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Crystal structure of $\text{Na}_2\text{HfSi}_2\text{O}_7$ by Rietveld refinement

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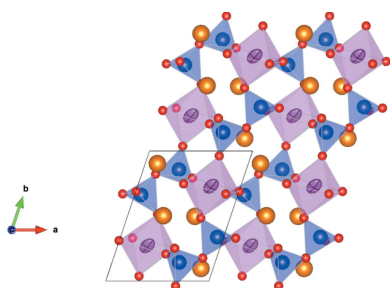
The structure of triclinic disodium hafnium disilicate, $\text{Na}_2\text{HfSi}_2\text{O}_7$, has been determined by laboratory powder X-ray diffraction and refined by the Rietveld refinement. The structure is a framework made of alternate layers of HfO_6 octahedra and SiO_4 tetrahedra linked by common O atoms. Sodium atoms are located in the voids of the framework, aligned into tunnels along the [010] direction. $\text{Na}_2\text{HfSi}_2\text{O}_7$ is isostructural with the parakeldyshite $\text{Na}_2\text{ZrSi}_2\text{O}_7$ phase.

1. Chemical context

Laboratory work in order to explore the chemistry of compounds with radioactive elements such as actinides is difficult because of the emission of ionizing radiation. To overcome this problem, these radionuclides are often replaced by a stable element having similar properties as the radioactive element, for instance by using elements with a similar ionic radius or with the same oxidation state. Hence actinides are often replaced by neodymium, zirconium, europium, or hafnium (Ramsey *et al.*, 1995). The reactivity of uranium with an Na–Si–O glass at high temperatures was thus simulated by using hafnium instead of uranium. We have obtained samples with different phases among which was a sodium hafnium disilicate, similar to the sodium zirconium silicate already observed in a similar glass (Plaisted *et al.*, 1999). The structure of the sodium hafnium disilicate is discussed in this paper.

2. Structural commentary

The $\text{Na}_2\text{HfSi}_2\text{O}_7$ phase is isostructural with the parakeldyshite phase (Voronkov *et al.*, 1970; Fleischer *et al.*, 1979). As reported in Table 1, the cell parameters of the $\text{Na}_2\text{HfSi}_2\text{O}_7$ phase are slightly smaller than those of parakeldyshite, and the volume of the cell is 0.8% smaller. For the $\text{Na}_2\text{HfSi}_2\text{O}_7$ phase, the HfO_6 octahedral and the SiO_4 tetrahedral volumes are about the same as the analogous Zr octahedral and Si tetrahedral volumes in parakeldyshite. The SiO_4 tetrahedral volume of the $\text{Na}_2\text{HfSi}_2\text{O}_7$ phase is about 5% smaller than that in parakeldyshite. It is thus in the latter tetrahedron that the bond lengths differ significantly whereas the other bond lengths are quite similar in both phases. The sodium coordination polyhedral volumes are quite similar in volume for the two phases, about 30.1 \AA^3 . A polyhedral view of the $\text{Na}_2\text{HfSi}_2\text{O}_7$ structure is given in Fig. 1. The $\text{Na}_2\text{ZrSi}_2\text{O}_7$ phase is capable of ion exchange on the sodium site thanks to the sufficient dimension of the sodium tunnels in the [010]



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Table 1

Cell parameters, selected distances (Å), angles (°) and volumes (Å³) for the title phase compared to parakeldyshite.

Cell parameters of Na₂ZrSi₂O₇ are from Ferreira *et al.* (2001).

| Na ₂ HfSi ₂ O ₇ | | Na ₂ ZrSi ₂ O ₇ | |
|--|--------------------------------------|--|------------------------------------|
| <i>a, b, c</i> | 6.6123 (2), 8.7948 (3), 5.41074 (15) | <i>a, b, c</i> | 6.6364 (4), 8.8120 (5), 5.4233 (3) |
| <i>α, β, γ</i> | 92.603 (2), 94.084 (2), 71.326 (2) | <i>α, β, γ</i> | 92.697 (4), 94.204 (3), 71.355 (3) |
| <i>V</i> _{cell} | 297.25 (2) | <i>V</i> _{cell} | 299.61 (3) |
| Hf1 octahedron | | Zr octahedron | |
| O1—O7 | 4.15 (4) | O1—O7 | 4.22 (2) |
| O4—O5 | 4.28 (3) | O4—O5 | 4.24 (2) |
| O3—O6 | 4.22 (4) | O3—O6 | 4.18 (2) |
| Hf1—O7 | 2.23 (3) | Zr—O7 | 2.13 (2) |
| Hf1—O1 | 1.92 (3) | Zr—O1 | 2.08 (2) |
| Hf1—O3 | 2.30 (3) | Zr—O3 | 2.11 (2) |
| Hf1—O4 | 2.04 (2) | Zr—O4 | 2.16 (3) |
| Hf1—O5 | 2.26 (3) | Zr—O5 | 2.09 (3) |
| Hf1—O6 | 1.93 (2) | Zr—O6 | 2.03 (2) |
| Hf1—O7—Si2 | 116.7 (6) | Zr—O7—Si2 | 124.0 (4) |
| Polyhedron volume | 12.5 | Polyhedron volume | 12.4 |
| Si1 tetrahedron | | Si1 tetrahedron | |
| Si1—O2 ⁱ | 1.55 (3) | Si1—O2 ⁱ | 1.62 (2) |
| Si1—O3 ⁱ | 1.37 (4) | Si1—O3 ⁱ | 1.58 (1) |
| Si1—O4 ⁱ | 1.66 (3) | Si1—O4 ⁱ | 1.55 (1) |
| Si1—O1 | 1.68 (3) | Si1—O1 | 1.57 (1) |
| Polyhedron volume | 1.94 | Polyhedron volume | 2.02 |
| Si2 tetrahedron | | Si2 tetrahedron | |
| Si2—O2 | 1.77 (3) | Si2—O2 | 1.67 (2) |
| Si2—O7 ⁱ | 1.61 (3) | Si2—O7 ⁱ | 1.64 (1) |
| Si2—O5 | 1.61 (3) | Si2—O5 | 1.62 (1) |
| Si2—O6 | 1.60 (3) | Si2—O6 | 1.53 (1) |
| Polyhedron volume | 2.12 | Polyhedron volume | 2.14 |
| Si1—O—Si2 bridging angle | 136.7 (5) | Si1—O—Si2 bridging angle | 130.9 (5) |

Symmetry code: (i) $-x, -y, -z$.

direction (Kostov-Kytin *et al.*, 2008). Since these dimensions are the same in both phases, ion exchange should also be possible in the Na₂HfSi₂O₇ phase. A numerical comparison of the structures of the parakeldyshite and the Na₂HfSi₂O₇ phase

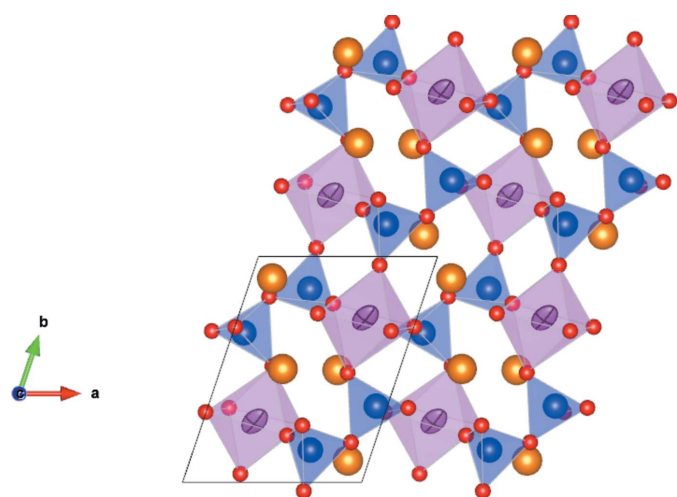


Figure 1

Polyhedral representation of the Na₂HfSi₂O₇ phase with SiO₄ units (blue), HfO₆ units (green) and sodium (yellow) with displacement ellipsoids drawn at the 99% probability level.

was performed with *COMPSTRU* (de la Flor *et al.*, 2016). The structures' similarities were estimated by different parameters such as the measure of similarity Δ (Bergerhoff *et al.*, 1999). This parameter was determined to be 0.018 for a maximum distance between paired atoms of 1 Å, indicating that structures are effectively isostructural. Since hafnium simulates uranium, the existence of the Na₂USi₂O₇ phase can also be supposed.

3. Database survey

The crystal chemistry of zirconosilicates can be described in terms of an *MT* framework with MO₆ octahedra and TO₄ tetrahedra (*M* = Zr, *T* = Si; Ilyushin & Blatov, 2002). The voids in the *MT* framework are filled with alkaline or alkaline earth elements coordinated in an eight-vertex polyhedron. The crystal system of sodium zirconosilicates can vary from triclinic (Na₂ZrSi₂O₇) to monoclinic (Na₂ZrSi₄O₁₁) or trigonal (Na₈ZrSi₆O₁₈). If we focus on the chemistry of zirconosilicates with Si₂O₇ diortho groups and their analogs (Pekov *et al.*, 2007), the triclinic phase is privileged such as the parakeldyshite Na₂ZrSi₂O₇ phase (Ferreira *et al.*, 2001) or the keldyshite (Na,H)₂ZrSi₂O₇ phase (Khalilov *et al.*, 1978). The potassium analogue, however, is monoclinic as in the case of khibinskite K₂ZrSi₂O₇ (Chernov *et al.*, 1970; Nosyrev *et al.*, 1976).

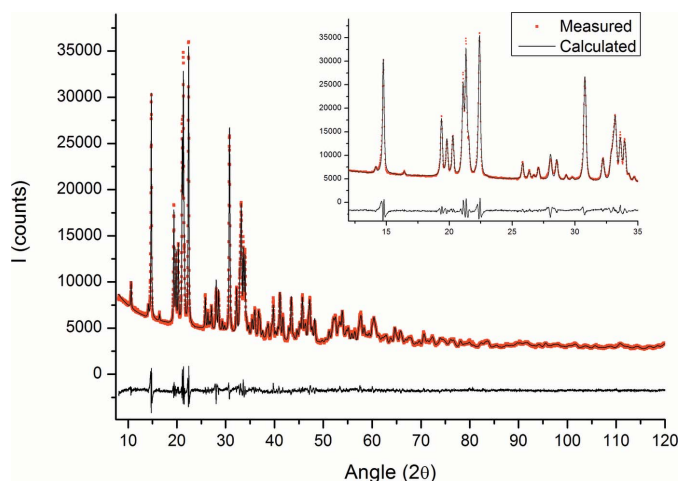


Figure 2
Comparison of observed (red squares) and calculated (solid line) intensities for Na₂HfSi₂O₇. The difference pattern appears below. Inset: focus on the 12–35° 2θ range.

4. Synthesis and crystallization

The synthesis of sodium hafnium disilicate was based on the two-step synthesis protocol of parakelyshite Na₂ZrSi₂O₇ (Lin *et al.*, 1999; Ferreira *et al.*, 2001). The first step was the synthesis of the Hf–petarasite phase Na₅Zr₂Si₆O₁₈(Cl·OH)₂·H₂O with zirconium totally substituted by hafnium. Adequate quantities of sodium silicate solution (27% SiO₂, 8% Na₂O), sodium chloride, hafnium chloride, potassium chloride, sodium hydroxide and water were mixed thoroughly in a polytetrafluoroethylene (PTFE) vessel at room temperature for 30 minutes. A gel was obtained with a pH value around 13. The PTFE vessel was put in a Parr digestion apparatus for a hydrothermal synthesis over 10 days at 523 K. The resulting powder was washed, filtered, and dried overnight at 393 K. In spite of the drying process, the powder was still hydrated. Powder X-ray diffraction showed the compound to be isostructural to petarasite. The second step was the calcination of Hf–petarasite over 15 h at 1373 K under air which lead to a white powder. SEM observation of the powder showed large grains with Na, Hf, Si and O and smaller grains with supplementary K. The chemical composition of the major phase was determined by EDS to have the following stoichiometry Na_{1.7±0.2}Hf_{1.0}Si_{2.3±0.1}O_{7.3±0.9} as compared to the theoretical stoichiometry of Na₂HfSi₂O₇. Thus the major phase is very close to the expected one. The sample was analysed by differential thermal analysis to determine its melting point. There was no thermal event indicating a melting until 1623 K and the sample was still in powder form. The Na₂HfSi₂O₇ phase therefore has a higher melting point than parakelyshite which is below 1523 K (Ferreira *et al.*, 2001).

5. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. Observed and calculated intensities for Na₂HfSi₂O₇ are shown in Fig. 2 along with the

Table 2
Experimental details.

| | |
|--------------------------------------|--|
| Crystal data | |
| Chemical formula | Na ₂ HfSi ₂ O ₇ |
| <i>M_r</i> | 392.6 |
| Crystal system, space group | Triclinic, <i>P</i> $\bar{1}$ |
| Temperature (K) | 293 |
| <i>a</i> , <i>b</i> , <i>c</i> (Å) | 6.6123 (2), 8.7948 (3), 5.41074 (15) |
| α , β , γ (°) | 92.603 (2), 94.0843 (18), 71.3262 (18) |
| <i>V</i> (Å ³) | 297.25 (2) |
| <i>Z</i> | 2 |
| Radiation type | Cu <i>K</i> α ₁ , λ = 1.540562, 1.544390 Å |
| Specimen shape, size (mm) | Flat sheet, 25 × 25 |
| Data collection | |
| Diffractometer | Panalytical XPert MPD Pro |
| Specimen mounting | Packed powder pellet |
| Data collection mode | Reflection |
| Scan method | Step |
| 2θ values (°) | 2θ _{min} = 8.013 2θ _{max} = 120.013 2θ _{step} = 0.017 |
| Refinement | |
| <i>R</i> factors and goodness of fit | <i>R_p</i> = 0.024, <i>R_{wp}</i> = 0.032, <i>R_{exp}</i> = 0.015, <i>R</i> (<i>F</i>) = 0.024, χ^2 = 4.973 |
| No. of parameters | 67 |

Computer programs: *X'Pert Data Collector* (PANalytical, 2011), *JANA2006* (Petříček *et al.*, 2014), *VESTA* (Momma & Izumi, 2011) and *publCIF* (Westrip, 2010).

difference pattern. The reliability factors of the refinement were quite poor because of an amorphous bump attributed to the second minor phase. Hence the reliability factors were negatively impacted. The isotropic ADP's of the oxygen atoms were constrained to be equal in volume in order to avoid a slightly negative ADP value on O5. The residual electron density is about 2.4 e Å⁻³, which is less than 10% of the electron density of a Hf atom. The occupancies of all atoms were fixed to unity.

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Crystal structure of Na₂HfSi₂O₇ by Rietveld refinement

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Computing details

Data collection: *X'Pert Data Collector* (PANalytical, 2011); cell refinement: *JANA2006* (Petříček *et al.*, 2014); data reduction: *JANA2006* (Petříček *et al.*, 2014); program(s) used to solve structure: *JANA2006* (Petříček *et al.*, 2014); program(s) used to refine structure: *JANA2006* (Petříček *et al.*, 2014); molecular graphics: *VESTA* (Momma & Izumi, 2011); software used to prepare material for publication: *publCIF* (Westrip, 2010).

Disodium hafnium disilicate

Crystal data

| | |
|--|--|
| Na ₂ HfSi ₂ O ₇ | $Z = 2$ |
| $M_r = 392.6$ | $F(000) = 356$ |
| Triclinic, $P\bar{1}$ | $D_x = 4.387 \text{ Mg m}^{-3}$ |
| $a = 6.6123 (2) \text{ \AA}$ | Cu $K\alpha_1$ radiation, $\lambda = 1.540562, 1.544390 \text{ \AA}$ |
| $b = 8.7948 (3) \text{ \AA}$ | $T = 293 \text{ K}$ |
| $c = 5.41074 (15) \text{ \AA}$ | Particle morphology: plate-like |
| $\alpha = 92.603 (2)^\circ$ | white |
| $\beta = 94.0843 (18)^\circ$ | flat_sheet, $25 \times 25 \text{ mm}$ |
| $\gamma = 71.3262 (18)^\circ$ | Specimen preparation: Prepared at 1393 K and |
| $V = 297.25 (2) \text{ \AA}^3$ | 100 kPa |

Data collection

| | |
|--|---|
| Panalytical XPert MPD Pro diffractometer | Data collection mode: reflection |
| Radiation source: sealed X-ray tube | Scan method: step |
| Specimen mounting: packed powder pellet | $2\theta_{\min} = 8.013^\circ, 2\theta_{\max} = 120.013^\circ, 2\theta_{\text{step}} = 0.017^\circ$ |

Refinement

| | |
|--------------------------------|---|
| $R_p = 0.024$ | 67 parameters |
| $R_{\text{wp}} = 0.032$ | 0 restraints |
| $R_{\text{exp}} = 0.015$ | 6 constraints |
| $R(F) = 0.024$ | Weighting scheme based on measured s.u.'s |
| 6423 data points | $(\Delta/\sigma)_{\max} = 0.005$ |
| Profile function: pseudo-Voigt | Background function: Legendre polynoms |

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

| | x | y | z | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|-------------|-------------|-------------|----------------------------------|
| Na1 | 0.8823 (15) | 0.0970 (12) | 0.2630 (18) | 0.035 (4)* |
| Na2 | 0.3456 (14) | 0.5024 (10) | 0.7608 (18) | 0.011 (3)* |
| Hf1 | 0.2880 (3) | 0.2710 (2) | 0.2201 (3) | 0.0158 (7) |
| Si1 | 0.6528 (13) | 0.1435 (9) | 0.7769 (13) | 0.010 (3)* |

| | | | | |
|-----|-------------|-------------|-------------|--------------|
| Si2 | 0.9381 (12) | 0.3380 (8) | 0.6861 (15) | 0.006 (2)* |
| O1 | 0.307 (2) | 0.0382 (17) | 0.172 (3) | 0.0030 (15)* |
| O2 | 0.865 (2) | 0.1777 (14) | 0.727 (2) | 0.0030 (15)* |
| O3 | 0.494 (2) | 0.2081 (15) | 0.530 (3) | 0.0030 (15)* |
| O4 | 0.562 (2) | 0.2522 (15) | 0.020 (3) | 0.0030 (15)* |
| O5 | -0.003 (2) | 0.3116 (14) | 0.401 (3) | 0.0030 (15)* |
| O6 | 0.120 (2) | 0.3300 (14) | 0.872 (3) | 0.0030 (15)* |
| O7 | 0.284 (2) | 0.5148 (14) | 0.288 (3) | 0.0030 (15)* |

Atomic displacement parameters (Å²)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|-------------|-------------|-------------|------------|------------|------------|
| Hf1 | 0.0148 (10) | 0.0177 (11) | 0.0126 (10) | 0.0003 (7) | 0.0035 (7) | 0.0111 (8) |

Geometric parameters (Å, °)

| | | | |
|---|------------|---|------------|
| O1—Hf1 | 2.017 (15) | Na1—Na1 ^{vii} | 3.169 (13) |
| O1—Si1 ⁱ | 1.568 (17) | Na1—Na2 ^v | 3.363 (13) |
| O2—Si1 | 1.567 (18) | Na1—Hf1 ^{viii} | 3.513 (12) |
| O2—Si2 | 1.660 (17) | Na1—Si1 ⁱⁱ | 2.919 (12) |
| O3—Hf1 | 2.060 (13) | Na1—Si1 | 3.210 (13) |
| O3—Si1 | 1.644 (15) | Na1—Si1 ^{vii} | 3.140 (11) |
| O4—Na1 | 2.450 (15) | Na1—Si2 | 3.132 (13) |
| O4—Si1 ⁱⁱ | 1.622 (15) | Na2—Na2 ^v | 3.590 (14) |
| O5—Na1 ⁱⁱⁱ | 2.323 (18) | Na2—Na2 ^{ix} | 3.174 (13) |
| O5—Si2 ⁱⁱⁱ | 1.605 (16) | Na2—Hf1 | 3.556 (9) |
| O6—Hf1 ^{iv} | 2.115 (13) | Na2—Hf1 ^{iv} | 3.399 (10) |
| O6—Si2 ⁱⁱⁱ | 1.497 (16) | Na2—Hf1 ^v | 3.590 (10) |
| O7—Na2 ^v | 2.441 (18) | Na2—Si1 | 3.161 (10) |
| O7—Si2 ^v | 1.625 (13) | Na2—Si2 ^v | 3.052 (11) |
| Na1—Na1 ^{vi} | 3.453 (14) | | |
| Hf1—O1—Si1 ⁱ | 161.7 (9) | Na2 ^{ix} —Na2—Si1 | 76.2 (3) |
| Si1—O2—Si2 | 136.8 (8) | Na2 ^{ix} —Na2—Si2 ^v | 153.7 (4) |
| Hf1—O3—Si1 | 175.1 (10) | Hf1—Na2—Hf1 ^{iv} | 102.1 (3) |
| Na1—O4—Si1 ⁱⁱ | 89.2 (6) | Hf1—Na2—Hf1 ^v | 119.7 (3) |
| Na1 ⁱⁱⁱ —O5—Si2 ⁱⁱⁱ | 104.3 (9) | Hf1—Na2—Si1 | 66.6 (2) |
| Hf1 ^{iv} —O6—Si2 ⁱⁱⁱ | 153.3 (10) | Hf1—Na2—Si2 ^v | 59.6 (2) |
| Na2 ^v —O7—Si2 ^v | 134.4 (9) | Hf1 ^{iv} —Na2—Hf1 ^v | 126.1 (3) |
| O4—Na1—O5 ^{viii} | 97.2 (6) | Hf1 ^{iv} —Na2—Si1 | 62.6 (2) |
| O4—Na1—Na1 ^{vi} | 91.7 (4) | Hf1 ^{iv} —Na2—Si2 ^v | 134.1 (4) |
| O4—Na1—Na1 ^{vii} | 152.6 (6) | Hf1 ^v —Na2—Si1 | 102.9 (3) |
| O4—Na1—Na2 ^v | 51.1 (4) | Hf1 ^v —Na2—Si2 ^v | 97.7 (3) |
| O4—Na1—Hf1 ^{viii} | 109.2 (5) | Si1—Na2—Si2 ^v | 125.7 (4) |
| O4—Na1—Si1 ⁱⁱ | 33.8 (4) | O1—Hf1—O3 | 88.5 (5) |
| O4—Na1—Si1 | 95.1 (5) | O1—Hf1—O6 ⁱⁱ | 91.8 (5) |
| O4—Na1—Si1 ^{vii} | 143.7 (5) | O1—Hf1—Na1 ⁱⁱⁱ | 51.7 (4) |
| O4—Na1—Si2 | 103.7 (5) | O1—Hf1—Na2 ⁱⁱ | 123.8 (4) |

| | | | |
|---|-----------|---|-----------|
| O5 ^{viii} —Na1—Na1 ^{vi} | 114.1 (6) | O1—Hf1—Na2 | 131.8 (4) |
| O5 ^{viii} —Na1—Na1 ^{vii} | 89.9 (5) | O1—Hf1—Na2 ^v | 136.4 (4) |
| O5 ^{viii} —Na1—Na2 ^v | 46.9 (4) | O3—Hf1—O6 ⁱⁱ | 171.1 (6) |
| O5 ^{viii} —Na1—Hf1 ^{viii} | 36.4 (4) | O3—Hf1—Na1 ⁱⁱⁱ | 107.6 (5) |
| O5 ^{viii} —Na1—Si1 ⁱⁱ | 113.7 (5) | O3—Hf1—Na2 ⁱⁱ | 124.6 (5) |
| O5 ^{viii} —Na1—Si1 | 85.7 (5) | O3—Hf1—Na2 | 50.0 (4) |
| O5 ^{viii} —Na1—Si1 ^{vii} | 94.3 (5) | O3—Hf1—Na2 ^v | 71.4 (5) |
| O5 ^{viii} —Na1—Si2 | 29.8 (4) | O6 ⁱⁱ —Hf1—Na1 ⁱⁱⁱ | 79.4 (4) |
| Na1 ^{vi} —Na1—Na1 ^{vii} | 109.5 (3) | O6 ⁱⁱ —Hf1—Na2 ⁱⁱ | 48.7 (4) |
| Na1 ^{vi} —Na1—Na2 ^v | 116.9 (4) | O6 ⁱⁱ —Hf1—Na2 | 133.2 (3) |
| Na1 ^{vi} —Na1—Hf1 ^{viii} | 79.2 (3) | O6 ⁱⁱ —Hf1—Na2 ^v | 102.6 (4) |
| Na1 ^{vi} —Na1—Si1 ⁱⁱ | 58.3 (3) | Na1 ⁱⁱⁱ —Hf1—Na2 ⁱⁱ | 127.8 (2) |
| Na1 ^{vi} —Na1—Si1 | 158.2 (4) | Na1 ⁱⁱⁱ —Hf1—Na2 | 111.9 (2) |
| Na1 ^{vi} —Na1—Si1 ^{vii} | 52.3 (2) | Na1 ⁱⁱⁱ —Hf1—Na2 ^v | 171.0 (2) |
| Na1 ^{vi} —Na1—Si2 | 141.2 (4) | Na2 ⁱⁱ —Hf1—Na2 | 102.1 (2) |
| Na1 ^{vii} —Na1—Na2 ^v | 125.8 (4) | Na2 ⁱⁱ —Hf1—Na2 ^v | 53.9 (2) |
| Na1 ^{vii} —Na1—Hf1 ^{viii} | 92.0 (3) | Na2—Hf1—Na2 ^v | 60.3 (2) |
| Na1 ^{vii} —Na1—Si1 ⁱⁱ | 156.1 (5) | O1 ⁱ —Si1—O2 | 111.9 (8) |
| Na1 ^{vii} —Na1—Si1 | 59.0 (3) | O1 ⁱ —Si1—O3 | 113.6 (9) |
| Na1 ^{vii} —Na1—Si1 ^{vii} | 61.2 (3) | O1 ⁱ —Si1—O4 ^{iv} | 109.9 (9) |
| Na1 ^{vii} —Na1—Si2 | 70.6 (3) | O1 ⁱ —Si1—Na1 | 97.9 (6) |
| Na2 ^v —Na1—Hf1 ^{viii} | 71.7 (3) | O1 ⁱ —Si1—Na1 ^{iv} | 76.2 (6) |
| Na2 ^v —Na1—Si1 ⁱⁱ | 76.5 (3) | O1 ⁱ —Si1—Na1 ^{vii} | 61.5 (6) |
| Na2 ^v —Na1—Si1 | 83.1 (3) | O1 ⁱ —Si1—Na2 | 150.4 (7) |
| Na2 ^v —Na1—Si1 ^{vii} | 135.6 (5) | O2—Si1—O3 | 104.6 (8) |
| Na2 ^v —Na1—Si2 | 55.9 (3) | O2—Si1—O4 ^{iv} | 105.7 (9) |
| Hf1 ^{viii} —Na1—Si1 ⁱⁱ | 104.5 (4) | O2—Si1—Na1 | 52.6 (6) |
| Hf1 ^{viii} —Na1—Si1 | 117.6 (3) | O2—Si1—Na1 ^{iv} | 77.6 (6) |
| Hf1 ^{viii} —Na1—Si1 ^{vii} | 64.0 (3) | O2—Si1—Na1 ^{vii} | 50.5 (5) |
| Hf1 ^{viii} —Na1—Si2 | 62.2 (3) | O2—Si1—Na2 | 97.4 (6) |
| Si1 ⁱⁱ —Na1—Si1 | 123.9 (4) | O3—Si1—O4 ^{iv} | 110.8 (7) |
| Si1 ⁱⁱ —Na1—Si1 ^{vii} | 110.6 (4) | O3—Si1—Na1 | 64.3 (6) |
| Si1 ⁱⁱ —Na1—Si2 | 132.4 (4) | O3—Si1—Na1 ^{iv} | 167.4 (6) |
| Si1—Na1—Si1 ^{vii} | 120.1 (3) | O3—Si1—Na1 ^{vii} | 121.8 (6) |
| Si1—Na1—Si2 | 56.5 (3) | O3—Si1—Na2 | 59.9 (5) |
| Si1 ^{vii} —Na1—Si2 | 103.3 (3) | O4 ^{iv} —Si1—Na1 | 150.5 (8) |
| O7 ^v —Na2—Na1 ^v | 99.3 (5) | O4 ^{iv} —Si1—Na1 ^{iv} | 57.1 (5) |
| O7 ^v —Na2—Na2 ^v | 45.5 (4) | O4 ^{iv} —Si1—Na1 ^{vii} | 125.7 (6) |
| O7 ^v —Na2—Na2 ^{ix} | 60.6 (4) | O4 ^{iv} —Si1—Na2 | 55.6 (5) |
| O7 ^v —Na2—Hf1 | 96.4 (4) | Na1—Si1—Na1 ^{iv} | 123.9 (4) |
| O7 ^v —Na2—Hf1 ^{iv} | 113.5 (4) | Na1—Si1—Na1 ^{vii} | 59.9 (3) |
| O7 ^v —Na2—Hf1 ^v | 35.8 (3) | Na1—Si1—Na2 | 103.3 (3) |
| O7 ^v —Na2—Si1 | 68.4 (4) | Na1 ^{iv} —Si1—Na1 ^{vii} | 69.4 (3) |
| O7 ^v —Na2—Si2 ^v | 110.4 (5) | Na1 ^{iv} —Si1—Na2 | 107.6 (3) |
| Na1 ^v —Na2—Na2 ^v | 91.8 (3) | Na1 ^{vii} —Si1—Na2 | 147.9 (4) |
| Na1 ^v —Na2—Na2 ^{ix} | 97.3 (3) | O2—Si2—O5 ^{viii} | 100.7 (8) |
| Na1 ^v —Na2—Hf1 | 117.5 (3) | O2—Si2—O6 ^{viii} | 106.7 (8) |
| Na1 ^v —Na2—Hf1 ^{iv} | 124.7 (3) | O2—Si2—O7 ^v | 102.8 (8) |

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| Na1 ^v —Na2—Hf1 ^v | 64.7 (3) | O2—Si2—Na1 | 55.3 (5) |
| Na1 ^v —Na2—Si1 | 167.6 (4) | O2—Si2—Na2 ^v | 103.7 (6) |
| Na1 ^v —Na2—Si2 ^v | 58.2 (3) | O5 ^{viii} —Si2—O6 ^{viii} | 116.1 (9) |
| Na2 ^v —Na2—Na2 ^{ix} | 106.1 (3) | O5 ^{viii} —Si2—O7 ^v | 109.8 (8) |
| Na2 ^v —Na2—Hf1 | 60.3 (2) | O5 ^{viii} —Si2—Na1 | 46.0 (6) |
| Na2 ^v —Na2—Hf1 ^{iv} | 142.8 (3) | O5 ^{viii} —Si2—Na2 ^v | 53.3 (5) |
| Na2 ^v —Na2—Hf1 ^v | 59.4 (2) | O6 ^{viii} —Si2—O7 ^v | 118.2 (8) |
| Na2 ^v —Na2—Si1 | 80.2 (3) | O6 ^{viii} —Si2—Na1 | 131.2 (6) |
| Na2 ^v —Na2—Si2 ^v | 68.4 (3) | O6 ^{viii} —Si2—Na2 ^v | 149.4 (8) |
| Na2 ^{ix} —Na2—Hf1 | 141.7 (3) | O7 ^v —Si2—Na1 | 110.3 (6) |
| Na2 ^{ix} —Na2—Hf1 ^{iv} | 66.1 (3) | O7 ^v —Si2—Na2 ^v | 57.1 (6) |
| Na2 ^{ix} —Na2—Hf1 ^v | 60.0 (3) | Na1—Si2—Na2 ^v | 65.9 (3) |

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