



**HAL**  
open science

## Crystal structure of Na<sub>2</sub>HfSi<sub>2</sub>O<sub>7</sub> by Rietveld refinement

Nicolas Massoni, Pierrick Chevreux

► **To cite this version:**

Nicolas Massoni, Pierrick Chevreux. Crystal structure of Na<sub>2</sub>HfSi<sub>2</sub>O<sub>7</sub> by Rietveld refinement. Acta Crystallographica Section E: Structure Reports Online [2001-2014], 2016, 72, pp.1434. 10.1107/S2056989016014225 . cea-01368805

**HAL Id: cea-01368805**

**<https://cea.hal.science/cea-01368805v1>**

Submitted on 20 Sep 2016

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution 4.0 International License



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

Nicolas Massoni<sup>a,\*</sup> and Pierrick Chevreux<sup>a,b</sup><sup>a</sup>CEA, DEN, DTCD, Marcoule, BP17171, F-30207 Bagnols sur Ceze, France, and <sup>b</sup>CRPG, CNRS UMR-5873, Université de Lorraine, BP 20, F-54501 Vandoeuvre les Nancy cedex, France. \*Correspondence e-mail: nicolas.massoni@cea.fr

Received 1 September 2016

Accepted 6 September 2016

Edited by A. Van der Lee, Université de Montpellier II, France

**Keywords:** crystal structure; powder diffraction; sodium hafnium disilicate.**CCDC reference:** 1502957**Supporting information:** this article has supporting information at journals.iucr.org/e

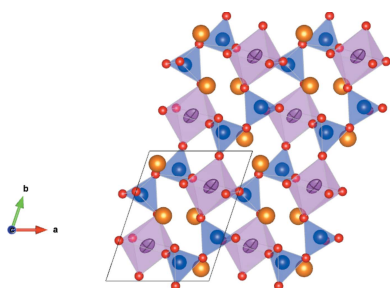
The structure of triclinic disodium hafnium disilicate,  $\text{Na}_2\text{HfSi}_2\text{O}_7$ , has been determined by laboratory powder X-ray diffraction and refined by the Rietveld refinement. The structure is a framework made of alternate layers of  $\text{HfO}_6$  octahedra and  $\text{SiO}_4$  tetrahedra 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  $\text{HfO}_6$  octahedral and the  $\text{SiO}_4$  tetrahedral volumes are about the same as the analogous Zr octahedral and Si tetrahedral volumes in parakeldyshite. The  $\text{SiO}_4$  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  $30.1 \text{ \AA}^3$ . 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]



OPEN ACCESS

**Table 1**

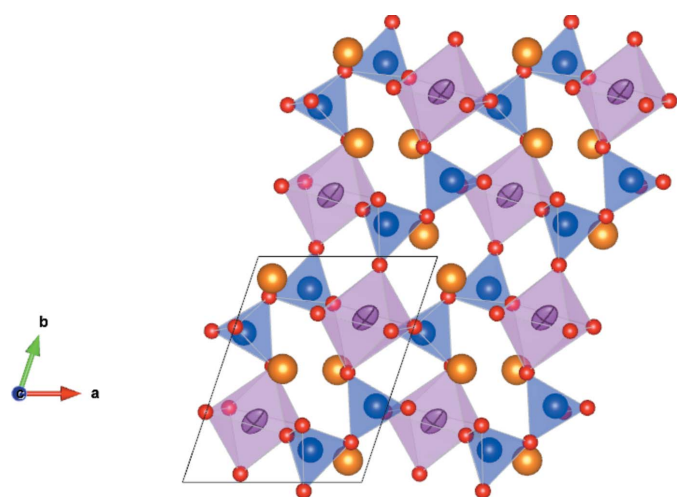
 Cell parameters, selected distances (Å), angles (°) and volumes (Å<sup>3</sup>) for the title phase compared to parakeldyshite.

 Cell parameters of Na<sub>2</sub>ZrSi<sub>2</sub>O<sub>7</sub> are from Ferreira *et al.* (2001).

Na <sub>2</sub> HfSi <sub>2</sub> O <sub>7</sub>		Na <sub>2</sub> ZrSi <sub>2</sub> O <sub>7</sub>	
<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> <sub>cell</sub>	297.25 (2)	<i>V</i> <sub>cell</sub>	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 <sup>i</sup>	1.55 (3)	Si1—O2 <sup>i</sup>	1.62 (2)
Si1—O3 <sup>i</sup>	1.37 (4)	Si1—O3 <sup>i</sup>	1.58 (1)
Si1—O4 <sup>i</sup>	1.66 (3)	Si1—O4 <sup>i</sup>	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 <sup>i</sup>	1.61 (3)	Si2—O7 <sup>i</sup>	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 Na<sub>2</sub>HfSi<sub>2</sub>O<sub>7</sub> phase. A numerical comparison of the structures of the parakeldyshite and the Na<sub>2</sub>HfSi<sub>2</sub>O<sub>7</sub> phase

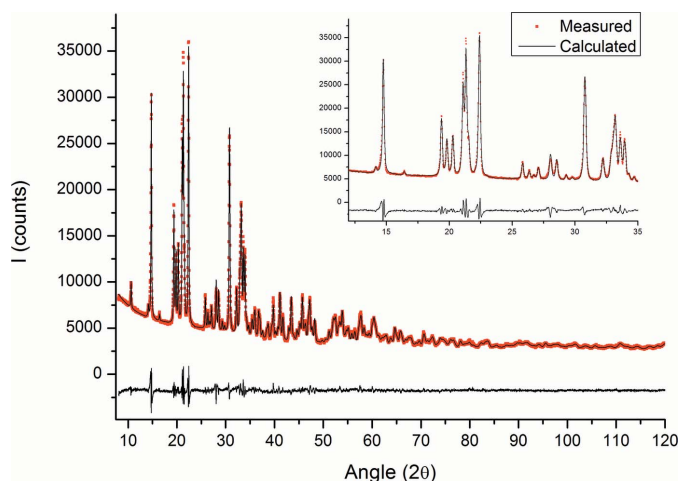

**Figure 1**

Polyhedral representation of the Na<sub>2</sub>HfSi<sub>2</sub>O<sub>7</sub> phase with SiO<sub>4</sub> units (blue), HfO<sub>6</sub> 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  $\Delta$  (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 Na<sub>2</sub>USi<sub>2</sub>O<sub>7</sub> phase can also be supposed.

### 3. Database survey

The crystal chemistry of zirconosilicates can be described in terms of an *MT* framework with MO<sub>6</sub> octahedra and TO<sub>4</sub> 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 (Na<sub>2</sub>ZrSi<sub>2</sub>O<sub>7</sub>) to monoclinic (Na<sub>2</sub>ZrSi<sub>4</sub>O<sub>11</sub>) or trigonal (Na<sub>8</sub>ZrSi<sub>6</sub>O<sub>18</sub>). If we focus on the chemistry of zirconosilicates with Si<sub>2</sub>O<sub>7</sub> diortho groups and their analogs (Pekov *et al.*, 2007), the triclinic phase is privileged such as the parakeldyshite Na<sub>2</sub>ZrSi<sub>2</sub>O<sub>7</sub> phase (Ferreira *et al.*, 2001) or the keldyshite (Na,H)<sub>2</sub>ZrSi<sub>2</sub>O<sub>7</sub> phase (Khalilov *et al.*, 1978). The potassium analogue, however, is monoclinic as in the case of khibinskite K<sub>2</sub>ZrSi<sub>2</sub>O<sub>7</sub> (Chernov *et al.*, 1970; Nosyrev *et al.*, 1976).



**Figure 2**  
Comparison of observed (red squares) and calculated (solid line) intensities for  $\text{Na}_2\text{HfSi}_2\text{O}_7$ . The difference pattern appears below. Inset: focus on the  $12\text{--}35^\circ$   $2\theta$  range.

#### 4. Synthesis and crystallization

The synthesis of sodium hafnium disilicate was based on the two-step synthesis protocol of parakelyshite  $\text{Na}_2\text{ZrSi}_2\text{O}_7$  (Lin *et al.*, 1999; Ferreira *et al.*, 2001). The first step was the synthesis of the Hf-petarasite phase  $\text{Na}_5\text{Zr}_2\text{Si}_6\text{O}_{18}(\text{Cl}\cdot\text{OH})_2\cdot\text{H}_2\text{O}$  with zirconium totally substituted by hafnium. Adequate quantities of sodium silicate solution (27%  $\text{SiO}_2$ , 8%  $\text{Na}_2\text{O}$ ), 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  $\text{Na}_{1.7\pm 0.2}\text{Hf}_{1.0}\text{Si}_{2.3\pm 0.1}\text{O}_{7.3\pm 0.9}$  as compared to the theoretical stoichiometry of  $\text{Na}_2\text{HfSi}_2\text{O}_7$ . 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  $\text{Na}_2\text{HfSi}_2\text{O}_7$  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  $\text{Na}_2\text{HfSi}_2\text{O}_7$  are shown in Fig. 2 along with the

**Table 2**  
Experimental details.

Crystal data	$\text{Na}_2\text{HfSi}_2\text{O}_7$
Chemical formula	392.6
$M_r$	Triclinic, $P\bar{1}$
Crystal system, space group	293
Temperature (K)	6.6123 (2), 8.7948 (3), 5.41074 (15)
$a, b, c$ (Å)	92.603 (2), 94.0843 (18),
$\alpha, \beta, \gamma$ (°)	71.3262 (18)
$V$ (Å <sup>3</sup> )	297.25 (2)
$Z$	2
Radiation type	Cu $K\alpha_1$ , $\lambda = 1.540562, 1.544390$ Å
Specimen shape, size (mm)	Flat sheet, $25 \times 25$
Data collection	Panalytical XPert MPD Pro
Diffractometer	Packed powder pellet
Specimen mounting	Reflection
Data collection mode	Step
Scan method	$2\theta_{\min} = 8.013$ $2\theta_{\max} = 120.013$ $2\theta_{\text{step}} = 0.017$
$2\theta$ values (°)	
Refinement	
$R$ factors and goodness of fit	$R_p = 0.024, R_{\text{wp}} = 0.032,$ $R_{\text{exp}} = 0.015, R(F) = 0.024,$ $\chi^2 = 4.973$
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  $2.4 \text{ e } \text{Å}^{-3}$ , which is less than 10% of the electron density of a Hf atom. The occupancies of all atoms were fixed to unity.

#### Acknowledgements

NM would like to thank Professor Philippe Deniard (Institut des Matériaux de Nantes) for his continuous support of the Rietveld refinements. The authors gratefully acknowledge AREVA and ANDRA for their financial support of this work.

#### References

- Bergerhoff, G., Berndt, M., Brandenburg, K. & Degen, T. (1999). *Acta Cryst.* **B55**, 147–156.
- Chernov, A. N., Maksimov, B. A., Ilyukhin, V. V. & Belov, N. V. (1970). *Dokl. Akad. Nauk SSSR*, **193**, 1293–1296.
- Ferreira, P., Ferreira, A., Rocha, J. & Soares, M. R. (2001). *Chem. Mater.* **13**, 355–363.
- Fleischer, M., Chao, G. Y. & Mandarino, J. A. (1979). *Am. Mineral.* **64**, 652–659.
- Flor, G. de la, Orobengoa, D., Tasci, E., Perez-Mato, J. M. & Aroyo, M. I. (2016). *J. Appl. Cryst.* **49**, 653–664.
- Ilyushin, G. D. & Blatov, V. A. (2002). *Acta Cryst.* **B58**, 198–218.
- Khalilov, A. D., Khomyakov, A. P. & Makhmudov, S. A. (1978). *Dokl. Akad. Nauk SSSR*, **238**, 573–575.
- Kostov-Kytin, V., Fujiwara, K., Nakayama, N. & Nikolova, R. (2008). *Proc. Bulg. Geol. Soc.* pp. 13–14.

- Lin, Z., Rocha, J., Ferreira, P., Thursfield, A., Agger, J. R. & Anderson, M. W. (1999). *J. Phys. Chem. B*, **103**, 957–963.
- Momma, K. & Izumi, F. (2011). *J. Appl. Cryst.* **44**, 1272–1276.
- Nosyrev, N. A., Treushnikov, E. N. & Voronkov, A. A. (1976). *Dokl. Akad. Nauk SSSR*, **231**, 1351–1353.
- PANalytical (2011). *X'Pert Data Collector*. PANalytical BV, Almelo, The Netherlands.
- Pekov, I. V., Zubkova, N. V., Pushcharovsky, D. Yu., Kolitsch, U. & Tillmanns, E. (2007). *Crystallogr. Rep.* **52**, 1066–1071.
- Petříček, V., Dušek, M. & Palatinus, L. (2014). *Z. Kristallogr. Cryst. Mater.* **229**, 345–352.
- Plaisted, T., Hrma, P., Vienna, J. & Jiricka, A. (1999). *Proceedings of MRS* **608**, 13–14.
- Ramsey, W. G., Bibler, N. E. & Meaker, T. F. (1995). *WM Symposia, Waste Management*, **95**, 23828–23907.
- Voronkov, A. A., Shumyatskaya, N. G. & Pyatenko, Yu. A. (1970). *Zh. Strukt. Khim.* **11**, 932–933.
- Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.

## supporting information

*Acta Cryst.* (2016). E72, 1434-1437 [doi:10.1107/S2056989016014225]

Crystal structure of Na<sub>2</sub>HfSi<sub>2</sub>O<sub>7</sub> by Rietveld refinement

Nicolas Massoni and Pierrick Chevreux

## 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 <sub>2</sub> HfSi <sub>2</sub> O <sub>7</sub>	$Z = 2$
$M_r = 392.6$	$F(000) = 356$
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 ( $\text{\AA}^2$ )

	$x$	$y$	$z$	$U_{\text{iso}}^*/U_{\text{eq}}$
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 (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
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 <sup>vii</sup>	3.169 (13)
O1—Si1 <sup>i</sup>	1.568 (17)	Na1—Na2 <sup>v</sup>	3.363 (13)
O2—Si1	1.567 (18)	Na1—Hf1 <sup>viii</sup>	3.513 (12)
O2—Si2	1.660 (17)	Na1—Si1 <sup>ii</sup>	2.919 (12)
O3—Hf1	2.060 (13)	Na1—Si1	3.210 (13)
O3—Si1	1.644 (15)	Na1—Si1 <sup>vii</sup>	3.140 (11)
O4—Na1	2.450 (15)	Na1—Si2	3.132 (13)
O4—Si1 <sup>ii</sup>	1.622 (15)	Na2—Na2 <sup>v</sup>	3.590 (14)
O5—Na1 <sup>iii</sup>	2.323 (18)	Na2—Na2 <sup>ix</sup>	3.174 (13)
O5—Si2 <sup>iii</sup>	1.605 (16)	Na2—Hf1	3.556 (9)
O6—Hf1 <sup>iv</sup>	2.115 (13)	Na2—Hf1 <sup>iv</sup>	3.399 (10)
O6—Si2 <sup>iii</sup>	1.497 (16)	Na2—Hf1 <sup>v</sup>	3.590 (10)
O7—Na2 <sup>v</sup>	2.441 (18)	Na2—Si1	3.161 (10)
O7—Si2 <sup>v</sup>	1.625 (13)	Na2—Si2 <sup>v</sup>	3.052 (11)
Na1—Na1 <sup>vi</sup>	3.453 (14)		
Hf1—O1—Si1 <sup>i</sup>	161.7 (9)	Na2 <sup>ix</sup> —Na2—Si1	76.2 (3)
Si1—O2—Si2	136.8 (8)	Na2 <sup>ix</sup> —Na2—Si2 <sup>v</sup>	153.7 (4)
Hf1—O3—Si1	175.1 (10)	Hf1—Na2—Hf1 <sup>iv</sup>	102.1 (3)
Na1—O4—Si1 <sup>ii</sup>	89.2 (6)	Hf1—Na2—Hf1 <sup>v</sup>	119.7 (3)
Na1 <sup>iii</sup> —O5—Si2 <sup>iii</sup>	104.3 (9)	Hf1—Na2—Si1	66.6 (2)
Hf1 <sup>iv</sup> —O6—Si2 <sup>iii</sup>	153.3 (10)	Hf1—Na2—Si2 <sup>v</sup>	59.6 (2)
Na2 <sup>v</sup> —O7—Si2 <sup>v</sup>	134.4 (9)	Hf1 <sup>iv</sup> —Na2—Hf1 <sup>v</sup>	126.1 (3)
O4—Na1—O5 <sup>viii</sup>	97.2 (6)	Hf1 <sup>iv</sup> —Na2—Si1	62.6 (2)
O4—Na1—Na1 <sup>vi</sup>	91.7 (4)	Hf1 <sup>iv</sup> —Na2—Si2 <sup>v</sup>	134.1 (4)
O4—Na1—Na1 <sup>vii</sup>	152.6 (6)	Hf1 <sup>v</sup> —Na2—Si1	102.9 (3)
O4—Na1—Na2 <sup>v</sup>	51.1 (4)	Hf1 <sup>v</sup> —Na2—Si2 <sup>v</sup>	97.7 (3)
O4—Na1—Hf1 <sup>viii</sup>	109.2 (5)	Si1—Na2—Si2 <sup>v</sup>	125.7 (4)
O4—Na1—Si1 <sup>ii</sup>	33.8 (4)	O1—Hf1—O3	88.5 (5)
O4—Na1—Si1	95.1 (5)	O1—Hf1—O6 <sup>ii</sup>	91.8 (5)
O4—Na1—Si1 <sup>vii</sup>	143.7 (5)	O1—Hf1—Na1 <sup>iii</sup>	51.7 (4)
O4—Na1—Si2	103.7 (5)	O1—Hf1—Na2 <sup>ii</sup>	123.8 (4)



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



Na1 <sup>v</sup> —Na2—Hf1 <sup>v</sup>	64.7 (3)	O2—Si2—Na1	55.3 (5)
Na1 <sup>v</sup> —Na2—Si1	167.6 (4)	O2—Si2—Na2 <sup>v</sup>	103.7 (6)
Na1 <sup>v</sup> —Na2—Si2 <sup>v</sup>	58.2 (3)	O5 <sup>viii</sup> —Si2—O6 <sup>viii</sup>	116.1 (9)
Na2 <sup>v</sup> —Na2—Na2 <sup>ix</sup>	106.1 (3)	O5 <sup>viii</sup> —Si2—O7 <sup>v</sup>	109.8 (8)
Na2 <sup>v</sup> —Na2—Hf1	60.3 (2)	O5 <sup>viii</sup> —Si2—Na1	46.0 (6)
Na2 <sup>v</sup> —Na2—Hf1 <sup>iv</sup>	142.8 (3)	O5 <sup>viii</sup> —Si2—Na2 <sup>v</sup>	53.3 (5)
Na2 <sup>v</sup> —Na2—Hf1 <sup>v</sup>	59.4 (2)	O6 <sup>viii</sup> —Si2—O7 <sup>v</sup>	118.2 (8)
Na2 <sup>v</sup> —Na2—Si1	80.2 (3)	O6 <sup>viii</sup> —Si2—Na1	131.2 (6)
Na2 <sup>v</sup> —Na2—Si2 <sup>v</sup>	68.4 (3)	O6 <sup>viii</sup> —Si2—Na2 <sup>v</sup>	149.4 (8)
Na2 <sup>ix</sup> —Na2—Hf1	141.7 (3)	O7 <sup>v</sup> —Si2—Na1	110.3 (6)
Na2 <sup>ix</sup> —Na2—Hf1 <sup>iv</sup>	66.1 (3)	O7 <sup>v</sup> —Si2—Na2 <sup>v</sup>	57.1 (6)
Na2 <sup>ix</sup> —Na2—Hf1 <sup>v</sup>	60.0 (3)	Na1—Si2—Na2 <sup>v</sup>	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)  $-x+1, -y+1, -z+2$ .