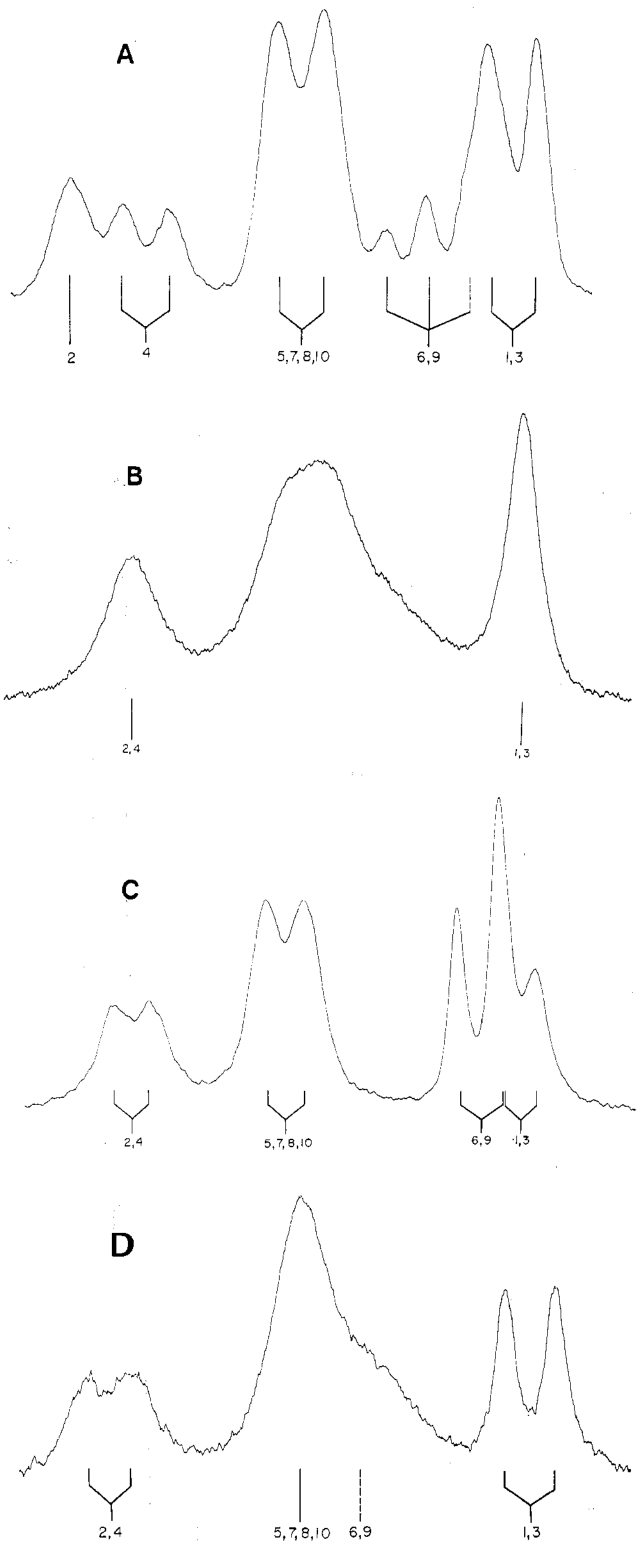

Figure 1.—^{11}B nmr spectra (32.1 Mc) of (A) $Rb_2(2\text{-}BrB_{10}H_{12}CN)$, (B) $1,2,3,4\text{-}D_4B_{10}H_8[S(C_2H_5)_2]_2$, (C) $B_{10}H_{12}(C_2H_5NC)_2$, and (D) 5,6,7,8,9,10,bridge-$D_8B_{10}H_4[S(C_2H_5)_2]_2$ (partially deuterated).

$B_{10}H_{12}$(ligand)$_2$ compounds (see Table I) indicates that the variance of the 2,4 (4.5 ppm), 5,7,8,10 (4.1 ppm), and 1,3 (6 ppm) positions is far less than that observed for the 6,9 (14 ppm) positions. All other factors being equal, the 6,9 doublet appears to move to higher field as the base strength of the attached ligand increases. Further studies may indicate that these general trends are applicable to all compounds of the 2632, $B_{10}H_{14}^{2-}$ type.

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CONTRIBUTION FROM THE DIVISION OF MINERAL CHEMISTRY,
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Calcium Indate, an Isotype of Calcium Ferrite and Sodium Scandium Titanate

BY A. F. REID

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The calcium ferrite structure type,[1,2] characterized by an orthorhombic unit cell and a short (3 A) *b* axis, has been established for a number of AB_2O_4 compounds including $SrFe_2O_4$,[1] CaV_2O_4,[2] β-$CaCr_2O_4$,[2] Eu_3O_4,[3] $CaSc_2O_4$,[4] and $MgSc_2O_4$,[5] and powder patterns also indicate isomorphism for a series of compounds where atom A is Ba or Sr and atom B is a rare earth.[6-8]

The calcium ferrite structure is built up of double blocks of edge-shared octahedra, extending infinitely in the *b*-axis direction, with each double string joined by octahedral corners to other double strings in such a way as to produce tunnels large enough to accommodate the calcium atoms. An alternative arrangement of double blocks is found in the calcium titanate ($CaTi_2O_4$) structure[9-11] which has similar tunnels but a different edge-sharing arrangement fitted within an orthorhombic unit cell with axes very similar to those of $CaFe_2O_4$.

In the course of our work on the reasons for variations in double-block arrangements we have reexamined calcium indate, $CaIn_2O_4$, variously reported to have space group either Pca2$_1$ or Pbcm[12] or, on the basis of powder pattern and density, to be of calcium ferrite type.[6] Structure factor calculations show it in fact to be of calcium ferrite structure type, space group Pnma, isomorphous with calcium scandate[4] and with sodium scandium titanate.[13]

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Experimental Section

$CaIn_2O_4$ was prepared[6,12] by heating stoichiometric amounts of 99.99% In_2O_3 with Analytical reagent grade $CaCO_3$, first at 1000°, then at 1200° for 15 hr, and after further grinding, at 1200° for a further period of 15 hr to ensure good crystallization for diffraction intensity measurements. After the initial weight loss due to $CaCO_3$ decomposition, further weight loss was less than 0.2%, and it has been shown[12] that, from 45 to 55 mole % of CaO, $CaIn_2O_4$ is the only CaO–In_2O_3 compound formed at temperatures up to 1300°. The calculated density for 4 formula units per unit cell is 6.34 g cm^{-3}, and a value of $d^{22}{}_4$ 6.30 g cm^{-3} has been found.[6] $CaFe_2O_4$ and $CaSc_2O_4$ samples were similarly prepared at 1300°.

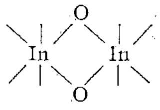
Powder diffraction data were obtained with a Philips diffractometer, using Ni-filtered Cu Kα radiation and a Geiger counter detector, scans being made at 0.125°/min. Intensities were determined by measurement of diffraction peak areas. Lattice parameters were determined by inclusion of silicon powder (a_0 = 5.4307 A) as an internal standard in a separate sample.

After preliminary indexing, least-squares lattice parameter and index selection programs were employed to determine final lattice parameters and indices. All observed peaks could be indexed, with a standard deviation between $\sin^2 \theta_{obsd}$ and $\sin^2 \theta_{calcd}$ of 9.7×10^{-5}. Structure factors were calculated employing $CaSc_2O_4$ fractional atomic coordinates[4] and the averages of the individual anisotropic temperature factors found for $NaScTiO_4$[13] as individual isotropic temperature factors.

Results and Discussion

The observed and calculated intensities are shown in Table I. The intensity discrepancy factor, $R_{I_o} = \Sigma|I_o - I_c|/\Sigma I_o$, was 14.3% and for 30 noncoincident reflections (omitting the very weak reflection 008) the structure factor discrepancy was 8.8%. Alterations from the $CaSc_2O_4$ fractional coordinates[4] of more than 0.005 for metals or 0.008 for oxygens sharply increased these discrepancies, and it is evident that $CaIn_2O_4$ and $CaSc_2O_4$ are strictly isomorphous. $NaScTiO_4$ was found[13] to have metal atom positions within 0.002 and, except for O(2), oxygen atom positions within 0.008 of those for $CaSc_2O_4$. Lattice parameters for several $CaFe_2O_4$ isotypes are given in Table II. Those for $CaFe_2O_4$[1] and $CaSc_2O_4$[4,14] were redetermined in the present work using the same procedures as for $CaIn_2O_4$. The a_0 value is somewhat different from that of Schwarz and Bommert,[6] although b_0 and c_0 values agree closely with theirs. In view of the consistency of the results in Table I, the present value is preferred.

The unit cell volume of $CaIn_2O_4$ is significantly greater than that of $CaSc_2O_4$, and the 0.075 A increase in the b axis is the actual increase in the In-to-In separation in the configuration



Bond length calculations based on the present lattice parameters show the average indium–oxygen distance to be 0.04 A greater than that for scandium–oxygen, Table III, rather than equal to it as indicated in ionic radii tabulations.[15]

TABLE I

POWDER DIFFRACTION DATA FOR $CaIn_2O_4$[a]

h	k	l	d_{obsd}	d_{calcd}	I_{obsd}	I_{calcd}
0	0	2	5.647	5.645	17	20
1	0	2	4.870	4.872	115	155
2	0	0	4.823	4.821	132	211
2	0	2	3.669	3.666	20	24
0	0	4	2.825	2.823	170	186
3	0	2	2.793	2.793	376	391
1	1	2	2.684	2.682	390	405
2	1	0	2.674	2.674	175	178
0 2	1 0	3 4	2.439	2.444 2.436	42	36
2	1	2	2.414	2.417	19	12
1	1	3	2.370	2.369	44	38
3	1	1	2.228	2.228	16	19
4	0	2	2.216	2.217	16	14
1	1	4	2.071	2.071	46	42
2	1	4	1.943	1.941	190	155
4	1	0	1.928	1.928	123	119
4	1	1	1.899	1.901	20	19
0	0	6	1.882	1.882	6	7
0 1 3	1 0 0	5 6 5	1.847	1.848 1.847 1.848	22	20
4 5	1 0	2 2	1.825	1.825	39	39
2	0	6	1.753	1.753	30	26
3	0	6	1.624	1.624	64	54
0 6	2 0	0 0	1.606	1.607 1.607	108	94
1	1	6	1.602	1.601	93	77
4 5	1 0	4 4	1.592	1.592	108	105
5	1	2	1.587	1.587	91	58
2	1	6	1.539	1.539	35	30
1 2	2 2	2 0	1.524	1.526 1.524	22	21
0	0	8	1.4114	1.4114	7	33
0 1 6	2 0 0	4 8 4	1.3963	1.3964 1.3967 1.3965	90	77
3	2	2	1.3926	1.3927	97	76
4 5	1 0	6 6	1.3462	1.3468	27	26
3	0	8	1.2922	1.2923	11	9
1 6	1 1	8 4	1.2808	1.2808 1.2807	18	20
2	1	8	1.2480	1.2482	14	12
5	1	6	1.2422	1.2421	15	11
7	1	2	1.2351	1.2352	33	32
1 3 6	2 2 1	6 5 5	1.2122	1.2122 1.2124 1.2125	9	8
5 8	2 0	2 0	1.2058	1.2058 1.2051	13	18
2	2	6	1.1846	1.1845	8	10
3	2	5	1.1421	1.1422	27	28
4 5	1 0	4 8	1.1392	1.1389 1.1389	28	19
6	2	0	1.1362	1.1361	20	18

[a] Cu Kα_1, λ 1.5405 A; Si internal standard, a_0 = 5.4037 A.

TABLE II

LATTICE PARAMETERS[a] FOR $CaFe_2O_4$ ISOTYPES, SPACE GROUP Pnma

Compd	$a \pm 0.004$, A	$b \pm 0.003$, A	$c \pm 0.005$, A	$V \pm 0.1$, A^3
CaF_2O_4	9.217	3.018	10.702	298.2
$CaSc_2O_4$	9.460	3.138	11.110	329.8
$CaIn_2O_4$	9.461	3.213	11.292	349.8
$NaScTiO_4$	9.277	3.048	10.917	308.7

[a] Cu radiation, Kα_1 1.5405 A; Si internal standard, a_0 = 5.4307 A.

TABLE III

OCTAHEDRAL METAL[a]–OXYGEN DISTANCES IN $CaIn_2O_4$ AND $CaSc_2O_4$ (±0.03 A)

	$CaIn_2O_4$	$CaSc_2O_4$
M(1)–O(1)[b]	2.18	2.14
M(1)–O(3)	2.13	2.10
M(1)–O(4)[b]	2.19	2.15
M(1)–O(4′)	2.06	2.03
M(2)–O(2)[b]	2.18	2.14
M(2)–O(2′)	2.19	2.15
M(2)–O(3)[b]	2.09	2.05
M(2)–O(1)	2.22	2.18

[a] M(1) and M(2) are the two different crystallographic sites occupied by In or Sc. [b] These distances occur twice.

Cruickshank, Taylor, and Glasser[12] in reporting $CaIn_2O_4$ not to be of calcium ferrite structure type based their indexing on a single crystal obtained from a calcium indate–lithium fluoride mixture. However, their powder data, allowing for the absence of an internal standard, are consistent with the present data in Table I. It is possible that for their single crystal a charge compensation substitution of F for O and Li for Ca, even in small amount, could have altered the internal symmetry of the unit cell and thus the arrangement of double blocks in the structure.

Acknowledgments.—Lattice parameter and structure factor calculations were performed with the Elliott 803 computer of the Division of Mineral Chemistry,

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The Rapid Interaction between Sodium Chlorite and Dissolved Chlorine[1]

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The reactions

$$2HClO_2 + HClO \longrightarrow 2ClO_2 + Cl^- + H_2O + H^+ \quad (1)$$

$$2HClO_2 + Cl_2 \longrightarrow 2ClO_2 + 2Cl^- + 2H^+ \quad (2)$$

are interesting not only by themselves but in that they may play a key role in the oxidation reactions of metal ions by chlorine-containing oxidizing agents.[2-5] Reactions 1 and 2 have been found inevitably to be accompanied by reactions which lead to the formation of ClO_3^-, for example

$$HClO + HClO_2 \longrightarrow ClO_3^- + Cl^- + 2H^+ \quad (3)$$

We have observed that the lower the concentration of $HClO_2$, the more ClO_3^- that is produced. However, the addition of the product ClO_3^- has little or no influence on the over-all course of reaction 1, 2, or 3.

When $HClO_2$ is oxidized by dissolved Cl_2, less ClO_3^- is formed than when HOCl is the oxidizing agent (*i.e.*, the stoichiometry approaches that given by reaction 2). Reaction 2 is considerably faster than reaction 1.

Kinetic studies on both reactions 1 and 2 which are indeed rapid are complicated by the fact that of all the species involved, only ClO_2 can be conveniently determined. This fact coupled with the concentration dependence of the stoichiometry allows only qualitative observations to be reported at this time. It should be pointed out that these qualitative observations themselves are sufficient to provide verification for the model used to understand the mechanism for the production of chlorate in the uranium(IV)–chlorite[2a,3] and in the vanadium(II)–chlorite reactions.[4]

Experimental Section

All the chemicals and analytical procedures used for this study have been described elsewhere.[2b,4] The concentration of dissolved chlorine dioxide was measured spectrophotometrically. The molar absorbance was calculated to be 1240 M^{-1} cm^{-1} at 360 mμ.[5] The rate of formation of dissolved chlorine dioxide was followed by means of the rapid mixing apparatus described by Thompson and Gordon.[6]

Three different procedures were used to initiate the reaction between sodium chlorite and the oxidizing agents used (dissolved chlorine or hypochlorite). The first procedure involved the rapid acidification of a slightly basic mixture of sodium chlorite and sodium hypochlorite by the addition of perchloric acid of the appropriate concentration. The second procedure involved the rapid addition of aqueous sodium chlorite to an acidic solution of hypochlorous acid. The third procedure involved the addition of aqueous sodium chlorite to an acidic solution of dissolved chlorine. In all cases, a 2-cm spectrophotometer cell was stoppered with a rubber serum cap, and the reagent was added by means of the rapid mixing syringe which has been shown to have a mixing time of 30 msec.[6]

Results and Discussion

The reaction between sodium chlorite[7] and hypochlorous acid has been discussed by Taube and Dodgen.[8] The results of our study of the stoichiometry of reaction 1 and the subsequent formation of chlorate are shown in Table I.

TABLE I
THE REACTION BETWEEN SODIUM CHLORITE AND HYPOCHLOROUS ACID[a]

10^4[NaOCl), M	10^4[NaClO$_2$], M	10^4[ClO$_2$][b] produced, M
15.0	6.0	2.5 ± 0.1[c]
7.5	3.0	0.60 ± 0.10[c]
3.0	3.0	0.49 ± 0.09[c]
1.5	3.0	0.42 ± 0.08[c]
1.5	6.0	2.4 ± 0.05[c]
1.5	15.0	3.8 ± 0.04[c]
1.5	30.0	4.3 ± 0.04[c]
. . .	30.0	0.03[e]
15.0	3.0	0.84 ± 0.03[d]
7.5	3.0	1.1 ± 0.1[d]
3.0	3.0	1.4 ± 0.1[d]
1.5	6.0	2.8 ± 0.1[d]
1.5	15.0	3.5 ± 0.1[d]

[a] Final acidity was 0.20 M $HClO_4$. [b] Each data point is the average of several experiments and the errors are deviations from the mean. [c] Rapid acidification of basic mixture of sodium chlorite and sodium hypochlorite. [d] Rapid addition of aqueous sodium chlorite to an acidic solution of hypochlorous acid. [e] Acidification of sodium chlorite in the absence of other oxidizing agents such as chlorine. Result reported after 20 sec. After 5 min only 1.25×10^{-4} M ClO_2 was produced. For additional results of the disproportionation of chlorous acid see the work of Kieffer.[5]

These data show that there is a marked influence on the stoichiometry as the amount of excess oxidizing agent is changed. However, as soon as sodium chlorite is in excess, the production of chlorine dioxide markedly improves. Actually, the theoretical amount predicted by eq 1 is exceeded, which perhaps can be explained by a chlorine or hypochlorous acid catalysis of the disproportionation of sodium chlorite. The difference in yield of chlorine dioxide as the method of mixing is changed suggests that the chlorite–hypochlorite or

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[1] This research was supported in part by Grant No. 14-0001-01-405 from the Office of Saline Water.

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