

Non-Stoichiometric Sodium Iron Titanate, $\text{Na}_x\text{Fe}_x\text{Ti}_{2-x}\text{O}_4$, $0.90 > x > 0.75$

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(Received 18 April 1967 and in revised form 14 August 1967)

The new, congruently melting, compound $\text{Na}_x\text{Fe}_x\text{Ti}_{2-x}\text{O}_4$, $0.90 > x > 0.75$, was prepared as a powder at 1000°C and in crystalline form by melting NaFeTiO_4 in air at 1220°C . It is orthorhombic, space group $Pnma$, with unit-cell dimensions $a = 9.248$, $b = 2.973$ and $c = 11.344$ Å at the composition $x = 0.90$. The Fe and Ti atoms randomly occupy octahedral positions, and the octahedra within a unit cell are joined by extensive edge-sharing into Z-shaped groups of four. These groups extend in infinite ribbons in the b -axis direction, and are corner joined to each other, thereby providing double tunnels of sodium-ion sites, not all occupied. The structure is a rearrangement, with a necessary sodium loss, of the limiting composition NaFeTiO_4 , which is a CaFe_2O_4 isotype with similar crystallographic constants, but containing pairs of edge-shared octahedra corner joined to form single tunnels for sodium ions.

Introduction

In a concurrent study (Reid, Wadsley & Sienko, 1968) we reported that NaFeTiO_4 has the calcium ferrite structure type, and is isomorphous with sodium scandium titanate NaScTiO_4 and a series of other $\text{NaA}^{3+}\text{B}^{4+}\text{O}_4$ compounds including NaScZrO_4 , NaScHfO_4 , NaFeSnO_4 and NaScSnO_4 . NaFeTiO_4 and NaScTiO_4 were found to form a complete solid solution series (Reid, Perkins & Sienko, 1968), of which at least the members NaFeTiO_4 , $\text{NaFe}_{\frac{1}{3}}\text{Sc}_{\frac{2}{3}}\text{TiO}_4$ and NaScTiO_4 melted congruently when sealed in platinum capsules.

In the present work it was found that NaFeTiO_4 melted at approximately 1180°C , but when heated in air at 1220°C and slowly cooled lost sodium and formed a new, intrinsically non-stoichiometric compound characterized by the formula $\text{Na}_x\text{Fe}_x\text{Ti}_{2-x}\text{O}_4$ with $0.90 > x > 0.75$. This compound has the same space group as NaFeTiO_4 , as well as similar lattice parameters, and the two may be regarded as structurally related polymorphs with $x < 0.90$ in the one and $x = 1$ in the other.

Experimental

Well formed prismatic crystals of $\text{Na}_{0.9}\text{Fe}_{0.9}\text{Ti}_{1.1}\text{O}_4$ developed in the b -axis direction were made by melting the composition NaFeTiO_4 at 1220°C and then cooling

it to 900°C at a rate of approximately 100° per hour. During this time 2% weight loss occurred from 300 mg of sample held in a small platinum dish. A small amount of an unidentified phase was also present.

The nature and composition of the crystals were confirmed by powder preparations and lattice parameter measurements for the composition range $\text{Na}_x\text{Fe}_x\text{Ti}_{2-x}\text{O}_4$ for $x = 1.00$ to $x = 0.50$. Between $x = 0.90$ and $x = 0.75$ a phase was obtained which had lattice parameters almost identical with those of the material obtained by melting NaFeTiO_4 , and whose reflexion intensities were also closely similar. The small variation of lattice parameters with change of composition (Table 1) did not allow lattice parameter evaluation of the value of x for the crystalline material, but because they were formed from a melt containing an excess of sodium and iron, it could safely be assumed that the crystals obtained from melted NaFeTiO_4 had the upper limit of composition $\text{Na}_{0.9}\text{Fe}_{0.9}\text{Ti}_{1.1}\text{O}_4$.

Powder preparations were made by heating finely ground mixtures of sodium oxalate and the appropriate quantities of Fe_2O_3 and TiO_2 overnight at 1000°C , followed by regrinding and reheating. At $x = 0.90$, some weak peaks corresponding to the strongest reflexions of NaFeTiO_4 (calcium ferrite type) were still present while below $x = 0.75$ increasing amounts of the pattern of $\text{Na}_2\text{Fe}_2\text{Ti}_6\text{O}_{16}$, sodium titanium bronze type (Andersson & Wadsley, 1962; Bayer

Table 1. Crystallographic data for $\text{Na}_x\text{Fe}_x\text{Ti}_{2-x}\text{O}_4$ and NaFeTiO_4

	$\text{Na}_{0.75}\text{Fe}_{0.75}\text{Ti}_{1.25}\text{O}_4$ $\text{Na}_x\text{Fe}_x\text{Ti}_{2-x}\text{O}_4$	$\text{Na}_{0.90}\text{Fe}_{0.90}\text{Ti}_{1.10}\text{O}_4$ $\text{Na}_x\text{Fe}_x\text{Ti}_{2-x}\text{O}_4$	NaFeTiO_4 CaFe_2O_4
Structure type	<i>Pnma</i>	<i>Pnma</i>	<i>Pnma</i>
Space group	<i>Pnma</i>	<i>Pnma</i>	<i>Pnma</i>
a (Å \pm 0.004)	9.255	9.248	9.175
b (Å \pm 0.002)	2.970	2.973	2.962
c (Å \pm 0.004)	11.342	11.344	10.741
V (Å ³ \pm 0.1)	311.8	311.9	291.9
Z	4	4	4
d_{calc} , (g.cm ⁻³)	3.897	3.995	4.339

& Hoffman, 1965; Reid & Sienko, 1967) were present. The range of homogeneity of $\text{Na}_x\text{Fe}_x\text{Ti}_{2-x}\text{O}_4$ is thus $0.90 > x > 0.75$.

Powder diffractometer data were obtained at slow scan rates and relative intensities were determined from peak areas. For lattice parameter calibration, potassium chloride was included as an internal standard in separate samples. A proportional counter with pulse height discrimination was used as detector to distinguish $\text{Cu } K\alpha$ radiation from Fe fluorescence. A least-squares program was used in conjunction with an index selection program to determine final indices and lattice parameters. When reflexions were coincident, those contributing less than 5% of the calculated intensity were excluded. Crystallographic data for $\text{Na}_x\text{Fe}_x\text{Ti}_{2-x}\text{O}_4$ are given in Table 1, and powder diffraction data in Table 2, where calculated intensities are derived from the structure factors of Table 3 by appropriate Lorentz-polarization and multiplicity corrections.

Table 2. Powder diffraction data for $\text{Na}_{0.90}\text{Fe}_{0.90}\text{Ti}_{1.10}\text{O}_4$

KCl internal standard, $a_0 = 6.293 \text{ \AA}$; $\text{Cu } K\alpha_1$ radiation

<i>h</i>	<i>k</i>	<i>l</i>	$\sin^2 \theta$ obs.	$\sin^2 \theta$ calc.	<i>I</i> obs.	<i>I</i> calc.
1	0	1	0.01153	0.01155	100	70
0	0	2	0.01844	0.01844	5	10
1	0	2	0.02536	0.02538	40	45
2	0	2	0.04618	0.04619	25	13
1	0	3	0.04848	0.04843	6	6
3	0	1	0.06697	0.06704	20	18
0	0	4	0.07374	0.07377	25	25
1	1	1	0.07863	0.07864	5	4
{	1	0	0.08081	0.08070	35	3
{	3	0		0.08087		25
1	1	2	0.09249	0.09248	5	23
2	1	0	0.09524	0.09482	2	2
2	1	1	0.09948	0.09943	8	40
3	0	3	0.10391	0.10393	17	8
2	1	2	0.11330	0.11326	6	22
{	3	0	0.13623	0.13620	16	7
{	2	1		0.13631		8
2	0	5	0.14295	0.14301	8	4
3	1	2	0.14787	0.14792	4	7
3	1	3	0.17098	0.17097	4	15
{	3	0	0.17781	0.17769	12	8
{	4	1		0.17801		8
4	0	4	0.18466	0.18476	36	7
2	0	6	0.19382	0.19372	4	4
2	1	5	0.21008	0.21008	7	15
1	1	6	0.24009	0.24001	4	8
5	0	4	0.24706	0.24719	6	2
5	1	2	0.25912	0.25886	4	8
0	2	0	0.26828	0.26849	3	10
{	3	0	0.28853	0.28834	15	2
{	5	0		0.28868		4

Single-crystal data

Intensity data for the levels $k=0, 1, 2$ were collected from a crystal measuring $0.2 \times 0.04 \times 0.04 \text{ mm}^3$ rotated about the b axis and recorded with $\text{Cu } K\alpha$ radiation on multiple films using the integrating Weissenberg technique. The space group alternatives were determined from systematic absences in these photographs.

Zero level relative intensities recorded with both $\text{Cu } K\alpha$ and $\text{Co } K\alpha$ were virtually identical and for speed of collection with our facilities the remaining levels were also photographed using $\text{Cu } K\alpha$.

Intensities were measured visually by comparison with a standard scale, and the reduction to structure amplitudes, and all subsequent computing, was made in the Division's Elliot 803 computer using the programming system devised by Daly, Stephens & Wheatley (1963), and kindly made available to us by Dr P. J. Wheatley. Interlayer scaling for the three levels of data was adjusted after each least-squares refinement cycle, and the scaled observed data and structure amplitudes calculated from the final model are given in Table 3. Scattering curves for Na, Fe and Ti were taken from *International Tables for X-ray Crystallography* (1962, page 201 *et seq.*). The scattering curve for O^{2-} was that of Suzuki (1960).

Determination of the structure

The presence of a 2.9 \AA axis indicated that all atoms should be resolved in the (010) projection, and for this reason the structure determination by Fourier methods was confined to the $h0l$ level. Initial results indicated that the new structure might in some way be a subtle rearrangement of the low temperature form. The sharpened Patterson function $P(u, w)$ shown in Fig. 1 could be interpreted to indicate a pair of edge-shared octahedra across the origin as in CaFe_2O_4 (Fig. 5), and the strong vector interaction O-A (Fig. 1) had the right length but with a slightly different orientation. The symmetry-related pair of octahedra was placed at the centre of the unit cell, and the problem was then to join the two units by one further octahedron. Of the limited possibilities, joining the double blocks by another octahedron which shares corners with both of them, as has been found in $\text{NaTi}_2\text{Al}_5\text{O}_{12}$ (Mumme & Wadsley, 1967) would require an additional strong vec-

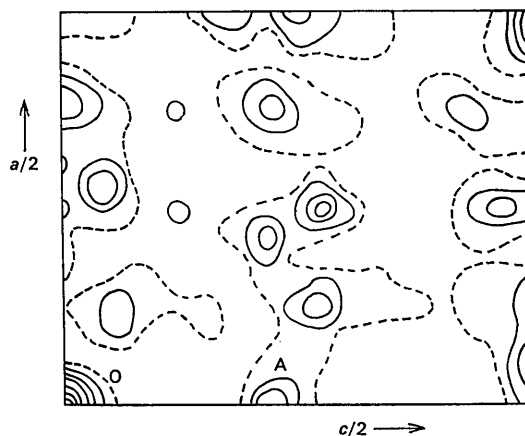


Fig. 1. Patterson function $P(u, w)$ projected on (010). The vector O-A connects metals in the edge-shared pair of octahedra across the origin.

tor interaction of length 2.9 Å, but this could not be found. The Patterson function did however support two possible ways in which a bridging octahedron could be inserted either to face or edge-share with one double block and corner share with the other.

Structure factors were therefore calculated for these two possibilities with metal atoms placed firstly at (0, 0.11) and (0.234, 0.176) and secondly at (0, 0.11) and (0.202, 0.344). Two-dimensional electron density maps projected onto (010) were calculated from the two sets of structure factors. From the second model it was then found possible to determine the approximate positions of the four oxygen atoms at (0.106, 0.176), (0.040, 0.365), (0.351, 0.264) and (0.372, 0.476) while a strong peak at (0.375, 0.125) suggested the position of the sodium atom, and clearly indicated this second model to be correct. The two-dimensional data

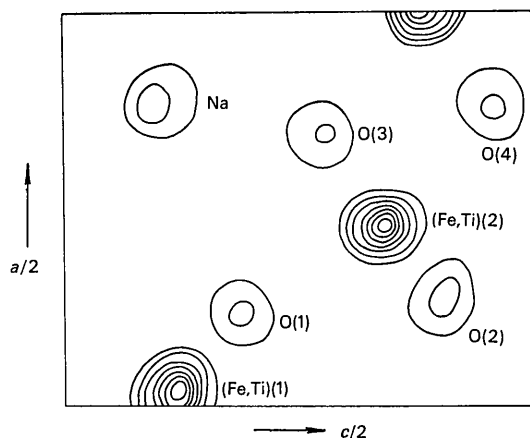


Fig. 2. Electron density projection on (010). Contours are at arbitrary intervals.

were then refined by progressive two-dimensional Fourier analysis (Fig. 2) until the *R* value had dropped to 12.4%.

At this stage the upper level data were included in the calculations, it being assumed that the atoms were situated in the mirror planes at $y = \frac{1}{2}$ and $\frac{3}{2}$ of space group *Pnma*, all in 4(c). For the asymmetric unit the octahedral metal atoms were placed at $\frac{1}{4}$ and $\frac{3}{4}$ while the sodium was placed at $\frac{1}{2}$. It was initially assumed that Fe and Ti randomly occupied the available octahedral sites, and that all sodium sites were occupied. From this point refinement was carried out by a number of least-squares cycles, varying coordinates and isotropic temperature factors. After several cycles *R* dropped from 13.5% to 11.5%. Further refinements with anisotropic temperature factors reached a steady state at the final *R* value of 10.02% and no further improvement was obtained by allowing for 90% rather than 100% occupation of sodium sites. Observed and calculated structure factors are given in Table 3. The positional and thermal parameters are listed in Table 4 and the bond lengths in Table 5.

Octahedral site occupancy and significance of anisotropic temperature factors

To determine if Fe and Ti were ordered several cycles of least-squares structure factor refinements for the two ordered possibilities were made in which coordinates and anisotropic temperature factors, 42 parameters in all, were allowed to vary from those given in Table 4. Initial *R* values of approximately 12.5% fell to final values of 11.7% for each of the ordered possibilities, compared with 10.02% for random occupancy. While these values strongly indicated that random occupancy of the octahedral positions by Fe and Ti is the preferred structural model, it is desirable to

Table 3. Observed and calculated structure factors

H	K	L	F ₀	F _c	H	K	L	F ₀	F _c	H	K	L	F ₀	F _c	H	K	L	F ₀	F _c			
2	2	0	0	239	215	1	0	0	547	546	10	1	4	315	334	1	2	2	-379	-764		
2	2	0	0	1553	1577	1	1	1	317	291	1	1	1	466	461	1	2	2	-291	-694		
2	2	0	0	1595	1470	1	1	1	646	601	1	1	1	-337	-376	1	2	2	1029	949		
2	2	0	0	895	1072	1	1	1	-895	-825	1	1	1	175	173	1	2	2	801	854		
2	2	0	0	1359	1401	1	1	1	-885	-782	1	1	1	169	165	1	2	2	245	282		
2	2	0	0	491	492	1	1	1	481	370	1	1	1	761	866	1	2	2	357	476		
2	2	0	0	-253	-492	1	1	1	-357	-368	1	1	1	943	825	1	2	2	365	306		
2	2	0	0	-1152	313	1	1	1	984	830	1	1	1	453	489	1	2	2	174	140		
2	2	0	0	185	119	1	1	1	-357	-368	1	1	1	398	457	1	2	2	527	647		
2	2	0	0	-1009	313	1	1	1	-980	-895	1	1	1	1475	1469	1	2	2	541	493		
2	2	0	0	464	441	1	1	1	497	454	1	1	1	657	689	1	2	2	-354	-314		
2	2	0	0	-716	-758	1	1	1	-655	-624	1	1	1	694	753	1	2	2	1557	1359		
2	2	0	0	1030	1232	1	1	1	-646	-604	1	1	1	531	524	1	2	2	497	418		
2	2	0	0	774	992	1	1	1	-355	-233	1	1	1	453	377	1	2	2	1061	1059		
2	2	0	0	-146	-1945	1	1	1	-341	-354	1	1	1	6	6	1	2	2	4	4	487	418
2	2	0	0	-371	-375	1	1	1	-791	-799	1	1	1	6	6	1	2	2	4	4	1061	1059
2	2	0	0	-303	-1041	1	1	1	-1246	-1179	1	1	1	6	6	1	2	2	4	4	511	491
2	2	0	0	407	376	1	1	1	-751	-655	1	1	1	1765	2035	1	2	2	293	342		
2	2	0	0	-157	-776	1	1	1	-679	-713	1	1	1	-995	-1022	1	2	2	469	469		
2	2	0	0	-712	-654	1	1	1	-403	-345	1	1	1	613	673	1	2	2	949	803		
2	2	0	0	384	-1209	1	1	1	-293	-251	1	1	1	722	848	1	2	2	895	888		
2	2	0	0	-186	-631	1	1	1	-571	-571	1	1	1	-601	-596	1	2	2	-485	-386		
2	2	0	0	-1185	-1186	1	1	1	-679	-674	1	1	1	435	438	1	2	2	-305	-470		
2	2	0	0	157	299	1	1	1	327	327	1	1	1	-435	-438	1	2	2	741	711		
2	2	0	0	-471	-293	1	1	1	-702	-847	1	1	1	309	317	1	2	2	-635	-552		
2	2	0	0	-243	-2665	1	1	1	-749	-308	1	1	1	-1405	-1535	1	2	2	-664	-597		
2	2	0	0	-940	-931	1	1	1	149	467	1	1	1	-542	-458	1	2	2	-469	-469		
2	2	0	0	631	-649	1	1	1	-2005	-1838	1	1	1	479	495	1	2	2	-202	-209		
2	2	0	0	1157	1317	1	1	1	-1049	-688	1	1	1	291	293	1	2	2	469	519		
2	2	0	0	-1391	-1544	1	1	1	-1103	-1336	1	1	1	-631	-643	1	2	2	-301	-288		
2	2	0	0	-960	-904	1	1	1	-1289	-1336	1	1	1	895	933	1	2	2	-495	-501		
2	2	0	0	-731	157	1	1	1	-449	-449	1	1	1	-435	-438	1	2	2	-166	-99		
2	2	0	0	1137	1065	1	1	1	-309	-357	1	1	1	625	629	1	2	2	-481	-507		
2	2	0	0	-162	-1676	1	1	1	-1405	-1419	1	1	1	-889	-899	1	2	2	-515	-515		
2	2	0	0	-1630	-1648	1	1	1	-157	-149	1	1	1	-252	-242	1	2	2	-714	-705		
2	2	0	0	1043	595	1	1	1	-1513	-1491	1	1	1	-815	-793	1	2	2	-467	-479		
2	2	0	0	-1247	-1262	1	1	1	291	307	1	1	1	-304	-304	1	2	2	-491	-518		
2	2	0	0	108	1086	1	1	1	-425	-499	1	1	1	-1197	-1212	1	2	2	469	469		
2	2	0	0	1063	1073	1	1	1	-425	-499	1	1	1	134	134	1	2	2	-268	-309		
2	2	0	0	473	452	1	1	1	-565	-366	1	1	1	487	549	1	2	2	319	309		
2	2	0	0	491	413	1	1	1	-637	632	1	1	1	13	13	1	2	2	-747	-833		
2	2	0	0	-716	-645	1	1	1	-1034	-1034	1	1	1	-365	-341	1	2	2	523	507		
2	2	0	0	679	633	1	1	1	-149	-1516	1	1	1	514	578	1	2	2	353	371		
2	2	0	0	646	592	1	1	1	-943	-951	1	1	1	-956	-765	1	2	2	-1097	-1057		
2	2	0	0	851	768	1	1	1	1429	1456	1	1	1	653	680	1	2	2	287	336		
2	2	0	0	823	894	1	1	1	497	754	1	1	1	260	260	1	2	2	507	605		
2	2	0	0	383	360	1	1	1	-637	-640	1	1	1	-846	-846	1	2	2	336	409		
2	2	0	0	1157	1182	1	1	1	729	776	1	1	1	336	336	1	2	2	279	367		
2	2	0	0	-519	-583	1	1	1	-405	-428	1	1	1	670	702	1	2	2	358	364		
2	2	0	0	787	616	1	1	1	601	751	1	1	1	670	702	1	2	2	279	367		
2	2	0	0	565	840	1	1	1	405	427	1	1	1	-649	-651	1	2	2	112	154		
2	2	0	0	731	622	1	1	1	969	1005	1	1	1	493	690	1	2	2	611	663		
2	2	0	0	-536	-446	1	1	1	479	499	1	1	1	605	494	1	2	2	12	12		

place some statistical weight on this result, obtained from 227 observations.

Hamilton (1965) has compiled tables in which the variance ratios $F_{b,n-m}$ (Hamilton, 1964) are converted to critical R factor ratios \mathcal{R} for comparing alternate hypotheses at a given significance level (Reid, Wadsley & Sienko, 1968). The effects (inherent in simple analysis-of-variance tests) of assumed linearities and of weightings introduced by particular computational schemes, provided these are used consistently, should be largely cancelled by taking the R factor ratio for alternative models. Similarly the effects of using either $|F_o| - |F_c|$ differences, or weighted least-squares deviations to calculate individual R factors should also cancel.

For the present case we find the critical R ratio at the 0.025 significance level to be $\mathcal{R}_{42, 272-42, 0.025} = 1.162$. The observed R factor ratio is $\mathcal{R} = 11.68/10.02 = 1.165$, and thus random occupancy can be accepted as the correct statistical model at a 97.5% confidence level. This result was not significantly altered whether 100% or 90% sodium occupancy was assumed.

Considering now the improvement in the random occupancy refinement when seven isotropic temperature factors are replaced with twenty-eight anisotropic ones, we wish to determine whether the change in R from 11.5% to 10.02% is significant, or whether we

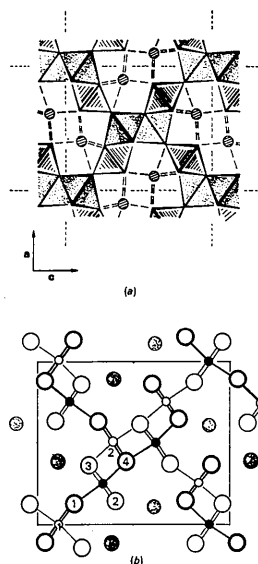


Fig. 3. (a) Crystal structure of $\text{Na}_x\text{Fe}_x\text{Ti}_{2-x}\text{O}_4$. Heavy markings show sites at $y = \frac{3}{4}$ and light markings show sites at $y = \frac{1}{4}$. Shaded circles are Na atoms. (b) Crystallographic sites in $\text{Na}_x\text{Fe}_x\text{Ti}_{2-x}\text{O}_4$. Heavy circles show sites at $y = \frac{3}{4}$, light circles atoms at $y = \frac{1}{4}$. Small circles (Fe, Ti) sites, large open circles oxygen and stippled circles Na. The unprimed numbers in the asymmetric unit cell correspond to those in Table 3.

Table 4. Fractional atomic coordinates and thermal parameters for high temperature NaFeTiO_4

Space group $Pnma$ (no. 62).

All atoms at point positions $4(c), \pm(x, \frac{1}{2}, z); \pm(\frac{1}{2} - x, \frac{1}{2}, \frac{1}{2} + z)$. All $U_{12} = U_{23} = 0$. e.s.d.'s are given in parentheses, e.g. 0.3935 ± 0.0024 .

	x	y	z	U_{11}	U_{22}	U_{33}	$2U_{13}$
Na	0.3925 (24)	$\frac{1}{2}$	0.1082 (16)	0.034 (10)	0.136 (25)	0.024 (9)	0.014 (15)
M(1)	0.0185 (5)	$\frac{1}{2}$	0.1206 (4)	0.005 (2)	0.013 (4)	0.003 (2)	-0.006 (3)
M(2)	0.2296 (6)	$\frac{1}{2}$	0.3404 (4)	0.009 (2)	0.018 (4)	0.012 (8)	-0.003 (4)
O(1)	0.1248 (30)	$\frac{1}{2}$	0.1877 (17)	0.028 (12)	0.020 (16)	-0.014 (8)	0.000 (15)
O(2)	0.1240 (27)	$\frac{1}{2}$	0.4059 (18)	0.016 (11)	0.016 (17)	0.000 (10)	-0.003 (17)
O(3)	0.3586 (24)	$\frac{1}{2}$	0.2708 (20)	0.006 (10)	0.002 (15)	0.013 (10)	-0.017 (17)
O(4)	0.3918 (21)	$\frac{1}{2}$	0.4626 (19)	-0.006 (8)	0.023 (18)	0.005 (9)	0.013 (15)

Table 5. Interatomic distances and e.s.d.'s for $\text{Na}_{0.90}\text{Fe}_{0.90}\text{Ti}_{1.10}\text{O}_4$

All sites have a b axis repeat distance of 2.973 ± 0.006 Å. Site numbers correspond to those in Fig. 3(b).

(Fe, Ti) and Na separations			(Fe, Ti) octahedron			Na-O polyhedron		
	No.	Distance		No.	Distance		No.	Distance
Na—Na	2	2.973 ± 0.006	(Fe, Ti)(2) octahedron			Na—O(1)	1	2.64 ± 0.025
Na—Na*	2	3.48 ± 0.02	(Fe, Ti)(2)—O(1)	1	1.985 ± 0.020	O(2)	2	2.60 ± 0.025
(Fe, Ti)(1)—(Fe, Ti)(1)	2	2.973 ± 0.006	O(2)	2	1.927 ± 0.019	O(2')	1	2.30 ± 0.025
(Fe, Ti)(1)—(Fe, Ti)(1')	2	3.13 ± 0.01	O(3)	2	2.063 ± 0.019	O(3)	2	2.39 ± 0.025
(Fe, Ti)(1)—(Fe, Ti)(2)	2	3.50 ± 0.01	O(4)	1	2.042 ± 0.017	O(1')	1	3.15 ± 0.025
(Fe, Ti)(2)—(Fe, Ti)(1')	2	3.09 ± 0.01	O(1)—O(2)	2	2.89 ± 0.027	O(1')	2	3.45 ± 0.013
(Fe, Ti)(1) octahedron			O(1)—O(3)	2	2.79 ± 0.027	O(2)	2	2.79 ± 0.027
(Fe, Ti)(1)—O(1)	2	1.938 ± 0.020	O(2)—O(3)	2	2.66 ± 0.026	O(2')	2	3.47 ± 0.026
O(3')	1	1.926 ± 0.019	O(2)—O(4)	2	2.96 ± 0.025	O(4')	2	2.96 ± 0.025
O(4')	2	2.115 ± 0.017	O(3)—O(4)	2	2.65 ± 0.025	O(1)—O(1')	2	2.92 ± 0.027
O(4'')	1	1.975 ± 0.027				O(3)—O(1')	2	2.92 ± 0.027
O(1)—O(3')	2	2.92 ± 0.027				O(1)—O(2')	2	2.89 ± 0.027
O(1)—O(4')	2	2.75 ± 0.026				O(2)—O(2')	2	3.47 ± 0.026
O(1)—O(4'')	2	2.96 ± 0.026				O(2'')—O(4')	2	2.96 ± 0.025
O(3')—O(4')	2	2.65 ± 0.025				O(4')—O(1)	2	2.96 ± 0.026
O(4')—O(4'')	2	2.64 ± 0.024						

* Oblique separation in a double tunnel.

have perhaps overdetermined the problem. From Hamilton's tables we find $R_{28-7, 227-21, 0.005} = 1.110$. The observed R is $11.5/10.02$, i.e. 1.15, and thus an improvement at a greater than 99.5% confidence level

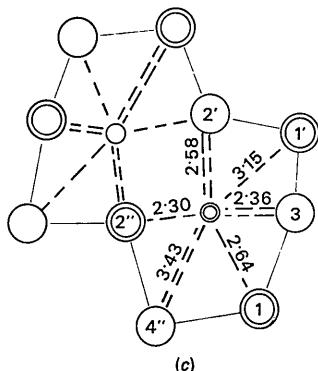
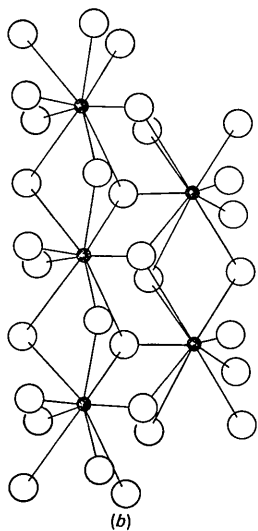
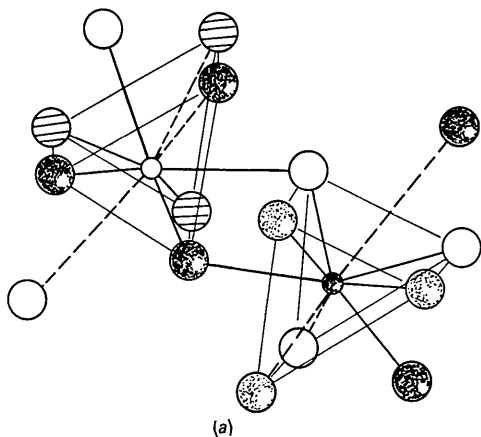


Fig. 4. Na-O coordination polyhedra in $\text{Na}_x\text{Fe}_x\text{Ti}_{2-x}\text{O}_4$. Small circles Na, large circles O. (a) The disposition of the paired coordination polyhedra viewed obliquely along b . These atoms with similar shadings are at the same level. (b) Sequence of staggered Na atoms down a double tunnel. (c) Actual Na-O separations shown on the (010) projection. The numbers correspond to Fig. 3(b).

has been obtained. There seems no reason to suppose that the large anisotropic Na vibration in the y direction is not real, and presumably associated with 90% occupancy of the sodium ion sites, but since even modest systematic errors in, say, upper level intensity data, could quite strongly affect the actual value of U_{22} , its present value should only be taken to show that considerable anisotropy exists. Indeed when 90% sodium occupancy was considered, an attempted further refinement of the data gave increasingly large and presumably unreal values of U_{22} .

Description

The structure is illustrated in Fig. 3. There are two crystallographically non-equivalent octahedral sites, randomly occupied by Fe and Ti, and indicated by dotted and shaded markings respectively. As required by space group $Pnma$, all atoms lie in planes at $y = \frac{1}{4}$ or $y = \frac{3}{4}$, the b -axis repeat distance of 2.973 Å being the octahedron edge length and necessarily also the b -axis metal-metal separation distance.

The basic unit of the structure, as in NaFeTiO_4 and other calcium ferrite isomorphs, is a pair, or double block, of edge-shared octahedra with their axes normal to the b axis. In the present structure however, the double blocks are further condensed by edge sharing, giving a distorted Z-shaped group of four octahedra, as viewed in projection down the b axis. This Z section extends in an infinite ribbon in the b -axis direction, and is corner-joined to four other Z sections reversed with respect to it. The corner-joining of the relatively large ribbons of four octahedra leaves double tunnels between the ribbons, instead of single tunnels as in the calcium ferrite structure. These 'double barrelled' tunnels are occupied by double rows of sodium atoms separated vertically by 2.973 Å and staggered alternately in each 'barrel' of the tunnels, giving each sodium atom an unusual sixfold coordination to its nearest oxygen neighbours (Fig. 4). Of the total of nine neighbours, three at $y = \frac{3}{4}$ and three at $y = \frac{1}{4}$ are located about the central Na atom at the corners of a right triangular prism whose interfacial angles are $35\frac{1}{2}^\circ$, $84\frac{1}{2}^\circ$ and 60° . Three additional oxygen atoms are located out from the three prism faces. The six nearest neighbours comprise the four oxygen atoms at the corners of the smallest face of the prism, and the two out from the two longer faces. A somewhat similar coordination is found for Mg^{2+} , Ca^{2+} , Eu^{2+} and Na^+ in the calcium ferrite isotypes, except that in them the prism is more regular and all six oxygen atoms defining it are at approximately equal distance from Mg^{2+} (Müller-Buschbaum, 1966), Ca^{2+} (Hill, Peiser & Rait, 1956; Bertaut, Blum & Magnano, 1956; Decker & Kasper, 1957; Müller-Buschbaum & Schnering, 1965), Eu^{2+} (Rau, 1966) or Na^+ (Reid, Wadsley & Sienko, 1968). These ions therefore have eight nearest neighbours rather than six. In $\text{Na}_x\text{Fe}_x\text{Ti}_{2-x}\text{O}_4$ furthermore, the coordination polyhedra have come together

in pairs, as illustrated in Figs. 3 and 4. The shorter Na–O bonds vary between 2.30 and 2.64 Å while the three longer ones vary between 3.43 and 3.15 Å.

The (Fe, Ti)–O distances in the metal–oxygen octahedra vary between 1.93 and 2.12 Å, a normal range for titanates (Andersson & Wadsley, 1962) and compare with 1.97 to 2.03 Å estimated for NaFeTiO₄ from NaScTiO₄ fractional coordinates and NaFeTiO₄ lattice parameters.

Discussion

Examination of Figs. 3, Na_xFe_xTi_{2-x}O₄, and 5, NaFeTiO₄, shows that the framework of the non-stoichiometric structure can be obtained from that of NaFeTiO₄ by a relatively modest displacement of the octahedra containing metal atoms at sites (2). Metal atoms at sites (1) are not displaced, the double blocks containing them being merely rotated to positions more nearly parallel to the *c* axis. The arranging of Na⁺ ions in double tunnels rather than in single ones apparently necessitates less than total occupancy, and despite the lower sodium content compared with NaFeTiO₄, the unit-cell volume for Na_{0.90}Fe_{0.90}Ti_{1.10}O₄ is 6.8% greater.

Double tunnels in 3 Å repeat structures are unusual, and even in psilomelane for example (Wadsley, 1953), the double tunnels are occupied by Ba²⁺ and H₂O with a consequent lessening of repulsion compared to that for occupation by charged ions. One of the noticeable features of the present structure is the large amplitude of thermal vibration of the Na⁺ ions in the *y* direction (*U*₂₂ in Table 4). A similar vibration has been discussed in some detail for Na⁺ in NaTi₂Al₅O₁₂ (Mumme & Wadsley, 1967) and it appears to be a real consequence of relatively unhindered vibration along the tunnel directions.

Another apparently equally likely form of Na_xFe_xTi_{2-x}O₄ might have been that shown in Fig. 6, in which face as well as edge sharing is involved. Although it did not form in the present case it could well do so in others.

The present structure is a further example of the relatively numerous class of compounds in which double blocks of edge-shared octahedra are combined in a lattice framework which provides tunnels for the accommodation of alkali or alkaline earth ions. These structures are characterized by a 3 Å (octahedron edge length) repeat distance, by the general formula A_xB₂O₄, and frequently also by having four double blocks in a unit cell with fourfold symmetry, leading to unit-cell axes approximately 10 Å × 10 Å and unit-cell volumes of 300 Å³ for an oxygen content of sixteen atoms. Besides Na_xFe_xTi_{2-x}O₄, *Pnma*, these 'fourfold' structures include the calcium ferrite type, typified by NaFeTiO₄, *Pnma* (Reid, Wadsley & Sienko, 1968), calcium titanite, *Bbmm*, (Bertaut & Blum, 1956) the hollandite structure, *I4/m*, (Byström & Byström, 1950) typified by K₂Al₂Ti₆O₁₆ (Bayer & Hoffman, 1966), and CaMn₂O₄, *Pmab*, (Lepicard & Protas, 1966).

The compound Na_xFe_xTi_{2-x}O₄ also provides an interesting addition to the pseudo-binary system NaFeO₂–TiO₂, which is now known to contain the following compounds of octahedral Fe³⁺: NaFeO₂ (rhombohedral), NaFeTiO₄ (orthorhombic), Na_xFe_xTi_{2-x}O₄, 0.90 > *x* > 0.75, (orthorhombic) and Na_xFe_xTi_{8-x}O₁₆, 2 ≥ *x* > 1.2, (monoclinic) (Bayer & Hoffman, 1965; Wadsley, 1964; Reid & Sienko, 1967).

The authors are indebted to Dr A. D. Wadsley for valuable discussions and suggestions.

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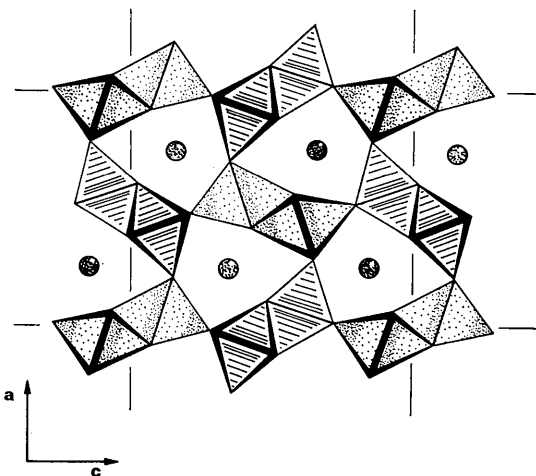


Fig. 5. NaFeTiO₄ (calcium ferrite isotype) crystal structure.

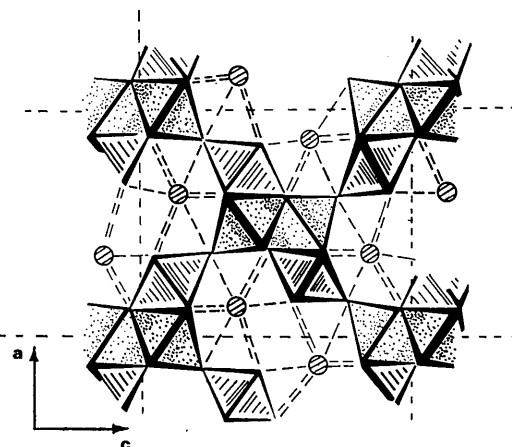


Fig. 6. Postulated alternative to the structure of Na_xFe_xTi_{2-x}O₄.

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The Crystal Structure of Dihydroxyfumaric Acid Dihydrate

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(Received 7 May 1965 and in revised form 12 September 1967)

Dihydroxyfumaric acid dihydrate $C_4H_4O_6 \cdot 2H_2O$ is monoclinic, $a = 6.40$, $b = 13.03$, $c = 5.34 \text{ \AA}$; $\beta = 126.5^\circ$. Space group $P2_1/c$, two centrosymmetric molecules in the unit cell. The atomic positions were determined by the [100], [010], [001] projections and by least-squares refinement of X-ray diffraction data. In the crystal structure the dihydroxyfumaric acid molecules are arranged in sheets, alternate sheets being separated by 1.60 \AA . The binding of the sheets of molecules in alternate layers is provided *via* the water molecules which are linked through oxygen atoms of the COOH groups (O-H \cdots O) by hydrogen bonds of 2.56 and 2.85 \AA . The molecule is nearly planar with generally accepted bond lengths and angles.

Dihydroxyfumaric acid $C_4H_4O_6 \cdot 2H_2O$ has of late assumed importance in biochemistry and has variously been described in the past as having either the *cis* or the *trans* configuration. Chemical evidence for or against these alternative configurations has been presented by Hartree (1953). In a previous communication the senior author (Gupta, 1953) was able to show conclusively from X-ray diffraction data that the molecule in the crystalline state must have the *trans* configuration since it crystallized in the monoclinic system, class $2/m$, space group $P2_1/c$ with two molecules in the unit cell of dimensions,

$$a = 6.40 \pm 0.02, \quad b = 13.03 \pm 0.03, \quad c = 5.34 \pm 0.01 \text{ \AA}; \\ \beta = 126.5 \pm 0.1^\circ.$$

The observed density is 1.715 g.cm^{-3} , calculated 1.708 g.cm^{-3} . The systematic absences of the X-ray reflexions are: $h0l$ absent when l is odd and $0k0$ absent when k is odd, so that the space group is determined uniquely as $P2_1/c$. Details of crystal morphology and pseudo-orthorhombic symmetry displayed by the crystal are given by Gupta (1953).

In a preliminary note Gupta (1955) gave the results of a Fourier analysis of the $0kl$ data from the dihydroxyfumaric acid dihydrate crystal. The structure determination, however, remained incomplete for more than nine years. The present paper, therefore, describes the results of fresh investigation by the authors using new experimental data.

Table 1. Final atomic coordinates and standard deviations

	x/a	$\sigma(x)$ (\AA)	y/b	$\sigma(y)$ (\AA)	z/c	$\sigma(z)$ (\AA)
C(1)	0.0880	0.014	0.0112	0.013	0.1516	0.011
C(2)	0.2162	0.013	-0.0696	0.012	0.3970	0.012
O(1)	0.3426	0.010	-0.0354	0.009	0.6748	0.010
O(2)	0.1980	0.010	-0.1603	0.008	0.3182	0.008
O(3)	0.1147	0.009	0.1097	0.008	0.2689	0.008
O ₄ (H ₂ O)	0.4296	0.009	0.1777	0.009	0.9164	0.008