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# Rietveld refinement of the crystal structures of $\text{Rb}_2\text{XSi}_5\text{O}_{12}$ ( $X = \text{Ni}, \text{Mn}$ )

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The synthetic leucite silicate framework mineral analogues  $\text{Rb}_2\text{XSi}_5\text{O}_{12}$  ( $X = \text{Ni}$  [dirubidium nickel(II) pentasilicate] and  $\text{Mn}$  [dirubidium manganese(II) pentasilicate]) have been prepared by high-temperature solid-state synthesis. The results of Rietveld refinements, using X-ray powder diffraction data collected using  $\text{Cu } K\alpha$  X-rays, show that the title compounds crystallize in the space group  $Pbca$  and adopt the cation-ordered structure of  $\text{Cs}_2\text{CdSi}_5\text{O}_{12}$  and other leucites. The structures consist of tetrahedral  $\text{SiO}_4$  and  $\text{XO}_4$  units sharing corners to form a partially substituted silicate framework. Extraframework  $\text{Rb}^+$  cations sit in channels in the framework. All atoms occupy the  $8c$  general position for this space group. In these refined structures, silicon and  $X$  atoms are ordered onto separate tetrahedrally coordinated sites (T-sites). However, the Ni displacement parameter and the Ni–O bond lengths suggest that for the  $X = \text{Ni}$  sample, there may actually be some T-site cation disorder.

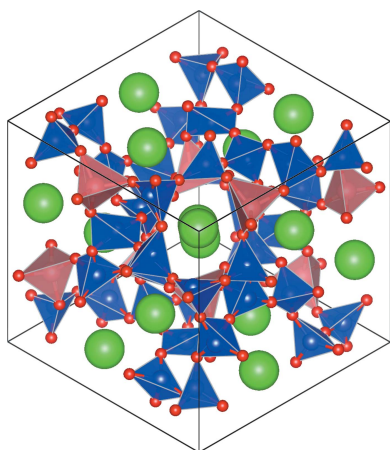
## 1. Chemical context

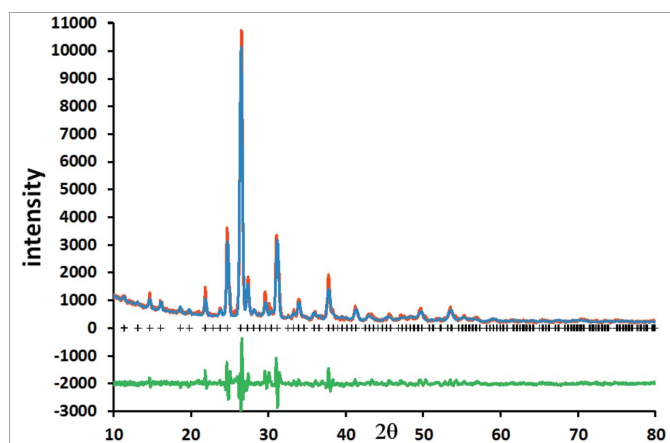
Synthetic analogues of the silicate framework minerals leucite  $\text{KAlSi}_2\text{O}_6$  (Mazzi *et al.*, 1976) and pollucite  $\text{CsAlSi}_2\text{O}_6$  (Dimitrijevic *et al.*, 1991) can be prepared with the general formulae  $\text{ABSi}_2\text{O}_6$  and  $\text{A}_2\text{CSi}_5\text{O}_{12}$ .  $A$  is an alkali metal cation (K, Rb, Cs),  $B$  is a trivalent cation (Al, B,  $\text{Fe}^{3+}$ ) and  $C$  is a divalent cation (Be, Mg, Mn,  $\text{Fe}^{2+}$ , Co, Ni, Cu, Zn, Cd). The title compounds are leucite analogues with  $A = \text{Rb}$  and  $C = \text{Ni}$  and  $\text{Mn}$ , these structures are in the space group  $Pbca$  and are isostructural with  $\text{Cs}_2\text{CdSi}_5\text{O}_{12}$  (Bell *et al.*, 1994b).

These leucite structures all have the same topology, a silicate framework structure with  $B$  or  $C$  cations partially substituting on the tetrahedrally coordinated silicon sites (T-sites).  $A$  cations sit in the extraframework channels, these extraframework cations can be removed by ion exchange which makes them of technological interest as a possible storage medium for radioactive Cs from nuclear waste (Gatta *et al.*, 2008).

## 2. Structural commentary

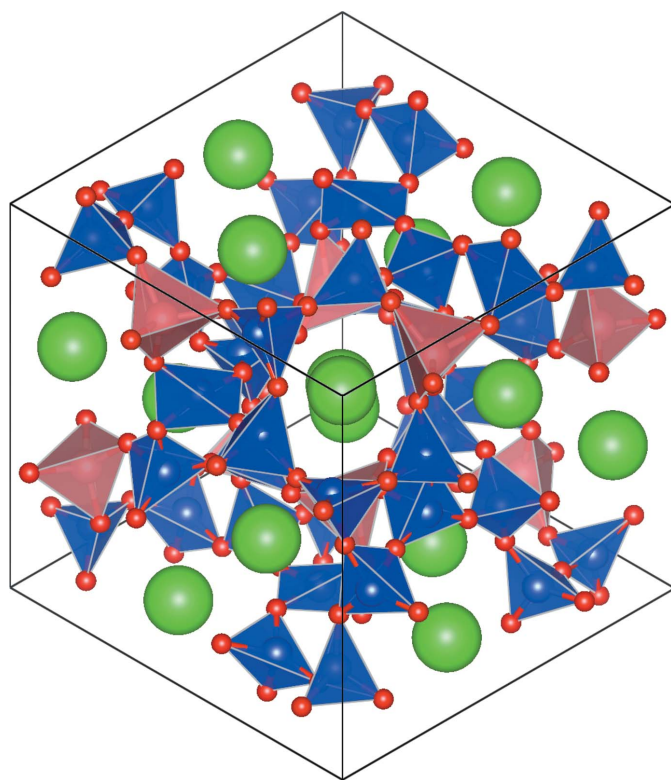
For the  $X = \text{Ni}$  refinement, the Ni site isotropic temperature factor was larger than expected [ $B_{\text{iso}} = 7.5$  (9)  $\text{\AA}^2$ ]. Also the mean Ni–O bond length for the  $\text{NiO}_4$  tetrahedron is 1.90 (2)  $\text{\AA}$ , shorter than that seen in tetrahedrally coordinated  $\text{NiO}_4$  units.  $\text{NiCr}_2\text{O}_4$  has the cubic spinel structure with Ni in tetrahedral coordination. A single-crystal structure refinement (Crottaz *et al.*, 1997) gives the Ni–O distance as 1.967 (3)  $\text{\AA}$ .



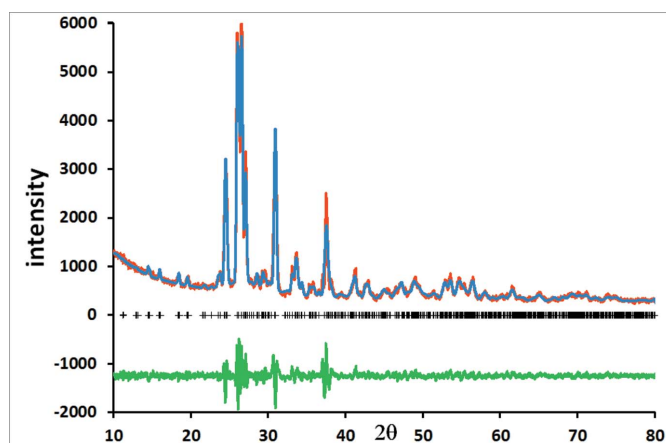


**Figure 1**  
Rietveld difference plot for the single-phase refinement of  $\text{Rb}_2\text{NiSi}_5\text{O}_{12}$ . The red, blue and green lines show, respectively, the observed, calculated and difference plots. Calculated Bragg reflection positions are indicated by crosses.

An EXAFS/XANES study (Farges *et al.*, 2001) gives the Ni–O distance as 1.96 (1) Å. The mean Si–O bond length for the  $\text{SiO}_4$  tetrahedra in the title structure is 1.643 (18) Å, which is slightly larger than the range of Si–O distances for silicates [1.59–1.63 Å; *International Tables for X-ray Crystallography* (1975, Vol. III, Table 4.1.1)]. These differences in the Ni–O and Si–O distances suggest some possible T-site cation



**Figure 2**  
The crystal structure of  $\text{Rb}_2\text{NiSi}_5\text{O}_{12}$ . Green spheres show Rb cations, blue polyhedra show  $\text{SiO}_4$  units, pink polyhedra show  $\text{NiO}_4$  units and red spheres represent O atoms.



**Figure 3**  
Rietveld difference plot for the single-phase refinement of  $\text{Rb}_2\text{MnSi}_5\text{O}_{12}$ . The red, blue and green lines show, respectively, the observed, calculated and difference plots. Calculated Bragg reflection positions are indicated by crosses.

disorder with some Si on the Ni site. A future higher quality neutron/synchrotron X-ray powder diffraction study may show if there really is Ni/Si T-site cation disorder.

Fig. 1 shows the Rietveld difference plot for  $\text{Rb}_2\text{NiSi}_5\text{O}_{12}$ . The crystal structure of  $\text{Rb}_2\text{NiSi}_5\text{O}_{12}$  is displayed in Fig. 2 and consists of a framework of corner-sharing tetrahedral  $\text{SiO}_4$  and  $\text{NiO}_4$  units, and  $\text{Rb}^+$  cations sitting in the extraframework channels.

For the  $X = \text{Mn}$  refinement, unlike in the  $X = \text{Ni}$  sample, the mean Mn–O distance is 2.02 (1) Å. This is in agreement with the mean Mn–O distance for  $\text{Cs}_2\text{MnSi}_5\text{O}_{12}$  (1.98 (3) Å; Bell & Henderson, 1996). This would suggest that this structure has complete T-site cation ordering. However, the isotropic temperature factors for the Mn site and the O sites could not be refined to chemically sensible positive values, so these were both fixed at  $B_{\text{iso}} = 0.1 \text{ \AA}^2$ . This refinement was done assuming that Mn was present as  $\text{Mn}^{2+}$  and that all sites were fully occupied. If some or all of the Mn atoms were present with a higher oxidation state, then this could account for the problem with refining these temperature factors. However, a higher quality neutron/synchrotron X-ray powder diffraction study may also be needed for a more precise determination of the state of Mn in this structure.

Fig. 3 shows the Rietveld difference plot for  $\text{Rb}_2\text{MnSi}_5\text{O}_{12}$ . The crystal structure of  $\text{Rb}_2\text{MnSi}_5\text{O}_{12}$  is displayed in Fig. 4 and consists of a framework of corner-sharing tetrahedral  $\text{SiO}_4$  and  $\text{MnO}_4$  units; Rb cations sit in the extraframework channels. Note how inclusion of the larger Mn cation in the silicate framework compared to Ni causes the central channel of the crystal structure to be slightly more distorted for  $\text{Rb}_2\text{MnSi}_5\text{O}_{12}$  (Fig. 4) compared to  $\text{Rb}_2\text{NiSi}_5\text{O}_{12}$  (Fig. 2).

### 3. Database survey

Many different leucite analogue crystal structures are known at ambient temperature. Table 1 gives compositions, space

**Table 1**  
Crystal structure parameters (Å°) for room-temperature leucite analogues.

Stoichiometry	SG	<i>a</i>	<i>b</i>	<i>c</i>	$\beta$	<i>V</i>
K <sub>2</sub> MgSi <sub>5</sub> O <sub>12</sub> <sup>a</sup>	<i>Ia</i> $\bar{3}d$	13.4190 (1)	13.4190 (1)	13.4190 (1)	90	2416.33 (5)
K <sub>2</sub> MgSi <sub>5</sub> O <sub>12</sub> <sup>a</sup>	<i>P2</i> <sub>1</sub> / <i>c</i>	13.168 (5)	13.652 (1)	13.072 (5)	91.69 (5)	2348 (2)
Cs <sub>2</sub> CdSi <sub>5</sub> O <sub>12</sub> <sup>b</sup>	<i>Pbca</i>	13.6714 (1)	13.8240 (1)	13.8939 (1)	90	2625.83 (6)
Cs <sub>2</sub> CuSi <sub>5</sub> O <sub>12</sub> <sup>c</sup>	<i>Pbca</i>	13.58943 (6)	13.57355 (5)	13.62296 (4)	90	2512.847 (13)
Cs <sub>2</sub> CuSi <sub>5</sub> O <sub>12</sub> <sup>c</sup>	<i>Ia</i> $\bar{3}d$	13.6322 (4)	13.6322 (4)	13.6322 (4)	90	2533.4 (2)
Cs <sub>2</sub> MgSi <sub>5</sub> O <sub>12</sub> <sup>d</sup>	<i>Pbca</i>	13.6371 (5)	13.6689 (5)	13.7280 (5)	90	2559.0 (2)
Rb <sub>2</sub> MgSi <sub>5</sub> O <sub>12</sub> <sup>d</sup>	<i>Pbca</i>	13.422 (1)	13.406 (1)	13.730 (1)	90	2470.6 (4)
Cs <sub>2</sub> ZnSi <sub>5</sub> O <sub>12</sub> <sup>d</sup>	<i>Pbca</i>	13.6415 (9)	13.6233 (8)	13.6653 (9)	90	2539.6 (3)
Rb <sub>2</sub> CdSi <sub>5</sub> O <sub>12</sub> <sup>e</sup>	<i>Pbca</i>	13.4121 (1)	13.6816 (1)	13.8558 (1)	90	2542.51 (5)
Cs <sub>2</sub> MnSi <sub>5</sub> O <sub>12</sub> <sup>e</sup>	<i>Pbca</i>	13.6878 (3)	13.7931 (3)	13.7575 (3)	90	2597.4 (2)
Cs <sub>2</sub> CoSi <sub>5</sub> O <sub>12</sub> <sup>e</sup>	<i>Pbca</i>	13.6487 (4)	13.7120 (4)	13.6828 (4)	90	2560.7 (2)
Cs <sub>2</sub> NiSi <sub>5</sub> O <sub>12</sub> <sup>e</sup>	<i>Pbca</i>	13.6147 (3)	13.6568 (5)	13.6583 (5)	90	2539.5 (1)
Rb <sub>2</sub> ZnSi <sub>5</sub> O <sub>12</sub> <sup>f</sup>	<i>Ia</i> $\bar{3}d$	13.4972 (1)	13.4972 (1)	13.4972 (1)	90	2458.86 (3)
KFeSi <sub>5</sub> O <sub>6</sub> <sup>g</sup>	<i>I4</i> <sub>1</sub> / <i>a</i>	13.2207 (3)	13.2207 (3)	13.9464 (3)	90	2437.6 (2)
RbFeSi <sub>5</sub> O <sub>6</sub> <sup>g</sup>	<i>I4</i> <sub>1</sub> / <i>a</i>	13.4586 (1)	13.4586 (1)	13.9380 (1)	90	2524.63 (5)
CsFeSi <sub>5</sub> O <sub>6</sub> <sup>g</sup>	<i>Ia</i> $\bar{3}d$	13.8542 (1)	13.8542 (1)	13.8542 (1)	90	2653.98 (3)
CsBSi <sub>5</sub> O <sub>6</sub> <sup>h</sup>	<i>I4</i> <sub>1</sub> / <i>a</i>	13.019 (2)	13.019 (2)	12.899 (3)	90	2186 (1)
CsAlSi <sub>5</sub> O <sub>6</sub> <sup>i</sup>	<i>Ia</i> $\bar{3}d$	13.647 (3)	13.647 (3)	13.647 (3)	90	2541.6 (6)
KAlSi <sub>5</sub> O <sub>6</sub> <sup>j</sup>	<i>I4</i> <sub>1</sub> / <i>a</i>	13.09 (1)	13.09 (1)	13.75 (1)	90	2356 (5)
Cs <sub>0.814</sub> B <sub>1.092</sub> Si <sub>1.977</sub> O <sub>6</sub> <sup>k</sup>	<i>Ia</i> - <i>3d</i>	13.009 (8)	13.009 (8)	13.009 (8)	90	2202 (1)
Rb <sub>2</sub> MgSi <sub>5</sub> O <sub>12</sub> <sup>l</sup>	<i>Ia</i> $\bar{3}d$	13.530 (1)	13.530 (1)	13.530 (1)	90	2476.8 (2)
Cs <sub>2</sub> BeSi <sub>5</sub> O <sub>12</sub> <sup>m</sup>	<i>Ia</i> $\bar{3}d$	13.406 (1)	13.406 (1)	13.406 (1)	90	2409.3 (2)

Notes: SG = space group; all  $\alpha$  and  $\gamma$  angles = 90°; (a) Bell *et al.* (1994a); (b) Bell *et al.* (1994b); (c) Bell *et al.* (2010); (d) Bell & Henderson (2009); (e) Bell & Henderson (1996); (f) Bell & Henderson (1994a); (g) Bell & Henderson (1994b); (h) Agakhanov *et al.* (2012); (i) Dimitrijevic *et al.* (1991); (j) Mazzi *et al.* (1976); (k) Bubnova *et al.* (2004); (l) Torres-Martinez & West (1986); (m) Torres-Martinez *et al.* (1984).

groups, lattice parameters, and references for some known ambient temperature leucite crystal structures. In addition, a high-temperature structure for Cs<sub>2</sub>ZnSi<sub>5</sub>O<sub>12</sub> in the space

group *Pa* $\bar{3}$  has been reported above 566 K (Bell & Henderson, 2012).

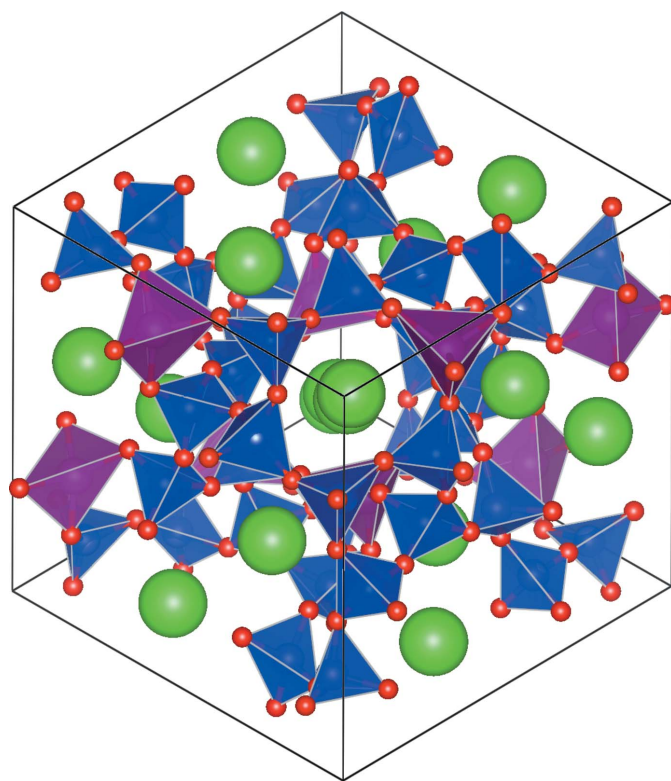
#### 4. Synthesis and crystallization

The samples were made from stoichiometric mixtures of Rb<sub>2</sub>CO<sub>3</sub>, SiO<sub>2</sub> and NiO (*X* = Ni) or MnO (*X* = Mn). These mixtures were ground together and then heated overnight at 873 K to decompose the carbonates, then melted in platinum crucibles at 1573 K for 1.5 h (*X* = Ni) or 1673 K for 2 h (*X* = Mn) before quenching to form glasses. The glasses were dry-crystallized at ambient pressure and 1193 K for 12 d.

#### 5. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. For each sample, a small amount of powder was ground and mounted on a low-background silicon wafer with a drop of acetone. These were mounted in flat-plate mode on a PANalytical X'Pert Pro MPD diffractometer. X-ray powder diffraction data were collected at 293 K using CuK $\alpha$  X-rays over the range 10–80°/2 $\theta$  using a PANalytical X'Celerator area detector. The powder diffraction data collection time for each sample was 8 h 20 min.

All Bragg reflections in both of the powder diffraction patterns could be indexed in the space group *Pbca* with similar lattice parameters to that for the Cs<sub>2</sub>CdSi<sub>5</sub>O<sub>12</sub> leucite (Bell *et al.*, 1994a). The crystal structures (Bell & Henderson, 1996) of Cs<sub>2</sub>NiSi<sub>5</sub>O<sub>12</sub> (*X* = Ni) and Cs<sub>2</sub>MnSi<sub>5</sub>O<sub>12</sub> (*X* = Mn) were respectively used as starting models for Rietveld (1969) refinements. In both cases, Rb<sup>+</sup> replaced Cs<sup>+</sup> as the extra-framework cation. Isotropic atomic displacement parameters



**Figure 4**  
The crystal structure of Rb<sub>2</sub>MnSi<sub>5</sub>O<sub>12</sub>. Green spheres show Rb cations, blue polyhedra show SiO<sub>4</sub> units, purple polyhedra show MnO<sub>4</sub> units and red spheres represent O atoms.

**Table 2**  
Experimental details.

	Rb <sub>2</sub> NiSi <sub>5</sub> O <sub>12</sub>	Rb <sub>2</sub> MnSi <sub>5</sub> O <sub>12</sub>
Crystal data		
Chemical formula	Rb <sub>2</sub> NiSi <sub>5</sub> O <sub>12</sub>	Rb <sub>2</sub> MnSi <sub>5</sub> O <sub>12</sub>
$M_r$	562.06	557.92
Crystal system, space group	Orthorhombic, <i>Pbca</i>	Orthorhombic, <i>Pbca</i>
Temperature (K)	293	293
$a, b, c$ (Å)	13.469 (3), 13.480 (3), 13.442 (2)	13.4085 (10), 13.6979 (11), 13.5761 (10)
$V$ (Å <sup>3</sup> )	2440.7 (8)	2493.5 (3)
$Z$	8	8
Radiation type	Cu $K\alpha$ , $\lambda = 1.540560$ Å	Cu $K\alpha$ , $\lambda = 1.540560$ Å
Specimen shape, size (mm)	Irregular, 10 × 10	Irregular, 10 × 10
Data collection		
Diffractometer	PANalytical X'Pert Pro MPD	PANalytical X'Pert Pro MPD
Specimen mounting	Flat plate	Flat plate
Data collection mode	Reflection	Reflection
Scan method	Step	Step
$2\theta$ values (°)	$2\theta_{\min} = 9.897$ $2\theta_{\max} = 79.883$ $2\theta_{\text{step}} = 0.017$	$2\theta_{\min} = 10.139$ $2\theta_{\max} = 80.125$ $2\theta_{\text{step}} = 0.017$
Refinement		
$R$ factors and goodness of fit	$R_p = 9.048$ , $R_{\text{wp}} = 12.007$ , $R_{\text{exp}} = 4.263$ , $R_{\text{Bragg}} = 10.421$ , $\chi^2 = 7.935$	$R_p = 6.527$ , $R_{\text{wp}} = 8.847$ , $R_{\text{exp}} = 3.909$ , $R_{\text{Bragg}} = 5.989$ , $\chi^2 = 5.121$
No. of parameters	73	71
No. of restraints	24	24

Computer programs: *X'Pert Data Collector* (PANalytical, 2006), *FULLPROF* (Rodríguez-Carvajal, 1993), *VESTA* (Momma & Izumi, 2008) and *pubCIF* (Westrip, 2010).

were used for all atoms in these phases. In both refinements, the isotropic atomic displacement parameters were constrained to be the same for all sites occupied by the same element, each Rb site had the same displacement parameter as did each Si site and each O site. Soft constraints were used for both refinements, in both cases the Si–O distances were constrained to be  $1.61 \pm 0.02$  Å. For  $X = \text{Ni}$ , the Ni–O distances were constrained to be  $1.88 \pm 0.02$  Å, the mean Ni–O distance for Cs<sub>2</sub>NiSi<sub>5</sub>O<sub>12</sub>. For  $X = \text{Mn}$ , the Mn–O distances were constrained to be  $1.98 \pm 0.02$  Å, the mean Mn–O distance for Cs<sub>2</sub>MnSi<sub>5</sub>O<sub>12</sub>. In both cases, Si and  $X$  atoms were ordered onto separate tetrahedrally coordinated sites, both refined structures are similar.

## References

- Agakhanov, A. A., Pautov, L. A., Karpenko, V. Y., Sokolova, E. & Hawthorne, F. C. (2012). *Can. Mineral.* **50**, 523–529.
- Bell, A. M. T. & Henderson, C. M. B. (1994a). *Acta Cryst.* **C50**, 984–986.
- Bell, A. M. T. & Henderson, C. M. B. (1994b). *Acta Cryst.* **C50**, 1531–1536.
- Bell, A. M. T. & Henderson, C. M. B. (1996). *Acta Cryst.* **C52**, 2132–2139.
- Bell, A. M. T. & Henderson, C. M. B. (2009). *Acta Cryst.* **B65**, 435–444.
- Bell, A. M. T. & Henderson, C. M. B. (2012). *Mineral. Mag.* **76**, 1257–1280.
- Bell, A. M. T., Henderson, C. M. B., Redfern, S. A. T., Cernik, R. J., Champness, P. E., Fitch, A. N. & Kohn, S. C. (1994a). *Acta Cryst.* **B50**, 31–41.
- Bell, A. M. T., Knight, K. S., Henderson, C. M. B. & Fitch, A. N. (2010). *Acta Cryst.* **B66**, 51–59.
- Bell, A. M. T., Redfern, S. A. T., Henderson, C. M. B. & Kohn, S. C. (1994b). *Acta Cryst.* **B50**, 560–566.
- Bubnova, R. S., Stepanov, N. K., Levin, A. A., Filatov, S. K., Paufler, P. & Meyer, D. C. (2004). *Solid State Sci.* **6**, 629–637.
- Crottaz, O., Kubel, F. & Schmid, H. (1997). *J. Mater. Chem.* **7**, 143–146.
- Dimitrijevic, R., Dondur, V. & Petranovic, N. (1991). *J. Solid State Chem.* **95**, 335–345.
- Farges, F., Brown, G. E., Petit, P.-E. & Munoz, M. (2001). *Geochim. Cosmochim. Acta.* **65**, 1665–1678.
- Gatta, G. D., Rotiroti, N., Fisch, M., Kadiyski, M. & Armbruster, T. (2008). *Phys. Chem. Miner.* **35**, 521–533.
- Mazzi, F., Galli, E. & Gottardi, G. (1976). *Am. Mineral.* **61**, 108–115.
- Momma, K. & Izumi, F. (2008). *J. Appl. Cryst.* **41**, 653–658.
- PANalytical (2006). *X'Pert Data Collector*. PANalytical, Almelo, The Netherlands.
- Rietveld, H. M. (1969). *J. Appl. Cryst.* **2**, 65–71.
- Rodríguez-Carvajal, J. (1993). *Phys. B: Condens. Matter.* **192**, 55–69.
- Torres-Martinez, L. M., Gard, J. A., Howie, R. A. & West, A. R. (1984). *J. Solid State Chem.* **51**, 100–103.
- Torres-Martinez, L. M. & West, A. R. (1986). *Z. Kristallogr.* **175**, 1–7.
- Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.

## supporting information

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Rietveld refinement of the crystal structures of  $\text{Rb}_2\text{XSi}_5\text{O}_{12}$  ( $\text{X} = \text{Ni}, \text{Mn}$ )

Anthony M. T. Bell and C. Michael B. Henderson

## Computing details

For both compounds, data collection: *X'Pert Data Collector* (PANalytical, 2006). Program(s) used to refine structure: *FULLPROF* (Rodríguez-Carvajal, 1993) for  $\text{Rb}_2\text{NiSi}_5\text{O}_{12}$ ; *FULLPROF* (Rodríguez-Carvajal, 2001) for  $\text{Rb}_2\text{MnSi}_5\text{O}_{12}$ . For both compounds, molecular graphics: *VESTA* (Momma & Izumi, 2008); software used to prepare material for publication: *pubCIF* (Westrip, 2010).

(Rb<sub>2</sub>NiSi<sub>5</sub>O<sub>12</sub>) Dirubidium nickel(II) pentasilicate

## Crystal data

$\text{Rb}_2\text{NiSi}_5\text{O}_{12}$	$Z = 8$
$M_r = 562.06$	$D_x = 3.059 (1) \text{ Mg m}^{-3}$
Orthorhombic, <i>Pbca</i>	Cu <i>K</i> $\alpha$ radiation, $\lambda = 1.540560 \text{ \AA}$
Hall symbol: -P 2ac 2ab	$T = 293 \text{ K}$
$a = 13.469 (3) \text{ \AA}$	purple-blue
$b = 13.480 (3) \text{ \AA}$	irregular, $10 \times 10 \text{ mm}$
$c = 13.442 (2) \text{ \AA}$	Specimen preparation: Prepared at 1193 K and
$V = 2440.7 (8) \text{ \AA}^3$	100 kPa

## Data collection

PANalytical X'Pert Pro MPD diffractometer	Data collection mode: reflection
Radiation source: X-ray tube	Scan method: step
Specimen mounting: flat plate	$2\theta_{\min} = 9.897^\circ$ , $2\theta_{\max} = 79.883^\circ$ , $2\theta_{\text{step}} = 0.017^\circ$

## Refinement

$R_p = 9.048$	Profile function: T-C-H Pseudo-Voigt
$R_{\text{wp}} = 12.007$	73 parameters
$R_{\text{exp}} = 4.263$	24 restraints
$R_{\text{Bragg}} = 10.421$	Background function: cubic splines
$\chi^2 = 7.935$	interpolation
4189 data points	

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Rb1	0.1367 (17)	0.1209 (19)	0.134 (2)	0.128 (4)*
Rb2	0.4100 (17)	0.3755 (18)	0.4037 (19)	0.128 (4)*
Ni1	0.3641 (11)	0.8370 (10)	0.9075 (10)	0.095 (12)*
Si2	0.1383 (12)	0.6631 (11)	0.6170 (13)	0.082 (6)*
Si3	0.5913 (12)	0.1289 (16)	0.6577 (12)	0.082 (6)*

Si4	0.6419 (14)	0.5703 (13)	0.1057 (11)	0.082 (6)*
Si5	0.9207 (11)	0.3702 (12)	0.8320 (14)	0.082 (6)*
Si6	0.8342 (11)	0.9051 (13)	0.3647 (13)	0.082 (6)*
O1	0.4680 (13)	0.383 (4)	0.155 (5)	0.017 (3)*
O2	0.143 (5)	0.4529 (14)	0.415 (3)	0.017 (3)*
O3	0.378 (5)	0.130 (5)	0.499 (2)	0.017 (3)*
O4	0.7369 (14)	0.436 (3)	0.618 (6)	0.017 (3)*
O5	0.658 (2)	0.7205 (19)	0.353 (6)	0.017 (3)*
O6	0.416 (3)	0.628 (6)	0.7182 (13)	0.017 (3)*
O7	0.9625 (14)	0.861 (6)	0.691 (2)	0.017 (3)*
O8	0.633 (5)	0.977 (2)	0.860 (6)	0.017 (3)*
O9	0.903 (2)	0.633 (6)	0.961 (2)	0.017 (3)*
O10	0.2157 (13)	0.928 (2)	0.146 (5)	0.017 (3)*
O11	0.169 (3)	0.2028 (17)	0.898 (5)	0.017 (3)*
O12	0.881 (5)	0.096 (5)	0.223 (2)	0.017 (3)*

*Geometric parameters (Å, °)*

Rb1—O1 <sup>i</sup>	3.51 (6)	Rb2—O11 <sup>ii</sup>	3.41 (5)
Rb1—O2 <sup>ii</sup>	3.11 (5)	Rb2—O12 <sup>iv</sup>	4.15 (7)
Rb1—O3 <sup>iii</sup>	3.84 (7)	Ni1—O4 <sup>xvii</sup>	1.93 (4)
Rb1—O3 <sup>iv</sup>	3.92 (7)	Ni1—O7 <sup>xvi</sup>	1.90 (3)
Rb1—O4 <sup>v</sup>	3.68 (8)	Ni1—O9 <sup>xviii</sup>	1.89 (3)
Rb1—O5 <sup>vi</sup>	3.08 (4)	Ni1—O11 <sup>xix</sup>	1.87 (3)
Rb1—O6 <sup>vii</sup>	3.64 (8)	Si2—O1 <sup>xx</sup>	1.64 (4)
Rb1—O7 <sup>viii</sup>	2.72 (4)	Si2—O3 <sup>xix</sup>	1.66 (4)
Rb1—O8 <sup>viii</sup>	3.37 (7)	Si2—O5 <sup>xii</sup>	1.64 (4)
Rb1—O9 <sup>viii</sup>	3.59 (8)	Si2—O10 <sup>xxi</sup>	1.66 (3)
Rb1—O10 <sup>ix</sup>	2.81 (4)	Si3—O1 <sup>xxii</sup>	1.67 (2)
Rb1—O11 <sup>x</sup>	3.39 (7)	Si3—O2 <sup>xxiii</sup>	1.63 (4)
Rb1—O12 <sup>xi</sup>	3.65 (7)	Si3—O6 <sup>xiii</sup>	1.67 (2)
Rb1—O12 <sup>iv</sup>	3.84 (6)	Si3—O11 <sup>xxiv</sup>	1.63 (5)
Rb2—O1	3.43 (7)	Si4—O2 <sup>xxv</sup>	1.61 (3)
Rb2—O2	3.75 (7)	Si4—O3 <sup>xxvi</sup>	1.64 (4)
Rb2—O3	3.58 (7)	Si4—O4 <sup>xv</sup>	1.64 (3)
Rb2—O4 <sup>viii</sup>	3.23 (4)	Si4—O12 <sup>xxvii</sup>	1.65 (4)
Rb2—O5 <sup>vi</sup>	4.14 (7)	Si5—O5 <sup>xxviii</sup>	1.64 (3)
Rb2—O5 <sup>viii</sup>	3.64 (8)	Si5—O7 <sup>xxix</sup>	1.61 (3)
Rb2—O6 <sup>viii</sup>	2.85 (4)	Si5—O8 <sup>xxx</sup>	1.65 (4)
Rb2—O7 <sup>xii</sup>	3.84 (8)	Si5—O12 <sup>xxii</sup>	1.62 (4)
Rb2—O8 <sup>xiii</sup>	3.51 (8)	Si6—O6 <sup>xxxi</sup>	1.64 (4)
Rb2—O8 <sup>xiv</sup>	3.65 (6)	Si6—O8 <sup>xxxii</sup>	1.65 (4)
Rb2—O9 <sup>xv</sup>	2.63 (4)	Si6—O9 <sup>xiv</sup>	1.67 (4)
Rb2—O9 <sup>xvi</sup>	3.92 (8)	Si6—O10 <sup>xxv</sup>	1.63 (2)
Rb2—O10 <sup>i</sup>	3.92 (7)		
O4 <sup>xvii</sup> —Ni1—O7 <sup>xvi</sup>	104 (3)	O5 <sup>xxviii</sup> —Si5—O7 <sup>xxix</sup>	127 (3)
O4 <sup>xvii</sup> —Ni1—O9 <sup>xviii</sup>	102 (4)	O5 <sup>xxviii</sup> —Si5—O8 <sup>xxx</sup>	109 (3)

O4 <sup>xvii</sup> —Ni1—O11 <sup>xix</sup>	119 (3)	O5 <sup>xxviii</sup> —Si5—O12 <sup>xxii</sup>	99 (5)
O7 <sup>xvi</sup> —Ni1—O9 <sup>xviii</sup>	115 (2)	O7 <sup>xxix</sup> —Si5—O8 <sup>xxx</sup>	123 (5)
O7 <sup>xvi</sup> —Ni1—O11 <sup>xix</sup>	106 (4)	O7 <sup>xxix</sup> —Si5—O12 <sup>xxii</sup>	99 (4)
O9 <sup>xviii</sup> —Ni1—O11 <sup>xix</sup>	110 (4)	O8 <sup>xxx</sup> —Si5—O12 <sup>xxii</sup>	80 (4)
O1 <sup>xx</sup> —Si2—O3 <sup>xix</sup>	95 (4)	O6 <sup>xxxi</sup> —Si6—O8 <sup>xxxii</sup>	93 (5)
O1 <sup>xx</sup> —Si2—O5 <sup>xii</sup>	115 (4)	O6 <sup>xxxi</sup> —Si6—O9 <sup>xiv</sup>	94 (3)
O1 <sup>xx</sup> —Si2—O10 <sup>xxi</sup>	101 (2)	O6 <sup>xxxi</sup> —Si6—O10 <sup>xxv</sup>	131 (4)
O3 <sup>xix</sup> —Si2—O5 <sup>xii</sup>	121 (5)	O8 <sup>xxxii</sup> —Si6—O9 <sup>xiv</sup>	100 (5)
O3 <sup>xix</sup> —Si2—O10 <sup>xxi</sup>	96 (4)	O8 <sup>xxxii</sup> —Si6—O10 <sup>xxv</sup>	94 (4)
O5 <sup>xii</sup> —Si2—O10 <sup>xxi</sup>	123 (3)	O9 <sup>xiv</sup> —Si6—O10 <sup>xxv</sup>	132 (4)
O1 <sup>xxii</sup> —Si3—O2 <sup>xxiii</sup>	110 (4)	Si2 <sup>vii</sup> —O1—Si3 <sup>ii</sup>	147 (2)
O1 <sup>xxii</sup> —Si3—O6 <sup>xiii</sup>	87 (3)	Si3 <sup>v</sup> —O2—Si4 <sup>iv</sup>	124 (2)
O1 <sup>xxii</sup> —Si3—O11 <sup>xxiv</sup>	134 (4)	Si2 <sup>i</sup> —O3—Si4 <sup>vi</sup>	158 (3)
O2 <sup>xxiii</sup> —Si3—O6 <sup>xiii</sup>	128 (4)	Ni1 <sup>xiii</sup> —O4—Si4 <sup>xxviii</sup>	130 (2)
O2 <sup>xxiii</sup> —Si3—O11 <sup>xxiv</sup>	82 (3)	Si2 <sup>xxxi</sup> —O5—Si5 <sup>xv</sup>	131 (2)
O6 <sup>xiii</sup> —Si3—O11 <sup>xxiv</sup>	120 (5)	Si3 <sup>xvii</sup> —O6—Si6 <sup>xii</sup>	129 (2)
O2 <sup>xxv</sup> —Si4—O3 <sup>xxvi</sup>	110 (4)	Ni1 <sup>xxiv</sup> —O7—Si5 <sup>xxxiii</sup>	124.2 (18)
O2 <sup>xxv</sup> —Si4—O4 <sup>xv</sup>	88 (3)	Si5 <sup>xxvii</sup> —O8—Si6 <sup>xxxiv</sup>	165 (3)
O2 <sup>xxv</sup> —Si4—O12 <sup>xxvii</sup>	112 (4)	Ni1 <sup>xxxv</sup> —O9—Si6 <sup>xxi</sup>	129 (2)
O3 <sup>xxvi</sup> —Si4—O4 <sup>xv</sup>	106 (5)	Si2 <sup>xiv</sup> —O10—Si6 <sup>iv</sup>	117.0 (19)
O3 <sup>xxvi</sup> —Si4—O12 <sup>xxvii</sup>	133 (3)	Ni1 <sup>i</sup> —O11—Si3 <sup>xvi</sup>	118 (2)
O4 <sup>xv</sup> —Si4—O12 <sup>xxvii</sup>	96 (4)	Si4 <sup>xxx</sup> —O12—Si5 <sup>ii</sup>	171 (3)

Symmetry codes: (i)  $-x+1/2, y-1/2, z$ ; (ii)  $x, -y+1/2, z-1/2$ ; (iii)  $-x+1/2, -y, z-1/2$ ; (iv)  $x-1/2, y, -z+1/2$ ; (v)  $x-1/2, -y+1/2, -z+1$ ; (vi)  $-x+1, y-1/2, -z+1/2$ ; (vii)  $-x+1/2, -y+1, z-1/2$ ; (viii)  $-x+1, -y+1, -z+1$ ; (ix)  $x, y-1, z$ ; (x)  $x, y, z-1$ ; (xi)  $x-1, y, z$ ; (xii)  $x-1/2, -y+3/2, -z+1$ ; (xiii)  $-x+1, y-1/2, -z+3/2$ ; (xiv)  $x, -y+3/2, z-1/2$ ; (xv)  $-x+3/2, -y+1, z-1/2$ ; (xvi)  $x-1/2, y, -z+3/2$ ; (xvii)  $-x+1, y+1/2, -z+3/2$ ; (xviii)  $x-1/2, -y+3/2, -z+2$ ; (xix)  $-x+1/2, y+1/2, z$ ; (xx)  $-x+1/2, -y+1, z+1/2$ ; (xxi)  $x, -y+3/2, z+1/2$ ; (xxii)  $x, -y+1/2, z+1/2$ ; (xxiii)  $x+1/2, -y+1/2, -z+1$ ; (xxiv)  $x+1/2, y, -z+3/2$ ; (xxv)  $x+1/2, y, -z+1/2$ ; (xxvi)  $-x+1, y+1/2, -z+1/2$ ; (xxvii)  $-x+3/2, y+1/2, z$ ; (xxviii)  $-x+3/2, -y+1, z+1/2$ ; (xxix)  $-x+2, y-1/2, -z+3/2$ ; (xxx)  $-x+3/2, y-1/2, z$ ; (xxxii)  $-x+3/2, -y+2, z-1/2$ ; (xxxiii)  $-x+2, y+1/2, -z+3/2$ ; (xxxiv)  $-x+3/2, -y+2, z+1/2$ ; (xxxv)  $x+1/2, -y+3/2, -z+2$ .

### (Rb<sub>2</sub>MnSi<sub>5</sub>O<sub>12</sub>) Dirubidium manganese(II) pentasilicate

#### Crystal data

Rb<sub>2</sub>MnSi<sub>5</sub>O<sub>12</sub>

$M_r = 557.92$

Orthorhombic, *Pbca*

Hall symbol: -P 2ac 2ab

$a = 13.4085$  (10) Å

$b = 13.6979$  (11) Å

$c = 13.5761$  (10) Å

$V = 2493.5$  (3) Å<sup>3</sup>

$Z = 8$

$D_x = 2.975$  (1) Mg m<sup>-3</sup>

Cu  $K\alpha$  radiation,  $\lambda = 1.540560$  Å

$T = 293$  K

pale brown-pink

irregular, 10 × 10 mm

Specimen preparation: Prepared at 1193 K and 100 kPa

#### Data collection

PANalytical X'Pert Pro MPD diffractometer

Radiation source: X-ray tube

Specimen mounting: flat plate

Data collection mode: reflection

Scan method: step

$2\theta_{\min} = 10.139^\circ$ ,  $2\theta_{\max} = 80.125^\circ$ ,  $2\theta_{\text{step}} = 0.017^\circ$

#### Refinement

$R_p = 6.527$

$R_{\text{wp}} = 8.847$

$R_{\text{exp}} = 3.909$

$R_{\text{Bragg}} = 5.989$

$\chi^2 = 5.121$

4189 data points

Profile function: T-C-H Pseudo-Voigt

71 parameters

24 restraints

Background function: cubic splines  
interpolation*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Rb1	0.1311 (8)	0.1348 (8)	0.1535 (6)	0.0544 (19)*
Rb2	0.3811 (10)	0.3968 (7)	0.3953 (7)	0.0544 (19)*
Mn1	0.3707 (9)	0.8342 (7)	0.9432 (6)	0.00127*
Si2	0.1328 (11)	0.6601 (10)	0.6011 (10)	0.024 (2)*
Si3	0.5921 (11)	0.1146 (10)	0.6255 (10)	0.024 (2)*
Si4	0.6449 (10)	0.5993 (11)	0.1054 (10)	0.024 (2)*
Si5	0.9006 (10)	0.3583 (11)	0.8208 (10)	0.024 (2)*
Si6	0.8312 (11)	0.9317 (10)	0.3329 (11)	0.024 (2)*
O1	0.4758 (12)	0.355 (3)	0.1607 (19)	0.00127*
O2	0.083 (2)	0.4973 (12)	0.399 (3)	0.00127*
O3	0.397 (2)	0.150 (3)	0.4890 (13)	0.00127*
O4	0.7328 (12)	0.4230 (19)	0.620 (2)	0.00127*
O5	0.659 (2)	0.7326 (14)	0.360 (2)	0.00127*
O6	0.363 (4)	0.632 (2)	0.7605 (17)	0.00127*
O7	0.9822 (15)	0.877 (3)	0.645 (2)	0.00127*
O8	0.659 (3)	0.9530 (13)	0.860 (3)	0.00127*
O9	0.893 (2)	0.635 (2)	0.9119 (13)	0.00127*
O10	0.2099 (14)	0.9281 (18)	0.135 (3)	0.00127*
O11	0.132 (3)	0.1885 (12)	0.9545 (17)	0.00127*
O12	0.892 (3)	0.139 (3)	0.2068 (12)	0.00127*

*Geometric parameters ( $\text{\AA}$ ,  $^\circ$ )*

Rb1—O1 <sup>i</sup>	4.09 (4)	Rb2—O10 <sup>i</sup>	3.76 (4)
Rb1—O2 <sup>ii</sup>	3.51 (3)	Rb2—O11 <sup>iii</sup>	3.63 (4)
Rb1—O2 <sup>iii</sup>	3.95 (4)	Rb2—O12 <sup>iv</sup>	3.80 (4)
Rb1—O3 <sup>iv</sup>	3.69 (3)	Mn1—O4 <sup>xvii</sup>	2.04 (2)
Rb1—O4 <sup>v</sup>	3.46 (3)	Mn1—O7 <sup>xvi</sup>	2.00 (3)
Rb1—O5 <sup>vi</sup>	3.12 (3)	Mn1—O9 <sup>xviii</sup>	2.03 (2)
Rb1—O6 <sup>vii</sup>	3.51 (3)	Mn1—O11 <sup>xix</sup>	2.002 (19)
Rb1—O7 <sup>viii</sup>	3.13 (3)	Si2—O1 <sup>xx</sup>	1.68 (2)
Rb1—O8 <sup>viii</sup>	3.07 (4)	Si2—O3 <sup>xix</sup>	1.58 (2)
Rb1—O9 <sup>viii</sup>	3.29 (3)	Si2—O5 <sup>xii</sup>	1.60 (2)
Rb1—O10 <sup>ix</sup>	3.03 (3)	Si2—O10 <sup>xxi</sup>	1.66 (3)
Rb1—O11 <sup>x</sup>	2.80 (2)	Si3—O1 <sup>xxii</sup>	1.68 (2)
Rb1—O12 <sup>xi</sup>	3.29 (4)	Si3—O2 <sup>xxiii</sup>	1.57 (2)
Rb1—O12 <sup>iv</sup>	3.98 (4)	Si3—O6 <sup>xiv</sup>	1.68 (3)
Rb2—O1	3.48 (3)	Si3—O11 <sup>xxiv</sup>	1.58 (3)
Rb2—O2	4.23 (3)	Si4—O2 <sup>xxv</sup>	1.63 (2)
Rb2—O3	3.62 (4)	Si4—O3 <sup>xxvi</sup>	1.56 (3)
Rb2—O4 <sup>viii</sup>	2.91 (3)	Si4—O4 <sup>xv</sup>	1.68 (2)
Rb2—O5 <sup>vi</sup>	4.17 (3)	Si4—O12 <sup>xxvii</sup>	1.56 (3)



Rb2—O5 <sup>viii</sup>	3.80 (3)	Si5—O5 <sup>xxviii</sup>	1.57 (3)
Rb2—O6 <sup>vii</sup>	3.77 (5)	Si5—O7 <sup>xxix</sup>	1.66 (3)
Rb2—O6 <sup>viii</sup>	4.05 (5)	Si5—O8 <sup>xiii</sup>	1.61 (3)
Rb2—O7 <sup>xii</sup>	3.43 (4)	Si5—O12 <sup>xxii</sup>	1.55 (2)
Rb2—O7 <sup>xiii</sup>	3.86 (3)	Si6—O6 <sup>xxx</sup>	1.60 (3)
Rb2—O8 <sup>xiv</sup>	3.45 (4)	Si6—O8 <sup>xxxi</sup>	1.63 (2)
Rb2—O9 <sup>xv</sup>	3.07 (3)	Si6—O9 <sup>xxxii</sup>	1.63 (3)
Rb2—O9 <sup>xvi</sup>	4.19 (3)	Si6—O10 <sup>xxv</sup>	1.68 (3)
O4 <sup>xvii</sup> —Mn1—O7 <sup>xvi</sup>	94.7 (15)	O5 <sup>xxviii</sup> —Si5—O7 <sup>xxix</sup>	121 (3)
O4 <sup>xvii</sup> —Mn1—O9 <sup>xviii</sup>	112.6 (18)	O5 <sup>xxviii</sup> —Si5—O8 <sup>xiii</sup>	106 (2)
O4 <sup>xvii</sup> —Mn1—O11 <sup>xix</sup>	128.0 (19)	O5 <sup>xxviii</sup> —Si5—O12 <sup>xxii</sup>	109 (3)
O7 <sup>xvi</sup> —Mn1—O9 <sup>xviii</sup>	114.1 (18)	O7 <sup>xxix</sup> —Si5—O8 <sup>xiii</sup>	105 (3)
O7 <sup>xvi</sup> —Mn1—O11 <sup>xix</sup>	111 (2)	O7 <sup>xxix</sup> —Si5—O12 <sup>xxii</sup>	110 (3)
O9 <sup>xviii</sup> —Mn1—O11 <sup>xix</sup>	97.8 (16)	O8 <sup>xiii</sup> —Si5—O12 <sup>xxii</sup>	106 (3)
O1 <sup>xx</sup> —Si2—O3 <sup>xix</sup>	104 (2)	O6 <sup>xxx</sup> —Si6—O8 <sup>xxxi</sup>	134 (3)
O1 <sup>xx</sup> —Si2—O5 <sup>xii</sup>	98 (2)	O6 <sup>xxx</sup> —Si6—O9 <sup>xxxii</sup>	94 (2)
O1 <sup>xx</sup> —Si2—O10 <sup>xxi</sup>	109 (2)	O6 <sup>xxx</sup> —Si6—O10 <sup>xxv</sup>	117 (3)
O3 <sup>xix</sup> —Si2—O5 <sup>xii</sup>	117 (3)	O8 <sup>xxxi</sup> —Si6—O9 <sup>xxxii</sup>	111 (2)
O3 <sup>xix</sup> —Si2—O10 <sup>xxi</sup>	111 (3)	O8 <sup>xxxi</sup> —Si6—O10 <sup>xxv</sup>	93 (2)
O5 <sup>xii</sup> —Si2—O10 <sup>xxi</sup>	116 (2)	O9 <sup>xxxii</sup> —Si6—O10 <sup>xxv</sup>	108 (2)
O1 <sup>xxii</sup> —Si3—O2 <sup>xxiii</sup>	103 (3)	Si2 <sup>vii</sup> —O1—Si3 <sup>iii</sup>	134.2 (18)
O1 <sup>xxii</sup> —Si3—O6 <sup>xiv</sup>	92 (3)	Si3 <sup>v</sup> —O2—Si4 <sup>iv</sup>	142.2 (18)
O1 <sup>xxii</sup> —Si3—O11 <sup>xxiv</sup>	111 (3)	Si2 <sup>i</sup> —O3—Si4 <sup>vi</sup>	137.6 (19)
O2 <sup>xxiii</sup> —Si3—O6 <sup>xiv</sup>	111 (3)	Mn1 <sup>xiv</sup> —O4—Si4 <sup>xxviii</sup>	120.5 (14)
O2 <sup>xxiii</sup> —Si3—O11 <sup>xxiv</sup>	120 (2)	Si2 <sup>xxx</sup> —O5—Si5 <sup>xv</sup>	136.4 (19)
O6 <sup>xiv</sup> —Si3—O11 <sup>xxiv</sup>	115 (2)	Si3 <sup>xvii</sup> —O6—Si6 <sup>xii</sup>	138 (2)
O2 <sup>xxv</sup> —Si4—O3 <sup>xxvi</sup>	100 (3)	Mn1 <sup>xxiv</sup> —O7—Si5 <sup>xxxiii</sup>	146.0 (16)
O2 <sup>xxv</sup> —Si4—O4 <sup>xv</sup>	110 (2)	Si5 <sup>xxvii</sup> —O8—Si6 <sup>xxxiv</sup>	138.2 (19)
O2 <sup>xxv</sup> —Si4—O12 <sup>xxvii</sup>	100 (3)	Mn1 <sup>xxxv</sup> —O9—Si6 <sup>xxi</sup>	132.5 (15)
O3 <sup>xxvi</sup> —Si4—O4 <sup>xv</sup>	122 (2)	Si2 <sup>xxxii</sup> —O10—Si6 <sup>iv</sup>	134.1 (18)
O3 <sup>xxvi</sup> —Si4—O12 <sup>xxvii</sup>	117 (2)	Mn1 <sup>i</sup> —O11—Si3 <sup>xvi</sup>	125.5 (15)
O4 <sup>xv</sup> —Si4—O12 <sup>xxvii</sup>	106 (3)	Si4 <sup>xiii</sup> —O12—Si5 <sup>iii</sup>	155.7 (19)

Symmetry codes: (i)  $-x+1/2, y-1/2, z$ ; (ii)  $-x, y-1/2, -z+1/2$ ; (iii)  $x, -y+1/2, z-1/2$ ; (iv)  $x-1/2, y, -z+1/2$ ; (v)  $x-1/2, -y+1/2, -z+1$ ; (vi)  $-x+1, y-1/2, -z+1/2$ ; (vii)  $-x+1/2, -y+1, z-1/2$ ; (viii)  $-x+1, -y+1, -z+1$ ; (ix)  $x, y-1, z$ ; (x)  $x, y, z-1$ ; (xi)  $x-1, y, z$ ; (xii)  $x-1/2, -y+3/2, -z+1$ ; (xiii)  $-x+3/2, y-1/2, z$ ; (xiv)  $-x+1, y-1/2, -z+3/2$ ; (xv)  $-x+3/2, -y+1, z-1/2$ ; (xvi)  $x-1/2, y, -z+3/2$ ; (xvii)  $-x+1, y+1/2, -z+3/2$ ; (xviii)  $x-1/2, -y+3/2, -z+2$ ; (xix)  $-x+1/2, y+1/2, z$ ; (xx)  $-x+1/2, -y+1, z+1/2$ ; (xxi)  $x, -y+3/2, z+1/2$ ; (xxii)  $x, -y+1/2, z+1/2$ ; (xxiii)  $x+1/2, -y+1/2, -z+1$ ; (xxiv)  $x+1/2, y, -z+3/2$ ; (xxv)  $x+1/2, y, -z+1/2$ ; (xxvi)  $-x+1, y+1/2, -z+1/2$ ; (xxvii)  $-x+3/2, y+1/2, z$ ; (xxviii)  $-x+3/2, -y+1, z+1/2$ ; (xxix)  $-x+2, y-1/2, -z+3/2$ ; (xxx)  $x+1/2, -y+3/2, -z+1$ ; (xxxi)  $-x+3/2, -y+2, z-1/2$ ; (xxxii)  $x, -y+3/2, z-1/2$ ; (xxxiii)  $-x+2, y+1/2, -z+3/2$ ; (xxxiv)  $-x+3/2, -y+2, z+1/2$ ; (xxxv)  $x+1/2, -y+3/2, -z+2$ .