

# Synthesis and crystal structure of a new microporous silicate with a mixed octahedral-tetrahedral framework: $\text{Cs}_3\text{ScSi}_8\text{O}_{19}$

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## ABSTRACT

During investigations of the system  $\text{Sc}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-TiO}_2\text{-SiO}_2$ , a new, unusual microporous compound,  $\text{Cs}_3\text{ScSi}_8\text{O}_{19}$ , was synthesized as colourless plates from a  $\text{CsF-MoO}_3$  flux. The crystal structure was determined from single-crystal X-ray diffraction data (Mo- $K\alpha$  radiation, CCD area detector). The compound is orthorhombic, space group  $Pnma$ , with  $a = 11.286(2)$ ,  $b = 7.033(1)$ ,  $c = 26.714(5)$  Å, and  $Z = 4$  ( $R_1(F) = 2.6\%$  and  $wR_{2\text{all}}(F^2) = 7.3\%$ , using 3066 ‘observed’ reflections with  $F_o > 4\sigma(F_o)$ ). The crystal structure of  $\text{Cs}_3\text{ScSi}_8\text{O}_{19}$  represents a new microporous framework structure type (‘MCV-1’), and the compound is exceptional in being the first representative of a mixed octahedral-tetrahedral framework structure, in which the  $[\text{TO}_4]:[\text{MO}_6]$  ratio is  $>6:1$ . The structure is based on isolated, nearly regular  $\text{ScO}_6$  octahedra [ $d_{\text{av}}(\text{Sc-O}) = 2.112$  Å] sharing corners with  $\text{SiO}_4$  tetrahedra to form an open framework with four-, six- and eight-membered rings; the latter are formed by  $\text{SiO}_4$  tetrahedra only. Two fully occupied Cs positions are located in large framework voids close to the six-membered rings, whereas four partly occupied and disordered Cs positions are close to very large framework voids bordered by the puckered eight-membered rings. The cavities are linked into channels parallel to  $[100]$  and  $[010]$ . The structure is compared with that of  $\text{Cs}_2\text{TiSi}_6\text{O}_{15}$  and related microporous scandium-, REE-, titano- and zirconosilicate minerals and compounds.  $\text{Cs}_3\text{ScSi}_8\text{O}_{19}$  or derivatives may be important in the context of immobilization of radioactive  $^{137}\text{Cs}$  waste, cationic conductivity or catalysis.

**KEYWORDS:** caesium scandium silicate ( $\text{Cs}_3\text{ScSi}_8\text{O}_{19}$ ), crystal structure, microporous, eight-membered rings, disorder.

## Introduction

As part of a project on phases and phase equilibria in the previously uninvestigated quaternary system  $\text{Sc}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-TiO}_2\text{-SiO}_2$ , which contains several refractory phases important in the field of applied mineralogy, a number of oxidic scandium compounds have been prepared using flux-growth techniques, and their crystal structures and crystal chemistry have been studied (Kolitsch and Tillmanns, 2003*a,b,c,d*). Recently, we have synthesized two new, unusual alkali scandium silicates,  $\text{K}_2\text{ScFSi}_4\text{O}_{10}$  (Kolitsch and Tillmanns,

2004), which is very closely related to narsarsukite  $[\text{Na}_2(\text{Ti,Fe}^{3+})(\text{O,F})\text{Si}_4\text{O}_{10}]$ , and  $\text{Cs}_3\text{ScSi}_8\text{O}_{19}$ , to be characterized in the present paper on the basis of single-crystal X-ray diffraction (XRD) studies. As will be shown,  $\text{Cs}_3\text{ScSi}_8\text{O}_{19}$  has a microporous character and represents a novel structure type among mixed-framework octahedral-tetrahedral frameworks. The latter include a large number of titano- and zirconosilicate minerals, and have recently attracted considerable interest due to their zeolite-like properties and potential applications in catalysis, adsorption, ion-exchange and separation (e.g. Rocha and Anderson, 2000; Anderson and Rocha, 2002) and as luminescent materials (e.g. Ananias *et al.*, 2002; Vidican *et al.*, 2003). Due to its structural features,  $\text{Cs}_3\text{ScSi}_8\text{O}_{19}$  or derivatives may be

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useful in the immobilization of radioactive  $^{137}\text{Cs}$  waste or as a cationic conductor. In line with the common tradition of giving three-letter names to new microporous framework structure types we have designated  $\text{Cs}_3\text{ScSi}_8\text{O}_{19}$  as 'MCV-1', for the Institute of Mineralogy and Cystallography Vienna.

## Experimental

### Synthesis

$\text{Cs}_3\text{ScSi}_8\text{O}_{19}$  has been synthesized during flux-growth preparations of Sc silicates and titanates. The new compound crystallized in air from a CsF-MoO<sub>3</sub> flux containing dissolved Sc<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub> and TiO<sub>2</sub> (experimental parameters: 6.0 g CsF, 1.5 g MoO<sub>3</sub>, 0.2299 g Sc<sub>2</sub>O<sub>3</sub>, 0.0901 g SiO<sub>2</sub>, 0.0133 g TiO<sub>2</sub>; Pt crucible covered with lid,  $T_{\text{max}}$  1150°C, holding time 6 h, cooling rate 1.5 K/h,  $T_{\text{min}}$  900°C, slow cooling to room temperature after switching off furnace; total weight loss 54.6%). The colourless, tabular {001}, indistinctly rectangular (elongation parallel to [100]) crystals of  $\text{Cs}_3\text{ScSi}_8\text{O}_{19}$  are up to 2 mm in their longest dimension. The crystals were found attached to the upper part of the inner crucible wall, an observation suggesting that vapour transport played a role in their formation. The white, water-soluble flux matrix contained colourless, transparent cubes of Sc<sub>2</sub>O<sub>3</sub> (up to 1 mm in size) and colourless, transparent, thick tabular, partly twinned crystals of synthetic thortveitite, Sc<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> (up to 1.5 mm). Semiquantitative chemical analysis (SEM-EDS) of the title compound showed no metals other than Cs, (minor) Sc, and Si.

### X-ray crystallography

Fragments of selected tabular crystals were studied with a Nonius KappaCCD diffractometer equipped with a 300  $\mu\text{m}$  diameter capillary-optics collimator to provide increased resolution. All fragments investigated showed a high crystal quality and the same primitive orthorhombic cell (see abstract). For the intensity data collection, a full sphere of reciprocal space was measured from a small tabular fragment using Mo-K $\alpha$  radiation (see Table 1 for details). The measured intensity data were processed with the Nonius program suite DENZO-SMN and corrected for Lorentz, polarization, background and absorption effects. Analysis of the extinction conditions and intensity statistics of the measured data clearly indicated

the centrosymmetric space group *Pnma*. The crystal structure was solved in *Pnma* by direct methods (SHELXS-97, Sheldrick, 1997a) and subsequent Fourier and difference Fourier syntheses, followed by anisotropic full-matrix least-squares refinements on  $F^2$  (SHELXL-97, Sheldrick, 1997b) (Table 1). The unit cell was found to contain, apart from clearly defined Cs, Sc, Si and O sites, four partly occupied and considerably disordered Cs sites. Refinement of their occupancies led to a nearly charge-balanced formula (38.04 positive charges vs. 38.00 negative charges); therefore, in order to obtain a fully electroneutral formula, the occupancies of the four partly occupied and disordered Cs sites were very slightly modified and then fixed. The last step of refinement gave the final residuals  $R1(F) = 2.64\%$  and  $wR2_{\text{all}}(F^2) = 7.59\%$ , using 3066 reflections with  $F_o > 4\sigma(F_o)$  and 189 parameters (Table 1). All the largest residual peaks in the final electron density map were close to the disordered Cs positions. A determination of the unit-cell parameters at 120 K suggests no phase transition during cooling, and only a small volume shrinkage of  $\sim 0.4\%$ .

Final positional and anisotropic displacement parameters are given in Tables 2 and 3. Selected bond lengths and calculated bond-valences are presented in Table 4. A list of observed and calculated structure factors (Table 5) has been deposited with the Principal Editor of *Mineralogical Magazine* and is also available upon request from the authors or from the Mineralogical Society website:

[www.minersoc.org/pages/e\\_journals/dep\\_mat.htm](http://www.minersoc.org/pages/e_journals/dep_mat.htm).

## Results and discussion

### Crystal structure and topology

$\text{Cs}_3\text{ScSi}_8\text{O}_{19}$  has a three-dimensional, microporous framework structure which is unique among mixed-framework octahedral-tetrahedral frameworks. It contains six unique Cs sites, four of which are partly occupied and considerably disordered (with approximate occupancies of 0.80 for Cs(3a), 0.05 for Cs(3b), 0.10 for Cs(3c) and 0.05 for Cs(3d)). Furthermore, there is one Sc site, six Si sites and 13 O sites. The majority of these sites are located on special positions with  $y = \frac{1}{4}$  (Table 2). The framework is built from corner-sharing SiO<sub>4</sub> tetrahedra, connected to an isolated ScO<sub>6</sub> octahedron. The connectivity results in eight-, six- and four-membered rings, and large voids and channels which host the Cs atoms

CRYSTAL STRUCTURE OF Cs<sub>3</sub>ScSi<sub>8</sub>O<sub>19</sub>TABLE 1. Crystal data, data collection information and refinement details for Cs<sub>3</sub>ScSi<sub>8</sub>O<sub>19</sub>.

|   |   |
|---|---|
| Crystal data  |   |
| Space group   | <i>Pnma</i>   |
| <i>a</i> , <i>b</i> , <i>c</i> (Å)  | 11.286(2), 7.033(1), 26.714(5)                              |
| <i>V</i> (Å <sup>3</sup> ), <i>Z</i>  | 2120.4(6), 4  |
| <i>F</i> (000), ρ <sub>calc</sub> (g·cm <sup>-3</sup> )                         | 1800, 3.046   |
| μ (mm <sup>-1</sup> )   | 5.96  |
| Absorption correction   | multi-scan*   |
| Crystal dimensions (mm)   | 0.03 × 0.12 × 0.20  |
| Data collection   |   |
| Diffractometer  | Nonius KappaCCD system                                      |
| <i>T</i> (K), λ (Mo- <i>K</i> α) (Å)  | 293, 0.71073  |
| Crystal-detector dist. (mm)   | 48  |
| Rotation axis; rotat. width (°)   | φ, ω; 1.0   |
| Total no. of frames   | 1092  |
| Collect. time per degree (s)  | 145   |
| Collection mode; 2θ <sub>max</sub>  | full sphere; 60   |
| <i>h</i> , <i>k</i> , <i>l</i> ranges   | -15 → 15, -9 → 9, -37 → 37                                  |
| Total reflections measured  | 5999  |
| Unique reflections  | 3325 ( <i>R</i> <sub>int</sub> = 1.25%)                     |
| Refinement  |   |
| <i>R</i> 1( <i>F</i> ), w <i>R</i> 2 <sub>all</sub> ( <i>F</i> <sup>2</sup> )** | 2.64%, 7.59%  |
| 'Observed' reflections  | 3066 [ <i>F</i> <sub>o</sub> > 4σ( <i>F</i> <sub>o</sub> )] |
| Extinction coefficient  | 0.00099(12)   |
| No. of refined parameters   | 189   |
| Goof; (Δ/σ) <sub>max</sub>  | 1.122; 0.001  |
| Δρ <sub>min</sub> , Δρ <sub>max</sub> (e/Å <sup>3</sup> )                       | -1.6, 2.1   |

Unit-cell parameters were refined from 3543 recorded reflections. Scattering factors for neutral atoms were employed in the refinement.

\* Otwinowski and Minor (1997)

\*\*  $w = 1/[\sigma^2(F_o^2) + (0.036P)^2 + 7.25P]$ , where  $P = ([\max \text{ of } (0 \text{ or } F_o^2)] + 2F_c^2)/3$

(Figs 1–3). Each O atom is coordinated to either two Si atoms or one Si and one Sc atom; all additional bonds are longer (>3.0 Å) bonds to the Cs atoms.

The eight-membered, puckered rings are built from SiO<sub>4</sub> tetrahedra only. Different sets of rings are oriented approximately parallel to (010), (102) and (10 $\bar{2}$ ) (Figs 1,3). The (010) rings are characterized by the Si numeral sequence 1-2-3-4-5-6-2-3 (the sequence numbers refer to the atom labels given in Table 2). Two different (10 $\bar{2}$ ) rings have the sequences 1-1-2-6-5-5-6-2 and 1-1-2-3-1-1-3-2, while two (102) rings show the sequences 1-1-3-2-1-1-2-3 and 5-5-6-2-1-1-2-6 (the latter ring being strongly puckered). Using the up/down classification (Liebau, 1985), the (010) rings can, in a simplified way, be characterized with the sequence *UUUDUUUD*.

The other sets of rings are too puckered and irregular to be classified in such a way. Adjacent (010) rings are connected parallel to [010] via shared O atoms of two Si(1)- and Si(5)O<sub>4</sub> tetrahedra (Fig. 3). Interestingly, the Si–O–Si angles of the tetrahedra involved in this linkage are considerably different: Si(1)–O(2)–Si(1) = 154.0° vs. Si(5)–O(12)–Si(5) = 131.4° (cf. Fig. 3). This observation may be explained by the influence of neighbouring SiO<sub>4</sub> groups and Cs atoms.

The six-membered, equally corrugated rings result from the linkage between two ScO<sub>6</sub> octahedra and four SiO<sub>4</sub> tetrahedra (best seen in Fig. 1), whereas the four-membered rings are formed due to the linkage between either one ScO<sub>6</sub> octahedron and three SiO<sub>4</sub> tetrahedra, or four interconnected SiO<sub>4</sub> tetrahedra.

TABLE 2. Fractional atomic coordinates and displacement parameters for Cs<sub>3</sub>ScSi<sub>8</sub>O<sub>19</sub>.

| Atom   | <i>x</i>    | <i>y</i>    | <i>z</i>     | <i>U</i> <sub>eq</sub> | Occupancy |
|--------|-------------|-------------|--------------|------------------------|-----------|
| Cs(1)  | 0.08833(2)  | ¼           | 0.451216(10) | 0.01849(9)             |           |
| Cs(2)  | 0.44959(2)  | ¼           | 0.453276(10) | 0.01806(9)             |           |
| Cs(3a) | -0.06753(7) | ¼           | 0.27852(3)   | 0.0553(2)              | 0.80*     |
| Cs(3b) | 0.0542(16)  | ¼           | 0.2320(6)    | 0.114(11)              | 0.05*     |
| Cs(3c) | -0.3636(13) | ¼           | 0.3136(4)    | 0.137(6)               | 0.10*     |
| Cs(3d) | -0.2460(11) | 0.050(2)    | 0.3034(3)    | 0.062(5)               | 0.025*    |
| Sc     | 0.27253(6)  | -¼          | 0.44425(3)   | 0.00708(14)            |           |
| Si(1)  | 0.25573(6)  | 0.02635(11) | 0.33686(3)   | 0.00826(14)            |           |
| Si(2)  | 0.05993(9)  | ¼           | 0.79830(4)   | 0.00857(19)            |           |
| Si(3)  | -0.05747(9) | ¼           | 0.68963(4)   | 0.00895(19)            |           |
| Si(4)  | 0.04073(9)  | ¼           | 0.58493(4)   | 0.00815(19)            |           |
| Si(5)  | -0.24354(6) | 0.03814(11) | 0.44130(3)   | 0.00813(14)            |           |
| Si(6)  | 0.42851(9)  | ¼           | 0.60048(4)   | 0.00856(19)            |           |
| O(1)   | 0.2699(2)   | -0.0203(3)  | 0.39362(8)   | 0.0187(4)              |           |
| O(2)   | 0.2515(3)   | ¼           | 0.32322(12)  | 0.0183(6)              |           |
| O(3)   | 0.1386(2)   | 0.0601(4)   | 0.80222(9)   | 0.0253(5)              |           |
| O(4)   | -0.1335(2)  | 0.0587(4)   | 0.68689(10)  | 0.0285(6)              |           |
| O(5)   | 0.0073(3)   | ¼           | 0.74288(11)  | 0.0192(6)              |           |
| O(6)   | -0.0429(3)  | ¼           | 0.83932(11)  | 0.0204(7)              |           |
| O(7)   | 0.0407(3)   | ¼           | 0.64614(12)  | 0.0293(8)              |           |
| O(8)   | -0.0850(3)  | ¼           | 0.56010(13)  | 0.0194(6)              |           |
| O(9)   | -0.1165(2)  | -0.0651(3)  | 0.43189(10)  | 0.0223(5)              |           |
| O(10)  | 0.27761(19) | -0.0436(3)  | 0.50126(7)   | 0.0150(4)              |           |
| O(11)  | 0.3445(2)   | 0.0635(3)   | 0.59311(8)   | 0.0191(4)              |           |
| O(12)  | -0.2284(3)  | ¼           | 0.41692(11)  | 0.0163(6)              |           |
| O(13)  | 0.5402(3)   | ¼           | 0.56519(12)  | 0.0192(6)              |           |

\* Occupancies fixed to achieve completely charge-balanced formula (see text).

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \mathbf{a}_j \text{ (Fischer and Tillmanns, 1988)}$$

The two fully occupied Cs positions, Cs(1) and Cs(2), are located in the large voids close to the six-membered rings. Both Cs(1) and Cs(2) are coordinated to 11 O atoms (Table 4). All four partially occupied and considerably disordered Cs atoms, Cs(3a) to Cs(3d), have very irregular coordinations to approximately seven to eight O atoms, and are located close to the eight-membered rings (Figs 1,2). Seemingly, the very large voids created by the linkage between these eight-membered rings provide several energetically similar positions. The minimum free diameter of the (010) silicate rings is  $\sim 2.8 \times 3.4$  Å, based on an oxygen radius of 1.35 Å. The corresponding diameters of the two similar (102) rings are  $\sim 4.2 \times 4.3$  and  $3.7 \times 4.3$  Å; those of the two (10 $\bar{2}$ ) rings are  $\sim 3.5 \times 4.3$  and  $3.5 \times 4.2$  Å. Thus, the Cs<sup>+</sup> cations, with a diameter of at least 3.5 Å, should be able to migrate through the majority of these rings. Consequently, measurable cationic conductivity,

predominantly in the *ab* plane, at high temperatures may be predicted from the atomic arrangement (cf. Figs 1,2). This is also indicated by the orientation of the strongly elongate displacement ellipsoids of the four disordered sites (see bottom part of Fig. 1 and Table 3). We further note that the short Cs–Cs distances between all of the four disordered Cs sites Cs(3a) to Cs(3d) (Table 4) prevent their simultaneous occupation.

The average Si–O bond lengths show a small range between 1.600 and 1.619 Å (Table 4). The isolated ScO<sub>6</sub> octahedron (Fig. 4) is fairly regular, with Sc–O bond lengths between 2.105(2) and 2.129(3) Å (Table 4), and maximum deviations of 10.1° from an ideally octahedral geometry. The mean Sc–O bond length, 2.112 Å, is very close to the commonly observed value in oxidic Sc compounds, 2.105 Å (Baur, 1981).

Results of bond-valence calculations are given in Table 4. Bond-valence sums (BVS) of Si atoms range between 4.07 and 4.27 v.u. (valence units).

CRYSTAL STRUCTURE OF Cs<sub>3</sub>ScSi<sub>8</sub>O<sub>19</sub>TABLE 3. Anisotropic displacement parameters for Cs<sub>3</sub>ScSi<sub>8</sub>O<sub>19</sub>.

| Atom   | $U_{11}$    | $U_{22}$    | $U_{33}$    | $U_{23}$    | $U_{13}$    | $U_{12}$    |
|--------|-------------|-------------|-------------|-------------|-------------|-------------|
| Cs(1)  | 0.01806(15) | 0.01939(14) | 0.01803(14) | 0.0         | -0.00029(9) | 0.0         |
| Cs(2)  | 0.01513(14) | 0.01866(14) | 0.02038(14) | 0.0         | 0.00024(9)  | 0.0         |
| Cs(3a) | 0.0819(5)   | 0.0232(2)   | 0.0609(4)   | 0.0         | -0.0468(4)  | 0.0         |
| Cs(3b) | 0.181(18)   | 0.005(3)    | 0.157(16)   | 0.0         | -0.163(16)  | 0.0         |
| Cs(3c) | 0.150(12)   | 0.176(14)   | 0.086(7)    | 0.0         | -0.033(7)   | 0.0         |
| Cs(3d) | 0.074(8)    | 0.102(11)   | 0.010(4)    | 0.003(5)    | 0.009(4)    | -0.013(7)   |
| Sc     | 0.0077(3)   | 0.0074(3)   | 0.0062(3)   | 0.0         | -0.0001(2)  | 0.0         |
| Si(1)  | 0.0105(3)   | 0.0054(3)   | 0.0089(3)   | 0.0004(2)   | -0.0005(2)  | -0.0001(2)  |
| Si(2)  | 0.0095(4)   | 0.0099(5)   | 0.0063(4)   | 0.0         | -0.0017(3)  | 0.0         |
| Si(3)  | 0.0087(4)   | 0.0106(5)   | 0.0075(4)   | 0.0         | -0.0023(3)  | 0.0         |
| Si(4)  | 0.0064(4)   | 0.0091(4)   | 0.0089(4)   | 0.0         | 0.0017(3)   | 0.0         |
| Si(5)  | 0.0090(3)   | 0.0057(3)   | 0.0096(3)   | -0.0009(2)  | 0.0001(2)   | -0.0001(2)  |
| Si(6)  | 0.0073(4)   | 0.0103(5)   | 0.0082(4)   | 0.0         | -0.0015(3)  | 0.0         |
| O(1)   | 0.0290(11)  | 0.0160(10)  | 0.0111(9)   | 0.0063(8)   | -0.0001(8)  | 0.0006(9)   |
| O(2)   | 0.0344(18)  | 0.0058(13)  | 0.0146(14)  | 0.0         | -0.0010(12) | 0.0         |
| O(3)   | 0.0312(12)  | 0.0220(12)  | 0.0227(11)  | -0.0041(9)  | -0.0118(9)  | 0.0153(10)  |
| O(4)   | 0.0257(12)  | 0.0180(11)  | 0.0417(14)  | 0.0056(11)  | -0.0180(11) | -0.0111(10) |
| O(5)   | 0.0196(15)  | 0.0278(17)  | 0.0101(13)  | 0.0         | -0.0058(11) | 0.0         |
| O(6)   | 0.0199(15)  | 0.0289(18)  | 0.0124(14)  | 0.0         | 0.0054(11)  | 0.0         |
| O(7)   | 0.0222(17)  | 0.057(3)    | 0.0089(13)  | 0.0         | 0.0032(12)  | 0.0         |
| O(8)   | 0.0089(13)  | 0.0249(17)  | 0.0243(16)  | 0.0         | -0.0021(11) | 0.0         |
| O(9)   | 0.0147(10)  | 0.0180(11)  | 0.0342(12)  | -0.0054(10) | 0.0016(9)   | 0.0056(9)   |
| O(10)  | 0.0245(10)  | 0.0105(9)   | 0.0098(8)   | -0.0006(7)  | 0.0027(7)   | -0.0024(8)  |
| O(11)  | 0.0194(10)  | 0.0193(11)  | 0.0186(10)  | -0.0035(8)  | -0.0045(8)  | -0.0078(9)  |
| O(12)  | 0.0283(16)  | 0.0080(13)  | 0.0125(13)  | 0.0         | 0.0051(11)  | 0.0         |
| O(13)  | 0.0097(13)  | 0.0295(17)  | 0.0184(14)  | 0.0         | 0.0019(11)  | 0.0         |

These values clearly depend on the number of O ligands in each SiO<sub>4</sub> tetrahedron which bridge to adjacent SiO<sub>4</sub> tetrahedra: the only two Si atoms with four bridging O ligands, Si(2) and Si(3) (Fig. 3), have the highest BVS, 4.25 and 4.27 v.u.; they also show the most regular geometry among all six non-equivalent SiO<sub>4</sub> groups. The average Si–O bond-length in the Si(2)O<sub>4</sub> and Si(3)O<sub>4</sub> tetrahedra, 1.602 and 1.600 Å, respectively (Table 4), agree well with commonly observed values in framework silicates (~1.60 Å; e.g. Liebau, 1985; Nyfeler and Armbruster, 1997, and references therein). The BVS for the unique Sc atom, 3.05 v.u. (Table 4), is in good accordance with the theoretical value. The two fully occupied Cs sites, Cs(1) and Cs(2), have BVS of 0.97 and 0.99 v.u., also very close to theoretical values. By contrast, the four partially occupied and disordered sites, Cs(3a–d) give BVS between 0.41 and 0.66 v.u. (Table 4). Thus, the oxygen environments of these sites (located close to very large voids) do not allow a full saturation with necessary bond-strength contribu-

tions. An alternative explanation is that fully occupied Cs(3a–d) sites would lead to severe oversaturation of adjacent O sites. Computed BVS for the O atoms range between 1.82 and 2.21 v.u. (Table 4); an analysis of the reasons for this relatively large numerical range clearly showed that the bond-valence parameters for Cs–O bonds are somewhat inflexible, similar to the situation of other *M*–O bonds, where *M* = large metal ion: contributions of short Cs–O bonds are underestimated, whereas those of long Cs–O bonds are overestimated.

According to the classification of zirconosilicates and their analogues recently proposed by Ilyushin and Blatov (2002), Cs<sub>3</sub>ScSi<sub>8</sub>O<sub>19</sub> belongs to the PME ('polyhedral microensembles') type A-1 which is rather common among zircono- and titanosilicates. This PME type is characterized by MO<sub>6</sub> octahedra which share each corner with a SiO<sub>4</sub> tetrahedron. We point out that Cs<sub>3</sub>ScSi<sub>8</sub>O<sub>19</sub> is the first representative of a mixed octahedral-tetrahedral microporous framework structure, in which the [TO<sub>4</sub>]:[MO<sub>6</sub>] ratio is >6:1.

TABLE 4. Selected bond distances (Å) and angles (°), and calculated bond valence sums (v.u.) for the coordination polyhedra in Cs<sub>3</sub>ScSi<sub>8</sub>O<sub>19</sub>.

|                 |            |                  |                   |            |                  |
|-----------------|------------|------------------|-------------------|------------|------------------|
| Cs(1)—O(1) × 2  | 3.191(2)   | 0.124            | Cs(2)—O(10) × 2   | 3.110(2)   | 0.155            |
| —O(9) × 2       | 3.244(2)   | 0.108            | —O(13)            | 3.160(3)   | 0.135            |
| —O(10) × 2      | 3.258(2)   | 0.104            | —O(1) × 2         | 3.205(2)   | 0.12             |
| —O(9) × 2       | 3.397(3)   | 0.071            | —O(11) × 2        | 3.435(2)   | 0.064            |
| —O(8)           | 3.506(3)   | 0.053            | —O(13) × 2        | 3.5528(7)  | 0.047            |
| —O(8) × 2       | 3.5297(6)  | <u>0.050</u>     | —O(10) × 2        | 3.614(2)   | <u>0.040</u>     |
| <Cs(1)—O>       | 3.34       | <u>0.97</u> v.u. | <Cs(2)—O>         | 3.363      | <u>0.99</u> v.u. |
| Cs(3a)—O(3) × 2 | 3.171(2)   | 0.131            | Cs(3b)—O(4) × 2   | 3.195(8)   | 0.123            |
| —O(4) × 2       | 3.274(3)   | 0.099            | —O(3) × 2         | 3.214(9)   | 0.117            |
| —O(2)           | 3.399(3)   | 0.071            | —O(2)             | 3.300(8)   | 0.093            |
| —O(5) × 2       | 3.6269(10) | <u>0.038</u>     | —O(5) × 2         | 3.646(6)   | 0.036            |
| <Cs(3a)—O>      | 3.363      | <u>0.61</u> v.u. | —O(2)             | 3.721(12)* | <u>0.030</u>     |
| Cs(3c)—O(12)    | 3.155(12)  | 0.137            | <Cs(3a)—O>        | 3.391      | <u>0.55</u> v.u. |
| —O(11) × 2      | 3.335(9)   | 0.084            | Cs(3d)—O(11)      | 3.085(9)   | 0.166            |
| —O(6) × 2       | 3.735(5)*  | 0.029            | —O(4)             | 3.168(10)  | 0.132            |
| —O(3) × 2       | 3.805(12)* | <u>0.024</u>     | —O(7)             | 3.324(14)  | 0.087            |
| <Cs(3c)—O>      | 3.558      | <u>0.41</u> v.u. | —O(12)            | 3.347(11)  | 0.082            |
| Sc—O(10) × 2    | 2.105(2)   | 0.518            | —O(7)             | 3.412(15)  | 0.068            |
| —O(1) × 2       | 2.107(2)   | 0.515            | —O(4)             | 3.483(10)  | 0.057            |
| —O(8)           | 2.119(3)   | 0.499            | —O(5)             | 3.639(15)  | 0.037            |
| —O(13)          | 2.129(3)   | <u>0.485</u>     | —O(2)             | 3.664(10)  | <u>0.035</u>     |
| <Sc—O>          | 2.112      | <u>3.05</u> v.u. | <Cs(3d)—O>        | 3.39       | <u>0.66</u> v.u. |
| Si(1)—O(1)      | 1.560(2)   | 1.189            | Cs(3a)⋯Cs(3b)     | 1.85(2)    |                  |
| —O(2)           | 1.6154(11) | 1.024            | Cs(3a)⋯Cs(3d) × 2 | 2.544(13)  |                  |
| —O(3)           | 1.628(2)   | 0.989            | Cs(3a)⋯Cs(3c)     | 3.369(12)  |                  |
| —O(4)           | 1.632(2)   | <u>0.979</u>     | Cs(3a)⋯Cs(3c)     | 3.471(15)  |                  |
| <Si(1)—O>       | 1.609      | <u>4.18</u> v.u. | Cs(3b)⋯Cs(3c)     | 1.53(2)    |                  |
| Si(3)—O(4) × 2  | 1.598(2)   | 1.073            | Cs(3b)⋯Cs(3d) × 2 | 2.82(2)    |                  |
| —O(5)           | 1.600(3)   | 1.067            | Cs(3c)⋯Cs(3d) × 2 | 1.952(19)  |                  |
| —O(7)           | 1.605(4)   | <u>1.053</u>     | Cs(3d)⋯Cs(3d)     | 2.81(3)    |                  |
| <Si(3)—O>       | 1.600      | <u>4.27</u> v.u. | Si(2)—O(5)        | 1.595(3)   | 1.082            |
| Si(5)—O(10)     | 1.582(2)   | 1.12             | —O(6)             | 1.597(3)   | 1.076            |
| —O(9)           | 1.626(2)   | 0.995            | —O(3) × 2         | 1.607(2)   | <u>1.047</u>     |
| —O(11)          | 1.629(2)   | 0.987            | <Si(2)—O>         | 1.602      | <u>4.25</u> v.u. |
| —O(12)          | 1.6350(14) | <u>0.971</u>     | Si(4)—O(8)        | 1.567(3)   | 1.167            |
| <Si(5)—O>       | 1.618      | <u>4.07</u> v.u. | —O(9) × 2         | 1.620(2)   | 1.011            |
|                 |            |                  | —O(7)             | 1.635(3)   | <u>0.971</u>     |
|                 |            |                  | <Si(4)—O>         | 1.611      | <u>4.16</u> v.u. |
|                 |            |                  | Si(6)—O(13)       | 1.574(3)   | 1.145            |
|                 |            |                  | —O(11) × 2        | 1.630(2)   | 0.984            |
|                 |            |                  | —O(6)             | 1.640(3)   | <u>0.958</u>     |
|                 |            |                  | <Si(6)—O>         | 1.619      | <u>4.07</u> v.u. |

Bond-valence sums (v.u.) for the oxygen atoms O(1) to O(13) are as follows:

O(1) – 1.95; O(2) – 2.11; O(3) – 2.14; O(4) – 2.13; O(5) – 2.21; O(6) – 2.03; O(7) – 2.02; O(8) – 1.82; O(9) – 2.19; O(10) – 1.94; O(11) – 2.04; O(12) – 1.97; O(13) – 1.86

Bond-valence parameters used are from Brese and O'Keeffe (1991) (Cs–O, Si–O) and Brown (1996; updated values from [www.ccp14.ac.uk/ccp/web-mirrors/i\\_d\\_brown](http://www.ccp14.ac.uk/ccp/web-mirrors/i_d_brown)) (Sc–O). Bond-valence contributions from the low-occupancy sites Cs(3b), Cs(3c) and Cs(3d) have been ignored. Bond-valence contributions from the Cs(3a) site (occupancy 80%) have been scaled down according to the occupancy.

\* These Cs–O distances are probably too long to be considered as bonds, but have been included because of the disordered nature and irregular environment of the Cs(3b) and Cs(3c) sites (cf. Fig. 1).

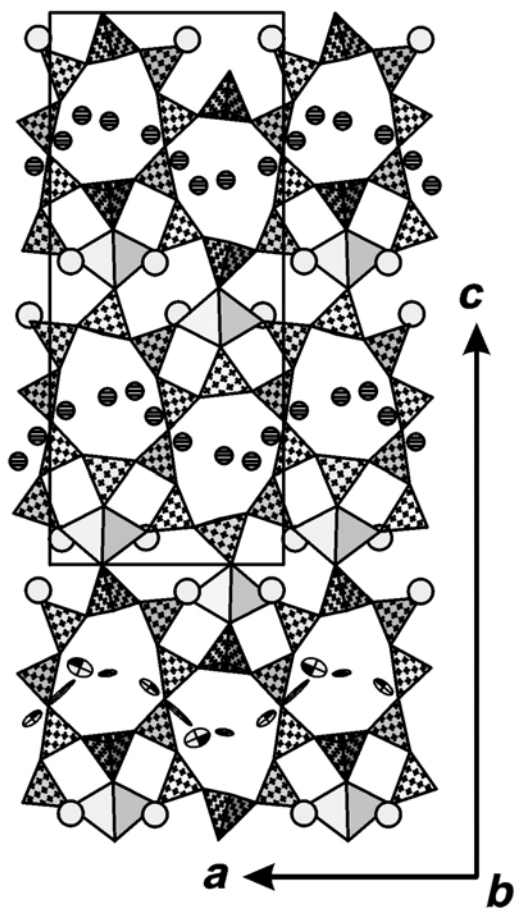


FIG. 1. The complex framework structure of  $\text{Cs}_3\text{ScSi}_8\text{O}_{19}$  projected along  $[010]$ . The  $\text{ScO}_6$  octahedron is unmarked.  $\text{SiO}_4$  tetrahedra are marked with crosses. The two large circles represent Cs(1) and Cs(2), whereas the four smaller, hatched circles represent the partially occupied and strongly disordered Cs(3a–d) sites which, in the bottom part of the figure, are shown as displacement ellipsoids. All drawings were done using *ATOMS* (Shape Software, 1999).

#### Relation to similar compounds and minerals

$\text{Cs}_3\text{ScSi}_8\text{O}_{19}$  represents the first known caesium scandium silicate. Previously reported alkali scandium silicates are restricted to the two sodium compounds  $\text{Na}_5\text{ScSi}_4\text{O}_{12}$  (hexagonal), containing  $\text{Si}_{12}\text{O}_{36}$  rings, isolated  $\text{ScO}_6$  octahedra and Na–O polyhedra (Merinov *et al.*, 1980) and  $\text{Na}_4\text{Sc}_2\text{Si}_4\text{O}_{13}$  (orthorhombic), which contains  $\text{Si}_4\text{O}_{13}$  radicals and  $\text{Sc}_2\text{O}_{10}$  dimers composed of two edge-sharing  $\text{ScO}_6$  octahedra (Maksimov *et*

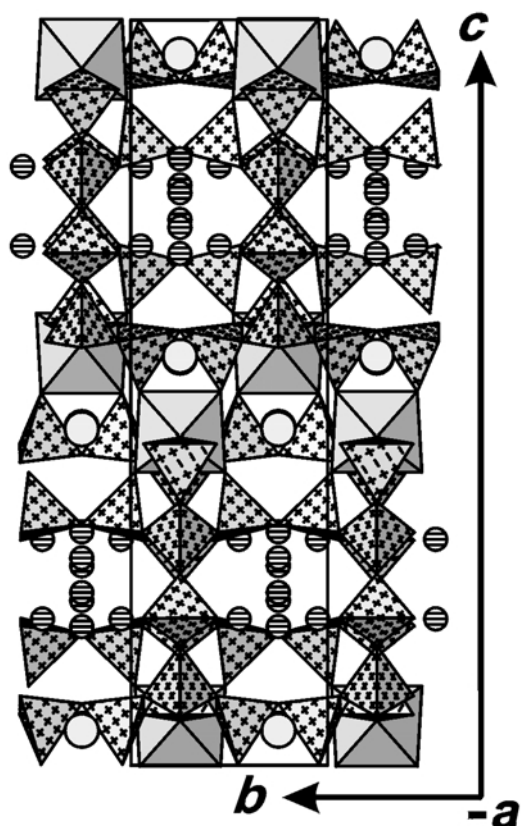


FIG. 2. The structure of  $\text{Cs}_3\text{ScSi}_8\text{O}_{19}$  projected along  $[100]$ . Note the partially occupied and disordered Cs(3a–d) sites in the channels parallel to  $[100]$ . Legend as in Fig. 1.

*al.*, 1980). Neither of these two compounds shows any significant structural resemblance to the title compound.

Among alkali- and  $\text{SiO}_2$ -rich alkali- $\text{REE}^{3+}$ -silicates, mainly the small to very small, heavy  $\text{REE}^{3+}$  ions are known to occur in octahedral environments, i.e. similar to  $\text{Sc}^{3+}$ . For the  $\text{REE}^{3+}$  ion which is smallest and most similar to  $\text{Sc}^{3+}$ , i.e.  $\text{Lu}^{3+}$ , three related compounds have been described:  $\text{Na}_5\text{LuSi}_4\text{O}_{12}$  (Merinov *et al.*, 1978; Filipenko *et al.*, 1997) which is isotopic with the already mentioned  $\text{Na}_5\text{ScSi}_4\text{O}_{12}$ ,  $\text{K}_3\text{LuSi}_2\text{O}_7$  (Vidican *et al.*, 2003) which has a layered hexagonal structure based on isolated  $\text{LuO}_6$  octahedra and interlinking  $\text{Si}_2\text{O}_7$  groups, and  $\text{K}_6\text{Lu}_2\text{Si}_6\text{O}_{18}$  (Filipenko *et al.*, 1988) which contains infinite  $\text{Si}_6\text{O}_{18}$  chains. None of these or other reported compounds with octahedrally coordinated  $\text{REE}^{3+}$  ions exhibits any structural

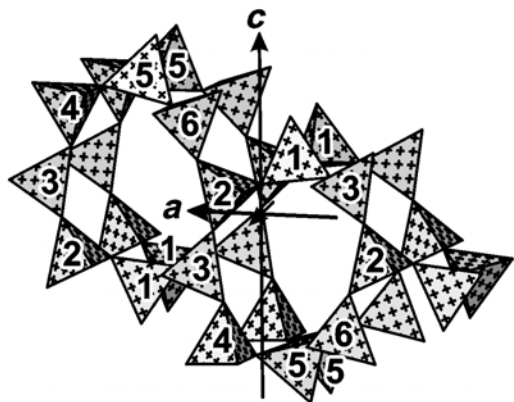


FIG. 3. The linkage between the eight-membered, puckered silicate rings in the structure of  $\text{Cs}_3\text{ScSi}_8\text{O}_{19}$ . The numbering of the Si atoms is shown. Note that the pairs of equivalent  $\text{Si}(5)\text{O}_4$  and  $\text{Si}(1)\text{O}_4$  tetrahedra are each linked along  $[010]$  via common O atoms (obscured). The axes have been scaled to 50% of their actual lengths.

similarity to  $\text{Cs}_3\text{ScSi}_8\text{O}_{19}$ . Apparently, the very large  $\text{Cs}^+$  cations enforce a rather different atomic arrangement with very large voids.

Only a very small number of alkali- and  $\text{SiO}_2$ -rich alkali- $M^{3+}$  silicates is known where  $M$  = medium-large metal such as V, Cr, Ga, In, Rh and Sc. One example is hydrothermally synthesized  $\text{Na}_3\text{V}^{3+}(\text{Si}_4\text{O}_{11})\cdot\text{H}_2\text{O}$  (VSH-16Na) reported by Huang *et al.* (2002). This compound contains unbranched  $[\text{Si}_8\text{O}_{22}]^{12-}$  double chains, which are connected by isolated  $\text{VO}_6$  octahedra to form an open framework structure with eight-ring channels.

If  $\text{Cs}_3\text{ScSi}_8\text{O}_{19}$  is compared with mixed octahedral-tetrahedral framework silicates containing tetravalent metal cations ( $\text{Ti}^{4+}$ ,  $\text{Zr}^{4+}$ ,  $\text{Sn}^{4+}$ ; Rocha and Anderson, 2000; Anderson and Rocha, 2002), it is found that a relatively close structural relation exists with  $\text{Cs}_2\text{TiSi}_6\text{O}_{15}$  (two very similar polymorphs with space groups  $C2/c$  and  $Cc$  are known: Grey *et al.*, 1997; Nyman *et al.*, 2000a). The crystal structure of the polymorph described by Grey *et al.* (1997) is used here for the comparison: it contains isolated  $\text{TiO}_6$  octahedra and  $\text{SiO}_4$  tetrahedra (both quite regular), which share all corners to form an open framework structure containing large cavities hosting the  $\text{Cs}^+$  ions. Each cavity is bound by three five-, two six-, and two eight-membered rings. The average Cs–O bond length is 3.336 Å, very close to the values observed in  $\text{Cs}_3\text{ScSi}_8\text{O}_{19}$  (Table 4). Thus, all the major

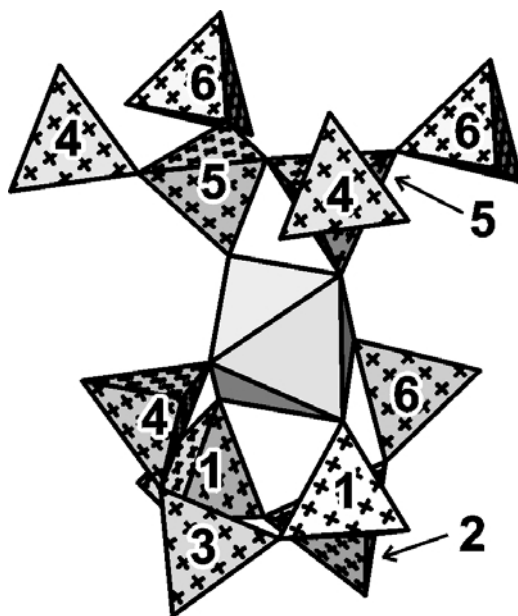


FIG. 4. The polyhedral environment of the nearly regular  $\text{ScO}_6$  octahedron in  $\text{Cs}_3\text{ScSi}_8\text{O}_{19}$ . The numbering of the Si atoms is shown.

structural features of  $\text{Cs}_2\text{TiSi}_6\text{O}_{15}$  are, on a local scale, fairly similar to those in  $\text{Cs}_3\text{ScSi}_8\text{O}_{19}$ . However, the long-scale connectivities are otherwise rather different:  $\text{Cs}_2\text{TiSi}_6\text{O}_{15}$  contains narrow blocks of  $\text{TiO}_6$  octahedra separated by blocks containing zigzag chains of  $\text{Si}_2\text{O}_7$  groups.  $\text{Cs}_2\text{TiSi}_6\text{O}_{15}$  and related compounds were studied in view of their excellent properties with regards to application in ceramic nuclear waste forms (e.g. Nyman *et al.*, 2000a,b, 2001). Accordingly, the structural features of  $\text{Cs}_3\text{ScSi}_8\text{O}_{19}$  suggest that it may also be useful in the immobilization of radioactive  $^{137}\text{Cs}$  waste.

Another comparable mineral crystal structure is that of umbite,  $\text{K}_2\text{ZrSi}_3\text{O}_9\cdot\text{H}_2\text{O}$ , which has recently been the subject of several research groups studying its microporous properties. In both umbite (Ilyushin, 1993; Poojary *et al.*, 1997; Jale *et al.*, 1999; Lin *et al.*, 1997, 1999a,b) and its two isostructural Ti and Sn analogues,  $\text{K}_2\text{TiSi}_3\text{O}_9\cdot\text{H}_2\text{O}$  (Dadachov and Le Bail, 1997; Lin *et al.*, 1999a; Valtchev *et al.*, 1999; Bortun *et al.*, 2000; Zhao *et al.*, 2002) and  $\text{K}_2\text{SnSi}_3\text{O}_9\cdot\text{H}_2\text{O}$  (Lin *et al.*, 1999b), respectively, infinite  $(\text{SiO}_3)_n^{2n-}$  silicate chains are connected by isolated  $\text{TiO}_6$  octahedra to form a mixed framework. Distorted eight-membered ring channels are filled with  $\text{K}^+$



cations and H<sub>2</sub>O molecules which can be reversibly exchanged. However, unlike in Cs<sub>3</sub>ScSi<sub>8</sub>O<sub>19</sub>, the channels in the umbite-type compounds are based on eight-membered rings composed of both octahedra and tetrahedra. The large K<sup>+</sup> cations can be exchanged with other alkali cations such as Cs<sup>+</sup> (Poojary *et al.*, 1997). It was also shown that the Zr-rich (umbite) silicates, which have comparatively large channels, exhibit affinity for Rb<sup>+</sup> and Cs<sup>+</sup> ions, whereas the Ti-rich analogues with much smaller channels show a preference for K<sup>+</sup> ions (Clearfield *et al.*, 1998; see also Valtchev *et al.*, 1999). Thus, the Cs<sup>+</sup> ions in Cs<sub>3</sub>ScSi<sub>8</sub>O<sub>19</sub> may, at least partly, be easily exchanged with other, smaller alkali cations, and it is planned to investigate the ion-exchange behaviour of title compound in the near future.

Finally, we point out that some minor similarities exist concerning the connectivities of the silicate rings in Cs<sub>3</sub>ScSi<sub>8</sub>O<sub>19</sub> and rhodesite, KHCa<sub>2</sub>Si<sub>8</sub>O<sub>19</sub>·5H<sub>2</sub>O (Hesse *et al.*, 1992), which has a similar space group (*Pmā*) and roughly similar unit-cell parameters,  $a = 23.42$  ( $\sim c_{\text{CsScSi}}$ ),  $b = 6.56$  ( $\sim 0.5a_{\text{CsScSi}}$ ),  $c = 7.05$  Å ( $\sim b_{\text{CsScSi}}$ ).

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Giovanni Ferraris is thanked for making us aware of apparent structural relations between Cs<sub>3</sub>ScSi<sub>8</sub>O<sub>19</sub> and rhodesite. We also thank Mark Welch and an anonymous reviewer for their helpful comments. Financial support by the Austrian Science Foundation (FWF) (Grant P15220-N06) is gratefully acknowledged.

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