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Crystal Chemistry of Sodium Scandium Titanate, $NaScTiO_4$, and Its Isomorphs[1]

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$NaScTiO_4$, $NaFeTiO_4$, $NaScSnO_4$, $NaFeSnO_4$, $NaScZrO_4$, and $NaScHfO_4$, as well as high-pressure $NaAlGeO_4$, are strictly isomorphous with the orthorhombic calcium ferrite type structure, space group Pnma. Each pair of tri- and quadrivalent elements randomly occupies two sets of crystallographically nonequivalent octahedral positions in the structure, the local site symmetries of which are almost identical. Uniform bond lengths and normal thermal vibration parameters for the randomized atoms in $NaScTiO_4$, determined by single-crystal structure analysis, are interpreted to mean that the randomness of the ions Sc^{3+} and Ti^{4+} leads to a real averaging of ionic sizes. No calcium ferrite structure was found by replacing Na with Li, K, Rb, or Cs nor for the $NaA^{3+}B^{4+}O_4$ compounds where A^{3+} = Mn, Cr, Co, Y, La, or In, although a number of other phases were formed. Calcium ferrite isotypes form only when A^{3+} and B^{4+} can be constrained to match one another both in size and in a local site symmetry which is nearly spherical.

Introduction

The crystal chemistry of metal oxides may be classified into two major groups. The familiar cubic or hexagonal close-packing description is convenient for those compounds where the bonding is largely ionic or the structure is highly symmetrical. For many transition metals, however, a form of covalent bonding generates arrangements of atoms where packing descriptions are cumbersome, and in these circumstances it is preferable to refer to specific coordination polyhedra. Two broad subdivisions in this latter case are based upon the length of a short axis of symmetry, which can be in the range 3.6–4.0 A and corresponds to the length of an octahedral body diagonal (linear O–M–O bond disposition), or an even shorter length 2.8–3.1 A, which is an octahedral or tetrahedral edge (an oxygen–oxygen contact).

Transition metal octahedra, displaying variations of internuclear distances characteristic of individual metals, show a pronounced tendency to cluster together into groups of finite cross section but of infinite extension, with one or the other of these periodicities. Within such groups the octahedra share a *maximum* number of edges. This concept, for which there is ample experimental evidence, leads to major unifying features in structural chemistry,[4] as a particular group appears in the structures of a great variety of compounds whether or not they have similar stoichiometries.

The group we are currently examining is derived from double octahedral elements sharing edges and has a repeat distance of 3.0 A (Figure 1), giving in idealized form an infinitely long parallelepiped. The way these groups join by additional edge or corner sharing to form a three-dimensional network is influenced, among other things, by the presence of electrostatically bonded positive ions at suitable interstices, where their size assumes considerable importance by virtue of their buttressing function.

With any one such ion, however, there may be more than one method of arranging the same strings of double octahedra to form energetically favorable structures. The well-known cases of $CaFe_2O_4$[5–7] and $CaTi_2O_4$[8] contain the double octahedral groups of Figure 1 arranged in two different ways, but in both cases the oxygen environments of the buttressing Ca ions are virtually identical. A third equally probable orthorhombic structure with the same stoichiometry can also be devised, and the three are represented in stylized form by Figures 2a–c. Two further almost identical ways have been described by Mumme and Reid,[9] although only one of the structures, a high-temperature nonstoichiometric phase $Na_xFe_xTi_{2-x}O_4$ ($0.75 < x < 0.90$), was found experimentally. The unit cell dimensions and space groups for typical members of the three known structures, together with approximate values for the structure shown in Figure 2c, are given in Table I. All five are orthorhombic and four have closely similar unit cell dimensions, three having the space group Pnma and the other two Cmcm. Consequently, the determination of the crystallographic constants alone cannot uniquely characterize such a phase, and in this paper, which is concerned with a family of substances $NaA^{3+}B^{4+}O_4$ with a wide range of transition elements A and B, the diffraction data have been very carefully analyzed to ensure that each isotype has the structure claimed for it.

All five possible structures have eight octahedrally coordinated metal atoms in the unit cell. For Cmcm all of these are represented as a single eightfold position and are therefore crystallographically identical. This could arise only if the two different ions A and B were randomized. For Pnma the atoms must occupy two

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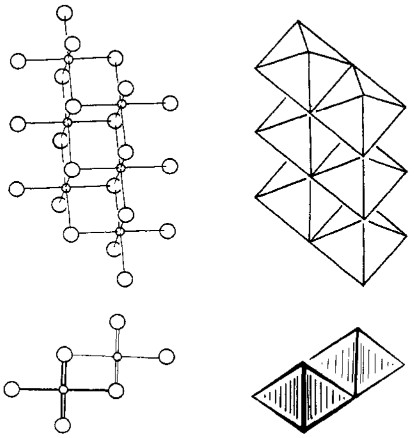

Figure 1.—Double octahedral group of infinite extension with a repeat distance of 3 A: upper, in clinographic perspective; lower, in projection; left, ball-and-spoke drawing; right, octahedra.

sets of fourfold positions, so the possibility of forming these structures may well depend upon A and B ordering. The plane of symmetry in Cmcm, replaced in Pnma by the *n* glide operation, presents a striking difference between the two classes. This mirror plane, which brings two octahedral groups together at the same level perpendicular to the 3-A axis, reflects the organization of the groups, and it is important to know whether the local symmetry of each metal ion exerts a dominant role in deciding which of the several competing structures, with small differences in lattice energy, is most likely to form.

The present paper describes the compounds $NaA^{3+}B^{4+}O_4$ crystallizing with the $CaFe_2O_4$ structure. The X-ray diffraction examination of $NaScTiO_4$ has been conducted at two levels; a careful refinement of the structure with three-dimensional single-crystal data, followed by a similar refinement with counter data collected with a powder diffractometer to establish a basis for the comparison of the isotypic compounds. A number of additional phases were identified during the present study of Na compounds, and the field of occurrence for calcium ferrite structures containing A^{3+} and B^{4+} ions has been explored for the alkali metals Li, K, Rb, and Cs.

Experimental Section

Materials.—Sodium oxalate and SnO_2 were analytical reagent grade, TiO_2 Fisher Certified reagent, and HfO_2 spectroscopic reagent grade. Sc_2O_3 (99.5%) was obtained from the Australian Mineral Development Laboratories, South Australia, and contained 0.3% of SiO_2 as chief impurity. Fe_2O_3 was Baker Laboratory reagent, and all other materials were laboratory reagent grade or better.

Most of the compounds described were readily prepared by heating finely ground and weighed mixtures of sodium oxalate and the appropriate metal oxides, first at 600° and then at 950–1000° for 15 hr in air, followed by regrinding and reheating. The more refractory materials $NaScSnO_4$, $NaScZrO_4$, and $NaScHfO_4$ were prefired at 1000° and then heated at 1300° for 40 hr in sealed platinum capsules. The stoichiometries of the compounds listed in Table II were assumed to be correct; weight losses other than from the decomposition of oxalate were negligible, and X-ray powder patterns showed no traces of the starting materials. $NaScTiO_4$, fused at 1200° and slowly cooled, gave

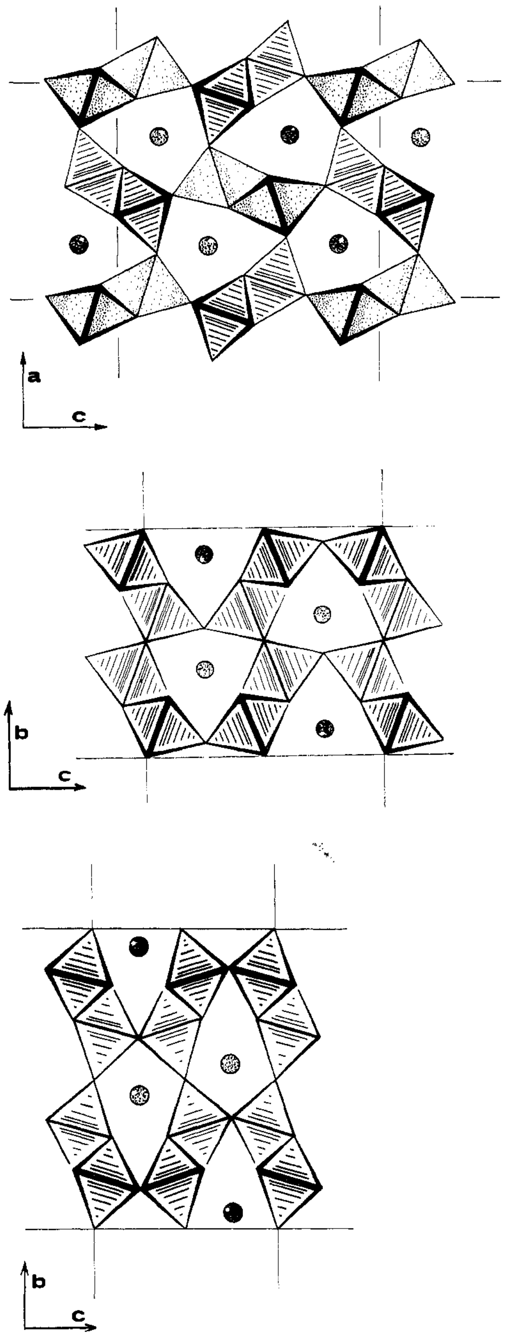

Figure 2.—Three alternative structures for compounds with stoichiometry $NaA^{3+}B^{4+}O_4$ containing groups of Figure 1. Circles are Na^+. Heavy and light markings indicate the two levels in the unit cell: (a) $CaFe_2O_4$ structure type; the stippled- and line-shaded octahedra are crystallographically different; (b) $CaTi_2O_4$ structure; (c) hypothetical structure, a possible alternative to b. The octahedra in b and c each are identical.

TABLE I

LATTICE PARAMETERS FOR SOME ALTERNATIVE ORTHORHOMBIC STRUCTURES OF STOICHIOMETRY AB_2O_4

	$NaScTiO_4$[a]	$Na_xFe_xTi_{2-x}O_4$[b]	$CaTi_2O_4$[8]	Unknown
a, A	9.277	9.255	3.136	3.0
b, A	3.048	2.875	9.727	12.5
c, A	10.917	11.337	9.976	7.8
Space group	Pnma	Pnma	Cmcm	Cmcm
Z	4	4	4	4

[a] Present work. [b] Ideal composition $NaFeTiO_4$, but with $0.75 < x < 0.90$ found experimentally.[9]

material suitable for single-crystal analysis. Attempts to pull crystals from the melt resulted in considerable decomposition accompanied by the volatilization of sodium oxide, and although $NaScTiO_4$ melts congruently, or at least crystallizes from temperatures above the liquidus, it is evidently unstable in the fused state except perhaps in a sealed system.

X-Ray Diffraction.—Three-dimensional intensity data for $NaScTiO_4$ were obtained with Cu Kα radiation from a needle crystal measuring $0.02 \times 0.2 \times 0.03$ mm³ and oriented for rotation around the axis of elongation (b), by integrated Weissenberg photographs using the multiple-film technique. Estimations of intensity were made visually with a calibrated scale, and each reflection was measured at least three times. Individual anomalies appearing during refinement were critically reevaluated. The linear absorption coefficient for $NaScTiO_4$ was 423 cm^{-1}, giving an optimum crystal size of 0.05 mm, so that no absorption correction was necessary. Scattering curves, adjusted for ionicity and for both real and imaginary components of anomalous dispersion,[10] were take from Table 3.3.1A in Vol. III of the "International Tables for Crystallography," except for O^{2-} where we used Suzuki's values.[11]

All calculations were made on the Elliott 803 computer of the Division of Mineral Chemistry, using the programs of Daly, Stephens, and Wheatley,[12] kindly made available by Wheatley and Daly. The weighting scheme of Cruickshank, *et al.*,[13] was adopted for the least-squares cycles, and the matrix inversion involved the block diagonal approximation. The scale factors for each level of the single-crystal investigation were adjusted after each cycle by comparison with the calculated structure factors. Overlapping reflections in the powder data were omitted from the refinement cycles. Each study was judged to be complete when shifts of all variables dropped to less than a fourth of the estimated standard deviations.

Powder diffraction data were obtained with a General Electric XRD-5 diffractometer, using Ni-filtered Cu Kα radiation. Intensity scans were usually made at least twice on reground samples, while $NaScTiO_4$ was also annealed. For Fe compounds the rate meter was arbitrarily biased to place the fluorescence background near zero on the chart recording, and diffraction intensities were measured above the background. Chart recordings were made at slow scan rates (0.2°/min) and intensities determined by measuring peak areas with an accurate planimeter. All peaks were traced at least twice, and up to 8 times when of small area. The diffractometer 2θ scale was calibrated with W and Si powders, and checks on the results for $NaScTiO_4$ and $NaFeTiO_4$ with W powder as an internal standard showed that 2θ values were accurate to ±0.02°. Iterative index selection and least-squares refinement procedures were employed to determine lattice parameters, and for each compound listed in Table II the standard deviation in $\sin^2 \theta_{\text{calcd}} - \sin^2 \theta_{\text{obsd}}$ was approximately 10×10^{-5}.

Table II

Lattice Parameters for $NaScTiO_4$ Isomorphs, Space Group Pnma, $Z = 4$

	a ± 0.003, A	b ± 0.002, A	c ± 0.004 A	V ± 0.1, A³	d_{calcd} ± 0.01, g cm⁻³
$NaFeTiO_4$	9.175	2.962	10.741	291.9	4.33
$NaScTiO_4$	9.277	3.048	10.917	308.7	3.87
$NaFeSnO_4$	9.347	3.067	11.000	315.3	5.51
$NaScSnO_4$	9.466	3.139	11.177	332.1	5.02
$NaScHfO_4$	9.511	3.169	11.226	338.4	6.10
$NaScZrO_4$	9.534	3.184	11.254	341.6	4.34
$NaAlGeO_4$[a]	*8.871*	*2.840*	*10.402*	*262.1*	*4.73*

[a] High-pressure phase,[14] zero-pressure parameters.

(a) **Single Crystal Study.**—Table I contains the crystallographic constants for $NaScTiO_4$. The structure was initially assumed to be of the $CaFe_2O_4$ type[5-7] for which we have used the standard setting Pnma instead of other settings used to date. Adopting the positions found for the atoms in a recent study of $CaSc_2O_4$ by Müller-Buschbaum and von Schnering[15] (described in the setting Pbam and hence requiring the b and c axes interchanged), averaging out the nearly identical scattering curves for Sc^{3+} and Ti^{4+}, and using fixed isotropic temperature factors, the initial reliability factor of 18% dropped to 8.5% after three least-squares refinement cycles. Allowing individual isotropic temperature factors to vary reduced this to 7.5%, and finally three cycles with individual anisotropic vibration parameters U_{ij} leveled off at 6.5%, a highly significant improvement in view of the relatively large number of reflections. The coordinates and the six vibrational mean-square-amplitude tensors U_{ij} as defined by Cruickshank[16] are given for all atoms in Table III, bond lengths in Table IV, and the observed and calculated structure factors in Table V. Bond lengths were not corrected for thermal vibration effects. The structure is illustrated as a ball and spoke drawing in Figure 3 and in stylized form in Figure 2a.

(b) **Powder Diffraction Study of $NaScTiO_4$.**—The intensities of 50 noncoincident reflections were reduced to F_o values by applying multiplicities and Lorentz polarization factors. Starting once again with the $CaSc_2O_4$ positions for the atoms, the data were refined by least squares allowing the positions to vary and using fixed isotropic temperatue factors for each atom averaged from the single-crystal U_{ii} values (Table III). An R factor of 7.5% was obtained after four cycles. The final coordinates were essentially identical with those in Table III, the metals being within 0.02 A and the oxygens 0.05 A of the positions found from the single-crystal data, except that the standard deviations were several times larger, a direct consequence of the fewer data provided by the powder method. A comparison of the observed and calculated intensities is given in Table VI where coincident reflections are also included.

Results

The field of occurrence of the isomorphous $NaA^{3+}B^{4+}O_4$ compounds as a function of ionic size is shown in Figure 4, in which Ahrens'[17] values have been adopted for convenience. The corresponding lattice parameters show a regular trend, well beyond experimental error, as the size of the metal ion increases with $Fe^{3+} < Sc^{3+}$ and $Ti^{4+} < Sn^{4+} < Hf^{4+} < Zr^{4+}$. Although the ionic sizes of the 3+ and 4+ ions in a given compound appear to be important to the extent that they must be nearly equal, it is clear that this is not the sole deciding factor in the formation of the calcium ferrite isotypes. It does appear that as the size of the 4+ ion and the free energy of formation of its dioxide increase, the $NaA^{3+}B^{4+}O_4$ structure becomes relatively less stable. Thus Th^{4+} will not enter the structure with Sc^{3+}, nor Zr^{4+} with Fe^{3+}. The absence of "$NaInTiO_4$" even though $CaIn_2O_4$ exists,[18] is probably due to the high stability of the competing phase $Na_2Ti_3O_7$,[19] rather than to the inability of the spherically symmetrical In^{3+} ion to enter the lattice with the somewhat smaller Ti^{4+} ion.

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TABLE III

POSITIONAL AND THERMAL PARAMETERS FOR $NaScTiO_4$[a]

Atom	x	z	U_{11}	U_{22}	U_{33}	$2U_{12}$	$2U_{23}$	$2U_{13}$
Na	0.2437 (10)	0.3477 (8)	0.0182 (43)	0.0363 (72)	0.0158 (40)	0 (0)	0 (0)	−0.0017 (77)
Sc or Ti(1)	0.0669 (5)	0.1106 (4)	0.0150 (19)	0.0163 (39)	0.0144 (20)	0 (0)	0 (0)	−0.0026 (32)
Sc or Ti(2)	0.0798 (4)	0.6057 (3)	0.0089 (16)	0.0102 (37)	0.0088 (17)	0 (0)	0 (0)	−0.0004 (31)
O(1)	0.2899 (18)	0.6508 (14)	0.0187 (83)	0.0279 (141)	0.0168 (80)	0 (0)	0 (0)	−0.0119 (139)
O(2)	0.3862 (18)	−0.0161 (14)	0.0194 (82)	0.0093 (135)	0.0177 (78)	0 (0)	0 (0)	−0.0145 (135)
O(3)	0.4789 (16)	0.2156 (13)	0.1038 (71)	0.0245 (125)	0.0091 (78)	0 (0)	0 (0)	−0.0198 (117)
O(4)	0.0744 (15)	−0.0729 (13)	0.0072 (64)	0.0332 (148)	0.0090 (73)	0 (0)	0 (0)	0.0069 (117)

[a] Space group Pnma (No. 62). All atoms in point position 4(c), $\pm(x, {}^1/_4, z)$; $\pm({}^1/_2 - x, {}^3/_4, {}^1/_2 + z)$. Esd's given in parentheses ($\times 10^4$).

TABLE IV

INTERATOMIC DISTANCES FOR $NaScTiO_4$[a] (A)

Sc,Ti(1) octahedron	Sc,Ti(2) octahedron	Na polyhedron
Sc,Ti(1)–O(1) 2 × 2.069 (14)	Sc,Ti(2)–O(2) 2 × 2.047 (14)	Na–O(1) 2 × 2.653 (15)
–O(3) 1 × 2.066 (13)	–O(2′) 1 × 2.045 (14)	–O(2) 2 × 2.477 (15)
–O(4) 2 × 2.052 (12)	–O(3) 2 × 2.015 (12)	–O(4) 2 × 2.434 (14)
–O(4′) 1 × 2.004 (12)	–O(1) 1 × 2.010 (13)	–O(3) 1 × 2.616 (14)
O(1)–O(4) 2 × 2.773 (17)	O(2)–O(1) 2 × 2.883 (19)	–O(3′) 1 × 2.552 (14)
–O(3) 2 × 3.008 (18)	O(2)–O(2′) 2 × 2.628 (19)	–O(1′) 1 × 3.337 (15)
–O(4′) 2 × 3.142 (17)	O(2)–O(3) 2 × 2.672 (18)	O(4)–O(4) 1 × 3.048[b]
O(4)–O(3) 2 × 2.810 (17)	O(3)–O(2′) 2 × 2.938 (18)	O(3)–O(3) 1 × 3.048[b]
O(4)–O(4′) 2 × 2.600 (16)	O(3)–O(1′) 2 × 3.007 (18)	O(1)–O(1) 1 × 3.048[b]
O(1)–O(1) 1 × 3.048[b]	O(2)–O(2) 1 × 3.048[b]	
O(4)–O(4) 1 × 3.048[b]	O(3)–O(3) 1 × 3.048[b]	

[a] Esd's × 10^3 given in parentheses; *e.g.*, 2.069 (14) = 2.069 ± 0.014 A. [b] b-axis length, Esd ±0.002 A.

TABLE V

OBSERVED AND CALCULATED STRUCTURE FACTORS[a] FOR SINGLE-CRYSTAL $NaScTiO_4$

h	k	l	F_o	F_c
0	0	2	286	280
0	0	4	-1120	-1242
0	0	6	-322	-297
0	0	8	580	552
0	0	10	421	406
1	0	2	-431	-359
1	0	3	-99	-91
1	0	4	-117	-108
1	0	5	-450	-402
1	0	6	376	363
1	0	8	405	406
1	0	10	-165	-157
1	0	12	-254	-243
2	0	0	647	708
2	0	2	238	250
2	0	3	110	108
2	0	4	-124	-130
2	0	5	198	204
2	0	6	-758	-769
2	0	7	-200	-180
2	0	8	188	188
2	0	9	-276	-258
2	0	10	587	569
2	0	12	-196	-188
3	0	1	152	154
3	0	2	-959	-1104
3	0	3	273	267
3	0	5	-174	-181
3	0	6	825	846
3	0	8	500	475
3	0	10	-346	-323
3	0	12	-403	-377
4	0	1	322	322
4	0	2	-555	-570
4	0	3	115	124
4	0	6	297	304
4	0	10	-298	-288
4	0	11	-144	-132
5	0	1	202	195
5	0	2	-441	-453
5	0	4	-234	-237
5	0	6	285	312
5	0	7	210	212
5	0	8	442	459
5	0	10	-328	-313
5	0	12	-340	-375
6	0	0	-1075	-1127
6	0	1	-138	-144
6	0	2	-305	-289
6	0	3	-205	-200
6	0	4	786	838
6	0	5	314	300
6	0	6	271	283
6	0	8	-391	-327
6	0	10	-292	-258
7	0	1	-175	-160
7	0	2	-177	-187
7	0	4	162	152
7	0	8	-175	-157
8	0	0	-400	-395
8	0	2	-164	-168
8	0	3	-233	-244
8	0	4	499	473
8	0	6	487	444
8	0	7	210	208
8	0	8	-213	-200
8	0	9	141	137
8	0	10	-295	-292
9	0	1	-230	-221
9	0	2	519	522
9	0	6	-483	-464
9	0	8	-106	-95
10	0	3	-212	-198
11	0	2	196	197
11	0	4	189	217
0	1	1	-234	-186
0	1	3	480	446
0	1	5	326	284
0	1	13	144	173
1	1	1	135	99
1	1	2	-871	-761
1	1	3	-671	-598
1	1	4	-475	-456
1	1	5	-107	-83
1	1	6	714	732
1	1	7	245	251
1	1	8	297	317
1	1	9	-140	-146
1	1	10	-288	-303
1	1	12	-473	-525
2	1	0	-767	-757
2	1	1	-103	-105
2	1	2	-169	-164
2	1	3	303	249
2	1	4	798	901
2	1	6	569	619
2	1	8	-267	-227
2	1	10	-336	-375
2	1	11	-154	-159
3	1	1	-543	-535
3	1	2	-236	-223
3	1	3	254	257
3	1	5	-117	-128
3	1	6	309	322
3	1	7	-232	-219
3	1	11	120	138
4	1	0	-943	-1081
4	1	1	-389	-408
4	1	2	-262	-288
4	1	3	-194	-169
4	1	4	883	936
4	1	6	472	472
4	1	8	-309	-338
4	1	10	-365	-361
5	1	2	701	710
5	1	6	-320	-334
5	1	7	244	236
5	1	8	-220	-208
5	1	9	-118	-152
5	1	10	267	267
6	1	0	-278	-275
6	1	2	-268	-252
6	1	5	-295	-277
6	1	8	-189	-150
6	1	9	212	202
6	1	10	-167	-171
7	1	2	491	485
7	1	3	342	332
7	1	4	222	195
7	1	5	140	152
7	1	6	-427	-382
7	1	8	-456	-449
7	1	10	268	276
8	1	0	378	374
8	1	4	-238	-237
8	1	6	-264	-266
9	1	2	324	309
9	1	6	-235	-231
10	1	0	567	603
10	1	1	200	212
10	1	2	138	119
10	1	3	210	213
10	1	4	-335	-323
10	1	5	-151	-137
10	1	6	-270	-275
11	1	2	-155	-162
0	2	2	-255	-155
0	2	4	790	772
0	2	6	260	246
0	2	8	-387	-399
0	2	10	-300	-348
1	2	2	329	246
1	2	4	153	115
1	2	5	184	173
1	2	6	-232	-243
1	2	8	-265	-273
2	2	0	-456	-421
2	2	2	-191	-140
2	2	4	181	170
2	2	6	476	454
2	2	8	-131	-156
2	2	9	172	175
2	2	10	-385	-401
3	2	2	722	752
3	2	3	-128	-106
3	2	6	-541	-569
3	2	8	-331	-378
3	2	10	220	244
4	2	2	318	290
4	2	6	-164	-183
4	2	8	122	99
4	2	10	191	200
5	2	2	350	352
5	2	4	191	169
5	2	6	-226	-246
5	2	7	-123	-134
5	2	8	-329	-328
5	2	10	200	237
6	2	0	734	734
6	2	2	165	191
6	2	4	-562	-576
6	2	5	-203	-189
6	2	6	-229	-232
6	2	7	-94	-87
6	2	8	280	259
7	2	2	92	92
7	2	8	110	104
8	2	0	314	318
8	2	2	117	114
8	2	3	161	186
8	2	4	-334	-375
8	2	6	-280	-322
9	2	1	158	159
9	2	2	-368	-393

[a] Absolute units ×10.

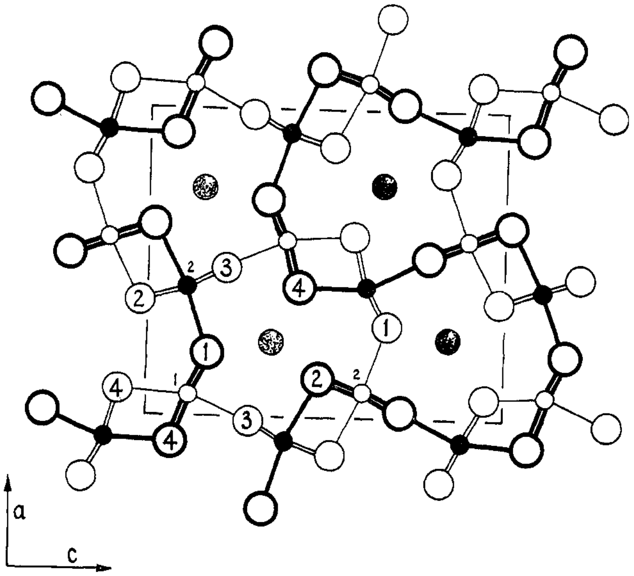

Figure 3.—Structure of $NaScTiO_4$: small circles, Sc or Ti; larger circles, oxygen. Na is stippled. The numbered sites correspond to the positions given in Table III.

$NaYTiO_4$ and $NaLaTiO_4$ appear to be the only sodium-containing phases with this same stoichiometry, and each has a unique structure at present under investigation. $NaTi_2Al_5O_{12}$,[20] $Na_2Ti_7O_{15}$,[21] and probably $NaAlO_2$,[22] were formed from the starting composition "$NaAlTiO_4$," while $Na_2Co^{2+}TiO_4$,[23] isomorphous with rhombohedral $NaFeO_2$,[24] resulted from attempts to form "$NaCo^{3+}TiO_4$." "$NaFeZrO_4$" gave $NaFeO_2$ + ZrO_2, "$NaScThO_4$" gave $NaScO_2$[25] + ThO_2, and "$NaInTiO_4$" gave a mixture of In_2O_3, Na_2TiO_3,[26] and $Na_2Ti_3O_7$.[19] Chromium formed a sodium-containing hollandite[27] structure $NaCr^{3+}Ti_3O_8$, together with a water-soluble chromate or dichromate, and it was found by magnetic and reflectance spectral measurements that neither 10% nor as little as 0.1% of Cr^{3+} would go into the $NaScTiO_4$ lattice, diamagnetic chromates being formed instead. "$NaMnTiO_4$" gave $Na_4Mn_4Ti_5O_{18}$, an unusual structure containing Mn^{3+} in square-pyramidal coordination.[28]

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(21) W. G. Mumme and A. D. Wadsley, *ibid.*, in press.
(22) J. Théry, A. M. Lejus, D. Briançon, and R. Collongues, *Bull. Soc. Chim. France*, 973 (1961).
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(25) R. Hoppe, *Naturwissenschaften*, **71**, 457 (1959).
(26) G. Lang, *Z. Anorg. Allgem. Chem.*, **276**, 77 (1954).
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(28) W. G. Mumme, *Acta Cryst.*, in press.

Table VI

Powder Diffraction Data[a] for $NaScTiO_4$ Isomorphs

$NaScTiO_4$

h	k	l	I_o	I_c
0	0	2	79	77
1	0	2	258	225
2	0	0	395	393
2	0	2	52	56
3	0	1	20	11
0	1	1	19	17
0	0	4	348	359
3	0	2	527	526
1	1	2	342	426
2	1	0	232	223
3	0	3	39	23
0	1	3	58	56
2	1	2	14	13
1	1	3	216	215
4	0	2}	274	231
3	1	1}		
2	1	3	30	27
3	1	2	27	24
1	1	4	94	89
2	1	4	306	296
4	1	0	221	325
0	0	6}	49	67
4	1	1}		
1	0	6	24	22
0	1	5	11	9
5	0	2	26	36
4	1	2	27	19
2	0	6	69	77
3	0	6	91	83
6	0	0	73	71
1	1	6	121	126
4	1	4	211	206
0	2	0	184	145
5	1	2	79	110
2	1	6	100	82
3	1	6	19	19
0	0	8	13	14
1	0	8	8	12
6	0	4	49	55
0	2	4	47	54
3	2	2	79	94
4	1	6	42	39
3	0	8	12	14
4	2	2	15	11
1	1	8	12	15
5	1	6	16	13
7	1	2	34	32
5	2	2	23	15
2	2	6	26	25
3	2	6	45	37
6	2	0	41	38
8	0	4	13	14
9	0	2	24	14
6	2	4	49	37
2	1	10	20	15

$NaFeTiO_4$

h	k	l	I_o	I_c
0	0	2	62	79
1	0	2	286	258
2	0	0	417	393
2	0	2	83	144
0	0	4	334	333
3	0	2	522	535
1	1	2}	631	716
2	1	0}		
0	1	3	35	48
1	1	3	124	153
4	0	2	78	62
3	1	1}	156	135
1	0	5}		
1	1	4}	93	95
2	0	5}		
2	1	4	155	299
4	1	0	114	192
4	1	1	93	45
2	0	6	99	77
3	0	6	120	50
6	0	0	114	67
5	0	4}	52	9
6	0	1}		
1	1	6	124	119
4	1	4	187	183
5	1	2	172	128
0	2	0	151	127
2	1	6	98	72
0	2	4	67	49
3	2	2	104	59

$NaFeSnO_4$

h	k	l	I_o	I_c
0	0	2	245	260
1	0	2	879	1120
2	0	0	1047	1314
2	0	2	115	107
0	0	4	894	952
3	0	2	1688	1723
1	1	2}	2853	2789
2	1	0}		
1	1	3	253	172
3	1	1}	219	188
4	0	2}		
3	0	4	75	41
3	1	2	65	61
1	1	4	253	242
2	1	4	911	802
4	1	0	641	612
0	0	6}	202	130
4	1	1}		
1	0	6	101	73
5	0	2	253	179
2	0	6	135	148
3	0	6	270	237
6	0	0	203	153
1	1	6	371	370
4	1	4	557	566
0	2	0}	658	623
5	1	2}		
6	0	4	149	155
0	2	4	155	158
3	2	2	321	314

$NaScSnO_4$

h	k	l	I_o	I_c
0	0	2	179	229
1	0	2	973	1050
2	0	0	1015	1097
2	0	2	82	67
3	0	1	50	33
2	0	3	47	16
1	1	1	25	22
0	0	4	848	908
3	0	2	1284	1540
1	1	2	1374	1652
2	1	0	680	767
2	0	4}	231	102
3	0	3}		
4	0	0	71	61
2	1	2		
1	1	3	192	180
4	0	2}	192	203
3	1	1}		
2	1	3	42	22
3	0	4	38	27
3	1	2	35	37
1	1	4	192	185
2	1	4}	680	790
3	1	3}		
4	1	0	501	538
0	0	6}	146	123
4	1	1}		
1	0	6	71	60
5	0	2	179	130
2	0	6	128	105
4	1	3	35	36
3	0	6	218	243
1	1	6	282	348
6	0	0	205	168
0	2	0	326	280
4	1	4	490	502
5	1	2	308	293
6	0	2}	205	182
2	1	6}		
1	2	2	64	55
2	2	0	55	53
3	1	6	38	25
0	0	8	39	50
1	0	8}	35	28
2	2	3}		
6	0	4	154	151
0	2	4	154	153
3	2	2	306	293
2	0	8	14	12
4	1	6	113	79
2	2	4	35	32
3	0	8	61	55
1	1	8	61	25
3	2	4	23	12
2	1	8	60	45
5	1	6	52	59
7	1	2	125	125
5	2	1}	39	10
2	0	9}		
1	2	6	29	23
5	2	2	67	55
2	2	6	38	38
4	1	8}	83	75
5	0	8}		
3	2	6	145	118
6	2	0	91	83
6	2	1}	24	28
8	1	0}		
1	1	10	78	35
6	2	4}	249	212
7	1	6}		
9	0	2}		
2	1	10	87	48
1	3	2	116	72
3	2	8	64	49
9	1	2	23	18
4	1	10}	73	58
5	0	10}		
2	3	4	87	66
4	3	0	87	48
7	1	8	73	51
9	0	6}	47	46
8	2	3}		
10	1	0}	132	142
4	3	4}		
5	3	2	132	54
8	2	4}	96	50
5	0	11}		
2	2	10	96	39
1	1	12	109	85
6	2	8}	38	49
5	3	4}		
8	2	6	44	27
7	3	2	102	87

$NaScZrO_4$

h	k	l	I_o	I_c
0	0	2	130	156
1	0	2	654	608
2	0	0	892	777
2	0	2	58	78
3	0	1}	33	57
0	1	1}		
2	0	3	49	10
1	1	1	115	13
0	0	4	666	659
3	0	2	1189	1119
1	1	2	832	1187
2	1	0	344	546
0	1	3}	130	135
3	0	3}		
2	0	4}		
2	1	2	54	39
1	1	3	154	193
4	0	1	42	24
3	1	1	126	130
4	0	2	126	80
2	1	3	42	21
3	0	4	22	14
3	1	2	45	43
1	1	4	126	166
2	1	4}	523	583
3	1	3}		
4	1	0	380	413
4	1	1}	60	78
5	0	1}		
0	0	6	60	30
0	1	5}	55	70
1	0	6}		
3	0	5}		
5	0	2}	190	146
4	1	2}		
2	0	6	116	112
3	0	6	237	160
0	2	0}	475	483
1	1	5}		
6	0	0	142	126
4	1	4}	392	404
5	0	4}		
5	1	2	231	213
2	1	6}	154	139
0	2	2}		
3	1	6	27	26
0	0	8	53	25
0	2	4	83	109
6	0	4	154	106
3	2	2}	202	210
5	1	2}		
2	0	8	14	9
4	1	6}	65	96
5	0	6}		
3	0	8	45	40
1	1	8	52	45
2	1	8	38	22
5	1	6	45	33
7	1	2	107	75
6	0	6	35	13
4	2	6	21	16
5	2	2	35	40
8	0	0	23	13
2	2	6	26	38
3	2	6	70	73
4	1	9}	70	51
5	0	9}		
6	2	0}	86	71
0	0	10}		
2	0	10	40	25
5	1	8	16	14

$NaScHfO_4$

h	k	l	I_o	I_c
0	0	2	355	385
1	0	2	1939	1711
2	0	0	1939	1927
2	0	2	150	148
3	0	1}	81	60
0	1	1}		
2	0	3	60	19
1	1	1	38	20
0	0	4	1939	1475
3	0	2	2731	2723
1	0	4	65	60
1	1	2	2731	3350
2	1	0	1163	1468
0	1	3}	382	361
2	0	4}		
2	1	2	99	109
1	1	3	163	188
3	1	1	136	112
4	0	2	136	96
2	1	3	24	17
3	0	4	87	94
3	1	2	57	104
1	1	4	270	408
2	1	4	1283	1299
4	1	0	901	1025
4	1	1}	90	139
5	0	1}		
0	0	6	95	139
1	0	6	191	117
5	0	2}	450	417
4	1	2}		
2	0	6	245	204
3	0	6	491	389
1	1	6	682	605
6	0	0}	764	744
0	2	0}		
4	1	4}	901	946
5	0	4}		
5	1	2	546	509
0	2	2}	382	354
2	1	6}		
6	0	2}		
2	2	0	210	133
3	1	6	65	46
6	1	0	51	41
0	0	8	120	73
0	2	4	518	534
6	0	4		
6	1	2}	515	582
3	2	2}		
4	1	6}	204	265
5	0	6}		
6	1	3}	71	99
2	2	4}		
4	2	2	58	17
1	1	8	95	177
2	1	8	98	90
5	1	6	84	100
7	1	2	254	272
6	0	6	84	45
5	2	2	139	143
2	2	6	54	79
3	2	6}	392	210
6	1	6}		
0	0	10}	163	196
5	2	0}		

[a] I_c are in absolute units $\times 10^{-2}$, and I_o are normalized with respect to them.

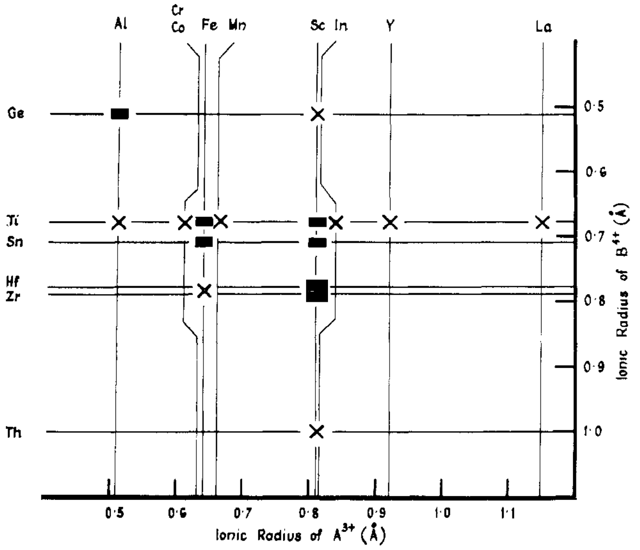

Figure 4.—Field of occurrence of $NaScTiO_4$ isomorphs, black rectangles, as a function of ionic radii (Ahrens[17]). Crosses are compositions giving different phases. $NaAlGeO_4$ was prepared at 120 kbars pressure and 900°.[14]

Figure 4 is, in effect, a cross section, constrained to $NaABO_4$ stoichiometry, of a three-dimensional figure where the third axis is the size of the alkali metal ion. We have made limited excursions into the third dimension of Figure 4 by attempting to prepare Li and K compounds corresponding to each of the $NaScTiO_4$ isomorphs, together with some corresponding Rb and Cs compounds. However, no calcium ferrite structure is formed as these other regions of the Figure encroach into the stability fields of other structural types. For the smaller Li^+ ion these structures are spinels such as $LiFeTiO_4$, reported by Blasse,[29] or the lithium ferrite type Li_2FeTiO_4, several of which have already been described by Brixner.[30] A number of new phases containing the larger ions K^+, Rb^+, and Cs^+ have been isolated, and these will be described in due course.

Isomorphism and Site Occupancy in the $NaA^{3+}B^{4+}O_4$ Compounds.—The lattice parameters of the six compounds similar to $NaScTiO_4$ are listed in Table II. We now wish to determine first whether they are all isomorphous and second whether the A^{3+} and B^{4+} ions go into the two different fourfold sites (1) and (2) either in that order ("ordered 1, 2") or its reverse ("ordered 2, 1") or, alternatively, whether occupation of the two sites is random so far as X-ray diffraction can determine. The bond lengths obtained from single-crystal data for $NaScTiO_4$ did not distinguish an Sc^{3+} site from a Ti^{4+} site (Table IV), and since these two isoelectronic ions are virtually identical scattering units, intensity data could not be expected to provide evidence for ordering or randomness.

To keep computations within reasonable bounds, we have initially assumed strict isomorphism between the various phases; that is to say the atoms in all cases have the same fractional coordinates as in $NaScTiO_4$. To test this hypothesis the powder intensities for $NaScSnO_4$ were refined by a number of least-squares cycles, but the reduction in R value from 10.6 to 9.7%, although ensuring a more self-consistent set of results, was not significant according to the ratio tests outlined below, and atom shifts were within the observed standard deviations of 0.05 A for Na, 0.02 A for Sc and Sn, and 0.15 A for O's. A comparison of observed and calculated intensities for all six compounds is given in Table VI, and $R_{|F_o|}$ for noncoincident and R_{I_o} for all observed reflections for each compound are given in Table VII.

Table VII

Final $R_{|F_o|}$ and R_{I_o} for $NaScTiO_4$ Isomorphs; Random Occupancy

	$R_{\|F_o\|}$,[a] all noncoincident reflections	R_{I_o},[a] all reflections
$NaScTiO_4$	7.6 (50)	11.6 (53)
$NaFeTiO_4$	11.6 (24)	19.4 (26)
$NaScSnO_4$	5.1 (24)	9.6 (26)
$NaFeSnO_4$	10.6 (52)	17.3 (77)
$NaScZrO_4$	18.2 (38)	18.3 (56)
$NaScHfO_4$	12.8 (37)	14.3 (52)
$NaAlGeO_4$[b]		22.5 (37)

[a] Numbers of observations are given in parentheses. [b] High-pressure phase.[13]

Diffraction data for the compounds with the greatest atomic number differences between A and B will show the greatest sensitivity to ordering. We have therefore calculated sets of structure factors for the three occupancy alternatives for the three compounds $NaScSnO_4$, $NaScZrO_4$, and $NaScHfO_4$. For $NaFeTiO_4$

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(29) G. Blasse, *J. Inorg. Nucl. Chem.*, **25**, 230 (1963).

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TABLE VIII

R FACTORS FOR ORDERED AND RANDOM OCCUPANCY OF A^{3+} AND B^{4+} IN $NaScSnO_4$, $NaScZrO_4$, AND $NaScHfO_4$[a]

	N^b	$R_{1,2}$	$R_{2,1}$	R_{random}	$R_{1,2}/R_{random}$	$R_{2,1}/R_{random}$
$NaScSnO_4$	30	20.5	17.7	14.0	1.464 (0.001)	1.264 (0.013)
$NaScZrO_4$	19	26.0	26.9	18.9	1.405 (0.030)	1.455 (0.018)
$NaScHfO_4$	27	27.0	23.8	13.5	2.044 (0.001)	1.763 (0.001)

[a] Significance levels for the rejection of the ordered models are given in parentheses. A significance level of 0.001 indicates that the random model is preferred with a 1 − 0.001, or 99.9%, probability. [b] Number of sensitive reflections considered; see text.

and $NaFeSnO_4$ too few data were obtained for significant comparisons to be made. Although there is a big difference in scattering power between Sc^{3+} (atomic number 21) and Zr (40), Sn (50), or Hf (72), it was found that a number of reflections were quite insensitive to the ordering model chosen. To increase the sensitivity of the comparisons, only those reflections were considered for which the structure factors calculated for "ordered 1, 2" differed from those for "ordered 2, 1" by 10% or more. The percentage discrepancy factors $R = 100\Sigma(|F_o| - |F_c|)/\Sigma|F_o|$ obtained from this procedure were then compared to determine the best model.

Hamilton[31,32] has shown that the ratio of the R factors obtained for two alternate models provides a simple test for statistical significance equivalent to performing an analysis of variance on the two sets of structure factor data and has compiled tables of critical R factor ratios $\mathcal{R}_{b,n-m,\alpha}$ which enable alternate hypotheses to be tested at a given significance level α. Here b is the dimension of the hypothesis to be tested, usually equivalent to the number of independent parameters which are deliberately constrained or varied, n is the number of observations, and $n - m$ is the number of degrees of freedom, with m usually equal to b. Strictly the R factors should be calculated from weighted standard deviations, but the use of simple differences is substantially canceled by taking their ratios. For example, Bailey and Dahl[33,34] found almost identical ratios using both methods in comparing various models for benzenechromium tricarbonyl and hexamethylbenzenechromium tricarbonyl. The R factor ratio test contains the assumptions,[31,32] as do variance ratio tests, that errors are random and that changes in structure factor differences $|F_o| - |F_c|$ are linear with respect to changes in structural parameters over the region of interest. This latter does not appear to be a serious constraint in ordering–random considerations, where parameter changes are usually small. A difficulty in the application of the tests lies in deciding the dimension of the hypothesis tested, but, assuming this to be known, the value of α at which $\mathcal{R}$ exceeds the critical value gives us the statistical significance level at which a hypothesis A is rejected in favor of some alternative B. The probability that hypothesis B is correct is then $1 - \alpha$, and for $\alpha = 0.005$, for example, it would be 99.5%.

In the present case, "ordered 1, 2" puts A^{3+} ions at x_1, $^1/_4$, y_1, and B^{4+} ions at x_2, $^3/_4$, y_2. In comparing this model with "ordered 2, 1" or "random," all other parameters are kept constant, and therefore only four independent variables, x_1, y_1, x_2, y_2, are used in deciding the positions of A^{3+} and B^{4+}, and the dimension of our hypothesis is four. It could be argued that fixing x_1, y_1 for one atom fixes x_2, y_2 for the other, a hypothesis of dimension two, but this gives a less strict test, and will be ignored.

Table VIII shows the R factors, their ratios $\mathcal{R}$, and the significance levels at which the observed ratios exceed the calculated ratios. We note that log α *vs.* $\mathcal{R}_{b,n-m,\alpha}$ is a linear function, and α is obtainable by interpolation or extrapolation as necessary. Table VIII shows that on the basis of the R factor test the random occupancy model is at least 97% probable in the worst case, and more than 99.9% probable for $NaScHfO_4$. The case for the zirconium compound suffers slightly from too few data, but is still strongly significant. Since the size disparity between Sc and Ti, or Fe and Ti, is much less than that for Sc and Hf, and the outer electronic configurations of Ti, Zr, and Hf are the same, we can justifiably assume that randomness extends to $NaScTiO_4$ and most probably also to $NaFeTiO_4$ and $NaFeSnO_4$. In addition, we have found[35] that Fe isomorphously replaces Sc in $NaSc_{1-x}Fe_xTiO_4$ with a regular change of lattice parameter and that in $Na_xFe_xTi_{2-x}O_4$ the structural framework of octahedral sites is randomly occupied by Fe and Ti. The exact nature of the random occupancies cannot be deduced from the X-ray studies. It may be that, within any given string of double blocks, ordering in the b-axis direction occurs, but that it is unrelated to that in the adjacent corner connected blocks, which are, in any case, of a crystallographically nonequivalent kind. However, neither for Fe^{3+} in $NaSc_{1-x}Fe_xTiO_4$ nor for small amounts of Fe^{3+} in $CaSc_2O_4$[36] could any evidence of site preference be inferred from electron spin resonance measurements on powdered samples.

Discussion

The calcium ferrite structure[5-7] has been confirmed by single-crystal studies or by comparison of observed and calculated powder diffraction intensities for the compounds β-$CaCr_2O_4$,[6] CaV_2O_4,[6] $CaSc_2O_4$,[15] $MgSc_2O_4$,[37] Eu_3O_4,[38] $SrEu_2O_4$,[38] $CaIn_2O_4$,[18] $CaYb_2O_4$,[39] and $NaAlGeO_4$.[14] Powder patterns also indicate isomorphism for $SrFe_2O_4$,[5]

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$SrSc_2O_4$,[40] and $SrIn_2O_4$[41] and for a series of Ba and Sr compounds BaM_2O_4 and SrM'_2O_4, where M is a rare earth Nd to Lu and M' is yttrium or a rare earth La to Ho,[41-43] as well as for the rare earth double sulfides $(Eu,Sm,Pb,Sr,Ba)^{2+}(Y,Ho,Er,Tm,Yb,Lu)_2{}^{3+}S_4$.[44]

The phases described in the present paper are, by single-crystal and powder intensity data (Tables IV and V), strictly isomorphous with $CaFe_2O_4$, and within the limits of experimental error there is among them an exact correspondence of atomic positions. All six substances have the same space group Pnma with all atoms in reflection planes at either $y = {}^1/_4$ or $y = {}^3/_4$.

For this structure there are two crystallographically different double groups of closely knit octahedra of the kind shown in Figure 2. Each one is joined by corners to four groups of the other kind and they extend infinitely in the direction of the *b* axis, the length of which is equivalent to an oxygen–oxygen distance along an octahedral edge. This three-dimensional structure, Figures 2a and 3, provides interconnected holes or *tunnels* which in the present instance contain the sodium ions in distorted eightfold coordination, a trigonal prism of oxygens with two additional atoms through the centers of two of the three rectangular faces. A ninth oxygen, which would otherwise give a symmetrical coordination, is too far away to be bonded. The two sodium atoms at each of the two levels in the unit cell, $y = {}^1/_4$ and $y = {}^3/_4$, connect across an oxygen at the same level, so that these oxygen atoms O(3) are each bonded to five metals in approximately a trigonal-bipyramidal configuration, while the remaining oxygens O(1), O(2), and O(4) are all near the centers of distorted square pyramids of metal atoms.

The strong crystallographic evidence that the A^{3+} and B^{4+} metal atoms are randomized shows that they have no significant preference for either of the two different octahedral double groups. This means that differences in site occupation energies are no more than thermal energies, kT, at the temperatures of formation. It is possible that the alkali metals in the tunnel interstices of the structure hinder the diffusion paths having the lowest activation energy, as has been discussed for reactions of other oxy compounds of transition metals.[45]

Evidence for the similarity of the two metal sites is also contained in the single-crystal determination of the $NaScTiO_4$ structure. The (Sc,Ti)–O bond distances in Table IV, showing individual variability within each of the two different octahedra, are identical within narrow limits of experimental error, even though the ionic radii of Sc^{3+} and Ti^{4+} usually differ by more than 0.1 A.[17] We note that the mean Sc–O bond length in $CaSc_2O_4$ is 2.12 A,[18] while Ti–O distances in rutile and alkali titanates[19] center around 1.96 A. The average of these two is 2.04 A, which is identical with the (Sc,Ti)–O average distance in $NaScTiO_4$, Table IV. The usual effect of random occupancy on the diffraction of X-rays is to superimpose two metals upon each other to produce an apparent mean metal–oxygen separation. Since Sc^{3+}–O distances are consistently larger than Ti^{4+}–O distances in other oxides, it might be supposed that in the present structure the oxygens would be smeared out in the x–z plane, and the temperature factors would therefore become anomalous. In fact, they are entirely normal for alkali transition metal titanates with the y-axis amplitude, if anything, the largest (Table III), and the averaging effect is real.

We conclude that the space group requirements of the structure fix the oxygen positions for a given combination of metals, and impose a specific size on the ions entering the octahedral sites. Random occupancy within a double block then occurs at sites of equivalent dimensions. Except for $NaFeTiO_4$ and $NaFeSnO_4$ containing the spherically symmetrical d^5 ion Fe^{3+}, the absence of $NaScTiO_4$ isomorphs with transition metal 3+ ions other than Sc^{3+} thus appears due to three interdependent effects.

First, the space group imposes the condition that the two sites in a given double block are symmetry equivalent and of the same size. Second, the lattice occupation energies for sites (1) and (2) are very similar, so that random occupation occurs and *all* sites are therefore of almost the same size and local symmetry. Finally, the choice for B^{4+} of the diamagnetic ions Ti^{4+}, Sn^{4+}, Zr^{4+}, or Hf^{4+} then requires that the A^{3+} ion be able to match them in size and near-spherical local symmetry. Transition metal ions with unpaired electrons and strong ligand field distortions from octahedral symmetry are therefore particularly unwelcome when Na is the "tunnel" ion.

Although β-$CaCr_2O_4$[6] and CaV_2O_4[6] do indeed have the calcium ferrite structure, site symmetry matching in their case is between identical 3+ ions, and not between dissimilar 3+ and 4+ ions. Thus in the formation of $NaScTiO_4$ isomorphs, and calcium ferrite isotypes generally, metal ion symmetries are playing a decisive role, which not only decides the symmetry of the individual coordination polyhedra, but which in combination with the space group symmetry also determines the formation of more extended structural blocks and thus in turn the final structure.

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