# Structural news from the quaternary system $Na_2O$-$K_2O$-CaO-$SiO_2$

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The crystalline compounds and sub-solidus equilibria in the ternary subsystems $Na_2O$-CaO-$SiO_2$ and $K_2O$-CaO-$SiO_2$ have been studied frequently in the past. On the contrary, the quaternary system containing both alkali oxides is rather uncharted territory and no thermodynamic or detailed phase-analytical data are available. So far, only a few potassium-sodium-calcium silicates such as $K_{1.08}Na_{0.92}Ca_6Si_4O_{15}$ (Kahlenberg et al. 2018a) or $Na_{1.5}K_{0.5}Ca_6Si_4O_{15}$ (Kahlenberg et al. 2018b) or $NaKCa_4[Si_9O_{23}]$ (Kasatkin et al. 2019) have been structurally characterized. While the first two members are mixed-anion silicates and isostructural with ternary phases, the latter compound corresponding to the mineral patynite represents a previously unknown structure type and belongs to the group of tubular inosilicates.

Our own recent synthesis experiments in the quaternary system $K_2O$-$Na_2O$-CaO-$SiO_2$ proved that there exists a complete solid-solution series between $Na_4CaSi_3O_9$ and its K-counterpart: $Na_{4-x}K_xSi_3O_9$. Lattice parameters of the cubic materials (space group $Pa\bar{3}$) obtained in polycrystalline form from solid-state reactions vary between 15.0998 (x = 0) and 15.9472 (x=4) Å. The silicate anions form strongly corrugated 12-membered tetrahedral rings.

Furthermore, we were able to prepare a previously unknown compound with composition $K_{0.72}Na_{1.71}Ca_{5.79}Si_6O_{19}$. Single-crystals of sufficient size and quality could be retrieved from a starting mixture with a $K_2O$:$Na_2O$:CaO:$SiO_2$ ratio of 1.5:0.5:2:3. The crystal structure was determined by direct methods at 25 °C from single crystal X-ray diffraction data (tetragonal symmetry, space group $P4_122$, $a$ = 7.3659(2) Å, $c$ = 32.2318(18) Å, V = 1748.78(12) Å$^3$, Z = 4, $R_1$ = 0.026, $wR_2$ = 0.063, for 1690 observed reflections with I > 2σ(I)). The silicate anion consists of highly puckered unbranched six-membered oligogroups of composition $[Si_6O_{19}]$ having point-group symmetry 2 ($C_2$). Even though several thousands of natural and synthetic oxidosilicates have been structurally characterized, the present compound is the first representative for this type of catena-hexasilicate anion - at least to the best of our knowledge.

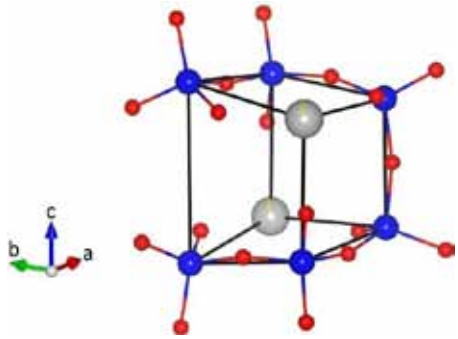


Figure 1. Conformation of a single $[Si_6O_{19}]$ group in $K_{0.72}Na_{1.71}Ca_{5.79}Si_6O_{19}$. The six Si atoms (blue) can be thought of as being located at the corners of an imaginary distorted cube with edge lengths between 3.22 and 4.60 Å. The remaining two corners are occupied by Na/Ca cations (grey/yellow). Oxygen atoms are shown in red.

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