The Canadian Mineralogist
Vol. 47, pp. 421-431 (2009)
DOI: 10.3749/canmin.47.2.421

CRYSTAL CHEMISTRY AND TOPOLOGY OF TWO FLUX-GROWN YTTRIUM SILICATES, $BaKYSi_2O_7$ AND $Cs_3YSi_8O_{19}$

Uwe KOLITSCH[§]

Mineralogisch-Petrographische Abt., Naturhistorisches Museum, Burgring 7, A–1010 Wien, Austria

Maria WIERZBICKA-WIECZOREK and Ekkehart TILLMANNS

Institut für Mineralogie und Kristallographie, Geozentrum, Universität Wien, Althanstr. 14, A–1090 Wien, Austria

Abstract

Two new yttrium silicates have been synthesized by a high-temperature flux-growth technique in air. The phase $BaKYSi_2O_7$ is monoclinic, with space group $P2_1/n$, a 9.775(2), b 5.718(1), c 13.096(3) Å, β 104.61(3)°, V 708.3(3) Å^3, and $Z = 4$; $Cs_3YSi_8O_{19}$ is orthorhombic, space group *Pnma*, with a 11.476(2), b 7.059(1), c 26.971(5) Å, V 2184.9(6) Å^3, and $Z = 4$. The crystal structures were determined from single-crystal X-ray-diffraction data and refined to $R1(F) = 2.0\%$ ($BaKYSi_2O_7$) and $R1(F) = 2.9\%$ ($Cs_3YSi_8O_{19}$). The phase $BaKYSi_2O_7$ represents a novel structure-type, and a compound that may also occur in nature. It has a mixed tetrahedron–octahedron framework structure containing Si_2O_7 groups and octahedrally coordinated Y atoms ($\langle Y–O \rangle$ = 2.256 Å). Voids in the framework host [9]-coordinated Ba atoms and [8]-coordinated K atoms. The YO_6 octahedron shares each of its apices with oxygen atoms of the Si_2O_7 groups. The unusually small Si–O–Si angle of the disilicate group [124.51(9)°] is noteworthy. The diphosphates $Na_2CaP_2O_7$, $M_2SrP_2O_7$ (M = K, Rb, Cs) and $K_2CdP_2O_7$, and the diarsenate $K_2CaAs_2O_7$, have closely related structures. The phase $Cs_3YSi_8O_{19}$ is isotypic with isoelectronic $Cs_3ScSi_8O_{19}$ and the second representative of the microporous framework structure-type MCV–1. The silicate has a mixed octahedron–tetrahedron framework structure with a $[TO_4]$:$[MO_6]$ ratio of 8:1. The structure contains isolated YO_6 octahedra ($\langle Y–O \rangle$ = 2.251 Å) sharing corners with SiO_4 tetrahedra to form an open framework with four-, six- and eight-membered rings. Large voids host two fully occupied Cs positions and four partly occupied and disordered Cs positions.

Keywords: flux growth, crystal structure, crystal chemistry, topology, yttrium, framework silicate, $BaKYSi_2O_7$, $Cs_3YSi_8O_{19}$, Si_2O_7 groups.

Sommaire

Nous avons synthétisé deux nouveaux silicates d'yttrium par une technique employant un fondant à haute température à un atmosphère. La phase $BaKYSi_2O_7$ est monoclinique, groupe spatial $P2_1/n$, a 9.775(2), b 5.718(1), c 13.096(3) Å, β 104.61(3)°, V 708.3(3) Å^3, et $Z = 4$; $Cs_3YSi_8O_{19}$ est orthorhombique, groupe spatial *Pnma*, avec a 11.476(2), b 7.059(1), c 26.971(5) Å, V 2184.9(6) Å^3, et $Z = 4$. Les structures cristallines ont été établies à partir de données en diffraction X prélevées sur monocristal, et affinées jusqu'à un résidu $R1(F) = 2.0\%$ ($BaKYSi_2O_7$) et $R1(F) = 2.9\%$ ($Cs_3YSi_8O_{19}$). La phase $BaKYSi_2O_7$ représente un nouveau type de structure; un tel composé pourrait avoir un analogue naturel. Elle possède une charpente mixte, avec tétraèdres et octaèdres, contenant des groupes Si_2O_7 et des atomes Y en coordinence octaédrique ($\langle Y–O \rangle$ = 2.256 Å). Les lacunes dans cette charpente contiennent des atomes Ba en coordinence [9] et des atomes K en coordinence [8]. Les octaèdres YO_6 partagent chacun de leurs coins avec des atomes d'oxygène des groupes Si_2O_7. L'angle Si–O–Si anormalement faible du groupe disilicate [124.51(9)°] est notable. Les diphosphates $Na_2CaP_2O_7$, $M_2SrP_2O_7$ (M = K, Rb, Cs) et $K_2CdP_2O_7$, et le diarsenate $K_2CaAs_2O_7$, possèdent une structure semblable. La phase $Cs_3YSi_8O_{19}$ est isotypique avec le composé isoélectronique $Cs_3ScSi_8O_{19}$; c'est le second représentant de la structure à charpente microporeuse de type MCV–1. Ce silicate possède une charpente mixte avec tétraèdres $[TO_4]$ et octaèdres $[MO_6]$ dans un rapport 8:1. La structure contient des octaèdres YO_6 isolés ($\langle Y–O \rangle$ = 2.251 Å) qui partagent leurs coins avec les tétraèdres SiO_4 pour former une trame ouverte d'anneaux à quatre, six et huit membres. Le césium remplit pleinement deux lacunes volumineuses; quatre autres sites du Cs sont seulement remplis en partie, et l'occupation du Cs y est désordonnée.

(Traduit par la Rédaction)

Mots-clés: croissance dans un fondant, structure cristalline, chimie cristalline, topologie, yttrium, silicate à charpente, $BaKYSi_2O_7$, $Cs_3YSi_8O_{19}$, groupes Si_2O_7.

[§] *E-mail address*: uwe.kolitsch@nhm-wien.ac.at

INTRODUCTION

Mixed-framework (SiO_4–$Ti^{4+}O_6$) titanosilicate materials (either natural or synthetic) have, in the last decade, attracted considerable interest owing to their microporous (zeolite-type) properties and potential applications in catalysis, adsorption, ion exchange, and separation (*e.g.,* Murugavel & Roesky 1997, Rocha & Anderson 2000, Sokolova & Hawthorne 2004, Rocha & Lin 2005) and as luminescent materials (*e.g.,* Ananias *et al.* 2002, Vidican *et al.* 2003; see also Kolitsch & Tillmanns 2004a). Their high thermal, chemical and radiation stability is of particular advantage. These properties are in part superior to those of established alumosilicate zeolites (*e.g.,* the extreme capacity for adsorption of toxic Pb^{2+} of the unique framework structure of the synthetic titanosilicate ETS–10; Zhao *et al.* 2003). Although substantial research efforts have been devoted to mixed (tetrahedral–octahedral) framework titanosilicates (as well as the similarly behaving zircono- and stannosilicates), mixed-framework silicates with $M^{3+}O_6$ octahedra only have been studied very recently (*cf.* Rocha & Lin 2005).

In the present contribution, we focus on the previously unknown crystal structures of two such mixed-framework silicates, $BaKYSi_2O_7$ and $Cs_3YSi_8O_{19}$. The crystal chemistry and topology of both silicates will be discussed and relations to other compounds will be addressed. The compound $BaKYSi_2O_7$ may well be encountered in natural environments such as pegmatites and other differentiates in alkaline provinces.

BACKGROUND INFORMATION

As part of a comprehensive study of the synthesis (by hydrothermal and flux-growth methods), crystal chemistry and topology of M^+–(M^{2+}–)M^{3+} silicates (M^+ = Na, K, Rb, Cs; M^{2+} = Sr, Ba; M^{3+} = Sc, V, Cr, Fe, In, Y, Yb) characterized by mixed octahedron–tetrahedron frameworks, the two compounds mentioned in the title were prepared from molybdate-based flux solvents. The two new yttrium silicates join the following other silicates that have also been synthesized thus far in the context of the study mentioned: $BaY_2Si_3O_{10}$ (Kolitsch *et al.* 2006a); $SrY_2Si_3O_{10}$ and $BaY_2Si_3O_{10}$-type $BaREE_2Si_3O_{10}$ (REE^{3+} = Gd, Y, Er, Yb) (Kolitsch *et al.* 2006b, Wierzbicka-Wieczorek *et al.* 2009b); $BaNa ScSi_2O_7$, $Sr_6KScSi_4O_{16}$ and $BaRbScSi_3O_9$ (Wierzbicka *et al.* 2007a); $BaY_4Si_5O_{17}$ and isotypic $SrSc_4Si_5O_{17}$ (Wierzbicka-Wieczorek 2007, Wierzbicka *et al.*, in prep.); $Ba_2Gd_2Si_4O_{13}$ (Wierzbicka-Wieczorek *et al.*, in prep.); $(Cs,Rb)_9Y_7Si_{24}O_{63}$ and several analogues (Wierzbicka-Wieczorek 2007, Wierzbicka-Wieczorek *et al.* 2008a); $\sim Na_4(Sr,M^{3+})_4(Si_2O_7)(SiO_4)_2$ (M^{3+} = Sc, Y, In) homeotypic with $Na_2Ca_6(Si_2O_7)(SiO_4)_2$ (Wierzbicka *et al.* 2007b, Wierzbicka-Wieczorek 2007); leucite-type $CsFeSi_2O_6$ and $RbFeSi_2O_6$; $Na_3YbSi_2O_7$ (isotypic with other $Na_3REESi_2O_7$ compounds), $NaScSi_2O_6$ (synthetic jervisite, a clinopyroxene), $RbSi_2O_4(OH)$ (Bull & Parise 2003) and isotypic $KSi_2O_4(OH)$; apatite-type $\sim Sr_4Y_6(SiO_4)_6O_2$, and various well-known rare-earth silicates with the REE_2SiO_5 and $REE_2Si_2O_7$ stoichiometries (*cf.* Felsche 1973).

The flux-growth preparations, which employed a variety of different solvent mixtures, also yielded several new molybdates. These include $Rb_5In(MoO_4)_4$ (Tillmanns *et al.* 2005, Wierzbicka-Wieczorek *et al.* 2008b), isotypic with $Rb_5Er(MoO_4)_4$ (Klevtsova & Glinskaya 1976), the novel structure-type $Rb_5Fe(MoO_4)_4$ (Wierzbicka *et al.* 2006, Wierzbicka-Wieczorek *et al.* 2009a), $K_2Ba(MoO_4)_2$ isotypic with the mineral palmierite, $K_2Pb(SO_4)_2$, as well as $K_5Y(MoO_4)_4$, $RbFe(MoO_4)_2$, and $Rb_2Mo_4O_{13}$ (isotypic with the triclinic modification of $K_2Mo_4O_{13}$) (Wierzbicka-Wieczorek *et al.* 2009a).

EXPERIMENTAL

Synthesis

The compound $BaKYSi_2O_7$ was prepared in air from a BaO–K_2O–MoO_3 flux containing dissolved precursor compounds of Ba, K, Y and Si (experimental parameters: 1 g $BaCO_3$, 1 g K_2CO_3, 1 g MoO_3, 0.1614 g Y_2O_3, 0.1718 g SiO_2; Pt crucible covered with lid, T_{max} = 1150°C, holding time 3 h, cooling rate 2 K/h, T_{min} = 900°C, slow cooling to room temperature after switching off the furnace). The reaction products were recovered by dissolving the flux in distilled water. The compound $BaKYSi_2O_7$ forms small (maximum diameter 0.7 mm), more or less isometric colorless transparent crystals. Chemical analyses by SEM–EDS showed the presence of Ba, K, Y and Si. Accompanying phases were a new tetragonal Ba–Y silicate (colorless prisms with the provisional formula $\sim Ba_{5+x}Y_{13}Si_8O_{41}$ according to a single-crystal refinement of the structure) and an unidentified Ba–K–Y silicate [primitive hexagonal cell, a = 9.898(1), c = 7.518(2) Å].

The compound $Cs_3YSi_8O_{19}$ crystallized in air from a CsF–MoO_3 flux containing dissolved precursor compounds of Cs, Y and Si (experimental parameters: 6 g CsF, 2.5 g MoO_3, 0.1614 g Y_2O_3, 0.1718 g SiO_2; Pt crucible covered with lid, T_{max} = 1150°C, holding time 3 h, cooling rate 1.5 K/h, T_{min} = 900°C, slow cooling to room temperature after switching off the furnace). The reaction products were recovered by dissolving the flux in distilled water. The large majority of these products consisted of large colorless glassy crystals of thortveitite-type ("C-type") $Y_2Si_2O_7$ (Felsche 1970, 1973, Redhammer & Roth 2003). The compound $Cs_3YSi_8O_{19}$ is present as a subordinate phase, forming small colorless prisms up to about 0.15 mm in length; SEM–EDS showed the presence of Cs, Y and Si.

Determination of the crystal structure

Selected crystals and crystal fragments were investigated with a NoniusKappa CCD single-crystal X-ray diffractometer (see Table 1 for details). All samples showed good quality of crystals, with no evidence of any twinning or other unusual features. The measured intensities were processed with the Nonius program suite DENZO-SMN and corrected for Lorentz, polarization, background and absorption effects.

Systematic extinctions in the dataset for $BaKYSi_2O_7$ and structure-factor statistics unambiguously indicated the centrosymmetric space-group $P2_1/n$. The crystal structure was determined by direct methods (SHELXS-97, Sheldrick 1997a) and subsequent Fourier and difference-Fourier syntheses, followed by a full-matrix least-squares refinement on F^2 (SHELXL-97, Sheldrick 1997b), leading to convergence at $R(F) = 2.0\%$ (for details, see Table 1). No significant deviation from unit occupancy was observed for any of the atoms in $BaKYSi_2O_7$. The refined positional and displacement parameters are given in Table 2, and selected bond-lengths and calculated bond-valence sums (BVS; in valence units, *vu*), in Table 3.

As input values for the structure model of $Cs_3YSi_8O_{19}$, the positional parameters for isotypic $Cs_3ScSi_8O_{19}$ (space group *Pnma*; Kolitsch & Tillmanns 2004b) were used. A full-matrix least-squares refinement (SHELXL-97, Sheldrick 1997b), with anisotropic treatment of all atoms and unrestrained refinement of the site occupancies of the four partially occupied and disordered Cs positions (Cs3a–d; see discussion) resulted in convergence at $R(F) = 2.9\%$ (for details, see Table 1). The refined model corresponds to a nearly charge-balanced formula (38.08 positive charges *versus* 38.00 negative charges); in order to obtain full electroneutrality, the occupancies of the four Cs positions Cs3a–d were restrained. All the largest residual peaks in the final electron-density map were close to the disordered Cs positions.

The refined positional and displacement parameters are given in Tables 4 and 5, and selected bond- lengths and calculated bond-valence sums are provided in Table 6. Tables of structure factors for both silicates

TABLE 1. CRYSTAL DATA, DATA COLLECTION INFORMATION AND REFINEMENT DETAILS FOR $BaKYSi_2O_7$ AND $Cs_3YSi_8O_{19}$

	Crystal data	
Formula	$BaKYSi_2O_7$	$Cs_3YSi_8O_{19}$
Formula weight	433.53	1016.36
Space group, *Z*	$P2_1/n$ (no. 14), 4	*Pnma* (no. 62), 4
a, *b*, *c* (Å)	9.775(2), 5.718(1), 13.096(3)	11.476(2), 7.059(1), 26.971(5)
β (°)	104.61(3)	-
V (Å^3)	708.3(3)	2184.9(6)
F(000), ρ_{calc} (g•cm^{-3})	792, 4.065	1872, 3.090
μ (mm^{-1})	14.597	8.117
Absorption correction	multi-scan[1)]	multi-scan[1)]
Crystal dimensions (mm)	0.05 × 0.06 × 0.07	0.08 × 0.10 × 0.15
	Data collection	
Diffractometer	Nonius Kappa CCD system	Nonius Kappa CCD system
λ (Mo*K*α) (Å), *T* (K)	0.71073, 293	0.71073, 293
Crystal–detector dist. (mm)	30	48
Rotation axis, width (°)	φ, ω, 2	φ, ω, 1
Total no. of frames	545	1402
Collect. time per degree (s)	100	31
Collection mode, $2\theta_{max}$ (°)	sphere, 70	sphere, 70
h, k, l ranges	-15 → 15, -9 → 9, -21 → 20	-18 → 18, -11 → 11, -43 → 43
Total reflections measured	5955	9349
Unique reflections	3107 (R_{int} 1.55%)	5119 (R_{int} 1.62%)
	Refinement	
$R1(F)$, $wR2_{all}(F^2)$[2)]	2.04%, 4.71%	2.94%, 8.12%
"Observed" reflections	2669 [$F_o > 4\sigma(F_o)$]	4274 [$F_o > 4\sigma(F_o)$]
Extinction coefficient	0.00300(13)	0.00086(9)
No. of refined parameters	110	189
GooF	1.049	1.046
$(\Delta/\sigma)_{max}$	0.001	0.001
$\Delta\rho_{min}$, $\Delta\rho_{max}$ (e/Å^3)	-1.00 (0.56 Å from Ba), 1.52 (0.65 Å from K)	-2.07, 2.95

Note: Unit-cell parameters were refined from 3357 and 5412 recorded reflections for $BaKYSi_2O_7$ and $Cs_3YSi_8O_{19}$, respectively. Scattering factors for neutral atoms were employed in the refinement.
[1)] Otwinowski *et al.* (2003). [2)] $BaKYSi_2O_7$: $w = 1/[\sigma^2(F_o^2) + (0.018P)^2 + 0.83P]$; $P = ([\max \text{ of } (0 \text{ or } F_o^2)] + 2F_c^2)/3$. $Cs_3YSi_8O_{19}$: $w = 1/[\sigma^2(F_o^2) + (0.037P)^2 + 4.05P]$; $P = ([\max \text{ of } (0 \text{ or } F_o^2)] + 2F_c^2/3$.

TABLE 2. FRACTIONAL COORDINATES AND DISPLACEMENT PARAMETERS (Å^2) OF ATOMS IN $BaKYSi_2O_7$

Atom	*x*	*y*	*z*	U_{eq}
Ba	0.636758(13)	0.76922(2)	0.172119(10)	0.00926(4)
K	0.13201(5)	0.26406(8)	0.13885(5)	0.01916(10)
Y	0.760689(19)	0.24063(3)	0.021620(14)	0.00554(4)
Si1	0.44792(6)	0.27157(9)	0.12132(4)	0.00521(9)
Si2	0.97508(6)	0.75487(9)	0.14618(4)	0.00563(9)
O1	0.36322(16)	0.0804(3)	0.03933(12)	0.0126(3)
O2	0.39106(16)	0.5349(3)	0.09229(12)	0.0126(3)
O3	0.61843(15)	0.2582(2)	0.13816(12)	0.0088(3)
O4	0.41496(15)	0.2031(3)	0.23643(11)	0.0108(3)
O5	1.07325(17)	0.7608(3)	0.06444(12)	0.0123(3)
O6	0.86372(16)	0.5381(3)	0.12693(12)	0.0110(3)
O7	0.89240(15)	1.0007(2)	0.15120(11)	0.0091(3)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ba	0.00893(6)	0.00803(6)	0.01092(6)	0.00081(4)	0.00267(4)	-0.00069(4)
K	0.0088(2)	0.0149(2)	0.0337(3)	-0.00130(18)	0.00517(19)	0.00003(16)
Y	0.00541(8)	0.00568(8)	0.00556(8)	-0.00013(5)	0.00145(6)	-0.00011(5)
Si1	0.0051(2)	0.0052(2)	0.0051(2)	-0.00001(16)	0.00090(17)	-0.00040(17)
Si2	0.0050(2)	0.0057(2)	0.0064(2)	-0.00045(16)	0.00178(18)	-0.00012(16)
O1	0.0132(7)	0.0126(7)	0.0114(7)	-0.0041(5)	0.0017(5)	-0.0044(5)
O2	0.0108(7)	0.0089(6)	0.0158(7)	0.0024(5)	-0.0008(5)	0.0015(5)
O3	0.0069(6)	0.0096(6)	0.0103(6)	-0.0007(5)	0.0026(5)	-0.0001(5)
O4	0.0078(6)	0.0166(7)	0.0081(6)	0.0008(5)	0.0021(5)	-0.0037(5)
O5	0.0111(7)	0.0167(8)	0.0116(7)	0.0012(5)	0.0072(5)	0.0021(5)
O6	0.0109(7)	0.0078(6)	0.0146(7)	-0.0029(5)	0.0039(5)	-0.0026(5)
O7	0.0103(7)	0.0072(6)	0.0102(6)	0.0005(5)	0.0033(5)	0.0021(5)

TABLE 3. SELECTED BOND-DISTANCES (Å) AND ANGLES (°) AND CALCULATED BOND-VALENCE SUMS (*vu*) FOR THE COORDINATION POLYHEDRA IN $BaKYSi_2O_7$

Ba	–O2	2.7184(16)	0.314	K	–O4	2.7607(17)	0.182
	–O6	2.7715(16)	0.272		–O7	2.8233(16)	0.154
	–O3	2.8298(14)	0.232		–O5	2.905(2)	0.123
	–O7	2.8505(15)	0.220		–O5	3.0107(16)	0.093
	–O1	2.8995(16)	0.193		–O6	3.0251(16)	0.089
	–O7	2.9011(15)	0.192		–O5	3.0460(16)	0.084
	–O3	2.9542(14)	0.166		–O1	3.0652(18)	0.080
	–O3	2.9840(18)	0.153		–O4	3.0917(16)	0.074
	–O6	3.0489(16)	0.129	<K–O>		$^{[8]}$2.966*	0.88 *vu**
<Ba–O>		$^{[9]}$2.884	1.87 *vu*				
Y	–O5	2.1973(16)	0.609	Si1	–O1	1.6076(16)	1.045
	–O2	2.2263(16)	0.563		–O2	1.6170(16)	1.019
	–O1	2.2331(15)	0.553		–O3	1.6270(16)	0.992
	–O6	2.2603(15)	0.514		–O4	1.6658(16)	0.893
	–O7	2.3059(15)	0.454	<Si1–O>		1.629	3.95 *vu*
	–O3	2.3116(16)	0.447				
<Y–O>		$^{[6]}$2.256	3.14 *vu*				
Si2	–O5	1.6081(17)	1.044	Si1–O–Si2		124.51(9)°	
	–O6	1.6267(15)	0.993				
	–O7	1.6310(15)	0.981				
	–O4	1.6651(16)	0.895				
<Si2–O>		1.633	3.91 *vu*				

Note: The bond-valence parameters are from Brese & O'Keeffe (1991). Bond-valence sums (BVS, *vu*) for the oxygen atoms O1 – O7 are as follows: 1.87 (O1), 1.90 (O2), 1.99 (O3), 2.04 (O4), 1.95 (O5), 1.99 (O6), 2.00 (O7).

* The ninth oxygen neighbor at 3.1562(17) Å has not been considered a bonding ligand as there is small, but distinct gap between the eighth and the ninth oxygen neighbor. Furthermore, in inorganic K compounds, the average coordination-number of K^+ cations is 7.9 (Brown 1988), and the average K–O bond length is 2.85 Å (Baur 1981).

TABLE 4. FRACTIONAL COORDINATES AND DISPLACEMENT PARAMETERS (Å^2) OF ATOMS IN $Cs_3YSi_8O_{19}$

Atom	*x*	*y*	*z*	U_{eq}	Occupancy
Cs1	0.08478(2)	¼	0.452882(9)	0.02132(6)	
Cs2	0.44859(2)	¼	0.452902(9)	0.02050(6)	
Cs3a	-0.06384(6)	¼	0.27777(2)	0.0595(2)	0.7550(16)*
Cs3b	0.0513(6)	¼	0.2318(2)	0.084(3)	0.100(2)*
Cs3c	-0.3717(14)	¼	0.3112(5)	0.141(6)	0.082(3)*
Cs3d	-0.2447(8)	0.0362(18)	0.3026(2)	0.052(3)	0.0314(11)*
Y	0.27068(3)	-¼	0.444322(11)	0.00861(6)	
Si1	0.25429(5)	0.03007(9)	0.33403(2)	0.00964(11)	
Si2	0.06203(8)	¼	0.79791(3)	0.00855(15)	
Si3	-0.05905(8)	¼	0.69138(3)	0.00923(15)	
Si4	0.04507(8)	¼	0.58776(3)	0.00940(15)	
Si5	-0.24528(5)	0.03564(9)	0.43776(2)	0.00959(11)	
Si6	0.42692(8)	¼	0.60258(3)	0.01003(15)	
O1	0.26638(19)	-0.0041(3)	0.39112(7)	0.0216(4)	
O2	0.2499(2)	¼	0.31699(10)	0.0161(5)	
O3	0.13989(19)	0.0610(3)	0.80173(8)	0.0259(4)	
O4	-0.13496(19)	0.0600(3)	0.68895(9)	0.0298(5)	
O5	0.0078(2)	¼	0.74333(9)	0.0199(5)	
O6	-0.0393(3)	¼	0.83851(10)	0.0214(6)	
O7	0.0360(3)	¼	0.64806(11)	0.0337(8)	
O8	-0.0751(2)	¼	0.55988(11)	0.0205(5)	
O9	-0.12050(18)	-0.0642(3)	0.42692(9)	0.0256(4)	
O10	0.27715(18)	-0.0326(3)	0.50513(7)	0.0183(4)	
O11	0.34430(17)	0.0633(3)	0.59686(7)	0.0210(4)	
O12	-0.2322(2)	¼	0.41536(10)	0.0162(5)	
O13	0.5338(2)	¼	0.56619(11)	0.0228(6)	

Note: $U_{eq} = (⅓)\ \Sigma_i\ \Sigma_j\ U_{ij}\ a_i^* a_j^*\ \mathbf{a}_i\ \mathbf{a}_j$ (Fischer & Tillmanns 1988). * Occupancies were subsequently restrained to achieve a completely charge-balanced formula (see text).

TABLE 5. ANISOTROPIC DISPLACEMENT PARAMETERS FOR $Cs_3YSi_8O_{19}$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cs1	0.02058(12)	0.02209(11)	0.02129(11)	0.000	0.00045(8)	0.000
Cs2	0.01708(11)	0.02085(11)	0.02357(12)	0.000	-0.00009(8)	0.000
Cs3a	0.0881(5)	0.0253(2)	0.0651(4)	0.000	-0.0516(4)	0.000
Cs3b	0.124(6)	0.0170(15)	0.111(5)	0.000	-0.104(5)	0.000
Cs3c	0.158(12)	0.151(12)	0.114(9)	0.000	-0.025(8)	0.000
Cs3d	0.064(6)	0.084(7)	0.008(3)	0.003(3)	0.011(3)	0.010(5)
Y	0.00849(13)	0.00964(13)	0.00771(12)	0.000	-0.00021(9)	0.000
Si1	0.0112(3)	0.0066(2)	0.0111(3)	0.0006(2)	-0.00050(19)	0.0000(2)
Si2	0.0090(4)	0.0094(3)	0.0072(3)	0.000	-0.0010(3)	0.000
Si3	0.0085(4)	0.0108(4)	0.0084(3)	0.000	-0.0017(3)	0.000
Si4	0.0070(4)	0.0108(4)	0.0104(4)	0.000	0.0013(3)	0.000
Si5	0.0102(3)	0.0076(2)	0.0110(2)	-0.0015(2)	-0.00038(19)	0.0000(2)
Si6	0.0078(4)	0.0124(4)	0.0099(4)	0.000	-0.0017(3)	0.000
O1	0.0337(10)	0.0179(9)	0.0130(8)	0.0063(7)	0.0004(7)	0.0006(8)
O2	0.0276(14)	0.0059(9)	0.0146(11)	0.000	-0.0020(9)	0.000
O3	0.0287(10)	0.0217(10)	0.0273(10)	-0.0031(8)	-0.0120(8)	0.0140(8)
O4	0.0257(10)	0.0180(9)	0.0457(13)	0.0049(9)	-0.0181(9)	-0.0099(8)
O5	0.0190(13)	0.0312(15)	0.0095(10)	0.000	-0.0055(9)	0.000
O6	0.0231(14)	0.0290(15)	0.0121(11)	0.000	0.0081(10)	0.000
O7	0.0225(15)	0.067(3)	0.0114(12)	0.000	0.0050(10)	0.000
O8	0.0101(11)	0.0285(15)	0.0228(13)	0.000	-0.0047(9)	0.000
O9	0.0157(9)	0.0195(9)	0.0415(12)	-0.0066(9)	0.0016(8)	0.0069(7)
O10	0.0303(10)	0.0138(8)	0.0108(7)	-0.0011(6)	0.0018(7)	-0.0034(7)
O11	0.0212(9)	0.0211(9)	0.0209(8)	-0.0027(7)	-0.0053(7)	-0.0098(7)
O12	0.0273(14)	0.0068(9)	0.0146(11)	0.000	0.0041(10)	0.000
O13	0.0107(12)	0.0367(16)	0.0209(13)	0.000	0.0031(10)	0.000

are available from the Depository of Unpublished Data, on the MAC website [document Yttrium silicates CM47_421].

DESCRIPTION OF THE STRUCTURES

$BaKYSi_2O_7$

The phase $BaKYSi_2O_7$ represents a novel structure-type. It has a framework of tetrahedra and octahedra containing Si_2O_7 groups and octahedrally coordinated Y atoms (<Y–O> = 2.256 Å). Voids in the framework contain [9]-coordinated Ba atoms (<Ba–O> = 2.884 Å) and [8]-coordinated K atoms (<K–O> = 2.966 Å). The asymmetric unit contains one Ba, one K, one Y, two Si and seven O atoms.

The framework of $BaKYSi_2O_7$ is based on a YO_6 octahedron that shares each of its apices with an oxygen atom of the Si_2O_7 group. The YO_6 octahedra show a (001) layered arrangement and are linked to neighboring octahedra by Si_2O_7 groups oriented along the *c* axis (Fig. 1). The overall charge of the tetrahedron–octahedron framework is 3+. This charge is balanced by the Ba^{2+} and K^+ cations, which occupy voids in the framework. Figure 2a shows that the two cations are "stacked" in narrow channels parallel to $[10\bar{1}]$, with a strict sequence ...–Ba–K–Ba–K–... . Diffusion along $[10\bar{1}]$ is, however, not possible because the cation-containing voids are separated by bottlenecks in the framework. Further narrow channels containing the Ba^{2+} and K^+ cations are also recognizable in a view along [121] (Fig. 2b). The BaO_9 polyhedra and KO_8 polyhedra share only one O6–O7 edge with each other. However, the irregular BaO_9 polyhedron shares four-sided O3–O7–O3'–O6 faces with adjacent BaO_9 polyhedra in a zigzag-like fashion parallel to the *b* axis. The BaO_9 polyhedron also shares triangular faces (O1–O3–O7) with YO_6 octahedra. The irregular KO_8 polyhedron shares one polyhedron edge (O5–O5') with adjacent KO_8 polyhedra and triangular faces (O5–O6–O7) and edges (O1–O5) with YO_6 octahedra. A bond-valence analysis (Table 3) yields BVS in good agreement with formal valences.

The Si–O–Si angle of the disilicate group in $BaKYSi_2O_7$ is unusually small [124.51(9)°]. Values commonly observed in silicates range between 135 and 180°, with maxima of 139, 157 and 180°, and a mean of 154° (Baur 1980, Liebau 1985). Very few other silicates show such small Si–O–Si angles; for example, in barysilite, $Pb_8Mn(Si_2O_7)_3$, Si–O–Si is 120.9° (Kolitsch & Holtstam 2002). A comparison of $BaKYSi_2O_7$ with related simple disilicate compounds containing more or less large cations leads to the large family of simple REE disilicates $REE_2Si_2O_7$. In the LREE members of this family (types A, F, G; Felsche 1973), the Si–O–Si angle ranges from 130 to 135°, whereas in the HREE members, an angle of 180° is observed (type C; thortveitite-type). In the recently discovered high-pressure type K (observed for REE = Nd, Sm, Eu and Gd; Fleet & Liu 2001), the angle decreases further

TABLE 6. SELECTED BOND-DISTANCES (Å) AND ANGLES (°) AND CALCULATED BOND-VALENCE SUMS (*vu*) FOR THE COORDINATION POLYHEDRA IN $Cs_3YSi_8O_{19}$

Cs(1)	–O(1)	×2	3.215(2)	0.117	Cs(2)	–O(10)	×2	3.1362(19)	0.144
	–O(10)	×2	3.292(2)	0.095		–O(13)		3.208(3)	0.119
	–O(9)	×2	3.310(2)	0.090		–O(1)	×2	3.220(2)	0.115
	–O(8)		3.420(3)	0.067		–O(11)	×2	3.513(2)	0.052
	–O(9)	×2	3.521(3)	0.051		–O(13)	×2	3.5726(7)	0.044
	–O(8)	×2	3.5480(6)	0.047		–O(10)	×2	3.680(2)	0.033
<Cs(1)–O>			3.381	0.87 *vu*	<Cs(2)–O>			3.405	0.90 *vu*
Cs(3a)	–O(3)	×2	3.190(2)	0.125	Cs(3b)	–O(4)	×2	3.205(4)	0.120
	–O(4)	×2	3.286(2)	0.096		–O(3)	×2	3.233(4)	0.111
	–O(2)		3.332(3)	0.085		–O(2)		3.235(4)	0.111
	–O(5)	×2	3.6325(9)*	0.038		–O(5)	×2	3.656(2)*	0.035
<Cs(3a)–O>			3.364	0.60 *vu*		–O(2)		3.702(6)*	0.031
					<Cs(3a)–O>			3.391	0.67 *vu*
Cs(3c)	–O(12)		3.232(14)	0.111	Cs(3d)	–O(11)		3.024(7)	0.195
	–O(11)	×2	3.336(10)	0.084		–O(3)***		3.137(7)	0.144
	–O(2)		3.729(15)**	0.029		–O(6)***		3.341(11)	0.083
	–O(6)	×2	3.747(5)*	0.028		–O(12)		3.397(8)	0.071
	–O(3)	×2	3.789(13)*	0.025		–O(7)		3.404(10)	0.070
<Cs(3c)–O>			3.588	0.41*vu*		–O(4)		3.431(8)	0.065
						–O(2)*		3.563(8)	0.046
						–O(5)*		3.607(10)	0.040
					<Cs(3d)–O>			3.363	0.71 *vu*
Y	–O(10)	×2	2.2472(19)	0.532	Cs(3a)···Cs(3b)			1.811(9)	
	–O(8)		2.247(3)	0.532	Cs(3a)···Cs(3d)			2.652(11)	
	–O(1)	×2	2.2527(19)	0.525	Cs(3a)···Cs(3d)			2.652(10)	
	–O(13)		2.261(3)	0.513	Cs(3a)···Cs(3c)			3.260(14)	
<Y–O>			2.251	3.16*vu*	Cs(3a)···Cs(3c)			3.646(16)	
					Cs(3b)···Cs(3c)			1.460(15)	
					Cs(3b)···Cs(3d)		×2	2.936(12)	
					Cs(3c)···Cs(3d)		×2	2.111(15)	
					Cs(3d)···Cs(3d)			3.02(3)	
Si(1)	–O(1)		1.565(2)	1.117	Si(2)	–O(6)		1.597(3)	1.076
	–O(2)		1.6198(10)	1.101		–O(5)		1.598(3)	1.073
	–O(3)		1.627(2)	0.992		–O(3)	×2	1.609(2)	1.041
	–O(4)		1.632(2)	0.979	<Si(2)–O>			1.603	4.23*vu*
<Si(1)–O>			1.611	4.16*vu*					
Si(3)	–O(4)	×2	1.598(2)	1.073	Si(4)	–O(8)		1.567(3)	1.167
	–O(5)		1.600(3)	1.067		–O(9)	×2	1.620(2)	1.011
	–O(7)		1.605(4)	1.053		–O(7)		1.635(3)	0.971
<Si(3)–O>			1.600	4.27*vu*	<Si(4)–O>			1.611	4.16*vu*
Si(5)	–O(10)		1.582(2)	0.112	Si(6)	–O(13)		1.574(3)	1.145
	–O(9)		1.626(2)	0.995		–O(11)	×2	1.630(2)	0.984
	–O(11)		1.629(2)	0.987		–O(6)		1.640(3)	0.958
	–O(12)		1.6350(14)	0.971	<Si(6)–O>			1.619	4.07 *vu*
<Si(5)–O>			1.618	4.07 *vu*					

Note: The bond-valence parameters are from Brese & O'Keeffe (1991). Bond-valence contributions from the low-occupancy sites Cs(3b), Cs(3c) and Cs(3d) have been neglected. Bond-valence contributions from the Cs(3a) site (occupancy *ca.* 76%) have been scaled down according to the occupancy.
* These Cs–O distances probably are too long to be considered as bonds, but have been included here because of the disordered nature and irregular environment of the Cs(3b) and Cs(3c) sites (*cf.* Fig. 4).
** Note that the corresponding distance Cs(3c)–O(2) in $Cs_3ScSi_8O_{19}$ is, for unknown reasons, not listed in the SHELXL97 cif file of the structure refinement of $Cs_3ScSi_8O_{19}$, and was therefore not listed in Kolitsch & Tillmanns (2004b); this distance is 3.879 Å.
*** Atoms O(3) and O(6) are misprinted as O(4) and O(7) in Kolitsch & Tillmanns (2004b).

to 122.7–124.4° in order to allow a volume reduction under applied pressure. These observations indicate that the two large cations present in $BaKYSi_2O_7$ (Ba^{2+}, K^+) apparently favor a small Si–O–Si angle of the Si_2O_7 group.

$BaKYSi_2O_7$: structural relations to other compounds

To the best of our knowledge, $BaKYSi_2O_7$ has no isoelectronic equivalent among either natural or synthetic silicates or germanates. The connectivity between YO_6 octahedra and Si_2O_7 groups in its structure

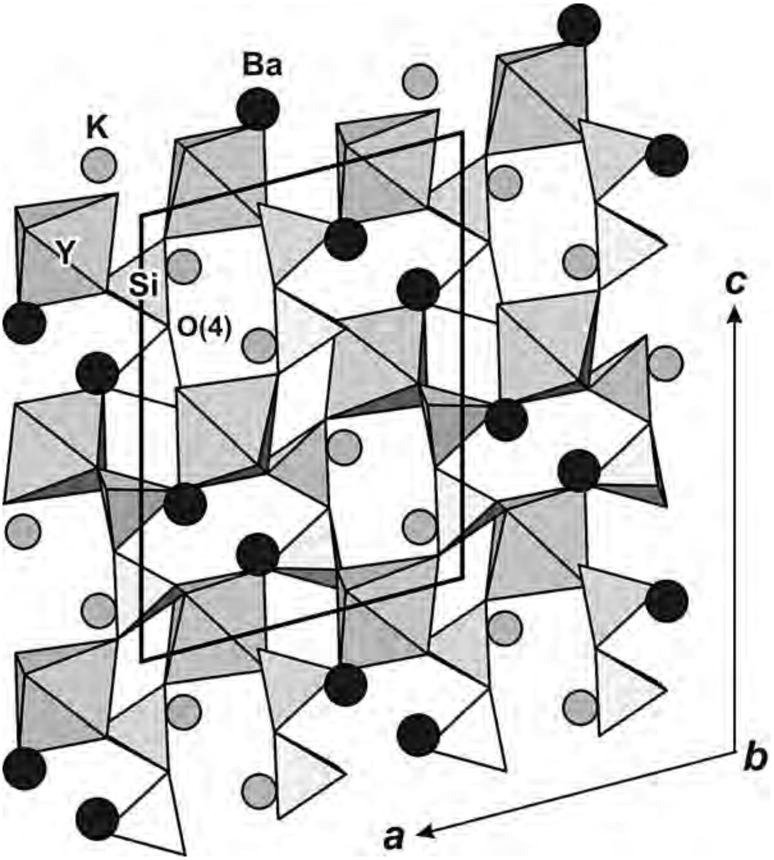

FIG. 1. The framework structure of $BaKYSi_2O_7$ seen along [010]. Each apex of the YO_6 octahedron is corner-linked to Si_2O_7 groups. The Ba^{2+} and K^+ cations occupy voids in the framework. All drawings were done with ATOMS (Shape Software 1999).

is, however, commonly encountered in related silicate compounds: according to the classification of zirconosilicates and their analogues proposed by Ilyushin & Blatov (2002), $BaKYSi_2O_7$ belongs to the PME ("polyhedral microensembles") of type A–1, which is rather common among zirconosilicates and titanosilicates. This PME type is characterized by MO_6 octahedra that share each corner with a SiO_4 tetrahedron. The new silicate $Cs_3YSi_8O_{19}$ described below also contains the PME of type A–1.

The crystal structure of $BaKYSi_2O_7$ shows some distinct similarity to those of several synthetic diphosphates and diarsenates containing octahedrally coordinated M^{2+} cations such as Ca^{2+}, Sr^{2+} and Cd^{2+}. These compounds have either triclinic–pseudomonoclinic or monoclinic symmetry and similar topologies (Fig. 3). They include $Na_2CaP_2O_7$ ($P\overline{1}$; Bennazha *et al.* 1999; Fig. 3a), $K_2CaAs_2O_7$ ($P2_1/c$; Faggiani & Calvo 1976; Fig. 3b) and the isotypic $K_2SrP_2O_7$ (Trunov *et al.* 1991b), $K_2CdP_2O_7$ ($C2/c$; Faggiani & Calvo 1976; Fig. 3c) and isotypic $M_2SrP_2O_7$ (M = Rb, Cs) (Trunov *et al.* 1991a).

The arrangement of the atoms in all these pyrocompounds is based on $M^{2+}O_6$ octahedra sharing each of their corners with an X_2O_7 group (X = P or As). As in $BaKYSi_2O_7$, the X_2O_7 groups link the $M^{2+}O_6$ octahedra in different directions, resulting in three-dimensional tetrahedron–octahedron frameworks, with voids occupied by the more or less large M^+ cations (Fig. 3). However, the linkage between the polyhedral units shows some differences concerning the polyhedron orientations and conformations, thus resulting in different space-group symmetries (the highest symmetry apparently achievable is $C2/c$, and seems to be preferred by the compounds with larger M^+ and M^{2+} ions). The two lower-symmetry structure-types ($Na_2CaP_2O_7$ and $K_2CaAs_2O_7$) each have two non-equivalent Na, K and P, As sites in their respective asymmetric units (Figs.

3a,b), whereas the $K_2CdP_2O_7$ structure-type only has one K site and one P site (Fig. 3c).

It is apparent from the above data that the common topology is relatively flexible. We predict that more silicates (and germanates) isotypic with $BaKYSi_2O_7$ or at least closely related to it will be found in the future. Recent results from single-crystal structure-refinements in fact demonstrate that flux-grown Sc and Yb analogues of $BaKYSi_2O_7$ can be prepared. They have the following unit-cell parameters: $BaKScSi_2O_7$: a 9.523(2), b 5.601(1), c 12.800(3) Å, β 104.38(3)°, V 661.3(2) $Å^3$; $BaKYbSi_2O_7$: a 9.722(2), b 5.695(1), c 13.025(3) Å, β 104.59(3)°, V 697.9(2) $Å^3$ (Wierzbicka-Wieczorek 2007). As expected from the ionic radii of $^{[6]}M^{3+}$, the unit-cell volume of these two analogues is smaller than that of $BaKYSi_2O_7$, the smallest being that of the Sc analogue.

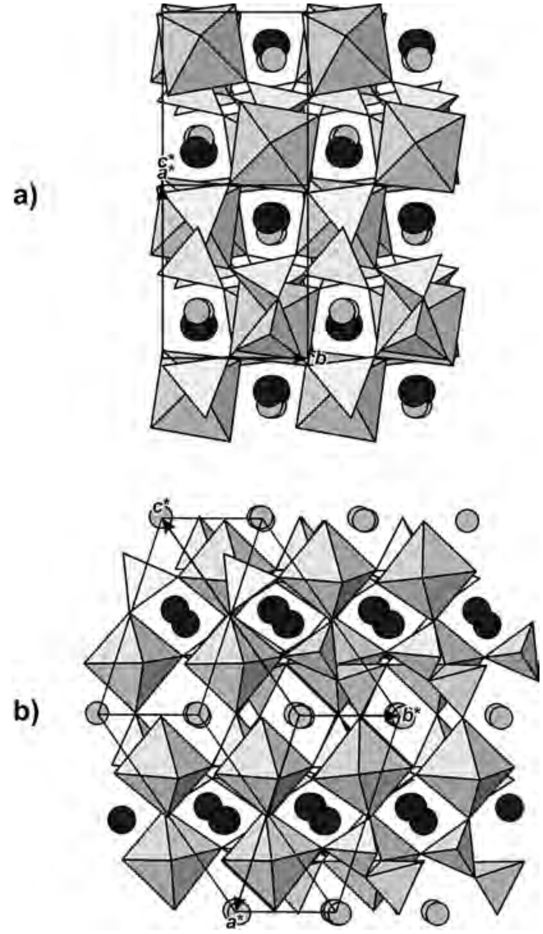

FIG. 2. View of the Ba- and K-containing channels in the framework structure of $BaKYSi_2O_7$: a) along [10$\bar{1}$], and b) along [121]. Labels as in Figure 1.

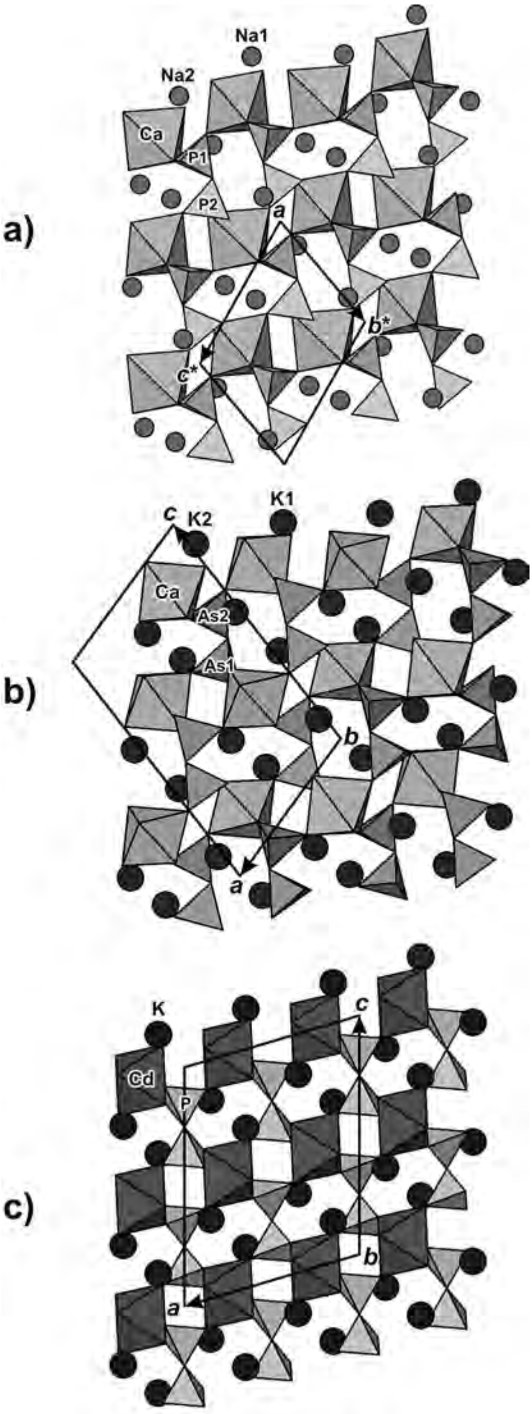

FIG. 3. Structure types of some metal diphosphates and diarsenates with topologies very similar to that of $BaKYSi_2O_7$ (compare Fig. 1). a) $Na_2CaP_2O_7$ (Bennazha *et al.* 1999), b) $K_2CaAs_2O_7$ (Faggiani & Calvo 1976), c) $K_2CdP_2O_7$ (Faggiani & Calvo 1976).

The compound $Cs_3YSi_8O_{19}$

The new silicate $Cs_3YSi_8O_{19}$ is isotypic with its isoelectronic Sc analogue $Cs_3ScSi_8O_{19}$ (Kolitsch & Tillmanns 2004b). The latter was the first representative of a mixed octahedron–tetrahedron framework structure, in which the $[TO_4]$:$[MO_6]$ ratio is greater than 6:1. The following description and discussion of the atomic arrangement of $Cs_3YSi_8O_{19}$ will focus on its most important features and a comparison with the features of $Cs_3ScSi_8O_{19}$. For a more detailed description of the connectivity, the reader is referred to Kolitsch & Tillmanns (2004b).

The crystal structure of $Cs_3YSi_8O_{19}$ (Fig. 4) is based on isolated YO_6 octahedra sharing corners with SiO_4 tetrahedra to form an open framework that contains four-, six- and eight-membered rings; the latter only involve by SiO_4 tetrahedra. The range of Y–O bond lengths in the YO_6 octahedron [2.2472(19) to 2.261(3) Å] is considerably shorter than that in $BaKYSi_2O_7$ [2.1973(16) to 2.3116(16) Å], although the average bond-lengths are very similar [d_{av}(Y–O) = 2.251 and 2.256 Å for $Cs_3YSi_8O_{19}$ and $BaKYSi_2O_7$, respectively]. The bond-angle distortion in $Cs_3YSi_8O_{19}$ [O–Y–O: 86.13(10) to 100.81(11)° and 169.91(12) to 172.65(7)°] is also considerably weaker than in $BaKYSi_2O_7$ [79.29(5) to 102.58(6)° and 162.70(6) to 171.91(6)°].

As in isotypic $Cs_3ScSi_8O_{19}$, two fully occupied Cs positions are located in large voids in the framework close to the six-membered rings. Their mean Cs–O bond lengths [3.381 and 3.405 Å for Cs(1) and Cs(2), respectively] are slightly longer than those in $Cs_3ScSi_8O_{19}$, 3.340 and 3.363 Å, respectively (Kolitsch & Tillmanns 2004b). Four further, partly occupied and disordered Cs positions with very irregular coordinations to O atoms [Cs(3a)–Cs(3d)] are located close to very large voids bordered by the puckered eight-membered rings. These cavities are linked into spacious channels parallel to [100] and [010]. The connectivity results in each O atom being coordinated to either two Si atoms or one Si and one Sc atom; all additional bonds are longer (> 3.0 Å) to the Cs atoms. Calculated BVS of the cations (Table 6) are very close to those in $Cs_3ScSi_8O_{19}$, and in reasonable agreement with formal valences.

The approximate occupancies of the four partly occupied and more or less disordered Cs sites are similar to those in $Cs_3ScSi_8O_{19}$ (values in brackets): Cs(3a) 0.76 (0.80); Cs(3b) 0.10 (0.05); Cs(3c) 0.08 (0.10); Cs(3d) 0.03 (0.025). Note that the combined occupancy of all four sites was constrained to be 1.00, in order to achieve a completely charge-balanced formula; the freely refined occupancies are given in Table 4.

The average Si–O bond lengths range between 1.600 and 1.619 Å (Table 6), identical to the range in $Cs_3ScSi_8O_{19}$. The sequence from shortest to longest Si–O bonds in the individual SiO_4 tetrahedra is also practically identical in both compounds, thus demonstrating the behavior of the SiO_4 tetrahedra as rigid units.

The structure of $Cs_3YSi_8O_{19}$ is related to that of $Cs_2TiSi_6O_{15}$ and some other microporous scandium-, REE-, titanosilicate and zirconosilicate minerals and compounds; for details, see the article on $Cs_3ScSi_8O_{19}$ by Kolitsch & Tillmanns (2004b). Since the topology of $Cs_3YSi_8O_{19}$ is characterized by large voids and channels, we argued in the previous article that the topology or its derivatives may be important in the context of immobilization of radioactive ^{137}Cs waste, cationic conductivity or catalysis. The large channels would facilitate ionic movement, and the high-temperature

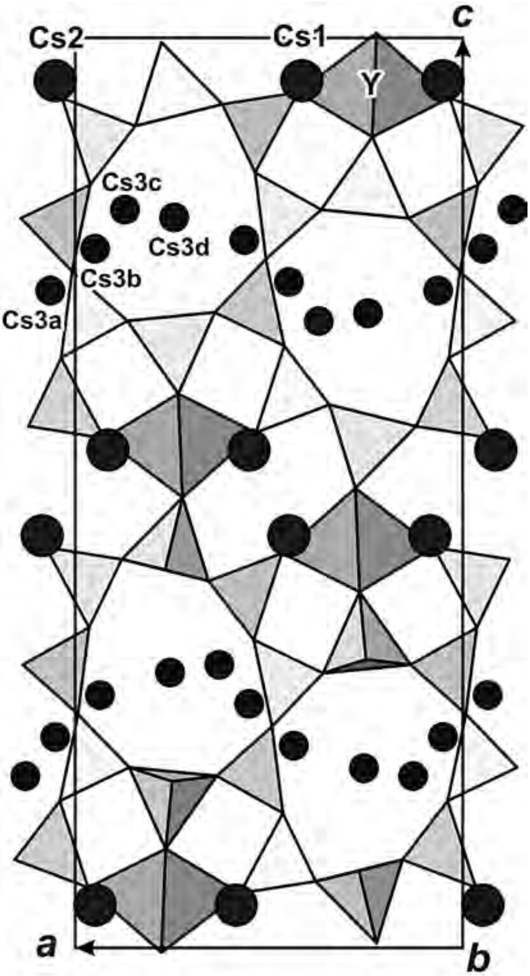

FIG. 4. The complex framework-structure of $Cs_3YSi_8O_{19}$ in a projection along [010]. The two large dark circles represent Cs(1) and Cs(2), whereas the four smaller, hatched circles represent the partially occupied and strongly disordered Cs(3a–d) sites.

preparation attests to a considerable thermodynamic stability.

Conclusions

Two novel metal–Y silicates with mixed octahedron–tetrahedron framework structures, $BaKYSi_2O_7$ and $Cs_3YSi_8O_{19}$, have been prepared, and their crystal structures have been determined. Both belong to the PME ("polyhedral microensembles"), type A-1 of Ilyushin & Blatov (2002). We anticipate that a larger number of isotypic $HREE^{3+}$ analogues exist and will be reported in the future.

Acknowledgements

Financial support by the Austrian Science Foundation (FWF) (Grant P17623–N10) is gratefully acknowledged. The article benefitted from constructive reviews by E. Sokolova and an anonymous reviewer, and patient editorial assistance by Bob Martin.

References

Ananias, D., Rainho, J.P., Ferreira, A., Lopes, M., Morais, C.M., Rocha, J. & Carlos, L.D. (2002): Synthesis and characterization of Er(III) and Y(III) sodium silicates: $Na_3ErSi_3O_9$, a new infrared emitter. *Chem. Mater.* **14**, 1767-1772.

Baur, W.H. (1980): Straight Si–O–Si bridging bonds do exist in silicates and silicon dioxide polymorphs. *Acta Crystallogr.* **B36**, 2198-2202.

Baur, W.H. (1981): Interatomic distance predictions for computer simulation of crystal structures. *In* Structure and Bonding in Crystals II (M. O'Keeffe & A. Navrotsky, eds.). Academic Press, New York, N.Y. (31-52).

Bennazha, J., Boukhari, A. & Holt, E.M. (1999): Synthesis and crystal structure of $Na_2CaP_2O_7$. *Solid State Sci.* **1**, 373-380.

Brese, N.E. & O'Keeffe, M. (1991): Bond-valence parameters for solids. *Acta Crystallogr.* **B47**, 192-197.

Brown, I.D. (1988): What factors determine cation coordination numbers? *Acta Crystallogr.* **B44**, 545-553.

Bull, I. & Parise, J.B. (2003): $Cs[Si_3O_6(OH)]$ and $Rb[Si_2O_4(OH)]$: two novel phyllosilicates. *Acta Crystallogr.* **C59**, i100-i102.

Faggiani, R. & Calvo, C. (1976): Crystal structure of $CaK_2As_2O_7$ and $CdK_2P_2O_7$. *Can. J. Chem.* **54**, 3319-3324.

Felsche, F. (1970): Crystal data on the polymorphic disilicate $Y_2Si_2O_7$. *Naturwiss.* **57**, 127-128.

Felsche, F. (1973): The crystal chemistry of rare-earth silicates. *Structure and Bonding* **13**, 99-197.

Fischer, R.X. & Tillmanns, E. (1988): The equivalent isotropic displacement factor. *Acta Crystallogr.* **C44**, 775-776.

Fleet, M.E. & Liu, Xiaoyang (2001): High-pressure rare earth disilicates $REE_2Si_2O_7$ (REE = Nd, Sm, Eu, Gd): type K. *J. Sol. State Chem.* **161**, 166-172.

Ilyushin, G.D. & Blatov, V.A. (2002): Crystal chemistry of zirconosilicates and their analogs: topological classification of MT frameworks and suprapolyhedral invariants. *Acta Crystallogr.* **B58**, 198-218.

Klevtsova, R.F. & Glinskaya, L.A. (1976): Crystal structure of rubidium erbium molybdate $Rb_5Er(MoO_4)_4$. *Dokl. Akad. Nauk SSSR* **230**, 1337-1340 (in Russ.).

Kolitsch, U. & Holtstam, D. (2002): Barysilite from Garpenberg Norra, Dalarna, Sweden: occurrence and crystal structure refinement. *Mineral. Mag.* **66**, 353-363.

Kolitsch, U. & Tillmanns, E. (2004a): The structural relation between the new synthetic silicate $K_2ScFSi_4O_{10}$ and narsarsukite, $Na_2(Ti,Fe^{3+})(O,F)Si_4O_{10}$. *Eur. J. Mineral.* **16**, 143-149.

Kolitsch, U. & Tillmanns, E. (2004b): Synthesis and crystal structure of a new microporous silicate with a mixed octahedral–tetrahedral framework: $Cs_3ScSi_8O_{19}$. *Mineral. Mag.* **68**, 677-686.

Kolitsch, U., Wierzbicka, M. & Tillmanns, E. (2006a): $BaY_2Si_3O_{10}$, a new flux-grown trisilicate. *Acta Crystallogr.* **C62**, i97-i99.

Kolitsch, U., Wierzbicka, M. & Tillmanns, E. (2006b): Monoclinic $BaY_2Si_3O_{10}$ and triclinic $SrY_2Si_3O_{10}$: flux-growth and atomic arrangements of two new silicates containing finite Si_3O_{10} units. *In* 15th Slovenian-Croatian Crystallographic Meeting (Jezersko, Slovenia), Book of Abstracts, 22.

Liebau, F. (1985): *Structural Chemistry of Silicates*. Springer-Verlag, Berlin, Germany.

Murugavel, R. & Roesky, H.W. (1997): Titanosilicates: recent developments in synthesis and use as oxidation catalysts. *Angew. Chem., Int. Ed.* **36**, 477-479.

Otwinowski, Z., Borek, D., Majewski, W. & Minor, W. (2003): Multiparametric scaling of diffraction intensities. *Acta Crystallogr.* **A59**, 228-234.

Redhammer, G.J. & Roth, G. (2003): β-$Y_2Si_2O_7$, a new thortveitite-type compound, determined at 100 and 280 K. *Acta Crystallogr.* **C59**, i103-i106.

Rocha, J. & Anderson, M.W. (2000): Microporous titanosilicates and other novel mixed octahedral-tetrahedral framework oxides. *Eur. J. Inorg. Chem.*, 801-818.

ROCHA, J. & LIN, ZHE (2005): Microporous mixed octahedral-pentahedral-tetrahedral framework silicates. *In* Micro- and Mesoporous Mineral Phases (G. Ferraris & S. Merlino, eds.). *Rev. Mineral. Geochem.* **57**, 173-201.

SHAPE SOFTWARE (1999): ATOMS for Windows and Macintosh V5.0.4. Kingsport, Tennessee 37663, U.S.A.

SHELDRICK, G.M. (1997a): SHELXS–97, a program for the solution of crystal structures. University of Göttingen, Göttingen, Germany.

SHELDRICK, G.M. (1997b): SHELXL–97, a program for crystal structure refinement. University of Göttingen, Göttingen, Germany.

SOKOLOVA, E. & HAWTHORNE, F.C. (2004): The crystal chemistry of silicate minerals with chains of (TiO_6) octahedra. *Can. Mineral.* **42**, 807-824.

TILLMANNS, E., WIERZBICKA, M. & KOLITSCH, U. (2005): $Rb_5In(MoO_4)_4$: crystal structure of a possible laser material. *Acta Crystallogr.* **A61** *Suppl.*, C370.

TRUNOV, V.K., OBOZNENKO, YU.V., SIROTINKIN, S.P. & TSKHELASHVILI, N.B. (1991a): Crystal structures of the double diphosphates $Rb_2SrP_2O_7$ and $Cs_2SrP_2O_7$. *Neorg. Mater.* **27**, 2370-2374 (in Russ.).

TRUNOV, V.K., OBOZNENKO, YU.V., SIROTINKIN, S.P. & TSKHELASHVILI, N.B. (1991b): Accurate definition of $K_2SrP_2O_7$ crystal structure. *Neorg. Mater.* **27**, 1993-1994 (in Russ.).

VIDICAN, I., SMITH, M.D. & ZUR LOYE, H.-C. (2003): Crystal growth, structure determination, and optical properties of new potassium-rare-earth silicates $K_3RESi_2O_7$ (RE = Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu). *J. Sol. State Chem.* **170**, 203-210.

WIERZBICKA, M., KOLITSCH, U. & TILLMANNS, E. (2006): $Rb_5Fe(MoO_4)_4$ – a novel stucture type with isolated $Fe_2Mo_8O_{32}$ clusters. *Z. Kristallogr., Suppl.* **24**, 176.

WIERZBICKA, M., KOLITSCH, U. & TILLMANNS, E. (2007a): Three new complex silicates of scandium: flux growth and topologies of $Sr_6KScSi_4O_{16}$, $BaNaScSi_2O_7$ and $BaRbScSi_3O_9$. *Z. Kristallogr., Suppl.* **25**, 079-61-id51 (CD-ROM).

WIERZBICKA, M., KOLITSCH, U. & TILLMANNS, E. (2007b): Flux synthesis and crystal structure of the new mixed silicates $Na_4Sr_2M^{3+}{}_2(Si_2O_7)(SiO_4)_2$ (M^{3+} = Y, In, Sc). *In* 16th Croatian-Slovenian Crystallographic Meeting (Petrčane, Croatia), Book of Abstracts, 37.

WIERZBICKA-WIECZOREK, M. (2007): *Syntheses, Crystal Structures and Crystal Chemistry of New Mixed-Framework Silicates and a New Molybdate Structure Type.* Ph.D. thesis, Institute of Mineralogy and Crystallography, University of Vienna, Vienna, Austria.

WIERZBICKA-WIECZOREK, M., KOLITSCH, U. & TILLMANNS, E. (2008a): Novel synthetic alkali–yttrium silicates with a new microporous mixed framework topology: $(Rb,Cs)_9Y_7Si_{24}O_{63}$ and isotypic $Rb_9Y_7Si_{24}O_{63}$. *Crystal Res. Technol.* **43**, 1210-1219.

WIERZBICKA-WIECZOREK, M., KOLITSCH, U. & TILLMANNS, E. (2008b): Flux syntheses and crystal structures of new compounds with decorated kröhnkite-like chains. *Acta Chim. Slov.* **55**, 909-917.

WIERZBICKA-WIECZOREK, M., KOLITSCH, U. & TILLMANNS, E. (2009b): Preparation and structural study of five new trisilicates, $SrY_2Si_3O_{10}$ and $BaREE_2Si_3O_{10}$ (REE = Gd, Er, Yb, Sc), including a review on the geometry of the Si_3O_{10} unit. *Eur. J. Mineral.* (in press).

WIERZBICKA-WIECZOREK, M., KOLITSCH, U. & TILLMANNS, E. (2009a): Crystal chemistry and topology of Rb–M^{III}-molybdates (M = Fe, Sc, In) and triclinic $Rb_2Mo_4O_{13}$: novel clusters, decorated chains and layers. *Z. Kristallogr.* **224**, 151-162.

ZHAO, G.X.S., LEE, J.L. & CHIA, P.A. (2003): Unusual adsorption properties of microporous titanosilicate ETS–10 toward heavy metal lead. *Langmuir* **19**, 1977-1979.

Received December 23, 2006, revised manuscript accepted March 17, 2009.