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Ilmenite-type $\text{Na}_2(\text{Fe}_{2/3}\text{Te}_{4/3})\text{O}_6$

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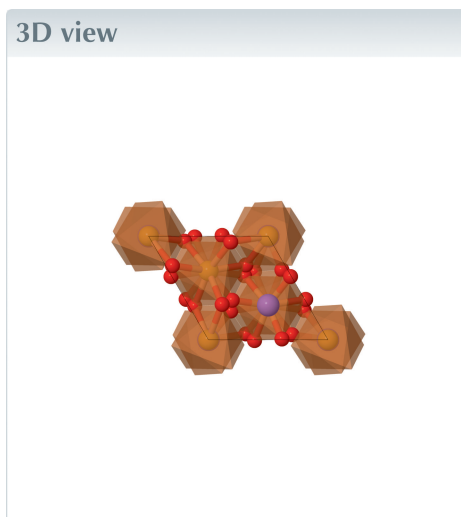
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$\text{Na}_2(\text{Fe}_{2/3}\text{Te}_{4/3})\text{O}_6$ ($Z = 3$) or $\text{Na}_3(\text{FeTe}_2)\text{O}_9$ ($Z = 2$), trisodium iron(III) ditellurium(VI) nonaoxide, adopts the ilmenite (FeTiO_3 , $Z = 6$) structure type with the Ti site (site symmetry 3.) replaced by Na and the Fe site (site symmetry 3.) replaced by a mixed-occupied ($\text{Fe}^{\text{III}}, \text{Te}^{\text{VI}}$) site in a Fe:Te ratio of 1:2. Whereas the $[(\text{Fe}, \text{Te})\text{O}_6]$ octahedron is only slightly distorted, the $[\text{NaO}_6]$ octahedron shows much stronger distortions, as revealed by a larger spread of the bond lengths and some distortion parameters.



Structure description

Crystals of $\text{Na}_2(\text{Fe}_{2/3}\text{Te}_{4/3})\text{O}_6$ were inadvertently obtained during hydrothermal synthesis attempts originally aiming at a phase with composition $\text{Na}_{12}\text{Fe}^{\text{III}}_6\text{Te}^{\text{VI}}_4\text{O}_{27}\cdot 3\text{H}_2\text{O}$ and for which possible relationships with the potassium phase $\text{K}_{12}\text{Fe}^{\text{III}}_6\text{Te}^{\text{VI}}_4\text{O}_{27}\cdot 3\text{H}_2\text{O}$ (Eder, 2023) were to be investigated.

$\text{Na}_2(\text{Fe}_{2/3}\text{Te}_{4/3})\text{O}_6$ ($Z = 3$) or $\text{Na}_3(\text{FeTe}_2)\text{O}_9$ ($Z = 2$) crystallizes in the ilmenite structure type (FeTiO_3 , $Z = 6$). The Na^+ cations take the Ti sites and the occupationally disordered ($\text{Fe}^{\text{III}}/\text{Te}^{\text{VI}}$) atoms (ratio $\text{Fe}^{\text{III}}:\text{Te}^{\text{VI}} = 1:2$) take the Fe sites of the ilmenite structure. The latter is a twofold superstructure of the corundum structure where two-thirds of the octahedral voids of the hexagonal close packed (hcp) structure defined by O atoms are occupied (Wells, 1975). The two types of metal sites in the ilmenite structure, both with site symmetry 3. (multiplicity 6, Wyckoff letter c), have a distorted octahedral oxygen environment. The $[(\text{Fe}, \text{Te})\text{O}_6]$ octahedron is only slightly distorted, the $[\text{NaO}_6]$ octahedron more clearly as evidenced by their bond lengths distribution $[(\text{Fe}, \text{Te})-\text{O} = 1.951(3) \text{ \AA} (3\times), 1.993(3) \text{ \AA} (3\times); \text{Na}-\text{O} = 2.297(3) \text{ \AA} (3\times), 2.545(4) \text{ \AA} (3\times)]$, and by quantitative distortion parameters (Robinson *et al.*, 1971) [quadratic elongation: $[(\text{Fe}, \text{Te})\text{O}_6] = 1.018$; $[\text{NaO}_6] = 1.062$; angle variance: $[(\text{Fe}, \text{Te})\text{O}_6] = 62.99^\circ$; $[\text{NaO}_6] = 204.27^\circ$]. The polyhedral volume of $[(\text{Fe}, \text{Te})\text{O}_6]$ amounts to 9.950 \AA^3 , and that of $[\text{NaO}_6]$ to 17.378 \AA^3 as calculated with the VOLCAL option in *PLATON* (Spek, 2020).



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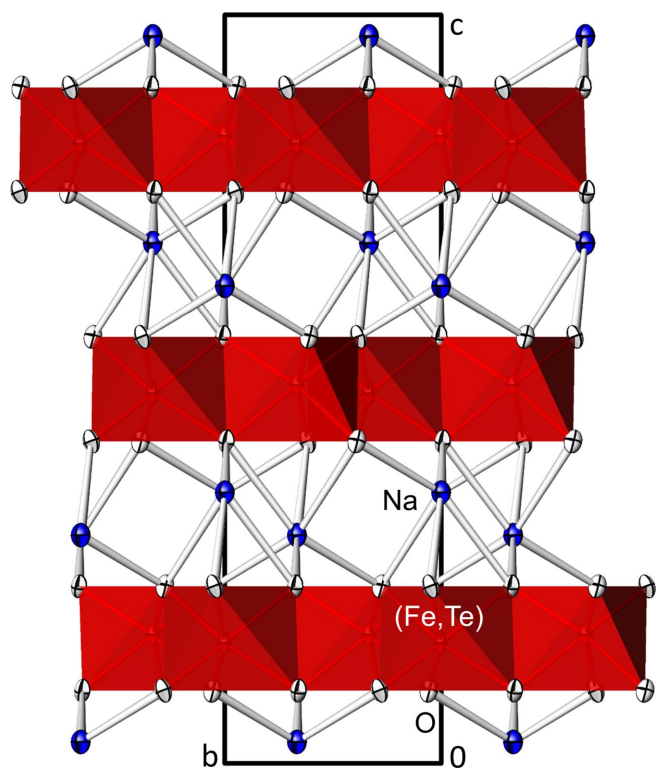


Figure 1
Crystal structure of ilmenite-type $\text{Na}_2(\text{Fe}_{2/3}\text{Te}_{4/3})\text{O}_6$ in a projection along $[\bar{1}00]$ showing the layer stacking along $[001]$. $[(\text{Fe},\text{Te})\text{O}_6]$ units are shown in the polyhedral representation (red octahedra), Na atoms (blue) with bonds to the O atoms. Displacement ellipsoids are drawn at the 74% probability level.

The only other Te-containing compounds adopting the ilmenite structure type deposited with the Inorganic Crystal Structure Database (ICSD, release 2023–1; Zagorac *et al.*, 2019) are $\text{Na}_2(\text{Ti}^{\text{IV}}\text{Te}^{\text{VI}})\text{O}_6$ and $\alpha\text{-Na}_2(\text{Ge}^{\text{IV}}\text{Te}^{\text{VI}})\text{O}_6$ (Woodward *et al.*, 1999).

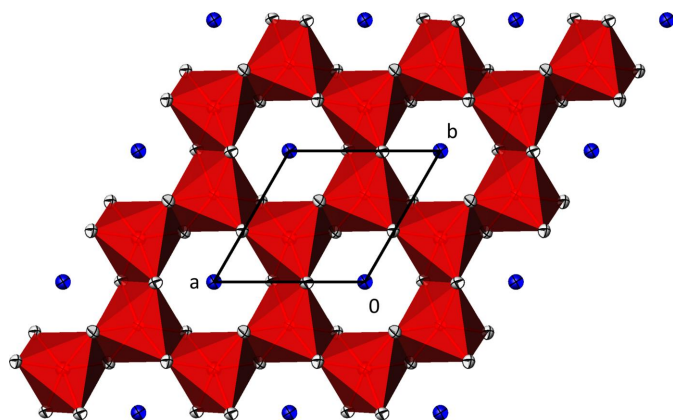


Figure 2
Projection of the crystal structure of $\text{Na}_2(\text{Fe}_{2/3}\text{Te}_{4/3})\text{O}_6$ onto (001) , showing only one layer of $[(\text{Fe},\text{Te})\text{O}_6]$ units (red polyhedra) and of Na atoms (blue). For clarity, Na–O bonds are omitted. Displacement ellipsoids are drawn at the 74% probability level.

Table 1
Experimental details.

Crystal data	
Chemical formula	$\text{Na}_2(\text{Fe}_{2/3}\text{Te}_{4/3})\text{O}_6$
M_r	349.33
Crystal system, space group	Trigonal, $R\bar{3}:H$
Temperature (K)	300
a, c (\AA)	5.2598 (8), 15.778 (3)
V (\AA^3)	378.02 (14)
Z	3
Radiation type	Mo $K\alpha$
μ (mm^{-1})	9.76
Crystal size (mm)	$0.05 \times 0.04 \times 0.01$
Data collection	
Diffractometer	Stoe Stadivari
Absorption correction	Multi-scan (<i>LANA</i> ; Koziskova <i>et al.</i> , 2016)
T_{\min}, T_{\max}	0.519, 0.596
No. of measured, independent and observed $[I > 2\sigma(I)]$ reflections	3266, 454, 383
R_{int}	0.043
$(\sin \theta/\lambda)_{\text{max}}$ (\AA^{-1})	0.731
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.027, 0.066, 1.03
No. of reflections	454
No. of parameters	17
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e \AA^{-3})	1.64, -1.30

Computer programs: *X-AREA* (Stoe, 2021), *SHELXT* (Sheldrick, 2015a), *SHELXL* (Sheldrick, 2015b), *ATOMS* (Dowty, 2006) and *pubCIF* (Westrip, 2010).

The ilmenite-type crystal structure of $\text{Na}_2(\text{Fe}_{2/3}\text{Te}_{4/3})\text{O}_6$ is shown in Figs. 1 and 2.

Synthesis and crystallization

Hydrothermal synthesis conditions were the same as detailed for garnet-type $\text{Na}_3\text{Te}_2(\text{FeO}_4)_3$ (Eder & Weil, 2023). Small

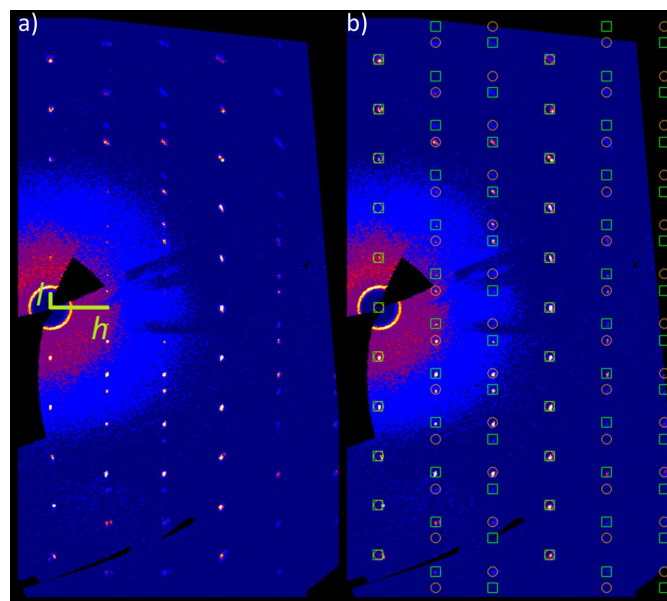


Figure 3
(a) Reconstructed reciprocal $h0l$ plane of $\text{Na}_2(\text{Fe}_{2/3}\text{Te}_{4/3})\text{O}_6$; (b) reflections belonging to the two twin domains are marked in green squares (domain 1) and orange circles (domain 2); reflections of the two domains overlap in every third row h .

amounts of yellowish (nearly colourless) crystals of $\text{Na}_2(\text{Fe}_{2/3}\text{Te}_{4/3})\text{O}_6$ with a plate-like form were harvested from the reaction mixture that also contained very few colourless crystals of $\text{NaFe}^{\text{III}}(\text{Te}^{\text{IV}}\text{O}_3)_2$ (Weil & Stöger, 2008).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1.

All crystals under investigation were systematically twinned with at least two twin domains present. During the integrating and scaling process of the finally chosen crystal, a pseudo-Laue class of $\bar{3}m$ was suggested by *X-AREA* (Stoe, 2021) with similar R_{int} values compared to the Laue class corresponding to the actual structure ($\bar{3}$). From this pseudo-symmetry imposed by the twinning, one possible twin law ($m_{(210)}$) with a transformation of **a**, $-\mathbf{a}-\mathbf{b}$, **c** was derived. The intensity data were integrated on basis of a hexagonal primitive unit-cell of same dimensions to include the reflections of both twin domains (Fig. 3). By applying the twin law given above, the ratios of the respective domains refined to values of 0.540:0.460 (2). For the sake of charge-neutrality, the mixed-occupied ($\text{Fe}^{\text{III}}/\text{Te}^{\text{VI}}$) site was constrained to a ratio of 1:2 for Fe:Te. The two atom types located at this site were refined with common displacement parameters.

Structure data of $\text{Na}_2(\text{Fe}_{2/3}\text{Te}_{4/3})\text{O}_6$ were standardized with *STRUCTURE-TIDY* (Gelato & Parthé, 1987).

Acknowledgements

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full crystallographic data

IUCrData (2024). **9**, x240482 [https://doi.org/10.1107/S2414314624004826]

Ilmenite-type $\text{Na}_2(\text{Fe}_{2/3}\text{Te}_{4/3})\text{O}_6$

Felix Eder and Matthias Weil

Trisodium iron(III) ditellurium(VI) nonaoxide

Crystal data

$\text{Na}_2\text{Fe}_{0.6666}\text{Te}_{1.3333}\text{O}_6$

$M_r = 349.33$

Trigonal, $R\bar{3}:H$

$a = 5.2598$ (8) Å

$c = 15.778$ (3) Å

$V = 378.02$ (14) Å³

$Z = 3$

$F(000) = 470$

$D_x = 4.604$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 3735 reflections

$\theta = 3.9\text{--}31.3^\circ$

$\mu = 9.76$ mm⁻¹

$T = 300$ K

Plate, yellowish

$0.05 \times 0.04 \times 0.01$ mm

Data collection

Stoe Stadivari

diffractometer

Radiation source: Axo_Mo

rotation method, ω scans

Absorption correction: multi-scan

(*LANA*; Koziskova *et al.*, 2016)

$T_{\min} = 0.519$, $T_{\max} = 0.596$

3266 measured reflections

454 independent reflections

383 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.043$

$\theta_{\max} = 31.3^\circ$, $\theta_{\min} = 4.7^\circ$

$h = -4 \rightarrow 7$

$k = -7 \rightarrow 5$

$l = -22 \rightarrow 23$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.027$

$wR(F^2) = 0.066$

$S = 1.03$

454 reflections

17 parameters

0 restraints

$w = 1/[\sigma^2(F_o^2) + (0.0446P)^2]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 1.64$ e Å⁻³

$\Delta\rho_{\min} = -1.30$ e Å⁻³

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refined as a 2-component inversion twin.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Te	0.000000	0.000000	0.16114 (4)	0.0138 (2)	0.6667

Fe	0.000000	0.000000	0.16114 (4)	0.0138 (2)	0.3333
Na	0.000000	0.000000	0.3619 (2)	0.0215 (6)	
O	0.3411 (6)	0.0563 (7)	0.0969 (2)	0.0181 (6)	

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Te	0.0101 (2)	0.0101 (2)	0.0212 (3)	0.00503 (11)	0.000	0.000
Fe	0.0101 (2)	0.0101 (2)	0.0212 (3)	0.00503 (11)	0.000	0.000
Na	0.0183 (9)	0.0183 (9)	0.0278 (15)	0.0091 (4)	0.000	0.000
O	0.0126 (14)	0.0156 (13)	0.0260 (15)	0.0068 (11)	0.0020 (11)	-0.0026 (12)

Geometric parameters (Å, °)

Te—O	1.951 (3)	Na—O ^{vi}	2.297 (3)
Te—O ⁱ	1.951 (3)	Na—O ^{vii}	2.297 (3)
Te—O ⁱⁱ	1.951 (3)	Na—O ^{viii}	2.297 (3)
Te—O ⁱⁱⁱ	1.993 (3)	Na—O ⁱⁱⁱ	2.545 (4)
Te—O ^{iv}	1.993 (3)	Na—O ^{iv}	2.545 (4)
Te—O ^v	1.993 (3)	Na—O ^v	2.545 (4)
O—Te—O ⁱ	95.42 (13)	O ^{vi} —Na—O ^{viii}	98.45 (11)
O—Te—O ⁱⁱ	95.42 (13)	O ^{vii} —Na—O ^{viii}	91.78 (15)
O ⁱ —Te—O ⁱⁱ	95.42 (13)	O ^{viii} —Na—O ^{viii}	156.33 (16)
O—Te—O ⁱⁱⁱ	98.82 (19)	O ^{vi} —Na—O ^{iv}	91.78 (15)
O ⁱ —Te—O ⁱⁱⁱ	79.08 (15)	O ^{vii} —Na—O ^{iv}	156.34 (16)
O ⁱⁱ —Te—O ⁱⁱⁱ	165.14 (16)	O ^{viii} —Na—O ^{iv}	98.45 (11)
O—Te—O ^{iv}	79.08 (15)	O ⁱⁱⁱ —Na—O ^{iv}	65.98 (14)
O ⁱ —Te—O ^{iv}	165.15 (16)	O ^{vi} —Na—O ^v	156.34 (16)
O ⁱⁱ —Te—O ^{iv}	98.82 (19)	O ^{vii} —Na—O ^v	98.45 (11)
O ⁱⁱⁱ —Te—O ^{iv}	88.08 (14)	O ^{viii} —Na—O ^v	91.77 (15)
O—Te—O ^v	165.14 (16)	O ⁱⁱⁱ —Na—O ^v	65.98 (14)
O ⁱ —Te—O ^v	98.82 (19)	O ^{iv} —Na—O ^v	65.98 (14)
O ⁱⁱ —Te—O ^v	79.08 (15)	Te—O—Te ^{iv}	100.92 (15)
O ⁱⁱⁱ —Te—O ^v	88.08 (14)	Te—O—Na ^{ix}	120.25 (14)
O ^{iv} —Te—O ^v	88.08 (14)	Te ^{iv} —O—Na ^{ix}	123.88 (14)
O ^{vi} —Na—O ^{vii}	99.80 (15)	Te—O—Na ^{iv}	142.72 (16)
O ^{vi} —Na—O ^{viii}	99.80 (15)	Te ^{iv} —O—Na ^{iv}	87.65 (11)
O ^{vii} —Na—O ^{viii}	99.80 (15)	Na ^{ix} —O—Na ^{iv}	81.55 (11)

Symmetry codes: (i) $-x+y, -x, z$; (ii) $-y, x-y, z$; (iii) $x-y-1/3, x-2/3, -z+1/3$; (iv) $-x+2/3, -y+1/3, -z+1/3$; (v) $y-1/3, -x+y+1/3, -z+1/3$; (vi) $-x+y+2/3, -x+1/3, z+1/3$; (vii) $-y-1/3, x-y-2/3, z+1/3$; (viii) $x-1/3, y+1/3, z+1/3$; (ix) $x+1/3, y-1/3, z-1/3$.