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# Na$M^{II}$Zr$_2$F$_{11}$ ($M^{II}$ = Mn, Fe, Co, Ni, Zn) Fluorides

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## Abstract

The structures of $NaMnZr_2F_{11}$ (sodium manganese undecafluorodizirconate), $NaFeZr_2F_{11}$, $NaCoZr_2F_{11}$, $NaNiZr_2F_{11}$ and $NaZnZr_2F_{11}$ have been refined from single-crystal X-ray diffraction data. These compounds are isostructural with $AgPdZr_2F_{11}$. They are characterized by isolated compressed octahedra, which are slightly tetragonally distorted, surrounding the divalent cations of the first-row transition metals. Attempts at the growth of single crystals of divalent chromium ($d^4$) and copper ($d^9$) failed, probably because these cations are unstable as a result of the Jahn–Teller effect.

## Comment

Compounds of the general formula Na$M^{II}$Zr$_2$F$_{11}$ can be divided into two very different structure types according to the nature of the divalent cation, $M^{2+}$. For a divalent cation of the second transition series, such as $Pd^{2+}$ or $Ag^{2+}$, a three-dimensional layered structure with triclinic space group $P\bar{1}$ has been observed (Müller, 1987). In this structure type, the $Pd^{2+}$ ions have regular octahedral coordination, whereas the F-atom environment about $Ag^{2+}$ is pseudotetragonally elongated. It can be inferred that the distortion of the $Ag^{2+}$ octahedra is Jahn–Teller induced. A slightly less distorted variant of this structure type has been observed for $AgPdZr_2F_{11}$, which crystallizes in the monoclinic space group *C*2/*m* (Müller, 1987). Here, the $Pd^{2+}$ ion also has regular octahedral coordination. We report herein the structures of a series of fluorides with general formula Na$M^{II}$Zr$_2$F$_{11}$ ($M^{II}$ = Mn, Fe, Co, Ni, Zn) which are closely related to that of $AgPdZr_2F_{11}$. In these compounds, the divalent cations are in slightly compressed octahedra. Assuming that the Jahn–Teller effect may operate in Na$M^{II}$Zr$_2$F$_{11}$ compounds since such a strong effect has already been observed for $Ag^{2+}$ in $NaAgZr_2F_{11}$, the lack of representatives for $Cr^{2+}$ ($d^4$) and $Cu^{2+}$ ($d^9$), for which a strong Jahn–Teller effect could be expected, may be interpreted as due to such an effect being stronger for divalent cations of the first transition row than for $Ag^{2+}$, leading to unstable structures. For the $Co^{2+}$ compounds the stabilization of the high-spin state is related to the weak crystal field generally induced by an F-atom environment.

The $Zr^{IV}$ ions are located in corner-linked *trans* chains of $(Zr_2F_{12})^{4-}$ binuclear units comprising pairs of edge-sharing pentagonal bipyramids. The $Na^+$ and $M^{2+}$ ions are ordered within chains of edge-linked polyhedra, made up of alternating hexagonal bipyramids and octahedra. Both types of chains are joined by sharing corners and edges, resulting in layers as illustrated in Fig. 1. These layers are perpendicular to [201] and are further linked to form a three-dimensional framework by sharing corners. The layers are stacked along [201] in the sequence *A*,*B*,*C*,*D*,*E* and are related by a translation in such a way that one layer is displaced relative to the other by $\frac{1}{2}\mathbf{b} - \frac{1}{4}\mathbf{c}$ so that an additional Na–Zr–$M^{II}$–Zr ordering occurs within the corner-linked *trans* chains of composition $(NaM^{II}Zr_2F_{24})_n^{13n-}$, extended along [201].

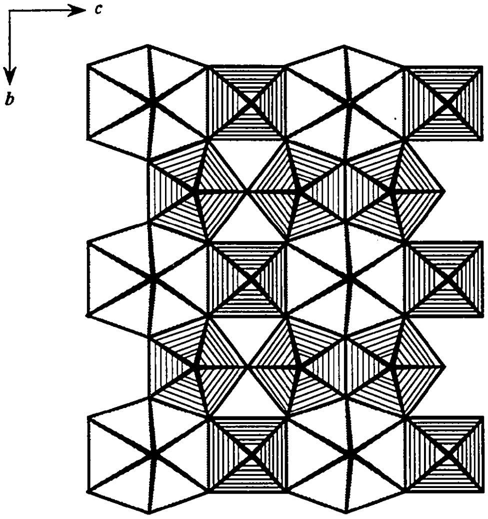

Fig. 1. Polyhedral layer showing the linkage between octahedra ($M^{II}$), pentagonal bipyramids (Zr) and hexagonal bipyramids (Na).

## Experimental

Single crystals of $NaMnZr_2F_{11}$ were obtained by heating a stoichiometric mixture of the dried binary fluorides at 1073 K for 2 d in a sealed platinum tube followed by slow cooling to room temperature at 4 K h$^{-1}$. For the other Na$M^{II}$Zr$_2$F$_{11}$ fluorides ($M^{II}$ = Fe, Co, Ni, Zn), single crystals were obtained by heating stoichiometric mixtures of the dried starting fluorides to 1073 K in sealed platinum tubes, as above, but once this temperature had been reached the samples were allowed to cool slowly to 913 K at 4 K h$^{-1}$. The temperature was maintained at 913 K for 3 d before quenching the samples in air. Annealing of the samples at 913 K over 3 d gave crystals of better quality, suitable for crystal structure determination.

### Compound (1)

*Crystal data*

$NaMnZr_2F_{11}$
$M_r = 469.35$
Monoclinic
$C2/m$
$a = 9.131\,(2)$ Å
$b = 6.775\,(1)$ Å
$c = 7.769\,(2)$ Å
$\beta = 116.22\,(2)^\circ$
$V = 431.1\,(2)$ Å$^3$
$Z = 2$
$D_x = 3.62$ Mg m$^{-3}$

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 3$–$19^\circ$
$\mu = 3.92$ mm$^{-1}$
$T = 293$ K
Prismatic
0.12 × 0.11 × 0.10 mm
Colourless

*Data collection*

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: $\psi$ scan (North, Phillips & Mathews, 1968)
$T_{min} = 0.958$, $T_{max} = 0.998$
1421 measured reflections
1421 independent reflections

1131 observed reflections $[I > 3\sigma(I)]$
$\theta_{max} = 40^\circ$
$h = 0 \rightarrow 16$
$k = 0 \rightarrow 12$
$l = -14 \rightarrow 14$
3 standard reflections
frequency: 60 min
intensity decay: none

*Refinement*

Refinement on $F$
$R = 0.036$
$wR = 0.051$
$S = 1.621$
1108 reflections
46 parameters
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{max} = 0.01$
$\Delta\rho_{max} = 1.782$ e Å$^{-3}$
$\Delta\rho_{min} = -1.687$ e Å$^{-3}$

Extinction correction: $|F_c| = |F_o|(1 + gI_c)$ (Stout & Jensen, 1968)
Extinction coefficient: $g = 1.7\,(2) \times 10^{-6}$
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

### Compound (2)

*Crystal data*

$NaFeZr_2F_{11}$
$M_r = 470.26$
Monoclinic
$C2/m$
$a = 9.069$ (3) Å
$b = 6.736$ (1) Å
$c = 7.757$ (1) Å
$\beta = 116.22\ (1)^\circ$
$V = 425.1$ (2) Å$^3$
$Z = 2$
$D_x = 3.67$ Mg m$^{-3}$

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 5$–$19^\circ$
$\mu = 4.25$ mm$^{-1}$
$T = 293$ K
Prismatic
0.19 × 0.16 × 0.14 mm
Colourless

*Data collection*

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: $\psi$ scan (North, Phillips & Mathews, 1968)
$T_{min} = 0.955$, $T_{max} = 0.999$
1454 measured reflections
1454 independent reflections

1326 observed reflections $[I > 3\sigma(I)]$
$\theta_{max} = 40^\circ$
$h = 0 \rightarrow 16$
$k = 0 \rightarrow 12$
$l = -14 \rightarrow 14$
3 standard reflections
frequency: 60 min
intensity decay: none

*Refinement*

Refinement on $F$
$R = 0.022$
$wR = 0.030$
$S = 1.092$
1323 reflections
46 parameters
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{max} = 0.01$
$\Delta\rho_{max} = 1.559$ e Å$^{-3}$
$\Delta\rho_{min} = -2.293$ e Å$^{-3}$

Extinction correction: $|F_c| = |F_o|(1 + gI_c)$ (Stout & Jensen, 1968)
Extinction coefficient: $g = 3.8\,(1) \times 10^{-6}$
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

### Compound (3)

*Crystal data*

$NaCoZr_2F_{11}$
$M_r = 473.35$
Monoclinic
$C2/m$
$a = 9.037$ (1) Å
$b = 6.700$ (1) Å
$c = 7.725$ (2) Å
$\beta = 116.26\ (1)^\circ$
$V = 419.5$ (1) Å$^3$
$Z = 2$
$D_x = 3.75$ Mg m$^{-3}$

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 3$–$18^\circ$
$\mu = 4.56$ mm$^{-1}$
$T = 293$ K
Prismatic
0.15 × 0.10 × 0.09 mm
Colourless

*Data collection*

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: $\psi$ scan (North, Phillips & Mathews, 1968)
$T_{min} = 0.939$, $T_{max} = 0.999$
1372 measured reflections
1372 independent reflections

1129 observed reflections $[I > 3\sigma(I)]$
$\theta_{max} = 40^\circ$
$h = 0 \rightarrow 16$
$k = 0 \rightarrow 12$
$l = -14 \rightarrow 14$
3 standard reflections
frequency: 60 min
intensity decay: none

*Refinement*

Refinement on $F$
$R = 0.024$
$wR = 0.032$
$S = 1.037$
1129 reflections
46 parameters
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{max} = 0.01$
$\Delta\rho_{max} = 1.348$ e Å$^{-3}$
$\Delta\rho_{min} = -1.904$ e Å$^{-3}$

Extinction correction: $|F_c| = |F_o|(1 + gI_c)$ (Stout & Jensen, 1968)
Extinction coefficient: $g = 1.5\,(2) \times 10^{-6}$
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

**Compound (4)**

*Crystal data*

$NaNiZr_2F_{11}$
$M_r = 473.12$
Monoclinic
$C2/m$
$a = 9.002$ (2) Å
$b = 6.675$ (1) Å
$c = 7.709$ (1) Å
$\beta = 116.24$ (2)°
$V = 415.5$ (2) Å$^3$
$Z = 2$
$D_x = 3.78$ Mg m$^{-3}$
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 5$–18°
$\mu = 4.88$ mm$^{-1}$
$T = 293$ K
Prismatic
0.17 × 0.08 × 0.07 mm
Colourless

*Data collection*

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: $\psi$ scan (North, Phillips & Mathews, 1968)
$T_{\min} = 0.847$, $T_{\max} = 0.999$
1357 measured reflections
1357 independent reflections
1210 observed reflections $[I > 3\sigma(I)]$
$\theta_{\max} = 40°$
$h = 0 \rightarrow 16$
$k = 0 \rightarrow 12$
$l = -14 \rightarrow 14$
3 standard reflections
frequency: 60 min
intensity decay: none

*Refinement*

Refinement on $F$
$R = 0.034$
$wR = 0.042$
$S = 1.468$
1210 reflections
46 parameters
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{\max} = 0.01$
$\Delta\rho_{\max} = 2.026$ e Å$^{-3}$
$\Delta\rho_{\min} = -2.926$ e Å$^{-3}$
Extinction correction: $|F_c| = |F_o|(1 + gI_c)$ (Stout & Jensen, 1968)
Extinction coefficient: $g = 4.7 (2) \times 10^{-6}$
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

**Compound (5)**

*Crystal data*

$NaZnZr_2F_{11}$
$M_r = 479.78$
Monoclinic
$C2/m$
$a = 9.025$ (3) Å
$b = 6.695$ (1) Å
$c = 7.721$ (1) Å
$\beta = 116.18$ (1)°
$V = 418.7$ (1) Å$^3$
$Z = 2$
$D_x = 3.81$ Mg m$^{-3}$
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 6$–18°
$\mu = 5.52$ mm$^{-1}$
$T = 293$ K
Prismatic
0.18 × 0.10 × 0.08 mm
Colourless

*Data collection*

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: $\psi$ scan (North, Phillips & Mathews, 1968)
$T_{\min} = 0.946$, $T_{\max} = 0.999$
1369 measured reflections
1369 independent reflections
1192 observed reflections $[I > 3\sigma(I)]$
$\theta_{\max} = 40°$
$h = 0 \rightarrow 16$
$k = 0 \rightarrow 12$
$l = -14 \rightarrow 14$
3 standard reflections
frequency: 60 min
intensity decay: none

*Refinement*

Refinement on $F$
$R = 0.028$
$wR = 0.035$
$S = 1.230$
1192 reflections
46 parameters
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{\max} = 0.01$
$\Delta\rho_{\max} = 2.200$ e Å$^{-3}$
$\Delta\rho_{\min} = -2.073$ e Å$^{-3}$
Extinction correction: $|F_c| = |F_o|(1 + gI_c)$ (Stout & Jensen, 1968)
Extinction coefficient: $g = 2.0 (2) \times 10^{-6}$
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å$^2$)

$B_{eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$

| | $x$ | $y$ | $z$ | $B_{eq}$ |
|---|---|---|---|---|
| Compound (1) | | | | |
| Na | 0 | 0 | 0 | 3.36 (9) |
| Mn | 0 | 0 | 1/2 | 0.70 (1) |
| Zr | 0.50168 (4) | 0 | 0.23286 (5) | 0.651 (5) |
| F(1) | 0 | 1/2 | 1/2 | 2.69 (8) |
| F(2) | 0 | 0.3310 (4) | 0 | 1.48 (4) |
| F(3) | 0.2537 (3) | 0 | 0.6489 (4) | 1.98 (6) |
| F(4) | 0.2652 (3) | 0 | 0.1082 (5) | 2.35 (7) |
| F(5) | 0.0116 (2) | 0.2104 (3) | 0.3074 (3) | 1.57 (3) |
| Compound (2) | | | | |
| Na | 0 | 0 | 0 | 3.36 (4) |
| Fe | 0 | 0 | 1/2 | 0.713 (4) |
| Zr | 0.50364 (2) | 0 | 0.23462 (2) | 0.609 (2) |
| F(1) | 0 | 1/2 | 1/2 | 2.76 (4) |
| F(2) | 0 | 0.3301 (2) | 0 | 1.37 (2) |
| F(3) | 0.2504 (1) | 0 | 0.6497 (2) | 1.86 (3) |
| F(4) | 0.2665 (2) | 0 | 0.1094 (3) | 2.46 (3) |
| F(5) | 0.0143 (1) | 0.2076 (1) | 0.3095 (1) | 1.54 (1) |
| Compound (3) | | | | |
| Na | 0 | 0 | 0 | 3.73 (6) |
| Co | 0 | 0 | 1/2 | 0.642 (6) |
| Zr | 0.50490 (2) | 0 | 0.23574 (3) | 0.541 (3) |
| F(1) | 0 | 1/2 | 1/2 | 3.01 (6) |
| F(2) | 0 | 0.3292 (3) | 0 | 1.31 (2) |
| F(3) | 0.2479 (2) | 0 | 0.6494 (3) | 1.66 (3) |
| F(4) | 0.2668 (3) | 0 | 0.1095 (4) | 2.43 (4) |
| F(5) | 0.0154 (1) | 0.2066 (2) | 0.3124 (2) | 1.38 (2) |
| Compound (4) | | | | |
| Na | 0 | 0 | 0 | 3.97 (8) |
| Ni | 0 | 0 | 1/2 | 0.632 (6) |
| Zr | 0.50626 (3) | 0 | 0.23708 (3) | 0.543 (3) |
| F(1) | 0 | 1/2 | 1/2 | 3.98 (7) |
| F(2) | 0 | 0.3281 (3) | 0 | 1.25 (3) |
| F(3) | 0.2454 (2) | 0 | 0.6490 (3) | 1.68 (4) |
| F(4) | 0.2671 (3) | 0 | 0.1093 (4) | 2.63 (5) |
| F(5) | 0.0168 (2) | 0.2047 (2) | 0.3154 (2) | 1.32 (2) |
| Compound (5) | | | | |
| Na | 0 | 0 | 0 | 3.72 (6) |
| Zn | 0 | 0 | 1/2 | 0.704 (5) |
| Zr | 0.50534 (2) | 0 | 0.23615 (3) | 0.555 (3) |
| F(1) | 0 | 1/2 | 1/2 | 3.38 (6) |
| F(2) | 0 | 0.3293 (2) | 0 | 1.26 (2) |

| | | | | |
|---|---|---|---|---|
| F(3) | 0.2472 (2) | 0 | 0.6498 (3) | 1.74 (3) |
| F(4) | 0.2670 (2) | 0 | 0.1089 (3) | 2.50 (4) |
| F(5) | 0.0159 (1) | 0.2061 (2) | 0.3138 (2) | 1.40 (2) |

Table 2. *Selected geometric parameters* (Å)

| | | | |
|---|---|---|---|
| Compound (1) | | | |
| Na—F(4) | 2.184 (3) | Mn—F(5$^{ii}$) | 2.103 (2) |
| Na—F(4$^{i}$) | 2.184 (3) | Mn—F(5$^{v}$) | 2.103 (2) |
| Na—F(2) | 2.242 (3) | Mn—F(5$^{iv}$) | 2.103 (2) |
| Na—F(2$^{i}$) | 2.242 (3) | Zr—F(4) | 1.937 (3) |
| Na—F(5) | 2.743 (2) | Zr—F(3$^{vi}$) | 2.005 (3) |
| Na—F(5$^{ii}$) | 2.743 (2) | Zr—F(5$^{vii}$) | 2.036 (2) |
| Na—F(5$^{iii}$) | 2.743 (2) | Zr—F(5$^{viii}$) | 2.036 (2) |
| Na—F(5$^{i}$) | 2.743 (2) | Zr—F(1$^{vii}$) | 2.082 (1) |
| Mn—F(3) | 2.083 (2) | Zr—F(2$^{vii}$) | 2.135 (2) |
| Mn—F(3$^{iv}$) | 2.083 (2) | Zr—F(2$^{ix}$) | 2.135 (2) |
| Mn—F(5) | 2.103 (2) | | |
| Compound (2) | | | |
| Na—F(4) | 2.179 (1) | Fe—F(5$^{ii}$) | 2.080 (1) |
| Na—F(4$^{i}$) | 2.179 (1) | Fe—F(5$^{v}$) | 2.080 (1) |
| Na—F(2) | 2.223 (1) | Fe—F(5$^{iv}$) | 2.080 (1) |
| Na—F(2$^{i}$) | 2.223 (1) | Zr—F(4) | 1.929 (1) |
| Na—F(5) | 2.731 (1) | Zr—F(3$^{vi}$) | 2.003 (1) |
| Na—F(5$^{ii}$) | 2.731 (1) | Zr—F(5$^{vii}$) | 2.044 (1) |
| Na—F(5$^{iii}$) | 2.731 (1) | Zr—F(5$^{viii}$) | 2.044 (1) |
| Na—F(5$^{i}$) | 2.731 (1) | Zr—F(1$^{vii}$) | 2.074 (1) |
| Fe—F(3) | 2.043 (1) | Zr—F(2$^{vii}$) | 2.138 (1) |
| Fe—F(3$^{iv}$) | 2.043 (1) | Zr—F(2$^{ix}$) | 2.138 (1) |
| Fe—F(5) | 2.080 (1) | | |
| Compound (3) | | | |
| Na—F(4) | 2.174 (2) | Co—F(5$^{ii}$) | 2.053 (1) |
| Na—F(4$^{i}$) | 2.174 (2) | Co—F(5$^{v}$) | 2.053 (1) |
| Na—F(2) | 2.206 (2) | Co—F(5$^{iv}$) | 2.053 (1) |
| Na—F(2$^{i}$) | 2.206 (2) | Zr—F(4) | 1.930 (2) |
| Na—F(5) | 2.731 (1) | Zr—F(3$^{vi}$) | 2.006 (1) |
| Na—F(5$^{ii}$) | 2.731 (1) | Zr—F(5$^{vii}$) | 2.043 (1) |
| Na—F(5$^{iii}$) | 2.731 (1) | Zr—F(5$^{viii}$) | 2.043 (1) |
| Na—F(5$^{i}$) | 2.731 (1) | Zr—F(1$^{vii}$) | 2.061 (1) |
| Co—F(3) | 2.016 (1) | Zr—F(2$^{vii}$) | 2.135 (1) |
| Co—F(3$^{iv}$) | 2.016 (1) | Zr—F(2$^{ix}$) | 2.135 (1) |
| Co—F(5) | 2.053 (1) | | |
| Compound (4) | | | |
| Na—F(4) | 2.168 (2) | Ni—F(5$^{ii}$) | 2.026 (1) |
| Na—F(4$^{i}$) | 2.168 (2) | Ni—F(5$^{v}$) | 2.026 (1) |
| Na—F(2) | 2.190 (2) | Ni—F(5$^{iv}$) | 2.026 (1) |
| Na—F(2$^{i}$) | 2.190 (2) | Zr—F(4) | 1.932 (2) |
| Na—F(5) | 2.734 (1) | Zr—F(3$^{vi}$) | 2.008 (2) |
| Na—F(5$^{ii}$) | 2.734 (1) | Zr—F(5$^{vii}$) | 2.051 (1) |
| Na—F(5$^{iii}$) | 2.734 (1) | Zr—F(5$^{viii}$) | 2.051 (1) |
| Na—F(5$^{i}$) | 2.734 (1) | Zr—F(1$^{vii}$) | 2.052 (1) |
| Ni—F(3) | 1.989 (2) | Zr—F(2$^{vii}$) | 2.138 (1) |
| Ni—F(3$^{iv}$) | 1.989 (2) | Zr—F(2$^{ix}$) | 2.138 (1) |
| Ni—F(5) | 2.026 (1) | | |
| Compound (5) | | | |
| Na—F(4) | 2.174 (2) | Zn—F(5$^{ii}$) | 2.043 (1) |
| Na—F(4$^{i}$) | 2.174 (2) | Zn—F(5$^{v}$) | 2.043 (1) |
| Na—F(2) | 2.205 (2) | Zn—F(5$^{iv}$) | 2.043 (1) |
| Na—F(2$^{i}$) | 2.205 (2) | Zr—F(4) | 1.931 (2) |
| Na—F(5) | 2.737 (1) | Zr—F(3$^{vi}$) | 2.007 (1) |
| Na—F(5$^{ii}$) | 2.737 (1) | Zr—F(5$^{vii}$) | 2.047 (1) |
| Na—F(5$^{iii}$) | 2.737 (1) | Zr—F(5$^{viii}$) | 2.047 (1) |
| Na—F(5$^{i}$) | 2.737 (1) | Zr—F(1$^{vii}$) | 2.059 (1) |
| Zn—F(3) | 2.010 (1) | Zr—F(2$^{vii}$) | 2.134 (1) |
| Zn—F(3$^{iv}$) | 2.010 (1) | Zr—F(2$^{ix}$) | 2.134 (1) |
| Zn—F(5) | 2.043 (1) | | |

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

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *MolEN* (Fair, 1990). Program used to solve and refine structure: *MolEN*. Molecular graphics: *ORTEP* (Johnson, 1965).

Lists of structure factors and anisotropic displacement parameters have been deposited with the IUCr (Reference: AB1265). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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# Zirconium Tungstate

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## Abstract

Zirconium tungstate, $Zr(WO_4)_2$, has been prepared by solid-state reaction at 1473 K. The structure was determined from X-ray and neutron powder diffraction data and refined by the Rietveld method. The final $R$ indices are $R_F = 0.032$, $R_I = 0.027$ and $R_P = 0.065$. The structure contains $WO_4$ tetrahedra, each linked by three corners to three $ZrO_6$ octahedra; each tetrahedron has a terminal O atom with a short W—O distance. This arrangement is closely related to that of the $Zr(MoO_4)_2$ high-temperature form.

## Comment

$M(XO_4)_2$ phases with $M$ = Zr or Hf and $X$ = Mo or W have been studied extensively by vibration spectroscopy (Auray & Tarte, 1982). In the case of the high-temperature form (HT) of $Zr(MoO_4)_2$, the results were correlated to the crystallographic features: the gap