

Al(1)	24 (l)	0.2341 (4)	0.3952 (4)	0.1635 (2)	0.009 (1)
Al(2)	12 (k)	0.1560 (5)	0	0.1149 (3)	0.011 (2)
Al(3)	12 (k)	0.2529 (5)	0	0.5289 (3)	0.009 (2)
Al(4)	12 (j)	0.1481 (6)	0.5472 (6)	1/4	0.010 (2)
Al(5)	12 (i)	0.2495 (3)	2x	0	0.029 (2)
Al(6)†	8 (h)	1/3	2/3	0.1313 (2)	0.010 (1)
Al(7)	6 (g)	0.8498 (7)	0	1/4	0.006 (2)

† Al(6) site occupied by 44 (2)% Cr; set isotropic.

Table 2. *Interatomic distances* (<4 Å)

Yb—Al(4)	×2	3.044 (6)	Al(2)—Al(7)	×2	2.897 (6)
Yb—Al(5)	×2	3.057 (5)	Al(2)—Al(2)	×2	2.936 (7)
Yb—Al(1)	×2	3.062 (4)	Al(2)—Yb		3.389 (4)
Yb—Al(3)		3.190 (4)	Al(2)—Al(5)	×2	3.900 (8)
Yb—Al(6)	×2	3.219 (1)	Al(3)—Al(2)		2.737 (6)
Yb—Al(1)	×2	3.232 (8)	Al(3)—Al(5)	×2	2.740 (9)
Yb—Al(3)		3.270 (4)	Al(3)—Cr(2)		2.795 (8)
Yb—Al(5)	×2	3.369 (5)	Al(3)—Al(2)	×2	2.837 (11)
Yb—Al(2)		3.389 (4)	Al(3)—Al(1)	×2	2.885 (6)
Yb—Yb		3.444 (1)	Al(3)—Al(3)	×2	2.930 (12)
Yb—Cr(1)		3.498 (2)	Al(3)—Yb		3.190 (4)
Cr(1)—Al(7)	×2	2.478 (4)	Al(3)—Yb		3.270 (4)
Cr(1)—Al(2)	×2	2.638 (5)	Al(4)—Cr(1)		2.681 (6)
Cr(1)—Al(1)	×4	2.681 (8)	Al(4)—Al(1)	×2	2.730 (14)
Cr(1)—Al(4)	×2	2.681 (6)	Al(4)—Al(6)	×2	2.732 (12)
Cr(1)—Yb	×2	3.498 (2)	Al(4)—Al(1)	×2	2.764 (6)
Cr(2)—Al(2)	×6	2.635 (6)	Al(4)—Al(4)		2.787 (17)
Cr(2)—Al(3)	×6	2.795 (8)	Al(4)—Yb	×2	3.044 (6)
Al(1)—Al(6)		2.647 (8)	Al(4)—Al(4)	×2	3.062 (24)
Al(1)—Cr(1)		2.681 (8)	Al(5)—Al(5)	×2	2.734 (13)
Al(1)—Al(2)		2.709 (8)	Al(5)—Al(3)	×2	2.740 (9)
Al(1)—Al(4)		2.730 (14)	Al(5)—Al(6)	×2	2.794 (6)
Al(1)—Al(4)		2.764 (6)	Al(5)—Yb	×2	3.057 (5)
Al(1)—Al(7)		2.792 (9)	Al(5)—Al(1)	×2	3.057 (4)
Al(1)—Al(3)		2.885 (6)	Al(5)—Yb	×2	3.369 (5)
Al(1)—Al(1)		3.032 (7)	Al(5)—Al(2)	×2	3.900 (8)
Al(1)—Al(1)		3.038 (4)	Al(6)—Al(1)	×3	2.647 (8)
Al(1)—Al(5)		3.057 (4)	Al(6)—Al(4)	×3	2.732 (12)
Al(1)—Yb		3.062 (4)	Al(6)—Al(5)	×3	2.794 (6)
Al(1)—Yb		3.232 (8)	Al(6)—Yb	×3	3.219 (1)
Al(2)—Cr(2)		2.635 (6)	Al(7)—Cr(1)	×2	2.478 (4)
Al(2)—Cr(1)		2.638 (5)	Al(7)—Al(1)	×4	2.792 (9)
Al(2)—Al(1)	×2	2.709 (8)	Al(7)—Al(7)	×2	2.827 (9)
Al(2)—Al(3)		2.737 (6)	Al(7)—Al(2)	×4	2.897 (6)
Al(2)—Al(3)	×2	2.837 (11)			

The structure was solved by *MULTAN87* (Debaerdemaeker, Germain, Main, Tate & Woolfson, 1987) and refined by least-squares techniques varying the scale factor, isotropic extinction, atomic positional and anisotropic displacement parameters. The Al(6) site, about half occupied by Cr, was set isotropic and its occupancy parameter was refined. *Xtal3.2* (Hall, Flack & Stewart, 1992) was used for the data reduction and structure refinement. The high value of the displacement parameter of the Al(5) site has been noted. Refinement of the occupancy and displacement parameters of the Al(5) site did not improve the results.

Lists of structure factors and anisotropic displacement parameters have been deposited with the IUCr (Reference: DU1079). 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 Structures of Dry-Synthesized $M\text{Fe}^{\text{III}}\text{Si}_2\text{O}_6$ Leucites ($M = \text{K}, \text{Rb}, \text{Cs}$) by Synchrotron X-ray Powder Diffraction

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Abstract

Analyses of high-resolution synchrotron X-ray powder diffraction patterns of dry-synthesized $M\text{Fe}^{\text{III}}\text{Si}_2\text{O}_6$ leucites ($M = \text{K}, \text{Rb}, \text{Cs}$) showed that the K- and Rb-containing leucites (iron potassium silicate, KFeSi_2O_6 , and iron rubidium silicate, $\text{RbFeSi}_2\text{O}_6$) each have a tetragonal $I4_1/a$ structure and the Cs-containing leucite (caesium iron silicate, $\text{CsFeSi}_2\text{O}_6$) has a cubic $Ia\bar{3}d$ structure. The structures of these materials have been refined by the Rietveld method. In $\text{CsFeSi}_2\text{O}_6$ leucite, Fe^{III} and Si are disordered on tetrahedral framework sites as required by space-group constraints. In KFeSi_2O_6 leucite, Fe shows significant ordering and is concentrated on the T_3 tetrahedral site. $\text{RbFeSi}_2\text{O}_6$ leucite shows less pronounced T -site ordering reflecting the fact that it is closer to the tetragonal–cubic phase transition at which the T sites become identical.

Comment

As part of a wider attempt to understand the controls and consequences of tetrahedral-site cation ordering in compounds with framework structures, we are studying a series of synthetic silicates with structures 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 their Al/Si analogues, and also display different *T*-site ordering arrangements depending on the conditions of their synthesis and on their chemical compositions (Bell, Henderson, Redfern, Cernik, Champness, Fitch & Kohn, 1994*a*; Bell, Redfern, Henderson & Kohn, 1994*b*).

The structure of leucite consists of a three-dimensional framework of interconnected SiO₄ and AlO₄ tetrahedra with K⁺ ions occupying channels within the framework. Other phases having the leucite structure include the natural minerals pollucite (CsAlSi₂O₆) and analcime (NaAlSi₂O₆·H₂O) and a wide variety of synthetic materials with different stoichiometries (for a review see Kohn, Dupree, Mortuza & Henderson, 1991) and which crystallize in different space groups (Torres-Martinez & West, 1989; Bell, Cernik, Champness, Fitch, Henderson, Kohn, Norledge & Redfern, 1993; Bell *et al.*, 1994*a,b*). All of these phases have the same topology with the different space groups being related by reversible displacive transitions and different tetrahedral-site ordering patterns. Thus natural leucite (KAlSi₂O₆) has a tetragonal *I4₁/a* structure with Al and Si distributed over three separate tetrahedral (*T*) sites (denoted *T*₁, *T*₂ and *T*₃) (Mazzi, Galli & Gottardi, 1976) while pollucite (CsAlSi₂O₆) is cubic *Ia $\bar{3}d$* with Si and Al disordered over a single *T* site (Beger, 1969). KAlSi₂O₆ leucite transforms rapidly and reversibly to a metrically cubic structure at high temperature. This high-temperature leucite was originally believed to be cubic *Ia $\bar{3}d$* (Peacor, 1968), leading to the conclusion that in the low-temperature form Si and Al were fully disordered over the three *T* sites. Recent magic-angle-spinning NMR work has, however, shown that natural leucite shows partial *T*-site ordering, although different ordering arrangements have been proposed (Brown, Cardile, MacKenzie, Ryan & Meinhold, 1987; Murdoch, Stebbins, Carmichael & Pines, 1988; Phillips, Kirkpatrick & Putnis, 1989; Kohn, Henderson & Dupree, 1994). Taylor & Henderson (1968) studied the thermal expansion of a natural leucite and synthetic samples having the stoichiometry *M*AlSi₂O₆, with *M* = K, Rb and Cs, and noted that tetragonal RbAlSi₂O₆ also showed a displacive transition to a cubic *Ia $\bar{3}d$* structure at high temperature.

Several workers have studied synthetic leucites with the stoichiometry *M*Fe^{III}Si₂O₆ in which Fe^{III} substitutes for Al in the tetrahedral sites. Faust (1963) showed that the X-ray powder diffraction pattern of the K,Fe compound could be indexed as tetragonal *I4₁/a* and that this

material underwent a phase transition at high temperature similar to that for KAlSi₂O₆ leucite. Hirao, Soga & Masanaga (1976) found that KFeSi₂O₆, RbFeSi₂O₆, (Rb_{0.9}Cs_{0.1})FeSi₂O₆ and (Rb_{0.8}Cs_{0.2})FeSi₂O₆ leucites all showed tetragonal–cubic phase transitions at high temperatures. Kopp, Harris, Clark & Lakel (1963) used the relative intensities of peaks in an X-ray powder diffraction pattern to deduce that synthetic CsFeSi₂O₆ leucite is cubic *Ia $\bar{3}d$* at room temperature; this space group has a single *T* site and so requires a disordered tetrahedral-site cation arrangement. However, Faust (1963) and Lange, Carmichael & Stebbins (1986) suggested that KFeSi₂O₆ leucite might contain an ordered arrangement of Fe^{III} and Si. Brown *et al.* (1987) studied KFeSi₂O₆ leucite by ⁵⁷Fe Mössbauer spectroscopy and fitted three doublets to the spectrum obtained. By assigning the doublets with the higher quadrupole splittings to the more distorted *T* sites (order of distortion *T*₁ > *T*₂ > *T*₃), they determined site occupancies for Fe of *T*₁ 0.19, *T*₂ 0.34 and *T*₃ 0.47. In a recent Mössbauer study of synthetic Fe leucites, England, Henderson, Charnock & Vaughan (1994) found similar values of 0.12, 0.35 and 0.52, respectively, for KFeSi₂O₆ leucite, while the Mössbauer spectrum of CsFeSi₂O₆ showed a broad doublet, reflecting the wide range of local environments for Fe in the cubic *Ia $\bar{3}d$* structure in which Fe and Si are disordered over a single *T* site.

Although structural relationships for *M*,Fe leucites have been deduced in previous work, no structures have been determined directly. In the present paper we describe the structures of three dry-synthesized leucites with the stoichiometry *M*Fe^{III}Si₂O₆, where *M* = K, Rb, Cs, determined using X-ray powder diffraction techniques and Rietveld analysis (Rietveld, 1969). Observed, calculated and difference profiles for the K, Rb and Cs Fe^{III} leucites are shown in Figs. 1, 2 and 3, respectively. The difference plots for the K- and Cs-containing compounds show that the agreement between the observed and calculated profiles is good, but the fit for RbFeSi₂O₆ is less good as a consequence of some [001] preferred orientation in the sample.

The refined *T*—O distances for KFeSi₂O₆ leucite decrease in the order *T*₃ > *T*₂ > *T*₁; these values represent weighted averages for Si—O and Fe^{III}—O distances for each *T* site. The mean *T*—O distances for the three *T* sites can be used to calculate the site occupancies based on tetrahedral bond lengths of 1.86 Å for Fe^{III}—O and 1.60 Å for Si—O. The values obtained for the Fe occupancies using this method are *T*₁ 0.28, *T*₂ 0.30 and *T*₃ 0.42. These values may be compared with the refined site occupancies of 0.29 (1), 0.35 (1) and 0.36 (1). Mazzi *et al.* (1976) found that for natural leucite the order of decreasing *T*-site distortion is *T*₁ > *T*₂ > *T*₃; the relative distortions can be assessed using the tetrahedral angle variances σ^2 (in degrees²) (Robinson,

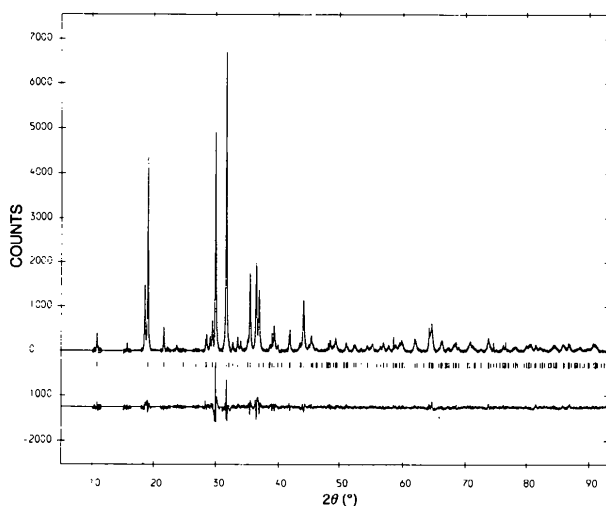


Fig. 1. Rietveld difference plot for dry-synthesized KFeSi_2O_6 .

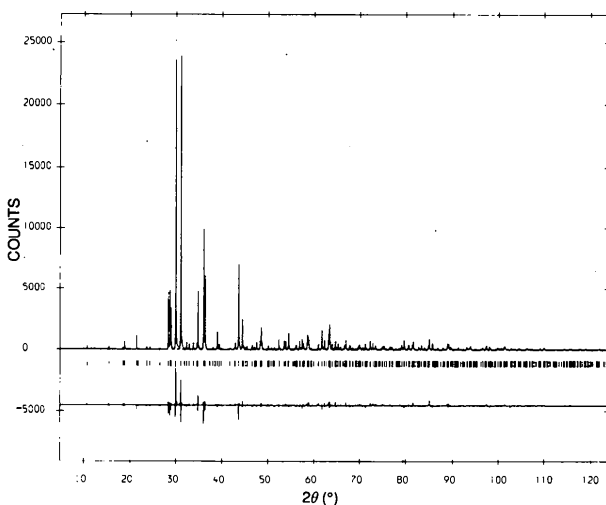


Fig. 2. Rietveld difference plot for dry-synthesized $\text{RbFeSi}_2\text{O}_6$.

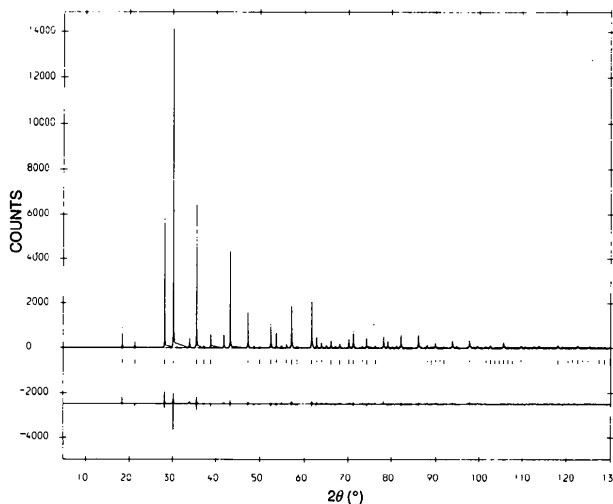


Fig. 3. Rietveld difference plot for dry-synthesized $\text{CsFeSi}_2\text{O}_6$.

Gibbs & Ribbe, 1971) of 8.7, 5.4 and 2.3, respectively. As expected, the angle variances for the Fe leucites studied here are considerably higher as a result of the presence of the larger Fe cations in the framework. Angle variances for KFeSi_2O_6 leucite are T_1 8.7, T_2 13.3 and T_3 28.0; thus Fe seems to be preferentially ordered into the most distorted T site, confirming the Mössbauer site assignments of Brown *et al.* (1987) and England *et al.* (1994). Note that these Fe leucites do not show the same relative distortions for the three T sites as natural leucite (Mazzi *et al.*, 1976), suggesting that Al and Fe have significantly different effects on the geometries of the TO_4 tetrahedra.

The tetrahedral angle variances in $\text{RbFeSi}_2\text{O}_6$ leucite are larger than those in KFeSi_2O_6 (T_1 30.6, T_2 23.1 and T_3 57.9); the T_3 site is again the most distorted. The mean T —O distances decrease in the order $T_3 > T_2 \approx T_1$ leading to values for the Fe occupancies of T_1 0.31, T_2 0.27 and T_3 0.42. These values may be compared with those obtained from the Rietveld refinement: 0.31 (1), 0.36 (1) and 0.33 (1), respectively. The occupancies calculated from the bond lengths might be the more reliable as the R factor for the refinement in which the possibility of ordering was included was little better than that for the refinement in which disorder was assumed. In addition, the model for the $\text{RbFeSi}_2\text{O}_6$ leucite structure is slightly less reliable than for the other two leucites because of preferred orientation in the sample. In $\text{RbFeSi}_2\text{O}_6$ leucite, therefore, Fe seems to be slightly ordered into the most distorted T site (T_3) but the degree of ordering is less than that in KFeSi_2O_6 leucite. $\text{RbFeSi}_2\text{O}_6$ leucite is less tetragonal than KFeSi_2O_6 leucite ($c/a = 1.036$ and 1.055 , respectively) with a lower tetragonal—cubic transition temperature [593 and 843 K, respectively (Hirao *et al.*, 1976)]. The differences between the local geometries of the three T sites decrease as temperature or mean size of the alkali-metal cations in the cavities increases and thus less T -site ordering might be expected in Rb leucites than in K leucites.

For the cubic $1a\bar{3}d$ $\text{CsFeSi}_2\text{O}_6$ leucite the refined T —O distance represents the weighted average of tetrahedral Si—O and Fe^{III} —O distances. The tetrahedral angle variance for the single T site is 47.3; this value compares well with the mean for the three T sites in $\text{RbFeSi}_2\text{O}_6$ leucite. The displacement factors for the framework components in $\text{CsFeSi}_2\text{O}_6$ leucite are larger than those for the KFeSi_2O_6 and $\text{RbFeSi}_2\text{O}_6$ leucites as a result of the more disordered nature of the structure. As might be expected, the alkali-metal cation displacement factors vary inversely with cation size.

Taylor & Henderson (1968) discussed the thermal expansion and tetragonal—cubic phase-transition behaviour of K, Rb and Cs aluminosilicate leucites in terms of collapse of the framework about the cavity cations. Decreasing temperature and decreasing mean cavity cation

size lead to structures that are more collapsed, as a cooperative rotation of the TO_4 units to form stronger bonds with the alkali-metal cations occurs. Hirao *et al.* (1976) used this same explanation to account for the behaviour of the analogous alkali-metal ferro-silicate leucites. The structures determined in this paper confirm these rela-

tionships as the mean $T-O-T$ angles decrease with decreasing alkali-metal cation size (Cs 140.1, Rb 135.3, K 135.0°). Note that the $T-O-T$ angles tend to increase as framework structures become more symmetrical, *i.e.* less collapsed.

Comparison of the projections of the structures of KFeSi₂O₆ and CsFeSi₂O₆ in Figs. 4 and 5, respectively, shows how the channels in the framework become distorted as the structure collapses. The structure of RbFeSi₂O₆ is similar to that of KFeSi₂O₆, but has slightly less distorted channels.

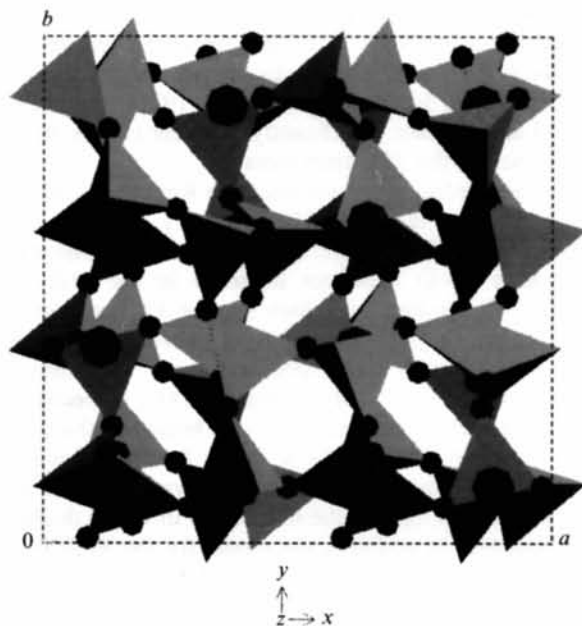


Fig. 4. A projection of the structure of KFeSi₂O₆ along [001]. Tetrahedra represent TO_4 units, large circles represent K^+ cations and small circles represent O^{2-} anions.

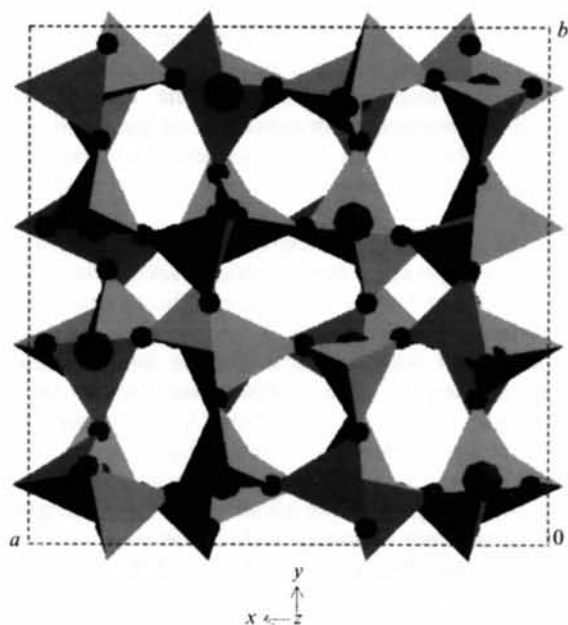


Fig. 5. A projection of the structure of CsFeSi₂O₆ along [001]. Tetrahedra represent TO_4 units, large circles represent Cs^+ cations and small circles represent O^{2-} anions.

Experimental

Appropriate proportions of the relevant alkali-metal carbonate, Fe_2O_3 and SiO_2 were ground together to provide the starting materials. The K-containing mix was melted at 1523 K for two days and was quenched to form a glass, followed by crystallization at 1073 K for four days. The Rb- and Cs-containing mixes were recrystallized at 1673 K for three days.

KFeSi₂O₆

Crystal data

KFeSi₂O₆
 $M_r = 247.11$
 Tetragonal
 $I4_1/a$
 $a = 13.2207(3) \text{ \AA}$
 $c = 13.9464(3) \text{ \AA}$
 $V = 2437.6(2) \text{ \AA}^3$
 $Z = 16$

Synchrotron radiation

$\lambda = 1.80067 \text{ \AA}$
 $T = 293 \text{ K}$
 Powder
 Sample mounted in
 reflection mode

Data collection

High resolution powder
 diffractometer, SRS
 station 8.3 (Cernik,
 Murray, Pattison & Fitch,
 1990)
 Parallel beam non-focusing
 optics with channel-cut
 monochromator and
 scintillation detector

Method for scanning
 reciprocal space: step scan
 Absorption correction
 method: none
 8800 data points measured
 8800 data points in the
 processed diffractogram
 $2\theta_{\min} = 5.00$, $2\theta_{\max} =$
 92.99°
 Increment in $2\theta = 0.01^\circ$

Refinement

$R_I = 0.045$ (Young, Prince &
 Sparks, 1982)
 $R_{wp} = 0.154$ (Young, Prince
 & Sparks, 1982)
 $R_{\text{exp}} = 0.120$ (Young, 1993)
 $S = 1.645$
 352 reflections

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

Table 1. Fractional atomic coordinates, isotropic displacement parameters (\AA^2) and site occupancy factors for KFeSi₂O₆

	x	y	z	B_{iso}	Occupancy
K	0.3620 (5)	0.3641 (4)	0.1174 (5)	4.9 (2)	1.00
Si1	0.0570 (4)	0.3972 (4)	0.1643 (4)	0.87 (9)	0.71 (1)
Si2	0.1649 (4)	0.6130 (4)	0.1271 (4)	0.87 (9)	0.65 (1)
Si3	0.3914 (4)	0.6440 (4)	0.0851 (3)	0.87 (9)	0.64 (1)

Fe1	0.0570 (4)	0.3972 (4)	0.1643 (4)	0.87 (9)	0.29 (1)
Fe2	0.1649 (4)	0.6130 (4)	0.1271 (4)	0.87 (9)	0.35 (1)
Fe3	0.3914 (4)	0.6440 (4)	0.0851 (3)	0.87 (9)	0.36 (1)
O1	0.1299 (9)	0.3181 (9)	0.1165 (7)	0.25	1.00
O2	0.0890 (8)	0.5125 (9)	0.1322 (8)	0.25	1.00
O3	0.1486 (8)	0.6787 (7)	0.2299 (8)	0.25	1.00
O4	0.1279 (9)	0.6823 (7)	0.0382 (8)	0.25	1.00
O5	0.2885 (9)	0.5727 (8)	0.125 (1)	0.25	1.00
O6	0.4818 (8)	0.6131 (7)	0.1758 (7)	0.25	1.00

Table 2. Selected geometric parameters (\AA , $^\circ$)
for KFeSi_2O_6

T represents Si or Fe.

T1—O1	1.57 (1)	T3—O5	1.75 (1)
T1—O1'	1.72 (1)	T3—O6	1.79 (1)
T1—O2	1.64 (1)	T3—O6'	1.69 (1)
T1—O4	1.75 (1)	K—O1	3.13 (1)
T2—O2	1.67 (1)	K—O2	2.99 (1)
T2—O3	1.69 (1)	K—O3	3.11 (1)
T2—O4'	1.62 (1)	K—O4	3.03 (1)
T2—O5	1.72 (1)	K—O5	2.93 (1)
T3—O3'	1.65 (1)	K—O6	2.96 (1)
O1—T1—O1'	113.2 (6)	O3'—T3—O5	109.4 (6)
O1—T1—O2	110.2 (6)	O3'—T3—O6	110.6 (5)
O1—T1—O4	105.8 (6)	O3'—T3—O6'	108.6 (6)
O1'—T1—O2	107.6 (6)	O5—T3—O6	99.9 (6)
O1'—T1—O4	107.7 (6)	O5—T3—O6'	112.4 (6)
O2—T1—O4	112.5 (6)	O6—T3—O6'	115.6 (6)
O2—T2—O3	107.3 (6)	T1—O1—T1	145.7 (8)
O2—T2—O4'	107.6 (6)	T1—O2—T2	154.9 (7)
O2—T2—O5	109.0 (5)	T2—O3—T3	130.2 (6)
O3—T2—O4'	108.7 (5)	T1—O4—T2	139.3 (7)
O3—T2—O5	107.2 (6)	T2—O5—T3	125.4 (7)
O4'—T2—O5	116.7 (6)	T3—O6—T3	122.4 (6)

RbFeSi₂O₆

Crystal data

RbFeSi₂O₆

$M_r = 293.48$

Tetragonal

$I4_1/a$

$a = 13.4586 (1) \text{\AA}$

$c = 13.9380 (1) \text{\AA}$

$V = 2524.63 (5) \text{\AA}^3$

$Z = 16$

Data collection

High resolution powder diffractometer, SRS station 8.3 (Cernik, Murray, Pattison & Fitch, 1990)
Parallel beam non-focusing optics with channel-cut monochromator and scintillation detector

Refinement

$R_I = 0.089$ (Young, Prince & Sparks, 1982)

$R_{wp} = 0.174$ (Young, Prince & Sparks, 1982)

$R_{exp} = 0.102$ (Young, 1993)

$S = 2.898$

626 reflections

Synchrotron radiation

$\lambda = 1.80067 \text{\AA}$

$T = 293 \text{ K}$

Powder

Sample mounted in reflection mode

Method for scanning reciprocal space: step scan
Absorption correction method: none
11 876 data points measured
11 876 data points in the processed diffractogram
 $2\theta_{min} = 5.00$, $2\theta_{max} = 123.75^\circ$
Increment in $2\theta = 0.01^\circ$

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

Table 3. Fractional atomic coordinates, isotropic displacement parameters (\AA^2) and site occupancy factors for $\text{RbFeSi}_2\text{O}_6$

	<i>x</i>	<i>y</i>	<i>z</i>	B_{iso}	Occupancy
Rb	0.3655 (2)	0.3632 (2)	0.1213 (2)	4.51 (7)	1.00
Si1	0.0645 (4)	0.3937 (4)	0.1629 (3)	2.62 (9)	0.69 (1)
Si2	0.1685 (4)	0.6062 (4)	0.1272 (4)	2.62 (9)	0.64 (1)
Si3	0.3883 (4)	0.6473 (4)	0.0885 (4)	2.62 (9)	0.67 (1)
Fe1	0.0645 (4)	0.3937 (4)	0.1629 (3)	2.62 (9)	0.31 (1)
Fe2	0.1685 (4)	0.6062 (4)	0.1272 (4)	2.62 (9)	0.36 (1)
Fe3	0.3883 (4)	0.6473 (4)	0.0885 (4)	2.62 (9)	0.33 (1)
O1	0.136 (1)	0.3122 (8)	0.1040 (8)	3.0 (1)	1.00
O2	0.0959 (9)	0.5032 (9)	0.1227 (7)	3.0 (1)	1.00
O3	0.1463 (9)	0.6690 (7)	0.2226 (8)	3.0 (1)	1.00
O4	0.1332 (9)	0.6734 (7)	0.0357 (8)	3.0 (1)	1.00
O5	0.2911 (9)	0.559 (1)	0.1236 (9)	3.0 (1)	1.00
O6	0.4795 (9)	0.6110 (9)	0.1563 (9)	3.0 (1)	1.00

Table 4. Selected geometric parameters (\AA , $^\circ$)
for $\text{RbFeSi}_2\text{O}_6$

T represents Si or Fe.

T1—O1	1.67 (1)	T3—O5	1.83 (1)
T1—O1'	1.72 (1)	T3—O6	1.62 (1)
T1—O2	1.63 (1)	T3—O6'	1.70 (1)
T1—O4	1.73 (1)	Rb—O1	3.18 (1)
T2—O2	1.70 (1)	Rb—O2	3.20 (1)
T2—O3	1.60 (1)	Rb—O3	3.21 (1)
T2—O4'	1.63 (1)	Rb—O4	3.13 (1)
T2—O5	1.77 (1)	Rb—O5	2.82 (1)
T3—O3'	1.77 (1)	Rb—O6	3.25 (1)
O1—T1—O1'	117.3 (5)	O3'—T3—O5	101.3 (5)
O1—T1—O2	106.0 (6)	O3'—T3—O6	104.9 (6)
O1—T1—O4	112.3 (6)	O3'—T3—O6'	114.3 (6)
O1'—T1—O2	105.4 (6)	O5—T3—O6	101.0 (6)
O1'—T1—O4	102.9 (6)	O5—T3—O6'	117.8 (6)
O2—T1—O4	112.9 (6)	O6—T3—O6'	115.6 (7)
O2—T2—O3	110.7 (6)	T1—O1—T1	138.7 (8)
O2—T2—O4'	104.9 (6)	T1—O2—T2	150.9 (8)
O2—T2—O5	104.2 (5)	T2—O3—T3	134.2 (7)
O3—T2—O4'	107.5 (6)	T1—O4—T2	143.4 (7)
O3—T2—O5	112.7 (5)	T2—O5—T3	116.3 (8)
O4'—T2—O5	116.6 (5)	T3—O6—T3	134.2 (8)

CsFeSi₂O₆

Crystal data

CsFeSi₂O₆

$M_r = 340.92$

Cubic

$Ia\bar{3}d$

$a = 13.8542 (1) \text{\AA}$

$V = 2653.98 (3) \text{\AA}^3$

$Z = 16$

Data collection

High resolution powder diffractometer, SRS station 8.3 (Cernik, Murray, Pattison & Fitch, 1990)

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

Synchrotron radiation

$\lambda = 1.80067 \text{\AA}$

$T = 293 \text{ K}$

Powder

Sample mounted in reflection mode

Method for scanning reciprocal space: step scan
Absorption correction method: none
12 501 data points measured
12 501 data points in the processed diffractogram
 $2\theta_{min} = 5.00$, $2\theta_{max} = 130.00^\circ$
Increment in $2\theta = 0.01^\circ$

Refinement

$R_I = 0.106$ (Young, Prince & Sparks, 1982)	15 parameters
$R_{wp} = 0.173$ (Young, Prince & Sparks, 1982)	Atomic scattering factors from <i>International Tables for X-ray Crystallography</i> (1974, Vol. IV, Table 2.3.1)
$R_{exp} = 0.160$ (Young, 1993)	
$S = 1.171$	
122 reflections	

Table 5. Fractional atomic coordinates, isotropic displacement parameters (\AA^2) and site occupancy factors for CsFeSi₂O₆

CsFeSi ₂ O ₆					
	x	y	z	B_{iso}	Occupancy
Cs	1/8	1/8	1/8	3.10 (3)	1.00
Si	1/8	0.6628 (1)	0.5873 (1)	4.04 (6)	0.67
Fe	1/8	0.6628 (1)	0.5873 (1)	4.04 (6)	0.33
O	0.4686 (3)	0.3859 (3)	0.1509 (3)	4.5 (1)	1.00

Table 6. Selected geometric parameters (\AA , $^\circ$) for CsFeSi₂O₆

T represents Si or Fe.

T—O	× 2	1.706 (4)	Cs—O	× 6	3.573 (4)
T—O'	× 2	1.658 (4)	Cs—O'	× 6	3.365 (4)
O—T—O'	× 2	114.2 (2)	O'—T—O'		101.8 (2)
O'—T—O	× 2	113.8 (2)	T—O—T		140.1 (2)
O—T—O		99.7 (2)			

The systematic absences in the powder diffraction data for KFeSi₂O₆ and RbFeSi₂O₆ showed that these materials have the $I4_1/a$ leucite structure. Atomic coordinates from the low-temperature structure of natural leucite (Mazzi *et al.*, 1976) were used as a starting model for these refinements. The K compound contained a small but significant amount of haematite (Fe₂O₃) as an impurity. In this case, a two-phase refinement was performed using the structural parameters for haematite from Blake, Hessevick, Zoltai & Finger (1966). The systematic absences in the powder diffraction data for CsFeSi₂O₆ confirmed that this material has the cubic $Ia\bar{3}d$ structure, for which the atomic coordinates from the high-temperature structure of natural leucite (Peacor, 1968) were used as a starting model. The structures of the K- and Rb-containing leucites were initially refined in $I4_1/a$ assuming a disordered arrangement of Fe^{III} and Si on the tetrahedral sites, giving R_I factors of 0.064 and 0.097, respectively. In subsequent refinements the T-site occupancies were allowed to vary, leading to a significant improvement for KFeSi₂O₆ ($R_I = 0.045$) while RbFeSi₂O₆ showed a small improvement ($R_I = 0.089$). Data collection was performed using in-house software. The raw synchrotron powder diffraction data were normalized to account for the decay of the synchrotron radiation beam. Cell refinement was performed using *REFCEL* from the *Powder Diffraction Program Library (PDPL)* (Murray, Cockcroft & Fitch, 1990). Structure refinement was carried out using the program *MPROF* in *PDPL*. A pseudo-Voigt peak-shape function was used to model the shape of the Bragg peaks, and the least-squares weighting scheme used was weight = normalization factor/(profile intensity + background). Molecular graphics were prepared using *CERIUS* (Molecular Simulations Inc., 1994).

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Lists of raw powder data have been deposited with the IUCr (Reference: BR1077). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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