*Scientific paper*

# Flux Syntheses and Crystal Structures of New Compounds With Decorated Kröhnkite-like Chains

**Maria Wierzbicka-Wieczorek,**[a]* **Uwe Kolitsch**[b]
**and Ekkehart Tillmanns**[a]

[a] *Institute of Mineralogy and Crystallography, University of Vienna, Geocentre, Althanstr. 14, A-1090 Vienna, Austria*

[b] *Department of Mineralogy and Petrography, Natural History Museum Vienna, Burging 7, A-1010 Vienna, Austria*

* *Corresponding author: E-mail: maria.wierzbicka@univie.ac.at*

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***Dedicated to the memory of Professor Ljubo Golič***

## Abstract

The crystal structures of two novel compounds, $KSr_6Sc(SiO_4)_4$ and $Rb_5In(MoO_4)_4$, were determined from single-crystal X-ray diffraction data collected at room temperature. Both compounds have been synthesised by the flux growth technique in the course of a research project on new micro- and nanoporous alkali-$M^{3+}$ silicates. $KSr_6Sc(SiO_4)_4$ represents a new structure type and the first silicate containing decorated kröhnkite-like octahedral-tetrahedral chains. It is orthorhombic and crystallises in *Pnma*, with $a$ = 19.137(4), $b$ = 11.197(2), $c$ = 7.125(1) Å, $V$ = 1526.7(5) Å$^3$, Z = 8. $Rb_5In(MoO_4)_4$ has space group *P*2/*c* with $a$ = 11.391(2), $b$ = 7.983(2), $c$ = 11.100(2) Å,  = 113.74(3)°, $V$ = 924.0(3) Å$^3$, $Z$ = 2. It is isotypic with $Rb_5Er(MoO_4)_4$. The topologies of both compounds are characterised by isolated infinite decorated kröhnkite-like chains that are built from either $ScO_6$ or $InO_6$ octahedra corner-linked and decorated by $SiO_4$ or $MoO_4$ tetrahedra. These chains are separated by alkali or alkaline earth metals. A detailed comparison to the few other compounds based on decorated kröhnkite-like chains, *viz.* $Ba_2Ca(HPO_4)_2(H_2PO_4)_2$, $CsM^{3+}(H_{1.5}AsO_4)_2(H_2AsO_4)$ ($M^{3+}$ = Ga, Cr), $CsAl(H_2AsO_4)_2(HAsO_4)$, $K(H_2O)M^{3+}(H_{1.5}AsO_4)_2(H_2AsO_4)$ ($M^{3+}$ = Fe, Ga, In) and $K_5In(MoO_4)_4$ is given.

**Keywords:** Decorated kröhnkite-like chains, rubidium indium molybdate, strontium potassium scandium silicate, flux growth, single-crystal X-ray diffraction

## 1. Introduction

Kröhnkite-type chains (Figure 1) are infinite isolated octahedral-tetrahedral chains formed from the ladder-like corner-linkage of $MO_6$ octahedra and $XO_4$ tetrahedra. They are named after the mineral kröhnkite, $Na_2Cu(SO_4)_2 \cdot 2H_2O$, in which this type of chain was first described.[1] Kröhnkite-type chains are encountered in a large number of natural and synthetic compounds in different orientations and topological arrangements. Fleck, Kolitsch and coworkers provide a detailed classification and reviews of all compounds containing kröhnkite-type or kröhnkite-like chains (the latter are topologically very similar to, but not identical to kröhnkite-type chains *sensu strictu*), and decorated variants of the latter (the two 'free' apices of the $MO_6$ octahedra are further decorated with one or two $XO_4$ tetrahedra; only very few examples of such variants are known).[2–6] The mentioned classification encompasses (generally hydrated) $XO_4$ oxysalts, where $X$ = $P^{5+}$, $As^{5+}$, $S^{6+}$, $Se^{6+}$, $Cr^{6+}$, $Mo^{6+}$, $W^{6+}$.

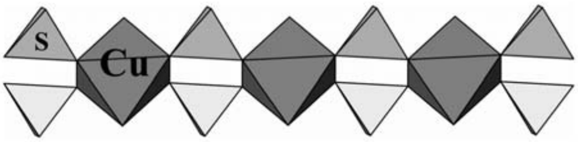

**Figure 1.** Kröhnkite-type octahedral-tetrahedral chain in kröhnkite, $Na_2Cu(SO_4)_2 \cdot 2H_2O$.

During a systematic research for new micro- and nanoporous silicates in the system $M^{1+}$–($M^{2+}$–)$M^{3+}$–Si–O ($M^{1+}$ = Na, K, Rb, Cs; $M^{2+}$ = Sr, Ba; $M^{3+}$ = Sc, V, Cr, Fe, In, Y, Yb, Gd) with the help of high-temperature flux growth syntheses, two novel compounds containing decorated kröhnkite-like chains, $KSr_6Sc(SiO_4)_4$ and $Rb_5In(MoO_4)_4$, were grown from molybdate-based flux solvents.[7,8] During this research project, more than 30 new crystalline compounds (including isotypic compounds) with 12 novel structure types have been studied in detail by single-crystal X-ray diffraction methods, supplemented by chemical analyses and Raman spectroscopy. The following novel silicates are described and summarised in a PhD Thesis completed at the University of Vienna[7]: $BaKREESi_2O_7$ (REE = Y,[9,10] Yb, Sc) and isotypic $SrKScSi_2O_7$ ($P2_1/n$), with the three structurally related compounds $BaNaScSi_2O_7$ ($P2_1/m$), $BaKYbSi_2O_7$ ($Cc$) and isotypic $SrKScSi_2O_7$, $BaY_2Si_3O_{10}$ ($P2_1/m$)[11,12] and isotypic $BaREE_2Si_3O_{10}$ (REE = Gd, Er, Yb, Sc), triclinic $SrY_2Si_3O_{10}$ ($P\bar{1}$),[12] $BaRbScSi_3O_9$ ($P2_1/c$),[13,14] $BaY_4Si_5O_{17}$ and isotypic $SrREE_4Si_5O_{17}$ (REE = Yb, Sc) ($P2_1/m$),[15] $Ba_2Gd_2Si_4O_{13}$ ($C2/c$),[14,16] $(M^{1+})_9REE_7Si_{24}O_{63}$ (REE = Yb, Y; $M^{1+}$ = K, Rb, Cs) ($R\bar{3}$), $Na_4Sr_2REE_2(Si_2O_7)(SiO_4)_2$ (REE = Y, In, Sc) ($P2_1/c$),[17] $Ba_{5.2}REE_{13}Si_8O_{41}$ (REE = Y, Ho) ($I\bar{4}2m$) and, finally, $Cs_3REESi_8O_{19}$ (REE = Y,[9] Yb) ($Pnma$) and isotypic $Rb_3YSi_8O_{19}$.

The flux syntheses also yielded several, partly new molybdates as reaction by-products, e.g., novel $Rb_5Fe(MoO_4)_4$,[18] $K_5Y(MoO_4)_4$, $RbFe(MoO_4)_2$ and isotypic $RbSc(MoO_4)_2$, and $Rb_2Mo_4O_{13}$ (isotypic with the triclinic modification of $K_2Mo_4O_{13}$).[8]

In the present paper we report the syntheses and the crystal structures (determined from single-crystal X-ray diffraction data) of $KSr_6Sc(SiO_4)_4$ and $Rb_5In(MoO_4)_4$, and we discuss and compare the decorated kröhnkite-like chains in their atomic arrangements with those of all other presently known compounds containing such chains.

# 2. Experimental

## 2. 1. Syntheses

The flux growth experiments were conducted in a Naber high-temperature furnace in air using platinum crucibles at $T_{max}$ = 1150 °C. Small, colourless, pseudo-tetragonal prisms of $KSr_6Sc(SiO_4)_4$ were grown from a $MoO_3$ flux containing dissolved reagent-grade starting materials of K, Sr, Sc and Si (experimental parameters: 1.0014 g $K_2CO_3$, 1.0001 g $Sr(OH)_2\cdot 8H_2O$, 0.1245 g $Sc_2O_3$, 0.2118 g $SiO_2$, 1.0010 g $MoO_3$). The Pt crucible filled with an intimate mixture of the starting materials was heated up during 12 h to 1150 °C, followed by a holding time of 3 h, and cooling during 125 h (2 K/h) to 900 °C, at which point the furnace was switched off. The reaction products were washed in distilled water, filtered and dried in air. This synthesis yielded three other reaction products, namely pseudo-octahedral crystals of $SrKScSi_2O_7$ ($Cc$), which is isotypic to $BaKYbSi_2O_7$, small colourless pseudohexagonal plates of $SrKScSi_2O_7$, which is isotypic to $BaKYSi_2O_7$ and $Sr_3(Si_3O_9)$.

Small colourless prisms of $Rb_5In(MoO_4)_4$ were obtained as a by-product during a flux growth experiment for which the following starting mixture of reagent-grade starting material was used: 1.5004 g RbF, 0.1824 g $In_2O_3$, 0.1019 g $SiO_2$ and 1.7733 g $MoO_3$. The used temperature programme was: heating up during 4 h to 1150 °C, holding time 3 h, cooling for 166.6 h (1.2 K/h) to 900 °C, after which the furnace was switched off. The crystals were accompanied only by one additional phase, $In_2O_3$.

## 2. 2. Data Collection and Structure Solution

The crystal structures of $KSr_6Sc(SiO_4)_4$ and $Rb_5In(MoO_4)_4$ were determined from single-crystal X-ray diffraction data obtained from selected crystal fragments of good diffracting quality. Measurements were made with a Nonius KappaCCD four-circle X-ray diffractometer, equipped with a capillary optics collimator (for further details on data collection strategies and data processing see Table 1). The intensity data were processed with the Nonius program suite DENZO-SMN[19] and corrected for Lorentz, polarization and background effects. Absorption was corrected according to the multi-scan method.[19] The program SHELXS-97 was used for the solution of the crystal structures, employing direct methods. The structure

**Table 1.** Crystal data, data collection information and refinement details for $KSr_6Sc(SiO_4)_4$ and $Rb_5In(MoO_4)_4$.

| | **$KSr_6Sc(SiO_4)_4$** | **$Rb_5In(MoO_4)_4$** |
|---|---|---|
| Space group | *Pnma* | *P2/c* |
| Crystal size ($mm^3$) | 0.02 × 0.03 × 0.04 | 0.08 × 0.10 × 0.17 |
| *a* (Å) | 19.137(4) | 11.391(2) |
| *b* (Å) | 11.197(2) | 7.983(2) |
| *c* (Å) | 7.125(1) | 11.100(2) |
| β (°) | 90 | 113.74(3) |
| *V* ($Å^3$) | 1526.7(5) | 924.0(3) |
| Z | 8 | 2 |
| *F* (000) | 1808 | 1060 |
| $\rho_{calc}$ ($g/cm^3$) | 4.255 | 4.248 |
| $\mu$ ($mm^{-1}$) | 21.895 | 17.025 |
| Crystal-detector distance (mm) | 34 | 30 |
| $2\theta_{max}$ (°), *T* (K) | 60, 293 | 70, 293 |
| Rotation width (°) | 1.5 | 2 |
| Frames | 564 | 519 |
| Time per frame (s) | 400 | 50 |
| *h, k, l* ranges | –26/26,<br>–10/10,<br>–12/12, | –15/15,<br>–18/18,<br>–17/17 |
| Total refls. measured | 4240 | 7876 |
| Unique reflections | 2334<br>($R_{int}$ 3.14%) | 4054<br>($R_{int}$ 1.56%) |
| 'Observed' refls.* | 1863 | 3697 |
| Variables | 146 | 120 |
| $R1(F)$, $wR2_{all}$ $(F^2)$ | 3.54, 7.95% | 2.27, 5.72% |
| Extinct. coefficient | 0.00009(4) | 0.00549(16) |
| GooF | 1.172 | 1.052 |
| $(\Delta/\sigma)_{max}$ | 0.001 | 0.001 |
| $\Delta\rho_{min}$, $\Delta\rho_{max}$ ($e/Å^3$) | –1.18, 1.86 | –1.80, 1.62 |
| *a, b*** | 0.025, 9.6 | 0.03, 0.9 |

* $F_o > 4\sigma(F_o)$

** $w = 1/[\sigma^2(F_o^2) + (a \times P^2 + b \times P]$; $P = [\max(0, F_o^2) + 2 \times F_c^2]/3$

models were refined by standard full-matrix least-squares techniques on $F^2$ using SHELXL-97.[20]

For the final refinement step of the structure model of $Rb_5In(MoO_4)_4$, the atomic coordinates of isotypic $Rb_5Er(MoO_4)_4$ were used as a starting model.[21]

The final cycles of least-squares refinement for $KSr_6Sc(SiO_4)_4$ gave the residuals $R1(F) = 3.55\%$ and $wR2_{all}(F^2) = 7.97\%$ using 1863 reflections with $F_o > 4\sigma(F_o)$ and 146 parameters. For $Rb_5In(MoO_4)_4$ the residuals are: $R1(F) = 2.27\%$, $wR2_{all}(F^2) = 5.72\%$ for 3697 reflections with $F_o > 4\sigma(F_o)$ and 120 parameters (see Table 1). The final difference Fourier maps were fairly smooth and showed a minimum of –1.18 e/Å$^3$ (Sr position) and a maximum of 1.86 e/Å$^3$ (close to the K position) for $KSr_6Sc(SiO_4)_4$. Corresponding values for $Rb_5In(MoO_4)_4$ were –1.80 and 1.62 e/Å$^3$, respectively (both close to Rb positions). The final positional and displacement parameters of $KSr_6Sc(SiO_4)_4$ and $Rb_5In(MoO_4)_4$ are given in Tables 2 and 5. Anisotropic displacement parameters are listed in Tables 3 and 6. Selected interatomic distances and calculated bond-valence sums (v.u.) for the coordination polyhedra are presented in Tables 4 and 7. All figures were drawn using the program ATOMS 5.1 version.[22]

# 3. Results and Discussion

## 3. 1. Crystal Structures and Topologies

### 3. 1. 1. $KSr_6Sc(SiO_4)_4$

$KSr_6Sc(SiO_4)_4$ represents a novel structure type, the first K–Sr–Sc silicate and the first silicate with decorated kröhnkite-like octahedral-tetrahedral chains.

Other reported scandium silicates containing alkali and/or alkaline earth cations comprise $K_2Sc(Si_2O_6)$,[23] $K_2ScF(Si_4O_{10})$,[24] $K_3Sc(Si_2O_7)$,[25] $Ba_9Sc_2(SiO_4)_6$,[26] as well as the above mentioned six compounds $BaKScSi_2O_7$, $BaNaScSi_2O_7$, $BaSc_2Si_3O_{10}$, $BaRbScSi_3O_9$, $SrSc_4Si_5O_{17}$, $Na_4Sr_2Sc_2(Si_2O_7)(SiO_4)_2$. None of these compounds shows a close structural relation to $KSr_6Sc(SiO_4)_4$.

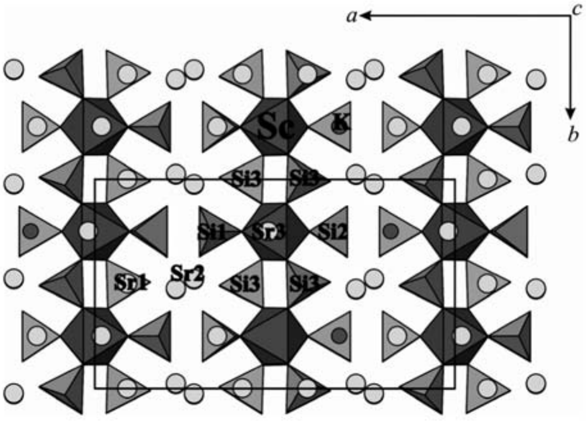

**Figure 2.** View of $KSr_6Sc(SiO_4)_4$ along [001], and perpendicular to the decorated kröhnkite-like octahedral-tetrahedral chains (in the central part of the figure, Sr atoms have been omitted in order to show the $SiO_4$ tetrahedra more clearly).

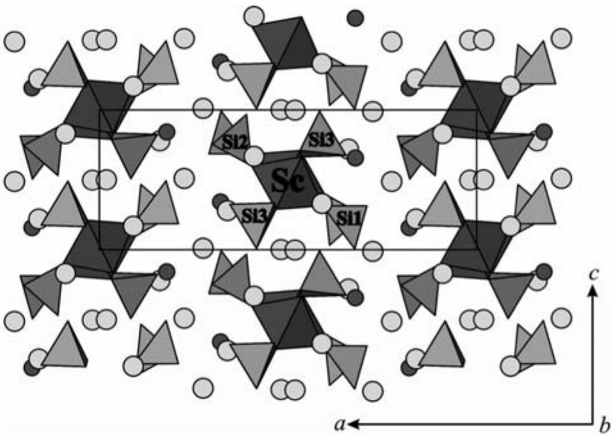

**Figure 3.** The structure of $KSr_6Sc(SiO_4)_4$ projected along [010], i.e., parallel to the isolated decorated kröhnkite-like octahedral-tetrahedral chains.

The new structure type of $KSr_6Sc(SiO_4)_4$ (Figures 2, 3) contains one octahedrally coordinated Sc site, three crystallographically non-equivalent $SiO_4$ tetrahedra, and five Sr sites, three of which are occupied by a mixture of Sr and K atoms (one with K > Sr) (Table 2). The majority of these sites are located on mirror planes in $y = ¼$. The $ScO_6$ octahedra share all of their oxygen corners with $SiO_4$ tetrahedra, forming isolated decorated octahedral-tetrahedral chains running parallel to [010], i.e., decorated kröhnkite-like chains (see Figure 2). The Sr/K atoms are located between these chains. The [8]- or [9]-coordinated Sr atoms have average Sr–O bond lengths of 2.61, 2.73 and 2.74 Å (Table 4). The average K–O bond length of the [8+2]-coordinated K atom is 2.87 Å. The average Si–O bond lengths lie within a small range from 1.62 to 1.64 Å. The isolated $ScO_6$ octahedron is only slightly distorted, with O–Sc–O bond angles ranging between 83.14° and 94.48 and between 170.9 and 177.58°. The average Sc–O bond length (2.10 Å) corresponds very well with literature values for oxidic Sc compounds (2.10 Å).[27] The bond-valence sums (BVSs) of Si atoms range between 3.86 and 4.02 v.u. (valence units). The BVSs for the Sr1 (1.84 v.u.), Sr2 (2.14 v.u.) and Sr3 (1.77 v.u.) atoms are close to the theoretical value.

In contrast, BVSs for the Sr4 (1.61 v.u.) and K5 (1.51 v.u.) atoms reflect the mixed (Sr/K) occupancies of these two sites (Table 4). We would like to point out that unrestrained occupancy refinements of the mixed Sr/K sites resulted in a nearly charge-balanced empirical formula (≈$KSr_6Sc(SiO_4)_4$), with 63.9 positive charges *vs.* 64 negative charges. For the final refinement the occupancies were slightly modified and then fixed to achieve a completely charge-balanced formula.

**Table 2.** Fractional atomic coordinates and equivalent isotropic displacement parameters (Å$^2$) for $KSr_6Sc(SiO_4)_4$. $U_{equiv}$ according to Fischer & Tillmanns.[28]

| Atom | *x* | *y* | *z* | $U_{equiv}$ | Occupancy* |
|---|---|---|---|---|---|
| Sr1 | 0.41000(2) | 0.00028(5) | 0.33110(7) | 0.01021(12) | 0.950 |
| K1 | 0.41000(2) | 0.00028(5) | 0.33110(7) | 0.01021(12) | 0.050 |
| Sr2 | 0.22493(2) | 0.02370(5) | 0.48859(7) | 0.01168(12) | |
| Sr3 | 0.48151(4) | –¼ | –0.00159(10) | 0.01361(16) | |
| Sr4 | 0.33940(5) | ¼ | 0.72011(13) | 0.0154(2) | 0.70 |
| K4 | 0.33940(5) | ¼ | 0.72011(13) | 0.0154(2) | 0.30 |
| K5 | 0.32136(6) | –¼ | 0.65769(15) | 0.0125(2) | 0.60 |
| Sr5 | 0.32136(6) | –¼ | 0.65769(15) | 0.0125(2) | 0.40 |
| Sc | 0.49987(7) | –¼ | 0.48125(19) | 0.0070(3) | |
| Si1 | 0.32788(10) | –¼ | 0.2314(3) | 0.0088(4) | |
| Si2 | 0.34565(10) | ¼ | 0.2244(3) | 0.0087(4) | |
| Si3 | 0.42300(7) | –0.00434(13) | 0.76985(19) | 0.0078(3) | |
| O1 | 0.3229(3) | –¼ | 0.0064(8) | 0.0169(12) | |
| O2 | 0.2905(2) | –0.3687(4) | 0.3133(6) | 0.0176(8) | |
| O3 | 0.4082(3) | –¼ | 0.3152(8) | 0.0130(11) | |
| O4 | 0.3902(3) | ¼ | 0.0323(8) | 0.0220(13) | |
| O5 | 0.29935(19) | 0.3700(3) | 0.2466(6) | 0.0147(8) | |
| O6 | 0.4036(3) | ¼ | 0.3985(9) | 0.0205(13) | |
| O7 | 0.41657(19) | –0.0331(3) | 0.9907(5) | 0.0137(8) | |
| O8 | 0.34586(19) | 0.0088(4) | 0.6753(6) | 0.0170(8) | |
| O9 | 0.46801(18) | 0.1152(3) | 0.7105(5) | 0.0119(8) | |
| O10 | 0.46390(19) | –0.1175(4) | 0.6657(5) | 0.0151(8) | |

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

**Table 3.** Anisotropic displacement parameters for (Å$^2$) $KSr_6Sc(SiO_4)_4$.

| Atom | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|
| Sr1 | 0.0099(2) | 0.0114(2) | 0.0093(2) | -0.00067(19) | -0.00048(17) | 0.00082(19) |
| K1 | 0.0099(2) | 0.0114(2) | 0.0093(2) | -0.00067(19) | -0.00048(17) | 0.00082(19) |
| Sr2 | 0.0114(2) | 0.0148(3) | 0.0088(2) | -0.00096(19) | 0.00127(17) | 0.00062(18) |
| Sr3 | 0.0176(4) | 0.0145(4) | 0.0088(3) | 0.0 | 0.0004(3) | 0.0 |
| Sr4 | 0.0147(4) | 0.0132(5) | 0.0182(4) | 0.0 | 0.0037(3) | 0.0 |
| K4 | 0.0147(4) | 0.0132(5) | 0.0182(4) | 0.0 | 0.0037(3) | 0.0 |
| K5 | 0.0141(5) | 0.0146(6) | 0.0088(5) | 0.0 | 0.0008(4) | 0.0 |
| Sr5 | 0.0141(5) | 0.0146(6) | 0.0088(5) | 0.0 | 0.0008(4) | 0.0 |
| Sc | 0.0086(6) | 0.0084(6) | 0.0041(6) | 0.0 | -0.0002(5) | 0.0 |
| Si1 | 0.0090(9) | 0.0074(10) | 0.0100(9) | 0.0 | -0.0005(7) | 0.0 |
| Si2 | 0.0083(9) | 0.0078(10) | 0.0100(9) | 0.0 | -0.0008(7) | 0.0 |
| Si3 | 0.0086(6) | 0.0079(7) | 0.0071(6) | -0.0005(5) | 0.0008(5) | -0.0009(5) |
| O1 | 0.029(3) | 0.009(3) | 0.012(3) | 0.0 | -0.007(2) | 0.0 |
| O2 | 0.020(2) | 0.009(2) | 0.024(2) | 0.0023(16) | 0.0016(16) | -0.0036(16) |
| O3 | 0.012(2) | 0.013(3) | 0.014(3) | 0.0 | -0.001(2) | 0.0 |
| O4 | 0.024(3) | 0.024(3) | 0.018(3) | 0.0 | 0.012(2) | 0.0 |
| O5 | 0.0132(18) | 0.0095(19) | 0.021(2) | 0.0008(16) | 0.0013(15) | 0.0017(15) |
| O6 | 0.016(3) | 0.023(3) | 0.022(3) | 0.0 | -0.011(2) | 0.0 |
| O7 | 0.0152(18) | 0.0171(19) | 0.0089(17) | 0.0017(16) | 0.0014(15) | 0.0006(15) |
| O8 | 0.0095(16) | 0.026(2) | 0.0150(18) | 0.0000(17) | -0.0031(15) | 0.0006(17) |
| O9 | 0.0136(18) | 0.010(2) | 0.0117(18) | 0.0027(15) | 0.0033(14) | -0.0030(15) |
| O10 | 0.0176(19) | 0.014(2) | 0.0140(19) | -0.0060(16) | 0.0039(15) | 0.0018(15) |

### 3.1.2. $Rb_5In(MoO_4)_4$

$Rb_5In(MoO_4)_4$ belongs to the large group of isoelectronic compounds with the general formula $A_5M^{3+}(XO_4)_4$ ($A$ = Rb, K, Tl; $M^{3+}$ = REE, Bi, Fe, In; $X$ = Mo, W). Most of them crystallise in a variety of layered structure types, related to the mineral palmierite, $K_2Pb(SO_4)_2$.[31,32] In contrast, $Rb_5Er(MoO_4)_4$ and isotypic $Rb_5In(MoO_4)_4$ represent a chain-based structure type, which is built from decorated kröhnkite-like chains. The crystal structure of $Rb_5Er(MoO_4)_4$ was determined by Klevtsova and Glinska-

**Table 4.** Selected interatomic distances (Å) and calculated bond-valence sums (v.u.) for the coordination polyhedra in $KSr_6Sc(SiO_4)_4$*.

| | **$KSr_6Sc(SiO_4)_4$** | |
|---|---|---|
| Sr1–O7 | 2.458(4) | 0.399 |
| Sr1–O5 | 2.637(4) | 0.246 |
| Sr1–O9 | 2.685(4) | 0.216 |
| Sr1–O2 | 2.724(4) | 0.194 |
| Sr1–O8 | 2.745(4) | 0.184 |
| Sr1–O10 | 2.747(4) | 0.182 |
| Sr1–O3 | 2.8050(8) | 0.156 |
| Sr1–O6 | 2.8396(13) | 0.142 |
| Sr1–O10 | 2.913(4) | 0.117 |
| Sr1–O9** | 3.193(4) | 0.055 |
| **Mean** | **2.73** | **1.84** |
| Sr2–O2 | 2.480(4) | 0.376 |
| Sr2–O5 | 2.533(4) | 0.326 |
| Sr2–O5 | 2.560(4) | 0.303 |
| Sr2–O2 | 2.625(4) | 0.254 |
| Sr2–O8 | 2.636(4) | 0.246 |
| Sr2–O8 | 2.675(4) | 0.222 |
| Sr2–O1 | 2.697(2) | 0.209 |
| Sr2–O7 | 2.710(4) | 0.202 |
| **Mean** | **2.61** | **2.14** |
| Sr3–O4 | 2.466(6) | 0.390 |
| Sr3–O3 | 2.658(5) | 0.232 |
| Sr3–O7 (2x) | 2.729(4) | 0.192 |
| Sr3–O (2x) | 2.741(4) | 0.187 |
| Sr3–O10 (2x) | 2.817(4) | 0.152 |
| Sr3–O1 | 3.036(6) | 0.087 |
| **Mean** | **2.74** | **1.77** |
| Sr4–O4 | 2.426(6) | 0.435 |
| Sr4–O6 | 2.600(6) | 0.272 |
| Sr4–O8 (2x) | 2.723(4) | 0.195 |
| Sr4–O9 (2x) | 2.888(4) | 0.125 |
| Sr4–O2 (2x) | 2.896(4) | 0.122 |
| **Mean** | **2.76** | **1.61** |
| K5–O1 | 2.485(6) | 0.383 |
| K5–O5 (2x) | 2.747(4) | 0.189 |
| K5–O2 (2x) | 2.852(4) | 0.142 |
| K5–O8 (2x) | 2.938(4) | 0.113 |
| K5–O3 | 2.952(5) | 0.108 |
| K5–O10 (2x) | 3.106(4) | 0.071 |
| **Mean** | **2.87** | **1.51** |
| Sc–O6 | 2.036(5) | 0.624 |
| Sc–O10 (2x) | 2.098(4) | 0.528 |
| Sc–O3 | 2.117(5) | 0.501 |
| Sc–O9 (2x) | 2.127(4) | 0.488 |
| **Mean** | **2.10** | **3.16** |
| Si1–O1 | 1.606(6) | 1.050 |
| Si1–O2 (2x) | 1.618(4) | 1.016 |
| Si1–O3 | 1.648(5) | 0.937 |
| **Mean** | **1.62** | **4.02** |
| Si2–O4 | 1.613(6) | 1.030 |
| Si2–O5 (2x) | 1.617(4) | 1.019 |
| Si2–O6 | 1.664(6) | 0.898 |
| **Mean** | **1.64** | **3.86** |
| Si3–O7 | 1.611(4) | 1.036 |
| Si3–O8 | 1.629(4) | 0.987 |
| Si3–O9 | 1.647(4) | 0.940 |
| Si3–O10 | 1.664(4) | 0.898 |
| **Mean** | **1.63** | **3.97** |

ya[21]; it is monoclinic, with space group *P*2/*c* and the unit-cell parameters *a* = 11.44, *b* = 7.99, *c* =11.19 Å, β = 113.3°. We point out that the crystal structure data of $Rb_5Er(MoO_4)_4$ are missing in the latest edition of the Inorganic Crystal Structure Database (ICSD). The ICDD-PDF contains a measured X-ray powder diffraction pattern of $Rb_5In(MoO_4)_4$ (PDF-entry no. 26-1367).[33] The pattern is indexed on the basis of a monoclinic (space group not given) unit cell with *a* = 18.78, *b* = 7.984, *c* = 12.30 Å, β = 91.58°, *V* = 1843.56 Å$^3$ which corresponds numerically to a *B*-centered cell with double volume as compared to the unit-cell parameters reported here (*a* = 11.391, *b* = 7.983, *c* = 11.100 Å, β = 113.74°, *V* = 924.0 Å$^3$, space group *P*2/*c*; transformation matrix *P*- to *B*-centred cell [10–1 010 101]). A comparison of the powder diffraction data reported in PDF-entry no. 26–1367 [33] with those calculated for the compound described in this work shows that all

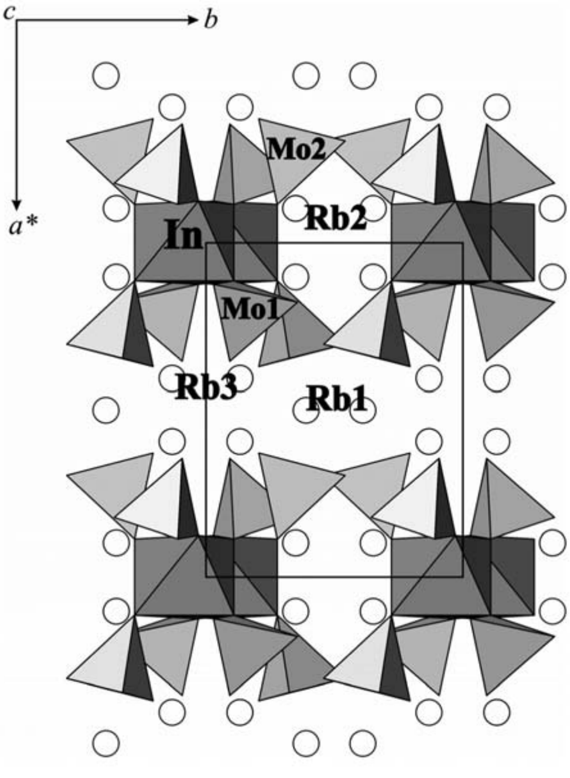

**Figure 4.** View of $Rb_5In(MoO_4)_4$ along [001], parallel to the decorated kröhnkite-like octahedral-tetrahedral chains.

Bond-valence sums (v.u.) for the oxygen atoms O1 to O10 are as follows: O1 = 1.94, O2 = 2.10, O3 = 2.09, O4 = 1.86, O5 = 1.89, O6 = 2.01, O7 = 1.83, O8 = 1.90, O9 = 2.01, O10 = 1.95.

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[*] Bond-valence calculations are based on parameters of Brese & O'Keeffe[29] and for Sc atoms, on Brown[30] (updated values from webmirrors/i_d_brown). Bond-valence sums for the mixed Sr/K sites Sr4 and K5 were calculated taking into account the respective occupancies (see Table 2).

[**] Not used for calculation of mean distances and BVSs.

strong and medium strong reflections of $Rb_5In(MoO_4)_4$ appear in the pattern. However, there are a number of additional strong reflections reported that clearly do not belong to the powder diffraction pattern of $Rb_5In(MoO_4)_4$.

The asymmetric unit of $Rb_5In(MoO_4)_4$ contains one In site, three Rb, two Mo and eight O sites. Two atoms, Rb1 and In, lie on special positions, whereas all remaining atoms are in general positions. The main building unit of its crystal structure (see Figures 4, 5) is a decorated kröhnkite-like [100] chain built from a distorted $InO_6$ octahedron corner-linked by $MoO_4$ tetrahedra and decorated by additional $MoO_4$ tetrahedra. These chains are separated in different directions by three non-equivalent Rb atoms. A somewhat layered character of the atomic arrangement parallel to (100) is evident from the view in Figure 5.

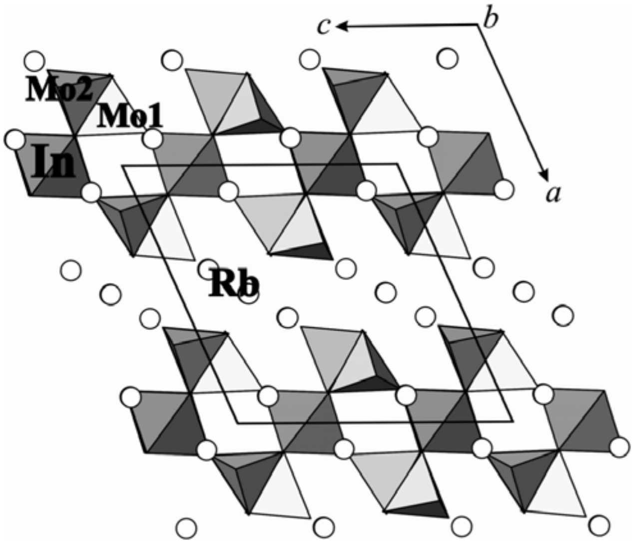

**Figure 5.** View of $Rb_5In(MoO_4)_4$ along [010], perpendicular to the decorated kröhnkite-like octahedral-tetrahedral chains.

The $InO_6$ octahedra are only slightly distorted with an average In–O bond length of 2.136 Å and O–In–O bond angles between 81.01 and 99.33 and between 156.08 and 178.74°. The Rb atoms are coordinated by eight or ten O atoms with average Rb–O bond lengths of 3.026 Å (for [8]–coordination), and 3.093 and 3.120 Å (for [10]–coordination).

According to the classification of molybdates with composition $A_5M^{3+}(MoO_4)_4$ ($A$ = K, Rb; $M^{3+}$ = REE, Y, In, Sc, Fe, Al, Bi) by Lazoryak and Efremov[31], $Rb_5Er(MoO_4)_4$ and isotypic $Rb_5In(MoO_4)_4$ adopt structure type VII. This type is structurally similar to type V adopted by $K_5M^{3+}(MoO_4)_4$ ($M^{3+}$ = Tm–Lu, In, Sc), and represented by $K_5In(MoO_4)_4$ discussed below.

## 3. 2. Comparison With Other Compounds Based on Decorated Kröhnkite-like Octahedral-Tetrahedral Chains

As already mentioned in the introduction, the kröhnkite-type chain *sensu strictu* is encountered in a fairly large number of compounds. In contrast, there exist only few compounds containing decorated kröhnkite-like chains. Figure 6 compares the chain units of nine known and two new compounds with decorated kröhnkite-like chains. All these compounds contain more or less distorted $MO_6$ octahedra linked and decorated by the $XO_4$ tetrahedra. However, there are distinct differences concerning both linkage and orientation of $XO_4$ tetrahedra with respect to the octahedra.

In $KSr_6Sc(SiO_4)_4$ (Figure 6a) and the protonated phosphate compound $Ba_2Ca(HPO_4)_2(H_2PO_4)_2$,[33] the two decorating tetrahedra are attached to the *trans* apices of the $MO_6$ octahedra. Specifically, in $KSr_6Sc(SiO_4)_4$ two Si3–centred tetrahedra corner-link neighbouring octahedra, whereas the two remaing Si1– and Si2–centred tetrahedra only decorate the chain. Although the overall topo-

**Table 5.** Fractional atomic coordinates and equivalent isotropic displacement parameters (Å$^2$) for $Rb_5In(MoO_4)_4$. $U_{equiv}$ according to Fischer & Tillmanns.[28]

| Atom | *x* | *y* | *z* | $U_{equiv}$ |
|---|---|---|---|---|
| Rb1 | ½ | 0.38964(4) | ¼ | 0.02177(7) |
| Rb2 | 0.10260(2) | 0.34909(3) | 0.65569(2) | 0.02542(6) |
| Rb3 | 0.40615(2) | 0.86800(3) | 0.35455(2) | 0.01999(5) |
| In | 0.0 | 0.08625(3) | ¼ | 0.01074(5) |
| Mo1 | 0.195171(15) | 0.85392(2) | 0.555916(16) | 0.01067(4) |
| Mo2 | 0.283066(18) | 0.33993(2) | 0.442361(17) | 0.01253(5) |
| O1 | 0.11442(15) | 0.8913(2) | 0.38167(14) | 0.0185(3) |
| O2 | 0.35569(15) | 0.9074(2) | 0.60628(16) | 0.0211(3) |
| O3 | 0.12492(15) | 0.9706(2) | 0.64853(15) | 0.0182(3) |
| O4 | 0.17831(19) | 0.6432(2) | 0.58073(19) | 0.0279(4) |
| O5 | 0.11423(15) | 0.2778(2) | 0.37620(16) | 0.0229(3) |
| O6 | 0.34680(16) | 0.3243(2) | 0.61421(15) | 0.0211(3) |
| O7 | 0.30474(18) | 0.5421(2) | 0.39453(18) | 0.0254(4) |
| O8 | 0.37157(17) | 0.2057(2) | 0.38808(17) | 0.0239(3) |

**Table 6.** Anisotropic displacement parameters (Å$^2$) for $Rb_5In(MoO_4)_4$.

| **Atom** | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|
| Rb1 | 0.02211(15) | 0.01526(13) | 0.02713(15) | 0.0 | 0.00905(12) | 0.0 |
| Rb2 | 0.02270(12) | 0.02601(13) | 0.02473(12) | 0.00352(9) | 0.00662(9) | –0.00855(9) |
| Rb3 | 0.02290(11) | 0.01753(10) | 0.01843(10) | –0.00186(8) | 0.00716(8) | 0.00038(8) |
| In | 0.00952(8) | 0.01248(9) | 0.00981(8) | 0.0 | 0.00345(6) | 0.0 |
| Mo1 | 0.00984(8) | 0.01184(8) | 0.01064(7) | 0.00178(5) | 0.00443(6) | 0.00112(5) |
| Mo2 | 0.01297(8) | 0.01153(8) | 0.01255(8) | –0.00024(5) | 0.00456(6) | –0.00114(5) |
| O1 | 0.0187(7) | 0.0220(8) | 0.0124(6) | 0.0036(6) | 0.0040(6) | 0.0069(6) |
| O2 | 0.0122(7) | 0.0289(9) | 0.0221(7) | 0.0005(7) | 0.0069(6) | 0.0001(6) |
| O3 | 0.0189(7) | 0.0214(8) | 0.0179(7) | 0.0011(6) | 0.0112(6) | 0.0036(6) |
| O4 | 0.0382(11) | 0.0141(8) | 0.0363(10) | 0.0053(7) | 0.0203(9) | 0.0008(7) |
| O5 | 0.0168(7) | 0.0244(8) | 0.0254(8) | –0.0106(7) | 0.0063(6) | –0.0065(6) |
| O6 | 0.0238(8) | 0.0221(8) | 0.0149(7) | 0.0015(6) | 0.0052(6) | 0.0007(6) |
| O7 | 0.0353(10) | 0.0151(7) | 0.0263(8) | 0.0040(6) | 0.0131(7) | –0.0036(7) |
| O8 | 0.0268(8) | 0.0216(8) | 0.0278(8) | –0.0024(7) | 0.0157(7) | 0.0022(7) |

**Table 7.** Selected interatomic distances (Å) and calculated bond-valence sums (v.u.) for the coordination polyhedra in $Rb_5In(MoO_4)_4$[*].

| **$Rb_5In(MoO_4)_4$** | | | | | |
|---|---|---|---|---|---|
| Rb1–O6 (2x) | 2.9007(19) | 0.177 | Rb3–O6 | 3.1003(18) | 0.103 |
| Rb1–O8 (2x) | 2.9069(18) | 0.174 | Rb3–O2 | 3.1328(17) | 0.094 |
| Rb1–O2 (2x) | 2.9594(19) | 0.151 | Rb3–O2 | 3.1407(18) | 0.092 |
| Rb1–O4 (2x)[**] | 3.389(2) | 0.047 | Rb3–O3[**] | 3.355(2) | 0.052 |
| Rb1–O7 (2x)[**] | 3.446(2) | 0.040 | Rb3–O1[**] | 3.4602(17) | 0.039 |
| **Mean** | **2.92** | **1.00** | **Mean** | **3.01** | **1.10** |
| Rb2–O4 | 2.7436(19) | 0.270 | In–O5 (2x) | 2.1274(17) | 0.544 |
| Rb2–O7 | 2.858(2) | 0.199 | In–O1 (2x) | 2.1730(16) | 0.481 |
| Rb2–O6 | 3.0033(18) | 0.134 | In–O3 (2x) | 2.1886(15) | 0.461 |
| Rb2–O1 | 3.0236(18) | 0.127 | **Mean** | **2.16** | **2.97** |
| Rb2–O3 | 3.0362(19) | 0.123 | Mo1–O4 | 1.7275(18) | 1.624 |
| Rb2–O1 | 3.1181(17) | 0.098 | Mo1–O2 | 1.7364(16) | 1.586 |
| Rb2–O5 | 3.2089(18) | 0.077 | Mo1–O3 | 1.7963(15) | 1.349 |
| Rb2–O4 | 3.220(2) | 0.075 | Mo1–O1 | 1.8011(16) | 1.331 |
| **Mean** | **3.03** | **1.10** | **Mean** | **1.77** | **5.90** |
| Rb3–O8 | 2.7715(19) | 0.251 | Mo2–O8 | 1.7366(17) | 1.587 |
| Rb3–O6 | 2.9119(17) | 0.172 | Mo2–O7 | 1.7474(17) | 1.541 |
| Rb3–O7 | 2.9517(18) | 0.154 | Mo2–O6 | 1.7511(17) | 1.524 |
| Rb3–O8 | 3.016(2) | 0.130 | Mo2–O5 | 1.8295(17) | 1.235 |
| Rb3–O2 | 3.0871(17) | 0.107 | **Mean** | **1.77** | **5.89** |

Bond-valence sums (v.u.) for the oxygen atoms O1 to O8 are as follows: O1 = 2.07, O2 = 2.03, O3 = 1.98, O4 = 2.02, O5 = 1.86, O6 = 2.11, O7 = 1.94, O8 = 2.14

[*] Bond–valence calculations are based on parameters of Brese & O'Keeffe.[29] [**] Not used for calculation of mean distances and BVSs.

logy of the decorated chains in both compounds is identical, the decorating P1–centred tetrahedra in $Ba_2Ca(HPO_4)_2(H_2PO_4)_2$ are considerably tilted with respect to the chain direction, and the chain is somewhat corrugated (see Figure 6b).

In $Rb_5In(MoO_4)_4$ (Figure 6c) the chain is formed by a different octahedral-tetrahedral linkage scheme: Mo1–centred tetrahedra link the $InO_6$ octahedra alternatively in a horizontal and vertical plane, whereas the two Mo2–centred decorating tetrahedra are attached to the *cis* apices of the $InO_6$ octahedra. This scheme results in a slightly wavy character of the chain.

The chain in $K_5In(MoO_4)_4$[35] (Figure 6d) is related to that in $Rb_5In(MoO_4)_4$, but considerably more distorted. The linkage of the $InO_6$ octahedra by Mo2– and Mo4–centred tetrahedra in a twisted sequence, and the *cis* decorating Mo1– and Mo3–centred tetrahedra result in a distinct zigzag-like character of the chain.

In the protonated arsenate compounds $CsM^{3+}(H_{1.5}AsO_4)_2(H_2AsO_4)$ ($M^{3+}$ = Ga, Cr), $CsAl(H_2AsO_4)_2(HAsO_4)$ and $K(H_2O)M^{3+}(H_{1.5}AsO_4)_2(H_2AsO_4)$ ($M^{3+}$ = Fe, Ga, In) described by Schwendtner and Kolitsch,[36–38] all $AsO_4$ tetrahedra are involved in the linkage system forming the chain, i.e., each $AsO_4$ tetrahedron corner-links

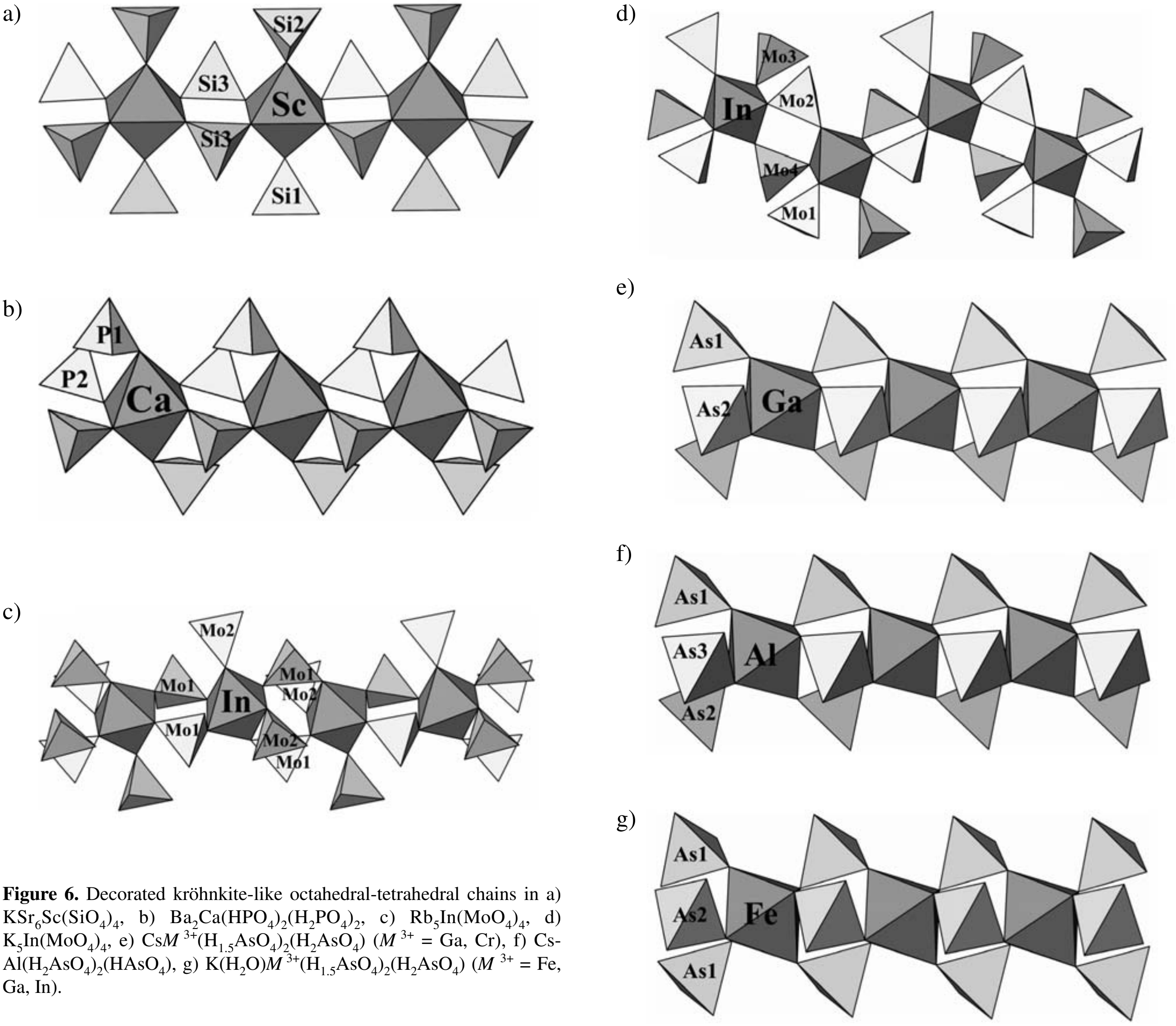

**Figure 6.** Decorated kröhnkite-like octahedral-tetrahedral chains in a) $KSr_6Sc(SiO_4)_4$, b) $Ba_2Ca(HPO_4)_2(H_2PO_4)_2$, c) $Rb_5In(MoO_4)_4$, d) $K_5In(MoO_4)_4$, e) $CsM^{3+}(H_{1.5}AsO_4)_2(H_2AsO_4)$ ($M^{3+}$ = Ga, Cr), f) $CsAl(H_2AsO_4)_2(HAsO_4)$, g) $K(H_2O)M^{3+}(H_{1.5}AsO_4)_2(H_2AsO_4)$ ($M^{3+}$ = Fe, Ga, In).

two $MO_6$ octahedra (see Figure 6 e-g). The overall topology of the chains in these arsenates is identical. It is probable that this chain type will also be found in protonated phosphates.

## 4. Conclusions

The present work demonstrates that decorated kröhnkite-like chains are not only encountered among arsenates, phosphates and molybdates, but also in silicates, with $KSr_6Sc(SiO_4)_4$ being the first such example. A comparison of all presently known compounds containing decorated kröhnkite-like chains reveals, firstly, different systems of corner-linkage forming the chains, and, secondly, different roles of additional tetrahedra (some only play a decorating role, while others provide an additional corner-linkage along the chain direction).

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# Povzetek

Z metodo rentgenske difrakcije sta bili pri sobni temperaturi določeni kristalni strukturi dveh novih spojin $KSr_6Sc(SiO_4)_4$ in $Rb_5In(MoO_4)_4$. Obe spojini sta bili sintetizirani iz fluksa pri študiju novih mikro in nanoporoznih alkalijskih-$M^{3+}$ silikaktov. $KSr_6Sc(SiO_4)_4$ predstavlja nov strukturni tip in je to prvi silikat, ki vsebuje dekorativne kröhnkitu podobne oktaedrsko-tetraedrske verige. Spojina je ortorombska v Pnma, with a = 19.137(4), b = 11.197(2), c = 7.125(1) Å, V = 1526.7(5) Å$^3$, Z = 8. $Rb_5In(MoO_4)_4$ kristalizira v P2/c with a = 11.391(2), b = 7.983(2), c = 11.100(2) Å, β = 113.74(3)°, V = 924.0(3) Å$^3$, Z = 2. Spojina je izotipična z $Rb_5Er(MoO_4)_4$. Narejena je bila tudi primerjava z ostalimi spojinami, ki vsebujejo kröhnkitu podobne verige npr. $Ba_2Ca(HPO_4)_2(H_2PO_4)_2$, $CsM^{3+}(H_{1.5}AsO_4)_2(H_2AsO_4)$ ($M^{3+}$ = Ga, Cr), $CsAl(H_2AsO_4)_2(HAsO_4)$, $K(H_2O)M^{3+}(H_{1.5}AsO_4)_2(H_2AsO_4)$ ($M^{3+}$ = Fe, Ga, In) in $K_5In(MoO_4)_4$.