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Disodium zinc germanium tetraoxide

A. M. Healey, M. Webster and M. T. Weller

Abstract

Hydrothermally grown single crystals of the title compound, Na_2ZnGeO_4, are monoclinic [space group Pn (No. 7)]. The structure is confirmed; recognition of the true monoclinic symmetry with pseudo-orthorhombic twinning enabled refinement to $R = 0.022$ from data measured at 150 K.

Comment

The compound Na_2ZnGeO_4 is well known and a structure was reported in 1968 (Kuz'min *et al.*, 1969) with $R = 0.155$. The present study confirms the earlier structure but with the Zn—O distances showing a much smaller spread of values and also with no evidence for any disorder in the Zn/Ge positions. The tetrahedral GeO_4 group has O—Ge—O angles in the range 108.0 (3)–113.1 (2)° and the angles in ZnO_4 are 107.1 (3)–113.5 (2)°.

A range of cristobalite related oxides are known and the various structural types have been reviewed recently in an informative article (Thompson *et al.*, 1998). Related compounds include the K analogue K_2ZnGeO_4 and Na_2ZnSiO_4 of which the former is known in tetragonal and orthorhombic forms and the latter as orthorhombic and monoclinic (Pn) polymorphs (Thompson *et al.*, 1998). A report (Grins & Nygren, 1983) of an orthorhombic modification of Na_2ZnGeO_4 is based on the indexing of an X-ray powder pattern.

Experimental

Single crystals of Na_2ZnGeO_4 were prepared by a method similar to that used by Shannon (1979). The powdered solid (0.5 g) was added to an aqueous sodium hydroxide solution (2 g in 2 ml) and the mixture sealed in a gold tube. The tube was heated to 973 K in a hydrothermal bomb apparatus for 1 day and then allowed to cool slowly to ambient temperatures over a second day (Healey, 1999).

Refinement

The initial experimental diffraction data were collected as orthorhombic following the strong indication in the Laue check routine. The systematic absences (*hkl*: none, *h*0*l*: h+l = 2n) lead to space groups $Pmn2_1$ (31) or Pmnm (59). In both space groups with an ordered model the Zn and Ge atoms would be on special positions and on attempting a structure solution no satisfactory models emerged. An alternative was to treat the system as monoclinic where by chance beta was extremely close to 90° and a recollection of the data even allowed for a triclinic crystal system by collecting four octants of the reciprocal lattice. The systematic absences now lead to space groups Pn (7) or P2/n (13) and a structure determination was carried out in the former.

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Using *SHELXL97* (Sheldrick, 1997), with no absorption correction and isotropic atomic displacement parameters (adp) R1 = 0.056. Introducing anisotropic adps for Zn and Ge gave non-positive definite U^{ij} values and several high correlation coefficients (R1 = 0.053) and finally introducing twin refinement (TWIN 1 0 0 0 − 1 0 0 0 − 1, BASF 0.23) reduced R1 to 0.046 with some restrictions applied to U11 of atoms Zn and Ge.

At this stage it was felt that the structure was essentially correct but that refinement was unsatisfactory due to the U^{ij} values probably caused by the lack of an absorption correction. The decision was taken to use the *DIFABS* absorption correction (Walker & Stuart, 1983) and this produced a convincing improvement in the refinement. *DIFABS* was applied to all the measured data using the non-twin isotropic model and after the correction R1 = 0.036. The anisotropic adps introduced for Zn and Ge were now well behaved and on adding the TWIN command gave R1 = 0.022 at convergence. There remained large correlations between Na(1) and Na(2) *x* coordinates and between U12 for Zn1 and Ge1.

The simulated powder X-ray pattern show a strong correlation between the intensity of *hkl* and hk-l reflections and this is the reason that the Laue symmetry measurements favoured (incorrectly) the orthorhombic crystal system.

A single-crystal was mounted on a glass fibre and held in position at 150 K using the oil-film crystal mounting technique. Diffraction data were obtained using a Rigaku AFC7S diffractometer fitted with Mo radiation and graphite monochromator. The diffractometer software in the Laue check routine strongly favoured an orthorhombic crystal system but as this had not resulted in a structure in the first experiment, the data were (re)collected as triclinic (four octants). No psi-scan measurements were possible and as the crystal faces were not identified the choices for an absorption correction were limited to none or *DIFABS* (Walker & Stuart, 1983).

The structure was solved by direct methods (Sheldrick, 1986) to locate the heavy atoms (Zn, Ge) and gradually the lighter atoms were added using structure factor and electron-density calculations. Initial data processing was carried out using the MSC software (1995).

The structure was refined using *SHELXL97* (Sheldrick, 1997).

Computing details

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988); cell refinement: MSC/AFC-7S diffractometer control software; data reduction: *TEXSAN* (Molecular Structure Corporation, 1995); program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997).

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Crystal data

$Na_2Zn_1Ge_1O_4$	V = 212.74 (5) Å^3
M_r = 247.94	Z = 2
Monoclinic, *Pn*	Mo *K*α
a = 7.1535 (9) Å	μ = 12.79 mm^{-1}
b = 5.5819 (10) Å	T = 150 (2) K
c = 5.3279 (4) Å	0.28 × 0.13 × 0.10 mm

β = 89.934 (8)°

Data collection

Rigaku AFC7S diffractometer	405 reflections with $I > 2\sigma(I)$
Absorption correction: part of the refinement model (ΔF) (Walker & Stuart, 1983)	R_{int} = 0.026
T_{min} = 0.207, T_{max} = 0.278	3 standard reflections
779 measured reflections	every 150 reflections
414 independent reflections	intensity decay: 1.3%

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.022	$\Delta\rho_{max}$ = 0.50 e Å^{-3}
$wR(F^2)$ = 0.054	$\Delta\rho_{min}$ = −1.06 e Å^{-3}
S = 1.26	Absolute structure: Flack (1983)
414 reflections	Flack parameter: 0.03 (4)
42 parameters	

Table 1
Selected geometric parameters (Å, °)

Ge1—O1^{i}	1.741 (5)	Na1—O4^{ii}	2.330 (17)
Ge1—O2	1.749 (5)	Na1—O2	2.324 (6)
Ge1—O3^{i}	1.750 (6)	Na1—O1	2.350 (11)
Ge1—O4^{i}	1.753 (7)	Na1—O3^{iv}	2.347 (17)
Zn1—O2^{ii}	1.947 (7)	Na2—O2^{v}	2.261 (17)
Zn1—O4^{ii}	1.968 (5)	Na2—O4^{vi}	2.288 (7)
Zn1—O3^{iii}	1.972 (4)	Na2—O1^{iv}	2.291 (17)
Zn1—O1^{i}	1.977 (6)	Na2—O3^{v}	2.321 (11)
O1^{i}—Ge1—O2	109.0 (2)	O4^{ii}—Zn1—O3^{iii}	107.3 (2)
O1^{i}—Ge1—O3^{i}	110.5 (3)	O2^{ii}—Zn1—O1^{i}	113.52 (19)
O2—Ge1—O3^{i}	108.0 (3)	O4^{ii}—Zn1—O1^{i}	108.1 (2)
O1^{i}—Ge1—O4^{i}	108.2 (3)	O3^{iii}—Zn1—O1^{i}	110.8 (3)
O2—Ge1—O4^{i}	108.0 (3)	Ge1^{vii}—O1—Zn1^{vii}	124.8 (3)
O3^{i}—Ge1—O4^{i}	113.1 (2)	Ge1—O2—Zn1^{viii}	125.1 (4)
O2^{ii}—Zn1—O4^{ii}	107.1 (3)	Ge1^{vii}—O3—Zn1^{ix}	125.6 (3)
O2^{ii}—Zn1—O3^{iii}	109.7 (2)	Ge1^{vii}—O4—Zn1^{viii}	126.1 (3)

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

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supplementary materials

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Crystal data

$Na_2Zn_1Ge_1O_4$	$F_{000} = 232$
$M_r = 247.94$	$D_x = 3.871$ Mg m^{-3}
Monoclinic, *Pn*	Mo *K*α radiation λ = 0.71073 Å
a = 7.1535 (9) Å	Cell parameters from 25 reflections
b = 5.5819 (10) Å	θ = 23.9–24.8º
c = 5.3279 (4) Å	μ = 12.79 mm^{-1}
β = 89.934 (8)º	*T* = 150 (2) K
V = 212.74 (5) Å^3	Block, colourless
Z = 2	0.28 × 0.13 × 0.10 mm

Data collection

Rigaku AFC7S diffractometer	$R_{int} = 0.026$
Radiation source: fine-focus sealed tube	$\theta_{max} = 25.0$º
Monochromator: graphite	$\theta_{min} = 3.7$º
T = 150(2) K	*h* = 0→8
ω–2θ scans	*k* = −6→6
Absorption correction: part of the refinement model (Δ*F*) (Walker & Stuart, 1983)	*l* = −6→6
$T_{min} = 0.207$, $T_{max} = 0.278$	3 standard reflections
779 measured reflections	every 150 reflections
414 independent reflections	intensity decay: 1.3%
405 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Calculated $w = 1/[\sigma^2(F_o^2) + (0.03P)^2 + 0.05P]$ where $P = (F_o^2 + 2F_c^2)/3$?
$R[F^2 > 2\sigma(F^2)] = 0.022$	$(\Delta/\sigma)_{max} = 0.002$
$wR(F^2) = 0.054$	$\Delta\rho_{max} = 0.50$ e Å^{-3}
S = 1.26	$\Delta\rho_{min} = -1.06$ e Å^{-3}
414 reflections	Extinction correction: none
42 parameters	Absolute structure: Flack (1983)
Primary atom site location: structure-invariant direct methods	Flack parameter: 0.03 (4)

Special details

Experimental. Crystal mounted using oil-film method on glass fibre for low temperature examination.

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

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit S are based on F^2, conventional *R*-factors *R* are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on F, and R– factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Ge1	0.24710 (12)	0.68457 (15)	0.0045 (2)	0.0050 (3)
Zn1	0	0.18611 (17)	0	0.0050 (4)
Na1	0.2504 (19)	0.3202 (5)	0.4891 (14)	0.0113 (13)*
Na2	0.9953 (19)	0.8197 (6)	0.4915 (15)	0.0124 (15)*
O1	0.2220 (10)	0.3841 (8)	0.9235 (10)	0.0067 (9)*
O2	0.2741 (10)	0.7067 (7)	0.3300 (10)	0.0074 (11)*
O3	0.0473 (10)	0.8465 (7)	0.9205 (10)	0.0079 (10)*
O4	0.4515 (10)	0.7933 (7)	0.8629 (10)	0.0074 (11)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ge1	0.0051 (4)	0.0056 (4)	0.0043 (4)	−0.0002 (5)	−0.0004 (4)	−0.0001 (2)
Zn1	0.0053 (5)	0.0049 (5)	0.0048 (5)	−0.0001 (5)	0.0000 (4)	0.0000 (3)

Geometric parameters (Å, °)

Ge1—O1^{i}	1.741 (5)	Na1—Na2^{xiii}	3.295 (5)
Ge1—O2	1.749 (5)	Na1—Na2^{vii}	3.337 (5)
Ge1—O3^{i}	1.750 (6)	Na1—Na2^{ii}	3.332 (5)
Ge1—O4^{i}	1.753 (7)	Na1—Zn1^{xiv}	3.341 (9)
Ge1—Na2^{ii}	3.246 (10)	Na2—O2^{xv}	2.261 (17)
Ge1—Na2^{iii}	3.289 (8)	Na2—O4^{xvi}	2.288 (7)
Ge1—Na1	3.287 (6)	Na2—O1^{xi}	2.291 (17)
Ge1—Na2^{iv}	3.328 (8)	Na2—O3^{xv}	2.321 (11)
Ge1—Na2^{v}	3.361 (10)	Na2—Ge1^{xv}	3.246 (10)
Ge1—Na1^{i}	3.417 (7)	Na2—Na1^{xii}	3.271 (4)
Ge1—Na1^{iv}	3.554 (14)	Na2—Ge1^{xvii}	3.289 (8)
Zn1—O2^{iv}	1.947 (7)	Na2—Na1^{xi}	3.295 (5)

Zn1—O4^{iv}	1.968 (5)	Na2—Zn1^{xviii}	3.323 (7)
Zn1—O3^{vi}	1.972 (4)	Na2—Ge1^{xii}	3.328 (8)
Zn1—O1^{i}	1.977 (6)	Na2—Na1^{xviii}	3.337 (5)
Zn1—Na1	3.251 (10)	Na2—Na1^{xv}	3.332 (5)
Zn1—Na1^{iv}	3.284 (8)	O1—Ge1^{xiv}	1.741 (5)
Zn1—Na2^{vii}	3.323 (7)	O1—Zn1^{xiv}	1.977 (6)
Zn1—Na1^{i}	3.341 (9)	O1—Na2^{xiii}	2.291 (17)
Zn1—Na1^{viii}	3.344 (8)	O2—Zn1^{xii}	1.947 (7)
Zn1—Na2^{ix}	3.395 (7)	O2—Na2^{ii}	2.261 (17)
Zn1—Na2^{iv}	3.543 (14)	O3—Ge1^{xiv}	1.750 (6)
Zn1—Na2^{x}	3.611 (14)	O3—Zn1^{xix}	1.972 (4)
Na1—O4^{iv}	2.330 (17)	O3—Na2^{ii}	2.321 (11)
Na1—O2	2.324 (6)	O3—Na1^{xiii}	2.347 (17)
Na1—O1	2.350 (11)	O4—Ge1^{xiv}	1.753 (7)
Na1—O3^{xi}	2.347 (17)	O4—Zn1^{xii}	1.968 (5)
Na1—Na2^{iv}	3.271 (4)	O4—Na2^{xx}	2.288 (7)
Na1—Zn1^{xii}	3.284 (8)	O4—Na1^{xii}	2.330 (18)
O1^{i}—Ge1—O2	109.0 (2)	O3^{xi}—Na1—Ge1	97.5 (4)
O1^{i}—Ge1—O3^{i}	110.5 (3)	Zn1—Na1—Ge1	60.55 (15)
O2—Ge1—O3^{i}	108.0 (3)	Na2^{iv}—Na1—Ge1	61.00 (18)
O1^{i}—Ge1—O4^{i}	108.2 (3)	O4^{iv}—Na1—Zn1^{xii}	137.1 (3)
O2—Ge1—O4^{i}	108.0 (3)	O2—Na1—Zn1^{xii}	35.7 (3)
O3^{i}—Ge1—O4^{i}	113.1 (2)	O1—Na1—Zn1^{xii}	84.3 (3)
O1^{i}—Ge1—Na2^{ii}	111.40 (19)	O3^{xi}—Na1—Zn1^{xii}	81.0 (4)
O2—Ge1—Na2^{ii}	41.7 (4)	Zn1—Na1—Zn1^{xii}	120.48 (19)
O3^{i}—Ge1—Na2^{ii}	68.4 (3)	Na2^{iv}—Na1—Zn1^{xii}	85.63 (16)
O4^{i}—Ge1—Na2^{ii}	136.5 (2)	Ge1—Na1—Zn1^{xii}	59.93 (10)
O1^{i}—Ge1—Na2^{iii}	149.43 (19)	O4^{iv}—Na1—Na2^{xiii}	131.2 (2)
O2—Ge1—Na2^{iii}	84.3 (2)	O2—Na1—Na2^{xiii}	118.5 (4)
O3^{i}—Ge1—Na2^{iii}	90.1 (3)	O1—Na1—Na2^{xiii}	44.0 (4)
O4^{i}—Ge1—Na2^{iii}	41.4 (3)	O3^{xi}—Na1—Na2^{xiii}	63.3 (3)
Na2^{ii}—Ge1—Na2^{iii}	96.92 (13)	Zn1—Na1—Na2^{xiii}	152.96 (9)
O1^{i}—Ge1—Na1	66.4 (2)	Na2^{iv}—Na1—Na2^{xiii}	108.49 (9)
O2—Ge1—Na1	42.62 (18)	Ge1—Na1—Na2^{xiii}	142.1 (2)
O3^{i}—Ge1—Na1	121.8 (2)	Zn1^{xii}—Na1—Na2^{xiii}	83.96 (17)
O4^{i}—Ge1—Na1	123.1 (2)	O4^{iv}—Na1—Na2^{vii}	43.23 (16)
Na2^{ii}—Ge1—Na1	61.33 (17)	O2—Na1—Na2^{vii}	144.9 (4)
Na2^{iii}—Ge1—Na1	122.2 (3)	O1—Na1—Na2^{vii}	94.4 (3)
O1^{i}—Ge1—Na2^{iv}	40.1 (4)	O3^{xi}—Na1—Na2^{vii}	99.4 (2)
O2—Ge1—Na2^{iv}	91.2 (2)	Zn1—Na1—Na2^{vii}	60.57 (12)

O3^{i}—Ge1—Na2^{iv}	150.1 (2)	Na2^{iv}—Na1—Na2^{vii}	95.49 (9)
O4^{i}—Ge1—Na2^{iv}	80.8 (2)	Ge1—Na1—Na2^{vii}	121.1 (2)
Na2^{ii}—Ge1—Na2^{iv}	120.6 (2)	Zn1^{xii}—Na1—Na2^{vii}	178.75 (18)
Na2^{iii}—Ge1—Na2^{iv}	115.0 (4)	Na2^{xiii}—Na1—Na2^{vii}	95.15 (9)
Na1—Ge1—Na2^{iv}	59.26 (12)	O4^{iv}—Na1—Na2^{ii}	74.10 (18)
O1^{i}—Ge1—Na2^{v}	87.65 (19)	O2—Na1—Na2^{ii}	42.7 (4)
O2—Ge1—Na2^{v}	148.2 (2)	O1—Na1—Na2^{ii}	79.8 (3)
O3^{i}—Ge1—Na2^{v}	40.3 (3)	O3^{xi}—Na1—Na2^{ii}	145.9 (2)
O4^{i}—Ge1—Na2^{v}	91.1 (3)	Zn1—Na1—Na2^{ii}	83.89 (15)
Na2^{ii}—Ge1—Na2^{v}	107.5 (4)	Na2^{iv}—Na1—Na2^{ii}	119.71 (13)
Na2^{iii}—Ge1—Na2^{v}	94.81 (14)	Ge1—Na1—Na2^{ii}	58.72 (19)
Na1—Ge1—Na2^{v}	141.4 (4)	Zn1^{xii}—Na1—Na2^{ii}	66.1 (2)
Na2^{iv}—Ge1—Na2^{v}	117.33 (19)	Na2^{xiii}—Na1—Na2^{ii}	119.13 (13)
O1^{i}—Ge1—Na1^{i}	39.5 (2)	Na2^{vii}—Na1—Na2^{ii}	113.65 (9)
O2—Ge1—Na1^{i}	146.91 (16)	O4^{iv}—Na1—Zn1^{xiv}	71.5 (3)
O3^{i}—Ge1—Na1^{i}	96.1 (2)	O2—Na1—Zn1^{xiv}	123.0 (4)
O4^{i}—Ge1—Na1^{i}	81.7 (3)	O1—Na1—Zn1^{xiv}	35.5 (3)
Na2^{ii}—Ge1—Na1^{i}	141.6 (4)	O3^{xi}—Na1—Zn1^{xiv}	121.5 (3)
Na2^{iii}—Ge1—Na1^{i}	118.7 (3)	Zn1—Na1—Zn1^{xiv}	107.8 (4)
Na1—Ge1—Na1^{i}	105.24 (7)	Na2^{iv}—Na1—Zn1^{xiv}	153.25 (10)
Na2^{iv}—Ge1—Na1^{i}	58.45 (12)	Ge1—Na1—Zn1^{xiv}	140.7 (4)
Na2^{v}—Ge1—Na1^{i}	58.88 (16)	Zn1^{xii}—Na1—Zn1^{xiv}	117.7 (2)
O1^{i}—Ge1—Na1^{iv}	83.3 (2)	Na2^{xiii}—Na1—Zn1^{xiv}	64.5 (2)
O2—Ge1—Na1^{iv}	97.8 (3)	Na2^{vii}—Na1—Zn1^{xiv}	61.10 (12)
O3^{i}—Ge1—Na1^{iv}	35.02 (18)	Na2^{ii}—Na1—Zn1^{xiv}	83.76 (14)
O4^{i}—Ge1—Na1^{iv}	145.69 (19)	O2^{xv}—Na2—O4^{xvi}	105.7 (5)
Na2^{ii}—Ge1—Na1^{iv}	57.7 (2)	O2^{xv}—Na2—O1^{xi}	123.6 (3)
Na2^{iii}—Ge1—Na1^{iv}	123.1 (2)	O4^{xvi}—Na2—O1^{xi}	107.7 (7)
Na1—Ge1—Na1^{iv}	91.2 (3)	O2^{xv}—Na2—O3^{xv}	104.5 (7)
Na2^{iv}—Ge1—Na1^{iv}	121.8 (2)	O4^{xvi}—Na2—O3^{xv}	104.8 (3)
Na2^{v}—Ge1—Na1^{iv}	56.4 (2)	O1^{xi}—Na2—O3^{xv}	109.0 (5)
Na1^{i}—Ge1—Na1^{iv}	89.0 (3)	O2^{xv}—Na2—Ge1^{xv}	30.96 (19)
O2^{iv}—Zn1—O4^{iv}	107.1 (3)	O4^{xvi}—Na2—Ge1^{xv}	93.2 (4)
O2^{iv}—Zn1—O3^{vi}	109.7 (2)	O1^{xi}—Na2—Ge1^{xv}	103.4 (3)
O4^{iv}—Zn1—O3^{vi}	107.3 (2)	O3^{xv}—Na2—Ge1^{xv}	135.5 (6)
O2^{iv}—Zn1—O1^{i}	113.52 (19)	O2^{xv}—Na2—Na1^{xii}	135.5 (3)
O4^{iv}—Zn1—O1^{i}	108.1 (2)	O4^{xvi}—Na2—Na1^{xii}	113.2 (4)
O3^{vi}—Zn1—O1^{i}	110.8 (3)	O1^{xi}—Na2—Na1^{xii}	63.5 (3)
O2^{iv}—Zn1—Na1	139.5 (2)	O3^{xv}—Na2—Na1^{xii}	45.8 (4)
O4^{iv}—Zn1—Na1	45.2 (4)	Ge1^{xv}—Na2—Na1^{xii}	152.73 (11)
O3^{vi}—Zn1—Na1	107.40 (18)	O2^{xv}—Na2—Ge1^{xvii}	135.9 (3)

O1^{i}—Zn1—Na1	66.0 (2)	O4^{xvi}—Na2—Ge1^{xvii}	30.4 (3)
O2^{iv}—Zn1—Na1^{iv}	44.2 (2)	O1^{xi}—Na2—Ge1^{xvii}	87.7 (4)
O4^{iv}—Zn1—Na1^{iv}	82.7 (2)	O3^{xv}—Na2—Ge1^{xvii}	90.7 (3)
O3^{vi}—Zn1—Na1^{iv}	153.65 (19)	Ge1^{xv}—Na2—Ge1^{xvii}	120.8 (2)
O1^{i}—Zn1—Na1^{iv}	87.9 (3)	Na1^{xii}—Na2—Ge1^{xvii}	83.98 (17)
Na1—Zn1—Na1^{iv}	96.95 (13)	O2^{xv}—Na2—Na1^{xi}	95.4 (3)
O2^{iv}—Zn1—Na2^{vii}	123.2 (2)	O4^{xvi}—Na2—Na1^{xi}	84.7 (3)
O4^{iv}—Zn1—Na2^{vii}	42.25 (17)	O1^{xi}—Na2—Na1^{xi}	45.5 (3)
O3^{vi}—Zn1—Na2^{vii}	65.1 (2)	O3^{xv}—Na2—Na1^{xi}	154.3 (4)
O1^{i}—Zn1—Na2^{vii}	120.9 (2)	Ge1^{xv}—Na2—Na1^{xi}	65.8 (2)
Na1—Zn1—Na2^{vii}	60.99 (16)	Na1^{xii}—Na2—Na1^{xi}	108.49 (9)
Na1^{iv}—Zn1—Na2^{vii}	121.7 (3)	Ge1^{xvii}—Na2—Na1^{xi}	85.92 (17)
O2^{iv}—Zn1—Na1^{i}	89.8 (3)	O2^{xv}—Na2—Zn1^{xviii}	82.2 (3)
O4^{iv}—Zn1—Na1^{i}	151.80 (19)	O4^{xvi}—Na2—Zn1^{xviii}	35.32 (19)
O3^{vi}—Zn1—Na1^{i}	87.06 (17)	O1^{xi}—Na2—Zn1^{xviii}	100.9 (4)
O1^{i}—Zn1—Na1^{i}	43.7 (2)	O3^{xv}—Na2—Zn1^{xviii}	137.3 (2)
Na1—Zn1—Na1^{i}	107.8 (4)	Ge1^{xv}—Na2—Zn1^{xviii}	60.52 (15)
Na1^{iv}—Zn1—Na1^{i}	95.09 (12)	Na1^{xii}—Na2—Zn1^{xviii}	142.2 (2)
Na2^{vii}—Zn1—Na1^{i}	141.7 (4)	Ge1^{xvii}—Na2—Zn1^{xviii}	60.24 (11)
O2^{iv}—Zn1—Na1^{viii}	78.9 (2)	Na1^{xi}—Na2—Zn1^{xviii}	60.69 (17)
O4^{iv}—Zn1—Na1^{viii}	88.43 (18)	O2^{xv}—Na2—Ge1^{xii}	104.03 (15)
O3^{vi}—Zn1—Na1^{viii}	43.5 (3)	O4^{xvi}—Na2—Ge1^{xii}	137.0 (6)
O1^{i}—Zn1—Na1^{viii}	153.88 (18)	O1^{xi}—Na2—Ge1^{xii}	29.33 (13)
Na1—Zn1—Na1^{viii}	120.21 (18)	O3^{xv}—Na2—Ge1^{xii}	96.9 (3)
Na1^{iv}—Zn1—Na1^{viii}	114.7 (4)	Ge1^{xv}—Na2—Ge1^{xii}	96.65 (14)
Na2^{vii}—Zn1—Na1^{viii}	59.23 (12)	Na1^{xii}—Na2—Ge1^{xii}	59.74 (14)
Na1^{i}—Zn1—Na1^{viii}	117.45 (19)	Ge1^{xvii}—Na2—Ge1^{xii}	115.0 (4)
O2^{iv}—Zn1—Na2^{ix}	78.8 (3)	Na1^{xi}—Na2—Ge1^{xii}	62.12 (16)
O4^{iv}—Zn1—Na2^{ix}	144.83 (15)	Zn1^{xviii}—Na2—Ge1^{xii}	122.8 (3)
O3^{vi}—Zn1—Na2^{ix}	41.5 (2)	O2^{xv}—Na2—Na1^{xviii}	75.5 (2)
O1^{i}—Zn1—Na2^{ix}	100.4 (2)	O4^{xvi}—Na2—Na1^{xviii}	44.2 (4)
Na1—Zn1—Na2^{ix}	141.7 (4)	O1^{xi}—Na2—Na1^{xviii}	151.9 (3)
Na1^{iv}—Zn1—Na2^{ix}	119.1 (3)	O3^{xv}—Na2—Na1^{xviii}	82.0 (3)
Na2^{vii}—Zn1—Na2^{ix}	104.94 (8)	Ge1^{xv}—Na2—Na1^{xviii}	83.60 (15)
Na1^{i}—Zn1—Na2^{ix}	59.38 (16)	Na1^{xii}—Na2—Na1^{xviii}	119.69 (13)
Na1^{viii}—Zn1—Na2^{ix}	58.07 (12)	Ge1^{xvii}—Na2—Na1^{xviii}	65.8 (2)
O2^{iv}—Zn1—Na2^{iv}	145.79 (19)	Na1^{xi}—Na2—Na1^{xviii}	119.11 (13)
O4^{iv}—Zn1—Na2^{iv}	100.8 (2)	Zn1^{xviii}—Na2—Na1^{xviii}	58.44 (18)
O3^{vi}—Zn1—Na2^{iv}	79.5 (2)	Ge1^{xii}—Na2—Na1^{xviii}	178.7 (2)
O1^{i}—Zn1—Na2^{iv}	36.81 (17)	O2^{xv}—Na2—Na1^{xv}	44.14 (16)
Na1—Zn1—Na2^{iv}	57.4 (2)	O4^{xvi}—Na2—Na1^{xv}	149.8 (4)

$Na1^{iv}$—Zn1—$Na2^{iv}$	123.4 (2)	$O1^{xi}$—Na2—$Na1^{xv}$	92.9 (3)
$Na2^{vii}$—Zn1—$Na2^{iv}$	90.8 (3)	$O3^{xv}$—Na2—$Na1^{xv}$	88.3 (3)
$Na1^{i}$—Zn1—$Na2^{iv}$	57.1 (2)	$Ge1^{xv}$—Na2—$Na1^{xv}$	59.94 (13)
$Na1^{viii}$—Zn1—$Na2^{iv}$	121.7 (2)	$Na1^{xii}$—Na2—$Na1^{xv}$	95.52 (10)
$Na2^{ix}$—Zn1—$Na2^{iv}$	89.7 (3)	$Ge1^{xvii}$—Na2—$Na1^{xv}$	178.88 (19)
$O2^{iv}$—Zn1—$Na2^{x}$	33.6 (2)	$Na1^{xi}$—Na2—$Na1^{xv}$	95.19 (10)
$O4^{iv}$—Zn1—$Na2^{x}$	80.7 (3)	$Zn1^{xviii}$—Na2—$Na1^{xv}$	120.46 (19)
$O3^{vi}$—Zn1—$Na2^{x}$	99.2 (2)	$Ge1^{xii}$—Na2—$Na1^{xv}$	65.5 (2)
$O1^{i}$—Zn1—$Na2^{x}$	143.65 (19)	$Na1^{xviii}$—Na2—$Na1^{xv}$	113.65 (9)
Na1—Zn1—$Na2^{x}$	124.3 (3)	$Ge1^{xiv}$—O1—$Zn1^{xiv}$	124.8 (3)
$Na1^{iv}$—Zn1—$Na2^{x}$	57.6 (2)	$Ge1^{xiv}$—O1—$Na2^{xiii}$	110.5 (4)
$Na2^{vii}$—Zn1—$Na2^{x}$	89.7 (3)	$Zn1^{xiv}$—O1—$Na2^{xiii}$	112.0 (3)
$Na1^{i}$—Zn1—$Na2^{x}$	121.8 (3)	$Ge1^{xiv}$—O1—Na1	112.4 (2)
$Na1^{viii}$—Zn1—$Na2^{x}$	57.2 (2)	$Zn1^{xiv}$—O1—Na1	100.8 (4)
$Na2^{ix}$—Zn1—$Na2^{x}$	88.5 (3)	$Na2^{xiii}$—O1—Na1	90.5 (5)
$Na2^{iv}$—Zn1—$Na2^{x}$	178.2 (2)	Ge1—O2—$Zn1^{xii}$	125.1 (4)
$O4^{iv}$—Na1—O2	102.4 (5)	Ge1—O2—$Na2^{ii}$	107.4 (5)
$O4^{iv}$—Na1—O1	104.3 (6)	$Zn1^{xii}$—O2—$Na2^{ii}$	118.0 (3)
O2—Na1—O1	103.0 (3)	Ge1—O2—Na1	106.7 (3)
$O4^{iv}$—Na1—$O3^{xi}$	132.7 (3)	$Zn1^{xii}$—O2—Na1	100.1 (5)
O2—Na1—$O3^{xi}$	104.2 (6)	$Na2^{ii}$—O2—Na1	93.2 (5)
O1—Na1—$O3^{xi}$	106.9 (6)	$Ge1^{xiv}$—O3—$Zn1^{xix}$	125.6 (3)
$O4^{iv}$—Na1—Zn1	36.8 (2)	$Ge1^{xiv}$—O3—$Na2^{ii}$	110.5 (5)
O2—Na1—Zn1	87.8 (3)	$Zn1^{xix}$—O3—$Na2^{ii}$	104.2 (3)
O1—Na1—Zn1	141.0 (6)	$Ge1^{xiv}$—O3—$Na1^{xiii}$	119.6 (3)
$O3^{xi}$—Na1—Zn1	106.4 (3)	$Zn1^{xix}$—O3—$Na1^{xiii}$	101.1 (4)
$O4^{iv}$—Na1—$Na2^{iv}$	101.1 (3)	$Na2^{ii}$—O3—$Na1^{xiii}$	89.0 (5)
O2—Na1—$Na2^{iv}$	83.5 (3)	$Ge1^{xiv}$—O4—$Zn1^{xii}$	126.1 (3)
O1—Na1—$Na2^{iv}$	151.6 (5)	$Ge1^{xiv}$—O4—$Na2^{xx}$	108.2 (5)
$O3^{xi}$—Na1—$Na2^{iv}$	45.2 (3)	$Zn1^{xii}$—O4—$Na2^{xx}$	102.4 (3)
Zn1—Na1—$Na2^{iv}$	65.8 (2)	$Ge1^{xiv}$—O4—$Na1^{xii}$	123.2 (3)
$O4^{iv}$—Na1—Ge1	86.2 (3)	$Zn1^{xii}$—O4—$Na1^{xii}$	98.0 (4)
O2—Na1—Ge1	30.64 (17)	$Na2^{xx}$—O4—$Na1^{xii}$	92.5 (6)
O1—Na1—Ge1	132.75 (18)		

Symmetry codes: (i) *x*, *y*, *z*−1; (ii) *x*−1, *y*, *z*; (iii) *x*−1/2, −*y*+2, *z*−1/2; (iv) *x*−1/2, −*y*+1, *z*−1/2; (v) *x*−1, *y*, *z*−1; (vi) *x*, *y*−1, *z*−1; (vii) *x*−1, *y*−1, *z*; (viii) *x*−1/2, −*y*, *z*−1/2; (ix) *x*−1, *y*−1, *z*−1; (x) *x*−3/2, −*y*+1, *z*−1/2; (xi) *x*+1/2, −*y*+1, *z*−1/2; (xii) *x*+1/2, −*y*+1, *z*+1/2; (xiii) *x*−1/2, −*y*+1, *z*+1/2; (xiv) *x*, *y*, *z*+1; (xv) *x*+1, *y*, *z*; (xvi) *x*+1/2, −*y*+2, *z*−1/2; (xvii) *x*+1/2, −*y*+2, *z*+1/2; (xviii) *x*+1, *y*+1, *z*; (xix) *x*, *y*+1, *z*+1; (xx) *x*−1/2, −*y*+2, *z*+1/2.