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MBO_3 Calcite-Type Borates of Al, Ga, Tl, and Rh

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The Al, Ga, and Tl isotypes of the known calcite-type borate $InBO_3$ as well as the $4d^6$ compound $RhBO_3$ of the same structure have been prepared at high pressure. Doping of $AlBO_3$ with traces of Cr gives pink crystals similarly to the formation of ruby from corundum. Properties of the above compounds are presented. In addition, crystal data for calcite-type borates, carbonates, and nitrates have been compiled and their relationships are discussed.

Introduction

The isotypism of borates, carbonates, and nitrates was pointed out by Goldschmidt and Hauptmann (*1*) in 1932. In this early work, $ScBO_3$ and $InBO_3$ were prepared by firing mixtures of $Sc(OH)_3$ or $In(OH)_3$ and H_3BO_3. Comparisons of their X-ray diffraction powder patterns with those of $ZnCO_3$ and $CdCO_3$ indicated these borates to have the calcite-type structure. In more recent work, Bernal et al. (*2*) prepared the series $Fe_{1-x}Ga_xBO_3$ ($0 < x \leqslant 0.8$) by fusion of the component oxides in a flux of Bi_2O_3 and confirmed the calcite structure in these borates. Other syntheses of MBO_3 compounds containing the $3d$ transition elements Sc (*3*), Ti (*4*), V (*4, 5*), Cr (*4–6*), and Fe (*7*), as well as Lu (*8, 9*) and Yb (*10*), the two smallest rare earths, have been reported in which these borates are also isotypes of this structure. Interest in the physical properties of VBO_3 (*5*), $CrBO_3$ (*5*), and $FeBO_3$ (*7, 11*) prompted a search for additional calcite-type borates. High-pressure syntheses have now been used to obtain the remaining group IIIA compounds $AlBO_3$, $GaBO_3$, and $TlBO_3$, as well as the $4d$ compound $RhBO_3$, all with this structure. Other high-pressure borates of Al and Ga were also obtained in the course of this work and will be reported separately.

Experimental

Reactions were carried out (1) at pressures of 25–65 kbar in platinum or gold capsules in a tetrahedral anvil device described previously (*12*), (2) at pressures of 5–30 kbar in boron nitride or welded platinum capsules in a piston–cylinder device similar to that of Boyd and England (*13*), and (3) under an external argon pressure of 3 kbar in sealed platinum or gold tubes. Reagent grade chemicals were used as reactants and were ground together in the desired ratios and pelleted prior to reaction. Following reaction at the desired temperatures and pressure, the products were extracted with hot water to remove soluble materials including excess B_2O_3 or H_3BO_3 and were then rinsed with acetone and air dried.

Single crystal data were obtained from precession photographs. X-ray powder diffraction patterns were taken at 25°C with a Debye–Scherrer camera or a Hägg–Guinier camera which used monochromatic $CuK\alpha_1$ radiation and a KCl internal standard ($a = 6.2931$ Å). Films were read on a David Mann film reader, Model No. 1222. Cell dimensions were refined by a least-squares method and showed a standard deviation of $\pm$ 0.001 Å or less.

Results

$AlBO_3$. Calcite-type $AlBO_3$ was obtained in an assortment of macrocrystalline habits including

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colorless powders, platelets, polyhedra, and rhombs by reaction of Al_2O_3 or $Al(OH)_3$ and B_2O_3 at atom ratios of Al:B of about 1:1.25 to 1:2 under a very wide range of high pressures. Typical synthesis conditions yielding this compound included reactions at (1) 65 kbars/1200°C-2 hr/cool 4 hr to 400°C/quench, (2) 30 kbars/800°C-6 hr/quench, and (3) 10 kbars/900°C-4 hr/quench. Reactions at lower pressures of 3–5 kbars gave the known borates $9Al_2O_3 \cdot 2B_2O_3$ (*14*) and/or $2Al_2O_3 \cdot B_2O_3$ (*14*). The latter phase was also formed in the reaction of $Al_2O_3/3H_3BO_3$ at 750°C and atmospheric pressure.

Oxygen analyses on polyhedral crystals obtained under reaction conditions (2) confirmed the formula $AlBO_3$; *Anal.* Calcd: O, 55.95. Found: O, 55.85. Single crystal X-ray data indicated that $AlBO_3$, like $InBO_3$, has rhombohedral symmetry in space group $R\bar{3}c$. Hexagonal cell dimensions $a_H = 4.463$ and $c_H = 13.746$ Å were obtained by refinement of both Guinier and Debye–Scherrer (Table I) X-ray powder data.

Although $AlBO_3$ was not isolated from syntheses run at pressures below 10 kbars, the pressure-quenched compound showed high thermal stability at ambient pressure with DTA measurements indicating decomposition around 1000°C. The decomposed product was the known orthorhombic $2Al_2O_3 \cdot B_2O_3$ phase (*14*). Crystals of $AlBO_3$ had a Knoop microhardness (KHN_{100}) in the range 1600–1800 (Al_2O_3, corundum, ~2100). No luminescence was noted under either short or long wavelength uv radiation. The infrared spectrum of $AlBO_3$ is similar to that of $InBO_3$ (*15*) in the regions around 1300–1100 cm^{-1} and 700 cm^{-1} because of contributions from the planar BO_3 anion. Shifts to lower frequencies observed in bands below 600 cm^{-1} may be attributed to the appreciably lower cation mass of Al vs In.

$AlBO_3$:Cr. By reaction under conditions described in the preceding section, but in the added presence of traces of Cr_2O_3 (Al:Cr ~ 1:0.005), $AlBO_3$ was doped to give pale-pink crystals of $AlBO_3$:Cr similarly to the formation of ruby from corundum. Hexagonal cell dimensions obtained from Guinier powder data, $a_H = 4.464$, $c_H = 13.750$ Å, indicated this $AlBO_3$:Cr to have a cell size just larger than that of the unmodified host.

Samples of calcite-type $AlBO_3$:Cr qualitatively showed red luminescence of moderate intensity when activated with 366 nm uv radiation. This fluorescence centered in a broad band (580–720 nm) with a maximum around 640 nm and superposed thereon were three narrow bands centering at 676, 690, and 704 nm. Moderate red-orange cathodo-luminescence was also noted upon bombardment *in vacuo* with low voltage ions. The infrared spectrum essentially duplicated that of unmodified $AlBO_3$.

$Al_xT_{1-x}BO_3$ Phases. In addition to the synthesis of pink, crystalline $AlBO_3$ doped with traces of Cr, mixed aluminum–transition-metal borates containing variable amounts of Fe, V, and Cr were also prepared. Polyphase products resulted and the calcite-type borates formed usually could not be isolated for characterization. Compositions were estimated from cell volumes of the intermediate calcite-type phases assuming Vegard's rule to apply.

Reaction of $Al_2O_3/Fe_2O_3/3.2\ B_2O_3$ at 65–25 kbars/1200–800°C gave dark, crystalline, mixed calcite-type phases in the composition range $Fe_{0.3-0.6}Al_{0.7-0.4}BO_3$ plus other borates. Qualitatively, none of these products showed a ferromagnetic transition to 1.7*K* using the Meissner technique (detection of rapid change in permeability with temperature). Small amounts of Al were introduced into $FeBO_3$ ($Fe_{1-x}Al_xBO_3$, $x < 0.05$) by reaction of $Fe_2O_3/0.2\ Fe(NO_3)_3 \cdot 9H_2O/0.05\text{–}0.1\ Al_2O_3/1.5\ B_2O_3$ at 65 kbars/800–1000°C. Dark-green fragmented crystals could be isolated. Magnetic measurements on the composition $Fe_{0.98}Al_{0.02}BO_3$ gave the values $\sigma_s = 4.3$ emu/g, $\mu_s = 0.088\ \mu_B$, $T_c = 347$ K as compared to $\sigma_s = 4.4$ emu/g, $\mu_s = 0.09\ \mu_B$, $T_c = 355$ K for dark-green crystals of unmodified $FeBO_3$ prepared similarly. The Al thus appears to act only as a diluent and brings about no change in the cant angle of the magnetic system so as to increase the effective magnetic moment.

Reactions of Al_2O_3/V_2O_3 or $Cr_2O_3/3.2\ B_2O_3$ were carried out under pressure as in the Al–Fe system. Dark, crystalline mixed calcite-type phases in the ranges $V_{0.75-0.25}Al_{0.25-0.75}BO_3$ and $Cr_{0.67-0.33}Al_{0.33-0.67}BO_3$ were isolated containing other borates. In the (Al,V)BO_3 compositions, Meissner measurements again indicated a dilution effect of Al in VBO_3 since its magnetic transition dropped from 32 K (*5*) to values around 13–9K.

$GaBO_3$. Although $GaBO_3$ has been reported (*16*) to show broad band luminescence upon excitation with short wave uv radiation, unit cell dimensions of this compound are not recorded. Calcite-type $GaBO_3$ was synthesized in the present work over a range of pressures in a

TABLE I

POWDER DIFFRACTION DATA FOR MBO_3 CALCITE-TYPE BORATES

	Al		Ga		Rh		Tl	
h k l	I/I_0	*d*	I/I_0	*d*	I/I_0	*d*	I/I_0	*d*
1 0 2	60	3.371	95	3.459	100	3.508	100	3.758
0 1 4	100	2.569	100	2.642	100	2.677	100	2.912
0 0 6	35	2.291	5	2.365	20	2.389	20	2.657
1 1 0	15	2.231	45	2.285	95	2.320	65	2.462
1 1 3	100	2.007	40	2.057	45	2.088	10	2.235
0 2 2	55	1.861	50	1.906	90	1.935	60	2.061
2 0 4	35	1.685	25	1.727	65	1.753	45	1.881
1 1 6	80	1.599	55	1.643	95	1.665	95	1.808
1 0 8	40	1.570	30	1.618	70	1.638		
1 2 1	10	1.453	5	1.487	–	–	–	–
2 1 2	30	1.429	25	1.462	75	1.486	60	1.581
1 2 4	35	1.345	30	1.377	70	1.399	70	1.496
0 1 10	–	–	5	1.334	30	1.351		
0 2 8	–	–	30	1.319	–	–	30	1.458
3 0 0	80	1.289			70	1.339	25	1.422
1 1 9	25	1.261	5	1.297	5	1.314	–	–
0 0 12	10	1.146	10	1.181	10	1.196	5	1.332
2 0 10	–	–	10	1.152	–	–	20	1.280
0 3 6	–	–			35	1.168	50	1.255
2 1 8	10	1.113	10	1.143	50	1.159		
2 2 0	–	–			–	–	10	1.233
2 2 3	10	1.084	5	1.110	–	–	–	–
1 3 2	2	1.059	5	1.084	25	1.101	40	1.172
1 1 12	–	–	15	1.048	50	1.064		
3 1 4	20	1.023			–	–	50	1.136
1 2 10	–	–	10	1.028	50	1.043		
2 2 6	20	1.003			–	–	20	1.119
1 0 14	–	–	20	0.9813	10	0.9937	10	1.103
4 0 2	–	–	5	0.9793	–	–	10	1.059
0 4 4	15	0.9302	10	0.9526	20	0.9670	20	1.032
1 3 8	25	0.9095	15	0.9329	30	0.9464	25	1.019
2 2 9	10	0.9010	5	0.9249	–	–	–	–
0 2 14	–	–	5	0.9015	–	–	15	1.007
3 2 2	10	0.8793	5	0.9001	30	0.9140	55	0.9730^a
2 3 4	10	0.8586	10	0.8801	–	–	30	0.9520^b
0 3 12	45	0.8561			50	0.8921	55	0.9730^a
1 1 15	5	0.8476	10	0.8737	–	–	–	–
3 1 10	–	–	5	0.8678	25	0.8800	30	0.9520^b
4 1 0	5	0.8434	5	0.8634	–	–	35	0.9325^c
4 0 8	15	0.8423			45	0.8765	10	0.9421
4 1 3	10	0.8295	5	0.8493	–	–	–	–
2 1 14	5	0.8149	10	0.8387	25	0.8495	35	0.9325^c
2 2 12	–	–	5	0.8213	25	0.8325	30	0.9054
1 4 6	30	0.7916	25	0.8109	60	0.8231	40	0.8803
3 2 8	15	0.7880	10	0.8079	30	0.8198		
a_{Hex}:	4.463 Å		4.568 Å		4.640 Å		4.932 Å	
c_{Hex}:	13.746 Å		14.182 Å		14.351 Å		15.988 Å	

^{a,b,c} = multiple reflections.

manner similar to that used to prepare $AlBO_3$. In contrast to $AlBO_3$, however, it was also possible to obtain $GaBO_3$ at atmospheric pressure by firing $Ga_2O_3/3H_3BO_3$ at 750°C for 48–72 hr.

Oxygen analyses on white microcrystals obtained from the reaction of $Ga_2O_3/6H_3BO_3$ at 30 kbars/900° C/6 hr/quench confirmed the formula $GaBO_3$; *Anal.* Calcd: O, 37.35. Found: O, 37.21, 37.02. X-ray diffraction powder data (Table I) indicated the calcite-type structure and refinement gave the hexagonal cell dimensions $a_H = 4.568$, $c_H = 14.182$Å.

Crystals of $GaBO_3$ showed the same high thermal stability as noted for $AlBO_3$. DTA measurements indicated decomposition to occur around 1000°C with β-Ga_2O_3 being the end product isolated. The white luminescence reported by Blasse and Bril (*16*) for $GaBO_3$ was observed in some but not all the samples prepared in this study. No correlation of this phenomenon with synthesis conditions was noted. The infrared spectrum of $GaBO_3$ more closely resembles that of $InBO_3$ than that of $AlBO_3$, as would be expected from the respective cation masses.

$GaBO_3$:Cr. Doping of $GaBO_3$ with Cr (Ga:Cr $\sim$ 1:0.005) was achieved in the manner used to prepare $AlBO_3$:Cr. In contrast to the pink color obtained in this latter borate (and as in Al_2O_3:Cr), the resultant crystals were light green. This green coloration also occurs in Cr-doped α-Ga_2O_3 prepared at high pressure (*17*) and is attributed to the difference in crystal field splitting due to the difference in size of the Al^{+3} and Ga^{3+} cations. Certain of the $GaBO_3$:Cr samples were qualitatively observed to luminesce a faint red when irradiated with short- (but not with long-) wave uv.

$TlBO_3$. Reaction of $TlNO_3/0.5$–$1\ B_2O_3$ at 65 kbars/1000°C–2 hr/cool 4 hr to 400°C/quench gave a product that after hot water extraction comprised a mixture of brown and white crystals. The former were not identified but the white crystals gave an X ray diffraction powder pattern (Table I) that could be indexed in the manner of the calcite-type MBO_3 compounds of Al, Ga, and In thus indicating formation of $TlBO_3$, the last member of this series. Refinement of the data gave the hexagonal cell dimensions $a_H = 4.932$, $c_H = 15.988$ Å.

In this reaction, the NO_3^- moiety in $TlNO_3$ acts as an oxidizing agent to convert Tl^+ to Tl^{3+} prior to formation of $TlBO_3$. This oxidation may be enhanced by the hydrous conditions that pertain in these syntheses since rigorously dried reactants were not used. At the lower reaction temperature of 600° instead of 1000°C, the reaction under pressure failed to produce $TlBO_3$ but gave the high-pressure corundum form of Tl_2O_3 (*18*) instead.

$RhBO_3$. In addition to the calcite-type MBO_3 compounds of Al through Tl, the high-pressure synthesis techniques used herein have also yielded a new transition-metal isotype in this borate series. Reaction of $Rh_2O_3/3.7\ H_3BO_3$ at 65 kbars/800°C–6 hr/quench gave a mixture of dark crystals plus a sludge that could be dispersed away in water, leaving prismatic, red-brown crystals up to 0.5 mm in length. The same crystals formed from the reactants $RhCl_3/3\ NaBO_2 \cdot 4H_2O$ but Rh metal was also isolated. Oxygen analyses on the red-brown crystals confirmed the formula $RhBO_3$; *Anal.* Calcd: O, 29.68. Found: O, 29.16. X-ray diffraction powder data (Table I) indicated the calcite-type structure and refinement gave the hexagonal cell dimensions $a_H = 4.640$, $c_H = 14.351$ Å. In contrast to the MBO_3 compounds of V (*5*), Cr (*5*), and Fe (*7*), magnetic susceptibility data showed no ordering to take place in $RhBO_3$ down to 4.2 K. Crystals of $RhBO_3$ had a high Knoop microhardness (KHN_{100}) of around 2500 (SiC $\sim$ 2500).

Discussion

Luminescence. From limited observations in this work, the luminescent behavior of the calcite-type compounds $AlBO_3$ and $GaBO_3$, both unmodified as well as doped with Cr, appears to resemble that reported (*16, 19*) for the compounds $YAl_3B_4O_{12}$ and $YGa_3B_4O_{12}$ in the related huntite-type structure. Thus $AlBO_3$ and $YAl_3B_4O_{12}$ fail to show fluorescence emission under short- or long-wave uv excitation, whereas; both Ga analogs show broad band (white) luminescence under short-wave uv excitation. In $YAl_3B_4O_{12}$:Cr and $YGa_3B_4O_{12}$:Cr, the Cr^{3+} emission (*19*) consists of two broad bands, a very weak one centering around 500 nm and a strong one around 700 nm with two sharp lines superposed thereon at 682 and 685 nm for the Al and at 690 and 692 nm for the Ga species, respectively. Less precise data suggest a similar situation to pertain for $AlBO_3$:Cr in which a strong, broad band centering around 640 nm has superposed thereon three narrow bands centering at 676, 690, and 704 nm. No data were obtained upon $GaBO_3$:Cr.

TABLE II

CRYSTAL DATA[a] FOR CALCITE-TYPE NITRATES AND CARBONATES

MZO_3	Cation[b] r, Å	Hex. cell dims., Å a	c	Room temp., c/a
$LiNO_3$	0.74	4.692	15.206	3.24
$NaNO_3$	1.02	5.070	16.829	3.32
$AgNO_3$	1.15	—	—	3.23[c]
KNO_3	1.38	—	—	3.42[c]
$RbNO_3$	1.49	5.483	21.410	3.90[d]
$NiCO_3$	0.690	4.5975	14.723	3.20
$MgCO_3$	0.720	4.6330	15.016	3.24
$CoCO_3$	0.745[e]	4.6581	14.958	3.21
$ZnCO_3$	0.750	4.6528	15.025	3.23
$FeCO_3$	0.780[e]	4.6887	15.373	3.28
$MnCO_3$	0.830[e]	4.7771	15.644	3.28
$CdCO_3$	0.95	4.9204	16.298	3.31
$CaCO_3$	1.00	4.9899	17.064	3.42

[a] Ref. 20.
[b] Ref. 21.
[c] Extrapolated to room temperature.
[d] At 250°C.
[e] High spin state.

Crystal Data. The structure of the isotypic, rhombohedral, calcite-type MZO_3 borates, carbonates, and nitrates is depicted by Wyckoff (*20*) as basically a rocksalt-like arrangement of M^{n+} cations and ZO_3^{n-} anions distorted by the spatial requirements of the latter. This cubic-type of packing may be regarded as one of the limits of this structure wherein the anions and cations are similar in size to each other, and, on a hexagonal basis, the ideal *c*/*a* ratio has a value of 4.90. The other limit may be regarded as the $LiNbO_3$-type wherein the cation is much smaller than the complex anion. In this arrangement, essentially a hexagonal close-packing of the oxygen atoms in the ZO_3^{n-} anion occurs with the cations located in the interstices. The ideal *c*/*a* ratio has a value of 2.82.

A brief compilation of crystal data for calcite-type nitrates and carbonates is given in Table II followed by a more detailed listing for borates in Table III. In both tables, the compounds are listed in the order of increasing cationic radius (*21*) for each anion grouping. Examination of the *c*/*a* values shows that all three sets of compounds are intermediate between the limiting structures discussed above since they have ratios at room temperature that range from 3.24 to 3.42, 3.20 to 3.42, and 3.08 to 3.32, respectively, for the nitrates, carbonates, and borates. The general trend is an increase in *c*/*a* as the cation size increases. It thus appears that in the calcite structure, the presence of large cations tends to force the structure toward a cubic, NaCl-type of packing, whereas smaller cations allow a collapse in the *c* direction of this array so as more

TABLE III

CRYSTAL DATA FOR CALCITE-TYPE BORATES

MBO_3	Effec. Ionic radius (a) r, Å	r^3, $Å^3$	Hex. cell dims., Å a	c	c/a	Unit cell vol., $Å^3$	Electron confign.	Reference
Al	0.530	0.149	4.463	13.746	3.08	237.1	$2p^6$	b
Cr	0.615	0.233	4.580	14.243	3.11	258.7	$3d^3$	c
Ga	0.620	0.238	4.568	14.182	3.11	256.3	$3d^{10}$	b
V	0.640	0.262	4.621	14.516	3.14	268.4	$3d^2$	c
Fe	0.645	0.268	4.624	14.470	3.13	267.9	$3d^5$	d
Rh	0.665	0.294	4.640	14.351	3.09	267.6	$4d^6$	b
Ti	0.67	0.30	4.670	14.90	3.19	281.4	$3d^1$	e
Sc	0.745	0.413	4.759	15.321	3.22	300.5	$3p^6$	f
In	0.800	0.512	4.823	15.456	3.21	311.4	$4d^{10}$	g
Lu	0.861	0.638	4.915	16.211	3.30	339.2	$4f^{14}$	b, g, h
Yb	0.868	0.654	4.924	16.322	3.32	342.7	$4f^{13}$	i
Tl	0.885	0.693	4.932	15.988	3.24	336.8	$5d^{10}$	b

[a] Ref. 21. [b] This work. [c] Ref. 5. [d] Ref. 7. [e] Ref. 4. [f] Ref. 3. [g] Ref. 8. [h] Ref. 9. [i] Ref. 10.

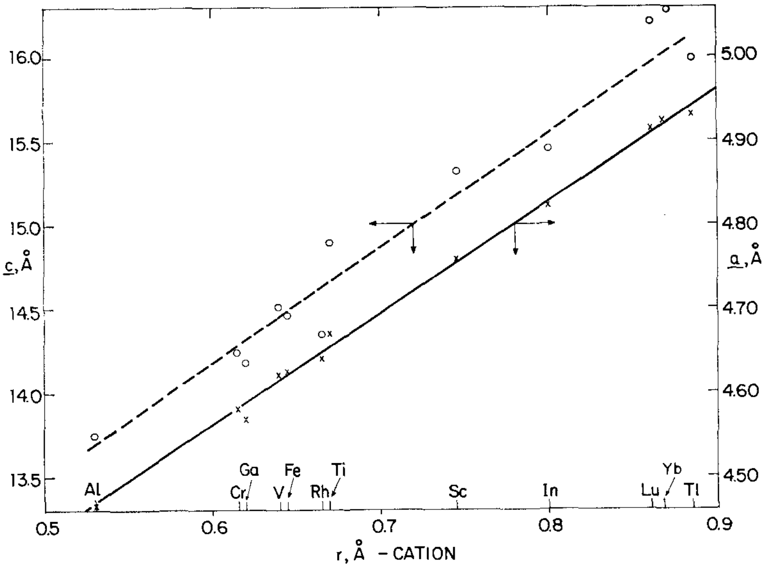

FIG. 1. Hexagonal cell dimensions of calcite-type borates vs. cation radii.

closely to simulate a hexagonal type of oxygen close-packing. The degree of ionicity of the specific cation also contributes in a secondary way to the packing in this structure since the more covalent of two ions of similar size is seen to lead to a smaller value of c/a. For example, this effect appears to pertain for $AgNO_3$, $CdCO_3$, and $RhBO_3$, $InBO_3$, and $TlBO_3$.

A plot of effective cationic volume vs unit cell volume has been presented by Prewitt et al. (*18*), for an M_2O_3 corundum series of compounds containing nine of the twelve cations present in the calcite-type borates listed in Table III. In this compilation, a well-defined linear relationship exists between cell volumes and cubed cation radii for this wide range of cations except for the compound Tl_2O_3 which appears to have an anomalously low cell volume. If a similar plot is made for the calcite-type borates, however, the data show considerable scatter and no clear linear-type of volume relationship is apparent. In Fig. 1, plots of hexagonal cell dimensions a and c vs appropriate cation radii would suggest from the linearity of a vs r as opposed to the irregularity of c vs r that the anomalous volume relationship of the borates arises as a consequence of the manner in which the cations pack in the c direction of this rhombohedral lattice and tend toward one limiting structure or the other, as discussed previously. In contrast, in the corundum structure a much more rigid adherence to hexagonal close-packing of the oxygen atoms pertains which would lead to the observed linear r^3 vs volume relationship.

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References

1. V. M. GOLDSCHMIDT AND H. HAUPTMANN, *Nach. Ges. Wiss. Göettingen Math.-Phys. Kl.* 53, (1932).
2. I. BERNAL, C. W. STRUCK, AND J. G. WHITE, *Acta Crystallogr.* **16**, 849 (1963).
3. A. BIEDL, *Amer. Mineral.* **51**, 521 (1966).
4. H. SCHMID, *Acta Crystallogr.* **17**, 1080 (1964).
5. T. A. BITHER, C. G. FREDERICK, T. E. GIER, J. F. WEIHER, AND H. S. YOUNG, *Solid State Commun.* **8**, 109 (1970).
6. N. C. TOMBS, W. J. CROFT, AND H. C. MATTRAW, *Inorg. Chem.* **2**, 872 (1963).
7. J. C. JOUBERT, T. SHIRK, W. B. WHITE, AND R. ROY, *Mater. Res. Bull.* **3**, 671 (1968).
8. E. M. LEVIN, R. S. ROTH, AND J. B. MARTIN, *Amer. Mineral.* **46**, 1030 (1961).

9. S. C. Abrahams, J. L. Bernstein, and E. T. Keve, *J. Appl. Crystallogr.* **4**, 284 (1971).
10. H. J. Meyer and A. Skokan, *Naturwissenschaften* **58**, 566 (1971).
11. A. J. Kurtzig, R. Wolfe, R. C. LeCraw, and J. W. Nielsen, *Appl. Phys. Lett.* **14**, 350 (1969).
12. A. W. Sleight and T. A. Bither, *Inorg. Chem.* **8**, 566 (1969).
13. F. R. Boyd and J. L. England, *J. Geophys. Res.* **65**, 741 (1960).
14. H. Scholzo, *Z. Anorg. Allg. Chem.* **284**, 272 (1956).
15. C. E. Weir and R. A. Schroeder, *J. Res. Nat. Bur. Stand.* **68A**, 465 (1964).
16. G. Blasse and A. Bril, *J. Inorg. Nucl. Chem.* **29**, 266 (1967).
17. J. P. Remeika and M. Marezio, *Appl. Phys. Lett.* **8**, 87 (1966).
18. C. T. Prewitt, R. D. Shannon, D. B. Rogers and A. W. Sleight, *Inorg. Chem.* **8**, 1985 (1969).
19. G. Blasse and A. Bril, *Phys. Status Solidi* **20**, 551 (1967).
20. R. W. G. Wyckoff, "Crystal Structures," Vol. 2, Chap. VII, A, Interscience Publishers, New York (1964).
21. R. D. Shannon and C. T. Prewitt, *Acta Crystallogr.* **B25**, 925 (1969); Ibid., **B26**, 1046 (1970).