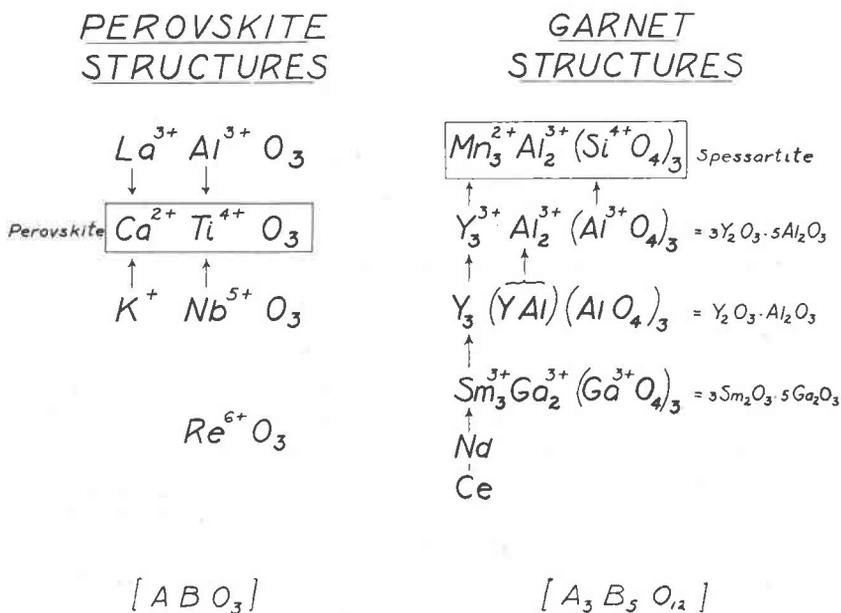Nd

Ce

$$[A_3 B_5 O_{12}]$$

FIG. 1. Examples of Cation Substitutions in Perovskite and Garnet Structures.

Some of the demonstrated cation substitutions in perovskite structures and garnet structures are shown as examples in Fig. 1. In perovskite, a bivalent cation (Ca^{2+}) is combined with a quadrivalent cation (Ti^{4+}). Within certain limits of cation size, other combinations of a bivalent and a quadrivalent cation have the perovskite structure with varying degrees of distortion from the ideal cubic form. Further (again within certain cation-size limitations), other cation combinations with a total charge of six can proxy for the $A^{2+}:B^{4+}$ combination. For example (Fig. 1),

both lanthanum aluminate,[a] with two trivalent cations, and potassium niobate, with a monovalent and a pentavalent cation, have the perovskite structure. As extreme examples of the substitution possibilities, rhenium oxide (ReO_3) and one form of tungsten oxide (WO_3), with cation valence of six, have distorted perovskite structures (Wyckoff, 1949, Ch. V, Text p. 15).

The garnet substitutions are somewhat more complex. Starting from the ideal formula of spessartite garnet, $Mn_3Al_2(SiO_4)_3$, it has been shown (Yoder and Keith, 1951), that yttrium can be substituted for manganese if aluminum is simultaneously substituted for silicon in order to maintain the charge balance. The result of complete substitution $Y^{3+}Al^{3+} \rightarrow Mn^{2+}Si^{4+}$ is a silica-free garnet of the formula $Y_3Al_2(AlO_4)_3$ which can be simplified to $3Y_2O_3 . 5Al_2O_3$, (yttrogarnet). The first form of the yttrogarnet formula above has the advantage of emphasizing that aluminum occurs both in six-fold and in four-fold coordination.

Previous Work

The earliest and most complete work to date is that of V. M. Goldschmidt and his students who prepared a large number of the ABO_3 compounds and determined their general structure type. Goldschmidt (1927–36) also studied the factors determining structure type and clearly demonstrated the influence of ionic radius and ionic polarizability as the controlling variables. Zachariasen (1927) made an extensive survey of the A_2O_3 structures, which may be considered as special cases of the ABO_3 structures. A large number of investigators since have prepared a few more compounds, or attempted to clarify or more closely define the relationships between ionic radius and structure type. Of the recent work especial mention may be made of the papers of Naray-Szabo (1943) and the recent classification by Wood (1951). Interest in this field has been stimulated by the exceptional dielectric properties of $BaTiO_3$ and related compounds. Much detailed information is collected in the publications of Megaw (1946), Matthias (1949), Jonker and van Santen (1949), and Roberts (1949, 1951), but with the exception of the last two studies referred to above, little attention has been given to the systematic preparation of new compounds and determination of structure types. It is worth noting that almost every oxide compound which has been found to be strongly ferroelectric was listed in Goldschmidt's original work on perovskite and related structures.

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[a] This terminology is used only for convenience, and the compound is no more an aluminate than a lanthanate. We adopt the convention of placing the smaller cation in the "B" position in writing formulae.
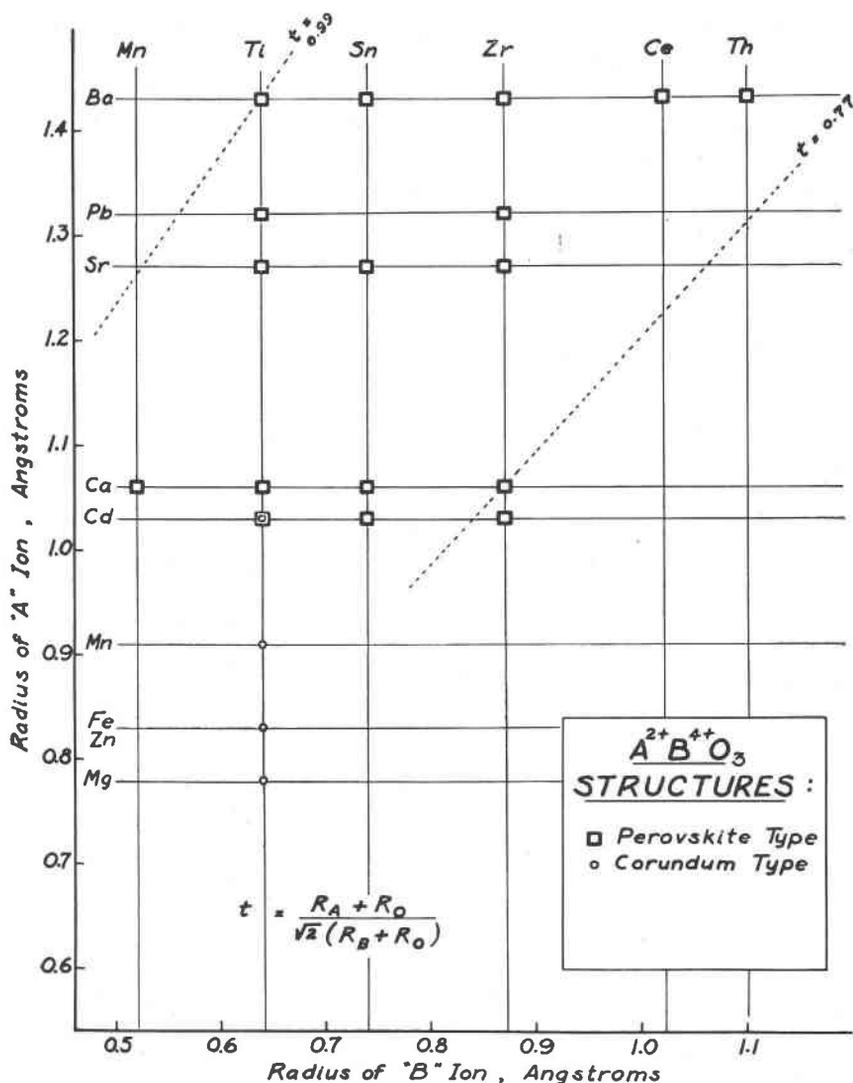
FIG. 2. Distribution of $A^{2+}B^{4+}O_3$ Structures in Relation to Cation Radii.

Figure 2 is a plot of the structures obtained in double-oxide combinations of bivalent and quadrivalent ions of different radius. The data are mostly from the literature and may be found summarized in Wyckoff (1951) or in Structure Reports (1951). Modified Goldschmidt radii are used (see Rankama and Sahama, 1950). The results are essentially

the same using any of the sets of ionic radii, the main difference being in the relative positions of In, Sc, and Y.[b]

Using the data shown in Fig. 2 . . . Goldschmidt (1927–36), developed the concept of what he called a "tolerance factor" to express, in terms of ionic radii, the limits within which a specific structure may be expected from combinations of various elements. His formula is:

$$t = \frac{R_A + R_0}{\sqrt{2}(R_B + R_0)} .**$$

** t = tolerance factor for the perovskite structure.
R_A = ionic radius of the larger cation in double oxides.
R_B = ionic radius of the smaller cation in double oxides.
R_0 = ionic radius of oxygen.

Goldschmidt concluded that the perovskite structure may be expected within the limits $t = 0.99$ to 0.77 (see Fig. 2). The present work confirms that those limits are substantially correct for double-oxide combinations of a bivalent and a quadrivalent cation. Subsequent to the work of Goldschmidt, some perovskite structures have been reported below the tolerance limit $t = 0.77$, but we have not been able to confirm those reports. For example: $CdCeO_3$, $CaCeO_3$, $CaThO_3$, and $MgCeO_3$, are listed (Wyckoff, 1948) as compounds with the perovskite structure. In the present investigation, mixtures of 1:1 molecular proportion in the four binary systems involved were sintered at temperatures up to $1900°$ C. All show some solid solution between the component oxides but no evidence of an intermediate compound. $CaCeO_3$ and $CdCeO_3$† solid solutions have the fluorite structure, and constitute therefore an interesting example of anion-deficient solid solution. Compounds of the formula $A^{2+}B^{4+}O_3$, in which both A and B are small show the corundum —ilmenite structure.

The $A^{2+}B^{4+}O_3$ compounds which are closest to a line from $SrTiO_3$ to $BaThO_3$ on the chart (Fig. 2), approach most nearly the ideal cubic perovskite structure. In a direction toward a higher tolerance factor the structures are progressively more distorted; $BaTiO_3$ for example is tetragonal at room temperature. In the opposite direction, toward a

[b] For example, trivalent scandium and indium are assigned the same ionic radius by Pauling although the published parameters of simple isostructural compounds of indium and scandium are not the same. L. H. Ahrens (1952) presents reasons for preferring the Pauling radii, and it is probable that inconsistencies will be cleared up as more accurate crystal structure data are accumulated. For purposes of the present investigation the ratios of ionic radii appear to be more significant than close approach to absolute values of the radii.

† Conclusions regarding $CdCeO_3$ are doubtful because of loss of CdO by volatilization, especially above 1200°C.

smaller tolerance factor, the structures are distorted away from the simple cubic form, but in a different manner. Perovskite itself ($CaTiO_3$) probably should be considered as monoclinic (Naray-Szabo, 1943), while $CaZrO_3$ is reported as orthorhombic (Megaw, 1946).

The available data on compounds in which both the A and B cations are trivalent are less extensive and less well established. Some literature values are included in the results presented, but in almost every case they have been checked. It was the object of the investigation to collect more extensive data on the compounds formed from binary equimolar mixtures of the trivalent oxides, and to classify them into general structure types. The influence of certain factors on the structures can thereby be evaluated.

PREPARATION AND TREATMENT OF MIXTURES

All of the materials used are from commercial sources and were not especially purified; the following are of C. P. grade or better; Al_2O_3, Ga_2O_3, Sc_2O_3, La_2O_3, Fe_2O_3, Cr_2O_3 and $Bi(OH)_3$. The following were quoted as being 99% pure: Y_2O_3,* Nd_2O_3,* Sm_2O_3,* and $Ce_2(C_2O_4)_3 \cdot 9H_2O$. Most of the starting materials are in an extremely fine state of subdivision.

Small batches, in most cases one gram or less, were weighed out in the required proportion and then finely ground together in a sintered alumina mortar. In some cases more reactive mixtures were prepared by dissolving the component oxides in nitric acid, diluting the solution and then simultaneously precipitating the hydroxides by adding the solution dropwise to an excess of ammonium hydroxide. The precipitated hydroxides were filtered and washed, dried below 300° C., and used especially for the low-temperature hydrothermal runs.

The general treatment procedure used was to fire the mixtures to progressively higher temperatures and to determine the phases present after different stages of treatment. For lower temperatures, charges were sintered in platinum crucibles in a globar furnace (to 1400° C.) and in a gas-air furnace (to 1650° C.). For higher temperatures (1650° to 1900° C.) a simple strip furnace was used. The strip furnace, modified slightly from the design of Roberts and Morey (1930), consists essentially of a thin sheet of 60% platinum 40% rhodium alloy, $\frac{1}{4}$ inch by $1\frac{1}{4}$ inches by .0015 inch thick, formed into a "U"-shaped element which constitutes both the resistor and the sample holder. The power source and control circuit for the strip resistor includes a constant voltage transformer, two variable transformers (Variacs), and a 25:1 stepdown transformer,

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* Small amounts of some of the mixtures were also made up with 99.9% pure oxides; in no case was there any significant difference, as compared with the compounds prepared from 99% pure oxides.

which supplies up to 200 amperes at about 5 volts. The "U"-shaped resistor is supported on sheet-copper cooling fins and connected to the low-voltage side of the stepdown transformer by means of two silver blocks held in place by beryllium copper springs.

A small sample placed in the bottom of the "U" shaped strip resistor can be held at a desired temperature long enough for attainment of equilibrium and then quenched to room temperature by shutting off the current. The furnace has no refractories and the size and heat content of the strip resistor are so small in relation to the size of the silver contact blocks and copper cooling fins that the quench is very rapid, even faster than that obtained by dropping a charge from a conventional vertical tube furnace into mercury. Temperatures were read with an optical pyrometer calibrated in conjunction with the strip furnace at the melting temperatures of diopside, $CaMgSi_2O_6$ (1391.5°);[e] pseudowollastonite, $CaSiO_3$ (1546°); SiO_2 90%: CaO 10% (1708°); and rhodium (1960°).

For lower temperature hydrothermal runs, mixtures were wrapped in gold or platinum foil envelopes and heated in pressure vessels at the desired temperature and water pressure. Most of this work was done in so-called test-tube bombs (Roy, Roy and Osborn, 1950).

EXAMINATION OF PRODUCTS

The products in each case were examined by optical and x-ray methods; in addition, a number of them were thermally analyzed with the object of detecting possible inversion phenomena. Differential thermal analysis was performed with an automatic controller-recorder apparatus.

A set of high refractive index liquids, prepared according to the outline of Larsen and Meyrowitz (1951) proved to be satisfactory and much superior to high-index liquids previously available.[d] However, even with the extended range of index measurement (up to 2.00), the indices of refraction of most of the phases encountered are too high to be matched. A further difficulty results from the fact that a number of the more refractory mixtures do not develop any liquid at the highest temperatures attained, and the grain size of products is so small as to preclude obtaining useful information with the microscope. In many cases the fine grain size of products also has an effect on x-ray measurements. For example, it is difficult in some cases to obtain sufficiently well-crystallized material to permit distinction between an orthorhombic and a tetragonal distortion of the perovskite structure. X-ray powder diffraction data were obtained either with a 90-degree North American Philips Geiger-Counter spectrometer or with the 165 degree GE XRD-3 unit.

[e] Temperatures in degrees C., 1948 International Scale (Stimson, 1949).

[d] It was found necessary to maintain the 4 highest index liquids at a temperature of about 35°C. in order to prevent crystallization.

TABLE 1. SUMMARY OF SIGNIFICANT RUNS AND CRYSTAL STRUCTURES OBTAINED

Preparation No.	Composition (Mol. Proportion of Oxides)		Initial Condition	Steam Pressure (p.s.i.)	Temperature (°C.)	Time	Color of Product (Refl. Light)	Results of Microscopic and X-Ray Examination
			Smaller Cation Aluminum					
60	La_2O_3 Al_2O_3	1:1	f.g. oxides	—	1,640	90 min.	white	anisotropic (nearly isotropic); $LaAlO_3$ (perovskite structure)
			f.g. oxides	5,000	700	3 days	white	—(same)—
59	CeO_2[1] Al_2O_3	1:1	f.g. oxides	—	1,640	90 min.	yel. green	mostly anisotropic, low birefringence: $CeAlO_3$ (perovskite struct.) and some CeO_2
58	CeO_2 Al_2O_3	3:5	f.g. oxides	—	1,650	90 min.	yel. green	mostly anisotropic, low birefringence: $CeAlO_3$ solid soln. (perovskite struct.) and some CeO_2
61	Nd_2O_3 Al_2O_3	1:1	f.g. oxides	—	1,650	90 min.	pale viol.	anisotropic, low birefringence: $NdAlO_3$ (perovskite structure)
			$NdAlO_3$	5,000	600	3 days	pale viol.	—(same)—
62	Sm_2O_3 Al_2O_3	1:1	f.g. oxides	—	1,650	90 min.	yel. white	anisotropic, moderate birefringence: $SmAlO_3$ (perovskite structure)
			ppt. hydrox.	5,000	700	3 days	yel. white	—(same)—
67	Y_2O_3 Al_2O_3	1:1	f.g. oxides	—	1,800	2 hrs.	white	anisotropic: $YAlO_3$ ($YCrO_3$ structure)
			garnet and minor $YAlO_3$	—	1,700	1 hr.	white	mostly isotropic: garnet solid solution and small amt. of unknown phase
			$YAlO_3$	—	1,600	1 hr.	white	garnet solid soln. and minor $YAlO_3$
70	Y_2O_3 Al_2O_3	3:5	f.g. oxides	—	1,760	5 min.	white	isotropic: $Y_3Al_2(AlO_3)_3$ (garnet struct.). Inverts to high form at 1,970±50° C. (Yoder and Keith, 1951)
71	In_2O_3 Al_2O_3	1:1	$InAlO_3$ (type "C")	—	1,700(L)	2 min.	pinkish white	anisotropic: unknown high form*[2]
			f.g. oxides	—	1,600	2 hrs.	pinkish white	isotropic, $InAlO_3$ (Tl_2O_3 structure)
			Smaller Cation Gallium					
103	La_2O_3 Ga_2O_3	1:1	f.g. $La(OH)_3$ and Ga_2O_3	—	1,000 1,475	24 hrs. 12 hrs.	colorless	$LaGaO_3$ (perovskite structure)
79	CeO_2 Ga_2O_3	1:1	f.g. oxides	—	1,700(L)	2 min.	pale brown	2 phases—1 isotropic, 1 anisotropic: CeO_2 and $CeGaO_3$ (perovskite structure)
			f.g. oxides ppt. hydrox.	5,000	1,430 595	20 hrs. 12 days	pale brown pale yellow	isotropic: garnet and CeO_2; isotropic: garnet and CeO_2 (Liquidus temp. higher than No. 99)
99	Ce_2O_3 Ga_2O_3	3:5	ppt. hydrox.	10,000	600	18 days	pale orange	isotropic: garnet and CeO_2. Note—minor amt. of green glass in charge quenched from 1,430° C.

[1] ceria was added as the oxalate, $Ce(C_2O_4)_3 \cdot 9H_2O$.
(L) =completely or mostly liquid at indicated temperature.
[2] $InAlO_3$ high form has x-ray reflections at $2\theta = 10.1$, 20.6, 31.0, 33.0, 37.7, 53.1, 55.6 deg, (for Cu K_α).

TABLE 1—(*continued*)

Preparation No.	Composition (Mol. Proportion of Oxides)		Initial Condition	Steam Pressure (p.s.i.)	Temperature (°C.)	Time	Color of Product (Refl. Light)	Results of Microscopic and X-Ray Examination
77	Nd_2O_3 Ga_2O_3	1:1	f.g. oxides / $NdGaO_3$ (fused) / f.g. oxides	— / — / 5,000	1,740(L) / 1200 / 595	2 min. / 3 hrs. / 12 days	pale violet / pale violet	anisotropic: $NdGaO_3$ (*perovskite structure*) / mostly isotropic: *garnet* and minor amt. of unknown phase
98	Nd_2O_3 Ga_2O_3	3:5	ppt. hydrox.	10,000	600	18 days	very pale violet	mostly isotropic: *garnet* and small amount of unknown phase
75	Sm_2O_3 Ga_2O_3	1:1	f.g. oxides / f.g. oxides	— / —	1,760(L) / 1,240	2 min. / 22 hrs.	very pale yellow / very pale yellow	acicular crystals, parallel extinction, uniaxial (+) moderate birefringence: (*unknown structure*) / mostly isotropic: *garnet* and Sm_2O_3
76	Sm_2O_3 Ga_2O_3	3:5	f.g. oxides / f.g. oxides / f.g. oxides	— / — / 5,000	1,715(L) / 1,460 / 650	2 min. / 8 hrs. / 9 days	very pale yellow / very pale yellow / very pale yellow	glass and rare acicular crystals: anisotropic high form (unknown structure); apparently inverts to *garnet* on grinding / isotropic: *garnet* (Liquidus temp. probably slightly higher than No. 75) / isotropic: *garnet*
74	Y_2O_3 Ga_2O_3	1:1	f.g. oxides / f.g. oxides / f.g. oxides	— / — / —	1,810(L) / 1,800(L) / 1,240	2 min. / 2 min. / 22 hrs.	— / white / white	glass, N = 1.98±0.01 (Liquidus temp. higher than No. 97) / anisotropic acicular cryst. formed on quench, parallel extinction; (unknown structure) / isotropic, *garnet* solid solution
97	Y_2O_3 Ga_2O_3	3:5	f.g. oxides	10,000	600	9 days	white	mostly isotrop., rare larger cryst. anisotropic: *garnet* and smaller amt. yttrium hydrate
				Smaller Cation Chromium				
94	La_2O_3 Cr_2O_3	1:1	f.g. oxides sintered 20 hrs. at 1,300 deg.	—	1,860	2 min.	green	anisotropic, low birefringence: $LaCrO_3$ (*perovskite structure*)
63	Ce_2O_3 Cr_2O_3	1:1	f.g. oxides / f.g. oxides	— / 5,000	1,700 / 600	1 hr. / 3 days	black / black	translucent on thin edges, anisotropic, very low birefringence: $CeCrO_3$ (*perovskite struct.*) and small amt. CeO_2 / —(*similar*)—
84	Nd_2O_3 Cr_2O_3	1:1	f.g. oxides sintered 12 hrs. at 1,300 deg.	—	1,860	1 min.	greenish brown	anisotropic, very low birefringence: $NdCrO_3$ (*perovskite struct.*) and rare Cr_2O_3
65	Sm_2O_3 Cr_2O_3	1:1	f.g. oxides sintered 1 hr. at 1,600 deg. / f.g. oxides	— / 10,000	1,670 / 596	75 min. / 6 days	green / green	anisotropic, very low birefringence: $SmCrO_3$ ($YCrO_3$ struct.) and rare Cr_2O_3 / anisotropic: very low birefringence: $SmCrO_3$ ($YCrO_3$ structure)
64	Y_2O_3 Cr_2O_3	1:1	f.g. oxides / f.g. oxides / f.g. oxides	— / — / 10,000	1,860 / 1,670 / 590	5 min. / 2 hrs. / 6 days	green / green / green	anisotropic, moderate birefringence: $YCrO_3$ (*type structure*) / —(*same*)— / —(*same and rare* Cr_2O_3)—
100	Y_2O_3 Cr_2O_3	3:5	ppt. hydrox.	10,000	600	9 days	bright green	anisotropic, very low birefringence: $YCrO_3$ *solid solution*; x-ray pattern essentially identical to that of charge No. 64 (above)

TABLE 1—(continued)

Preparation No.	Composition (Mol. Proportion of Oxides)		Initial Condition	Steam Pressure (p.s.i.)	Temperature (°C.)	Time	Color of Product (Refl. Light)	Results of Microscopic and X-Ray Examination
	Smaller Cation Iron							
85	La_2O_3 / Fe_2O_3	1:1	f.g. oxides sintered 1,300 deg.	—	1,650(L)	1 min.	dark brown	anisotropic, very low birefringence: *LaFeO₃ (perovskite structure)*
66	Ce_2O_3 / Fe_2O_3	1:1	f.g. oxides sintered 15 hrs. at 1,300 deg.	—	1,860(L)	3 min.	dark brown	translucent only on thin edges, anisotropic, weakly birefringent: *CeFeO₃ (perovskite struct.)* and small amt. of CeO_2
86	Nd_2O_3 / Fe_2O_3	1:1	f.g. oxides sintered 12 hrs. at 1,300 deg.	—	1,830(L)	1 min.	red brown	anisotropic, low birefringence: *NdFeO₃ (YCrO₃ structure)*
	Fe_2O_3		f.g. oxides	—	1,300	12 hrs.	red brown	—(same)—
69	Sm_2O_3 / Fe_2O_3	1:1	$SmFeO_3$ fused at 1,810 deg.	—	1,680	2 min.	red brown	anisotropic moder. birefringence, magnetic: *SmFeO₃ (YCrO₃ structure)* (Liquidus temp. higher than No. 101 and No. 102)
101	Sm_2O_3 / Fe_2O_3	3:5	f.g. oxides	—	1,760(L)	2 min.	dark brown	anisotropic: *SmFeO₃ solid soln. (YCrO₃ structure)* (Liquidus temp. approx. 170 deg. lower than No. 69)
102	Sm_2O_3 / Fe_2O_3	5:3	$SmFeO_3$ solid soln. fused at 1,760 deg.	—	1,550	2 min.	dark brown	anisotropic: *SmFeO₃ solid soln. (YCrO₃ structure)* (Liquidus temp. approx. 100 degrees lower than No. 69)
			$SmFeO_3$ solid soln. fused at 1,810 deg.	—	1,630	2 min.	brown	
68	Y_2O_3 / Fe_2O_3	1:1	f.g. oxides	—	1,860(L)	3 min.	dark brown	translucent only on thin edges, anisotrop., moder. birefr.: *YFeO₃ (YCrO₃ struct.)*
73	In_2O_3 / Fe_2O_3	1:1	f.g. oxides	—	1,600 (some liquid formed)	2 hrs.	yellow brown	isotrop: *InFeO₃ (Tl₂O₃ struct.)* and small amount of magnetite
	Smaller Cation Indium or Scandium							
80	La_2O_3 / Sc_2O_3	1:1	f.g. oxides sintered 12 hrs. at 1,475 deg.	—	1,860	1 min.	pale violet pink	anisotropic: *LaScO₃ (YCrO₃ struct.)* and some unreacted La_2O_3
87	Ce_2O_3 / Sc_2O_3	1:1	f.g. oxides sintered 12 hrs. at 1,300 deg.	—	1,860	1 min.	pale brown	anisotropic: *CeScO₃ (YCrO₃ struct.)*—incomplete reaction
			f.g. oxides	8,000	600	7 days	pale brown	—(same and some CeO_2)—
88	Nd_2O_3 / Sc_2O_3	1:1	f.g. oxides	—	1,800	2 min.	white	anisotropic, moderate birefringence: *NdScO₃ (YCrO₃ structure)*
			f.g. oxides	8,000	600	5 days	white	—(same)—
81	Y_2O_3 / Sc_2O_3	1:1	f.g. oxides	—	1,880	4 min.	very pale violet	Y_2O_3–Sc_2O_3 *solid soln. (Tl₂O₃ structure)* Some unreacted Y_2O_3 and Sc_2O_3 present
78	La_2O_3 / In_2O_3	1:1	f.g. oxides	—	1,880(L)	2 min.	white	anisotropic: *LaInO₃ (YCrO₃ struct.)*—
			f.g. oxides	5,000	650	9 days	white	—(same and unreacted La_2O_3)—

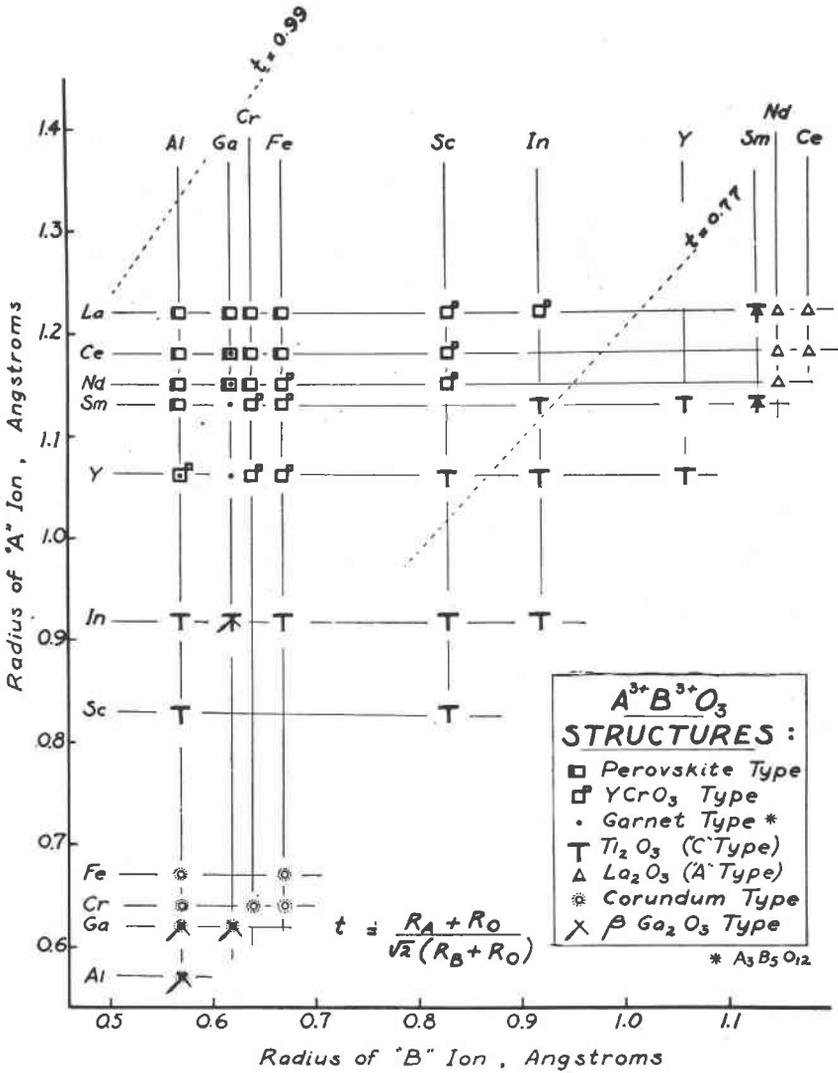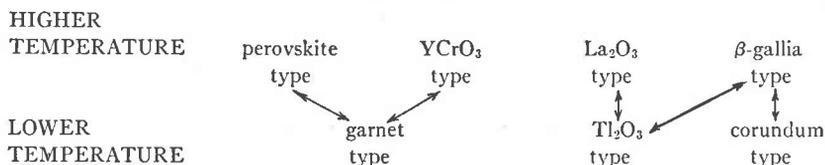FIG. 3. Distribution of $A^{3+}B^{3+}O_3$ Structures in Relation to Cation Radii.

With both instruments filtered copper radiation was used. The spacings recorded were calibrated by running a partial pattern for NaCl on each chart; all spacings are in Angstrom units.

RESULTS

Results of the investigation are summarized in Table 1 and are shown in a schematic diagram (Fig. 3), a plot of the radius of the A^{3+} cation

versus the radius of the B^{3+} cation. Several of the compounds included in Fig. 3 have previously been reported; each was checked in the present study.

At least seven different structure types are formed by various double-oxide combinations of the trivalent elements considered. Those which either can be obtained as a "stranded" phase at room temperature or are stable at low temperatures include: perovskite, garnet, La_2O_3,* Tl_2O_3,* corundum, $YCrO_3$, and β-gallia type structures. Each structure is formed within specific limits of radius ratio. Near the limits of occurrence of each structure-type on the ionic radius chart (Fig. 3), some of the compounds and solid solutions show one structure at a higher temperature and another structure at a lower temperature. The general relationship between the principal high and low forms is as follows:†

HIGHER
TEMPERATURE   perovskite $YCrO_3$ La_2O_3 β-gallia
                        type   type   type   type

LOWER   garnet Tl_2O_3 corundum
TEMPERATURE   type   type   type

It should be emphasized that the investigation here reported is in the nature of a preliminary survey; the many binary systems represented have not been studied in detail. In some of the systems there may exist intermediate compounds other than those of 1:1 or 3:5 molecular proportion, and there may of course be other polymorphs than those recognized. Some of the polymorphs encountered have not yet been identified as to structure type, e.g. high temperature polymorphs in charges of compositions $InAlO_3$, $SmGaO_3$, $YGaO_3$ (Table 1).

It would be desirable to make complete studies of phase equilibria in some of the binary systems involved; it is proposed to attempt investigation of one or two of them as examples. Many of the systems present considerable experimental difficulty due to high liquidus temperatures. Those which show formation of some liquid in 1:1 preparations at temperatures below 1800° are: In_2O_3—Al_2O_3 and the systems in which gallium oxide and iron oxide are components. In a few cases the liquids formed could be quenched to a glass by the use of small charges on the strip furnace. In the system In_2O_3—Al_2O_3 a small amount of colorless, high index glass was encountered in a 1:1 preparation quenched from 1810°. Preparations of 1:1 and 3:5 molecular proportions in the system Sm_2O_3—Ga_2O_3 showed some glass in charges quenched from temperatures in the range 1675–1715°, while a 3:5 preparation in the system Ce_2O_3—Ga_2O_3 contained some yellowish green glass in charges quenched from tempera-

* Often called the A and C type rare earth oxide structures after Zachariasen (1927).
† The B-type rare-earth oxide structure is not considered.

TABLE 2. POWDER DIFFRACTION DATA FOR COMPOUNDS CLASSED
AS HAVING THE PEROVSKITE STRUCTURE

$LaAlO_3$	$LaGaO_3$	$LaCrO_3$	$LaFeO_3$
Well-formed crystals $a_0 = 3.778 \pm .001$ Very nearly cubic Good pattern	Good pattern, a_0 (equiv.) $= 3.875 \pm .003$ V. slight distortion**	Fair pattern, a_0 (equiv.) $= 3.880 \pm .005$ V. slight distortion probably monoclinic (not tetragonal or rhombic)	Fair pattern, a_0 (equiv.) $= 3.915 \pm .005$ V. slight distortion possibly monoclinic
$CeAlO_3$	$CeGaO_3$	$CeCrO_3$	$CeFeO_3$
Fair pattern; little CeO_2 present, a_0 (equiv.) $= 3.77 \pm .02$ Tetragonal distortion reported*	Very poor pattern Abundant CeO_2, a_0 (equiv.) $= 3.87$	Fair pattern V. little CeO_2, a_0 (equiv.) $= 3.851 \pm .007$ Nearly cubic	Poor pattern CeO_2 present, a_0 (equiv.) $= 3.89 \pm .03$ Largest distortion probably monoclinic (not tetragonal)
$NdAlO_3$	$NdGaO_3$	$NdCrO_3$	
Good pattern, a_0 (equiv.) $= 3.73 \pm .01$ Rhombohedral distortion	Fair pattern, a_0 (equiv.) $= 3.86 \pm .015$ Rhombohedral or monoclinic distortion	Fair pattern, a_0 (equiv.) $= 3.84 \pm .02$ Rhombohedral or monoclinic distortion	
$SmAlO_3$			
Good pattern plus unknown phase, a_0 (equiv.) $= 3.71 \pm .01$ Probably rhombohedral distortion			

* Zachariasen (*Acta Cryst.*, **2**, 388, 1949) reported a tetragonal cell for $CeAlO_3$. Our results do not confirm this since the 111 reflection is a symmetrical doublet.

** Only a study of the first few reflections (at low angles) was made to classify the type of distortion (see Megaw, 1946). The a_0 (equivalent) reported for each of the perovskites is a somewhat arbitrary value arrived at by using a weighted average for each line which was split.

tures as low as 1430°. Only one preparation was obtained entirely as a glass: a charge of 1:1 molecular proportion in the system Y_2O_3—Ga_2O_3, quenched from 1880°, yielded a colorless glass with index of refraction $= 1.98 \pm .01$.

Liquids in the iron-oxide bearing systems crystallize very rapidly and could not be quenched to glass. Small charges in some cases undercool appreciably and then crystallize rapidly with an accompanying visible exothermic effect.

It should be noted that iron-oxide bearing systems in air cannot be considered as binary because of the presence of FeO in increasing proportion at higher temperatures. In several of the mixtures made up with Fe_2O_3 as a component, reduction in some runs was sufficient to yield a spinel phase. For the same reason, many of the earlier reports on ferrates are open to question, since no mention is made of the difficulty of maintaining iron in one valence state. The same qualification, based upon the

possibility of different valence states of cations as a function of temperature, applies to some other components of systems referred to, for example to cerium oxide.

By comparison of Figs. 2 and 3 it will be seen that $LaAlO_3$ occupies a chart position similar to that of $SrTiO_3$ (i.e. has similar ionic radius ratio); $LaAlO_3$ is the most nearly cubic‡ of the perovskite-structure combinations of double oxides of trivalent elements. If progressively smaller cations are substituted in the place of lanthanum, the structures are distorted more and more away from the simple cubic form. $LaAlO_3$ is isotropic or very nearly so, while the aluminates of cerium, neodymium and samarium exhibit low to moderate birefringence, greatest for $SmAlO_3$.

TABLE 3. POWDER X-RAY DIFFRACTION DATA FOR COMPOUNDS
CLASSED AS GARNET STRUCTURES

hkl	$3Y_2O_3:5Al_2O_3$		$Y_2O_3:Al_2O_3$*		$3Sm_2O_3:5Ga_2O_3$**	
	"d"	I/I_0	"d"	I/I_0	"d"	I/I_0
211	4.89	35	4.90	35	5.04	7
220	4.24	10	4.25	10		
321	3.21	20	3.202	25		
400	3.00	30	2.995	28	3.089	35
420	2.69	100	2.681	100	2.763	100
422	2.45	25	2.447	30	2.525	40
431	2.36	5	2.350	12	2.428	5
521	2.19	30	2.187	40	2.259	10
440	2.13	5	2.125	10	2.201	12
611	1.952	30	1.945	55	2.01	15
631	1.772	2	1.768	5		
444	1.734	25	1.7307	45	1.786	20
640	1.666	40	1.662	70	1.715	30
633	1.635	10	1.6313	25	1.68	2
642	1.608	35	1.602	65	1.6584	40
651	1.528	5	1.5234	10		
800	1.503	15	1.499	30	1.544	15

Unit cell edges for these compounds obtained from the above data and analogous data for other patterns are as follows: (given in Angstroms) $3Y_2O_3 \cdot 5Al_2O_3$ $a_0 = 12.01 \pm .02$; $Y_2O_3 \cdot Al_2O_3 = 11.989 \pm .005$; $Y_2O_3 \cdot Ga_2O_3 = 12.30 \pm .05$; $Sm_2O_3 \cdot Ga_2O_3$ $a_0 = 12.465 \pm .025$; $3Sm_2O_3 \cdot 5Ga_2O_3 a_0 = 12.355 \pm .015$; $Nd_2O_3 \cdot Ga_2O_3$ $a_0 = 12.54 \pm .02$.

* The anomalous decrease in cell size from $3Y_2O_3 \cdot 5Al_2O_3$ to $YAlO_3$ is noteworthy.

** The data are given for the 3:5 composition since the solid solution does not quite extend as far as $SmGaO_3$, and the latter pattern has some other lines in it.

‡ It would appear that $LaAlO_3$ is not perfectly cubic, since several lines in the back reflection region show an asymmetric broadening of the α_1 and α_2 reflections. The maximum splitting is such that the separation is less than half the separation between α_1 and α_2.

They still show the fundamental perovskite structure with some simple splitting of x-ray reflections, indicating a lower symmetry, but with no apparent doubling of the cell. All such compounds, though not isotropic, have been classified as perovskite structures. X-ray data are given in Table 2.

When yttrium is substituted in the place of samarium, we no longer obtain a perovskite structure at moderately high temperatures, but rather a garnet, of ideal formula $Y_3Al_2(AlO_4)_3$ or $3Y_2O_3 \cdot 5Al_2O_3$ (yttrogarnet), the structure of which has been worked out earlier (Yoder and Keith, 1951). A mixture of equal molecular proportions of Y_2O_3 and Al_2O_3 can be reacted by sintering to give a phase with the same structure; the garnet structure apparently is tolerant not only to Al^{3+} in both six-fold and four-fold coordination, but also to replacement of about half of the six-coordinated aluminum by yttrium, as represented by the formula $Y_3YAl(AlO_4)_3$. Yttrium, samarium, neodymium, and cerium oxides in combination with Ga_2O_3 similarly form intermediate compounds which have the garnet structure.

Above a temperature of about 1970° C. yttrogarnet inverts to a high form called yttroalumite, which is probably tetragonal. The indexing of the yttroalumite x-ray pattern arrived at by Dr. G. Donnay in a preliminary study (Yoder and Keith, 1951, p. 531) was found to be unsatisfactory; using Bunn type charts a more satisfactory cell was derived which is related to the earlier-determined cell by a simple doubling of the "a"-axis. In the present investigation nine other new compounds have been prepared which have essentially the same structure as yttroalumite but which form at lower temperatures; this group of isostructural compounds is referred to one of them, $YCrO_3$ as the type structure. We have not found any analogue to the $YCrO_3$ structure among double oxides of cations other than those of the trivalent group. The x-ray pattern bears a remote similarity to those of distorted perovskite structures, but the distortion is well beyond that which gives a simple splitting of the x-ray reflections of perovskite and there appears to be justification for classifying the $YCrO_3$ type structures separately. Powder diffraction data are listed in Table 4.

Extensive solid solution in both the $YCrO_3$ type structures and the garnet structures makes it difficult to decide whether the $YCrO_3$ type should be considered to have an ideal 1:1 molecular proportion rather than, say, a 3:5 molecular proportion. A final answer must await completion of phase equilibrium studies of the binary oxide systems involved. On the basis of preliminary studies in the system Sm_2O_3—Fe_2O_3 it is concluded that a 1:1 ideal molecular proportion is probably correct. The intermediate compound has the yttrium chromate structure and a preparation of 1:1 molecular proportion has a liquidus temperature about

TABLE 4. POWDER X-RAY DIFFRACTION DATA FOR $YCrO_3$-TYPE COMPOUNDS

hkl	$3Y_2O_3{:}5Al_2O_3$		$YCrO_3$		$SmCrO_3$		$NdFeO_3$		$SmFeO_3$		$NdScO_3$		$YFeO_3$		$LaScO_3$		$LaInO_3$	
	"d"	I/I_0	"d"	I/I_0	"d"	I/I_0	"d"	I/I_0	"d"	I/I_0	"d"	I/I_0	"d"	I/I_0	"d"	I/I_0	"d"	I/I_0
002	4.24	5	3.80	10			3.885(d)	15	3.867	7	3.98(d)	25						
102	3.70	45	3.754	10					3.83	7					4.07	30		
200	3.68	40			3.84(d)	15												
201	3.36	25																
112	3.32	20	3.389	35	3.43	15	3.478	7	3.445	10	3.56	5	3.427	15	3.63	7	3.707 / 3.2(d)	5 / VW
003	2.89	3	2.950	10	2.98	2			3.015	2								
103	2.67	40	2.750	35	2.75	25	2.783	20	2.797	25	2.88	20			3.017	15	2.96	25
212	2.62	100	2.67	100	2.675	100	2.738	100	2.72	100	2.825	100	2.78	20	2.867	100	2.903	100
220	2.59	30	2.607	40	2.615	30	2.714	20	2.67	20	2.78	20	2.694	100	2.73	10	2.85 / 2.79 / 2.72	30 / 5 / 5
113	2.51	25	2.585	20	2.593	20	2.62	5	2.628	2			2.622(d)	30				
203	2.26	3	2.485	5														
222	2.22	15	2.256	20	2.28	5				VW	2.405	5	2.270	7	2.42	7	2.455	5
213	2.16	25	2.222	12	2.227	10	2.259	7		VW	2.338	5	2.16(d)	7	2.36	15	2.30	5
302	2.12	20	2.143	20	2.2178	15	2.217	10		VW	2.28	10			2.33	20	2.27	15
104			2.125	7	2.146	10	2.18	7		VW	2.211	7	2.108	10	2.24	10		
312	2.05	15	2.094	20	2.113	10	2.15	10										
114	1.996	3	2.049	7	2.06	2												
321	1.972	3	1.998	3														
204	1.859	40	1.895	45	1.912	30	1.94(d)	35	1.933	30	1.977	30	1.920	20	2.025	50	2.053	70
400	1.845	30	1.877	35	1.899	25			1.918	5	1.953	5	1.895	20	1.973	25	2.014	5
214	1.806	20	1.852	20	1.866	10	1.886(d)	15	1.89	2	1.941	7	1.857(d)	15			1.993	10
331	1.694	2	1.838	25	1.855	20			1.873	7							1.87	12
412			1.685	30	1.701	10	1.74(d)	7	1.716	25	1.786	15	1.752	5	1.811	15	1.821	15
224	1.655	10									1.768	18	1.704(d)	20	1.781	15	1.698	25
304	1.640	25	1.664	7	1.692	20	1.713	15			1.727	2			1.666	50	1.686	15
314	1.605	10	1.626	10							1.650(d)	10			1.651	50	1.658	45

(d) indicates double reflection.

170° higher than that of the 3:5 composition and about 100° higher than that of the 5:3 composition. That is, there appears to be a maximum on the liquidus curve at a composition corresponding to $SmFeO_3$. Liquidus temperatures in the system Y_2O_3—Cr_2O_3 are too high to permit a similar study of the liquidus curve near $YCrO_3$ with available equipment.

Further work will be required in order to elucidate in detail the relationships among the garnet, perovskite, and $YCrO_3$ structures. It will be noted that perovskite structures give way to garnet and $YCrO_3$ structures as the tolerance factor is decreased below about 0.9; as the tolerance factor is further decreased, that is in combinations of smaller "A" cations with larger "B" cations, we move into a chart area in which cubic structures of the Tl_2O_3 type are obtained in the preparations of 1:1 molecular proportion (Fig. 3). In each case either one or both of the component oxides also has that structure, so that the 1:1 preparation should be considered as a member of a solid solution series rather than as an intermediate compound in the strict sense of the phase rule. In those cases in which both component oxides have the Tl_2O_3 structure, solid solution probably is complete.

At the extreme chart corner where the two combining cations represented are relatively large and of approximately the same effective radius, hexagonal structures of the La_2O_3 type are obtained in 1:1 preparations. At the opposite extreme chart corner, where are represented double-oxide combinations of two relatively small cations of approximately the same radius, structures are either the corundum type or the β-gallia type. In these cases (i.e. for La_2O_3, corundum, and β-gallia type structures) as in the case of the Tl_2O_3 structures discussed above, the structures obtained in 1:1 preparations are of the same type as that of one or both of the component oxides. The single known exception is the low temperature form of $GaAlO_3$ (Hill, Roy, and Osborn, 1952).

It will be noted that double-oxide combinations with trivalent bismuth as the "A" cation are not included in Fig. 3. $BiAlO_3$ and $BiCrO_3$ have been reported as having the perovskite structure (Naray-Szabo, 1943) and that structure would appear to be reasonable from consideration of the ionic radii. It was not found feasible to confirm the structures of double-oxide combinations with bismuth because the volatility of Bi_2O_3 makes it difficult to obtain solid state reactions with Al_2O_3 and Cr_2O_3. An investigation is being made of compounds formed hydrothermally at lower temperatures.

The ionic radius chart (Fig. 3) has not been extended to include boron. The ionic radius of B^{3+} is much smaller than that of Al^{3+} and the structures of double-oxides with boron are quite different. Mixtures corresponding to $LaBO_3$, YBO_3, and $InBO_3$ were prepared by the method used

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by Goldschmidt and Hauptmann (1932) and also by our usual methods. The present results confirm those of Goldschmidt and Hauptmann in regard to the formation and crystal structure of $InBO_3$ and $LaBO_3$; both form easily at 1000° C. The structure of $InBO_3$ was found to be of the calcite type with a somewhat larger unit cell than that reported by Goldschmidt. $LaBO_3$ formed by reaction at 600° and at 1000° has the aragonite structure (cell dimensions very similar to those of strontianite); it melts sharply at $1560 \pm 20°$ and crystallizes below that temperature to a high form which has a superficial resemblance to calcite, including similar birefringence and cleavage, but which is biaxial positive and has a powder pattern (Table 5) quite different from those of calcite and aragonite. There is a possibility of some compositional change due to loss of B_2O_3 but this was minimized by using very short heating time at the higher temperatures. No inversions were detected in the low temperature form up to 1050° C. Refractive indices for the high form were determined as: $\gamma(Na) = 1.860 \pm .003$, $\alpha(Na) = 1.820 \pm .003$.

YBO_3 is reported in the literature as having either the calcite structure or the vaterite structure, depending upon the temperature of formation

TABLE 5. X-RAY POWDER DIFFRACTION DATA FOR NEW BORATES

$LaBO_3$ (high form)		YBO_3	
"d"	I/I_0	"d"	I/I_0
5.64	7	4.375	30
3.91	20	3.277	100
3.10	100	3.06	10
3.01	90	2.62	60
2.86	5	2.195	10
2.54	7	1.885	35
2.13	10	1.82	25
2.085	3	1.73	20
2.07	2	1.631	7
2.01	15	1.532(d)	15
1.946	5	1.337	5
1.916	15	1.311	2
1.875	3	1.328	2
1.828	7	1.189	10
1.610	5		
1.51	10		
1.378	5		
1.281	5		
1.230	5		
1.207	10		
1.162	7		

(Goldschmidt and Hauptmann, *op. cit.*). The YBO_3 compound obtained in the present investigation exists in only one crystal form from room temperature to its melting point $(1580 \pm 20°)$; it has optical characteristics somewhat similar to those of calcite, but giving a positive uniaxial interference figure and an x-ray powder pattern (Table 5) which does not correspond to either the calcite type or the vaterite type as given by Brooks, Clark, and Thurston (1951). The refractive indices are $\alpha(Na) = 1.77 \pm .01 \ \gamma(Na) = 1.795 \pm .01$.

Mixtures of $CrBO_3$ composition did not yield an intermediate compound. After heating to 1000° C., the x-ray diffraction pattern showed the presence of only Cr_2O_3 as a crystalline phase. On prolonged heating (7 days), the B_2O_3 gradually volatilized and the Cr_2O_3 (originally very fine grained) was found to have grown into hexagonal crystals of much larger size (to 0.1 mm. diameter). A similar phenomenon was observed upon heating the $InBO_3$ mixture for a few minutes at 1700° C.; dissociation of the $InBO_3$ compound and volatilization of the B_2O_3, left behind well-formed yellowish brown cubes of In_2O_3. These observations suggest a method for growing the refractory oxides (and possibly some other compounds) into crystals large enough for single-crystal studies.

DISCUSSION OF RESULTS

A number of trivalent elements, including some which can exist in trivalent condition as well as in other valence states, were not included in the present study. However, the element combinations which have been studied are sufficiently representative of different ionic radius ratios to form a basis for predicting the probable structures in some cases. Actinium, with ionic radius slightly larger than that of lanthanum, as well as trivalent protoactinium and the trivalent ions of the transuranium elements, all slightly smaller than lanthanum, may form perovskite structures in double-oxide combinations with aluminum, gallium, chromium, and iron.

The 4f elements 63 to 66 inclusive, and trivalent thallium, with ionic radii between those of samarium and yttrium, may form garnet structures in double-oxide combinations with aluminum and gallium, and possibly $YCrO_3$ type structures with chromium and iron. In some cases a garnet structure may be stable at low temperatures and a $YCrO_3$ type structure at higher temperatures. Similar structural relations are possible for the double-oxides of elements 67 to 71 inclusive in combination with aluminum, gallium, chromium or iron. However, the smallest ion of the 4f group may more nearly fulfill size requirements for the formation of Tl_2O_3 type structures in double-oxide combinations with chromium and iron.

Other trivalent ions which have not been mentioned* have ionic radii in a range which suggests that they might form perovskite-type structures in double-oxide combinations with the largest of the "A" cations, e.g. with lanthanum (see Jonker and van Santen, 1948) and cerium. However, the Pauling radii place Sb^{3+} and V^{3+} closer to Sc^{3+} than to Fe^{3+}, that is in a chart area (Fig. 3) in which the $YCrO_3$-type structure would be more likely for combinations with La^{3+} and Ce^{3+}. All of the above suggestions should be qualified to the extent that predictions of probable structures are more likely to be correct for ions which have polarizabilities nearly the same as those of the cations whose double-oxide combinations have been studied, and on which the chart (Fig. 3) is based.

Goldschmidt, in his several publications, considered the importance of radius, polarizability and charge of an ion in determining the positions it could take in specific structures. The influence of ionic radius is discussed and illustrated in all textbooks on crystal chemistry. The present study does not include cations with sufficiently different polarizability to permit conclusions as to the effect of that variable. However, for the first time the effect of ionic charge can be demonstrated clearly; by comparison of Figs. 2 and 3 it can be seen that the extent of perovskite structures is more limited in the combinations of trivalent cations than in combinations of a bivalent and a tetravalent cation. The effect of cation charge ratio upon the lower limit of "t", the tolerance factor for perovskite structures, is as follows:

Compounds (A = larger cation)	Charge ratio, Z_A/Z_B	Lower Limit of "t"
$A^{3+}B^{3+}O_3$	1.0	0.89
$A^{2+}B^{4+}O_3$	0.5	0.77
$A^+ B^{5+}O_3$	0.2	0.71 to 0.81* (prob. closer to 0.71)

* Bracketed by the "t" values for $NaNbO_3$ (perovskite structure) and $LiNbO_3$ (corundum structure).

The so-called tolerance limits of Goldschmidt are therefore seen to be applicable only to compounds of cations with one combination of charges. Goldschmidt's original perovskite tolerance limits, for example, should be restricted to $A^{2+}B^{4+}O_3$, combinations and cannot be used indiscriminately for different charge combinations without appropriate modification.

Several discrepancies in the older literature have been clarified. For

* e.g. trivalent arsenic, antimony, vanadium, cobalt, and manganese.

example Goldschmidt (1927) listed $YAlO_3$ as having the perovskite structure and that listing has been copied in a number of later publications. Recently Wood (1951) noted the borderline position of $YAlO_3$ on the ionic radius chart between the perovskite structures and the corundum-ilmenite structures and raised the question as to which structure pure $YAlO_3$ would have. The present investigation shows that it has neither of these structures but forms a garnet structure which inverts to a $YCrO_3$ type structure at high temperature. Wood also commented on the anomalous position of $CaCeO_3$ and $CdCeO_3$; it has been shown that these compositions do not have the perovskite structure but contain members of solid-solution series which have the fluorite structure.

TABLE 6. PRELIMINARY MEASUREMENTS OF DIELECTRIC CONSTANT OF PRESSED DISCS OF SOME CRYSTALLINE COMPOUNDS PREPARED FOR THE INVESTIGATION OF DOUBLE OXIDES OF TRIVALENT ELEMENTS*

Preparation Number	Composition	Structure Type	Temperature Degrees C.	Dielectric Constant
104	$LaBO_3$	aragonite	-180	1.6
			25	13.5
			516	34.5
105	$InBO_3$	calcite	-180	3.6
			25	5.5
			562	21.5
63	$CeCrO_3$	perovskite	-180	4.0
			25	85
			165	665
84	$NdCrO_3$	perovskite		n.d.
		(too highly conducting to be measured)		
62	$SmAlO_3$	perovskite	-180	5.1
			25	5.9
			616	33
59	$CeAlO_3$	perovskite	-180	9.0
			25	209
			276	1796
67	$YAlO_3$	garnet solid solution	-180	1.8
			25	7
			467	366

* Measurements of Dielectric Constant by E. Francis and R. Eriks, Physics Department, Pennsylvania State University.

One of the reasons for undertaking a survey of crystal structures of double oxides as a function of ionic radii of the cations was to establish a basis for study of special properties of some of the compounds and the direction of change of properties as a result of substitution of cations of different radius. For example, an investigation is being undertaken of the variation of dielectric constant. Preliminary data for a few of the compounds (Table 6), based upon measurements made by E. Francis and R. Eriks of Dr. R. Pepinsky's laboratory, Pennsylvania State University, indicate that $CeAlO_3$ and $CeCrO_3$ may be of interest as dielectric materials. Both of those compounds have the perovskite structure. It should be emphasized that measurements were made on discs formed by compacting the powdered materials in a pellet press. No correction is made for porosity of the discs and the measurements of dielectric constant may be expected to be lower, as well as less significant, than measurements made on single crystals or crystal slices. Further work is needed in order to locate possible peaks on the curves of dielectric constant versus temperature.

Under contract with the Signal Corps, the investigation of ionic substitutions is being extended to include several other groups of multiple cation combinations than the 3 plus: 3 plus group, as well as some anion substitutions in the place of oxygen. It is believed that accumulation of data on general relationships between crystal structure types and electrical properties will contribute towards a basis for setting up a useful theory regarding the fundamental requirements for high dielectric constant and low power-factor.

Determination of the crystal structures of double oxides also has a bearing on studies of the natural occurrence of some comparatively rare elements. For example, those which form garnet structures in double-oxide combinations with more common elements may be found in appreciable quantity in natural garnets. Many of the new compounds, as well as the binary systems involved, thus offer potentially valuable studies in the fields of geochemistry and mineralogy as well as in the field of ceramic technology.

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