Data collection: CAD-4 Express (Enraf-Nonius, 1992). Cell refinement: CAD-4 Express. Data reduction: CADAK (Savariault, 1991a). Program(s) used to solve structure: SHELXS86 (Sheldrick, 1985). Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993). Molecular graphics: ORTEPII (Johnson, 1976). Software used to prepare material for publication: TABPUB (Savariault, 1991b).

The authors would like to thank Dr J. Galy for helpful discussions.

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.

References

- Brown, I. D. & Altermatt, D. (1985). Acta Cryst. B41, 244-247.
- Brown, I. D. & Shannon, R. D. (1973). Acta Cryst. A29, 266–282.
- Castro, A., Enjalbert, R., Schnuriger, B. & Galy, J. (1990). C. R. Acad. Sci. Paris Ser. C, 310, 1629-1632.
- Coppens, P., Leiserowitz, L. & Rabinovich, D. (1965). Acta Cryst. 18, 1035-1041.
- Darriet, J. & Galy, J. (1973). Cryst. Struct. Commun. 2, 237-243.
- Darriet, J., Guillaume, G., Wilhelmi, K. A. & Galy, J. (1972). Acta Chem. Scand. 26, 59-68.
- Déramond, E., Savariault, J. M. & Galy, J. (1994). Acta Cryst. C50, 164–166.
- Enjalbert, R., Savariault, J. M. & Galy, J. (1980). C. R. Acad. Sci. Paris Ser. C, 290, 239-242.
- Enraf-Nonius (1992). CAD-4 Express. Version 5.0. Enraf-Nonius, Delft, The Netherlands.
- Galy, J. (1992). J. Solid State Chem. 100, 229-236.
- Galy, J. & Carpy, A. (1975). Acta Cryst. B31, 1794-1795.
- Galy, J., Casalot, A., Pouchard, M. & Hagenmuller, P. (1966). C. R. Acad. Sci. Paris Ser. C, 262, 1055-1057.
- Galy, J. & Enjalbert, R. (1982). J. Solid State Chem. 44, 1-8.
- Galy, J., Meunier, G., Andersson, S. & Åström, A. (1975). J. Solid State Chem. 13, 142–148.
- Hirschinger, J., Mongrelet, T., Marichal, C., Granger, P., Savariault, J. M., Déramond, E. & Galy, J. (1993). J. Phys. Chem. 97, 10301– 10307.
- Johnson, C. K. (1976). ORTEPII. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Meunier, G., Darriet, J. & Galy, J. (1972). J. Solid State Chem. 5, 314-327.
- Meunier, G., Darriet, J. & Galy, J. (1973). J. Solid State Chem. 6, 67-78.
- Moore, P. B. & Louisnathan, J. (1969). Z. Kristallogr. 130, 438-442.
- Savariault, J. M. (1991a). CADAK. Programme de Réduction des Données du CAD-4. CEMES, France.
- Savariault, J. M. (1991b). TABPUB. Programme de Présentation des Tableaux pour Structure Cristalline. CEMES, France.
- Savariault, J. M., Déramond, E. & Galy, J. (1994). Z. Kristallogr. 209, 405-409.
- Savariault, J. M. & Galy, J. (1992). J. Solid State Chem. 101, 119-126.
- Sheldrick, G. M. (1985). SHELXS86. Crystallographic Computing 3, edited by G. M. Sheldrick, C. Krüger & R. Goddard, pp. 175–189. Oxford University Press.
- Sheldrick, G. M. (1993). SHELXL93. Program for Crystal Structure Refinement. University of Göttingen, Germany.

Acta Cryst. (1996). C52, 2132-2139

Rietveld Refinement of the Orthorhombic *Pbca* Structures of Rb₂CdSi₅O₁₂, Cs₂MnSi₅O₁₂, Cs₂CoSi₅O₁₂ and Cs₂NiSi₅O₁₂ Leucites by Synchrotron X-ray Powder Diffraction

A. M. T. BELL^a[†] AND C. M. B. HENDERSON^b

^aCCLRC Daresbury Laboratory, Daresbury, Warrington, Cheshire WA4 4AD, England, and ^bDepartment of Earth Sciences, University of Manchester, Manchester M13 9PL, England. E-mail: amtb2@cam.ac.uk

(Received 16 August 1995; accepted 4 March 1996)

Abstract

Analysis of high-resolution synchrotron X-ray powder diffraction patterns for hydrothermally synthesized $Rb_2CdSi_5O_{12}$ and $Cs_2MnSi_5O_{12}$ leucite analogues, and dry-synthesized $Cs_2CoSi_5O_{12}$ and $Cs_2NiSi_5O_{12}$ 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 $Cs_2MnSi_5O_{12}$, $Cs_2CoSi_5O_{12}$ and $Cs_2NiSi_5O_{12}$ leucite samples are unusual in containing SiO_4 tetrahedra which are more distorted, on average, than the larger MnO₄, CoO₄ and NiO₄ tetrahedra. The JCPDS file numbers for $Rb_2CdSi_5O_{12}$, $Cs_2MnSi_5O_{12}$ and $Cs_2CoSi_5O_{12}$ 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 $X_2ZSi_5O_{12}$ (X = K, Rb, Cs; Z = Mg, Mn, Fe²⁺, Co, Ni, Cu, Zn, Cd). The structures of these analogues are related to that of natural leucite (KAlSi₂O₆). 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. ²⁹Si magic-

[†] Present address: Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, England.

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, Rb₂CdSi₅O₁₂ and Cs₂MnSi₅O₁₂, and two drysynthesized leucites, Cs₂CoSi₅O₁₂ and Cs₂NiSi₅O₁₂. It is noteworthy that pairs of dry- and hydrothermally synthesized samples of the $Cs_2MnSi_5O_{12}$, $Cs_2CoSi_5O_{12}$ and Cs₂NiSi₅O₁₂ 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 Cs₂CdSi₅O₁₂ (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 Rb₂CdSi₅O₁₂, Cs₂MnSi₅O₁₂, $Cs_2CoSi_5O_{12}$ 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 Cs₂MnSi₅O₁₂, all of the atomic displacement parameters became negative, hence they were fixed at 0.25 $Å^2$. 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 Å^2 . ²⁹Si MAS NMR spectra (Kohn, Henderson & Dupree, 1994) of both Cs₂CdSi₅O₁₂ and Rb₂CdSi₅O₁₂ indicated



Fig. 1. Rietveld difference plot for hydrothermally synthesized Rb₂CdSi₅O₁₂.



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



Fig. 3. Rietveld difference plot for dry-synthesized Cs₂CoSi₅O₁₂.



Fig. 4. Rietveld difference plot for dry-synthesized Cs₂NiSi₅O₁₂.

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 $Cs_2CdSi_5O_{12}$. In $Cs_2CdSi_5O_{12}$, the Si—O distances within the SiO₄ tetrahedra are in the range 1.51-1.67 Å [mean 1.59 (5) Å]. The corresponding distances in $Rb_2CdSi_5O_{12}$, $Cs_2MnSi_5O_{12}$, $Cs_2OSi_5O_{12}$ and $Cs_2NiSi_5O_{12}$ 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 Cs₂CdSi₅O₁₂, 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 Rb₂CdSi₅O₁₂. The tetrahedral Mn—O, Co—O and Ni—O distances for Cs₂MnSi₅O₁₂, Cs₂CoSi₅O₁₂ and Cs₂NiSi₅O₁₂ 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 $Rb_2CdSi_5O_{12}$ (Fig. 5) to that of Cs in



Fig. 5. Projection of the structure of $Rb_2CdSi_5O_{12}$ along [111]. Dark tetrahedra represent CdO_4 units, light tetrahedra represent SiO_4 units, large circles represent Rb^+ cations and small circles represent O^{2-} anions.



Fig. 6. Projection of the structure of $Cs_2MnSi_5O_{12}$ along [111]. Dark tetrahedra represent MnO_4 units, light tetrahedra represent SiO_4 units, large circles represent Cs^+ cations and small circles represent O^{2-} anions.

 $Cs_2MnSi_5O_{12}$ (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 $Cs_2CoSi_5O_{12}$ and $Cs_2NiSi_5O_{12}$ are essentially the same as that of $Cs_2MnSi_5O_{12}$.

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 Δ) (*i.e.* greater distortion from the cubic *la3d* 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 Δ values of 1.033 and 1.016, respectively, and in the mean T-O-T angles of 135(12) and $140(13)^\circ$, respectively. Bell, Redfern, Henderson & Kohn (1994) pointed out that the O-T-O angle variances show that the divalentcation tetrahedra in K2MgSi5O12, Cs2CdSi5O12 and Cs₂CuSi₅O₁₂ leucite analogues are more distorted than the SiO₄ tetrahedra in each phase. Rb₂CdSi₅O₁₂ shows the same relationship, with O-T-O angle variances (σ^2 ; in units of degrees²) (Robinson, Gibbs & Ribbe, 1971) of 163 for CdO₄ and 26.4 for SiO₄. In each of these leucite analogues, the mean Si-O-Si intertetrahedral 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 Cs₂MnSi₅O₁₂, 1.005 for Cs₂CoSi₅O₁₂ and 1.003 for Cs₂NiSi₅O₁₂). 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)°, respectively, for $Cs_2MnSi_5O_{12}$; 137 (6) and 136 (8)° for $Cs_2CoSi_5O_{12}$, and 142 (10) and 135 (10)° for Cs₂NiSi₅O₁₂]. In addition (and unexpectedly), in all three samples the SiO₄ tetrahedra have larger tetrahedral-angle variances (degrees²) than the ZO₄ 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 intertetrahedral 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 SiO₄ tetrahedra in these three samples are more distorted. The different departures from pseudo-cubic symmetry for Rb₂CdSi₅O₁₂ and Cs₂MnSi₅O₁₂ 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 Rb₂CdSi₅O₁₂ 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 Cs₂MnSi₅O₁₂ 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.

Rb₂CdSi₅O₁₂

Crystal data

~	
$^{12}\text{CdSi}_{5}\text{O}_{12}$ = 615.76	Synchrotron radiation $\lambda = 1.40285 \text{ Å}$
- 015.70	$\lambda = 1.402$

Orthorhombic
Pbca
a = 13.4121 (1) Å
<i>b</i> = 13.6816 (1) Å
c = 13.8558 (1) Å
V = 2542.51 (5) Å ³
Z = 8
$D_{\rm r} = 3.217 {\rm Mg m^{-3}}$

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

T = 293 KPowder 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 $2\theta_{\min} = 5.00$,
$2\theta_{\rm max} = 125.00^{\circ}$
2θ increment = 0.01°
Dataset normalized for
decay of synchrotron
beam (PDPL PODSUM:
Murray, Cockcroft &
Fitch, 1990)
Al holder reflections
excluded

Refinement

0

08

09

0 0

0

$R_l = 0.073$	Weighting scheme: normal-
$R_{\rm wp} = 0.165$	ization factor/profile
$R_{\rm exp} = 0.174$	intensity + background
S = 0.903	Atomic scattering factors
Processed $2\theta_{\min} = 10.00$.	from International Tables
$2\theta_{\rm max} = 70.00^{\circ}$	for X-ray Crystallography
Increment in $2\theta = 0.01^{\circ}$	(1974, Vol. IV, Table
75 parameters	2.3.1)

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

	x	у	z	Biso
Rbl	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)
01	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)
04	0.7366 (9)	0.436(1)	0.611 (1)	0.2(1)
05	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)
07	0.984 (1)	0.897 (1)	0.671 (1)	0.2(1)
08	0.667 (1)	0.9683 (9)	0.838 (1)	0.2(1)
09	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)
011	0.134 (1)	0.1737 (8)	0.947 (1)	0.2(1)
012	0.884 (2)	0.159 (1)	0.1999 (9)	0.2 (1)

Table 2. Selected geometric parameters (Å, °) for Rb2CdSisO12

2.24 (1)	Rb1O1 ^{xxii}	3.79 (2)
2.20 (1)	Rb1O2 ^{xxiii}	3.37 (2)
2.20 (1)	Rb1-O3 ^{xxiv}	3.83 (2)
2.25 (1)	Rb1-O4 ^{xxv}	3.74 (2)
	2.24 (1) 2.20 (1) 2.20 (1) 2.25 (1)	$\begin{array}{llllllllllllllllllllllllllllllllllll$

 $O3^{xiii}$ —Si4—O4^{xiv}

 03^{xiii} —Si4—O12^{xv} O4^{xiv}—Si4—O12^{xv}

Rb₂CdSi₅O₁₂, Cs₂MnSi₅O₁₂, Cs₂CoSi₅O₁₂ AND Cs₂NiSi₅O₁₂

Si2 01 ⁹	1 50 (2)	Ph1 05XXVI	3 26 (2)	Data a	llastian				
512-01 512 03 ^{iv}	1.59 (2)	$P_{h1} = OS$	3.20(2)	Dala ce	niection				
512-05 512 05 ^{vi}	1.50 (1)		2 90 (2)	High-re	solution powd	er	Sample shape: in	regular	
Si2-010 ^{vii}	1.60(2)		3.08(2)	diffra	actometer. SRS	Method for scan	ning		
Si2_01 ^{viii}	1.57 (2)		340(2)	etatic	n 23 (Cernik				
Si3-01 Si3-02 ^{ix}	1.59 (2)	$Rb1 - O10^{xxix}$	3 56 (2)	Statuc	m 2.5 (Cermix,	F '. 1	acol 1	e. step scan	
Si3-06 ^x	1.62(2)	Rb1-O11 ^{xxx}	2.88 (2)	Murr	ay, Pattison &	Fitch,	9501 data points	measured	
Si3-Oll ^{xi}	1.57(2)	$Rb1 - O12^{xxxi}$	3.34(2)	1990	; Collins, Cern	ik,	6301 data points	in the	
Si4-O2 ^{xii}	1.64 (2)	Rb2-01	3.43 (2)	Pattis	son. Bell & Fit	ch.	processed diff	actogram	
Si4-03 ^{xiii}	1.61 (2)	Rb2—02	4.21 (2)	1002))	,	Measured 2A	- 5 00	
Si4-O4 ^{xiv}	1.56 (2)	Rb2—O3	3.34 (2)	D) 1	• • • •		- 5.00,	
Si4-012 ^{xv}	1.61 (2)	Rb2—O4 ^{xxviii}	2.85 (1)	Parallel	beam non-roc	using	$2\theta_{\rm max} = 100.00$)- 	
Si5-O5 ^{xvi}	1.63 (2)	Rb2—O5 ^{xxviii}	3.60 (2)	optic	s with channel	-	2θ increment = 0).01°	
Si5—O7 ^{xvii}	1.59 (2)	Rb2—O6 ^{xxvii}	3.39 (2)	cut n	nonochromator	and	Dataset normaliz	ed for	
Si5—O8 ^{xviii}	1.63 (2)	Rb2—O7 ^{vi}	3.42 (2)	scint	illation detector	r	decay of synch	rotron	
Si5—O12 ^{viii}	1.66 (2)	Rb2O8 ^x	4.13 (2)	Snaoim	an mounting.)5 mm	heem (PDPL)		
Si6—O6 ^{xix}	1.62 (2)	Rb2—O9 ^{xiv}	2.83 (2)	Specifi	en mountaing. 2	25 1111		ODSUM,	
Si6-08 ^{xx}	1.61 (2)	Rb2—O10 ^{xxii}	3.47 (2)	diam	eter $Si(100)$ su	bstrate	Murray, Cocke	croft &	
Si6-09 ^{xxi}	1.61 (2)	Rb2—O11 ^{xxxii}	3.42 (2)	in a l	Perspex sample	e	Fitch, 1990)		
Si6—O10 ^{xii}	1.62 (2)	Rb2-012xxiv	3.27 (2)	holde	er, sample mou	inted	Si substrate refle	ctions	
04 ⁱ Cd107 ⁱⁱ	89.2 (5)	O5 ^{xvi} —Si5—O7 ^{xvii}	117.9 (8)	on si	ubstrate with a	cetone	excluded		
O4 ⁱ Cd1O9 ⁱⁱⁱ	110.8 (6)	O5 ^{xvi} —Si5—O8 ^{xviii}	102.9 (8)						
04 ⁱ Cd1O11 ^{iv}	122.3 (6)	O5 ^{xvi} —Si5—O12 ^{viii}	107.2 (9)	Dafaan	ant				
07 ⁱⁱ Cd1O9 ⁱⁱⁱ	118.5 (5)	O7 ^{xvii} —Si5—O8 ^{xviii}	111.0 (9)	кејшен	ieni				
07 ⁱⁱ Cd1O11 ^{iv}	117.4 (6)	O7 ^{xvii} —Si5—O12 ^{viii}	109 (1)	$R_{i}=0.$	126		Weighting schem	ie: normal-	
O9 ⁱⁿ Cd1O11 ^{iv}	99.9 (6)	08 ^{xvm} —Si5—O12 ^{vm}	109 (1)	R = 0	140		ization factor/	orofile	
01 ^v —Si2—O3 ^{iv}	110 (1)	$O6^{x_1x}$ —Si6— $O8^{x_x}$	110.9 (9)	$\Lambda_{wp} = 0$	0.140		intensity + bac	kground	
01 ^v —Si2—O5 ^{vi}	113 (1)	O6 ^{x1x} —Si6—O9 ^{xx1}	107.4 (8)	$\kappa_{exp} = 0$	0.140		Atomic scottering	factors	
$O1^{v}$ —Si2—O10 ^{vu}	104.6 (9)	$O6^{x_1x}$ —Si6—O10 ^{x_1}	101.8 (8)	S = 1.0	19		Atomic scattering		
$O3^{1v}$ —Si2—O5 ^{v1}	106.3 (9)	O8 ^{xx} —Si6—O9 ^{xxi}	115.5 (9)	Process	ed $2\theta_{\min} = 15.0$	00.	from Internation	onal Tables	
$O3^{iv}$ —Si2—O10 ^{vii}	114.8 (9)	08 ^{xx} —Si6—O10 ^{xii}	101.9 (8)	28	$= 78.00^{\circ}$		for X-ray Crys	stallography	
O5 ^{**} —Si2—O10 ^{**}	108.3 (8)	O9***-Si6-O10***	118.5 (9)	Inonom	n = 70.00	10	(1974, Vol. IV	Table	
$O1^{\text{vin}}$ —Si3— $O2^{\text{ix}}$	104 (1)	Si2 ^{AAVII} —O1—Si3 ^{AAAII}	143 (1)	merem	20 = 0.0	1	231		
01 ^{viii} —Si3—O6 [*]	112 (1)	Si3***_O2_Si4***	140 (1)	71 para	meters		2.3.1)		
01 ^{viii} —Si3—011 ^{×i}	116 (1)	Si2***	143 (1)						
02^{14} —Si3—O6^	111.7 (9)	Cdl [^] -O4-Si4 ^{***}	120.0 (8)	Table	3. Fractional	l atomic	coordinates an	d isotropic	
02^011^*	107.7 (9)	S12 ⁿⁿ —O5—S15 ⁿⁿ	138 (1)				(12) for Co M	· C: O	
	104.9 (9)		144 (1)	ai	spiacement p	urameters	(A) for CS_2MP	13150_{12}	
02	105.1 (9)		127.2 (9)		x	v	z	Biso	
$02^{}51404^{7}$	107.8 (7)		141 (1)	Cs1	0.1294 (5)	0.1352 (4	0.1506 (3)	0.25	
$02 - 514 - 012^{22}$	108 (1)		119.3 (9)	Cs2	0.3777 (5)	0.3905 (3	0.3888 (3)	0.25	

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) $\begin{array}{c} x = \frac{1}{2}, \frac{1}{2} = y, 1 = 2; (\text{vir}) x, \frac{1}{2} = y, \frac{1}{2} + 2; (\text{virr}) x, \frac{1}{2} + x, \frac{1}{2} - 2; (\text{virr}) x, \frac{1}{$ $x = \frac{1}{2}, y, \frac{1}{2} = z;$ (xxv) $x = \frac{1}{2}, \frac{1}{2} = y, 1 = z;$ (xxvi) $1 = x, y = \frac{1}{2}, \frac{1}{2} = z;$ $(xxvii) \frac{1}{2} - x, 1 - y, z - \frac{1}{2}; (xxviii) 1 - x, 1 - y, 1 - z; (xxix) x, y - 1, z; (xxx) x, y, z - 1; (xxxi) x - 1, y, z; (xxxii) x, \frac{1}{2} - y, z - \frac{1}{2}; (xxxiii)$ $1-x, \frac{3}{2}+y, \frac{1}{2}-z; (xxxiv) 2-x, \frac{1}{2}+y, \frac{3}{2}-z; (xxxv) \frac{3}{2}-x, 2-y, \frac{1}{2}+z;$ $(xxxvi) \frac{1}{2} + x, \frac{3}{2} - y, 2 - z.$

Si2^{xxi}—O10—Si6^{xxiv}

 $\begin{array}{c} Si2 & -O10 & Si3^{ii} \\ Cd1^{xxii} - O11 - Si3^{ii} \\ Si4^{xviii} - O12 - Si5^{xxxii} \end{array}$

155 (1)

132 (1)

117.8 (9)

Mnl

Si2

Si3

Si4

Si5

Si6

01

02

O3

04

05

06

07

08

09

010

011

012

0.380(1)

0.126 (2)

0.584 (2)

0.654 (1)

0.898 (1)

0.834 (2)

0.465(2)

0.093 (2)

0.384 (3)

0.730 (2)

0.653 (3)

0.360 (3)

0.987 (2)

0.678 (2)

0.904 (2)

0.217 (2)

0.147 (3)

0.902 (3)

0.8374 (7)

0.665 (1)

0.110(1)

0.598 (1)

0.373 (1)

0.918 (1)

0.379 (3)

0.502 (2)

0.165 (2)

0.412 (3)

0.724 (2)

0.622 (2)

0.889 (3)

0.963 (2)

0.642 (2)

0.904 (3)

0.198 (2)

0.151 (2)

0.9337 (7)

0.596 (1)

0.634 (1)

0.111 (1)

0.818 (1)

0.353 (1)

0.166 (3)

0.416 (2)

0.475 (2)

0.625 (3)

0.364 (2)

0.756 (2)

0.650 (2)

0.851 (3)

0.926 (2)

0.143 (3)

0.923 (2)

0.200 (2)

0.25

0.25

0.25

0.25

0.25

0.25

0.25

0.25

0.25

0.25

0.25

0.25

0.25

0.25

0.25

0.25

0.25

0.25

116.0 (8)

104.4 (9)

114 (1)

		Table 4. Se	elected geomet	ric parameters	(Å, °) for
$Cs_2MnSi_5O_{12}$					
Crystal data		Mn104 ⁱ	1.99 (3)	Cs1—O1 ^{xxii}	3.76 (4)
		Mn107 ^u	1.99 (3)	Cs1—O2 ^{xxiii}	3.68 (3)
$Cs_2MnSi_5O_{12}$	Synchrotron radiation	Mn109 ¹¹¹	1.97 (2)	Cs1-O3 ^{xxiv}	3.80 (4)
$M_r = 653.17$	$\lambda = 1.29969 \text{ Å}$	Mn1—O11 ^{iv}	1.97 (2)	Cs1—O4 ^{xxv}	3.44 (4)
Orthorhombic	T = 293 K	Si2-O1	1.69 (4)	Cs1-O5 ^{xxvi}	3.23 (3)
Phog	I = 275 K	Si2-O3 ^{iv}	1.67 (3)	Cs1-O6 ^{xxvii}	3.66 (3)
	Powder	Si2—O5 ^{vi}	1.67 (3)	Cs1-07 ^{xxviii}	3.19 (3)
a = 13.68/8 (3) A	Pale pink	Si2—O10 ^{vii}	1.69 (4)	Cs1—O8 ^{xxviii}	2.96 (3)
b = 13.7931 (3) Å	Sample mounted in	Si3—O1 ^{viii}	1.70 (4)	Cs1—O9 ^{xxviii}	3.28 (3)
c = 137575(3)Å	reflection mode	Si3—O2 ^{ix}	1.69 (3)	Cs1-O10 ^{xxix}	3.41 (4)
$V = 2507 A(2) Å^{3}$	Teneedon mode	Si3—O6 ^x	1.71 (3)	Cs1011***	3.25 (3)
V = 2397.4 (2) A		Si3—O11 ^{xi}	1.69 (3)	Cs1-012***	3.19 (4)
Z = 8		Si4—O2 ^{xii}	1.61 (4)	Cs2—O1	3.29 (4)
$D_x = 3.341 \text{ Mg m}^{-3}$		Si4—O3 ^{xiii}	1.59 (3)	Cs2—O2	4.20 (3)

Si4—O4 ^{xiv}	1.61 (3)	Cs2—03	3.33 (3)
Si4-012 ^{xv}	1.63 (4)	Cs2—O4 ^{xxviii}	3.10 (3)
Si5-05 ^{xvi}	1.63 (3)	Cs2—O5 ^{xxviii}	3.77 (3)
Si5-07 ^{xvii}	1.66 (3)	Cs2—O6 ^{xxvii}	3.73 (4)
Si5-O8 ^{xviii}	1.68 (4)	Cs207 ^{vi}	3.43 (3)
Si5-O12 ^{viii}	1.65 (3)	Cs2—O8 ^x	3.80 (4)
Si6-O6 ^{xix}	1.64 (3)	Cs2—O9 ^{xiv}	3.06 (3)
Si6-08**	1.66 (3)	Cs2-010 ^{xx11}	3.62 (4)
Si6-09 ^{xxi}	1.62 (3)	Cs2	3.41 (3)
Si6—O10 ^{xii}	1.62 (3)	Cs2—O12 ^{xxiv}	3.54 (3)
O4 ⁱ Mn1O7 ⁱⁱ	98 (1)	O5 ^{xvi} —Si5—O7 ^{xvii}	114 (2)
O4 ⁱ —Mn1—O9 ⁱⁱⁱ	117 (2)	O5 ^{xvi} —Si5—O8 ^{xviii}	104 (2)
O4 ⁱ Mn1O11 ^{iv}	110 (1)	O5 ^{xvi} —Si5—O12 ^{viii}	104 (2)
07 ⁱⁱ —Mn1—O9 ⁱⁱⁱ	113 (1)	07 ^{xvii} Si5O8 ^{xviii}	114 (2)
07 ⁱⁱ Mn1011 ^{iv}	117 (2)	O7 ^{xvii} —Si5—O12 ^{viii}	105 (2)
O9 ⁱⁱⁱ —Mn1—O11 ^{iv}	104 (1)	O8 ^{xviii} Si5O12 ^{viii}	116 (2)
O1 ^v —Si2—O3 ^{iv}	120 (2)	$O6^{xix}$ —Si6— $O8^{xx}$	109 (1)
01 ^v Si2O5 ^{vi}	108 (2)	O6 ^{xix} —Si6—O9 ^{xxi}	106 (2)
O1 ^v Si2O10 ^{vii}	97 (2)	O6 ^{xix} —Si6—O10 ^{xii}	102 (2)
O3 ^{iv} —Si2—O5 ^{vi}	110 (2)	O8 ^{xx} —Si6—O9 ^{xxi}	126 (2)
O3 ^{iv} —Si2—O10 ^{vii}	117 (2)	O8 ^{xx} -Si6-O10 ^{xii}	91 (2)
O5 ^{vi} —Si2—O10 ^{vii}	103 (2)	O9 ^{xx} '—Si6—O10 ^x "	120 (2)
O1 ^{viii} —Si3—O2 ^{ix}	105 (2)	$Si2^{xxyu}$ —O1— $Si3^{xxxu}$	126 (2)
O1 ^{viii} —Si3—O6 ^x	101 (2)	$Si3^{xxv}$ —O2— $Si4^{xxv}$	134 (2)
O1 ^{viii} —Si3—O11 ^{xi}	124 (2)	Si2 ^{xxii} —O3—Si4 ^{xxvi}	135 (2)
O2 ^{ix} —Si3—O6 ^x	114 (2)	Mn I [*] —O4—Si4 ^{*vi}	131 (2)
O2 ^{ix} —Si3—O11 ^{xi}	115 (2)	Si2 ^{xix} —O5—Si5 ^{xiv}	142 (2)
O6 ^x —Si3—O11 ^{x1}	97 (2)	Si3 ¹ —O6—Si6 ^{v1}	152 (3)
O2 ^{xii} -Si4-O3 ^{xxxiii}	98 (2)	Mn1 ^{x1} —07—Si5 ^{xxx1v}	144 (2)
O2 ^{xii} —Si4—O4 ^{xiv}	118 (2)	Si5 ^{xv} —O8—Si6 ^{xxxv}	133 (2)
02 ^{x11} —Si4—O12 ^{xv}	108 (2)	Mn1 ^{xxxvi} —O9—Si6 ^{vii}	125 (2)
O3 ^{xiii} —Si4—O4 ^{xiv}	117 (2)	Si2xxi -O10-Si6xxiv	144 (3)
O3 ^{xiii} —Si4—O12 ^{xv}	98 (2)	Mn1 ^{xxn} —O11—Si3 ⁿ	130 (2)
O4 ^{xiv} —Si4—O12 ^{xv}	115 (2)	Si4 ^{xvm} —O12—Si5 ^{xxxn}	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) $x - \frac{1}{2}, \frac{3}{2} - y, 1 - z$; (vi) $x, \frac{3}{2} - y, \frac{1}{2} + z$; (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) $\frac{1}{2} + x, y, \frac{3}{2} - z$; (xi) $\frac{1}{2} + x, y, \frac{1}{2} - z;$ (xiii) $1 - x, \frac{1}{2} + y, \frac{1}{2} - z;$ (xiv) $\frac{3}{2} - x, 1 - y, z - \frac{1}{2};$ (xv) $\frac{1}{2} - x, \frac{1}{2} + y, z; (xvi) = -x, 1 - y, \frac{1}{2} + z; (xvii) = -x, y - \frac{1}{2}, \frac{3}{2} - z; (xvii) = -x, y - \frac{1}{2}, \frac{3}{2} - z; (xviii) = -x, y - \frac{1}{2}, \frac{3}{2} - z; (xviii) = -x, y - \frac{1}{2}, \frac{3}{2} - z; (xviii) = -x, y - \frac{1}{2}, \frac{3}{2} - z; (xviii) = -x, y - \frac{1}{2}, \frac{3}{2} - z; (xviii) = -x, y - \frac{1}{2}, \frac{3}{2} - z; (xviii) = -x, y - \frac{1}{2}, \frac{3}{2} - z; (xviii) = -x, y - \frac{1}{2}, \frac{3}{2} - z; (xviii) = -x, y - \frac{1}{2}, \frac{3}{2} - z; (xviii) = -x, y - \frac{1}{2}, \frac{3}{2} - z; (xvii) = -x, y - \frac{1}{2}, \frac{3}{2} - z; (xvii) = -x, y - \frac{1}{2}, \frac{3}{2} - z; (xvii) = -x, y - \frac{1}{2}, \frac{3}{2} - z; (xvii) = -x, y - \frac{1}{2}, \frac{3}{2} - z; (xvii) = -x, y - \frac{1}{2}, \frac{3}{2} - z; (xvi) = -x, y - \frac{1}{2}, \frac{3}{2} - z; (xvi) = -x, y - \frac{1}{2}, \frac{3}{2} - z; (xvi) = -x, y - \frac{1}{2}, \frac{3}{2} - z; (xvi) = -x, y - \frac{1}{2}, \frac{3}{2} - z; (xvi) = -x, y - \frac{1}{2}, \frac{3}{2} - z; (xvi) = -x, y - \frac{1}{2}, \frac{3}{2} - z; (xvi) = -x, y - \frac{1}{2}, \frac{1}{2}, \frac{1}{2} - z; (xvi) = -x, y - \frac{1}{2}, \frac{1}{2} - z; (xvi) = -x, y - \frac{1}{2}, \frac{1}{2} - x; (xvi) = -x, y - \frac{1}{2}, \frac{1}{2} - x; (xvi) = -x, y - \frac{1}{2}, \frac{1}{2} - x; (xv$ $\begin{array}{l} x, \frac{3}{2} - y, z - \frac{1}{2}; (xxii) \frac{1}{2} - x, y - \frac{1}{2}, z; (xxiii) -x, y - \frac{1}{2}, \frac{1}{2} - z; (xxiv) \\ x - \frac{1}{2}, y, \frac{1}{2} - z; (xxv) x - \frac{1}{2}, \frac{1}{2} - y, 1 - z; (xxvi) 1 - x, y - \frac{1}{2}, \frac{1}{2} - z; \end{array}$ $(xxvii) \frac{1}{2} - x, 1 - y, z - \frac{1}{2}; (xxviii) 1 - x, 1 - y, 1 - z; (xxix) x, y - 1, z;$ $\begin{array}{l} (xxx) & x, y, z - 1; (xxxi) & x - 1, y, z; (xxxii) & x, \frac{1}{2} - y, z - \frac{1}{2}; (xxxiii) \\ 1 - x, \frac{3}{2} + y, \frac{1}{2} - z; (xxxiv) & 2 - x, \frac{1}{2} + y, \frac{3}{2} - z; (xxxv) & \frac{3}{2} - x, 2 - y, \frac{1}{2} + z; \\ (xxxvi) & \frac{1}{2} + x, \frac{3}{2} - y, 2 - z. \end{array}$

Cs₂CoSi₅O₁₂

Crystal data

	Coursehungen andiation	Co1-O4 ⁱ	1.91 (4)	Cs1-O1 ^{xxii}	3.75 (5)
$Cs_2C0S1_5O_{12}$	Synchrotron radiation	Co1-07 ⁱⁱ	1.93 (4)	Cs1-O2 ^{xxiii}	3.66 (4)
$M_r = 657.16$	$\lambda = 1.301382 \text{ A}$	Col—O9 ⁱⁱⁱ	1.92 (3)	Cs1-O3 ^{xxiv}	3.73 (4)
Orthorhombic	T = 293 K	Col-Oll"	1.91 (3)	Cs1-O4 ^{xxv}	3.47 (4)
Phca	Powder	Si2-O1	1.66 (5)	Cs1-O5 ^{xxvi}	3.35 (5)
a = 12.6497 (A) Å	Cabalt blue	Si2—O3 ^{iv}	1.65 (4)	Cs1-O6****	3.90 (4)
u = 13.0487 (4) A		Si2—O5 ^{vi}	1.65 (4)	Cs1-07 ^{xxvm}	3.54 (5)
b = 13./120 (4) Å	Sample mounted in	Si2—O10 ^{vii}	1.67 (5)	Cs1-O8 ^{xxviii}	3.03 (4)
c = 13.6828 (4) Å	reflection mode	Si3-O1 ^{vin}	1.62 (4)	Cs1-O9 ^{xxviii}	3.04 (4)
V = 2560.7 (2) Å ³		Si3—O2 ^{1x}	1.60 (5)	Cs1-O10 ^{xx1x}	3.27 (5)
7 - 8		Si3—O6 ^x	1.61 (4)	Cs1-Oll ^{xxx}	3.37 (5)
L = 0		Si3-011 ^{x1}	1.63 (4)	$Cs1-O12^{xxx}$	3.35 (5)
$D_x = 3.409 \text{ Mg m}^{-1}$		Si4—O2 ^x "	1.60 (5)	Cs2—01	3.38 (5)
		Si4—O3 ^x	1.60 (5)	Cs2—02	4.20 (5)
Data collection		Si4—O4 ^{xiv}	1.61 (4)	Cs203	3.56 (4)
High resolution nowder	Sample shape: irregular	Si4—012**	1.62 (5)	Cs2-04****	3.23 (4)
	Sample shape. Inegular	Si5—O5 ^{xvi}	1.61 (5)	Cs2—O5***	3.74 (5)
diffractometer, SRS	Method for scanning	Si5—O7 ^{xvii}	1.62 (5)	Cs2—06****	3.38 (5)
station 2.3 (Cernik,	reciprocal space:	Si5—O8 ^{xviii}	1.64 (5)	Cs207 ^{vi}	3.26 (4)
Murray, Pattison & Fitch.	step scan	Si5—O12 ^{vm}	1.63 (5)	Cs2—O8 ^x	3.80 (5)
1000: Collins Cernik	8827 data points measured	Si6—O6 ^{xix}	1.66 (5)	$Cs2-09^{x1v}$	3.19 (5)
1990, Comis, Cernik,	6027 data points incasured	Si6—O8 ^{xx}	1.66 (4)	Cs2	3.75 (5)
Pattison, Bell & Fitch,	5776 data points in the	Si6—O9 ^{xxi}	1.66 (5)	Cs2—011****	3.42 (4)
1992)	processed diffractogram	Si6—O10 ^x "	1.65 (4)	$Cs2-O12^{xxiv}$	3.57 (4)

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

Refinement

 $R_{I} = 0.059$ $R_{wp} = 0.128$ $R_{\rm exp}=0.142$ S = 0.821Processed $2\theta_{\min} = 5.00$, $2\theta_{\text{max}} = 70.00^{\circ}$ Increment in $2\theta = 0.01^{\circ}$ 72 parameters

Measured $2\theta_{\min} = 5.00$, $2\theta_{\rm max} = 93.26^{\circ}$ 2θ increment = 0.01° Dataset normalized for decay of synchrotron beam (PDPL PODSUM; Murray, Cockcroft & Fitch, 1990) Si substrate 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 5. Fractional atomic coordinates and isotropic displacement parameters ($Å^2$) for $Cs_2CoSi_5O_{12}$

	x	у	z	Biso
Csl	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)
Col	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
01	0.470 (2)	0.380 (4)	0.158 (4)	0.1
02	0.092 (3)	0.490 (3)	0.407 (3)	0.1
03	0.384 (4)	0.147 (3)	0.478 (2)	0.1
04	0.733 (2)	0.404 (4)	0.627 (3)	0.1
05	0.644 (3)	0.724 (2)	0.365 (4)	0.1
06	0.409 (4)	0.600 (3)	0.744 (2)	0.1
07	0.988 (2)	0.896 (3)	0.624 (4)	0.1
08	0.673 (3)	0.960 (2)	0.848 (3)	0.1
09	0.892 (4)	0.656 (3)	0.927 (2)	0.1
O10	0.214 (3)	0.914 (3)	0.134 (4)	0.1
011	0.152 (3)	0.204 (2)	0.910 (4)	0.1
012	0.890 (4)	0.150 (3)	0.210 (3)	0.1

Table 6. Selected geometric parameters (Å, °) for $Cs_2CoSi_5O_{12}$

04 ⁱ Co1O7 ⁱⁱ 104 (2)	$O5^{xvi}$ —Si5— $O7^{xvii}$	113 (3)	Refinemen	t			
$O4^{i} = Co1 = O9^{ii}$ 121 (2) $O4^{i} = Co1 = O11^{iv}$ 104 (2)	05 - 315 - 08 $05^{xvi} - 815 - 012^{viii}$	96 (3)	$R_{I} = 0.057$	7	'	weighting scheme:	normai-
$O7^{ii}$ —Co1—O9 ⁱⁱⁱ 107 (2)	07 ^{xvii} —Si5—O8 ^{xviii}	112 (3)	$R_{wp} = 0.09$	91		ization factor/pr	onie
O7 ⁱⁱ —Co1—O11 ^{iv} 118 (2)	07 ^{xvii} —Si5—O12 ^{viii}	125 (3)	$R_{\rm exp} = 0.0$	27		intensity + back	grouna
$O9^{iii}$ —Co1—O11 ^{iv} 104 (2)	08 ^{xvm} Si5O12 ^{vm}	104 (3)	S = 11.810	D	1	Atomic scattering	actors
$O1^{v}$ —Si2— $O3^{iv}$ 112 (3)	$O6^{xix}$ —Si6— $O8^{xi}$	100 (2)	Processed	$2\theta_{\rm min} = 7.0$	0,	from Internation	al Tables
$O1^{v} = S12 = O5^{v} = 107(3)$	06^{xix} Si6 010^{xii}	135(2)	2 <i>θ</i>	52.00°	-,	for X-ray Crysta	llography
O_{3}^{iv} —Si2—O5 ^{vi} 117 (3)	08 ^{xx} —Si6—O9 ^{xxi}	131 (2)	Increment	in $2\theta = 0.0$)1°	(1974, Vol. IV, 1	lable
O3 ^{iv} —Si2—O10 ^{vii} 106 (3)	O8 ^{xx} —Si6—O10 ^{xii}	90 (2)	75 parame	eters	-	2.3.1)	
$O5^{vi}$ —Si2—O10 ^{vii} 113 (2)	09 ^{xx1} —Si6—O10 ^{x11}	111 (2)	75 purun				
$O1^{VIII}$ - Si3 - $O2^{IX}$ 97 (3)	$Si2^{xxxy} - O1 - Si3^{xxxy}$	135 (3)	Table 7	Frantiana	l atomic	coordinates and	isotropic
$O1^{vii}$ Si3 $O1^{vii}$ 126 (3)	$Si2^{xxii} - O3 - Si4^{xxvi}$	147 (4)			a atomic		· 0
$O2^{ix}$ —Si3— $O6^{x}$ 105 (3)	Col ^x O4Si4 ^{xvi}	138 (3)	disp	placement p	parameters	$S(A^2)$ for Cs_2NiS	$a_5 O_{12}$
$O2^{ix}$ —Si3—O11 ^{xi} 118 (2)	Si2 ^{xix} —O5—Si5 ^{xiv}	130 (3)		x	у	z	Biso
06^{x} —Si3—O11 ^{x1} 120 (3)	Si ³¹ —O6—Si ⁶	144 (3)	Csl	0.131 (1)	0.1306 (8)	0.1446 (6)	4.78 (8)
$O2^{AII}$ Si4 $O3^{AAIII}$ 96 (3)	$C01^{m} - 07 - 515^{m}$	145 (5)	Cs2	0.377 (1)	0.3848 (7)	0.3853(7)	4.78 (8)
$O2^{\text{xii}}$ $Si4$ $O2^{\text{xiv}}$ $115(3)$	Col^{xxxvi} — $O9$ — $Si6^{vii}$	126 (3)	N11 \$12	0.378(2) 0.124(3)	0.838(1) 0.672(2)	0.526(1)	2.0 (2)
O_{3}^{xiii} —Si4— O_{4}^{xiv} 110 (2)	Si2xxi -O10-Si6xxiv	141 (3)	Si2	0.584(2)	0.117 (2)	0.635 (2)	2.0 (2)
$O3^{xiii}$ —Si4—O12 ^{xv} 106 (3)	Col ^{xxii} —O11—Si3 ⁱⁱ	133 (3)	Si4	0.646 (2)	0.596 (2)	0.112 (2)	2.0 (2)
$O4^{xiv}$ —Si4—O12 ^{xv} 104 (3)	Si4 ^{xvm} —O12—Si5 ^{xxxn}	134 (3)	Si5	0.916 (2)	0.385 (2)	0.820 (2)	2.0 (2)
	2 . (1)	(:::)	Si6	0.831 (2)	0.913 (2)	0.355 (2)	2.0 (2)
Symmetry codes: (1) $1 - x, \frac{1}{2} + y$,	$\frac{3}{2} - z;$ (ii) $x - \frac{1}{2}, y, \frac{3}{2}$	- z; (III)	01	0.465 (2)	0.308(4) 0.487(2)	0.104(3) 0.416(3)	1.0(3)
$x - \frac{1}{2}, \frac{3}{2} - y, 2 - z;$ (1V) $\frac{1}{2} - x, \frac{1}{2} + \frac{1}{2}$	-y, z; (v) = -x, 1 - y,	$\frac{1}{2} + 2$, (VI)	02	0.401(4)	0.152 (4)	0.481 (3)	1.0 (3)
$x = \frac{1}{2}, \frac{3}{2} = y, 1 = z;$ (vii) $x, \frac{3}{2} = y$	$y_{\frac{1}{2}} + z_{1}$ (viii) $x_{1,\frac{1}{2}} - y_{1}$	$\frac{1}{2} + 2$, (IX)	04	0.737 (2)	0.397 (4)	0.617 (4)	1.0 (3)
$\frac{1}{2} + x, \frac{1}{2} - y, 1 - z, (x) - x, y - y$	$\frac{1}{2}, \frac{1}{2} = 2; (xi) \frac{1}{2} = x, j, \frac{1}{2}$	$z = \frac{1}{2}; (xy)$	05	0.618 (4)	0.711 (2)	0.380 (3)	1.0 (3)
$\frac{1}{2} + x, y, \frac{1}{2} - z, (xn) = x, \frac{1}{2} + y, \frac{1}{2}$	<i>z</i> ; (xvii) $2 - x, y - \frac{1}{2}, \frac{3}{2}$	-z; (xviii)	06	0.359 (3)	0.624 (4)	0.754(2)	1.0 (3)
$\frac{1}{2} - x, y = 1, 7; (xix) = 1 + x, \frac{3}{2} - y, 1$	$-z;$ (xx) $\frac{3}{2} - x, 2 - y, z$	$-\frac{1}{4}$; (xxi)	07	0.970(3)	0.891(4)	0.849(3)	1.0(3)
$x, \frac{3}{4} - y, z - \frac{1}{4}; (xxii)^2 - x, y - \frac{1}{4};$	z; (xxiii) $-x, y - \frac{1}{2}, \frac{1}{2}$	-z; (xxiv)	09	0.906 (3)	0.618 (4)	0.943 (2)	1.0 (3)
$x = \frac{1}{2}, y, \frac{1}{2} = z; (xxy) x = \frac{1}{2}, \frac{1}{2} = y,$	1 - z; (xxvi) $1 - x, y - z$	$-\frac{1}{2}, \frac{1}{2}-z;$	O10	0.215 (3)	0.890 (4)	0.145 (4)	1.0 (3)
$(xxvii) \frac{1}{2} - x, 1 - y, z - \frac{1}{2}; (xxviii) 1$	-x, 1-y, 1-z; (xxix)	x, y - 1, z;	011	0.141 (3)	0.201 (2)	0.937 (3)	1.0 (3)
(xxx) x, y, z - 1; (xxxi) x - 1, y, z	; (xxxii) $x, \frac{1}{2} - y, z - y$	$\frac{1}{3}$; (xxxiii)	012	0.919(3)	0.138 (3)	0.203(2)	1.0 (3)
	· · · · · · ·	1					
$1-x, \frac{3}{2}+y, \frac{1}{2}-z; (xxxiv) 2-x, \frac{1}{2}+$	$y, \frac{3}{2} - z; (x x x v) \frac{3}{2} - x, 2$	$2^2 - y, \frac{1}{2} + z;$	T-1-1- 0	Calanta		a nanamatana	$(\hat{\lambda} \circ)$ for
$\frac{1-x, \frac{3}{2}+y, \frac{1}{2}-z; (xxxiv) 2-x, \frac{1}{2}+}{(xxxvi) \frac{1}{2}+x, \frac{3}{2}-y, 2-z.}$	$y, \frac{3}{2} - z; (xxxy) \frac{3}{2} - x, 2$	$2^2 - y, \frac{1}{2} + z;$	Table 8	. Selected	geometri	ic parameters	(Å, °) for
$\frac{1-x, \frac{3}{2}+y, \frac{1}{2}-z; (xxxiv) 2-x, \frac{1}{2}+}{(xxxvi) \frac{1}{2}+x, \frac{3}{2}-y, 2-z.}$	$y, \frac{3}{2} - z; (xxxy) \frac{3}{2} - x, 2$	$2^2 - y, \frac{1}{2} + z;$	Table 8	S. Selected	geometri Cs ₂ NiS	ic parameters i ₅ O ₁₂	(\mathring{A}, \circ) for
$\frac{1-x, \frac{3}{2}+y, \frac{1}{2}-z; (xxxiv) 2-x, \frac{1}{2}+}{(xxxvi) \frac{1}{2}+x, \frac{3}{2}-y, 2-z.}$	$y, \frac{3}{2} - z; (x \bar{x} x v) \frac{3}{2} - x, 2$	$2^2 - y, \frac{1}{2} + z;$	Table 8	. Selected	geometri Cs ₂ NiS	ic parameters i_5O_{12} $Cs1-O1^{xxii}$ $Cs1-O2^{xxiii}$	(Å, °) for
$\frac{1-x, \frac{3}{2}+y, \frac{1}{2}-z; (xxxiv) 2-x, \frac{1}{2}+}{(xxxvi) \frac{1}{2}+x, \frac{3}{2}-y, 2-z.}$ Cs ₂ NiSi ₅ O ₁₂	$y, \frac{3}{2} - z; (x \bar{x} x v) \frac{3}{2} - x, 2$	$2^2 - y, \frac{1}{2} + z;$	Table 8 Ni104 ⁱ Ni1-07 ⁱⁱ Ni107 ⁱⁱ Ni1-09 ⁱⁱⁱ	. Selected	geometri Cs ₂ NiS 1.87 (4) 1.88 (5) 1.89 (4)	ic parameters i_5O_{12} Cs1-O1 ^{xxiii} Cs1-O2 ^{xxiiii} Cs1-O3 ^{xxiv}	(Å, °) for 3.83 (6) 3.50 (4) 3.58 (5)
$1 - x, \frac{3}{2} + y, \frac{1}{2} - z; (xxxiv) 2 - x, \frac{1}{2} + (xxxvi) \frac{1}{2} + x, \frac{3}{2} - y, 2 - z.$ Cs ₂ NiSi ₅ O ₁₂ Crystal data	$y, \frac{3}{2} - z; (x \bar{x} x v) \frac{3}{2} - x, 2$	$2^2 - y$, $\frac{1}{2} + z$;	Table 8 Ni104 ⁱ Ni1-07 ⁱⁱ Ni1-09 ⁱⁱⁱ Ni1-09 ⁱⁱⁱ Ni1-011 ⁱⁱ Ni1-011 ⁱⁱⁱ	S. Selected	geometri Cs ₂ NiS 1.87 (4) 1.88 (5) 1.89 (4) 1.89 (3)	ic parameters i_5O_{12} $Cs1-O1^{xxii}$ $Cs1-O2^{xxiii}$ $Cs1-O3^{xxiv}$ $Cs1-O4^{xxv}$	(Å, °) for 3.83 (6) 3.50 (4) 3.58 (5) 3.58 (5)
$1 - x, \frac{3}{2} + y, \frac{1}{2} - z; (xxxiv) 2 - x, \frac{1}{2} + (xxxvi) \frac{1}{2} + x, \frac{3}{2} - y, 2 - z.$ Cs ₂ NiSi ₅ O ₁₂ Crystal data Cs ₂ NiSi ₅ O ₁₂	$y, \frac{3}{2} - z; (xxxy) \frac{3}{2} - x, 2$ Synchrotron radiatio	$2^2 - y, \frac{1}{2} + z;$	Table 8 Ni1-04 ⁱ Ni1-07 ⁱⁱ Ni1-09 ⁱⁱⁱ Ni1-09 ⁱⁱⁱⁱ Ni1-011 ⁱⁱ Si2-01 ⁱⁱ	. Selected	geometri Cs ₂ NiS 1.87 (4) 1.88 (5) 1.89 (4) 1.89 (3) 1.62 (5)	ic parameters i_5O_{12} $C_{S1}-O_{1xiii}$ $C_{S1}-O_{2xiii}$ $C_{S1}-O_{3xiv}$ $C_{S1}-O_{4xv}$ $C_{S1}-O_{5xvi}$ $C_{S1}-O_{5xvi}$	(Å, °) for 3.83 (6) 3.50 (4) 3.58 (5) 3.58 (5) 3.61 (5) 3.61 (5)
$1 - x, \frac{3}{2} + y, \frac{1}{2} - z; (xxxiv) 2 - x, \frac{1}{2} + (xxxvi) \frac{1}{2} + x, \frac{3}{2} - y, 2 - z.$ Cs ₂ NiSi ₅ O ₁₂ Crystal data Cs ₂ NiSi ₅ O ₁₂ $M_{2} = 656.94$	y, $\frac{3}{2} - z$; (xxxy) $\frac{3}{2} - x$, 2 Synchrotron radiatio $\lambda = 0.99820$ Å	$2^2 - y, \frac{1}{2} + z;$	Table 8 Ni1-O7 ⁱⁱ Ni1-O7 ⁱⁱ Ni1-O9 ⁱⁱⁱ Ni1-O11 ⁱⁱⁱ Si2-O1 ⁱ Si2-O3 ^{iv} Si2-O3 ^{iv} Si2-O3 ^{iv}	. Selected	<i>geometric</i> <i>Cs</i> ₂ <i>NiS</i> 1.87 (4) 1.88 (5) 1.89 (4) 1.89 (3) 1.62 (5) 1.63 (5) 1.63 (5)	ic parameters i_5O_{12} $C_{S1}=O1^{xxii}$ $C_{S1}=O2^{xxii}$ $C_{S1}=O3^{xxiv}$ $C_{S1}=O4^{xxv}$ $C_{S1}=O5^{xxvi}$ $C_{S1}=O5^{xxvi}$ $C_{S1}=O5^{xxvii}$	(Å, °) for 3.83 (6) 3.50 (4) 3.58 (5) 3.58 (5) 3.61 (5) 3.67 (5) 3.07 (5)
$1 - x, \frac{3}{2} + y, \frac{1}{2} - z; (xxxiv) 2 - x, \frac{1}{2} + (xxxvi) \frac{1}{2} + x, \frac{3}{2} - y, 2 - z.$ Cs ₂ NiSi ₅ O ₁₂ Crystal data Cs ₂ NiSi ₅ O ₁₂ $M_r = 656.94$ Orthorhombic	Synchrotron radiatio $\lambda = 0.99820 \text{ Å}$ T = 293 K	$2^2 - y, \frac{1}{2} + z;$	Table 8 Ni1-O4 ⁱ Ni1-O7 ⁱⁱ Ni1-O9 ⁱⁱⁱ Ni1-O11 ⁱⁱ Si2-O1 ^v Si2-O3 ^{vi} Si2-O10 ^{vi} Si2-O10 ^{vi}	. Selected	<i>geometric</i> <i>Cs</i> ₂ <i>NiS</i> 1.87 (4) 1.88 (5) 1.89 (4) 1.89 (3) 1.62 (5) 1.63 (5) 1.63 (4) 1.64 (6)	ic parameters i_5O_{12} $C_{51}-O_{12}^{xxii}$ $C_{51}-O_{2xxii}^{xxii}$ $C_{51}-O_{3xiv}^{xxiv}$ $C_{51}-O_{4xvi}^{xxv}$ $C_{51}-O_{5xvii}^{5xvii}$ $C_{51}-O_{7xviii}^{5xviii}$	(Å, °) for 3.83 (6) 3.50 (4) 3.58 (5) 3.61 (5) 3.67 (5) 3.02 (5) 3.11 (4)
$1 - x, \frac{3}{2} + y, \frac{1}{2} - z; (xxxiv) 2 - x, \frac{1}{2} + (xxxvi) \frac{1}{2} + x, \frac{3}{2} - y, 2 - z.$ Cs ₂ NiSi ₅ O ₁₂ Crystal data Cs ₂ NiSi ₅ O ₁₂ $M_r = 656.94$ Orthorhombic Pbca	Synchrotron radiatio $\lambda = 0.99820$ Å T = 293 K Powder	$2^2 - y, \frac{1}{2} + z;$	Table 8 Ni1-O4 ⁱ Ni1-O7 ⁱⁱ Ni1-O9 ⁱⁱⁱ Ni1-O11 ⁱⁱ Si2-O1 ^v Si2-O3 ^v Si2-O5 ^{vi} Si2-O1 ^{vi} Si2-O1 ^{viii} Si2-O1 ^{viii}	. Selected	<i>geometric</i> <i>Cs</i> ₂ <i>NiS</i> 1.87 (4) 1.88 (5) 1.89 (4) 1.89 (3) 1.62 (5) 1.63 (5) 1.63 (4) 1.64 (6) 1.68 (4)	ic parameters i_5O_{12} $C_{51}-O_{12}^{xxii}$ $C_{51}-O_{2xxii}^{xxii}$ $C_{51}-O_{3xii}^{xxii}$ $C_{51}-O_{4xv}^{xv}$ $C_{51}-O_{5xvii}^{xxvii}$ $C_{51}-O_{5xvii}^{xxvii}$ $C_{51}-O_{5xvii}^{xxvii}$ $C_{51}-O_{9xvii}^{xxvii}$	(Å, °) for 3.83 (6) 3.50 (4) 3.58 (5) 3.58 (5) 3.61 (5) 3.67 (5) 3.02 (5) 3.11 (4) 3.67 (5)
$1 - x, \frac{3}{2} + y, \frac{1}{2} - z; (xxxiv) 2 - x, \frac{1}{2} + (xxxvi) \frac{1}{2} + x, \frac{3}{2} - y, 2 - z.$ Cs ₂ NiSi ₅ O ₁₂ Crystal data Cs ₂ NiSi ₅ O ₁₂ $M_r = 656.94$ Orthorhombic Pbca $a = 13.6147$ (3) Å	Synchrotron radiatio $\lambda = 0.99820$ Å T = 293 K Powder Purple-blue	$2^2 - y, \frac{1}{2} + z;$	Table 8 Ni1-O4 ⁱ Ni1-O7 ⁱⁱ Ni1-O9 ⁱⁱⁱ Ni1-O9 ⁱⁱⁱ Si2-O1 ^v Si2-O5 ^{vi} Si2-O5 ^{vi} Si2-O1 ^{viii} Si3-O1 ^{viii} Si3-O2 ^{ia}	. Selected	$\begin{array}{c} geometric \\ Cs_2NiS \\ 1.87 (4) \\ 1.88 (5) \\ 1.89 (4) \\ 1.89 (3) \\ 1.62 (5) \\ 1.63 (5) \\ 1.63 (4) \\ 1.64 (6) \\ 1.68 (4) \\ 1.67 (5) \end{array}$	ic parameters i_5O_{12} $C_{S1}=01^{xxii}$ $C_{S1}=02^{xxiii}$ $C_{S1}=03^{xxii}$ $C_{S1}=04^{xxv}$ $C_{S1}=06^{xxvii}$ $C_{S1}=06^{xxvii}$ $C_{S1}=06^{xxviii}$ $C_{S1}=08^{xxviii}$ $C_{S1}=008^{xxviii}$ $C_{S1}=010^{xxx}$	(Å, °) for 3.83 (6) 3.50 (4) 3.58 (5) 3.61 (5) 3.67 (5) 3.02 (5) 3.11 (4) 3.67 (5) 3.48 (6)
$1 - x, \frac{3}{2} + y, \frac{1}{2} - z; (xxxiv) 2 - x, \frac{1}{2} + (xxxvi) \frac{1}{2} + x, \frac{3}{2} - y, 2 - z.$ Cs ₂ NiSi ₅ O ₁₂ Crystal data Cs ₂ NiSi ₅ O ₁₂ M _r = 656.94 Orthorhombic Pbca a = 13.6147 (3) Å b = 13.6568 (5) Å	Synchrotron radiation $\lambda = 0.99820$ Å T = 293 K Powder Purple-blue Sample mounted in	$2^2 - y, \frac{1}{2} + z;$	Table 8 Ni1-O4 ⁱ Ni1-O7 ⁱⁱ Ni1-O9 ⁱⁱⁱ Ni1-O11 ⁱⁱ Si2-O1 ^v Si2-O5 ^{vi} Si2-O5 ^{vi} Si3-O1 ^{viii} Si3-O2 ^{ix} Si3-O6 ⁱ	. Selected	$\begin{array}{c} geometric \\ Cs_2NiS \\ 1.87 (4) \\ 1.88 (5) \\ 1.89 (4) \\ 1.89 (3) \\ 1.62 (5) \\ 1.63 (5) \\ 1.63 (4) \\ 1.64 (6) \\ 1.68 (4) \\ 1.67 (5) \\ 1.71 (4) \\ 1.71$	ic parameters i_5O_{12} Cs101 ^{xxii} Cs102 ^{xxiii} Cs103 ^{xxii} Cs104 ^{xxv} Cs106 ^{xxvii} Cs106 ^{xxvii} Cs106 ^{xxviii} Cs108 ^{xxviii} Cs109 ^{xxviii} Cs1010 ^{xxx} Cs1011 ^{xxx} Cs1012 ^{xxx}	(Å, °) for 3.83 (6) 3.50 (4) 3.58 (5) 3.61 (5) 3.67 (5) 3.02 (5) 3.11 (4) 3.67 (5) 3.48 (6) 2.99 (4) 3.00 (5)
$1-x, \frac{3}{2}+y, \frac{1}{2}-z; (xxxiv) 2-x, \frac{1}{2}+(xxxvi) \frac{1}{2}+x, \frac{3}{2}-y, 2-z.$ Cs ₂ NiSi ₅ O ₁₂ Crystal data Cs ₂ NiSi ₅ O ₁₂ M _r = 656.94 Orthorhombic Pbca a = 13.6147 (3) Å b = 13.6568 (5) Å c = 13.6583 (5) Å	Synchrotron radiation $\lambda = 0.99820 \text{ Å}$ T = 293 K Powder Purple-blue Sample mounted in reflection mode	$2^2 - y, \frac{1}{2} + z;$	Table 8 Ni1O4 ⁱ Ni1-O7 ⁱⁱ Ni1-O9 ⁱⁱⁱ Ni1-O9 ⁱⁱⁱ Si2-O1 ⁱ Si2-O5 ⁱⁱⁱ Si2-O5 ⁱⁱⁱ Si3-O1 ⁱⁱⁱⁱ Si3-O2 ⁱⁱⁱ Si3-O2 ⁱⁱⁱ Si3-O1 ⁱⁱⁱⁱ Si3-O1 ⁱⁱⁱⁱ Si3-O1 ⁱⁱⁱⁱ Si3-O1 ⁱⁱⁱⁱ	. Selected	$\begin{array}{c} geometric \\ Cs_2NiS \\ 1.87 (4) \\ 1.88 (5) \\ 1.89 (4) \\ 1.89 (3) \\ 1.62 (5) \\ 1.63 (5) \\ 1.63 (5) \\ 1.63 (4) \\ 1.64 (6) \\ 1.68 (4) \\ 1.67 (5) \\ 1.71 (4) \\ 1.71 (4) \\ 1.71 (4) \\ 1.60 (4) \\ \end{array}$	ic parameters i_5O_{12} $C_{S1} = 01^{xxii}$ $C_{S1} = 03^{xxii}$ $C_{S1} = 03^{xxii}$ $C_{S1} = 04^{xxv}$ $C_{S1} = 06^{xxvii}$ $C_{S1} = 06^{xxvii}$ $C_{S1} = 06^{xxvii}$ $C_{S1} = 00^{xxviii}$ $C_{S1} = 00^{xxviii}$ $C_{S1} = 010^{xxxi}$ $C_{S1} = 010^{xxxi}$ $C_{S1} = 012^{xxxi}$ $C_{S1} = 012^{xxxi}$	(Å, °) for 3.83 (6) 3.50 (4) 3.58 (5) 3.58 (5) 3.61 (5) 3.67 (5) 3.02 (5) 3.11 (4) 3.67 (5) 3.48 (6) 2.99 (4) 3.00 (5) 3.26 (5)
$1-x, \frac{3}{2}+y, \frac{1}{2}-z; (xxxiv) 2-x, \frac{1}{2}+(xxxvi) \frac{1}{2}+x, \frac{3}{2}-y, 2-z.$ Cs ₂ NiSi ₅ O ₁₂ Crystal data Cs ₂ NiSi ₅ O ₁₂ M _r = 656.94 Orthorhombic Pbca a = 13.6147 (3) Å b = 13.6568 (5) Å c = 13.6583 (5) Å V = 2539.5 (1) Å ³	Synchrotron radiation $\lambda = 0.99820$ Å T = 293 K Powder Purple-blue Sample mounted in reflection mode	$2^2 - y, \frac{1}{2} + z;$	Table 8 Ni1O4 ⁱ Ni1-O7 ⁱⁱ Ni1-O9 ⁱⁱⁱ Ni1-O11 ⁱⁱ Si2-O3 ⁱⁱⁱ Si2-O5 ⁱⁱⁱ Si3-O1 ⁱⁱⁱⁱ Si3-O2 ⁱⁱⁱ Si3-O1 ⁱⁱⁱⁱ Si3-O11 ^{xiii} Si4-O2 ^{xiii} Si4-O2 ^{xiiii}	. Selected	$\begin{array}{c} geometric \\ Cs_2NiS \\ 1.87 (4) \\ 1.88 (5) \\ 1.89 (4) \\ 1.89 (3) \\ 1.62 (5) \\ 1.63 (5) \\ 1.63 (4) \\ 1.64 (6) \\ 1.68 (4) \\ 1.67 (5) \\ 1.71 (4) \\ 1.71 (4) \\ 1.71 (4) \\ 1.60 (5) \\ \end{array}$	ic parameters i_5O_{12} $C_{S1} = 0^{1xii}$ $C_{S1} = 0^{2xiii}$ $C_{S1} = 0^{3xiv}$ $C_{S1} = 0^{5xvi}$ $C_{S1} = 0^{5xvi}$ $C_{S1} = 0^{5xvii}$ $C_{S1} = 0^{5xvii}$ $C_{S1} = 0^{7xviii}$ $C_{S1} = 0^{9xviii}$ $C_{S1} = 0^{9xviii}$ $C_{S1} = 0^{12xxi}$ $C_{S1} = 0^{12xxi}$ $C_{S1} = 0^{12xxi}$ $C_{S1} = 0^{12xxi}$ $C_{S2} = 0^{12xxi}$	(Å, °) for 3.83 (6) 3.50 (4) 3.58 (5) 3.61 (5) 3.67 (5) 3.02 (5) 3.11 (4) 3.67 (5) 3.48 (6) 2.99 (4) 3.00 (5) 3.26 (5) 3.73 (6)
$1-x, \frac{3}{2}+y, \frac{1}{2}-z; (xxxiv) 2-x, \frac{1}{2}+(xxxvi) \frac{1}{2}+x, \frac{3}{2}-y, 2-z.$ Cs ₂ NiSi ₅ O ₁₂ Crystal data Cs ₂ NiSi ₅ O ₁₂ M _r = 656.94 Orthorhombic Pbca a = 13.6147 (3) Å b = 13.6568 (5) Å c = 13.6583 (5) Å V = 2539.5 (1) Å ³ Z = 8	Synchrotron radiatio $\lambda = 0.99820$ Å T = 293 K Powder Purple-blue Sample mounted in reflection mode	$z^2 - y, \frac{1}{2} + z;$	Table 8 Ni1 -04^{i} Ni1 -07^{ii} Ni1 -09^{ii} Ni1 -011^{ii} Si2 -01^{v} Si2 -03^{v} Si2 -05^{vi} Si3 -01^{vii} Si3 -01^{vii} Si3 -02^{ix} Si3 -02^{ix} Si3 -01^{vii} Si3 -01^{vii}	. Selected	$\begin{array}{c} geometric \\ Cs_2NiS \\ 1.87 (4) \\ 1.88 (5) \\ 1.89 (4) \\ 1.89 (3) \\ 1.62 (5) \\ 1.63 (5) \\ 1.63 (5) \\ 1.63 (4) \\ 1.64 (6) \\ 1.68 (4) \\ 1.67 (5) \\ 1.71 (4) \\ 1.71 (4) \\ 1.71 (4) \\ 1.71 (4) \\ 1.60 (5) \\ 1.59 (4) \end{array}$	$\begin{array}{c} c parameters \\ i_5 O_{12} \\ Cs1 - O1^{xxii} \\ Cs1 - O2^{xxiii} \\ Cs1 - O3^{xxiv} \\ Cs1 - O4^{xxv} \\ Cs1 - O5^{xxvii} \\ Cs1 - O6^{xxvii} \\ Cs1 - O7^{xxviii} \\ Cs1 - O7^{xxviii} \\ Cs1 - O9^{xxviii} \\ Cs1 - O9^{xxviii} \\ Cs1 - O10^{xxx} \\ Cs1 - O10^{xxx} \\ Cs1 - O12^{xxxi} \\ Cs1 - O12^{xxxi} \\ Cs1 - O12^{xxxi} \\ Cs1 - O12^{xxxi} \\ Cs2 - O1 \\ Cs2 - O2 \\ Cs2 - O2 \\ Cs2 - O3 \\ Cs$	(\mathring{A}, \circ) for 3.83 (6) 3.50 (4) 3.58 (5) 3.58 (5) 3.61 (5) 3.67 (5) 3.02 (5) 3.11 (4) 3.67 (5) 3.48 (6) 2.99 (4) 3.00 (5) 3.26 (5) 3.73 (6) 3.45 (5)
$1-x, \frac{3}{2}+y, \frac{1}{2}-z; (xxxiv) 2-x, \frac{1}{2}+(xxxvi) \frac{1}{2}+x, \frac{3}{2}-y, 2-z.$ Cs ₂ NiSi ₅ O ₁₂ Crystal data Cs ₂ NiSi ₅ O ₁₂ M _r = 656.94 Orthorhombic Pbca a = 13.6147 (3) Å b = 13.6568 (5) Å c = 13.6583 (5) Å V = 2539.5 (1) Å ³ Z = 8 D _r = 3.437 Mg m ⁻³	Synchrotron radiatio $\lambda = 0.99820$ Å T = 293 K Powder Purple-blue Sample mounted in reflection mode	$2^2 - y, \frac{1}{2} + z;$	Table 8 Ni1-O4 ¹ Ni1-O7 ¹⁰ Ni1-O9 ¹⁰ Ni1-O9 ¹⁰ Ni1-O11 ¹⁰ Si2-O1 ¹⁰ Si2-O5 ¹¹ Si2-O5 ¹¹ Si3-O1 ¹¹⁰ Si3-O1 ¹¹⁰ Si3-O1 ¹¹⁰ Si3-O6 ¹¹ Si4-O2 ¹¹⁰ Si4-O2 ¹¹⁰ Si4-O2 ¹¹⁰ Si4-O2 ¹¹⁰ Si4-O2 ¹¹⁰ Si4-O2 ¹¹⁰	Selected	$\begin{array}{c} geometric \\ Cs_2NiS \\ 1.87 (4) \\ 1.88 (5) \\ 1.89 (4) \\ 1.89 (3) \\ 1.62 (5) \\ 1.63 (5) \\ 1.63 (4) \\ 1.64 (6) \\ 1.68 (4) \\ 1.67 (5) \\ 1.71 (4) \\ 1.71 (4) \\ 1.71 (4) \\ 1.71 (4) \\ 1.60 (5) \\ 1.59 (4) \\ 1.62 (5) \\ 1.62 (5) \\ 1.61 (6) \\ 1.61 (6) \\ 1.62 (5) \\ 1.62 (5) \\ 1.61 (6) \\ 1.61$	ic parameters i_5O_{12} $C_{S1} = 01^{xxii}$ $C_{S1} = 02^{xxiii}$ $C_{S1} = 03^{xxiv}$ $C_{S1} = 04^{xxv}$ $C_{S1} = 06^{xxvii}$ $C_{S1} = 06^{xxvii}$ $C_{S1} = 06^{xxvii}$ $C_{S1} = 00^{xxviii}$ $C_{S1} = 00^{xxviii}$ $C_{S1} = 00^{xxviii}$ $C_{S1} = 010^{xxix}$ $C_{S1} = 010^{xxix}$ $C_{S1} = 010^{xxix}$ $C_{S1} = 010^{xxix}$ $C_{S1} = 010^{xxix}$ $C_{S2} = 010^{xxviii}$ $C_{S2} = 02^{xxviii}$ $C_{S2} = 02^{xxviii}$	(\mathring{A}, \circ) for 3.83 (6) 3.50 (4) 3.58 (5) 3.58 (5) 3.61 (5) 3.67 (5) 3.02 (5) 3.11 (4) 3.67 (5) 3.48 (6) 2.99 (4) 3.00 (5) 3.26 (5) 3.36 (5) 3.36 (5) 3.47 (4)
$1-x, \frac{3}{2}+y, \frac{1}{2}-z; (xxxiv) 2-x, \frac{1}{2}+(xxxvi) \frac{1}{2}+x, \frac{3}{2}-y, 2-z.$ Cs ₂ NiSi ₅ O ₁₂ Crystal data Cs ₂ NiSi ₅ O ₁₂ M _r = 656.94 Orthorhombic Pbca a = 13.6147 (3) Å b = 13.6568 (5) Å c = 13.6583 (5) Å V = 2539.5 (1) Å ³ Z = 8 D _x = 3.437 Mg m ⁻³	Synchrotron radiatio $\lambda = 0.99820$ Å T = 293 K Powder Purple-blue Sample mounted in reflection mode	$2^2 - y, \frac{1}{2} + z;$	Table 8 Ni1-O4 ¹ Ni1-O7 ⁱⁱ Ni1-O9 ⁱⁱⁱ Ni1-O9 ⁱⁱⁱ Ni1-O1 ¹ⁱ Si2-O1 ² Si2-O1 ² Si2-O5 ¹ⁱ Si3-O1 ¹ Si3-O1 ²ⁱⁱ Si3-O1 ²ⁱⁱ Si3-O1 ²ⁱⁱ Si4-O2 ²ⁱⁱ Si4-O2 ²ⁱⁱ Si4-O1 ^{2^x} Si5-O5 ^{xii}	Selected	$\begin{array}{c} geometric \\ Cs_2NiS \\ 1.87 (4) \\ 1.88 (5) \\ 1.89 (4) \\ 1.89 (3) \\ 1.62 (5) \\ 1.63 (5) \\ 1.63 (4) \\ 1.64 (6) \\ 1.64 (6) \\ 1.68 (4) \\ 1.67 (5) \\ 1.71 (4) \\ 1.71 (4) \\ 1.71 (4) \\ 1.71 (4) \\ 1.60 (5) \\ 1.59 (4) \\ 1.62 (5) \\ 1.61 (5) \\ 1.59 (5) \\ \end{array}$	ic parameters i_5O_{12} $C_{S1} = 01^{xxii}$ $C_{S1} = 02^{xxiii}$ $C_{S1} = 03^{xxiv}$ $C_{S1} = 04^{xxv}$ $C_{S1} = 06^{xxvii}$ $C_{S1} = 06^{xxvii}$ $C_{S1} = 06^{xxviii}$ $C_{S1} = 008^{xxviii}$ $C_{S1} = 010^{xxix}$ $C_{S1} = 010^{xxix}$ $C_{S1} = 010^{xxix}$ $C_{S1} = 010^{xxix}$ $C_{S1} = 010^{xxix}$ $C_{S2} = 02$ $C_{S2} = 02$ $C_{S2} = 02^{xxviii}$ $C_{S2} = 06^{xxviii}$	(\mathring{A}, \circ) for 3.83 (6) 3.50 (4) 3.58 (5) 3.58 (5) 3.61 (5) 3.67 (5) 3.02 (5) 3.11 (4) 3.67 (5) 3.48 (6) 2.99 (4) 3.00 (5) 3.26 (5) 3.36 (5) 3.36 (5) 3.47 (4) 3.68 (5)
$1-x, \frac{3}{2}+y, \frac{1}{2}-z; (xxxiv) 2-x, \frac{1}{2}+(xxxvi) \frac{1}{2}+x, \frac{3}{2}-y, 2-z.$ Cs ₂ NiSi ₅ O ₁₂ Crystal data Cs ₂ NiSi ₅ O ₁₂ M _r = 656.94 Orthorhombic Pbca a = 13.6147 (3) Å b = 13.6568 (5) Å c = 13.6583 (5) Å V = 2539.5 (1) Å ³ Z = 8 D _x = 3.437 Mg m ⁻³ Data collection	Synchrotron radiatio $\lambda = 0.99820$ Å T = 293 K Powder Purple-blue Sample mounted in reflection mode	$2^2 - y, \frac{1}{2} + z;$	Table 8 Ni1-O4 ¹ Ni1-O7 ¹⁰ Ni1-O9 ¹⁰ Ni1-O9 ¹⁰ Ni1-O1 ¹⁰ Si2-O1 ¹⁰ Si2-O1 ¹⁰ Si2-O5 ¹⁰ Si3-O1 ¹⁰ Si3-O1 ¹⁰ Si3-O1 ¹⁰ Si3-O1 ¹⁰ Si4-O2 ¹¹⁰ Si4-O2 ¹²⁰ Si5-O5 ¹⁰⁰ Si5-O7 ¹⁰⁰	S. Selected	$\begin{array}{c} geometric \\ Cs_2NiS \\ 1.87 (4) \\ 1.88 (5) \\ 1.89 (4) \\ 1.89 (3) \\ 1.62 (5) \\ 1.63 (5) \\ 1.63 (4) \\ 1.64 (6) \\ 1.64 (6) \\ 1.68 (4) \\ 1.67 (5) \\ 1.71 (4) \\ 1.71 (4) \\ 1.71 (4) \\ 1.71 (4) \\ 1.59 (4) \\ 1.62 (5) \\ 1.59 (5) \\ 1.62$	ic parameters i_5O_{12} $C_{S1} = 01^{xxii}$ $C_{S1} = 02^{xxiii}$ $C_{S1} = 03^{xxiv}$ $C_{S1} = 04^{xxv}$ $C_{S1} = 06^{xxvii}$ $C_{S1} = 06^{xxvii}$ $C_{S1} = 07^{xxviii}$ $C_{S1} = 00^{xxviii}$ $C_{S1} = 010^{xxxi}$ $C_{S1} = 010^{xxxi}$ $C_{S1} = 010^{xxxi}$ $C_{S1} = 010^{xxxi}$ $C_{S1} = 010^{xxxi}$ $C_{S2} = 02$ $C_{S2} = 03$ $C_{S2} = 04^{xxviii}$ $C_{S2} = 05^{xxviii}$ $C_{S2} = 06^{xxviii}$ $C_{S2} = 07^{vi}$	(\mathring{A}, \circ) for 3.83 (6) 3.50 (4) 3.58 (5) 3.58 (5) 3.61 (5) 3.67 (5) 3.02 (5) 3.11 (4) 3.67 (5) 3.148 (6) 2.99 (4) 3.00 (5) 3.26 (5) 3.36 (5) 3.36 (5) 3.47 (4) 3.68 (5) 3.37 (6)
$1-x, \frac{3}{2}+y, \frac{1}{2}-z; (xxxiv) 2-x, \frac{1}{2}+(xxxvi) \frac{1}{2}+x, \frac{3}{2}-y, 2-z.$ Cs ₂ NiSi ₅ O ₁₂ Crystal data Cs ₂ NiSi ₅ O ₁₂ M _r = 656.94 Orthorhombic Pbca a = 13.6147 (3) Å b = 13.6568 (5) Å c = 13.6583 (5) Å V = 2539.5 (1) Å ³ Z = 8 D _x = 3.437 Mg m ⁻³ Data collection High-resolution powder	Synchrotron radiatio $\lambda = 0.99820$ Å T = 293 K Powder Purple-blue Sample mounted in reflection mode 9501 data points me	$2^2 - y, \frac{1}{2} + z;$	Table 8 Ni1 -04^{i} Ni1 -07^{ii} Ni1 -09^{iii} Ni1 -011^{ii} Si2 -01^{v} Si2 -03^{v} Si2 -05^{vi} Si3 -01^{viii} Si3 -02^{ii} Si3 -02^{ii} Si3 -02^{ii} Si3 -01^{viii} Si3 -02^{ii} Si3 -01^{viii} Si3 -07^{viii} Si5 -07^{viii} Si5 -012^{viii}	S. Selected	$\begin{array}{c} geometric \\ Cs_2NiS \\ 1.87 (4) \\ 1.88 (5) \\ 1.89 (4) \\ 1.89 (3) \\ 1.62 (5) \\ 1.63 (5) \\ 1.63 (4) \\ 1.64 (6) \\ 1.68 (4) \\ 1.67 (5) \\ 1.71 (4) \\ 1.71 (4) \\ 1.71 (4) \\ 1.71 (4) \\ 1.59 (4) \\ 1.69 (5) \\ 1.59 (4) \\ 1.62 (5) \\ 1.59 (5) \\ 1.62 (5) \\ 1.62 (5) \\ 1.62 (4) \end{array}$	ic parameters i_5O_{12} $C_{S1} = -02^{xxiii}$ $C_{S1} = -02^{xxiii}$ $C_{S1} = -03^{xxiv}$ $C_{S1} = -05^{xxvi}$ $C_{S1} = -06^{xxvi}$ $C_{S1} = -06^{xxviii}$ $C_{S1} = -07^{xxviii}$ $C_{S1} = -010^{xxxi}$ $C_{S1} = -010^{xxxi}$ $C_{S1} = -012^{xxxi}$ $C_{S1} = -012^{xxxi}$ $C_{S1} = -012^{xxxi}$ $C_{S2} = -02$ $C_{S2} = -03^{xxviii}$ $C_{S2} = -05^{xxviii}$ $C_{S2} = -07^{vi}$ $C_{S2} = -08^{x}$	(\mathring{A}, \circ) for 3.83 (6) 3.50 (4) 3.58 (5) 3.58 (5) 3.61 (5) 3.67 (5) 3.02 (5) 3.11 (4) 3.67 (5) 3.02 (5) 3.11 (4) 3.67 (5) 3.48 (6) 2.99 (4) 3.00 (5) 3.26 (5) 3.36 (5) 3.36 (5) 3.47 (4) 3.68 (5) 3.37 (6) 3.85 (4)
$1-x, \frac{3}{2}+y, \frac{1}{2}-z; (xxxiv) 2-x, \frac{1}{2}+(xxxvi) \frac{1}{2}+x, \frac{3}{2}-y, 2-z.$ Cs ₂ NiSi ₅ O ₁₂ Crystal data Cs ₂ NiSi ₅ O ₁₂ M _r = 656.94 Orthorhombic Pbca a = 13.6147 (3) Å b = 13.6568 (5) Å c = 13.6583 (5) Å V = 2539.5 (1) Å ³ Z = 8 D _x = 3.437 Mg m ⁻³ Data collection High-resolution powder diffractometer SRS	Synchrotron radiatio $\lambda = 0.99820$ Å T = 293 K Powder Purple-blue Sample mounted in reflection mode 9501 data points me 4501 data points in	$2^2 - y, \frac{1}{2} + z;$	Table 8 Ni1-O4 ¹ Ni1-O7 ¹⁰ Ni1-O9 ¹⁰ Ni1-O9 ¹⁰ Ni1-O1 ¹⁰ Si2-O1 ¹⁰ Si2-O1 ¹⁰ Si2-O5 ¹⁰ Si3-O1 ¹⁰ Si3-O1 ¹⁰ Si3-O1 ¹⁰ Si3-O1 ¹⁰ Si4-O2 ¹¹ Si4-O4 ¹⁰ Si5-O5 ¹⁰ Si5-O7 ¹⁰⁰ Si5-O7 ¹⁰⁰ Si5-O7 ¹⁰⁰ Si5-O12 ¹⁰ Si6-O6 ¹⁰⁰	S. Selected	$\begin{array}{c} geometric \\ Cs_2NiS \\ 1.87 (4) \\ 1.88 (5) \\ 1.89 (4) \\ 1.89 (3) \\ 1.62 (5) \\ 1.63 (5) \\ 1.63 (4) \\ 1.64 (6) \\ 1.68 (4) \\ 1.67 (5) \\ 1.71 (4) \\ 1.71 (4) \\ 1.71 (4) \\ 1.71 (4) \\ 1.59 (4) \\ 1.69 (5) \\ 1.59 (4) \\ 1.62 (5) \\ 1.61 (5) \\ 1.62$	ic parameters i_5O_{12} $C_{S1} = -02^{xxiii}$ $C_{S1} = -02^{xxiii}$ $C_{S1} = -03^{xxiv}$ $C_{S1} = -05^{xxvii}$ $C_{S1} = -06^{xxvii}$ $C_{S1} = -06^{xxviii}$ $C_{S1} = -07^{xxviii}$ $C_{S1} = -010^{xxxi}$ $C_{S1} = -010^{xxxi}$ $C_{S1} = -010^{xxxi}$ $C_{S1} = -010^{xxxi}$ $C_{S1} = -010^{xxxi}$ $C_{S1} = -010^{xxxi}$ $C_{S2} = -02$ $C_{S2} = -03^{xxviii}$ $C_{S2} = -07^{xi}$ $C_{S2} = -07^{xi}$ $C_{S2} = -07^{xi}$ $C_{S2} = -07^{xi}$	(\mathring{A}, \circ) for 3.83 (6) 3.50 (4) 3.58 (5) 3.58 (5) 3.61 (5) 3.67 (5) 3.02 (5) 3.11 (4) 3.67 (5) 3.02 (5) 3.11 (4) 3.67 (5) 3.48 (6) 2.99 (4) 3.00 (5) 3.26 (5) 3.36 (5) 3.37 (6) 3.37 (6) 3.37 (6) 3.57 (6) 3.65 (4) 3.06 (4) 2.66 (5) 3.71 (6) 3.57 (6)
$1-x, \frac{3}{2}+y, \frac{1}{2}-z; (xxxiv) 2-x, \frac{1}{2}+(xxxvi) \frac{1}{2}+x, \frac{3}{2}-y, 2-z.$ Cs ₂ NiSi ₅ O ₁₂ Crystal data Cs ₂ NiSi ₅ O ₁₂ M _r = 656.94 Orthorhombic Pbca a = 13.6147 (3) Å b = 13.6568 (5) Å c = 13.6583 (5) Å V = 2539.5 (1) Å ³ Z = 8 D _x = 3.437 Mg m ⁻³ Data collection High-resolution powder diffractometer, SRS station 9.1 (Bushnell-Wve	Synchrotron radiatio $\lambda = 0.99820 \text{ Å}$ T = 293 K Powder Purple-blue Sample mounted in reflection mode 9501 data points me 4501 data points in processed diffract	$2^2 - y, \frac{1}{2} + z;$	Table 8 Ni1-O1 ⁱⁱ Ni1-O7 ⁱⁱⁱ Ni1-O9 ⁱⁱⁱ Ni1-O9 ⁱⁱⁱ Ni1-O1 ⁱⁱ Si2-O1 ^v Si2-O1 ^v Si2-O5 ^{vi} Si2-O1 ^{vi} Si3-O1 ^{viii} Si3-O1 ^{viii} Si3-O1 ^{viii} Si3-O1 ^{viii} Si3-O1 ^{viii} Si4-O2 ^{xiii} Si5-O5 ^{viii} Si5-O7 ^{viii} Si5-O7 ^{viii} Si5-O12 ^{vi} Si6-O6 ^{xiii} Si6-O6 ^{xiii} Si6-O6 ^{xiii}	S. Selected	$\begin{array}{c} geometric \\ Cs_2NiS \\ 1.87 (4) \\ 1.88 (5) \\ 1.89 (4) \\ 1.89 (3) \\ 1.62 (5) \\ 1.63 (5) \\ 1.63 (4) \\ 1.64 (6) \\ 1.64 (6) \\ 1.68 (4) \\ 1.67 (5) \\ 1.71 (4) \\ 1.71 (4) \\ 1.71 (4) \\ 1.71 (4) \\ 1.71 (4) \\ 1.60 (5) \\ 1.59 (4) \\ 1.62 (5) \\ 1.62 (5) \\ 1.62 (5) \\ 1.62 (5) \\ 1.62 (5) \\ 1.63 (4) \\ 1.63 (5) \\ 1.64 (5) \\ 1.64$	ic parameters i_5O_{12} $C_{S1} = 01^{xxii}$ $C_{S1} = 02^{xxiii}$ $C_{S1} = 03^{xxiv}$ $C_{S1} = 05^{xxvi}$ $C_{S1} = 06^{xxvi}$ $C_{S1} = 06^{xxvii}$ $C_{S1} = 00^{xxviii}$ $C_{S1} = 00^{xxviii}$ $C_{S1} = 010^{xxix}$ $C_{S1} = 010^{xxix}$ $C_{S1} = 010^{xxix}$ $C_{S2} = 010^{xxviii}$ $C_{S2} = 06^{xxviii}$ $C_{S2} = 06^{xxviii}$ $C_{S2} = 07^{xi}$ $C_{S2} = 07^{xi}$ $C_{S2} = 07^{xi}$ $C_{S2} = 07^{xi}$ $C_{S2} = 07^{xi}$ $C_{S2} = 01^{xxxii}$	(\mathring{A}, \circ) for 3.83 (6) 3.50 (4) 3.58 (5) 3.58 (5) 3.61 (5) 3.67 (5) 3.02 (5) 3.11 (4) 3.67 (5) 3.48 (6) 2.99 (4) 3.00 (5) 3.26 (5) 3.36 (5) 3.36 (5) 3.36 (5) 3.37 (6) 3.85 (4) 3.06 (4) 3.51 (6) 3.49 (5)
$1-x, \frac{3}{2}+y, \frac{1}{2}-z; (xxxiv) 2-x, \frac{1}{2}+(xxxvi) \frac{1}{2}+x, \frac{3}{2}-y, 2-z.$ Cs ₂ NiSi ₅ O ₁₂ Crystal data Cs ₂ NiSi ₅ O ₁₂ M _r = 656.94 Orthorhombic Pbca a = 13.6147 (3) Å b = 13.6568 (5) Å c = 13.6583 (5) Å V = 2539.5 (1) Å ³ Z = 8 D _x = 3.437 Mg m ⁻³ Data collection High-resolution powder diffractometer, SRS station 9.1 (Bushnell-Wye & Cernik 1992)	Synchrotron radiatio $\lambda = 0.99820 \text{ Å}$ T = 293 K Powder Purple-blue Sample mounted in reflection mode 9501 data points me 4501 data points in processed diffract Measured $2\theta_{min} = 5$	easured the togram .00.	Table 8 Ni1-O4 ¹ Ni1-O7 ¹⁰ Ni1-O9 ¹⁰ Ni1-O9 ¹⁰ Ni1-O1 ¹⁰ Si2-O1 ¹⁰ Si2-O1 ¹⁰ Si2-O5 ¹⁰ Si3-O1 ¹⁰ Si3-O1 ¹⁰ Si3-O1 ¹⁰ Si3-O1 ¹⁰ Si3-O1 ²⁰ Si3-O1 ²⁰ Si4-O2 ¹¹⁰ Si5-O7 ¹⁰⁰ Si5-O7 ¹⁰⁰ Si5-O7 ¹⁰⁰ Si5-O12 ¹⁰ Si6-O6 ¹⁰ Si6-O10 ¹⁰ Si6-O1 ¹⁰	S. Selected	$\begin{array}{c} geometric \\ Cs_2NiS \\ 1.87 (4) \\ 1.88 (5) \\ 1.89 (4) \\ 1.89 (3) \\ 1.62 (5) \\ 1.63 (5) \\ 1.63 (5) \\ 1.63 (4) \\ 1.64 (6) \\ 1.68 (4) \\ 1.67 (5) \\ 1.71 (4) \\ 1.71 (4) \\ 1.71 (4) \\ 1.71 (4) \\ 1.71 (4) \\ 1.59 (4) \\ 1.62 (5) \\ 1.62 (5) \\ 1.62 (5) \\ 1.62 (5) \\ 1.62 (5) \\ 1.63 (5) \\ 1.62 (5) \\ 1.63 (5) \\ 1.62$	ic parameters i_5O_{12} $C_{S1} = 01^{xxii}$ $C_{S1} = 02^{xxiii}$ $C_{S1} = 03^{xxiv}$ $C_{S1} = 05^{xxvi}$ $C_{S1} = 06^{xxvi}$ $C_{S1} = 06^{xxvii}$ $C_{S1} = 07^{xxviii}$ $C_{S1} = 00^{xxviii}$ $C_{S1} = 010^{xxxi}$ $C_{S1} = 010^{xxxi}$ $C_{S1} = 010^{xxxi}$ $C_{S1} = 010^{xxxi}$ $C_{S2} = 002^{xxviii}$ $C_{S2} = 02^{xxviii}$ $C_{S2} = 02^{xxviii}$ $C_{S2} = 07^{vi}$ $C_{S2} = 003^{xxviii}$ $C_{S2} = 007^{vi}$ $C_{S2} = 007^{xxi}$ $C_{S2} = 010^{xxii}$ $C_{S2} = 010^{xxii}$	(\mathring{A}, \circ) for 3.83 (6) 3.50 (4) 3.58 (5) 3.58 (5) 3.61 (5) 3.67 (5) 3.02 (5) 3.11 (4) 3.67 (5) 3.11 (4) 3.67 (5) 3.48 (6) 2.99 (4) 3.00 (5) 3.26 (5) 3.36 (5) 3.36 (5) 3.37 (6) 3.85 (4) 3.06 (4) 3.51 (6) 3.43 (5) 3.63 (5)
$1-x, \frac{3}{2}+y, \frac{1}{2}-z; (xxxiv) 2-x, \frac{1}{2}+(xxxvi) \frac{1}{2}+x, \frac{3}{2}-y, 2-z.$ Cs ₂ NiSi ₅ O ₁₂ Crystal data Cs ₂ NiSi ₅ O ₁₂ M _r = 656.94 Orthorhombic Pbca a = 13.6147 (3) Å b = 13.6568 (5) Å c = 13.6583 (5) Å V = 2539.5 (1) Å ³ Z = 8 D _x = 3.437 Mg m ⁻³ Data collection High-resolution powder diffractometer, SRS station 9.1 (Bushnell-Wye & Cernik, 1992) Parallel beam pon-focusing	Synchrotron radiatio $\lambda = 0.99820 \text{ Å}$ T = 293 K Powder Purple-blue Sample mounted in reflection mode 9501 data points me 4501 data points in processed diffract Measured $2\theta_{\min} = 5$ $2\theta_{\max} = 100.00^{\circ}$	easured the togram .00,	Table 8 Ni1-O4 ⁱ Ni1-O7 ⁱⁱ Ni1-O9 ⁱⁱⁱ Ni1-O9 ⁱⁱⁱ Ni1-O1 ⁱⁱ Si2-O1 ^o Si2-O1 ^o Si2-O1 ^o Si3-O1 ⁱⁱⁱ Si3-O1 ⁱⁱⁱ Si3-O1 ⁱⁱⁱ Si3-O1 ⁱⁱⁱ Si3-O1 ⁱⁱⁱ Si3-O1 ⁱⁱⁱ Si4-O2 ⁱⁱⁱ Si5-O7 ^{ivii} Si5-O7 ^{ivii} Si5-O7 ^{ivii} Si5-O12 ^{vi} Si6-O8 ^{ixii} Si6-O12 ⁱⁱⁱ Si6-O10 ⁱⁱⁱ Si6-O10 ⁱⁱ Si6-O10 ⁱⁱⁱ		$\begin{array}{c} geometric \\ Cs_2NiS \\ 1.87 (4) \\ 1.88 (5) \\ 1.89 (4) \\ 1.89 (3) \\ 1.62 (5) \\ 1.63 (5) \\ 1.63 (5) \\ 1.63 (4) \\ 1.64 (6) \\ 1.68 (4) \\ 1.67 (5) \\ 1.71 (4) \\ 1.71 (4) \\ 1.71 (4) \\ 1.71 (4) \\ 1.71 (4) \\ 1.59 (4) \\ 1.62 (5) \\ 1.62 (5) \\ 1.62 (5) \\ 1.62 (5) \\ 1.62 (5) \\ 1.62 (5) \\ 1.63 (5) \\ 1.62 (5) \\ 1.63 (5) \\ 1.62$	ic parameters i_5O_{12} $C_{S1} = -02^{xxiii}$ $C_{S1} = -02^{xxiii}$ $C_{S1} = -03^{xxiv}$ $C_{S1} = -05^{xxvi}$ $C_{S1} = -06^{xxvi}$ $C_{S1} = -06^{xxvii}$ $C_{S1} = -07^{xxviii}$ $C_{S1} = -012^{xxxi}$ $C_{S1} = -012^{xxxi}$ $C_{S1} = -012^{xxxi}$ $C_{S2} = -012^{xxxi}$ $C_{S2} = -04^{xxviii}$ $C_{S2} = -06^{xxviii}$ $C_{S2} = -07^{vi}$ $C_{S2} = -07^{vi}$ $C_{S2} = -012^{xxiv}$ $C_{S2} = -012^{xxiv}$ $C_{S2} = -012^{xxiv}$	(\mathring{A}, \circ) for 3.83 (6) 3.50 (4) 3.58 (5) 3.58 (5) 3.61 (5) 3.67 (5) 3.02 (5) 3.11 (4) 3.67 (5) 3.02 (5) 3.11 (4) 3.67 (5) 3.48 (6) 2.99 (4) 3.00 (5) 3.26 (5) 3.36 (5) 3.36 (5) 3.37 (6) 3.35 (4) 3.06 (4) 3.51 (6) 3.43 (5) 103 (3)
$1-x, \frac{3}{2}+y, \frac{1}{2}-z; (xxxiv) 2-x, \frac{1}{2}+(xxxvi) \frac{1}{2}+x, \frac{3}{2}-y, 2-z.$ Cs ₂ NiSi ₅ O ₁₂ Crystal data Cs ₂ NiSi ₅ O ₁₂ M _r = 656.94 Orthorhombic Pbca a = 13.6147 (3) Å b = 13.6568 (5) Å c = 13.6583 (5) Å V = 2539.5 (1) Å ³ Z = 8 D _x = 3.437 Mg m ⁻³ Data collection High-resolution powder diffractometer, SRS station 9.1 (Bushnell-Wye & Cernik, 1992) Parallel beam non-focusing optics with channel-	Synchrotron radiatio $\lambda = 0.99820 \text{ Å}$ T = 293 K Powder Purple-blue Sample mounted in reflection mode 9501 data points me 4501 data points in processed diffract Measured $2\theta_{\min} = 5$ $2\theta_{\max} = 100.00^{\circ}$ 2θ increment = 0.01	easured the togram .00, 1°	Table 8 Ni1-O4 ⁱ Ni1-O7 ⁱⁱ Ni1-O9 ⁱⁱⁱ Ni1-O9 ⁱⁱⁱ Ni1-O1 ⁱⁱ Si2-O1 ^v Si2-O1 ^v Si2-O5 ^{vi} Si3-O1 ^{viii} Si3-O1 ^{viii} Si3-O1 ^{viii} Si3-O1 ^{viii} Si3-O1 ^{viii} Si3-O1 ^{viii} Si4-O2 ^{kii} Si5-O7 ^{xvii} Si5-O7 ^{xvii} Si5-O7 ^{xviii} Si5-O7 ^{xviii} Si6-O6 ^{kiii} Si6-O8 ^{viii} Si6-O8 ^{viii} Si6-O1 ^{viii} Si6-O1 ^{viii} O4 ⁱⁱ -Ni1-O1 ^{viii} Ni1-O1 ^{viii}	S. Selected	$\begin{array}{c} geometric \\ Cs_2NiS \\ 1.87 (4) \\ 1.88 (5) \\ 1.89 (4) \\ 1.89 (3) \\ 1.62 (5) \\ 1.63 (5) \\ 1.63 (4) \\ 1.64 (6) \\ 1.64 (6) \\ 1.67 (5) \\ 1.71 (4) \\ 1.71 (4) \\ 1.71 (4) \\ 1.71 (4) \\ 1.71 (4) \\ 1.59 (4) \\ 1.62 (5) \\ 1.62$	$\begin{array}{c} c parameters \\ i_5 O_{12} \\ Cs1 - O1^{xxii} \\ Cs1 - O2^{xxiii} \\ Cs1 - O2^{xxiii} \\ Cs1 - O3^{xxiv} \\ Cs1 - O5^{xxvi} \\ Cs1 - O5^{xxvii} \\ Cs1 - O7^{xxviii} \\ Cs1 - O7^{xxviii} \\ Cs1 - O9^{xxviii} \\ Cs1 - O10^{xxx} \\ Cs1 - O10^{xxxi} \\ Cs1 - O10^{xxxi} \\ Cs2 - O10^{xxxii} \\ Cs2 - O2 \\ Cs2 - O3 \\ Cs2 - O4^{xxviii} \\ Cs2 - O7^{vi} \\ Cs2 - O7^{vi} \\ Cs2 - O10^{xxii} \\ Cs2 - O11^{xxxii} \\ Cs2 - O12^{xxiv} \\ Cs2 - O12^{xxvii} \\ Cs2 - O12^{xxv$	(\mathring{A}, \circ) for 3.83 (6) 3.50 (4) 3.58 (5) 3.58 (5) 3.61 (5) 3.67 (5) 3.02 (5) 3.11 (4) 3.67 (5) 3.02 (5) 3.11 (4) 3.67 (5) 3.48 (6) 2.99 (4) 3.00 (5) 3.26 (5) 3.36 (5) 3.36 (5) 3.37 (6) 3.35 (4) 3.06 (4) 3.51 (6) 3.49 (5) 3.63 (5) 103 (3) 105 (2)
$1-x, \frac{3}{2}+y, \frac{1}{2}-z; (xxxiv) 2-x, \frac{1}{2}+(xxxvi) \frac{1}{2}+x, \frac{3}{2}-y, 2-z.$ Cs ₂ NiSi ₅ O ₁₂ Crystal data Cs ₂ NiSi ₅ O ₁₂ M _r = 656.94 Orthorhombic Pbca a = 13.6147 (3) Å b = 13.6568 (5) Å c = 13.6583 (5) Å V = 2539.5 (1) Å ³ Z = 8 D _x = 3.437 Mg m ⁻³ Data collection High-resolution powder diffractometer, SRS station 9.1 (Bushnell-Wye & Cernik, 1992) Parallel beam non-focusing optics with channel- cut monochromator and	Synchrotron radiatio $\lambda = 0.99820 \text{ Å}$ T = 293 K Powder Purple-blue Sample mounted in reflection mode 9501 data points ma 4501 data points in processed diffract Measured $2\theta_{\min} = 5$ $2\theta_{\max} = 100.00^{\circ}$ 2θ increment = 0.01 Dataset normalized	easured the togram .00, 1° for	Table 8 Ni1-O4 ⁱ Ni1-O7 ⁱⁱ Ni1-O9 ⁱⁱⁱ Ni1-O9 ⁱⁱⁱ Ni1-O1 ⁱⁱ Si2-O1 ^v Si2-O1 ^v Si2-O1 ^{viii} Si3-O1 ^{xiii} Si3-O1 ^{xiii} Si3-O1 ^{xiii} Si3-O1 ^{xiii} Si4-O2 ^{xiii} Si5-O5 ^{xvii} Si5-O7 ^{xviii} Si5-O7 ^{xviii} Si5-O12 ^{viii} Si6-O6 ^{xix} Si6-O6 ^{xix} Si6-O6 ^{xix} Si6-O10 ^{xiii} Si6-O10 ^{xiii} Si6-O10 ^{xiii} Si6-O10 ^{xiii} Si6-N ^{xiii} Si6-N ^{xiii} Si6-N ^{xiii} Si6-N ^{xiii} Si6-N ^{xiii} Si6-N ^{xiii}	S. Selected	$\begin{array}{c} geometric \\ Cs_2NiS \\ 1.87 (4) \\ 1.88 (5) \\ 1.89 (4) \\ 1.89 (3) \\ 1.62 (5) \\ 1.63 (5) \\ 1.63 (5) \\ 1.63 (4) \\ 1.64 (6) \\ 1.68 (4) \\ 1.67 (5) \\ 1.71 (4) \\ 1.71 (4) \\ 1.71 (4) \\ 1.71 (4) \\ 1.60 (4) \\ 1.60 (5) \\ 1.59 (4) \\ 1.62 (5) \\ 1.62$	ic parameters i_5O_{12} $C_{S1}=01^{xxii}$ $C_{S1}=02^{xxiii}$ $C_{S1}=03^{xxiv}$ $C_{S1}=04^{xxv}$ $C_{S1}=06^{xxvii}$ $C_{S1}=06^{xxvii}$ $C_{S1}=00^{xxviii}$ $C_{S1}=00^{xxviii}$ $C_{S1}=010^{xxxi}$ $C_{S1}=010^{xxxi}$ $C_{S1}=010^{xxxi}$ $C_{S2}=010^{xxxi}$ $C_{S2}=02^{xxviii}$ $C_{S2}=02^{xxviii}$ $C_{S2}=04^{xxviii}$ $C_{S2}=06^{xxvii}$ $C_{S2}=07^{vi}$ $C_{S2}=00^{xxvii}$ $C_{S2}=00^{xxvii}$ $C_{S2}=00^{xxvii}$ $C_{S2}=00^{xxvii}$ $C_{S2}=00^{xxvii}$ $C_{S2}=00^{xxvii}$ $C_{S2}=01^{xxxii}$ $C_{S2}=01^{xx}$ $C_{S2}=01^{xx}$ $C_{S2}=01^{xx}$ $C_{S2}=01^{xx}$ $C_{S2}=01^{xx}$ $C_{S2}=01^{xx}$ $C_{S2}=01^{xx}$ $C_{S2}=01^{xx}$ $C_{S2}=01^{xx}$ $C_{S2}=01^{xx}$ $C_{S2}=01^{xx}$ $C_{S2}=01^{xx}$ $C_{S2}=01^{x}$ $C_{S2}=01^{x}$ $C_{S2}=01^{x}$ $C_{S2}=01^{x}$ $C_{S2}=01^{x}$ $C_{S2}=01^{x}$ $C_{S2}=01^{x}$ $C_{S2}=01^{x}$ $C_{S2}=01^{x}$ $C_{S2}=01^{x}$ $C_{S2}=01^{x}$ $C_{S2}=01^{x}$ $C_{S2}=01^{x}$ $C_{S2}=01^{x}$ $C_{S2}=01^{x}$ $C_{S2}=01^{x}$	(\mathring{A}, \circ) for 3.83 (6) 3.50 (4) 3.58 (5) 3.58 (5) 3.61 (5) 3.67 (5) 3.02 (5) 3.11 (4) 3.67 (5) 3.02 (5) 3.11 (4) 3.67 (5) 3.48 (6) 2.99 (4) 3.00 (5) 3.26 (5) 3.36 (5) 3.37 (6) 3.37 (6) 3.37 (6) 3.37 (6) 3.37 (6) 3.37 (6) 3.51 (6) 3.49 (5) 3.63 (5) 103 (3) 105 (2) 111 (3)
$1-x, \frac{3}{2}+y, \frac{1}{2}-z; (xxxiv) 2-x, \frac{1}{2}+(xxxvi) \frac{1}{2}+x, \frac{3}{2}-y, 2-z.$ Cs ₂ NiSi ₅ O ₁₂ Crystal data Cs ₂ NiSi ₅ O ₁₂ M _r = 656.94 Orthorhombic Pbca a = 13.6147 (3) Å b = 13.6568 (5) Å c = 13.6583 (5) Å V = 2539.5 (1) Å ³ Z = 8 D _x = 3.437 Mg m ⁻³ 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	Synchrotron radiation $\lambda = 0.99820 \text{ Å}$ T = 293 K Powder Purple-blue Sample mounted in reflection mode 9501 data points me 4501 data points in processed diffract Measured $2\theta_{\min} = 5$ $2\theta_{\max} = 100.00^{\circ}$ 2θ increment = 0.01 Dataset normalized decay of synchro	easured the togram .00, 1° for tron	Table 8 Ni1-O4 ⁱ Ni1-O7 ⁱⁱ Ni1-O9 ⁱⁱⁱ Ni1-O9 ⁱⁱⁱ Ni1-O1 ⁱⁱ Si2-O1 ^v Si2-O1 ^v Si2-O5 ^{vi} Si3-O1 ^{viii} Si3-O1 ^{viii} Si3-O1 ^{viii} Si3-O1 ^{viii} Si3-O1 ^{xiii} Si4-O2 ^{xiii} Si4-O12 ^{xiii} Si5-O5 ^{xviii} Si5-O7 ^{viii} Si5-O12 ^{viii} Si6-O6 ^{xixii} Si6-O6 ^{xixii} Si6-O6 ^{xixii} Si6-O6 ^{xixii} Si6-O12 ^{viii} Si6-O12 ^{viii} Si6-O12 ^{viii} Si6-O12 ^{viiii} Si6-O10 ^{viiiii} Si6-O10 ^{viiii} Si6-O10 ^{viiii} Si6-O10 ^{viiii}	S. Selected	$\begin{array}{c} geometric \\ Cs_2NiS \\ 1.87 (4) \\ 1.88 (5) \\ 1.89 (4) \\ 1.89 (3) \\ 1.62 (5) \\ 1.63 (5) \\ 1.63 (5) \\ 1.63 (4) \\ 1.64 (6) \\ 1.64 (6) \\ 1.67 (5) \\ 1.71 (4) \\ 1.71 (4) \\ 1.71 (4) \\ 1.60 (4) \\ 1.60 (5) \\ 1.59 (4) \\ 1.62 (5) \\ 1.61 (5) \\ 1.59 (5) \\ 1.62$	ic parameters i_5O_{12} $C_{S1}=01^{xxii}$ $C_{S1}=02^{xxiii}$ $C_{S1}=03^{xxiv}$ $C_{S1}=06^{xxvi}$ $C_{S1}=06^{xxvi}$ $C_{S1}=06^{xxvii}$ $C_{S1}=007^{xviii}$ $C_{S1}=007^{xviii}$ $C_{S1}=010^{xxxi}$ $C_{S1}=010^{xxxi}$ $C_{S1}=010^{xxxi}$ $C_{S2}=010^{xxxi}$ $C_{S2}=012^{xxxi}$ $C_{S2}=02^{xxviii}$ $C_{S2}=06^{xxviii}$ $C_{S2}=06^{xxviii}$ $C_{S2}=007^{vi}$ $C_{S2}=007^{vi}$ $C_{S2}=007^{vi}$ $C_{S2}=007^{vi}$ $C_{S2}=007^{vi}$ $C_{S2}=007^{vi}$ $C_{S2}=007^{vi}$ $C_{S2}=012^{xxii}$ $C_{S2}=012^{xxii}$ $C_{S2}=012^{xxii}$ $C_{S2}=012^{xxii}$ $C_{S2}=012^{xxii}$ $C_{S2}=012^{xxii}$ $C_{S2}=012^{xxii}$ $C_{S2}=012^{xxii}$	(\mathring{A}, \circ) for 3.83 (6) 3.50 (4) 3.58 (5) 3.58 (5) 3.61 (5) 3.67 (5) 3.02 (5) 3.11 (4) 3.67 (5) 3.02 (5) 3.11 (4) 3.67 (5) 3.48 (6) 2.99 (4) 3.00 (5) 3.23 (6) 3.37 (6) 3.35 (4) 3.06 (4) 3.51 (6) 3.49 (5) 3.63 (5) 103 (3) 105 (2) 111 (3) 125 (3) 00 (2)
$1-x, \frac{3}{2}+y, \frac{1}{2}-z; (xxxiv) 2-x, \frac{1}{2}+(xxxvi) \frac{1}{2}+x, \frac{3}{2}-y, 2-z.$ Cs ₂ NiSi ₅ O ₁₂ Crystal data Cs ₂ NiSi ₅ O ₁₂ M _r = 656.94 Orthorhombic Pbca a = 13.6147 (3) Å b = 13.6568 (5) Å c = 13.6583 (5) Å V = 2539.5 (1) Å ³ Z = 8 D _x = 3.437 Mg m ⁻³ 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	Synchrotron radiation $\lambda = 0.99820 \text{ Å}$ T = 293 K Powder Purple-blue Sample mounted in reflection mode 9501 data points med 4501 data points in processed diffract Measured $2\theta_{\min} = 5$ $2\theta_{\max} = 100.00^{\circ}$ 2θ increment = 0.01 Dataset normalized decay of synchroider beam (PDPL PO)	easured the togram .00, 1° for tron DSUM:	Table 8 Ni1-O4 ⁱ Ni1-O7 ⁱⁱ Ni1-O9 ⁱⁱⁱ Ni1-O9 ⁱⁱⁱ Ni1-O1 ⁱⁱ Si2-O1 ^v Si2-O1 ^v Si2-O5 ^{vi} Si3-O1 ^{viii} Si3-O1 ^{viii} Si3-O1 ^{viii} Si3-O1 ^{viii} Si3-O1 ^{xiii} Si4-O2 ^{xiii} Si4-O2 ^{xiii} Si5-O5 ^{xvii} Si5-O7 ^{viii} Si5-O12 ^{viii} Si6-O6 ^{xix} Si6-O6 ^{xix} Si6-O6 ^{xix} Si6-O12 ^{viii} Si6-O12 ^{viii} Si6-O12 ^{viii} Si6-O12 ^{viii} Si6-O12 ^{viii} Si6-O12 ^{viii} Si6-O12 ^{viiii} Si6-O12 ^{viii} Si6-O12 ^{viii} Si6-O12 ^{viiii} Si6-O12 ^{viiii} Si6-O12 ^{viii} Si6-O12 ^{viii} Si6-O12 ^{viii} Si6-O12 ^{viiii} Si6-O10 ^{viiii} Si6-O10 ^{viiii} Si6-O10 ^{viiii} Ni1-O1 ^{viii} -Ni1-O1 ^{viiii} -Ni1-O1 ^{viii} -Ni1-O1 ^{viiii} -Ni1-O1 ^{viii} -Ni1-O1 ^{viiii} -Ni1-O1 ^{viii} -	S. Selected	$\begin{array}{c} geometric \\ Cs_2NiS \\ 1.87 (4) \\ 1.88 (5) \\ 1.89 (4) \\ 1.89 (3) \\ 1.62 (5) \\ 1.63 (5) \\ 1.63 (5) \\ 1.63 (4) \\ 1.64 (6) \\ 1.64 (6) \\ 1.67 (5) \\ 1.71 (4) \\ 1.71 (4) \\ 1.71 (4) \\ 1.71 (4) \\ 1.60 (4) \\ 1.60 (5) \\ 1.59 (4) \\ 1.62 (5) \\ 1.62$	ic parameters i_5O_{12} $C_{S1}=01^{xxii}$ $C_{S1}=02^{xxiii}$ $C_{S1}=03^{xxiv}$ $C_{S1}=04^{xxv}$ $C_{S1}=06^{xxvii}$ $C_{S1}=06^{xxvii}$ $C_{S1}=007^{xviii}$ $C_{S1}=007^{xviii}$ $C_{S1}=010^{xxix}$ $C_{S1}=010^{xxix}$ $C_{S1}=010^{xxix}$ $C_{S2}=010^{xxix}$ $C_{S2}=012^{xxviii}$ $C_{S2}=02^{xxviii}$ $C_{S2}=06^{xxviii}$ $C_{S2}=07^{vi}$ $C_{S2}=007^{vi}$ $C_{S2}=007^{vi}$ $C_{S2}=007^{vi}$ $C_{S2}=007^{vi}$ $C_{S2}=010^{xxii}$ $C_{S2}=010^{xxii}$ $C_{S2}=012^{xxii}$ $C_{S2}=012^{xxii}$ $C_{S2}=012^{xxii}$ $C_{S2}=012^{xxii}$ $C_{S2}=012^{xxii}$ $C_{S2}=012^{xxii}$ $C_{S2}=012^{xxii}$ $C_{S2}=012^{xxii}$ $C_{S2}=012^{xxii}$	(\mathring{A}, \circ) for 3.83 (6) 3.50 (4) 3.58 (5) 3.58 (5) 3.61 (5) 3.67 (5) 3.02 (5) 3.11 (4) 3.67 (5) 3.02 (5) 3.11 (4) 3.67 (5) 3.48 (6) 2.99 (4) 3.00 (5) 3.26 (5) 3.36 (5) 3.37 (6) 3.37 (6) 3.37 (6) 3.37 (6) 3.37 (6) 3.37 (6) 3.37 (6) 3.37 (6) 3.37 (6) 3.37 (6) 3.35 (4) 3.06 (4) 3.51 (6) 3.49 (5) 3.63 (5) 103 (3) 105 (2) 111 (3) 125 (3) 99 (3) 113 (3)
$1-x, \frac{3}{2}+y, \frac{1}{2}-z; (xxxiv) 2-x, \frac{1}{2}+(xxxvi) \frac{1}{2}+x, \frac{3}{2}-y, 2-z.$ Cs ₂ NiSi ₅ O ₁₂ Crystal data Cs ₂ NiSi ₅ O ₁₂ M _r = 656.94 Orthorhombic Pbca a = 13.6147 (3) Å b = 13.6568 (5) Å c = 13.6583 (5) Å V = 2539.5 (1) Å ³ Z = 8 D _x = 3.437 Mg m ⁻³ 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 cubstrate sample mounted	Synchrotron radiation $\lambda = 0.99820 \text{ Å}$ T = 293 K Powder Purple-blue Sample mounted in reflection mode 9501 data points me 4501 data points in processed diffract Measured $2\theta_{\min} = 5$ $2\theta_{\max} = 100.00^{\circ}$ 2θ increment = 0.01 Dataset normalized decay of synchron beam (<i>PDPL PO</i>) Murray Cockered	easured the togram .00, 1° for tron <i>DSUM</i> ; ff &	Table 8 Ni1-O4 ⁱ Ni1-O7 ⁱⁱⁱ Ni1-O9 ⁱⁱⁱ Ni1-O9 ⁱⁱⁱ Ni1-O1 ⁱⁱ Si2-O1 ^v Si2-O1 ^v Si2-O5 ^{vi} Si3-O1 ^{viii} Si3-O2 ⁱⁱⁱ Si3-O2 ⁱⁱⁱ Si3-O1 ^{viii} Si3-O2 ⁱⁱⁱ Si3-O1 ^{viii} Si4-O2 ^{xiii} Si5-O5 ^{vii} Si5-O5 ^{viii} Si5-O1 ^{2viii} Si5-O1 ^{2viii} Si6-O6 ^{xiii} Si6-O6 ^{xiii} Si6-O1 ^{2viii} Si6-O1 ^{xiii} Si6-O1 ^{xiii} Si6-O1 ^{xiii} Si6-O1 ^{xiii} Si6-O1 ^{xiii} Si6-O1 ^{xiiii} Si6-O1 ^{xiiii} Si6-O1 ^{xiiii} Si6-O1 ^{xiiii} Si6-O1 ^{xiiii} Si6-O1 ^{xiiiii} Si6-O1 ^{xiiii} Si6-O1 ^{xiiii} Si6-O1 ^{xiiii} Si6-O1 ^{xiiiii} Si6-O1 ^{xiiii} O ^{xiii} -Ni1-O ^{xiiii} -Ni1-O ^{xiii} -Ni1-O ^{xiii} -Ni1-O ^{xiii} -Ni1-O ^{xiii} -Ni1-O ^{xiii} -Ni1-O ^{xiii} -Ni1-O ^{xiiii} -Ni1-O ^{xiiii} -Ni1-O ^{xiiii} -Ni1-O ^{xiii} -Ni1-O ^{xiiii} -Ni1-O ^{xiii} -Ni1-O ^{xi}	S. Selected	$\begin{array}{c} geometric \\ Cs_2NiS \\ 1.87 (4) \\ 1.88 (5) \\ 1.89 (4) \\ 1.89 (3) \\ 1.62 (5) \\ 1.63 (5) \\ 1.63 (5) \\ 1.63 (4) \\ 1.64 (6) \\ 1.64 (6) \\ 1.67 (5) \\ 1.71 (4) \\ 1.71 (4) \\ 1.71 (4) \\ 1.71 (4) \\ 1.60 (4) \\ 1.60 (5) \\ 1.59 (4) \\ 1.62 (5) \\ 1.61 (5) \\ 1.62$	ic parameters i_5O_{12} $C_{S1}=01^{xxii}$ $C_{S1}=02^{xxiii}$ $C_{S1}=03^{xxiv}$ $C_{S1}=06^{xxvi}$ $C_{S1}=06^{xxvii}$ $C_{S1}=06^{xxvii}$ $C_{S1}=007^{xviii}$ $C_{S1}=010^{xxix}$ $C_{S1}=010^{xxix}$ $C_{S1}=010^{xxix}$ $C_{S1}=010^{xxix}$ $C_{S2}=010^{xxii}$ $C_{S2}=02^{xxviii}$ $C_{S2}=02^{xxviii}$ $C_{S2}=02^{xxviii}$ $C_{S2}=00^{xxviii}$ $C_{S2}=00^{xxviii}$ $C_{S2}=00^{xxviii}$ $C_{S2}=00^{xxviii}$ $C_{S2}=00^{xxviii}$ $C_{S2}=00^{xxviii}$ $C_{S2}=00^{xxviii}$ $C_{S2}=001^{xxxii}$ $C_{S2}=01^{xxxii}$ $C_{S2}=01^{xxxii}$ $C_{S2}=01^{xxxii}$ $C_{S2}=01^{xxxii}$ $C_{S2}=01^{xxxii}$ $C_{S2}=01^{xxxii}$ $C_{S2}=01^{xxxii}$ $C_{S2}=01^{xxxii}$ $C_{S2}=01^{xxxii}$ $C_{S2}=01^{xxxii}$ $C_{S2}=01^{xxii}$ $O_{S}^{xvi}=Si5=01^{2^{viii}}$ $O_{S}^{xvi}=Si5=012^{viii}$ $O_{S}^{xvi}=Si5=012^{viii}$ $O_{S}^{xvi}=Si5=012^{viii}$	(\mathring{A}, \circ) for 3.83 (6) 3.50 (4) 3.58 (5) 3.58 (5) 3.61 (5) 3.67 (5) 3.02 (5) 3.11 (4) 3.67 (5) 3.02 (5) 3.11 (4) 3.67 (5) 3.48 (6) 2.99 (4) 3.00 (5) 3.23 (6) 3.37 (6) 3.35 (4) 3.06 (4) 3.51 (6) 3.49 (5) 3.63 (5) 103 (3) 105 (2) 111 (3) 125 (3) 99 (3) 113 (3) 105 (3)
$1-x, \frac{3}{2}+y, \frac{1}{2}-z; (xxxiv) 2-x, \frac{1}{2}+(xxxvi) \frac{1}{2}+x, \frac{3}{2}-y, 2-z.$ Cs ₂ NiSi ₅ O ₁₂ Crystal data Cs ₂ NiSi ₅ O ₁₂ M _r = 656.94 Orthorhombic Pbca a = 13.6147 (3) Å b = 13.6568 (5) Å c = 13.6583 (5) Å V = 2539.5 (1) Å ³ Z = 8 D _x = 3.437 Mg m ⁻³ 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	Synchrotron radiation $\lambda = 0.99820 \text{ Å}$ T = 293 K Powder Purple-blue Sample mounted in reflection mode 9501 data points me 4501 data points in processed diffract Measured $2\theta_{\min} = 5$ $2\theta_{\max} = 100.00^{\circ}$ 2θ increment = 0.01 Dataset normalized decay of synchron beam (<i>PDPL PO</i>) Murray, Cockcron Fitch 1990)	easured the togram .00, 1° for tron <i>DSUM</i> ; ft &	Table 8 Ni1-O4 ⁱ Ni1-O7 ⁱⁱⁱ Ni1-O7 ⁱⁱⁱ Ni1-O7 ⁱⁱⁱ Ni1-O1 ⁱⁱ Si2-O1 ^v Si2-O1 ^v Si2-O5 ^{vi} Si3-O1 ^{viii} Si3-O1 ^{viii} Si3-O2 ⁱⁱⁱ Si3-O1 ^{viii} Si3-O2 ⁱⁱⁱ Si3-O1 ^{viii} Si4-O2 ^{xiii} Si5-O5 ^{vii} Si5-O5 ^{viii} Si5-O1 ^{2viii} Si5-O1 ^{2viii} Si6-O6 ^{xiii} Si6-O6 ^{xiii} Si6-O6 ^{xiii} Si6-O6 ^{xiii} Si6-O1 ^{2viii} Si6-O6 ^{xiii} Si6-O1 ^{2viii} Si6-O1 ^{xiii} Si6-O1 ^{xiii} Si6-O1 ^{xiii} Si6-O1 ^{xiii} Si6-O1 ^{xiiii} O ^{xiii} -Ni1-O ^{xiiii} -Ni1-O ^{xiii} -Ni1	S. Selected	$\begin{array}{c} geometric \\ Cs_2NiS \\ 1.87 (4) \\ 1.88 (5) \\ 1.89 (4) \\ 1.89 (3) \\ 1.62 (5) \\ 1.63 (5) \\ 1.63 (5) \\ 1.63 (4) \\ 1.64 (6) \\ 1.64 (6) \\ 1.67 (5) \\ 1.71 (4) \\ 1.71 (4) \\ 1.71 (4) \\ 1.71 (4) \\ 1.60 (4) \\ 1.60 (5) \\ 1.59 (4) \\ 1.62 (5) \\ 1.61 (5) \\ 1.59 (5) \\ 1.62$	ic parameters i_5O_{12} $C_{S1}=01^{xxii}$ $C_{S1}=02^{xxiii}$ $C_{S1}=03^{xxiv}$ $C_{S1}=06^{xxvi}$ $C_{S1}=06^{xxvi}$ $C_{S1}=06^{xxvii}$ $C_{S1}=007^{xviii}$ $C_{S1}=007^{xviii}$ $C_{S1}=010^{xxix}$ $C_{S1}=010^{xxix}$ $C_{S1}=010^{xxix}$ $C_{S2}=010^{xxix}$ $C_{S2}=010^{xxviii}$ $C_{S2}=02^{xxviii}$ $C_{S2}=007^{vi}$ $C_{S2}=007^$	(\mathring{A}, \circ) for 3.83 (6) 3.50 (4) 3.58 (5) 3.58 (5) 3.61 (5) 3.67 (5) 3.02 (5) 3.11 (4) 3.67 (5) 3.02 (5) 3.11 (4) 3.67 (5) 3.48 (6) 2.99 (4) 3.00 (5) 3.26 (5) 3.36 (5) 3.37 (6) 3.37 (6) 3.35 (4) 3.06 (4) 3.51 (6) 3.49 (5) 3.63 (5) 103 (3) 105 (2) 111 (3) 125 (3) 99 (3) 113 (3) 105 (3) 117 (2)
$1-x, \frac{3}{2}+y, \frac{1}{2}-z; (xxxiv) 2-x, \frac{1}{2}+(xxxvi) \frac{1}{2}+x, \frac{3}{2}-y, 2-z.$ Cs ₂ NiSi ₅ O ₁₂ Crystal data Cs ₂ NiSi ₅ O ₁₂ M _r = 656.94 Orthorhombic Pbca a = 13.6147 (3) Å b = 13.6568 (5) Å c = 13.6583 (5) Å V = 2539.5 (1) Å ³ Z = 8 D _x = 3.437 Mg m ⁻³ 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 share: irremular	Synchrotron radiation $\lambda = 0.99820 \text{ Å}$ T = 293 K Powder Purple-blue Sample mounted in reflection mode 9501 data points med 4501 data points in processed diffract Measured $2\theta_{\min} = 5$ $2\theta_{\max} = 100.00^{\circ}$ 2θ increment = 0.01 Dataset normalized decay of synchron beam (<i>PDPL PO</i>) Murray, Cockcron Fitch, 1990) Impurity reflections	easured the togram .00, 1° for tron <i>DSUM</i> ; ft & excluded	Table 8 Ni1-O4 ⁱ Ni1-O7 ⁱⁱⁱ Ni1-O9 ⁱⁱⁱ Ni1-O9 ⁱⁱⁱ Ni1-O1 ⁱⁱ Si2-O1 ^v Si2-O1 ^v Si2-O1 ^{viii} Si2-O1 ^{viii} Si3-O1 ^{viii} Si3-O2 ⁱⁱⁱ Si3-O1 ^{xiii} Si3-O2 ⁱⁱⁱ Si3-O1 ^{xiii} Si4-O2 ^{xiii} Si5-O5 ^{xvii} Si5-O5 ^{xviii} Si5-O1 ^{2viii} Si5-O1 ^{xiii} Si6-O6 ^{xxiii} Si6-O6 ^{xxiii} Si6-O6 ^{xxiii} Si6-O1 ^{xiii} Si6-O1 ^{xiiii} Si6-O1 ^{xiii} Si6-O1 ^{xiiii} Si6-O1 ^{xiiii} Si6-O1 ^{xiiii} Si6-O1 ^{xiiii} O ^{xiiii} -Ni1-O ^{xiiii} -Ni1-O ^{xiiii} -Ni1-O ^{xiiii} -Ni1-O ^{xiii} -Ni1-O	S. Selected -07^{ii} -09^{iii} -09^{iii} -011^{iv} -011^{iv} -011^{iv} -03^{iv} -03^{iv} -05^{vi} -010^{vii}	$\begin{array}{c} geometric \\ Cs_2NiS \\ 1.87 (4) \\ 1.88 (5) \\ 1.89 (4) \\ 1.89 (3) \\ 1.62 (5) \\ 1.63 (5) \\ 1.63 (5) \\ 1.63 (4) \\ 1.64 (6) \\ 1.64 (6) \\ 1.67 (5) \\ 1.71 (4) \\ 1.71 (4) \\ 1.71 (4) \\ 1.71 (4) \\ 1.60 (4) \\ 1.60 (5) \\ 1.59 (4) \\ 1.62 (5) \\ 1.61 (5) \\ 1.59 (4) \\ 1.62 (5) \\ 1.62$	ic parameters i_5O_{12} $C_{S1}=01^{xxii}$ $C_{S1}=02^{xxiii}$ $C_{S1}=03^{xxiv}$ $C_{S1}=06^{xxvi}$ $C_{S1}=06^{xxvi}$ $C_{S1}=06^{xxvii}$ $C_{S1}=007^{xviii}$ $C_{S1}=007^{xviii}$ $C_{S1}=010^{xxix}$ $C_{S1}=010^{xxix}$ $C_{S1}=010^{xxix}$ $C_{S2}=010^{xxii}$ $C_{S2}=010^{xxviii}$ $C_{S2}=02^{xxviii}$ $C_{S2}=007^{vi}$ $C_{S2}=007^{vi}$ $C_{S2}=007^{vi}$ $C_{S2}=007^{vi}$ $C_{S2}=007^{vi}$ $C_{S2}=007^{vi}$ $C_{S2}=007^{vi}$ $C_{S2}=012^{xxii}$ $C_{S2}=012^{xxii}$ $C_{S2}=012^{xxii}$ $C_{S2}=012^{xxii}$ $C_{S2}=012^{xxii}$ $C_{S2}=012^{xxii}$ $C_{S2}=012^{xxii}$ $C_{S2}=012^{xxii}$ $C_{S2}=012^{xxii}$ $C_{S2}=012^{xxii}$ $C_{S2}=012^{xxii}$ $C_{S3}=012^{viii}$ $O_{S1}^{xvi}=Si5=012^{viii}$ $O_{S1}^{xvi}=Si5=012^{viii}$ $O_{S1}^{xvi}=Si5=012^{viii}$ $O_{S1}^{xvi}=Si5=012^{viii}$ $O_{S1}^{xvi}=Si5=012^{viii}$ $O_{S1}^{xvi}=Si5=012^{viii}$ $O_{S1}^{xvi}=Si5=012^{viii}$ $O_{S1}^{xvi}=Si5=012^{viii}$ $O_{S1}^{xvi}=Si5=012^{viii}$ $O_{S1}^{xvi}=Si5=012^{viii}$ $O_{S1}^{xvi}=Si5=012^{viii}$ $O_{S1}^{xvi}=Si5=012^{viii}$ $O_{S1}^{xvi}=Si5=012^{viii}$ $O_{S1}^{xvi}=Si5=012^{viii}$ $O_{S1}^{xvi}=Si5=012^{viii}$ $O_{S1}^{xvi}=Si5=012^{viii}$ $O_{S1}^{xvi}=Si5=012^{viii}$	(\mathring{A}, \circ) for 3.83 (6) 3.50 (4) 3.58 (5) 3.58 (5) 3.61 (5) 3.67 (5) 3.02 (5) 3.11 (4) 3.67 (5) 3.02 (5) 3.11 (4) 3.67 (5) 3.48 (6) 2.99 (4) 3.00 (5) 3.26 (5) 3.37 (6) 3.37 (6) 3.49 (5) 3.65 (5) 103 (3) 105 (2) 111 (3) 125 (3) 99 (3) 113 (3) 105 (3) 117 (2) 99 (3) 106 (2) 107 (2) 99 (3) 106 (2) 107 (2) 99 (3) 107 (2) 99 (3) 106 (2) 107
$1-x, \frac{3}{2}+y, \frac{1}{2}-z; (xxxiv) 2-x, \frac{1}{2}+(xxxvi) \frac{1}{2}+x, \frac{3}{2}-y, 2-z.$ Cs ₂ NiSi ₅ O ₁₂ <i>Crystal data</i> Cs ₂ NiSi ₅ O ₁₂ <i>M_r</i> = 656.94 Orthorhombic <i>Pbca a</i> = 13.6147 (3) Å <i>b</i> = 13.6568 (5) Å <i>c</i> = 13.6583 (5) Å <i>V</i> = 2539.5 (1) Å ³ <i>Z</i> = 8 <i>D_x</i> = 3.437 Mg m ⁻³ <i>Data collection</i> 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	Synchrotron radiation $\lambda = 0.99820 \text{ Å}$ T = 293 K Powder Purple-blue Sample mounted in reflection mode 9501 data points med 4501 data points in processed diffract Measured $2\theta_{\min} = 5$ $2\theta_{\max} = 100.00^{\circ}$ 2θ increment = 0.01 Dataset normalized decay of synchron beam (<i>PDPL PO</i>) Murray, Cockcron Fitch, 1990) Impurity reflections	easured the togram .00, 1° for tron DSUM; ft & excluded	Table 8 Ni1-O4 ⁱ Ni1-O7 ⁱⁱⁱ Ni1-O1 ⁱⁱⁱ Ni1-O9 ⁱⁱⁱ Ni1-O1 ⁱⁱⁱ Si2-O1 ^v Si2-O1 ^v Si2-O1 ^v Si2-O1 ^{viii} Si3-O1 ^{xiii} Si3-O1 ^{xiii} Si3-O1 ^{xiii} Si3-O2 ^{ix} Si3-O1 ^{xiii} Si4-O2 ^{xiii} Si4-O2 ^{xiii} Si5-O5 ^{xvii} Si5-O7 ^{xviii} Si5-O1 ^{2viii} Si6-O6 ^{xix} Si6-O6 ^{xix} Si6-O10 ^{xiii} Si6-O10 ^{xiii} Ni1-O7 ⁱⁱⁱ -Ni1-O7 ⁱⁱ	S. Selected -07^{ii} -09^{iii} -011^{iv} -011^{iv} -011^{iv} -011^{iv} -011^{iv} -010^{vi} -010^{vi} -010^{vi}	$\begin{array}{c} geometric \\ Cs_2NiS \\ 1.87 (4) \\ 1.88 (5) \\ 1.89 (4) \\ 1.89 (3) \\ 1.62 (5) \\ 1.63 (5) \\ 1.63 (4) \\ 1.64 (6) \\ 1.64 (6) \\ 1.64 (4) \\ 1.67 (5) \\ 1.71 (4) \\ 1.71 (4) \\ 1.71 (4) \\ 1.71 (4) \\ 1.60 (4) \\ 1.62 (5) \\ 1.62$	ic parameters i_5O_{12} $C_{S1}=01^{xxii}$ $C_{S1}=02^{xxiii}$ $C_{S1}=03^{xxiv}$ $C_{S1}=04^{xxv}$ $C_{S1}=06^{xxvii}$ $C_{S1}=06^{xxvii}$ $C_{S1}=00^{xxviii}$ $C_{S1}=00^{xxviii}$ $C_{S1}=010^{xxix}$ $C_{S1}=010^{xxix}$ $C_{S1}=010^{xxix}$ $C_{S2}=01$ $C_{S2}=02$ $C_{S2}=03$ $C_{S2}=04^{xxviii}$ $C_{S2}=02^{xxviii}$ $C_{S2}=02^{xxviii}$ $C_{S2}=00^{xxviii}$ $C_{S2}=00^{xxviii}$ $C_{S2}=00^{xxviii}$ $C_{S2}=00^{xxviii}$ $C_{S2}=00^{xxviii}$ $C_{S2}=00^{xxviii}$ $C_{S2}=00^{xxviii}$ $C_{S2}=01^{xxxxii}$ $C_{S2}=01^{xxxii}$ $C_{S2}=01^{xxxii}$ $C_{S2}=01^{xxxi$	(\mathring{A}, \circ) for 3.83 (6) 3.50 (4) 3.58 (5) 3.58 (5) 3.61 (5) 3.67 (5) 3.02 (5) 3.11 (4) 3.67 (5) 3.02 (5) 3.11 (4) 3.67 (5) 3.48 (6) 2.99 (4) 3.00 (5) 3.26 (5) 3.36 (5) 3.37 (6) 3.36 (5) 3.37 (6) 3.35 (4) 3.06 (4) 3.51 (6) 3.49 (5) 3.63 (5) 103 (3) 105 (2) 111 (3) 125 (3) 99 (3) 105 (3) 117 (2) 99 (3) 104 (3) 104 (3)

122 (3)	Si2 ^{xxvii} _01_Si3 ^{xxxii}	120 (3)
122 (5)	512 -01515	127 (5)
103 (2)	Si3 ^{xxv} —O2—Si4 ^{xx} ^v	140 (3)
120 (3)	Si2 ^{xxii} —O3—Si4 ^{xxvi}	139 (3)
106 (2)	Ni1 ^x —04—Si4 ^{xvi}	147 (3)
100 (2)	Si2 ^{xix} —O5—Si5 ^{xiv}	156 (3)
105 (2)	Si3 ⁱ —O6—Si6 ^{vi}	155 (4)
100 (3)	Ni1 ^{xi} —O7—Si5 ^{xxxiv}	138 (3)
103 (2)	Si5 ^{xv} —O8—Si6 ^{xxxv}	138 (3)
114 (3)	Ni 1 ^{xxxvi} —O9—Si6 ^{vii}	129 (2)
115 (3)	Si2 ^{xxi} —O10—Si6 ^{xxiv}	147 (4)
104 (2)	Ni1 ^{xxii} —O11—Si3 ⁱⁱ	124 (3)
120 (3)	Si4 ^{xviii} —O12—Si5 ^{xxxii}	133 (3)
	122 (3) 103 (2) 120 (3) 106 (2) 100 (2) 105 (2) 100 (3) 103 (2) 114 (3) 115 (3) 104 (2) 120 (3)	$\begin{array}{llllllllllllllllllllllllllllllllllll$

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, $\frac{1}{2} + z$; (xviii) 2 - x, $y - \frac{1}{2}$, $\frac{3}{2} - z$; (xviii) $\frac{3}{2} - x$, $y - \frac{1}{2}$, z; (xxii) $\frac{1}{2} + x$, $\frac{3}{2} - y$, 1 - z; (xxii) 2 - x, $y - \frac{1}{2}$, $\frac{3}{2} - z$; (xviii) $\frac{3}{2} - x$, $y - \frac{1}{2}$, z; (xxii) $\frac{1}{2} + x$, $\frac{3}{2} - y$, 1 - z; (xxiii) -x, $y - \frac{1}{2}$, $\frac{1}{2} - z$; (xviii) x, $\frac{3}{2} - y$, $z - \frac{1}{2}$; (xxii) $\frac{1}{2} - x$, $y - \frac{1}{2}$, $\frac{1}{2}$; (xxiii) 1 - x, 1 - y, 1 - z; (xxii) x, $y - \frac{1}{2} - z$; (xxvii) $\frac{1}{2} - x$, 1 - y, $z - \frac{1}{2}$; (xxviii) 1 - x, 1 - y, 1 - z; (xxii) x, y - 1, $\frac{1}{2} - z$; (xxxiii) 1 - x, $y - z - \frac{1}{2}$; (xxxiii) x - 1, y, z; (xxxii) x, $\frac{1}{2} - y$, $2 - \frac{1}{2}$; (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 $Cs_2NiSi_5O_{12}$ 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 $Cs_2NiSi_5O_{12}$ 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).

We acknowledge the use of the EPSRC-funded Chemical Database Service at Daresbury and also thank the EPSRC for the award of synchrotron beam time. We would like to thank Dr Graham Bushnell-Wye of Daresbury Laboratory for assistance with the high-resolution powder diffractometer on station 9.1 of the Daresbury Laboratory SRS.

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.

References

- 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., Redfern, S. A. T., Cernik, R. J., Champness, P. E., Fitch, A. N. & Kohn, S. C. (1994). Acta Cryst. B50, 31–41.

Bell, A. M. T., Redfern, S. A. T., Henderson, C. M. B. & Kohn, S. C. (1994). Acta Cryst. B50, 560-566.

- Bushnell-Wye, G. & Cernik, R. J. (1992). Rev. Sci. Instrum. 63, 999-1001.
- Cernik, R. J., Murray, P. K., Pattison, P. & Fitch, A. N. (1990). J. Appl. Cryst. 23, 292–296.
- Collins, S. P., Cernik, R. J., Pattison, P., Bell, A. M. T. & Fitch, A. N. (1992). *Rev. Sci. Instrum.* 63, 1013–1014.
- Hill, R. J. & Gibbs, G. V. (1979). Acta Cryst. B35, 25-30.
- Kohn, S. C., Henderson, C. M. B. & Dupree, R. (1994). Phys. Chem. Miner. 21, 176–190.
- Molecular Simulations Inc. (1994). CERIUS. Molecular Simulations Inc., 240/250 The Quorum, Barnwell Road, Cambridge CB5 8RE, England.
- Murray, A. D., Cockcroft, J. K. & Fitch, A. N. (1990). PDPL. Powder Diffraction Program Library. University College, London.
- Rietveld, H. M. (1969). J. Appl. Cryst. 2, 65-71.
- Robinson, K., Gibbs, G. V. & Ribbe, P. H. (1971). Science, 172, 567-570.
- Shannon, R. D. (1976). Acta Cryst. A32, 751-767.
- Taylor, D. & Henderson, C. M. B. (1968). Am. Mineral. 53, 1476-1489.