O atoms of the SeO_4 tetrahedra translated along the *b* axis. The shortest O—O distances are as follows: $O(3)_{y+1}\cdots O(4)$ 2·556 (22), $O(7)_{y+1}\cdots O(8)$ 2·479 (21), $O(11)_{y+1}\cdots O(9)$ 2·605 (26) Å.

Assuming these O—O distances to be due to the hydrogen bonds, the crystal structure of RHSe can be described as consisting of SeO_4^{2-} chains similar to the SO_4^{2-} chains formed in AHS and RHS, although the mutual arrangement of the chains in RHSe is different.

The coordination polyhedra of the Rb ions are similar. Rb—O distances up to 3·5 Å are listed in Table 2. Assuming the radius of the coordination sphere of Rb to be equal to 3·5 Å, the coordination number of the Rb atom is 10.

The pseudosymmetry observed in RHSe in the ferroelectric phase points to the possible existence of an upper phase with higher symmetry, which might be treated as the starting phase (called the prototype) from which the ferroelectric phase can be derived by small displacements or deformations. Recent work performed in our laboratory showed that the symmetry of the high-temperature phase is monoclinic with space group $I2_1$, $\gamma = 90{\cdot}70\ (1)^\circ$ (Pietraszko *et al.*, 1978).

Detailed discussion of the spontaneous polarization and the phase-transition mechanism in RHSe will be given when the crystal structure of the paraelectric phase has been determined and more information on the ferroelectric properties of $RbHSeO_4$ is available.

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Non-Stoichiometric Sodium Iron(II) Titanium(IV) Oxide

BY T. ISHIGURO, K. TANAKA, F. MARUMO, M. G. M. U. ISMAIL,
S. HIRANO AND S. SŌMIYA

*Research Laboratory of Engineering Materials, Tokyo Institute of Technology, O-okayama, Meguro-ku,
Tokyo 152, Japan*

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Abstract. $Na_{0.56}Fe_{0.28}Ti_{1.72}O_4$, orthorhombic, *Pnma*, $a = 9{\cdot}083\ (6)$, $b = 2{\cdot}954\ (1)$, $c = 10{\cdot}718\ (3)$ Å, $Z = 4$, $D_x = 4{\cdot}04$ g cm^{-3}. The crystals were prepared by heating a mixture of Fe and TiO_2 in a 10 *M* NaOH solution sealed in a Au tube at 650°C and 1000 bar. After 7 d black prismatic crystals were obtained. The compound is isostructural with $CaFe_2O_4$, with mean *M*(1)—O, *M*(2)—O and Na—O distances of 2·00, 1·98 and 2·48 Å respectively.

Introduction. Oscillation and Weissenberg photographs showed the crystal to be orthorhombic. The systematic absences, 0*kl* with $k + l$ odd and *hk*0 with *h* odd, indicated the space group to be $Pn2_1a$ or *Pnma*; the structure refinement showed the latter to be correct. Cell dimensions were determined by the least-squares method from the 2θ values of 19 reflections.

A prismatic crystal with approximate dimensions 0·04 × 0·30 × 0·04 mm was used for intensity collection. Intensities were measured on a Philips automated four-circle diffractometer with Mo $K\alpha$ radiation monochromated by graphite up to $2\theta = 45°$, employing the ω–2θ scan technique. The scan speed was 4° min^{-1} in ω and scanning was repeated twice when the total counts were less than 1000. The scan width was varied for each reflection according to the formula $(1{\cdot}2 + 0{\cdot}3 \tan \theta)^\circ$. Intensities were corrected for the Lorentz, polarization and absorption factors ($\mu = 68{\cdot}61$ cm^{-1} for Mo $K\alpha$). 599 independent reflections, whose $|F|$'s were larger than $3\sigma(|F|)$, were obtained and used for the structure determination.

The structure was solved by the heavy-atom method. At the initial stage, the Fe^{2+} ions were treated as Ti^{4+}. The positions of the Ti^{4+} and Na^+ ions were obtained from the Patterson maps. The O^{2-} ions were found on the Fourier maps phased with the Ti^{4+} and Na^+ ions. The refinement of the structure was carried out with the full-matrix least-squares program *LINUS* (Coppens & Hamilton, 1970). The site populations of the metal ions were also varied at the final stage by constraining the net charge of the crystal to be neutral and by assuming that no vacancy exists at either of the (Ti^{4+},Fe^{2+}) sites. The final conventional R value was 0·064. The difference Fourier maps synthesized with the final atomic parameters were absolutely flat.

The atomic scattering and dispersion-correction factors for Na^+, Fe^{2+} and Ti^{4+} were taken from *International Tables for X-ray Crystallography* (1974), and the scattering factors given by Tokonami (1965) were used for O^{2-}. The final positional parameters and populations are given in Table 1.* The structure viewed along the b axis is shown in Fig. 1. The interatomic distances are given in Table 2 with their estimated standard deviations in parentheses.

Discussion. Intensive studies have been carried out on the synthesis of compounds in the Na_2O–Fe_2O_3–TiO_2 ternary oxide system with the dry method by Reid and co-workers (Reid & Sienko, 1967; Reid, Perkins & Sienko, 1968; Li, Reid & Saunders, 1971). They found four phases on the tie-line $NaFeO_2$–TiO_2 besides TiO_2: $Na_{1-x}Fe_{1-x}Ti_xO_2$ ($0 \le x \le 0{\cdot}28$), $NaFeTiO_4$, $Na_xFe_xTi_{2-x}O_4$ ($0{\cdot}75 \le x \le 0{\cdot}90$), and $Na_{1-x}Fe_{1-x}Ti_{3+x}O_8$ ($0 \le x \le 0{\cdot}33$). Of these, the crystal of $NaFeTiO_4$ was reported to have a $CaFe_2O_4$-type structure with cell dimensions: $a = 9{\cdot}175$, $b = 2{\cdot}962$, $c = 10{\cdot}741$ Å (Reid, Wadsley & Sienko, 1968), though the atomic parameters were not refined. However, non-stoichiometric sodium iron(III) titanium(IV) oxide $Na_xFe^{III}_xTi^{IV}_{2-x}O_4$ ($0{\cdot}75 \le x \le 0{\cdot}90$), obtained by melting $NaFeTiO_4$ in air at 1220 °C, has a structure related to, but different from, the $CaFe_2O_4$ structure (Mumme & Reid, 1968). The present compound $Na_xFe^{II}_{x/2}Ti^{IV}_{2-x/2}O_4$ ($x = 0{\cdot}555$), synthesized with a high P_{H_2} and at a lower temperature than in the dry method, is isostructural with $NaFe^{III}Ti^{IV}O_4$, having slightly smaller cell dimensions. The Fe^{2+} and Ti^{4+} ions occupy the octahedral sites statistically. The site-population

Table 1. *Final positional parameters and populations*

		Population	x	y	z
$M(1)$	Ti^{4+}	0·79 (2)	0·0598 (2)	0·25	0·1147 (1)
	Fe^{2+}	0·21 (2)			
$M(2)$	Ti^{4+}	0·93 (2)	0·4135 (2)	0·75	0·1029 (2)
	Fe^{2+}	0·07 (2)			
Na		0·55 (2)	0·2405 (8)	0·25	0·3462 (6)
O(1)		1	0·2045 (7)	0·75	0·1458 (6)
O(2)		1	0·1128 (6)	0·75	0·4841 (5)
O(3)		1	0·4231 (7)	0·75	0·4280 (5)
O(4)		1	0·4746 (7)	0·25	0·2146 (5)

Table 2. *Interatomic distances* (Å)

Symmetry code

None x,y,z
(i) $\frac{1}{2} - x, 1 - y, \frac{1}{2} + z$
(ii) $\frac{1}{2} + x, y, \frac{1}{2} - z$
(iii) $x - \frac{1}{2}, y, \frac{1}{2} - z$
(iv) $x, 1 + y, z$

$M(1)$–O(3^{i})	2·007 (6)	$M(2)$–O(4)	1·981 (4) ×2
$M(1)$–O(4^{iii})	1·987 (6)	O(1)–O(2^{i})	2·817 (7) ×2
$M(1)$–O(1)	2·005 (4) ×2	O(1)–O(4)	2·957 (3) ×2
$M(1)$–O(3^{iii})	1·983 (4) ×2	O(2^{ii})–O(2^{i})	2·549 (6) ×2
O(3^{i})–O(1)	2·995 (8) ×2	O(2^{ii})–O(4)	2·879 (7) ×2
O(3^{i})–O(3^{iii})	2·553 (7) ×2	O(2^{i})–O(4)	2·595 (8) ×2
O(4^{iii})–O(1)	2·964 (8) ×2	O(2^{i})–O(2^{iv})	2·954 (1) ×2
O(4^{iii})–O(3^{iii})	2·763 (7) ×2	Na–O(1)	2·627 (7) ×2
O(1)–O(3^{iii})	2·675 (9) ×2	Na–O(4)	2·552 (9)
O(1)–O(1^{iv})	2·954 (1) ×2	Na–O(3)	2·388 (7) ×2
$M(2)$–O(1)	1·953 (6)	Na–O(2)	2·390 (7) ×2
$M(2)$–O(2^{ii})	2·036 (6)	Na–O(4^{iii})	2·501 (10)
$M(2)$–O(2^{i})	1·965 (5) ×2	O(2)–O(3)	2·882 (8) ×2

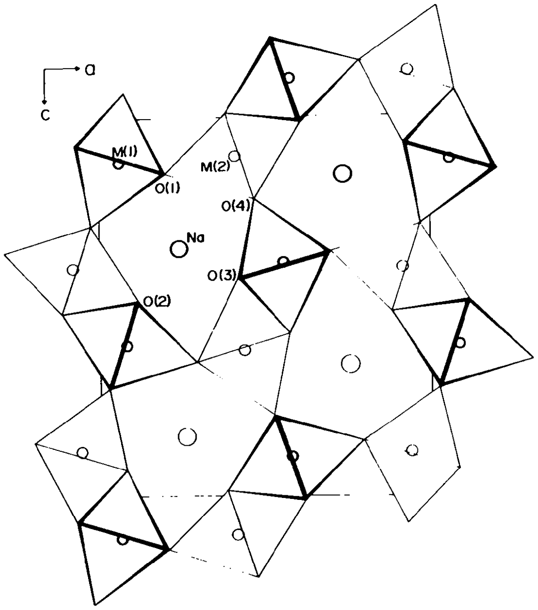

Fig. 1. The crystal structure of $Na_{0.56}Fe_{0.28}Ti_{1.72}O_4$ viewed along **b**, showing the linkage of (Ti,Fe)O_6 octahedra.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33773 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

analysis indicated that the Fe^{2+} ions have a higher concentration at the $M(1)$ site than at $M(2)$, and that the Na^+ site is approximately half-vacant, giving the chemical formula $Na_{0\cdot56}Fe^{II}_{0\cdot28}Ti^{IV}_{1\cdot72}O_4$. Though some of the Fe^{2+} ions might be oxidized to Fe^{3+}, the amount should not be large, since the final difference Fourier maps are quite flat around the Na^+ and (Ti^{4+},Fe^{2+}) sites.

The $(Ti,Fe)O_6$ octahedra share edges, constructing double chains parallel to [010]. The chains are further joined laterally with each other by sharing corners of the octahedra to form a three-dimensional framework with ditrigonal tunnels running parallel to [010]. The $M(1)$—O distances range from 1·98 to 2·01 Å (mean 2·00 Å), while the $M(2)$—O distances are in the range from 1·95 to 2·04 Å (mean 1·98 Å). These values are in agreement with the (Ti,Fe)—O distances found in $Na_{0\cdot90}Fe_{0\cdot90}Ti_{1\cdot10}O_4$ (Mumme & Reid, 1968) and freudenbergite (Ishiguro, Tanaka, Marumo, Ismail, Hirano & Sōmiya, 1978). In fact, the ionic radii given by Shannon & Prewitt (1969) suggest that the (Ti,Fe)—O distance in the present crystal should be longer than those in the above two crystals by only 0·005 and 0·013 Å respectively. It is notable that the Fe^{2+} ion with a larger ionic radius than Ti^{4+} is more concentrated at the $M(1)$ site which has a slightly larger octahedral environment than $M(2)$.

The Na—O distances range from 2·39 to 2·63 Å (mean 2·48 Å). Since the Na^+ ions lie in the wide tunnel spaces and approximately one half of their sites are vacant, this compound is expected to show ionic conduction by Na^+ ions in the [010] direction.

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Lead Zirconium Sulphide

BY R. LELIEVELD AND D. J. W. IJDO

Gorlaeus Laboratoria, Section of Solid State Chemistry, University of Leiden, PO Box 9502, 2300 *RA Leiden, The Netherlands*

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Abstract. $PbZrS_3$, *Pnma*, $a = 9\cdot0134\ (7)$, $b = 3\cdot7660\ (2)$, $c = 13\cdot9237\ (10)$ Å, $Z = 4$. Structure refinement based on neutron diffraction powder diagrams established the modified NH_4CdCl_3 structure of $PbZrS_3$. The compound is isostructural with $PbSnS_3$.

Introduction. We investigated the crystal structure of $PbZrS_3$ as a part of a research programme on the structural relations of compounds ABX_3, where A represents an alkaline or alkaline-earth metal, B a transition metal and X a halogen or S.

Sterzel & Horn (1970) reported the structures of $PbZrS_3$ and $PbHfS_3$, but their samples were contaminated with PbS. Their resulting X-ray powder pattern could be indexed like $PbSnS_3$ (Yamaoko & Okai, 1970), Table 1.

Table 1. *Crystal axes for* ABS_3

	a (Å)	b (Å)	c (Å)	Reference
$PbZrS_3$	9·031 (6)	3·770 (4)	13·919 (9)	Sterzel & Horn (1970), omitting their PbS pattern
$PbHfS_3$	8·989 (2)	3·738 (2)	13·924 (4)	
$PbZrS_3$	9·037 (5)	3·77 (2)	13·926 (5)	Yamaoko (1972)
$PbZrS_3$	9·0134 (7)	3·7660 (2)	13·923 (10)	This work
$PbSnS_3$	8·738	3·792	14·052	Jumas *et al.* (1972)
Sn_2S_3	8·864 (6)	3·747 (1)	14·020	Mootz & Puhl (1972)