First investigations on the quaternary system $\text{Na}_2\text{O}-\text{K}_2\text{O}-\text{CaO}-\text{SiO}_2$: synthesis and crystal structure of the mixed alkali calcium silicate $\text{K}_{1.08}\text{Na}_{0.92}\text{Ca}_6\text{Si}_4\text{O}_{15}$

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Abstract In the course of an exploratory study on the quaternary system $\text{Na}_2\text{O}-\text{K}_2\text{O}-\text{CaO}-\text{SiO}_2$ single crystals of the first anhydrous sodium potassium calcium silicate have been obtained from slow cooling of a melt in the range between 1250 and 1050 °C. Electron probe micro analysis suggested the following idealized molar ratios of the oxides for the novel compound: $\text{K}_2\text{O}:\text{Na}_2\text{O}:\text{CaO}:\text{SiO}_2 = 1:1:12:8$ (or $\text{KNaCa}_6\text{Si}_4\text{O}_{15}$). Single-crystal diffraction measurements on a crystal with chemical composition $\text{K}_{1.08}\text{Na}_{0.92}\text{Ca}_6\text{Si}_4\text{O}_{15}$ resulted in the following basic crystallographic data: monoclinic symmetry, space group $P 2_1/c$, $a = 8.9618(9)$ Å, $b = 7.3594(6)$ Å, $c = 11.2453(11)$ Å, $\beta = 107.54(1)^\circ$, $V = 707.2(1)$ Å³, $Z = 2$. Structure solution was performed using direct methods. The final least-squares refinement converged at a residual of $R(\text{IF}) = 0.0346$ for 1288 independent reflections and 125 parameters. From a structural point of view, $\text{K}_{1.08}\text{Na}_{0.92}\text{Ca}_6\text{Si}_4\text{O}_{15}$ belongs to the group of mixed-anion silicates containing $[\text{Si}_2\text{O}_7]^-$ and $[\text{SiO}_4]^-$ units in the ratio 1:2. The mono- and divalent cations occupy a total of four crystallographically independent positions located in voids between the tetrahedra. Three of these sites are exclusively occupied by calcium. The fourth site is occupied by 54(1)% K and 46(1)% Na, respectively. Alternatively, the structure can be described as a heteropolyhedral framework based on corner-sharing silicate tetrahedra and $[\text{CaO}_6]$ -octahedra. The network can build up from kröhnkite-like $[\text{Ca}(\text{SiO}_4)_2\text{O}_2]$ -chains running along $[001]$. A detailed

comparison with other $\text{A}_2\text{B}_6\text{Si}_4\text{O}_{15}$ -compounds including topological and group-theoretical aspects is presented.

Keywords Quaternary system · $\text{Na}_2\text{O}-\text{K}_2\text{O}-\text{CaO}-\text{SiO}_2$ · $\text{KNaCa}_6\text{Si}_4\text{O}_{15}$ · $\text{K}_{1.08}\text{Na}_{0.92}\text{Ca}_6\text{Si}_4\text{O}_{15}$ · Crystal growth · Heteropolyhedral framework

Introduction

The ternary systems $\text{Na}_2\text{O}-\text{CaO}-\text{SiO}_2$ and $\text{K}_2\text{O}-\text{CaO}-\text{SiO}_2$ have been studied for more than 90 years. Especially the sodium containing system has been in the focus of many research activities because of its fundamental importance for the production of commercial soda-lime-glasses (Varshneya 1994; Shelby 2009), which are the classical mass-produced types for windows and containers. However, the crystalline counterparts have also found quite a number of applications in Materials science. $\text{Na}_2\text{CaSiO}_4$ or $\text{Na}_2\text{Ca}_2\text{Si}_3\text{O}_9$ (combeite), for example, have been reported as major phases in bioactive glass ceramics or as host materials for inorganic phosphors, whereas overlapping fans of needles of $\text{Na}_2\text{Ca}_3\text{Si}_6\text{O}_{16}$ (devitrite) crystals have been successfully developed for manufacturing of low-cost optical diffusers (Kaygili 2014; Fujikura et al. 2012; Liu et al. 2014; Butt et al. 2014). The corresponding potassium system, on the other hand, has seen a revival of interest only recently. This is primarily related to the constantly increasing usage of renewable fuels such as biomass for the production of heat and/or electricity. Actually, the variation in composition of the silicate fraction of the bottom ashes and slags occurring during biomass combustion can be conveniently described in the triangle diagram $\text{K}_2\text{O}(+\text{Na}_2\text{O})-\text{CaO}(+\text{MgO})-\text{SiO}_2$. Consequently, the corresponding simplified ternary phase diagram has been frequently used for the interpretation of

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(i) melt formation/composition and (ii) the phase content at sub-solidus conditions (Lindberg et al. 2013 and references cited therein). Both aspects have implications for process control as well since slagging, fouling or sintering can cause severe problems in practical operation (deposition on or corrosion of heat transfer surfaces as well as bed agglomeration in fluidized beds) (Lindberg et al. 2013).

To the best of our knowledge, for the more complex quaternary system $\text{Na}_2\text{O}-\text{K}_2\text{O}-\text{CaO}-\text{SiO}_2$ no thermodynamic or phase-analytical data are available. This is somehow surprising because - at least among the amorphous materials of this system - it is known that the simultaneous presence of two different monovalent cations Na^+ and K^+ in the melt and the resulting glasses can induce dramatic changes in certain physicochemical properties (Dilmore et al. 1978; Grund and Jonson 2009). Actually, the term *mixed alkali effect* was coined a long time ago in silicate glass research to describe that chemical durability, electric conductivity or viscosity can vary in an extremely non-linear way if one alkali oxide is gradually substituted by another one (Shelby 2009). Furthermore, soda-potash-lime silicate glasses play also a role in archeology: the earliest known ancient Chinese glasses belong to this group of materials (Gan et al. 2006).

For the crystalline phases the situation is less understood. So far, not a single sodium-potassium-calcium silicate has been reported. However, simple structural extrapolations from the limiting calcium containing ternary systems have to be treated with care. First of all, the number of real ternary phases in the sub-systems $\text{Na}_2\text{O}-\text{CaO}-\text{SiO}_2$ and $\text{K}_2\text{O}-\text{CaO}-\text{SiO}_2$ is large (Kahlenberg and Maier 2016; Schmidmair et al. 2015) and for some phases reported in the older literature a final proof of existence is still missing. Furthermore, many of the well characterized compounds in the system $\text{Na}_2\text{O}-\text{CaO}-\text{SiO}_2$ have no direct chemical counterparts in the potassium system. Even for those cases where identical stoichiometries have been observed potential structural relationships between the two endmembers cannot be predicted. $\text{K}_2\text{Ca}_2\text{Si}_2\text{O}_7$ and $\text{Na}_2\text{Ca}_2\text{Si}_2\text{O}_7$, for example, represent different structure types based on $[\text{Si}_2\text{O}_7]$ -groups (Arroyabe and Kahlenberg 2011) and 1:1 mixtures of $[\text{Si}_3\text{O}_{10}]$ - and $[\text{SiO}_4]$ -moieties (Kahlenberg and Hösch 2002), respectively. $\text{K}_2\text{Ca}_6\text{Si}_4\text{O}_{15}$ (Arroyabe et al. 2009a) and $\text{Na}_2\text{Ca}_6\text{Si}_4\text{O}_{15}$ (Kahlenberg and Maier 2016) have related heteropolyhedral frameworks. Nevertheless, the topology of the networks is different. On the other hand, $\text{Na}_4\text{CaSi}_3\text{O}_9$ (Fischer and Tillmanns 1984) and $\text{K}_4\text{CaSi}_3\text{O}_9$ (Arroyabe et al. 2009b) are isotypic. However, the formation of a potential solid-solution series has not been studied.

In summary one can say that the phase equilibria and the structural landscape of the system $\text{Na}_2\text{O}-\text{K}_2\text{O}-\text{CaO}-\text{SiO}_2$ is rather uncharted territory. The main aim of the present work was to make a first step to fill this gap in solid-state knowledge. This paper reports the synthesis and the results of the

structural characterization of the first quaternary phase of the $\text{Na}_2\text{O}-\text{K}_2\text{O}-\text{CaO}-\text{SiO}_2$ system.

Experimental details

Synthesis experiments for a sample with nominal composition $(\text{Na}_{0.25}\text{K}_{0.75})_2\text{Ca}_2\text{Si}_2\text{O}_7$ were based on the following fine chemicals: Na_2CO_3 (Merck, 99.9%), CaCO_3 (Merck, >99.9%), K_2CO_3 (Alfa Aesar, 99.997%) and SiO_2 (Alfa Aesar, 99.995%). Before weighing on an analytical balance (Mettler Toledo LabStyle 204), the educts were dried at 300 °C for 12 h. A total of 3 g of the stoichiometric mixture was homogenized for 15 min in a planetary ball mill (Fritsch Pulverisette 7) under ethanol. Subsequently, the sample was dried again at 300 °C for complete removal of the alcohol and, finally, stored in a desiccator.

In order to obtain some basic information of the high temperature behavior of the sample, 35.44 mg were studied in an open platinum crucible by thermogravimetric (TGA) and differential thermal (DTA) analysis. The experiment was performed in a Setaram SetsysEvolution 2400 apparatus with a resolution of the electromagnetic compensated torsion balance of 0.03 µg and controlled carrier as well as auxiliary gas flows (mixing ranges: 50/50 to 1/99). The TGA - DTA is coupled with a mass spectrometer (OmniStar QMS200, Pfeifer Vacuum Quadrupol). The sample holder is equipped with Pt/Pt₉₀-Rh₁₀ thermocouples. The temperature program contained a heating/cooling ramp of 5 °C per minute from room temperature to $T_{\text{max}} = 1300$ °C and back to ambient conditions. The experiment was performed in air. The results can be summarized as follows: upon heating, the low-high quartz transformation (at 573 °C) as well as the stepwise CO_2 -release from the decomposition of the different carbonates in combination with starting solid-state reactions can be clearly identified (two effects with peak maxima at 748 and 1001 °C, respectively). A large endothermal signal (onset temperature: 1225 °C) indicated the formation of melt. At the maximum temperature of the experiment melting was still in progress. During cooling only one sharp intense exothermic effect could be detected (onset: 1125 °C, peak maximum: 1123 °C).

Single-crystal growth experiments were initiated in a resistance-heated chamber furnace using the following set of parameters: 1 g of the educt mixture confined in a lid-covered 50 ml platinum crucible was fired from 25 °C with a heating ramp of 50 °C/h to 1250 °C and annealed for 2 h. Subsequently, the sample was cooled with 5 °C/h to 1050 °C and immediately quenched in air by removing the crucible from the furnace. Weight loss was determined from weight differences before and after heating. The comparison of the theoretical (assuming a complete disintegration of the carbonates) and the experimental values revealed

a pronounced difference: 29.31 wt% vs. 37.06 wt%. This discrepancy of about 7.7 wt% has to be attributed to additional $\text{K}_2\text{O}/\text{Na}_2\text{O}$ -losses which are known to be the most volatile oxide components of this system. Notably, the corresponding difference in the DTA was much less distinct (2.1 wt%) although the maximum temperature was about 50 °C higher. This observation can be explained by the considerable shorter total run time of the heating/cooling cycle during thermal analysis.

A first optical examination of the shape of the quenched sample in the crucible indicated the presence of a melt phase in the course of the high-temperature treatment. After mechanical removal of the solidified melt cake from the container, it was slightly crushed in an agate mortar and further checked under a polarizing binocular. The visual inspection pointed to the presence of at least two different phases: (i) birefringent crystals up to 100 μm in diameter and (ii) an isotropic glassy matrix.

A part of the material from the growth experiment was further analyzed using X-ray powder diffraction (see Fig. 1). Data were collected on a Bruker D8-Discover diffractometer using a Cu-tube operated at 40 kV and 40 mA, a primary beam Ge-monochromator and a LYNXEYETM silicon strip detector. Data acquisition was performed in Bragg–Brentano θ - 2θ geometry at ambient temperature in the range between 3 and 135 ° 2θ with a counting time of 2 s per step and a step size of 0.01 °. A fixed 0.3° divergence slit as well as primary and secondary Soller slits were used. Analysis of the crystalline synthesis products was based on the LeBail method implemented in the program TOPAS Version 4.2 (Bruker-AXS 2009). Peak profiles were calculated using the fundamental parameter approach. For simulation of the background Chebyshev polynomials were selected. The contribution

of the amorphous phase was modeled as a single broad peak centered at 30.25 ° 2θ the position of which has been refined.

Several larger fragments of the sample were embedded in epoxy resin and polished with diamond paste (6, 3, 1 and 0.25 μm grain size) for chemical analysis and back-scattered electron (BSE) imaging using a JEOL JXA 8100 Superprobe electron probe micro-analyser (EPMA) operated in wavelength-dispersive mode with a focal-spot diameter of 2 μm . Measurements were performed with an acceleration voltage of 15 kV, a beam current of 10 nA and counting times of 20 s (peaks) and 10 s (background on each side of the peaks), respectively. For calibration, reference materials of jadeite ($\text{Na}-\text{K}_\alpha$), diopside ($\text{Ca}-\text{K}_\alpha$), orthoclase ($\text{K}-\text{K}_\alpha$) and quartz ($\text{Si}-\text{K}_\alpha$) were used. The intensities obtained were corrected for electron scattering, absorption and fluorescence radiation (ZAF correction). The BSE image of a characteristic region of the sample (Fig. 2) corroborates the observations under the optical microscope. Two phases can be clearly discriminated: light-grey partially isomorphous crystals alternate with darker grey regions representing the glassy constituents of the sample. A total number of 20 spots for each phase in various areas were analyzed. For the crystalline phase, they all yielded very similar chemical compositions giving no indication for chemical zoning with total sums based on oxides between 99.5 and 100.6 wt%. After normalization on 15 O atoms almost integral atomic ratios were obtained: $\text{K} : \text{Na} : \text{Ca} : \text{Si} : \text{O} = 1.04(1) : 0.97(2) : 6.06(3) : 3.97(1) : 15$ pointing to an idealized composition of $\text{KNaCa}_6\text{Si}_4\text{O}_{15}$. The analysis of the glassy phase was more problematic as it was not very stable under the electron beam: small “burned holes” appeared on the sample surface. Therefore, total

Fig. 1 LeBail plot of the X-ray powder diffraction pattern of the sample retrieved from the single-crystal growth experiment. Observed step intensities are represented by grey dots. Calculated step intensities (in red) for $\text{K}_{1.08}\text{Na}_{0.92}\text{Ca}_6\text{Si}_4\text{O}_{15}$ have been modelled using parameters given in Table 1 as starting values. Tick marks for the Bragg peaks of are given. The lower blue line represents the difference curve between observed and calculated step intensities. The presence of a glassy phase - indicated by an “amorphous hump” centered at about 30 ° 2θ - is clearly visible. (R_{wp} : 5.70%, R_{exp} : 4.77%, GOF: 1.20)

Fig. 2 BSE image of the sample obtained from the crystal-growth experiment. Light-grey, sometimes idiomorphically developed crystals of $\text{K}_{1.08}\text{Na}_{0.92}\text{Ca}_6\text{Si}_4\text{O}_{15}$ (I) are embedded in a glassy matrix (II). Black circular regions correspond to holes produced during sample preparation

sums for the oxides varied between 96 and 98 wt%. Corresponding average values (in weight percentages)

are as follows: Na_2O : 10.47(6), K_2O : 22.38(25), CaO : 16.15(28) and SiO_2 : 48.10(30).

For structural investigations, a single-crystalline, transparent and colorless fragment ($0.04 \times 0.06 \times 0.08$ mm in size) of good optical quality was selected. The crystal was mounted on the tip of a glass fiber using finger-nail hardener. Data were collected on an Oxford Diffraction Gemini R Ultra single-crystal diffractometer. Intensities corresponding to one hemisphere of reciprocal space were acquired at ambient temperature (25 °C) in 342 frames with ω -scans using 0.75° scan width per frame (exposure time per frame: 75 s). Subsequent integration and data reduction were performed with the CrysAlis^{PRO} software package (Rigaku 2015). Furthermore, a semi-empirical absorption correction (based on spherical harmonics) was applied. The diffraction pattern showed monoclinic Laue symmetry. Systematic absences pointed to space group $P-2_1/c$. The crystal structure was solved by direct methods (program SIR2004, Burla et al. 2005). Subsequent refinement calculations were performed with the program SHELX-97 (Sheldrick 1997) embedded in the software suite WinGX (Farrugia 1999). Neutral-atom scattering coefficients and anomalous-dispersion corrections were taken from the *International Tables for*

Table 1 Crystal data and structure refinement for $\text{K}_{1.08}\text{Na}_{0.92}\text{Ca}_6\text{Si}_4\text{O}_{15}$

Chemical formula	$\text{K}_{1.08}\text{Na}_{0.92}\text{Ca}_6\text{Si}_4\text{O}_{15}$	
Formula weight	656.15	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	$P-2_1/c$	
Unit cell dimensions	$a = 8.9618(9)$ Å	$\alpha = 90^\circ$
	$b = 7.3594(6)$ Å	$\beta = 107.54(1)^\circ$
	$c = 11.2453(11)$ Å	$\gamma = 90^\circ$
Volume	$707.2(1)$ Å ³	
Z	2	
Density (calculated)	3.081 Mg/m ³	
Absorption coefficient	3.027 mm ⁻¹	
F(000)	653.2	
Crystal size	$0.04 \times 0.06 \times 0.08$ mm	
Theta range for data collection	3.36 to 25.35°	
Index ranges	$-9 \leq h \leq 10$, $-8 \leq k \leq 7$, $-13 \leq l \leq 11$	
Reflections collected	4037	
Independent reflections	1288 [R(int)=0.0362]	
Completeness to $\theta = 25.35^\circ$	99.8%	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1288 / 0 / 125	
Goodness-of-fit on F^2	1.115	
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0346$, $wR2 = 0.0710$	
R indices (all data)	$R1 = 0.0482$, $wR2 = 0.0753$	
Largest diff. peak and hole	0.460 and -0.610 e/Å ³	

Crystallography, Volume C (Wilson 1995). Details of the data collection and refinement parameters are given in Table 1. Allocation of the cation species Na, K and Ca to specific sites were based on site-occupancy refinements and bond-distance considerations. Within four standard uncertainties three cation positions are exclusively occupied by calcium ions whereas the fourth site shows an almost balanced mixed potassium-sodium population (K: 54(1)%, Na: 46(1)%). Final full-matrix least-squares optimizations including fractional atomic coordinates and anisotropic displacement factors for all atoms converged to a residual value of $R1 = 3.46\%$ for 1288 independent observed reflections and 125 parameters. The largest shift/esd. in the last cycle was < 0.001 . The resulting chemical composition of $K_{1.08}Na_{0.92}Ca_6Si_4O_{15}$ compares well with the average composition of the crystals obtained from the EPM analysis. The final model was validated using the MISSYM algorithm included in the program PLATON (Spek 2009). No indications for unnecessarily low space group symmetry could be detected. Refined coordinates, equivalent isotropic displacement parameters, as well as selected interatomic distances and angles for $K_{1.08}Na_{0.92}Ca_6Si_4O_{15}$ are summarized in Tables 2 and 3. Anisotropic displacement parameters are listed in Table 4. Figures showing structural details were prepared using the program VESTA, Version 3 (Momma and Izumi 2011).

Table 2 Atomic coordinates and equivalent isotropic displacement parameters with estimated standard uncertainties (e.s.u.'s) in parentheses for $K_{1.08}Na_{0.92}Ca_6Si_4O_{15}$

Atom	x	y	z	U(eq)
Ca1	0.6780(1)	0.2411(1)	0.1665(1)	0.010(1)
Ca2	0.6630(1)	0.5053(1)	−0.0816(1)	0.016(1)
Ca3	0.0050(1)	0.4538(1)	0.2072(1)	0.013(1)
M	0.6768(1)	−0.0301(2)	−0.0874(1)	0.021(1)
Si1	0.9693(1)	0.2189(1)	−0.0211(1)	0.008(1)
Si2	0.6309(1)	0.7381(1)	0.1519(1)	0.009(1)
O1	0.7421(3)	0.5592(4)	0.1846(2)	0.018(1)
O2	0.8298(3)	0.2709(4)	0.0353(2)	0.017(1)
O3	0.9162(3)	0.2426(3)	0.3301(2)	0.013(1)
O4	0.4991(3)	0.2284(4)	0.2727(2)	0.021(1)
O5	0.7228(3)	−0.0689(4)	0.1807(2)	0.017(1)
O6	0.4688(3)	0.2811(4)	−0.0041(2)	0.020(1)
O7	0.1220(3)	0.3264(4)	0.0543(2)	0.016(1)
O8	0	0	0	0.022(1)

U(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor. Values are given in ($\text{\AA}^2$). M corresponds to a mixed cation site occupied by 54(1)% K and 46(1)% Na, respectively. The oxygen atom O8 resides on the special Wyckoff-position 2a. All other atoms occupy general positions

Table 3 Relevant bond lengths and angles for $K_{1.08}Na_{0.92}Ca_6Si_4O_{15}$

Bond lengths ($\text{\AA}$) up to 3.0 $\text{\AA}$:			
Ca1-O6	2.262(3)	Ca1-O4	2.271(3)
Ca1-O2	2.299(3)	Ca1-O5	2.313(3)
Ca1-O3	2.361(3)	Ca1-O1	2.405(3)
Ca2-O7	2.233(3)	Ca2-O6	2.341(3)
Ca2-O2	2.399(3)	Ca2-O4	2.520(3)
Ca2-O6	2.725(3)	Ca2-O1	2.888(3)
Ca2-O5	2.918(3)	Ca2-O4	2.947(3)
Ca3-O3	2.317(3)	Ca3-O3	2.371(3)
Ca3-O5	2.391(3)	Ca3-O1	2.419(3)
Ca3-O7	2.454(3)	Ca3-O2	2.487(3)
M-O4	2.642(3)	M-O6	2.643(3)
M-O2	2.747(3)	M-O8	2.7726(12)
M-O7	2.782(3)	M-O1	2.805(3)
M-O4	2.904(3)	M-O5	2.931(3)
Si1-O7	1.587(3)	Si1-O2	1.609(3)
Si1-O3	1.621(3)	Si1-O8	1.6396(10)
Si2-O5	1.625(3)	Si2-O1	1.625(3)
Si2-O4	1.637(3)	Si2-O6	1.638(3)
Bond angles ($^\circ$)			
O6-Ca1-O4	85.12(11)	O6-Ca1-O2	86.70(10)
O4-Ca1-O2	171.57(10)	O6-Ca1-O5	105.61(10)
O4-Ca1-O5	93.37(11)	O2-Ca1-O5	90.82(11)
O6-Ca1-O3	169.76(11)	O4-Ca1-O3	101.93(10)
O2-Ca1-O3	85.91(10)	O5-Ca1-O3	81.59(9)
O6-Ca1-O1	93.48(10)	O4-Ca1-O1	100.61(11)
O2-Ca1-O1	77.81(10)	O5-Ca1-O1	157.25(11)
O3-Ca1-O1	78.04(9)		
O3-Ca3-O3	151.74(8)	O3-Ca3-O5	80.87(10)
O3-Ca3-O5	96.60(10)	O3-Ca3-O1	91.55(10)
O3-Ca3-O1	77.55(10)	O5-Ca3-O1	152.15(10)
O3-Ca3-O7	90.33(10)	O3-Ca3-O7	116.56(10)
O5-Ca3-O7	76.07(9)	O1-Ca3-O7	131.07(9)
O3-Ca3-O2	120.76(9)	O3-Ca3-O2	81.60(9)
O5-Ca3-O2	132.62(10)	O1-Ca3-O2	74.05(10)
O7-Ca3-O2	63.37(9)		
O7-Si1-O2	108.60(15)	O7-Si1-O3	113.67(15)
O2-Si1-O3	110.14(15)	O7-Si1-O8	109.42(12)
O2-Si1-O8	107.05(12)	O3-Si1-O8	107.77(11)
O5-Si2-O1	115.07(16)	O5-Si2-O4	109.39(16)
O1-Si2-O4	109.33(16)	O5-Si2-O6	111.50(15)
O1-Si2-O6	105.62(15)	O4-Si2-O6	105.44(15)
Si1-O8-Si1	180.00		

Results

From a structural point of view, $K_{1.08}Na_{0.92}Ca_6Si_4O_{15}$ belongs to the group of mixed-anion silicates containing $[\text{SiO}_4]$ - and $[\text{Si}_2\text{O}_7]$ -groups in the ratio 2:1. Si-O bond distances (see Table 3) are in the normal range for silicate

Table 4 Anisotropic displacement parameters with estimated standard uncertainties (e.s.u.'s) in parentheses for $\text{K}_{1.08}\text{Na}_{0.92}\text{Ca}_6\text{Si}_4\text{O}_{15}$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ca1	0.008(1)	0.011(1)	0.011(1)	0.001(1)	0.002(1)	0.001(1)
Ca2	0.010(1)	0.011(1)	0.027(1)	−0.003(1)	0.005(1)	−0.001(1)
Ca3	0.012(1)	0.011(1)	0.016(1)	−0.001(1)	0.005(1)	−0.003(1)
M	0.018(1)	0.021(1)	0.020(1)	0.000(1)	0.003(1)	−0.009(1)
Si1	0.009(1)	0.007(1)	0.008(1)	0.000(1)	0.002(1)	0.000(1)
Si2	0.008(1)	0.009(1)	0.010(1)	−0.001(1)	0.003(1)	−0.001(1)
O1	0.015(2)	0.011(2)	0.027(2)	0.002(1)	0.007(1)	0.002(1)
O2	0.019(2)	0.017(2)	0.018(1)	0.000(1)	0.011(1)	0.001(1)
O3	0.014(2)	0.012(2)	0.011(1)	−0.001(1)	0.002(1)	0.000(1)
O4	0.014(2)	0.030(2)	0.021(2)	0.000(1)	0.011(1)	0.000(1)
O5	0.013(2)	0.010(2)	0.025(2)	0.001(1)	−0.001(1)	−0.001(1)
O6	0.012(2)	0.030(2)	0.014(2)	−0.005(1)	0.000(1)	0.002(1)
O7	0.013(2)	0.021(2)	0.013(1)	−0.002(1)	0.003(1)	−0.002(1)
O8	0.023(3)	0.010(2)	0.031(2)	0.004(2)	0.004(2)	0.003(2)

The anisotropic displacement factor exponent takes the form: $-2\pi^2(h^2a^{*2}U_{11} + \dots + 2hk a^* b^* U_{12})$. Values are given in ($\text{\AA}^2$)

compounds (Liebau 1985). Furthermore, the spread of the distances is in accordance with well-established trends among oxosilicates. The bridging oxygen of the dimer resides on an inversion centre, i.e. the point group symmetry of the $[\text{Si}_2\text{O}_7]$ -unit is $\bar{1}$ (or C_i). Consequently, the Si1–O8–Si1 bond angle is straight.

Two of the three solely calcium sites are coordinated by six O atoms. The coordination polyhedra can be described as distorted octahedra (about Ca1, Ca–O bond lengths: 2.26–2.41 Å) and distorted trigonal prisms (about Ca3, Ca–O bond lengths: 2.32–2.49 Å). A single prism is linked to two adjacent octahedra by sharing a common face or edge, respectively. The resulting trimers in turn form zig-zag chains running parallel $[010]$. The remaining cation sites are less regularly coordinated and occupy voids of the polyhedral network. Up to 3.0 Å eight oxygen ligands can be found for each of the two sites. Whereas the M-position shows a mixed K–Na population ($\langle \text{M–O} \rangle = 2.778$ Å) the second position is exclusively occupied by Ca^{2+} -cations (Ca3). Bond-valence sums for the cations have been calculated using the parameters of Brown and Altermatt (1985) (for (Na,Ca,K)–O bonds) and Brese and O’Keeffe (1991) (for Si–O bonds). The results in valence units are as follows: Ca1: 2.34, Ca2: 1.75, Ca3: 1.85, Si1: 4.11 and Si2: 3.92. Notably, the calcium positions show a pronounced deviation from the ideal value of 2 v.u., indicating a significant over- or underbonding, respectively. The estimation the K–Na occupancy on the mixed site from the average valence indicated an almost equal distribution of the two cation species which is in good agreement with the outcome of the site-population refinements.

The structure can be described as a mixed tetrahedral–octahedral framework (see Fig. 3). Basic building units of

this framework are so-called “kröhnkite-type” chains (named after the mineral kröhnkite, $\text{Na}_2\text{Cu}(\text{SO}_4)_2 \times 2\text{H}_2\text{O}$) which are well known in inorganic chemistry (Kolitsch and Fleck 2006 and references cited therein). These chains consist of a characteristic sequence of corner-linked $[\text{SiO}_4]$ -tetrahedra and octahedra. In the present compound these chains are running parallel to $[001]$ (Fig. 4a). The principal translation period of the kröhnkite-type chains t_K of about 5.5–5.6 Å is reflected on the c lattice parameter ($\approx 2 \times t_K$) of the present compound (see Table 5). The chains are located in layers running parallel to (010) at $y \approx \frac{1}{4}$ and $\frac{3}{4}$, respectively. In order to characterize the tetrahedral–octahedral network in more detail a topological analysis has been performed using the program TOPOS4.0 (Blatov 2012). Therefore, the crystal structure has been described by graphs composed of the vertices (sites of the tetrahedrally and octahedrally coordinated cations as well as O anions) and edges (bonds) between them. The nodes of the graph can be classified according to their *coordination sequences* $\{N_k\}$. They represent a set of integers $\{N_k\}$ ($k = 1, \dots, n$), where N_k is the number of sites in the k th coordination sphere of the respective atom that has been selected to be the central one. The corresponding values for the relevant symmetrically independent cation sites up to $n = 10$ (without the oxygen nodes) are listed in Table 6. Furthermore, the corresponding *extended point symbols* listing all shortest circuits for each angle for any non-equivalent atom have been determined.

Furthermore, for $\text{K}_{1.08}\text{Na}_{0.92}\text{Ca}_6\text{Si}_4\text{O}_{15}$ the *polyhedral microensembles* or *PME*’s have been constructed. On the lowest sublevel they are formed for *each* octahedron and tetrahedron in the asymmetric unit by considering all *directly* bonded $[\text{CaO}_6]$ - and $[\text{SiO}_4]$ -groups. They represent a geometrical interpretation of the coordination sequences up to

Fig. 3 Projection of the whole crystal structure of $\text{K}_{1.08}\text{Na}_{0.92}\text{Ca}_6\text{Si}_4\text{O}_{15}$ parallel to $[010]$. $[\text{SiO}_4]$ tetrahedra and $[\text{CaO}_6]$ octahedra are shown. Small red spheres: oxygen atoms; larger blue spheres: non-octahedrally coordinated Ca-cations; bicolored spheres: mixed Na (yellow) - K (violet) M-position

Fig. 4 Comparison of the tetrahedral-octahedral $[\text{X}(\text{SiO}_4)_2\text{O}_2]$ -chains in the isostructural compounds **a** $\text{K}_{1.08}\text{Na}_{0.92}\text{Ca}_6\text{Si}_4\text{O}_{15}$ ($\text{X} = \text{Ca}$) and **b** $\text{Na}_2\text{Ba}_6\text{Si}_4\text{O}_{15}$ ($\text{X} = \text{Na}$). The ϕ angles at the four O-O-O hinges between the tetrahedra and octahedra have the following values (data in parentheses refer to the sodium barium silicate): ϕ_1 : 66.07° (90.14°), ϕ_2 : 103.42° (90.29°), ϕ_3 : 74.49° (89.38°) and ϕ_4 : 116.01° (90.19°)

Table 5 Comparison between the basic crystallographic data of the structurally related compounds

Compound	Space group	a (Å)	b (Å)	c (Å)	β ($^\circ$)	Volume (Å ³)
$\text{K}_{1.08}\text{Na}_{0.92}\text{Ca}_6\text{Si}_4\text{O}_{15}$	$P 2_1/c$	8.9618	7.3594	11.2453	107.54	707.2
$\text{Na}_2\text{Ba}_6\text{Si}_4\text{O}_{15}$	$P 2_1/c$	9.508	7.856	11.528	107.63	820.6
$\beta\text{-Na}_2\text{Ca}_6\text{Si}_4\text{O}_{15}$	$P c$	9.0112	7.3171	10.9723	107.72	689.1

$\text{K}_{1.08}\text{Na}_{0.92}\text{Ca}_6\text{Si}_4\text{O}_{15}$: this paper; $\text{Na}_2\text{Ba}_6\text{Si}_4\text{O}_{15}$: Tamazyan et al. 1987; $\beta\text{-Na}_2\text{Ca}_6\text{Si}_4\text{O}_{15}$: Kahlenberg and Maier 2016. The unit cell of $\text{Na}_2\text{Ba}_6\text{Si}_4\text{O}_{15}$ has been transformed to monoclinic second setting

the index $k=3$. The PME 's of the first sublevel observed for the Ca1 nodes can be described as follows: each $[\text{CaO}_6]$ -octahedron is immediately linked to six tetrahedra (Fig. 5a). Using the classification based on the calculation of the coordination sequences up to $k=3$ (including the oxygen

atoms) (Ilyushin and Blatov (2002)) the PME 's of Ca1 can be denoted as $\{6,6,18\}$. For the PME 's of the two crystallographically independent tetrahedral Si nodes two groups of ensembles can be distinguished: $\{4,3,13\}$ (for Si1) and $\{4,4,20\}$ (for Si2) (see Fig. 5b, c).

Table 6 Coordination sequences $\{N_k\}$ of the tetrahedrally (Si) and octahedrally (Ca1) coordinated nodes (without the O atoms) as well as the extended point symbols for the mixed framework of $K_{1.08}Na_{0.92}Ca_6Si_4O_{15}$

Atom	Coordination sequences $\{N_k\}$ ($k=1-10$)										Extended point symbol
	1	2	3	4	5	6	7	8	9	10	
Si1	3	11	23	46	66	93	145	183	228	272	$4.8_2.8_2$
Si2	4	15	19	45	78	99	146	162	228	318	$4.4.4.4.4.6_2$
Ca1	6	10	28	43	70	112	129	185	232	280	$4.4.4.4.4.4.6_2.6_2.6_2.6_2.6_4.8.8_8$

Remark: $Na_2Ba_6Si_4O_{15}$ is topologically equivalent (see Kahlenberg and Maier 2016)

Fig. 5 Polyhedral microensembles of the crystallographically independent octahedral (Ca1) and tetrahedral (Si) nodes: **a** {6,6,18} (for Ca1), **b** {4,3,13} (for Si1) and **c** {4,4,20} (for Si2)

Discussion: comparison with related structures

A comparison with other known $A_2B_6Si_4O_{15}$ compounds revealed a close similarity between the lattice parameters and space group symmetry of $K_{1.08}Na_{0.92}Ca_6Si_4O_{15}$ and those reported for $Na_2Ba_6Si_4O_{15}$ (Tamazyan et al. 1987). Differences in the unit cell metrics can be attributed to differences in the sizes of divalent (Ba,Ca) and monovalent

(Na,K) cations. The abovementioned resemblance pointed to an isostructural relationship which was confirmed using a graphical comparison of both crystal structures. For the calculation of several quantitative descriptors for the characterization of the degree of similarity between the crystal structures of $K_{1.08}Na_{0.92}Ca_6Si_4O_{15}$ and $Na_2Ba_6Si_4O_{15}$ the program COMPSTRU (de la Flor et al. 2016) was used. Therefore, the original data of Tamazyan et al. (1987) have

been transformed to monoclinic second setting. For the given two materials, the degree of lattice distortion (S), i.e. the spontaneous strain obtained from the eigenvalues of the finite Lagrangian strain tensor calculated in a Cartesian reference system, has a value of $(S)=0.0325$. Subsequently, the structure of K_{1.08}Na_{0.92}Ca₆Si₄O₁₅ was mapped on the most similar configuration of Na₂Ba₆Si₄O₁₅. The calculations revealed the following atomic displacements (in Å) between the corresponding atoms in the Ba- (first entry) and the Ca- (second entry) compound: Ba1-Ca3: 0.462; Ba2-Ca2: 0.087; Ba3-M1: 0.136; Na1-Ca1: 0.097; Si1-Si1: 0.175; Si2-Si2: 0.169; O1-O7: 0.301; O2-O8: 0.000; O3-O3: 0.609; O4-O2: 0.562; O5-O4: 0.310; O6-O5: 0.082; O7-O1: 0.307; O8-O6: 0.349, i.e. the maximum displacement $d_{\max}$ is 0.609 Å. The arithmetic mean is $d_{\text{av}}=0.270$ Å. The measure of similarity Δ as defined by Bergerhoff et al. (1999) has a value of 0.071.

The shifts between equivalent atoms in the two isostructural compounds are reflected, for example, in the conformation of the individual kröhnkite-type chains (Fig. 4a, b). As can be clearly seen, the ϕ angles at the four O-O-O hinges between the tetrahedra and octahedra are quite different. In Na₂Ba₆Si₄O₁₅ values close to 90° are observed. On the other hand, for K_{1.08}Na_{0.92}Ca₆Si₄O₁₅ two acute (66.07, 74.49°) and two obtuse (103.42, 116.01°) angles can be distinguished. Furthermore, the [CaO₆]-group in the latter compound is much more distorted than the corresponding [NaO₆]-octahedron in Na₂Ba₆Si₄O₁₅. Unlike the Ba-containing phase, where the occurrence of twinning by reticular merohedry (mimicking an orthorhombic C-centred Bravais lattice) has been described to be a characteristic feature of almost all crystals, we could not observe similar twinning phenomena in our samples of K_{1.08}Na_{0.92}Ba₆Si₄O₁₅.

In a recent paper on the polymorphism of Na₂Ca₆Si₄O₁₅, different topologies among A₂B₆Si₄O₁₅ phases have been compared (Kahlenberg and Maier 2016). For the ambient temperature forms K₂Ca₆Si₄O₁₅ and Na₂Ca₆Si₄O₁₅ (α -modification), two different topologies of the mixed frameworks occur (though both are based on kröhnkite-type chains). The high-temperature polymorph of Na₂Ca₆Si₄O₁₅ (β -phase) has the same topology as K_{1.08}Na_{0.92}Ca₆Si₄O₁₅ and similar lattice parameters (Table 5). Furthermore, the symmetry of β -Na₂Ca₆Si₄O₁₅ (space group $P1c1$) is lower than in K_{1.08}Na_{0.92}Ca₆Si₄O₁₅ ($P12_1/c1$). Both structures are in a group-subgroup relationship. The symmetry loss is combined with a reduction in point group symmetry and results in a *translationengleiche* subgroup of index 2. Based on the crystal structures of the high- and low-symmetry compounds (and neglecting differences in site populations), a symmetry-mode analysis of the global structural-distortion patterns relating β -Na₂Ca₆Si₄O₁₅ and K_{1.08}Na_{0.92}Ca₆Si₄O₁₅ has been performed using the program AMPLIMODES (Perez-Mato et al. 2010). In the present case, the distortion field can be split into two contributions transforming according to the

irreducible representations Γ^+_1 and Γ^-_2 of $P2_1/c$. The absolute amplitudes of these two symmetry components of the global distortion are 3.03 Å (for Γ^+_1) and 4.23 Å (for Γ^-_2). As can be seen from the comparison of the values, both modes have large amplitudes and both have to be considered for an understanding of the formal symmetry break, i.e. a classification into a primary and a secondary distortion is impossible.

Our results show that there is a definite influence of the monovalent cation species on the stability of different A₂B₆Si₄O₁₅ structure types. However, further experimental data covering a larger range of Na/K-ratios are needed to draw a final conclusion. Additionally, synthesis temperature clearly plays a role as well and, hence, in-situ diffraction studies are also of importance to detect T-induced changes in the network topologies due to phase transformations.

Finally, we would like to mention that the investigation of crystalline compounds of the system Na₂O-K₂O-CaO-SiO₂ may have also implications for the field of Earth sciences. So far, no anhydrous sodium-potassium-calcium silicates have been observed in Nature. However, a number of water-containing minerals such as canasite, (Na,K)₆Ca₅Si₁₂O₃₀(OH,F)₄, (Rastsvetaeva et al. 2003), mountainite, KNa₂Ca₂[Si₈O₁₉(OH)]·6H₂O (Zubkova et al. 2009) or calcinaksite, KNaCa(Si₄O₁₀)·H₂O (Chukanov et al. 2015) are known from various mineralogically famous regions of the Earth: the Eifel volcanic area (Germany), kimberlite pipes in Kimberley (South Africa) or different Russian localities such as the Khibiny and Lovozero plutons (Kola Peninsula) or the Murun massif (Yakutia). Therefore, it is possible that water-free variants can be found in natural environments as well. Since crystal-structure determination of the above mentioned minerals was frequently complicated due to low diffraction quality and/or complex intergrowths of different species, diffraction studies on well-crystallized synthetic counterparts may ease the identification and structural characterization of potential new minerals.

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