

- Franzen, H. F. & Köckerling, M. (1995). *Prog. Solid State Chem.* **23**, 265–289.
- Kleinke, H. & Franzen, H. F. (1996a). *Angew. Chem.* Submitted.
- Kleinke, H. & Franzen, H. F. (1996b). *J. Alloys Compds.* In the press.
- Lundström, T. (1968). *Acta Chem. Scand.* **22**, 2191–2199.
- Molecular Structure Corporation (1989). *TEXSAN. Single Crystal Structure Analysis Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
- Molecular Structure Corporation (1993). *MSC/AFC Diffractometer Control Software*. Version 4.30. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
- Schönberg, N. (1954). *Acta Chem. Scand.* **8**, 226–239.
- Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures*. University of Göttingen, Germany.
- Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
- Tergenius, L.-E., Nöling, B. I. & Lundström, T. (1981). *Acta Chem. Scand. Ser. A*, **35**, 693–699.

Acta Cryst. (1996). **C52**, 2129–2132

Tricaesium Ditellurium Tetravanadium Chloride Tetradecaoxide

JEROME MARROT AND JEAN-MICHEL SAVARIAULT

Centre d'Elaboration de Matériaux et d'Etudes Structurales, CNRS, 29 Rue Jeanne Marvig, BP 4347, 31055 Toulouse CEDEX, France. E-mail: savariau@cemes.cemes.fr

(Received 6 December 1995; accepted 5 March 1996)

Abstract

The title compound, $(\text{CsCl})\text{Cs}_2(\text{TeV}_2\text{O}_7)_2$, was obtained at 700 K during the crystallization of a mixed tellurium-caesium vanadate using tellurium tetrachloride as a transport agent. The structure consists of stacks of $[\text{V}_2\text{TeO}_7]$ sheets alternately separated by layers of caesium atoms and layers of caesium and chlorine atoms. Within the sheets, the V atoms are distributed over two sites: a tetrahedral site containing V^{5+} ions and a square pyramidal site containing V^{4+} ions. The Te^{4+} ion lies within a tetrahedron formed by three O atoms and a lone pair. A maximum in the electron density is observed at the expected position of the lone pair.

Comment

In our long-term research, we are particularly interested in mixed valence transition metal (M) oxides, among them the vanadium bronzes, $M'_x\text{V}_{2-x}^{3+}\text{V}_x^{4+}\text{O}_5$ ($M' = \text{Li}, \text{Na}, \text{K}, \text{Rb}, \text{Ag}$) (Galy, 1992; Savariault, Déramond & Galy, 1994; Déramond, Savariault & Galy, 1994; Hirschinger *et al.*, 1993; Savariault & Galy, 1992), and the so-called lone-pair elements, M^* , characterized by unusual stereochemical effects ($M^* = \text{As}^{3+}, \text{Se}^{4+}, \text{Sn}^{2+}, \text{Sb}^{3+}, \text{Te}^{4+}, \text{Pb}^{2+}, \text{Bi}^{3+}$) (Galy, Meunier, Andersson

& Åström, 1975; Enjalbert, Savariault & Galy, 1980; Galy & Enjalbert, 1982; Castro, Enjalbert, Schnuriger & Galy, 1990). These oxides also give a rich series of double oxides, among which are the compounds $M\text{V}^{5+}\text{Te}^{4+}\text{O}_5$, which are related to the vanadium bronzes in formula but are completely different in structure and physical properties (Darriet, Guillaume, Wilhelmi & Galy, 1972). Several phases containing M and M^* metals have been synthesized, particularly for $M = \text{V}$, for example $\text{Te}_2\text{V}_2\text{O}_9$ and α - and β - TeVO_4 (Darriet & Galy, 1973; Meunier, Darriet & Galy, 1972, 1973), but with vanadium simultaneously present in two different valence states. During studies of the crystal growth of CsVTeO_5 by chemical transport using TeCl_4 , the title compound was discovered.

A projection of the structure of the title compound onto the $[001]$ plane is given in Fig. 1, showing the presence of sheets of vanadium and tellurium oxide separated alternately by layers of caesium atoms and layers of caesium and chlorine atoms. The corresponding average distances between successive metal oxide layers are 5.68 and 6.12 Å, respectively. A view of a metal oxide sheet is given in Fig. 2. The V atoms lie in two types of site: atom V1 in a VO_5 square pyramid and atom V2 in a VO_4 tetrahedron. The Te^{4+} ion, bonded to three O atoms, has a lone pair (E), thus forming a TeO_3E tetrahedron. The VO_4 and TeO_3E tetrahedra share atom O4 [$\text{V2}-\text{O4}-\text{Te}$ 132.2(4)°] to form a pair of tetrahedra in a staggered conformation with an angle between the O-atom basal planes of 57.6(1)°. The O atoms of each base, O2 and O3, are shared with the basal plane of the V1O_5 pyramid. This leads to a sheet of formula

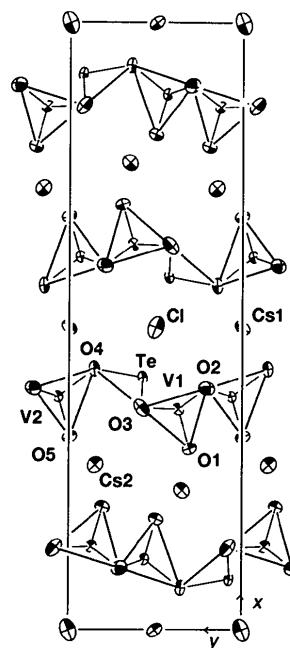


Fig. 1. A projection of the unit cell along the $[001]$ direction. Displacement ellipsoids are drawn at the 75% probability level.

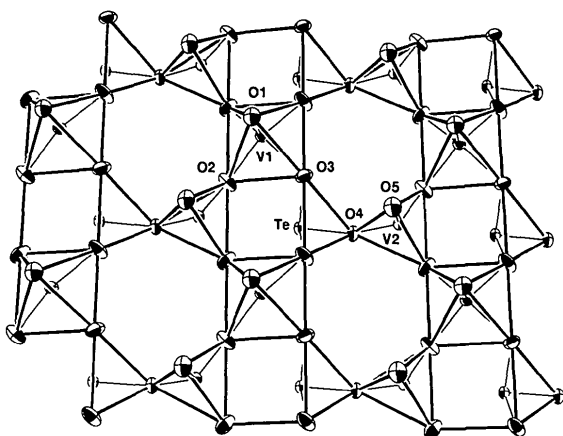


Fig. 2. A view of one layer showing the stacking of the vanadium and tellurium polyhedra. Displacement ellipsoids are drawn at the 75% probability level.

(VO)(VTeO₆E). This type of formula is also found in the compounds K₂VO(V₂O₇) (Galy & Carpy, 1975) and Ba₂(TiO)(Si₂O₇) (Moore & Louisnathan, 1969). However, the M₂O₇ moieties in these compounds are formed from tetrahedra in an eclipsed conformation and are arranged perpendicularly, whereas they are parallel in the title structure.

Within the sheets, the VIO₅ square pyramids and the V₂O₄ tetrahedra lie in the same orientation: their free apices, O1 and O5, are directed towards the intersheet space which contains caesium atoms but not chlorine atoms. The TeO₃E tetrahedra point towards the other intersheet space, which contains chlorine and caesium atoms. The V atoms are displaced from the basal planes (or the layer plane) towards the apices by 0.47 and 0.62 Å, respectively, such that the V—O(apex) bonds are the shortest V—O bonds in the polyhedra [V1—O1 1.591(5), V2—O5 1.616(5) Å]. The electroneutrality of this compound infers the ionic formula Cs₃⁺V₂⁴⁺V₂⁵⁺Te₂⁴⁺Cl⁻O₁₄⁴⁻. The two V-atom sites contain the V⁴⁺ and V⁵⁺ ions. Galy, Casalot, Pouchard & Hagenmuller (1966) have shown that in α'-NaV₂O₅, the volume of the square pyramidal V-atom sites varies with the oxidation state of vanadium: the V⁴⁺ ion, which has a greater ionic radius than V⁵⁺, occupies the largest site. Therefore, in the title compound, the V⁴⁺ ion must be found in the square pyramidal site and the V⁵⁺ ion in the tetrahedral site. Confirmation of this assignment is given using Brown's formula (Brown & Shannon, 1973; Brown & Altermatt, 1985): a valency of 4.18 is obtained for V1 in the pyramidal site and a valency of 4.99 for V2 in the tetrahedral site.

The structures of compounds containing the Te⁴⁺ ion show that the lone pair (E) has important stereochemical activity. The lone pair occupies a volume the same size as that of an anion (Galy, Meunier, Andersson & Åström, 1975). This infers that the Te atom is shifted out of the centre of its cavity, as the long and short

Te—O distances of ca 2.8 and 1.9 Å, respectively, demonstrate. In the title compound, a similar Te-atom environment is observed: there are three short distances, Te—O3 [1.857(3)], Te—O3ⁱ [1.857(3)] and Te—O4 [1.918(5)], and four long distances, Te—O2 [2.903(5)], Te—O2ⁱ [2.903(5)], Te—Cl and Te—Clⁱⁱ [3.419(1) Å]. The centre of the cavity ($x = 0.4226$, $y = 0.4908$, $z = 0.5$) is shifted 0.59 Å from the Te atom and its mean radius is 2.07 Å. Surprisingly, this shift is similar to the distance of the highest electron density maximum found in the Fourier difference synthesis from the Te atom (0.64 Å). The radius of the perturbation sphere of the lone pair, however, is larger than the radius of either the O²⁻ (1.42 Å) or the Cl⁻ (1.80 Å) anions. Assuming that the centre of the lone pair occupies the fourth corner of a regular tetrahedron built on the basal triangle of O atoms, Galy, Meunier, Andersson & Åström (1975) gave a formula for calculating the distance between the Te atom and the lone pair. An average Te—E distance of 1.25(9) Å was proposed. Applying the formula to the title compound, using the average distances O···O 2.801 and Te—O 1.882 Å, the calculated Te—E distance is 1.32 Å, close to the observed value of 1.25 Å. This structure confirms once more the stereoactivity of the lone pair.

The Cs atoms, which bind the vanadium–tellurium oxide sheets, have two types of environment. Cs1 lies within a square oblique prism of O atoms with two Cl atoms capping the two opposite faces. The average cation–anion distances are Cs1—O 3.22 and Cs1—Cl 3.41 Å. Cs2 is only surrounded by O atoms, which form a distorted trigonal prism with two O atoms pointing out of two contiguous faces. The average Cs2—O distance is 3.17 Å. The Cs-atom environments are shown in Fig. 3.

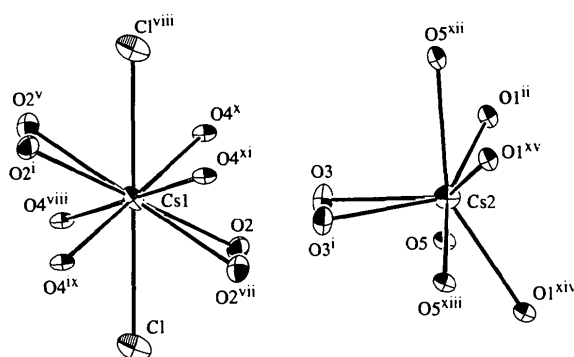


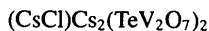
Fig. 3. The environments of the Cs atoms. Displacement ellipsoids are drawn at the 66% probability level.

Experimental

The synthesis of the title compound was a two-step process. First, CsVO₃ was prepared from a mixture of Cs₂CO₃ and V₂O₅ in a molar ratio of 1:1. The sample, carefully ground, was heated for 24 h at 673 K under oxygen. The reaction was terminated when the weight loss was equal to the calculated

weight of the carbon dioxide evolved. The purity of the compound was monitored by powder X-ray diffraction. TeO₂ was then added to CsVO₃ to form a mixture in the molar ratio 1:1 which, after grinding, was sealed under vacuum in a quartz container. CsVTeO₅ was obtained after heating the mixture at 780 K for 12 h. This compound looked like a brown glass, but gave a powder X-ray diffraction pattern characteristic of a pyrochlore-type structure which could be indexed using a cell parameter $a = 10.52(5) \text{ \AA}$. It rapidly became apparent that the pyrochlore phase could not be obtained without melting the mixture. After several unsuccessful attempts to grow crystals, the easily melted salt tellurium tetrachloride was used as a transport agent. A long quartz tube containing the above mixture and 1% TeCl₄ was evacuated and placed in a 573–700 K temperature gradient for a month. Two phases were obtained: the brown glass at the hot part of the tube and, a third of the way down the tube, black acicular crystals. Chemical analysis of the glass confirmed the formula CsVTeO₅: observed (calculated) Cs 33.75 (33.95), V 13.27 (13.01), Te 31.83 (32.60). EDX analysis of the crystals revealed the presence of chlorine in addition to the expected elements Cs, V and Te.

Crystal data



$M_r = 1117.124$

Orthorhombic

Pnmm

$a = 23.608(8) \text{ \AA}$

$b = 6.825(9) \text{ \AA}$

$c = 5.4908(13) \text{ \AA}$

$V = 884.7(13) \text{ \AA}^3$

$Z = 2$

$D_x = 4.194 \text{ Mg m}^{-3}$

D_m not measured

Data collection

Enraf–Nonius CAD-4

diffractometer

ω - 2θ scans

Absorption correction:

by integration from crystal shape, Gaussian grid:

6.4,34 (Coppens, Leis-erowitz & Rabinovich, 1965)

$T_{\min} = 0.5708$, $T_{\max} =$

0.7285

Refinement

Refinement on F^2

$R[F^2 > 2\sigma(F^2)] = 0.0407$

$wR(F^2) = 0.1011$

$S = 1.196$

2777 reflections

70 parameters

$w = 1/[\sigma^2(F_o^2) + (0.0389P)^2 + 8.6069P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = -0.001$

$\Delta\rho_{\max} = 3.58 \text{ e \AA}^{-3}$

$\Delta\rho_{\min} = -2.42 \text{ e \AA}^{-3}$

Mo $K\alpha$ radiation

$\lambda = 0.71069 \text{ \AA}$

Cell parameters from 25

reflections

$\theta = 11.5\text{--}22.8^\circ$

$\mu = 11.573 \text{ mm}^{-1}$

$T = 293(2) \text{ K}$

Needle

$0.2 \times 0.02 \times 0.015 \text{ mm}$

Black

3559 measured reflections

3559 independent reflections

$\theta_{\max} = 41.92^\circ$

$h = 0 \rightarrow 44$

$k = 0 \rightarrow 12$

$l = 0 \rightarrow 10$

3 standard reflections

frequency: 120 min

intensity decay: 0.10%

Extinction correction:

SHELXL93 (Sheldrick, 1993)

Extinction coefficient:

0.0011 (2)

Atomic scattering factors

from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
Te	0.41639 (2)	0.57398 (4)	1/2	0.01108 (7)
Cs1	0	1/2	1/2	0.01875 (10)
Cs2	0.27091 (2)	0.84715 (7)	0	0.02238 (9)
V1	0.36314 (4)	0.37055 (13)	0	0.01057 (13)
V2	0.38412 (4)	0.06332 (12)	1/2	0.00936 (12)
Cl	1/2	1/2	0.0	0.0293 (5)
O1	0.2986 (2)	0.3031 (8)	0	0.0225 (9)
O2	0.39843 (14)	0.2047 (5)	0.2483 (6)	0.0192 (5)
O3	0.3647 (2)	0.5811 (5)	0.2451 (6)	0.0220 (6)
O4	0.4311 (2)	0.8503 (6)	1/2	0.0177 (7)
O5	0.3181 (2)	0.0005 (8)	1/2	0.0211 (8)

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

Te—O3	1.857 (3)	Cs2—O5 ^{xi}	3.142 (3)
Te—O3 ⁱ	1.857 (3)	Cs2—O5 ^{xiii}	3.142 (3)
Te—O4	1.918 (5)	Cs2—O3 ^{xiii}	3.165 (4)
Te—O2	2.903 (5)	Cs2—O3	3.165 (4)
Te—O2 ⁱ	2.903 (5)	Cs2—O5 ^{vi}	3.165 (6)
Te—Cl	3.419 (1)	Cs2—O1 ^{xi}	3.180 (7)
Te—Cl ⁱⁱ	3.419 (1)	Cs2—O1 ^{xv}	3.213 (3)
Cs1—O2 ⁱⁱⁱ	3.092 (3)	Cs2—O1 ^{vi}	3.213 (3)
Cs1—O2 ^{iv}	3.092 (3)	V1—O1	1.591 (5)
Cs1—O2 ^v	3.092 (3)	V1—O2 ^{xiii}	1.958 (3)
Cs1—O2 ^{vi}	3.092 (3)	V1—O2	1.958 (3)
Cs1—O4 ^{vii}	3.350 (3)	V1—O3 ^{xiii}	1.969 (3)
Cs1—O4 ^{viii}	3.350 (3)	V1—O3	1.969 (3)
Cs1—O4 ^{ix}	3.350 (3)	V2—O5	1.616 (5)
Cs1—O4 ^x	3.350 (3)	V2—O2	1.719 (3)
Cs1—Cl ^{viii}	3.413 (5)	V2—O2 ⁱ	1.719 (3)
Cs1—Cl ^{vi}	3.413 (5)	V2—O4 ^{xv}	1.829 (5)
O3—Te—O3 ⁱ	97.8 (2)	O2 ^{xiii} —V1—O3	152.8 (2)
O3—Te—O4	95.36 (15)	O2—V1—O3	86.4 (2)
O3 ⁱ —Te—O4	95.36 (15)	O3 ^{xiii} —V1—O3	86.2 (2)
O1—V1—O2 ^{xiii}	103.9 (2)	O5—V2—O2	109.8 (2)
O1—V1—O2	103.9 (2)	O5—V2—O2 ⁱ	109.8 (2)
O2 ^{xiii} —V1—O2	88.2 (2)	O2—V2—O2 ⁱ	107.0 (3)
O1—V1—O3 ^{xiii}	103.3 (2)	O5—V2—O4 ^{xv}	112.0 (3)
O2 ^{xiii} —V1—O3 ^{xiii}	86.4 (2)	O2—V2—O4 ^{xv}	109.08 (15)
O2—V1—O3 ^{xiii}	152.8 (2)	O2 ⁱ —V2—O4 ^{xv}	109.08 (15)
O1—V1—O3	103.3 (2)		

Symmetry codes: (i) $x, y, l - z$; (ii) $x, y, l + z$; (iii) $x - \frac{1}{2}, \frac{1}{2} - y, \frac{1}{2} - z$; (iv) $x - \frac{1}{2}, \frac{1}{2} - y, \frac{1}{2} + z$; (v) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} + z$; (vi) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; (vii) $\frac{1}{2} - x, y - \frac{1}{2}, \frac{3}{2} - z$; (viii) $\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$; (ix) $x - \frac{1}{2}, \frac{3}{2} - y, z - \frac{1}{2}$; (x) $x - \frac{1}{2}, \frac{3}{2} - y, \frac{1}{2} + z$; (xi) $x, l + y, z$; (xii) $x, l + y, z - 1$; (xiii) $x, y, -z$; (xiv) $\frac{1}{2} - x, \frac{1}{2} + y, -\frac{1}{2} - z$; (xv) $x, y - 1, z$.

Preliminary studies were carried out on a crystal using the Weissenberg technique and Cu $K\alpha$ radiation. An orthorhombic cell with parameters $a = 23.61$, $b = 6.83$, $c = 5.49 \text{ \AA}$ was obtained and the *Pnmm* or *Pnn2* space groups proposed. Heavy atoms were obtained using the Patterson technique (Sheldrick, 1985) and other atoms from a series of refinements and Fourier summations (Sheldrick, 1993). Relationships between the coordinates of the atoms led to the choice of the centrosymmetric space group *Pnmm*. An absorption correction was performed using numerical integration over the crystal shape (Coppens, Leis-erowitz & Rabinovich, 1965) before the introduction of anisotropic displacement parameters for every atom. 785 poorly measured reflections were omitted from the final refinement. The final residual Fourier map reveals a maximum peak of electron density ($\rho = 3.58 \text{ e \AA}^{-3}$) near the Te atom (distance 0.64 \AA), 40% larger than the next largest peak (2.49 e \AA^{-3}).

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.

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

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

(Received 16 August 1995; accepted 4 March 1996)

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.

Abstract

Analysis of high-resolution synchrotron X-ray powder diffraction patterns for hydrothermally synthesized Rb₂CdSi₅O₁₂ and Cs₂MnSi₅O₁₂ leucite analogues, and dry-synthesized Cs₂CoSi₅O₁₂ and Cs₂NiSi₅O₁₂ 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 Cs₂MnSi₅O₁₂, Cs₂CoSi₅O₁₂ and Cs₂NiSi₅O₁₂ leucite samples are unusual in containing SiO₄ tetrahedra which are more distorted, on average, than the larger MnO₄, CoO₄ and NiO₄ tetrahedra. The JCPDS file numbers for Rb₂CdSi₅O₁₂, Cs₂MnSi₅O₁₂ and Cs₂CoSi₅O₁₂ 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 X₂ZSi₅O₁₂ (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 (KAISi₂O₆). 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.