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Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: BR1139). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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## Rietveld Refinement of the Orthorhombic *Pbca* Structures of Rb<sub>2</sub>CdSi<sub>5</sub>O<sub>12</sub>, Cs<sub>2</sub>MnSi<sub>5</sub>O<sub>12</sub>, Cs<sub>2</sub>CoSi<sub>5</sub>O<sub>12</sub> and Cs<sub>2</sub>NiSi<sub>5</sub>O<sub>12</sub> Leucites by Synchrotron X-ray Powder Diffraction

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### Abstract

Analysis of high-resolution synchrotron X-ray powder diffraction patterns for hydrothermally synthesized Rb<sub>2</sub>CdSi<sub>5</sub>O<sub>12</sub> and Cs<sub>2</sub>MnSi<sub>5</sub>O<sub>12</sub> leucite analogues, and dry-synthesized Cs<sub>2</sub>CoSi<sub>5</sub>O<sub>12</sub> and Cs<sub>2</sub>NiSi<sub>5</sub>O<sub>12</sub> leucite analogues showed that they have an orthorhombic *Pbca* structure. The structures have been refined by the Rietveld method, showing that the tetrahedrally coordinated atoms (Si, Cd, Mn, Co and Ni) are ordered on separate sites. The Cs<sub>2</sub>MnSi<sub>5</sub>O<sub>12</sub>, Cs<sub>2</sub>CoSi<sub>5</sub>O<sub>12</sub> and Cs<sub>2</sub>NiSi<sub>5</sub>O<sub>12</sub> leucite samples are unusual in containing SiO<sub>4</sub> tetrahedra which are more distorted, on average, than the larger MnO<sub>4</sub>, CoO<sub>4</sub> and NiO<sub>4</sub> tetrahedra. The JCPDS file numbers for Rb<sub>2</sub>CdSi<sub>5</sub>O<sub>12</sub>, Cs<sub>2</sub>MnSi<sub>5</sub>O<sub>12</sub> and Cs<sub>2</sub>CoSi<sub>5</sub>O<sub>12</sub> are 46-1491, 46-1492 and 46-1493, respectively.

### Comment

As part of a wider attempt to understand the controls and consequences of tetrahedral-site cation ordering in compounds with silicate framework structures, we are studying a series of synthetic leucite analogues with the stoichiometry X<sub>2</sub>ZSi<sub>5</sub>O<sub>12</sub> (X = K, Rb, Cs; Z = Mg, Mn, Fe<sup>2+</sup>, Co, Ni, Cu, Zn, Cd). The structures of these analogues are related to that of natural leucite (KAISi<sub>2</sub>O<sub>6</sub>). Many of these materials have framework-cation species that are more amenable to tetrahedral-site (*T*-site) analysis than Al/Si analogues and also display different *T*-site ordering arrangements depending on their conditions of synthesis and on their chemical compositions (Bell, Henderson, Redfern, Cernik, Champness, Fitch & Kohn, 1994; Bell & Henderson, 1994*a,b*; Bell, Redfern, Henderson & Kohn, 1994).

X-ray powder diffraction techniques and Rietveld analysis (Rietveld, 1969) have been used to determine the structures of these materials. <sup>29</sup>Si magic-

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angle spinning (MAS) NMR spectroscopy has also been used to characterize the number of distinct Si sites in a structure. Using these techniques, we have determined previously unknown monoclinic  $P2_1/c$  (Bell, Henderson, Redfern, Cernik, Champness, Fitch & Kohn, 1994) and orthorhombic  $Pbca$  (Bell, Redfern, Henderson & Kohn, 1994) structures which have the same basic topology as natural leucite; these low-symmetry leucites have fully ordered  $T$  sites. In this paper, we describe the structures of two hydrothermally synthesized leucites,  $Rb_2CdSi_5O_{12}$  and  $Cs_2MnSi_5O_{12}$ , and two dry-synthesized leucites,  $Cs_2CoSi_5O_{12}$  and  $Cs_2NiSi_5O_{12}$ . It is noteworthy that pairs of dry- and hydrothermally synthesized samples of the  $Cs_2MnSi_5O_{12}$ ,  $Cs_2CoSi_5O_{12}$  and  $Cs_2NiSi_5O_{12}$  leucites have essentially identical X-ray powder diffraction patterns.

Analysis of the powder diffraction patterns showed (from the systematic absences) that all of these materials have a  $Pbca$  structure consistent with the presence of ordered  $T$  sites. Therefore, the atomic coordinates of  $Pbca$   $Cs_2CdSi_5O_{12}$  (Bell, Redfern, Henderson & Kohn, 1994) were used as a starting model for Rietveld refinement. The structures were then refined using *MPROF* in the *Powder Diffraction Program Library* (PDPL; Murray, Cockcroft & Fitch, 1990). Figs. 1 to 4 show the observed, calculated and difference profiles which resulted for  $Rb_2CdSi_5O_{12}$ ,  $Cs_2MnSi_5O_{12}$ ,  $Cs_2CoSi_5O_{12}$  and  $Cs_2NiSi_5O_{12}$ . The good matches between the profiles indicate that the refined structures are reliable. During the refinement of the structure of  $Cs_2MnSi_5O_{12}$ , all of the atomic displacement parameters became negative, hence they were fixed at  $0.25 \text{ \AA}^2$ . During the refinement of the structure of  $Cs_2CoSi_5O_{12}$ , the atomic displacement parameters for the Co, Si and O atoms also became negative, so were fixed at  $0.10 \text{ \AA}^2$ .  $^{29}\text{Si}$  MAS NMR spectra (Kohn, Henderson & Dupree, 1994) of both  $Cs_2CdSi_5O_{12}$  and  $Rb_2CdSi_5O_{12}$  indicated

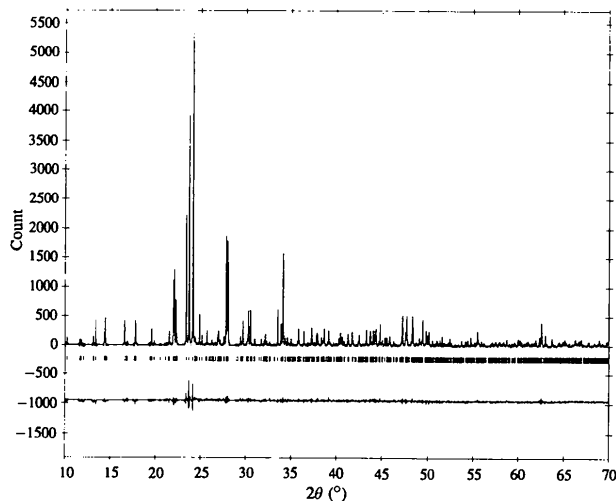


Fig. 1. Rietveld difference plot for hydrothermally synthesized  $Rb_2CdSi_5O_{12}$ .

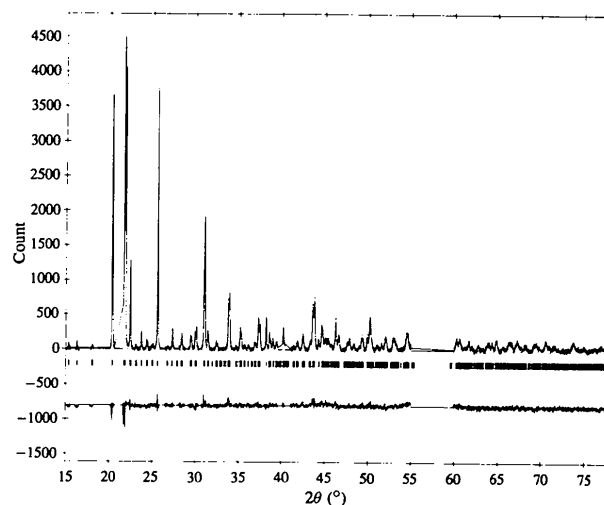


Fig. 2. Rietveld difference plot for hydrothermally synthesized  $Cs_2MnSi_5O_{12}$ .

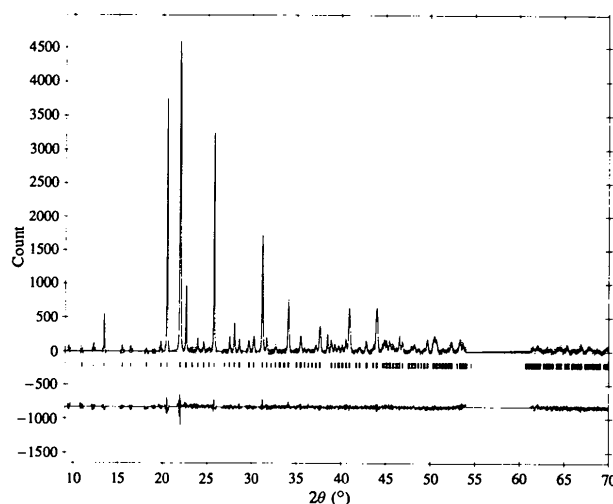


Fig. 3. Rietveld difference plot for dry-synthesized  $Cs_2CoSi_5O_{12}$ .

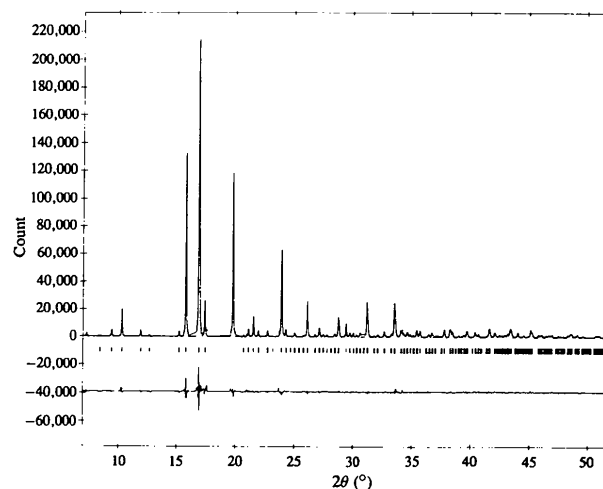


Fig. 4. Rietveld difference plot for dry-synthesized  $Cs_2NiSi_5O_{12}$ .

the presence of five chemically distinct Si sites; these assignments are in agreement with the *Pbca* structures.

All four of these compounds have structures similar to that of Cs<sub>2</sub>CdSi<sub>5</sub>O<sub>12</sub>. In Cs<sub>2</sub>CdSi<sub>5</sub>O<sub>12</sub>, the Si—O distances within the SiO<sub>4</sub> tetrahedra are in the range 1.51–1.67 Å [mean 1.59 (5) Å]. The corresponding distances in Rb<sub>2</sub>CdSi<sub>5</sub>O<sub>12</sub>, Cs<sub>2</sub>MnSi<sub>5</sub>O<sub>12</sub>, Cs<sub>2</sub>CoSi<sub>5</sub>O<sub>12</sub> and Cs<sub>2</sub>NiSi<sub>5</sub>O<sub>12</sub> are 1.56 (2)–1.66 (2) [mean 1.61 (3)], 1.59 (3)–1.71 (3) [mean 1.66 (4)], 1.61 (4)–1.67 (5) [mean 1.63 (2)] and 1.59 (4)–1.71 (4) Å [mean 1.62 (3) Å], respectively. These mean Si—O distances are within the range usually found in silicate framework structures after taking experimental error into account (1.59–1.63 Å; *International Tables for X-ray Crystallography*, 1985, Vol. III, Table 4.1.1).

In Cs<sub>2</sub>CdSi<sub>5</sub>O<sub>12</sub>, the tetrahedral Cd—O distances are in the range 2.21–2.27 Å, with comparable distances [2.20 (1)–2.25 (1) Å] in Rb<sub>2</sub>CdSi<sub>5</sub>O<sub>12</sub>. The tetrahedral Mn—O, Co—O and Ni—O distances for Cs<sub>2</sub>MnSi<sub>5</sub>O<sub>12</sub>, Cs<sub>2</sub>CoSi<sub>5</sub>O<sub>12</sub> and Cs<sub>2</sub>NiSi<sub>5</sub>O<sub>12</sub> are in the ranges 1.97 (2)–1.99 (3), 1.91 (3)–1.93 (4) and 1.87 (4)–1.89 (4) Å, respectively. Assuming a radius for oxygen of 1.40 Å, these distances yield four-coordinated radii for Cd, Mn, Co and Ni of 0.82, 0.58, 0.52 and 0.48 Å, respectively, compared with the literature values of 0.78, 0.66, 0.58 and 0.55 Å (Shannon, 1976).

The Cs and Rb extra-framework cations occupy large channels in the framework parallel to the [111] direction. By comparing the relatively more distorted environment of Rb in Rb<sub>2</sub>CdSi<sub>5</sub>O<sub>12</sub> (Fig. 5) to that of Cs in

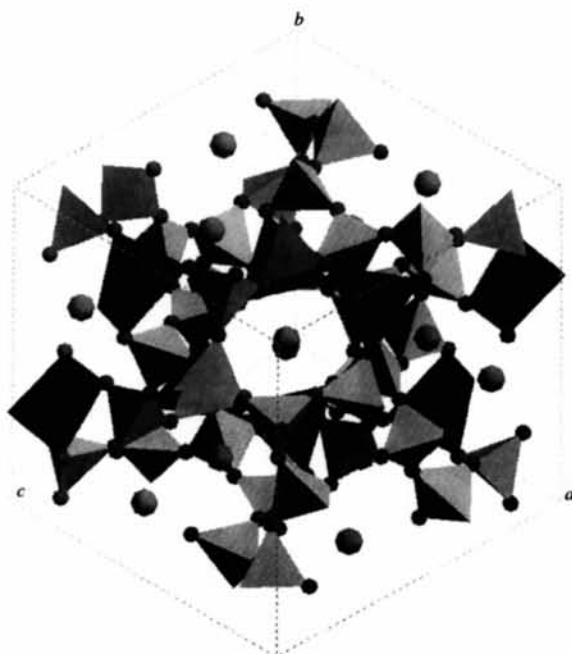


Fig. 5. Projection of the structure of Rb<sub>2</sub>CdSi<sub>5</sub>O<sub>12</sub> along [111]. Dark tetrahedra represent CdO<sub>4</sub> units, light tetrahedra represent SiO<sub>4</sub> units, large circles represent Rb<sup>+</sup> cations and small circles represent O<sup>2-</sup> anions.

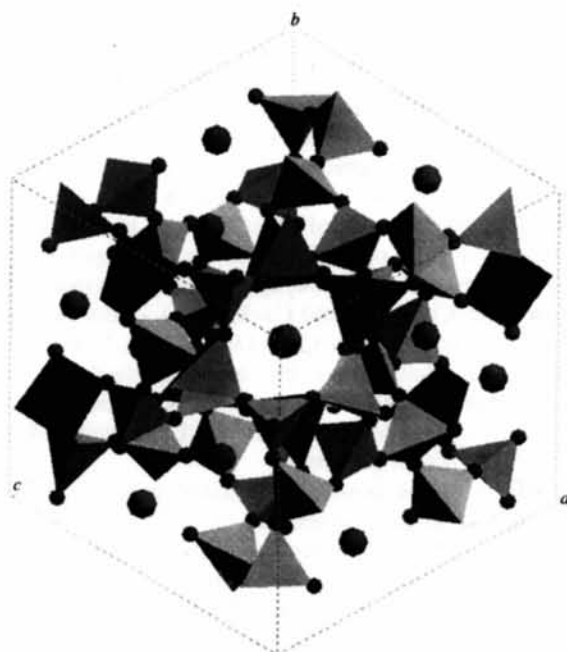


Fig. 6. Projection of the structure of Cs<sub>2</sub>MnSi<sub>5</sub>O<sub>12</sub> along [111]. Dark tetrahedra represent MnO<sub>4</sub> units, light tetrahedra represent SiO<sub>4</sub> units, large circles represent Cs<sup>+</sup> cations and small circles represent O<sup>2-</sup> anions.

Cs<sub>2</sub>MnSi<sub>5</sub>O<sub>12</sub> (Fig. 6), it can be seen that the shape of the channel around Cs is much closer to that of a regular hexagon than that around Rb. The structures of Cs<sub>2</sub>CoSi<sub>5</sub>O<sub>12</sub> and Cs<sub>2</sub>NiSi<sub>5</sub>O<sub>12</sub> are essentially the same as that of Cs<sub>2</sub>MnSi<sub>5</sub>O<sub>12</sub>.

It is interesting to analyse the structures of the *Pbca* leucite analogues in terms of different degrees of framework collapse (Taylor & Henderson, 1968), depending on the relative sizes of the framework cations and the cavity cations. We would expect larger degrees of collapse to be reflected in greater ratios between the largest and smallest cell edges (denoted  $\Delta$ ) (*i.e.* greater distortion from the cubic *Ia3d* pollucite structure), and smaller mean *T—O—T* angles. Thus, as expected for the cadmium analogues, the framework is more collapsed around the smaller Rb cation than around the larger Cs cation, as reflected in  $\Delta$  values of 1.033 and 1.016, respectively, and in the mean *T—O—T* angles of 135 (12) and 140 (13)°, respectively. Bell, Redfern, Henderson & Kohn (1994) pointed out that the *O—T—O* angle variances show that the divalent-cation tetrahedra in K<sub>2</sub>MgSi<sub>5</sub>O<sub>12</sub>, Cs<sub>2</sub>CdSi<sub>5</sub>O<sub>12</sub> and Cs<sub>2</sub>CuSi<sub>5</sub>O<sub>12</sub> leucite analogues are more distorted than the SiO<sub>4</sub> tetrahedra in each phase. Rb<sub>2</sub>CdSi<sub>5</sub>O<sub>12</sub> shows the same relationship, with *O—T—O* angle variances ( $\sigma^2$ ; in units of degrees<sup>2</sup>) (Robinson, Gibbs & Ribbe, 1971) of 163 for CdO<sub>4</sub> and 26.4 for SiO<sub>4</sub>. In each of these leucite analogues, the mean Si—O—Si inter-tetrahedral angle is larger than that for Si—O—Z, in agreement with the usual inverse relationship between

mean  $T-O$  bond length and mean  $T-O-T$  angle shown by framework silicates (Hill & Gibbs, 1979).

The  $Cs_2MnSi_5O_{12}$ ,  $Cs_2CoSi_5O_{12}$  and  $Cs_2NiSi_5O_{12}$  leucite structures described here show some significant differences from the relationships discussed above. All three samples show only small distortions from cubic symmetry ( $\Delta = 1.008$  for  $Cs_2MnSi_5O_{12}$ , 1.005 for  $Cs_2CoSi_5O_{12}$  and 1.003 for  $Cs_2NiSi_5O_{12}$ ). Despite the differences between the  $Si-O$  and  $Z-O$  ( $Z = Mn, Co$  and  $Ni$ ) bond lengths, the mean  $Si-O-Si$  and  $Si-O-Z$  angles are the same within error [ $137(9)$  and  $133(8)^\circ$ , respectively, for  $Cs_2MnSi_5O_{12}$ ;  $137(6)$  and  $136(8)^\circ$  for  $Cs_2CoSi_5O_{12}$ , and  $142(10)$  and  $135(10)^\circ$  for  $Cs_2NiSi_5O_{12}$ ]. In addition (and unexpectedly), in all three samples the  $SiO_4$  tetrahedra have larger tetrahedral-angle variances (degrees<sup>2</sup>) than the  $ZO_4$  tetrahedra (90 and 58, respectively, in  $Cs_2MnSi_5O_{12}$ ; 167 and 60 in  $Cs_2CoSi_5O_{12}$  and 79 and 47 in  $Cs_2NiSi_5O_{12}$ ). Although the errors in the tetrahedral-angle variances are large, we believe that it cannot be coincidental that all three samples show the same relationships. Thus, it appears that in the  $Cs_2MnSi_5O_{12}$ ,  $Cs_2CoSi_5O_{12}$  and  $Cs_2NiSi_5O_{12}$  leucites, the framework distortions are reflected by the presence of highly distorted intra-tetrahedral angles with little difference between mean  $Si-O-Si$  and  $Si-O-Z$  inter-tetrahedral angles. The small departures from isotropic unit-cell shapes are likely to result from distortions localized within the tetrahedra rather than distortions transmitted through the framework by cooperative rotations about the (usually) 'soft'  $T-O-T$  angles, which would be expected to introduce different  $T-O-T$  angles for different sizes of tetrahedra. However, at this stage, it remains unclear why the  $SiO_4$  tetrahedra in these three samples are more distorted. The different departures from pseudo-cubic symmetry for  $Rb_2CdSi_5O_{12}$  and  $Cs_2MnSi_5O_{12}$  leucite analogues are shown in Figs. 5 and 6, viewed down the large channels.

## Experimental

The starting materials were prepared from rubidium, caesium and cadmium carbonates, and silicon, manganese, cobalt and nickel oxides by mixing stoichiometric amounts in an agate mortar. These mixtures were then heated overnight at 873 K to decompose the carbonates and melted in a platinum crucible at 1673 K for 1.5 h before quenching to form glasses. The  $Rb_2CdSi_5O_{12}$  glass was ground and hydrothermally heated in a cold-seal bomb at 833 K and 50 MPa water-vapour pressure for 60 d to form a crystalline powder. The  $Cs_2MnSi_5O_{12}$  glass was similarly heated at 933 K and 50 MPa water-vapour pressure for 36 h. The  $Cs_2CoSi_5O_{12}$  and  $Cs_2NiSi_5O_{12}$  glasses were dry-crystallized at ambient pressure and 1393 K for 5 d.

### $Rb_2CdSi_5O_{12}$

#### Crystal data

$Rb_2CdSi_5O_{12}$   
 $M_r = 615.76$

Synchrotron radiation  
 $\lambda = 1.40285 \text{ \AA}$

Orthorhombic

$Pbca$

$a = 13.4121(1) \text{ \AA}$

$b = 13.6816(1) \text{ \AA}$

$c = 13.8558(1) \text{ \AA}$

$V = 2542.51(5) \text{ \AA}^3$

$Z = 8$

$D_x = 3.217 \text{ Mg m}^{-3}$

#### Data collection

High-resolution powder diffractometer, SRS station 2.3 (Cernik, Murray, Pattison & Fitch, 1990; Collins, Cernik, Pattison, Bell & Fitch, 1992)

Parallel beam non-focusing optics with channel-cut monochromator and scintillation detector

Specimen mounting: 25 mm diameter 1 mm deep Al sample holder

Sample shape: irregular

#### Refinement

$R_I = 0.073$

$R_{wp} = 0.165$

$R_{exp} = 0.174$

$S = 0.903$

Processed  $2\theta_{min} = 10.00^\circ$ ,

$2\theta_{max} = 70.00^\circ$

Increment in  $2\theta = 0.01^\circ$

75 parameters

$T = 293 \text{ K}$

Powder

White

Sample mounted in reflection mode

Method for scanning reciprocal space: step scan  
12 001 data points measured  
6000 data points in the processed diffractogram

Measured  $2\theta_{min} = 5.00^\circ$ ,  
 $2\theta_{max} = 125.00^\circ$

$2\theta$  increment =  $0.01^\circ$

Dataset normalized for decay of synchrotron beam (*PDPL PODSUM*; Murray, Cockcroft & Fitch, 1990)

All holder reflections excluded

Weighting scheme: normalization factor/profile intensity + background

Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.3.1)

Table 1. Fractional atomic coordinates and isotropic displacement parameters ( $\text{\AA}^2$ ) for  $Rb_2CdSi_5O_{12}$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> <sub>iso</sub>
Rb1	0.1256 (3)	0.1284 (3)	0.1501 (3)	3.09 (8)
Rb2	0.3715 (3)	0.3844 (3)	0.3781 (2)	3.09 (8)
Cd1	0.3847 (2)	0.8369 (2)	0.9414 (2)	0.99 (7)
Si2	0.1309 (7)	0.6749 (7)	0.5974 (5)	0.1 (1)
Si3	0.5797 (6)	0.1108 (7)	0.6321 (6)	0.1 (1)
Si4	0.6522 (7)	0.5977 (6)	0.1069 (6)	0.1 (1)
Si5	0.9013 (7)	0.3730 (6)	0.8140 (6)	0.1 (1)
Si6	0.8369 (7)	0.9144 (6)	0.3375 (6)	0.1 (1)
O1	0.4663 (9)	0.367 (1)	0.149 (1)	0.2 (1)
O2	0.082 (1)	0.5000 (9)	0.402 (1)	0.2 (1)
O3	0.378 (1)	0.165 (1)	0.4838 (8)	0.2 (1)
O4	0.7366 (9)	0.436 (1)	0.611 (1)	0.2 (1)
O5	0.649 (1)	0.7117 (9)	0.381 (1)	0.2 (1)
O6	0.356 (1)	0.627 (1)	0.7708 (9)	0.2 (1)
O7	0.984 (1)	0.897 (1)	0.671 (1)	0.2 (1)
O8	0.667 (1)	0.9683 (9)	0.838 (1)	0.2 (1)
O9	0.920 (1)	0.634 (1)	0.9064 (9)	0.2 (1)
O10	0.221 (1)	0.886 (1)	0.145 (1)	0.2 (1)
O11	0.134 (1)	0.1737 (8)	0.947 (1)	0.2 (1)
O12	0.884 (2)	0.159 (1)	0.1999 (9)	0.2 (1)

Table 2. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ) for  $Rb_2CdSi_5O_{12}$

Cd1—O4 <sup>i</sup>	2.24 (1)	Rb1—O1 <sup>xxii</sup>	3.79 (2)
Cd1—O7 <sup>ii</sup>	2.20 (1)	Rb1—O2 <sup>xxiii</sup>	3.37 (2)
Cd1—O9 <sup>iii</sup>	2.20 (1)	Rb1—O3 <sup>xxiv</sup>	3.83 (2)
Cd1—O11 <sup>iv</sup>	2.25 (1)	Rb1—O4 <sup>xxv</sup>	3.74 (2)

Si2—O1 <sup>v</sup>	1.59 (2)	Rb1—O5 <sup>xxvi</sup>	3.26 (2)
Si2—O3 <sup>iv</sup>	1.58 (1)	Rb1—O6 <sup>xxvii</sup>	3.75 (2)
Si2—O5 <sup>vi</sup>	1.60 (2)	Rb1—O7 <sup>xxviii</sup>	2.90 (2)
Si2—O10 <sup>vii</sup>	1.61 (2)	Rb1—O8 <sup>xxix</sup>	3.08 (2)
Si3—O1 <sup>viii</sup>	1.57 (2)	Rb1—O9 <sup>xxx</sup>	3.40 (2)
Si3—O2 <sup>ix</sup>	1.59 (2)	Rb1—O10 <sup>xxxi</sup>	3.56 (2)
Si3—O6 <sup>x</sup>	1.62 (2)	Rb1—O11 <sup>xxx</sup>	2.88 (2)
Si3—O11 <sup>xi</sup>	1.57 (2)	Rb1—O12 <sup>xxxii</sup>	3.34 (2)
Si4—O2 <sup>xii</sup>	1.64 (2)	Rb2—O1	3.43 (2)
Si4—O3 <sup>xiii</sup>	1.61 (2)	Rb2—O2	4.21 (2)
Si4—O4 <sup>xiv</sup>	1.56 (2)	Rb2—O3	3.34 (2)
Si4—O12 <sup>xv</sup>	1.61 (2)	Rb2—O4 <sup>xxviii</sup>	2.85 (1)
Si5—O5 <sup>xvi</sup>	1.63 (2)	Rb2—O5 <sup>xxviii</sup>	3.60 (2)
Si5—O7 <sup>xvii</sup>	1.59 (2)	Rb2—O6 <sup>xxvii</sup>	3.39 (2)
Si5—O8 <sup>xviii</sup>	1.63 (2)	Rb2—O7 <sup>vi</sup>	3.42 (2)
Si5—O12 <sup>viii</sup>	1.66 (2)	Rb2—O8 <sup>x</sup>	4.13 (2)
Si6—O6 <sup>xix</sup>	1.62 (2)	Rb2—O9 <sup>xiv</sup>	2.83 (2)
Si6—O8 <sup>xx</sup>	1.61 (2)	Rb2—O10 <sup>xxii</sup>	3.47 (2)
Si6—O9 <sup>xxi</sup>	1.61 (2)	Rb2—O11 <sup>xxxii</sup>	3.42 (2)
Si6—O10 <sup>xxii</sup>	1.62 (2)	Rb2—O12 <sup>xxiv</sup>	3.27 (2)
O4 <sup>i</sup> —Cd1—O7 <sup>ii</sup>	89.2 (5)	O5 <sup>xvi</sup> —Si5—O7 <sup>xvii</sup>	117.9 (8)
O4 <sup>i</sup> —Cd1—O9 <sup>iii</sup>	110.8 (6)	O5 <sup>xvi</sup> —Si5—O8 <sup>xxviii</sup>	102.9 (8)
O4 <sup>i</sup> —Cd1—O11 <sup>iv</sup>	122.3 (6)	O5 <sup>xvi</sup> —Si5—O12 <sup>viii</sup>	107.2 (9)
O7 <sup>ii</sup> —Cd1—O9 <sup>iii</sup>	118.5 (5)	O7 <sup>xvii</sup> —Si5—O8 <sup>xxviii</sup>	111.0 (9)
O7 <sup>ii</sup> —Cd1—O11 <sup>iv</sup>	117.4 (6)	O7 <sup>xvii</sup> —Si5—O12 <sup>viii</sup>	109 (1)
O9 <sup>iii</sup> —Cd1—O11 <sup>iv</sup>	99.9 (6)	O8 <sup>xxiii</sup> —Si5—O12 <sup>viii</sup>	109 (1)
O1 <sup>v</sup> —Si2—O3 <sup>iv</sup>	110 (1)	O6 <sup>xix</sup> —Si6—O8 <sup>xx</sup>	110.9 (9)
O1 <sup>v</sup> —Si2—O5 <sup>vi</sup>	113 (1)	O6 <sup>xix</sup> —Si6—O9 <sup>xxi</sup>	107.4 (8)
O1 <sup>v</sup> —Si2—O10 <sup>vii</sup>	104.6 (9)	O6 <sup>xix</sup> —Si6—O10 <sup>xii</sup>	101.8 (8)
O3 <sup>iv</sup> —Si2—O5 <sup>vi</sup>	106.3 (9)	O8 <sup>xx</sup> —Si6—O9 <sup>xxi</sup>	115.5 (9)
O3 <sup>iv</sup> —Si2—O10 <sup>vii</sup>	114.8 (9)	O8 <sup>xx</sup> —Si6—O10 <sup>xii</sup>	101.9 (8)
O5 <sup>vi</sup> —Si2—O10 <sup>vii</sup>	108.3 (8)	O9 <sup>xxi</sup> —Si6—O10 <sup>xii</sup>	118.5 (9)
O1 <sup>viii</sup> —Si3—O2 <sup>ix</sup>	104 (1)	Si2 <sup>xxvii</sup> —O1—Si3 <sup>xxxii</sup>	143 (1)
O1 <sup>viii</sup> —Si3—O6 <sup>x</sup>	112 (1)	Si3 <sup>xxv</sup> —O2—Si4 <sup>xxiv</sup>	140 (1)
O1 <sup>viii</sup> —Si3—O11 <sup>xi</sup>	116 (1)	Si2 <sup>xxii</sup> —O3—Si4 <sup>xxvi</sup>	143 (1)
O2 <sup>ix</sup> —Si3—O6 <sup>x</sup>	111.7 (9)	Cd1 <sup>x</sup> —O4—Si4 <sup>xvi</sup>	120.0 (8)
O2 <sup>ix</sup> —Si3—O11 <sup>xi</sup>	107.7 (9)	Si2 <sup>xix</sup> —O5—Si5 <sup>xiv</sup>	138 (1)
O6 <sup>x</sup> —Si3—O11 <sup>xi</sup>	104.9 (9)	Si3 <sup>o</sup> —O6—Si6 <sup>vi</sup>	144 (1)
O2 <sup>xii</sup> —Si4—O3 <sup>xxxiii</sup>	105.1 (9)	Cd1 <sup>xi</sup> —O7—Si5 <sup>xxxiv</sup>	127.2 (9)
O2 <sup>xii</sup> —Si4—O4 <sup>xiv</sup>	107.8 (7)	Si5 <sup>xv</sup> —O8—Si6 <sup>xxxv</sup>	141 (1)
O2 <sup>xii</sup> —Si4—O12 <sup>xv</sup>	108 (1)	Cd1 <sup>xxxvi</sup> —O9—Si6 <sup>vii</sup>	119.5 (9)
O3 <sup>xiii</sup> —Si4—O4 <sup>xiv</sup>	116.0 (8)	Si2 <sup>xxi</sup> —O10—Si6 <sup>xxiv</sup>	155 (1)
O3 <sup>xiii</sup> —Si4—O12 <sup>xv</sup>	104.4 (9)	Cd1 <sup>xxxii</sup> —O11—Si3 <sup>ii</sup>	117.8 (9)
O4 <sup>xiv</sup> —Si4—O12 <sup>xv</sup>	114 (1)	Si4 <sup>xxiii</sup> —O12—Si5 <sup>xxxii</sup>	132 (1)

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

### Cs<sub>2</sub>MnSi<sub>5</sub>O<sub>12</sub>

#### Crystal data

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

$M_r = 653.17$

Orthorhombic

*Pbca*

$a = 13.6878 (3) \text{ \AA}$

$b = 13.7931 (3) \text{ \AA}$

$c = 13.7575 (3) \text{ \AA}$

$V = 2597.4 (2) \text{ \AA}^3$

$Z = 8$

$D_x = 3.341 \text{ Mg m}^{-3}$

#### Synchrotron radiation

$\lambda = 1.29969 \text{ \AA}$

$T = 293 \text{ K}$

Powder

Pale pink

Sample mounted in reflection mode

#### Data collection

High-resolution powder diffractometer, SRS station 2.3 (Cernik, Murray, Pattison & Fitch, 1990; Collins, Cernik, Pattison, Bell & Fitch, 1992)

Parallel beam non-focusing optics with channel-cut monochromator and scintillation detector

Specimen mounting: 25 mm diameter Si(100) substrate in a Perspex sample holder, sample mounted on substrate with acetone

Sample shape: irregular  
Method for scanning reciprocal space: step scan

9501 data points measured  
6301 data points in the processed diffractogram

Measured  $2\theta_{\min} = 5.00$ ,  
 $2\theta_{\max} = 100.00^\circ$

$2\theta$  increment =  $0.01^\circ$   
Dataset normalized for decay of synchrotron beam (*PDPL PODSUM*; Murray, Cockcroft & Fitch, 1990)

Si substrate reflections excluded

#### Refinement

$R_i = 0.126$

$R_{wp} = 0.140$

$R_{exp} = 0.140$

$S = 1.019$

Processed  $2\theta_{\min} = 15.00$ ,

$2\theta_{\max} = 78.00^\circ$

Increment in  $2\theta = 0.01^\circ$

71 parameters

Weighting scheme: normalization factor/profile

intensity + background

Atomic scattering factors

from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.3.1)

Table 3. Fractional atomic coordinates and isotropic displacement parameters ( $\text{\AA}^2$ ) for Cs<sub>2</sub>MnSi<sub>5</sub>O<sub>12</sub>

	x	y	z	$B_{iso}$
Cs1	0.1294 (5)	0.1352 (4)	0.1506 (3)	0.25
Cs2	0.3777 (5)	0.3905 (3)	0.3888 (3)	0.25
Mn1	0.380 (1)	0.8374 (7)	0.9337 (7)	0.25
Si2	0.126 (2)	0.665 (1)	0.596 (1)	0.25
Si3	0.584 (2)	0.110 (1)	0.634 (1)	0.25
Si4	0.654 (1)	0.598 (1)	0.111 (1)	0.25
Si5	0.898 (1)	0.373 (1)	0.818 (1)	0.25
Si6	0.834 (2)	0.918 (1)	0.353 (1)	0.25
O1	0.465 (2)	0.379 (3)	0.166 (3)	0.25
O2	0.093 (2)	0.502 (2)	0.416 (2)	0.25
O3	0.384 (3)	0.165 (2)	0.475 (2)	0.25
O4	0.730 (2)	0.412 (3)	0.625 (3)	0.25
O5	0.653 (3)	0.724 (2)	0.364 (2)	0.25
O6	0.360 (3)	0.622 (2)	0.756 (2)	0.25
O7	0.987 (2)	0.889 (3)	0.650 (2)	0.25
O8	0.678 (2)	0.963 (2)	0.851 (3)	0.25
O9	0.904 (2)	0.642 (2)	0.926 (2)	0.25
O10	0.217 (2)	0.904 (3)	0.143 (3)	0.25
O11	0.147 (3)	0.198 (2)	0.923 (2)	0.25
O12	0.902 (3)	0.151 (2)	0.200 (2)	0.25

Table 4. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ) for Cs<sub>2</sub>MnSi<sub>5</sub>O<sub>12</sub>

Mn1—O4 <sup>i</sup>	1.99 (3)	Cs1—O1 <sup>xxii</sup>	3.76 (4)
Mn1—O7 <sup>ii</sup>	1.99 (3)	Cs1—O2 <sup>xxiii</sup>	3.68 (3)
Mn1—O9 <sup>iii</sup>	1.97 (2)	Cs1—O3 <sup>xxiv</sup>	3.80 (4)
Mn1—O11 <sup>iv</sup>	1.97 (2)	Cs1—O4 <sup>xxv</sup>	3.44 (4)
Si2—O1 <sup>v</sup>	1.69 (4)	Cs1—O5 <sup>xxvi</sup>	3.23 (3)
Si2—O3 <sup>iv</sup>	1.67 (3)	Cs1—O6 <sup>xxvii</sup>	3.66 (3)
Si2—O5 <sup>vi</sup>	1.67 (3)	Cs1—O7 <sup>xxviii</sup>	3.19 (3)
Si2—O10 <sup>vii</sup>	1.69 (4)	Cs1—O8 <sup>xxviii</sup>	2.96 (3)
Si3—O1 <sup>viii</sup>	1.70 (4)	Cs1—O9 <sup>xxviii</sup>	3.28 (3)
Si3—O2 <sup>ix</sup>	1.69 (3)	Cs1—O10 <sup>xxix</sup>	3.41 (4)
Si3—O6 <sup>x</sup>	1.71 (3)	Cs1—O11 <sup>xxx</sup>	3.25 (3)
Si3—O11 <sup>xi</sup>	1.69 (3)	Cs1—O12 <sup>xxxii</sup>	3.19 (4)
Si4—O2 <sup>xii</sup>	1.61 (4)	Cs2—O1	3.29 (4)
Si4—O3 <sup>xiii</sup>	1.59 (3)	Cs2—O2	4.20 (3)

Si4—O4 <sup>xiv</sup>	1.61 (3)	Cs2—O3	3.33 (3)
Si4—O12 <sup>xv</sup>	1.63 (4)	Cs2—O4 <sup>xxviii</sup>	3.10 (3)
Si5—O5 <sup>xvi</sup>	1.63 (3)	Cs2—O5 <sup>xxviii</sup>	3.77 (3)
Si5—O7 <sup>xvii</sup>	1.66 (3)	Cs2—O6 <sup>xxvii</sup>	3.73 (4)
Si5—O8 <sup>xviii</sup>	1.68 (4)	Cs2—O7 <sup>vi</sup>	3.43 (3)
Si5—O12 <sup>viii</sup>	1.65 (3)	Cs2—O8 <sup>†</sup>	3.80 (4)
Si6—O6 <sup>xix</sup>	1.64 (3)	Cs2—O9 <sup>xiv</sup>	3.06 (3)
Si6—O8 <sup>xx</sup>	1.66 (3)	Cs2—O10 <sup>xxii</sup>	3.62 (4)
Si6—O9 <sup>xxi</sup>	1.62 (3)	Cs2—O11 <sup>xxxi</sup>	3.41 (3)
Si6—O10 <sup>xxii</sup>	1.62 (3)	Cs2—O12 <sup>xxiv</sup>	3.54 (3)
O4 <sup>i</sup> —Mn1—O7 <sup>ii</sup>	98 (1)	O5 <sup>xvi</sup> —Si5—O7 <sup>xvii</sup>	114 (2)
O4 <sup>i</sup> —Mn1—O9 <sup>iii</sup>	117 (2)	O5 <sup>xvi</sup> —Si5—O8 <sup>xviii</sup>	104 (2)
O4 <sup>i</sup> —Mn1—O11 <sup>iv</sup>	110 (1)	O5 <sup>xvi</sup> —Si5—O12 <sup>viii</sup>	104 (2)
O7 <sup>ii</sup> —Mn1—O9 <sup>iii</sup>	113 (1)	O7 <sup>xvii</sup> —Si5—O8 <sup>xviii</sup>	114 (2)
O7 <sup>ii</sup> —Mn1—O11 <sup>iv</sup>	117 (2)	O7 <sup>xvii</sup> —Si5—O12 <sup>viii</sup>	105 (2)
O9 <sup>iii</sup> —Mn1—O11 <sup>iv</sup>	104 (1)	O8 <sup>xviii</sup> —Si5—O12 <sup>viii</sup>	116 (2)
O1 <sup>v</sup> —Si2—O3 <sup>iv</sup>	120 (2)	O6 <sup>xix</sup> —Si6—O8 <sup>xx</sup>	109 (1)
O1 <sup>v</sup> —Si2—O5 <sup>vi</sup>	108 (2)	O6 <sup>xix</sup> —Si6—O9 <sup>xxi</sup>	106 (2)
O1 <sup>v</sup> —Si2—O10 <sup>vii</sup>	97 (2)	O6 <sup>xix</sup> —Si6—O10 <sup>xxii</sup>	102 (2)
O3 <sup>iv</sup> —Si2—O5 <sup>vi</sup>	110 (2)	O8 <sup>xx</sup> —Si6—O9 <sup>xxi</sup>	126 (2)
O3 <sup>iv</sup> —Si2—O10 <sup>vii</sup>	117 (2)	O8 <sup>xx</sup> —Si6—O10 <sup>xxii</sup>	91 (2)
O5 <sup>vi</sup> —Si2—O10 <sup>vii</sup>	103 (2)	O9 <sup>xxi</sup> —Si6—O10 <sup>xxii</sup>	120 (2)
O1 <sup>viii</sup> —Si3—O2 <sup>ix</sup>	105 (2)	Si2 <sup>xxvii</sup> —O1—Si3 <sup>xxxii</sup>	126 (2)
O1 <sup>viii</sup> —Si3—O6 <sup>x</sup>	101 (2)	Si3 <sup>xxv</sup> —O2—Si4 <sup>xxiv</sup>	134 (2)
O1 <sup>viii</sup> —Si3—O11 <sup>xi</sup>	124 (2)	Si2 <sup>xxii</sup> —O3—Si4 <sup>xxvi</sup>	135 (2)
O2 <sup>ix</sup> —Si3—O6 <sup>x</sup>	114 (2)	Mn1 <sup>x</sup> —O4—Si4 <sup>xvi</sup>	131 (2)
O2 <sup>ix</sup> —Si3—O11 <sup>xi</sup>	115 (2)	Si2 <sup>xx</sup> —O5—Si5 <sup>xiv</sup>	142 (2)
O6 <sup>x</sup> —Si3—O11 <sup>xi</sup>	97 (2)	Si3 <sup>†</sup> —O6—Si6 <sup>vi</sup>	152 (3)
O2 <sup>xii</sup> —Si4—O3 <sup>xxxiii</sup>	98 (2)	Mn1 <sup>xi</sup> —O7—Si5 <sup>xxxiv</sup>	144 (2)
O2 <sup>xii</sup> —Si4—O4 <sup>xiv</sup>	118 (2)	Si5 <sup>xv</sup> —O8—Si6 <sup>xxxv</sup>	133 (2)
O2 <sup>xii</sup> —Si4—O12 <sup>xv</sup>	108 (2)	Mn1 <sup>xxxvi</sup> —O9—Si6 <sup>vii</sup>	125 (2)
O3 <sup>xiii</sup> —Si4—O4 <sup>xiv</sup>	117 (2)	Si2 <sup>xxi</sup> —O10—Si6 <sup>xxiv</sup>	144 (3)
O3 <sup>xiii</sup> —Si4—O12 <sup>xv</sup>	98 (2)	Mn1 <sup>xxii</sup> —O11—Si3 <sup>ii</sup>	130 (2)
O4 <sup>xiv</sup> —Si4—O12 <sup>xv</sup>	115 (2)	Si4 <sup>xxiii</sup> —O12—Si5 <sup>xxxii</sup>	129 (2)

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

**Cs<sub>2</sub>CoSi<sub>5</sub>O<sub>12</sub>***Crystal data*Cs<sub>2</sub>CoSi<sub>5</sub>O<sub>12</sub> $M_r = 657.16$ 

Orthorhombic

*Pbca* $a = 13.6487 (4) \text{ \AA}$  $b = 13.7120 (4) \text{ \AA}$  $c = 13.6828 (4) \text{ \AA}$  $V = 2560.7 (2) \text{ \AA}^3$  $Z = 8$  $D_x = 3.409 \text{ Mg m}^{-3}$ *Data collection*

High-resolution powder diffractometer, SRS station 2.3 (Cernik, Murray, Pattison & Fitch, 1990; Collins, Cernik, Pattison, Bell & Fitch, 1992)

## Synchrotron radiation

 $\lambda = 1.301382 \text{ \AA}$  $T = 293 \text{ K}$ 

Powder

Cobalt blue

Sample mounted in reflection mode

Sample shape: irregular

Method for scanning

reciprocal space:

step scan

8827 data points measured

5776 data points in the processed diffractogram

Parallel beam non-focusing optics with channel-cut monochromator and scintillation detector  
Specimen mounting: 25 mm diameter Si(100) substrate in a Perspex sample holder, sample mounted on substrate with acetone

Measured  $2\theta_{\min} = 5.00$ , $2\theta_{\max} = 93.26^\circ$  $2\theta$  increment =  $0.01^\circ$ 

Dataset normalized for decay of synchrotron beam (*PDPL PODSUM*; Murray, Cockcroft & Fitch, 1990)

Si substrate reflections excluded

*Refinement* $R_f = 0.059$  $R_{wp} = 0.128$  $R_{exp} = 0.142$  $S = 0.821$ Processed  $2\theta_{\min} = 5.00$ , $2\theta_{\max} = 70.00^\circ$ Increment in  $2\theta = 0.01^\circ$ 

72 parameters

Weighting scheme: normalization factor/profile intensity + background

Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.3.1)

Table 5. Fractional atomic coordinates and isotropic displacement parameters ( $\text{\AA}^2$ ) for Cs<sub>2</sub>CoSi<sub>5</sub>O<sub>12</sub>

	<i>x</i>	<i>y</i>	<i>z</i>	$B_{\text{iso}}$
Cs1	0.1270 (6)	0.1357 (6)	0.1459 (4)	1.73 (8)
Cs2	0.3826 (8)	0.3911 (6)	0.3889 (5)	1.73 (8)
Co1	0.373 (1)	0.8382 (9)	0.9347 (9)	0.1
Si2	0.127 (2)	0.663 (2)	0.597 (2)	0.1
Si3	0.587 (2)	0.117 (2)	0.640 (2)	0.1
Si4	0.650 (2)	0.588 (2)	0.117 (2)	0.1
Si5	0.907 (2)	0.374 (2)	0.825 (2)	0.1
Si6	0.834 (2)	0.919 (2)	0.350 (2)	0.1
O1	0.470 (2)	0.380 (4)	0.158 (4)	0.1
O2	0.092 (3)	0.490 (3)	0.407 (3)	0.1
O3	0.384 (4)	0.147 (3)	0.478 (2)	0.1
O4	0.733 (2)	0.404 (4)	0.627 (3)	0.1
O5	0.644 (3)	0.724 (2)	0.365 (4)	0.1
O6	0.409 (4)	0.600 (3)	0.744 (2)	0.1
O7	0.988 (2)	0.896 (3)	0.624 (4)	0.1
O8	0.673 (3)	0.960 (2)	0.848 (3)	0.1
O9	0.892 (4)	0.656 (3)	0.927 (2)	0.1
O10	0.214 (3)	0.914 (3)	0.134 (4)	0.1
O11	0.152 (3)	0.204 (2)	0.910 (4)	0.1
O12	0.890 (4)	0.150 (3)	0.210 (3)	0.1

Table 6. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ) for Cs<sub>2</sub>CoSi<sub>5</sub>O<sub>12</sub>

Co1—O4 <sup>i</sup>	1.91 (4)	Cs1—O1 <sup>xxii</sup>	3.75 (5)
Co1—O7 <sup>ii</sup>	1.93 (4)	Cs1—O2 <sup>xxiii</sup>	3.66 (4)
Co1—O9 <sup>iii</sup>	1.92 (3)	Cs1—O3 <sup>xxiv</sup>	3.73 (4)
Co1—O11 <sup>iv</sup>	1.91 (3)	Cs1—O4 <sup>xxv</sup>	3.47 (4)
Si2—O1 <sup>v</sup>	1.66 (5)	Cs1—O5 <sup>xxvi</sup>	3.35 (5)
Si2—O3 <sup>iv</sup>	1.65 (4)	Cs1—O6 <sup>xxvii</sup>	3.90 (4)
Si2—O5 <sup>vi</sup>	1.65 (4)	Cs1—O7 <sup>xxviii</sup>	3.54 (5)
Si2—O10 <sup>vii</sup>	1.67 (5)	Cs1—O8 <sup>xxviii</sup>	3.03 (4)
Si3—O1 <sup>viii</sup>	1.62 (4)	Cs1—O9 <sup>xxviii</sup>	3.04 (4)
Si3—O2 <sup>ix</sup>	1.60 (5)	Cs1—O10 <sup>xxix</sup>	3.27 (5)
Si3—O6 <sup>x</sup>	1.61 (4)	Cs1—O11 <sup>xxx</sup>	3.37 (5)
Si3—O11 <sup>xi</sup>	1.63 (4)	Cs1—O12 <sup>xxxi</sup>	3.35 (5)
Si4—O2 <sup>xii</sup>	1.60 (5)	Cs2—O1	3.38 (5)
Si4—O3 <sup>xiii</sup>	1.60 (5)	Cs2—O2	4.20 (5)
Si4—O4 <sup>xiv</sup>	1.61 (4)	Cs2—O3	3.56 (4)
Si4—O12 <sup>xv</sup>	1.62 (5)	Cs2—O4 <sup>xxxvii</sup>	3.23 (4)
Si5—O5 <sup>xvi</sup>	1.61 (5)	Cs2—O5 <sup>xxxviii</sup>	3.74 (5)
Si5—O7 <sup>xvii</sup>	1.62 (5)	Cs2—O6 <sup>xxxix</sup>	3.38 (5)
Si5—O8 <sup>xxviii</sup>	1.64 (5)	Cs2—O7 <sup>vi</sup>	3.26 (4)
Si5—O12 <sup>viii</sup>	1.63 (5)	Cs2—O8 <sup>x</sup>	3.80 (5)
Si6—O6 <sup>xix</sup>	1.66 (5)	Cs2—O9 <sup>xiv</sup>	3.19 (5)
Si6—O8 <sup>xx</sup>	1.66 (4)	Cs2—O10 <sup>xxii</sup>	3.75 (5)
Si6—O9 <sup>xxi</sup>	1.66 (5)	Cs2—O11 <sup>xxxii</sup>	3.42 (4)
Si6—O10 <sup>xxii</sup>	1.65 (4)	Cs2—O12 <sup>xxiv</sup>	3.57 (4)

O4 <sup>i</sup> —Co1—O7 <sup>ii</sup>	104 (2)	O5 <sup>xvi</sup> —Si5—O7 <sup>xvii</sup>	113 (3)
O4 <sup>i</sup> —Co1—O9 <sup>iii</sup>	121 (2)	O5 <sup>xvi</sup> —Si5—O8 <sup>xviii</sup>	105 (2)
O4 <sup>i</sup> —Co1—O11 <sup>iv</sup>	104 (2)	O5 <sup>xvi</sup> —Si5—O12 <sup>viii</sup>	96 (3)
O7 <sup>ii</sup> —Co1—O9 <sup>iii</sup>	107 (2)	O7 <sup>xvii</sup> —Si5—O8 <sup>xviii</sup>	112 (3)
O7 <sup>ii</sup> —Co1—O11 <sup>iv</sup>	118 (2)	O7 <sup>xvii</sup> —Si5—O12 <sup>viii</sup>	125 (3)
O9 <sup>iii</sup> —Co1—O11 <sup>iv</sup>	104 (2)	O8 <sup>xviii</sup> —Si5—O12 <sup>viii</sup>	104 (3)
O1 <sup>v</sup> —Si2—O3 <sup>iv</sup>	112 (3)	O6 <sup>xix</sup> —Si6—O8 <sup>xx</sup>	100 (2)
O1 <sup>v</sup> —Si2—O5 <sup>vi</sup>	107 (3)	O6 <sup>xix</sup> —Si6—O9 <sup>xxi</sup>	96 (2)
O1 <sup>v</sup> —Si2—O10 <sup>vii</sup>	101 (2)	O6 <sup>xix</sup> —Si6—O10 <sup>xii</sup>	135 (2)
O3 <sup>iv</sup> —Si2—O5 <sup>vi</sup>	117 (3)	O8 <sup>xx</sup> —Si6—O9 <sup>xxi</sup>	131 (2)
O3 <sup>iv</sup> —Si2—O10 <sup>vii</sup>	106 (3)	O8 <sup>xx</sup> —Si6—O10 <sup>xii</sup>	90 (2)
O5 <sup>vi</sup> —Si2—O10 <sup>vii</sup>	113 (2)	O9 <sup>xxi</sup> —Si6—O10 <sup>xii</sup>	111 (2)
O1 <sup>viii</sup> —Si3—O2 <sup>ix</sup>	97 (3)	Si2 <sup>xxvii</sup> —O1—Si3 <sup>xxxii</sup>	135 (3)
O1 <sup>viii</sup> —Si3—O6 <sup>x</sup>	84 (3)	Si3 <sup>xxv</sup> —O2—Si4 <sup>xxiv</sup>	135 (3)
O1 <sup>viii</sup> —Si3—O11 <sup>xi</sup>	126 (3)	Si2 <sup>xxii</sup> —O3—Si4 <sup>xxvi</sup>	147 (4)
O2 <sup>ix</sup> —Si3—O6 <sup>x</sup>	105 (3)	Co1 <sup>x</sup> —O4—Si4 <sup>xvi</sup>	138 (3)
O2 <sup>ix</sup> —Si3—O11 <sup>xi</sup>	118 (2)	Si2 <sup>xxix</sup> —O5—Si5 <sup>xiv</sup>	130 (3)
O6 <sup>x</sup> —Si3—O11 <sup>xi</sup>	120 (3)	Si3 <sup>i</sup> —O6—Si6 <sup>ii</sup>	144 (3)
O2 <sup>xii</sup> —Si4—O3 <sup>xxxiii</sup>	96 (3)	Co1 <sup>xi</sup> —O7—Si5 <sup>xxxiv</sup>	145 (3)
O2 <sup>xii</sup> —Si4—O4 <sup>xiv</sup>	124 (3)	Si5 <sup>xv</sup> —O8—Si6 <sup>xxxv</sup>	133 (3)
O2 <sup>xii</sup> —Si4—O12 <sup>xv</sup>	115 (3)	Co1 <sup>xxxvi</sup> —O9—Si6 <sup>viii</sup>	126 (3)
O3 <sup>xiii</sup> —Si4—O4 <sup>xiv</sup>	110 (2)	Si2 <sup>xxi</sup> —O10—Si6 <sup>xxiv</sup>	141 (3)
O3 <sup>xiii</sup> —Si4—O12 <sup>xv</sup>	106 (3)	Co1 <sup>xxii</sup> —O11—Si3 <sup>ii</sup>	133 (3)
O4 <sup>xiv</sup> —Si4—O12 <sup>xv</sup>	104 (3)	Si4 <sup>xviii</sup> —O12—Si5 <sup>xxxii</sup>	134 (3)

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

### Cs<sub>2</sub>NiSi<sub>5</sub>O<sub>12</sub>

#### Crystal data

Cs<sub>2</sub>NiSi<sub>5</sub>O<sub>12</sub>

*M<sub>r</sub>* = 656.94

Orthorhombic

*Pbca*

*a* = 13.6147 (3) Å

*b* = 13.6568 (5) Å

*c* = 13.6583 (5) Å

*V* = 2539.5 (1) Å<sup>3</sup>

*Z* = 8

*D<sub>x</sub>* = 3.437 Mg m<sup>-3</sup>

#### Data collection

High-resolution powder diffractometer, SRS station 9.1 (Bushnell-Wye & Cernik, 1992)

Parallel beam non-focusing optics with channel-cut monochromator and scintillation detector

Specimen mounting: Si substrate, sample mounted on substrate with acetone

Sample shape: irregular

Method for scanning reciprocal space: step scan

#### Synchrotron radiation

$\lambda$  = 0.99820 Å

*T* = 293 K

Powder

Purple-blue

Sample mounted in reflection mode

9501 data points measured

4501 data points in the processed diffractogram

Measured  $2\theta_{\min}$  = 5.00,

$2\theta_{\max}$  = 100.00°

$2\theta$  increment = 0.01°

Dataset normalized for decay of synchrotron beam (PDPL PODSUM; Murray, Cockcroft & Fitch, 1990)

Impurity reflections excluded

#### Refinement

*R<sub>i</sub>* = 0.057

*R<sub>wp</sub>* = 0.091

*R<sub>exp</sub>* = 0.027

*S* = 11.810

Processed  $2\theta_{\min}$  = 7.00,

$2\theta_{\max}$  = 52.00°

Increment in  $2\theta$  = 0.01°

75 parameters

Weighting scheme: normalization factor/profile intensity + background  
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.3.1)

Table 7. Fractional atomic coordinates and isotropic displacement parameters (Å<sup>2</sup>) for Cs<sub>2</sub>NiSi<sub>5</sub>O<sub>12</sub>

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B<sub>iso</sub></i>
Cs1	0.131 (1)	0.1306 (8)	0.1446 (6)	4.78 (8)
Cs2	0.377 (1)	0.3848 (7)	0.3853 (7)	4.78 (8)
Ni1	0.378 (2)	0.838 (1)	0.928 (1)	4.5 (4)
Si2	0.124 (3)	0.672 (2)	0.596 (2)	2.0 (2)
Si3	0.584 (2)	0.117 (2)	0.635 (2)	2.0 (2)
Si4	0.646 (2)	0.596 (2)	0.112 (2)	2.0 (2)
Si5	0.916 (2)	0.385 (2)	0.820 (2)	2.0 (2)
Si6	0.831 (2)	0.913 (2)	0.355 (2)	2.0 (2)
O1	0.465 (2)	0.368 (4)	0.164 (3)	1.0 (3)
O2	0.125 (5)	0.487 (2)	0.416 (3)	1.0 (3)
O3	0.401 (4)	0.152 (4)	0.481 (3)	1.0 (3)
O4	0.737 (2)	0.397 (4)	0.617 (4)	1.0 (3)
O5	0.618 (4)	0.711 (2)	0.380 (3)	1.0 (3)
O6	0.359 (3)	0.624 (4)	0.754 (2)	1.0 (3)
O7	0.970 (3)	0.891 (4)	0.660 (4)	1.0 (3)
O8	0.663 (3)	0.968 (2)	0.849 (3)	1.0 (3)
O9	0.906 (3)	0.618 (4)	0.943 (2)	1.0 (3)
O10	0.215 (3)	0.890 (4)	0.145 (4)	1.0 (3)
O11	0.141 (3)	0.201 (2)	0.937 (3)	1.0 (3)
O12	0.919 (3)	0.138 (3)	0.203 (2)	1.0 (3)

Table 8. Selected geometric parameters (Å, °) for Cs<sub>2</sub>NiSi<sub>5</sub>O<sub>12</sub>

Ni1—O4 <sup>i</sup>	1.87 (4)	Cs1—O1 <sup>xxii</sup>	3.83 (6)
Ni1—O7 <sup>ii</sup>	1.88 (5)	Cs1—O2 <sup>xxxiii</sup>	3.50 (4)
Ni1—O9 <sup>iii</sup>	1.89 (4)	Cs1—O3 <sup>xxiv</sup>	3.58 (5)
Ni1—O11 <sup>iv</sup>	1.89 (3)	Cs1—O4 <sup>xxv</sup>	3.58 (5)
Si2—O1 <sup>v</sup>	1.62 (5)	Cs1—O5 <sup>xxvi</sup>	3.61 (5)
Si2—O3 <sup>iv</sup>	1.63 (5)	Cs1—O6 <sup>xxvii</sup>	3.67 (5)
Si2—O5 <sup>vi</sup>	1.63 (4)	Cs1—O7 <sup>xxviii</sup>	3.02 (5)
Si2—O10 <sup>vii</sup>	1.64 (6)	Cs1—O8 <sup>xxviii</sup>	3.11 (4)
Si3—O1 <sup>viii</sup>	1.68 (4)	Cs1—O9 <sup>xxviii</sup>	3.67 (5)
Si3—O2 <sup>ix</sup>	1.67 (5)	Cs1—O10 <sup>xxix</sup>	3.48 (6)
Si3—O6 <sup>x</sup>	1.71 (4)	Cs1—O11 <sup>xxx</sup>	2.99 (4)
Si3—O11 <sup>xi</sup>	1.71 (4)	Cs1—O12 <sup>xxxi</sup>	3.00 (5)
Si4—O2 <sup>xii</sup>	1.60 (4)	Cs2—O1	3.26 (5)
Si4—O3 <sup>xiii</sup>	1.60 (5)	Cs2—O2	3.73 (6)
Si4—O4 <sup>xiv</sup>	1.59 (4)	Cs2—O3	3.45 (5)
Si4—O12 <sup>xv</sup>	1.62 (5)	Cs2—O4 <sup>xxxviii</sup>	3.36 (5)
Si5—O5 <sup>vi</sup>	1.61 (5)	Cs2—O5 <sup>xxxviii</sup>	3.47 (4)
Si5—O7 <sup>xvii</sup>	1.59 (5)	Cs2—O6 <sup>xxxvii</sup>	3.68 (5)
Si5—O8 <sup>xviii</sup>	1.62 (5)	Cs2—O7 <sup>vi</sup>	3.37 (6)
Si5—O12 <sup>viii</sup>	1.62 (4)	Cs2—O8 <sup>x</sup>	3.85 (4)
Si6—O6 <sup>xix</sup>	1.62 (5)	Cs2—O9 <sup>xiv</sup>	3.06 (4)
Si6—O8 <sup>xx</sup>	1.63 (4)	Cs2—O10 <sup>xxii</sup>	3.51 (6)
Si6—O9 <sup>xxi</sup>	1.63 (5)	Cs2—O11 <sup>xxiii</sup>	3.49 (5)
Si6—O10 <sup>xii</sup>	1.62 (5)	Cs2—O12 <sup>xiv</sup>	3.63 (5)
O4 <sup>i</sup> —Ni1—O7 <sup>ii</sup>	100 (2)	O5 <sup>xvi</sup> —Si5—O7 <sup>xvii</sup>	103 (3)
O4 <sup>i</sup> —Ni1—O9 <sup>iii</sup>	110 (2)	O5 <sup>xvi</sup> —Si5—O8 <sup>xviii</sup>	105 (2)
O4 <sup>i</sup> —Ni1—O11 <sup>iv</sup>	110 (2)	O5 <sup>xvi</sup> —Si5—O12 <sup>viii</sup>	111 (3)
O7 <sup>ii</sup> —Ni1—O9 <sup>iii</sup>	110 (2)	O7 <sup>xvii</sup> —Si5—O8 <sup>xviii</sup>	125 (3)
O7 <sup>ii</sup> —Ni1—O11 <sup>iv</sup>	121 (2)	O7 <sup>xvii</sup> —Si5—O12 <sup>viii</sup>	99 (3)
O9 <sup>iii</sup> —Ni1—O11 <sup>iv</sup>	106 (2)	O8 <sup>xviii</sup> —Si5—O12 <sup>viii</sup>	113 (3)
O1 <sup>v</sup> —Si2—O3 <sup>iv</sup>	110 (3)	O6 <sup>xix</sup> —Si6—O8 <sup>xx</sup>	105 (3)
O1 <sup>v</sup> —Si2—O5 <sup>vi</sup>	100 (3)	O6 <sup>xix</sup> —Si6—O9 <sup>xxi</sup>	117 (2)
O1 <sup>v</sup> —Si2—O10 <sup>vii</sup>	99 (3)	O6 <sup>xix</sup> —Si6—O10 <sup>xii</sup>	99 (3)
O3 <sup>iv</sup> —Si2—O10 <sup>vii</sup>	118 (3)	O8 <sup>xx</sup> —Si6—O9 <sup>xxi</sup>	106 (3)
O5 <sup>vi</sup> —Si2—O10 <sup>vii</sup>	117 (3)	O8 <sup>xx</sup> —Si6—O10 <sup>xii</sup>	104 (3)
O3 <sup>iv</sup> —Si2—O5 <sup>vi</sup>	110 (3)	O9 <sup>xxi</sup> —Si6—O10 <sup>xii</sup>	125 (3)

O1 <sup>viii</sup> —Si3—O2 <sup>ix</sup>	122 (3)	Si2 <sup>xxvii</sup> —O1—Si3 <sup>xxxii</sup>	129 (3)
O1 <sup>viii</sup> —Si3—O6 <sup>x</sup>	103 (2)	Si3 <sup>xxxv</sup> —O2—Si4 <sup>xxiv</sup>	140 (3)
O1 <sup>viii</sup> —Si3—O11 <sup>xi</sup>	120 (3)	Si2 <sup>xxii</sup> —O3—Si4 <sup>xxvi</sup>	139 (3)
O2 <sup>ix</sup> —Si3—O6 <sup>x</sup>	106 (2)	Ni1 <sup>x</sup> —O4—Si4 <sup>xvi</sup>	147 (3)
O2 <sup>ix</sup> —Si3—O11 <sup>xi</sup>	100 (2)	Si2 <sup>xxix</sup> —O5—Si5 <sup>xiv</sup>	156 (3)
O6 <sup>x</sup> —Si3—O11 <sup>xi</sup>	105 (2)	Si3 <sup>i</sup> —O6—Si6 <sup>vi</sup>	155 (4)
O2 <sup>xiii</sup> —Si4—O3 <sup>xxxiii</sup>	100 (3)	Ni1 <sup>xi</sup> —O7—Si5 <sup>xxxiv</sup>	138 (3)
O2 <sup>xiii</sup> —Si4—O4 <sup>xiv</sup>	103 (2)	Si5 <sup>xv</sup> —O8—Si6 <sup>xxxv</sup>	138 (3)
O2 <sup>xiii</sup> —Si4—O12 <sup>xv</sup>	114 (3)	Ni1 <sup>xxxvi</sup> —O9—Si6 <sup>vii</sup>	129 (2)
O3 <sup>xiii</sup> —Si4—O4 <sup>xiv</sup>	115 (3)	Si2 <sup>xxi</sup> —O10—Si6 <sup>xxxiv</sup>	147 (4)
O3 <sup>xiii</sup> —Si4—O12 <sup>xv</sup>	104 (2)	Ni1 <sup>xxii</sup> —O11—Si3 <sup>ii</sup>	124 (3)
O4 <sup>xiv</sup> —Si4—O12 <sup>xv</sup>	120 (3)	Si4 <sup>xviii</sup> —O12—Si5 <sup>xxxii</sup>	133 (3)

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

The high value of  $S$  for  $\text{Cs}_2\text{NiSi}_5\text{O}_{12}$  is due to some unknown impurity phases present in the material. While impurity reflections were excluded from the refinement, it is possible that some which overlapped with  $\text{Cs}_2\text{NiSi}_5\text{O}_{12}$  reflections remained, resulting in a peak-shape fit not quite as good as expected.

For all compounds, data collection: in-house software; cell refinement: *PDPL REFCEL* (Murray, Cockcroft & Fitch, 1990); program(s) used to refine structure: *PDPL MPROF*; molecular graphics: *CERIUS* (Molecular Simulations Inc., 1994).

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Lists of raw powder data have been deposited with the IUCR (Reference: BR1125). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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