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On the existence of a high-temperature polymorph of $Na_2Ca_6Si_4O_{15}$—implications for the phase equilibria in the system Na_2O-CaO-SiO_2

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Abstract Singe crystals of a new high-temperature polymorph of $Na_2Ca_6Si_4O_{15}$ have been obtained from solid state reactions performed at 1300 °C. The basic crystallographic data of this so-called β-phase at ambient conditions are as follows: space group $P1c1$, $a = 9.0112(5)$ Å, $b = 7.3171(5)$ Å, $c = 10.9723(6)$ Å, $\beta = 107.720(14)°$, $V = 689.14(7)$ Å^3, $Z = 2$. The crystals showed twinning by reticular merohedry (mimicking an orthorhombic *C*-centred unit cell) which was accounted for during data processing and structure solution. Structure determination was accomplished by direct methods. Least-squares refinements resulted in a residual of $R(|F|) = 0.043$ for 5811 observed reflections with $I > 2\sigma(I)$. From a structural point of view β-$Na_2Ca_6Si_4O_{15}$ can be attributed to the group of mixed-anion silicates containing [Si_2O_7]-dimers as well as isolated [SiO_4]-tetrahedra in the ratio 1:2, i.e. more precisely the formula can be written as $Na_2Ca_6[SiO_4]_2[Si_2O_7]$. The tetrahedral groups are arranged in layers parallel to (100). Sodium and calcium cations are located between the silicate anions for charge compensation and are coordinated by six to eight nearest oxygen ligands. Alternatively, the structure can be described as a mixed tetrahedral-octahedral framework based on kröhnkite-type [$Ca(SiO_4)_2O_2$]-chains in which the CaO_6-octahedra are corner-linked to bridging SiO_4-tetrahedra. The infinite chains are running parallel to [001] and are concentrated in layers parallel to (010). Adjacent layers are shifted relative to each other by an amount of +δ or −δ along a*. Consequently, a …ABABAB… stacking sequence is created. A detailed comparison with related structures such as α-$Na_2Ca_6Si_4O_{15}$ and other $A_2B_6Si_4O_{15}$ representatives including topological as well as group theoretical aspects is presented. There are strong indications that monoclinic $Na_2Ca_3Si_2O_8$ mentioned in earlier studies is actually misinterpreted β-$Na_2Ca_6Si_4O_{15}$. In addition to the detailed crystallographic analysis of the previously unknown compound our results will also help to improve the interpretation of the phase relationships between the compounds in the ternary system Na_2O-CaO-SiO_2 which are of interest for several applications related to the field of applied mineralogy and materials science.

Keywords $Na_2Ca_6Si_4O_{15}$ · $Na_2Ca_3Si_2O_8$ · Ternary system · Na_2O-CaO-SiO_2 · Sodium calcium silicates · Mixed framework structures

Introduction

Among the silicates containing alkali and alkaline earth cations the compounds belonging to the system Na_2O-CaO-SiO_2 have attracted the most attention. This is not really surprising, because the silica rich part of this system is of fundamental importance for manufacturing of so-called soda-lime-glasses which are the major commercial types used for the production of hollow and flat glasses such as containers or windows, respectively (Varshneya 1994; Shelby 2009).

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Since the landmark paper of Morey and Bowen (1925), several subsequent studies focused on the phase relationships as well as melting temperatures and melting behaviour of sodium calcium silicates (Thilo 1951; Segnit 1953; Shahid and Glasser 1970, 1971; Moir and Glasser 1974; Garza Montoya et al. 2003; Zhang et al. 2011; Knowles and Thompson 2014). However, especially the earlier investigations frequently lacked precise knowledge of the chemical formulas of the proposed phases. Therefore, many of the compounds disclosed in these phase equilibrium studies had to be later characterized by diffraction methods not only for the determination of their crystal structures but also for proving their suggested chemical compositions, i.e. structure analysis played the role of a convenient analytical probe. In the meantime crystal structure investigations have been performed for the following compounds: Na_2CaSiO_4 (Dollase and Ross 1991), $Na_2Ca_3Si_3O_{10}$ (Treushnikov et al. 1971), $Na_4CaSi_3O_9$ (Fischer and Tillmanns 1984), α-$Na_2Ca_2Si_3O_9$ (Ohsato et al. 1990), β-$Na_2Ca_2Si_3O_9$ (Fischer and Tillmanns 1987), $Na_2CaSi_2O_6$ (Ohsato et al. 1985), $Na_2Ca_3Si_6O_{16}$ (Ihara et al. 1984; Kahlenberg et al. 2010), $Na_2Ca_2Si_2O_7$ (Kahlenberg and Hösch 2002) and $Na_2Ca_6Si_4O_{15}$ (Armbruster and Röthlisberger 1990).

Due to their large variety in chemical composition the group of sodium-calcium-silicates is an excellent pool for the crystallographer to study the influence of the ratios between tetrahedrally and non-tetrahedrally coordinated cations on the topology of the resulting crystal structures. A summary of their structural characteristics can be found in Kahlenberg and Hösch (2002).

However, there is still a large number of ternary compounds in the system Na_2O-CaO-SiO_2 that have been mentioned in the literature for which no or only basic crystallographic data in terms of unit cell parameters are available. Therefore, to a certain extent suspicion has to be attached to their existence. One of the phases belonging to this group is $Na_2Ca_3Si_2O_8$ or $Na_2O \times 3CaO \times 2SiO_2$. To the best of our knowledge, Maki (1969) was the first who presented some information about this compound. According to his study which aimed on the preparation of new alkali oxide containing Ca_2SiO_4 analogues, a stable triclinic and a metastable monoclinic modification of $Na_2Ca_3Si_2O_8$ have to be distinguished. The monoclinic form could be prepared at 1300 °C and transformed slowly into a triclinic phase after prolongated annealing for more than 100 h at this temperature. He also presented indexed powder diffraction patterns of both polymorphs having the following sets of lattice parameters: triclinic form: $a = 5.47$ Å, $b = 7.32$ Å, $c = 9.02$ Å, $\alpha = 91.37°$, $\beta = 107.70$, $\gamma = 89.80°$; monoclinic form: $a = 10.99$ Å, $b = 7.33$ Å, $c = 9.01$ Å, $\beta = 107.75°$. Maki's efforts to index the powder patterns of both low-symmetry compounds from laboratory data cannot be appreciated enough. His high quality data were later used for creating the entries 00-023-0668 and 00-023-0670, respectively, of the PDF-4 Powder Diffraction File database issued by the International Centre for Diffraction Data (ICDD). These entries in turn were the primary source for phase identification of polycrystalline $Na_2Ca_3Si_2O_8$ in several subsequent papers using diffraction methods (Zhang et al. 2009; Kuo 2014; Jin et al. 2015; Fu and Hu 2016). Unfortunately, however, Maki did not perform a more detailed chemical analysis of his synthesis products.

The surprising lack of knowledge concerning more detailed crystallographic data on $Na_2Ca_3Si_2O_8$ prompted us to include this phase into an ongoing long-time study on the phase relationships and the crystal chemistry of silicates containing alkali as well as alkaline earth oxides. In this publication we present our results indicating that – at least – monoclinic $Na_2Ca_3Si_2O_8$ probably corresponds to a previously unknown high-temperature modification of $Na_2Ca_6Si_4O_{15}$.

Experimental details

Synthesis

Synthesis experiments of ternary oxides with the molar ratio $Na_2O:CaO:SiO_2 = 1:3:2$ were based on mixtures of the following dried educts: Na_2CO_3 (Alpha Aesar, 99.9 %), $CaCO_3$ (Merck, >99.9 %) and quartz (AlfaAesar, 99.995 %). The starting materials were homogenized for 45 min under ethanol in a planetary mill with 600 r.p.m., dried over night at 60 °C (in order to completely remove the ethanol) and stored in a desiccator. Afterwards, the educts were pressed into pellets (approximately 0.5 g, each having a diameter of 12 mm and a thickness of about 3 mm) and dried again at 300 °C. A single pellet was transferred into an open platinum crucible, placed into a resistance heated furnace and fired from 300 °C with a heating ramp of 50 °C per hour to 1300 °C. The crucible was removed after 44 h and finally quenched in air. Weight loss was determined from weight difference before and after heating.

Assuming a complete disintegration of the carbonates, one would expect a theoretical weight loss of 33.44 %. The corresponding value of our synthesis experiment performed at 1300 °C was 39.51 %, i.e. the experimentally determined loss is much higher. It seems to be likely to attribute the excess weight loss to an evaporation of Na_2O, which is known to be the most volatile oxide in this system.

A first inspection of the run-product indicated the presence of single crystals up 100 μm in diameter embedded in a polycrystalline matrix. The crystals could be separated mechanically. First investigations using a petrographic microscope showed that the optical quality of the colorless transparent crystals was only moderate. Except for very small samples most of the crystals exhibited undulose extinction when observed under crossed polarizers.

Chemical analysis

One of the crystals obtained from the synthesis experiment was embedded in epoxy resin and polished with diamond paste (3 and 1 μm grain size) for chemical analysis with an electron microprobe (JEOL JXA 8100 Superprobe) operated in wavelength-dispersive mode. Measurements were performed with an acceleration voltage of 15 kV and a 10 nA beam current. For calibration of sodium, calcium and silicon standard specimens of jadeite, diopside and quartz were used. The intensities obtained were corrected for electron scattering, absorption and fluorescence radiation (so-called ZAF correction). A total number of six spots in various areas of the crystal were analysed. They all yielded a very similar chemical composition giving no indication for a chemical zoning. The average values in weight-% are as follows: Na_2O: 9.32(3), CaO: 53.28(2) and SiO_2: 37.40(2). After normalization to 15 oxygen atoms almost integer atomic ratios were obtained: Na : Ca : Si : O = 1.92(2) : 6.06(2) : 3.97(1) : 15. This resulted in an idealized chemical formula of $Na_2Ca_6Si_4O_{15}$ and pointed to the presence of a phase the composition of which is significantly different from $Na_2Ca_3Si_2O_8$ (corresponding to 17.69 % Na_2O, 48.01 % CaO and 34.30 % SiO_2).

Single-crystal diffraction

Several single crystals of apparently good optical quality were fixed on the top of glass fibres with nail polish and examined on a Stoe IPDS-II imaging-plate diffractometer at room conditions. Many samples, however, showed reflections which were radially elongated making them unsuitable for more detailed data collections. Therefore, we focused on one of those that were of better diffraction quality. At a first glance, the diffraction pattern could be indexed with an orthorhombic *C*-centred unit cell. The corresponding lattice parameters had values of $a_{OR} = 34.332(2)$ Å, $b_{OR} = 10.9723(6)$ Å and $c_{OR} = 7.3171(5)$ Å. However, a more detailed inspection using precession-type reconstructions of reciprocal space revealed systematic absences that were not compatible with any orthorhombic space group. Actually, the diffraction pattern could be explained as the result of twinning by reticular merohedry of two monoclinic primitive individuals mimicking orthorhombic symmetry. Principally, two classes of reflections could be distinguished containing (i) contributions from only one domain each (complete separation) and (ii) contributions from both domains (complete overlap). The program X-Area (Stoe & Cie GmbH 2005) of the STOE diffractometer software package was employed to isolate the diffraction spots

Table 1 Crystal data and structure refinement for β-$Na_2Ca_6Si_4O_{15}$

Empirical formula	$Na_2Ca_6Si_4O_{15}$	
Formula weight	638.82	
Temperature	295(2) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	*P*1*c*1	
Unit cell dimensions	*a* = 9.0112(5) Å	α = 90°
	b = 7.3171(5) Å	β = 107.720(14)°
	c = 10.9723(6) Å	γ = 90°
Volume	689.14(7) $Å^3$	
Z	2	
Density (calculated)	3.079 Mg/m^3	
Absorption coefficient	2.815 mm^{-1}	
F(000)	636	
Crystal size	0.04 × 0.06 × 0.07 mm^3	
Theta range for data collection	2.37 to 26.75°	
Index ranges	−11 < = h < =11, −9 < = k < =9, −13 < = l < =12	
Reflections collected	7478	
Observed reflections [I > 2sigma(I)]	5811	
Completeness to theta = 26.75°	99.4 %	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	7478/2/246	
Goodness-of-fit on F^2	1.087	
Final R indices [I > 2sigma(I)]	R1 = 0.0430, wR2 = 0.1003	
R indices (all data)	R1 = 0.0657, wR2 = 0.1105	
Largest diff. peak and hole	1.138 and −1.123 e.$Å^{-3}$	

coming from the two different orientations of the domains. The diffraction peaks were indexed independently and the superimposed diffraction patterns were integrated simultaneously. Integration was repeated twice (with and without overlap check) for each twin domain. After transformation to monoclinic second setting the following lattice parameters were obtained for the domain I with the higher mean intensity: $a = 9.0112(5)$ Å, $b = 7.3171(5)$ Å, $c = 10.9723(6)$ Å, $\beta = 107.720(14)°$. Further data reduction included Lorentz and polarization corrections. No absorption correction was applied. Systematic absences pointed to space groups $P1c1$ or $P12/c1$. Structure solution was performed by direct methods (program SIR2004, Burla et al. 2005) using the data set containing the non-overlapping reflections from domain I only. However, only in the acentric space group $P1c1$ a crystal chemical reasonable model showing SiO_4-tetrahedra and additional Na/Ca cation sites was obtained. For the least-squares refinement of this initial model (program SHELX-97 (Sheldrick 1997) embedded in the WinGX software suite (Farrugia 1999)) the data set containing the overlapping and non-overlapping reflections from both domains (HKLF 5 command) was used. The volume fractions of the two twin domains refined to values of 70.9(2):29.1(2) respectively. Neutral atom scattering coefficients and anomalous dispersion corrections were taken from the *International Tables for Crystallography, Volume C* (Wilson 1995). A critical check

Table 2 Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3). U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor. The positions M(1) and M(3), respectively, represent mixed Na/Ca-sites with the following occupancies: M(1): 84(2)% Ca/16(2)% Na and M(3): 16(2)% Ca/84(2)% Na

	x	y	z	U(eq)
Si(1)	3664(3)	5049(3)	3381(2)	11(1)
Si(2)	6271(3)	−87(3)	6556(2)	13(1)
Si(3)	263(3)	−323(3)	347(2)	11(1)
Si(4)	9667(3)	5304(3)	206(2)	13(1)
O(1)	8207(8)	4832(7)	8963(7)	21(1)
O(2)	2666(8)	3166(8)	3293(6)	22(1)
O(3)	2631(8)	6918(8)	3234(7)	23(1)
O(4)	643(8)	−59(5)	1862(6)	16(1)
O(5)	7163(7)	−1852(8)	1874(6)	21(1)
O(6)	9277(8)	5119(6)	1535(6)	16(1)
O(7)	4970(9)	4776(9)	9780(7)	27(2)
O(8)	5282(8)	−241(8)	5029(6)	21(1)
O(9)	1732(9)	159(6)	9823(7)	19(1)
O(10)	11(11)	7477(14)	9997(5)	37(1)
O(11)	4988(8)	147(7)	2340(8)	26(2)
O(12)	4560(9)	5016(6)	2321(7)	21(1)
O(13)	7307(8)	1924(7)	1910(7)	23(1)
O(14)	8718(7)	697(10)	9485(5)	28(1)
O(15)	1138(7)	4252(10)	116(6)	31(2)
M(1)	3409(2)	2658(3)	766(2)	16(1)
Ca(2)	6782(3)	5047(2)	1731(2)	14(1)
M(3)	3179(5)	7180(6)	741(4)	44(1)
Ca(4)	3148(2)	44(2)	3329(2)	14(1)
Ca(5)	9978(2)	2541(2)	2736(1)	19(1)
Ca(6)	9967(2)	−2469(2)	3125(2)	14(1)
Ca(7)	6554(2)	2291(3)	9049(2)	21(1)
Na(8)	6731(4)	2144(4)	4123(3)	18(1)

Table 3 Selected bond lengths [Å] and angles [°] for β-$Na_2Ca_6Si_4O_{15}$

Si(1)-O(12)	1.606(8)	Si(1)-O(7)	1.630(8)
Si(1)-O(2)	1.632(6)	Si(1)-O(3)	1.635(6)
Si(2)-O(13)	1.615(6)	Si(2)-O(5)	1.616(6)
Si(2)-O(11)	1.638(8)	Si(2)-O(8)	1.645(7)
Si(3)-O(4)	1.603(7)	Si(3)-O(14)	1.608(6)
Si(3)-O(9)	1.634(7)	Si(3)-O(10)	1.655(10)
Si(4)-O(15)	1.562(7)	Si(4)-O(6)	1.607(7)
Si(4)-O(1)	1.618(7)	Si(4)-O(10)	1.650(10)
M(1)-O(15)	2.274(7)	M(1)-O(9)	2.397(6)
M(1)-O812)	2.426(6)	M(1)-O(7)	2.546(8)
M(1)-O(11)	2.624(7)	M(1)-O(3)	2.668(7)
M(1)-O(8)	2.731(7)		
Ca(2)-O(7)	2.272(8)	Ca(2)-O(12)	2.284(8)
Ca(2)-O(5)	2.293(6)	Ca(2)-O(6)	2.323(7)
Ca(2)-O(13)	2.330(6)	Ca(2)-O(1)	2.396(7)
M(3)-O(12)	2.398(8)	M(3)-O(9)	2.582(7)
M(3)-O(2)	2.596(8)	M(3)-O(10)	2.729(11)
M(3)-O(15)	2.770(9)	M(3)-O(7)	2.801(9)
M(3)-O(3)	2.931(8)	M(3)-O(11)	2.951(8)
Ca(4)-O(11)	2.243(8)	Ca(4)-O(8)	2.245(7)
Ca(4)-O(2)	2.323(6)	Ca(4)-O(3)	2.331(6)
Ca(4)-O(4)	2.341(7)	Ca(4)-O(9)	2.368(7)
Ca(5)-O(6)	2.277(6)	Ca(5)-O(4)	2.291(5)
Ca(5)-O(13)	2.344(7)	Ca(5)-O(2)	2.356(7)
Ca(5)-O(10)	2.472(5)	Ca(5)-O(1)	3.060(7)
Ca(5)-O(9)	3.073(7)		
Ca(6)-O(3)	2.409(7)	Ca(6)-O(6)	2.425(6)
Ca(6)-O(4)	2.433(6)	Ca(6)-O(15)	2.487(6)
Ca(6)-O(14)	2.490(7)	Ca(6)-O(5)	2.522(6)
Ca(6)-O(9)	2.656(7)	Ca(6)-O(1)	2.691(7)
Ca(7)-O(14)	2.197(6)	Ca(7)-O(8)	2.339(7)
Ca(7)-O(1)	2.402(6)	Ca(7)-O(7)	2.585(8)
Ca(7)-O(5)	2.626(7)	Ca(7)-O(11)	2.661(7)
Ca(7)-O(12)	2.938(6)	Ca(7)-O(13)	3.016(7)
Na(8)-O(8)	2.555(8)	Na(8)-O(11)	2.561(8)
Na(8)-O(1)	2.614(7)	Na(8)-O(13)	2.637(8)
Na(8)-O(14)	2.693(8)	Na(8)-O(10)	2.830(11)
Na(8)-O(5)	2.931(7)	Na(8)-O(7)	2.968(8)
O(12)-Si(1)-O(7)	107.8(4)	O(12)-Si(1)-O(2)	109.5(3)
O(7)-Si(1)-O(2)	110.4(4)	O(12)-Si(1)-O(3)	109.8(3)
O(7)-Si(1)-O(3)	104.7(4)	O(2)-Si(1)-O(3)	114.4(4)
O(13)-Si(2)-O(5)	117.8(4)	O(13)-Si(2)-O(11)	107.4(4)
O(5)-Si(2)-O(11)	107.2(3)	O(13)-Si(2)-O(8)	106.4(3)
O(5)-Si(2)-O(8)	111.1(3)	O(11)-Si(2)-O(8)	106.4(4)
O(4)-Si(3)-O(14)	115.3(3)	O(4)-Si(3)-O(9)	113.5(4)
O(14)-Si(3)-O(9)	110.0(4)	O(4)-Si(3)-O(10)	109.2(3)
O(14)-Si(3)-O(10)	106.4(4)	O(9)-Si(3)-O(10)	101.3(3)
O(15)-Si(4)-O(6)	116.1(3)	O(15)-Si(4)-O(1)	109.3(3)
O(6)-Si(4)-O(1)	113.6(4)	O(15)-Si(4)-O(10)	105.5(5)
O(6)-Si(4)-O(10)	108.0(3)	O(1)-Si(4)-O(10)	103.1(3)
Si(4)-O(10)-Si(3)	157.5(4)		

of the structure and its space group including the MISSYM algorithm implemented in the program PLATON (Spek 2009) did not reveal any indication that a wrong or unnecessarily low space group symmetry had been chosen. The final computations using anisotropic displacement parameters for all atoms as well as site occupancy refinements for the Na/Ca-positions resulted in a residual of $R1 = 0.0430$ for 246 parameters for all observed reflections (see Table 1). The difference electron density map turned out to be featureless, with maxima and minima of 1.14 and −1.13 e.Å^{-3}. The chemical formula derived from the structure analysis corresponds to $Na_2Ca_6Si_4O_{15}$ and is in excellent agreement with the results from the electron microprobe analysis. The optimized atomic coordinates, anisotropic displacement parameters as well as selected interatomic distances and angles are given in Tables 2, 3 and 4, respectively. Figures showing structural details were prepared using the program ATOMS6.4 (Dowty 2011).

Table 4 Anisotropic displacement parameters (Å^{2}x 10^3) for β-$Na_2Ca_6Si_4O_{15}$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11} + \ldots + 2\,h\,k\,a^*\,b^*\,U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Si(1)	8(1)	14(1)	10(1)	−2(1)	5(1)	−2(1)
Si(2)	14(1)	10(1)	16(2)	1(1)	7(1)	−3(1)
Si(3)	9(1)	13(1)	11(1)	1(1)	4(1)	−3(1)
Si(4)	16(1)	10(1)	13(1)	−1(1)	7(1)	−1(1)
O(1)	12(3)	30(3)	19(4)	5(2)	0(3)	−3(2)
O(2)	19(3)	14(3)	31(3)	0(2)	7(2)	2(2)
O(3)	16(3)	19(3)	39(4)	4(2)	16(3)	−2(2)
O(4)	24(3)	13(3)	10(3)	1(2)	5(3)	−1(2)
O(5)	12(3)	13(3)	35(4)	3(2)	3(2)	1(2)
O(6)	11(3)	22(3)	12(3)	−2(2)	1(2)	0(2)
O(7)	28(4)	44(4)	11(4)	4(2)	7(3)	−1(3)
O(8)	22(3)	27(3)	14(3)	−4(2)	5(3)	0(2)
O(9)	28(4)	19(3)	19(3)	−4(2)	20(3)	−3(2)
O(10)	71(3)	20(2)	26(2)	−4(3)	24(3)	−14(2)
O(11)	16(4)	32(3)	37(4)	2(2)	16(3)	6(2)
O(12)	13(3)	33(3)	20(3)	−6(2)	9(3)	−1(2)
O(13)	24(3)	5(2)	42(4)	1(2)	12(3)	−3(2)
O(14)	18(3)	41(4)	23(3)	8(3)	2(2)	10(3)
O(15)	20(3)	46(4)	26(3)	−15(3)	7(2)	3(3)
M(1)	8(1)	18(1)	22(1)	−1(1)	4(1)	−1(1)
Ca(2)	13(1)	13(1)	19(1)	−2(1)	8(1)	0(1)
M(3)	40(3)	55(3)	37(3)	10(2)	12(2)	23(2)
Ca(4)	11(1)	15(1)	17(1)	−1(1)	7(1)	0(1)
Ca(5)	16(1)	16(1)	23(1)	3(1)	5(1)	2(1)
Ca(6)	14(1)	14(1)	14(1)	−1(1)	4(1)	−1(1)
Ca(7)	22(1)	15(1)	32(1)	−3(1)	14(1)	−1(1)
Na(8)	24(2)	14(2)	20(2)	−5(1)	13(1)	−8(1)

Results

Description of the crystal structure

The present phase represents a second polymorph of $Na_2Ca_6Si_4O_{15}$. For sake of clarity the already known modification first described by Armbruster and Röthlisberger (1990) and the new form will be designated α- and β-$Na_2Ca_6Si_4O_{15}$, respectively. The crystal structure of β-$Na_2Ca_6Si_4O_{15}$ belongs to the group of mixed-anion silicates. It is built from isolated $[SiO_4]$-tetrahedra as well as $[Si_2O_7]$-units in the ratio of 2:1, i.e. more precisely the formula could be written as $Na_2Ca_6[SiO_4]_2[Si_2O_7]$. As shown in Fig. 1, the tetrahedral groups are arranged in layers parallel to (100). Sodium and calcium cations are located between the $[SiO_4]$-groups and $[Si_2O_7]$-dimers for charge compensation. In more detail, a total of eight symmetrically independent non-tetrahedral positions can be distinguished. With regard to the distribution of the Si-O bond lengths of the anion groups a pronounced distortion of the tetrahedra can be noticed. The spread of the Si-O distances ranges from 1.562–1.655 Å. Nevertheless, the observed values are in accordance with accepted values for silicate structures (Liebau 1985). The distortion is also reflected in the O-Si-O angles ranging from 101.3° to 117.8°. The average <O-Si-O> angles are, however, very close to those observed for an undistorted tetrahedron. The distortions can be expressed numerically via the quadratic elongations λ and the angle variances σ^2 (Robinson et al. 1971). The values of these parameters for the four crystallographically independent $[SiO_4]$-units are as follows: Si(1): $\lambda = 1.003$ and $\sigma^2 = 9.61$, Si(2): $\lambda = 1.005$ and $\sigma^2 = 20.96$, Si(3): $\lambda = 1.006$ and $\sigma^2 = 24.32$ and Si(4): $\lambda = 1.006$ and $\sigma^2 = 23.19$, i.e. the tetrahedra around Si(3) and Si(4) forming the dimer are slightly more distorted than the two isolated $[SiO_4]$-moieties around Si(1) and Si(2). Apart from O(10) all oxygen atoms in $Na_2Ca_6Si_4O_{15}$ are non-bridging. The Si(4)-O(10)-Si(3) angle

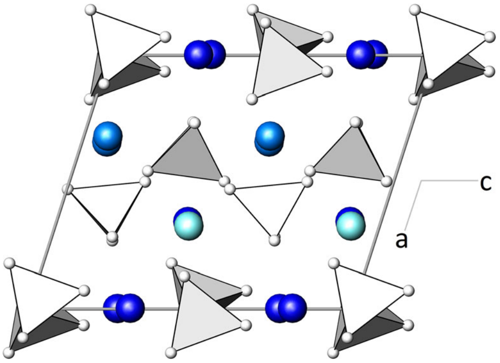

Fig. 1 Projection of the whole crystal structure of β-$Na_2Ca_6Si_4O_{15}$ parallel to [010]. Light and dark blue spheres correspond to pure sodium and cacium sites, respectively. Medium blue spheres represent positions with mixed Ca/Na populations. Oxygen atoms are shown as small grey spheres

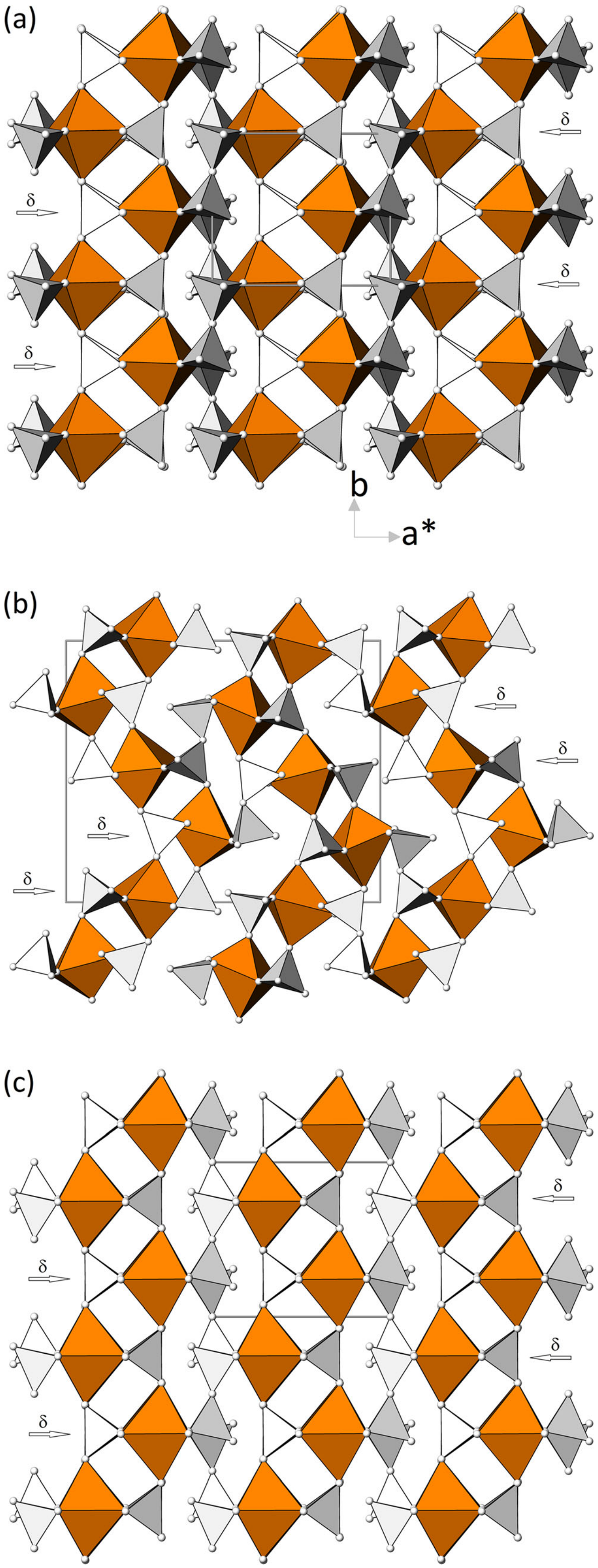

Fig. 2 Mixed tetrahedral-octahedral frameworks of (a) β-$Na_2Ca_6Si_4O_{15}$ (b) α-$Na_2Ca_6Si_4O_{15}$ and (c) $Na_2Ba_6Si_4O_{15}$ in projections parallel to the directions of the kröhnkite-type chains

has a value of 157.5(4)° indicating that the $[Si_2O_7]$-dimer is not straight but bended. The torsion angles <(O(1)-Si(4)-Si(3)-O(14)) = −19.3(9)°, <(O(6)-Si(4)-Si(3)-O(4)) = −21.8(9)° and <(O(15)-Si(4)-Si(3)-O(9)) = −19.1(9)° show that the conformation of the dimer can be considered as eclipsed. Initial site population refinements of the sodium and calcium ions on the non-tetrahedrally coordinated sites revealed that five out of eight positions are exclusively occupied by Ca ions (Ca(2), Ca(4), Ca(5), Ca(6) and Ca(7)), whereas the Na(8) position is a pure Na-site. The Na/Ca-distributions on the remaining two sites were optimized using the constraint that both positions are fully occupied. The derived populations (resulting in a charge balanced composition) are as follows: M(1): 84(2)% Ca/16(2)% Na and M(3): 16(2)% Ca/84(2)% Na. The positions Ca(2) and Ca(4) are coordinated by six nearest oxygen neighbors in form of distorted octahedra. Each octahedron shares common corners with four adjacent insular tetrahedra and two different $[Si_2O_7]$-dimers. The coordination spheres of the remaining Na/Ca-sites are much more irregular involving 7–8 oxygen ligands.

Alternatively, the structure can be described as a mixed tetrahedral-octahedral framework (see Fig. 2a). Within this network, infinite chains running parallel to [001] can be identified, in which the $[CaO_6]$-octahedra are corner-linked to bridging $[SiO_4]$-tetrahedra (see Fig. 3a). These so-called "kröhnkite-type" chains (named after the mineral kröhnkite, $Na_2Cu(SO_4)_2 \times 2H_2O$) are well known

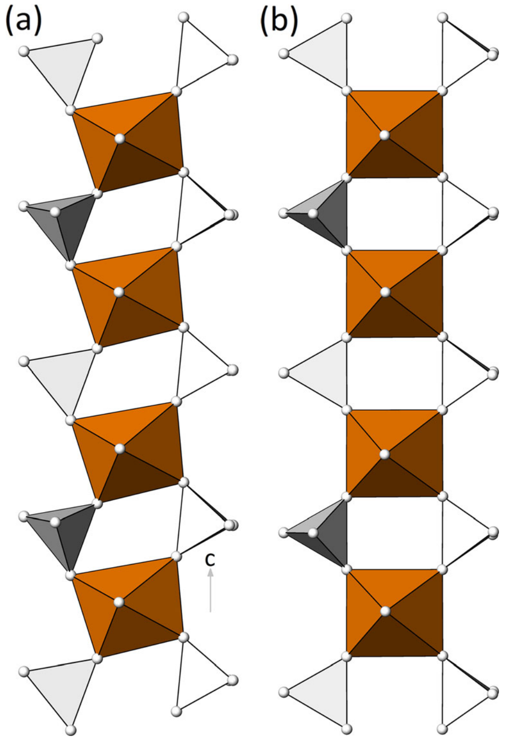

Fig. 3 Projections of a single kröhnkite-type chain in (a) β-$Na_2Ca_6Si_4O_{15}$ and (b) $Na_2Ba_6Si_4O_{15}$ perpendicular to the mean plane of the chain

Table 5 Summary of the basic crystallographic data of the different $A_2B_6Si_4O_{15}$-compounds based on kröhnkite-type chains with a translation period t_K. Remark: The unit cell of $Na_2Ba_6Si_4O_{15}$ has been transformed to monoclinic second setting

Compound	Space group	*a* [Å]	*b* [Å]	*c* [Å]	*β* [°]	Reference
$K_2Ca_6Si_4O_{15}$	*P* 2/*c*	7.3782	$5.5677 \approx t_K$	17.2466	90.005	Arroyabe et al. 2009
α-$Na_2Ca_6Si_4O_{15}$	*P* 2_1/*c*	$5.525 \approx t_K$	17.413	14.489	90.57	Armbruster and Röthlisberger 1990
$Na_2Ba_6Si_4O_{15}$	*P* 2_1/*c*	9.508	7.856	$11.528 \approx 2 \times t_K$	107.63	Tamazyan et al. 1987
β-$Na_2Ca_6Si_4O_{15}$	*P c*	9.0112	7.3171	$10.9723 \approx 2 \times t_K$	107.72	This paper

fundamental building blocks of structural inorganic chemistry (Kolitsch and Fleck 2006 and references cited therein). In the present compound, these chains are located in 4.55 Å wide layers running parallel to (010). Adjacent sheets are shifted relative to each other by an amount of +δ or −δ. Consequently, a …ABABAB… stacking sequence is created, where chains of neighboring layers are linked by corner sharing of common oxygen atoms (see Fig. 2a). The resulting three-dimensional network contains tunnel-like cavities in which the remaining more irregularly coordinated Na- and Ca-ions are incorporated. Principally, the α-form first described by Armbruster and Röthlisberger (1990) shows the same structure motifs. However, in this polymorph a four layer stacking …ABCDABCD… of the chains is observed. The series of relative shifts is…+δ,+δ,−δ,−δ,+δ,+δ,… (see Fig. 2b)

Comparison with related structures

Kröhnkite-type chains have been already shown to be major constituents of several silicates with the general composition $A_2B_6Si_4O_{15}$. Apart from both $Na_2Ca_6Si_4O_{15}$ polymorphs, $K_2Ca_6Si_4O_{15}$ (Arroyabe et al. 2009) and $Na_2Ba_6Si_4O_{15}$ (Tamazyan et al. 1987) also belong to this family of crystal structures. Table 5 presents a summary of the basic crystallographic data of these materials. It is obvious, that the translation period of the kröhnkite-type chains of about 5.5-5.6 Å is reflected in one of the lattice parameters of each phase. Furthermore, the comparisons of (i) the unit cell metrics as well as (ii) the graphical representations of β-$Na_2Ca_6Si_4O_{15}$ and $Na_2Ba_6Si_4O_{15}$ given in Figs. 2a/c and 3a/b point to a closer relationship between both compounds. In order to characterize the four mixed tetrahedral-octahedral frameworks in more detail a topological analysis has been performed using

Table 6 Coordination sequences $\{N_k\}$ of the tetrahedrally (T: Si) and octahedrally (M: Ca/Na) coordinated nodes (without the O atoms) as well as the extended point symbols for different mixed frameworks with composition $A_2B_6Si_4O_{15}$. Labels of the atoms correspond to those given in the publications

Compound	T/M-atom	Coordination sequences $\{N_k\}$ (k = 1–10)										Extended point symbol
		1	2	3	4	5	6	7	8	9	10	
$K_2Ca_6Si_4O_{15}$	Si(1)	3	12	17	38	54	78	111	143	192	231	4.4.4
	Si(2)	3	11	21	44	60	86	125	163	201	242	4.6.6
	Ca(1)	6	10	27	38	64	96	117	160	200	242	$4.4.4.4.4.4.6.6_2.6_2.6_2.6_2.6_2.6_4.8_9.8_9$
α-$Na_2Ca_6Si_4O_{15}$	Si(1)	3	12	17	38	54	78	111	143	192	231	4.4.4
	Si(2)	4	15	19	42	59	85	123	144	193	242	$4.4.4.4.4.6_2$
	Si(3)	3	12	20	33	53	83	116	156	187	229	$4.6_2.6_2$
	Si(4)	4	14	20	37	52	85	126	146	184	239	$4.6.4.6.4.6_2$
	Ca(3)	6	10	27	35	60	89	114	157	184	232	$4.4.4.4.4.4.6_2.6_2.6_2.6_2.6_2.6_3.8_8.8_9.8_9$
	Ca(7)	6	9	23	35	58	84	114	156	192	231	$4.4.4.4.4.4.6.6_2.6_2.6_2.6_3.6_3.6_4.8_{10}.8_{10}$
$Na_2Ba_6Si_4O_{15}$	Si(1)	3	11	23	46	66	93	145	183	228	272	$4.8_2.8_2$
	Si(2)	4	15	19	45	78	99	146	162	228	318	$4.4.4.4.4.6_2$
	Na(1)	6	10	28	43	70	112	129	185	232	371	$4.4.4.4.4.4.6_2.6_2.6_2.6_2.6_2.6_4.8.8_8.\ 8_8$
β-$Na_2Ca_6Si_4O_{15}$	Si(3)	3	11	23	46	66	93	145	183	228	272	$4.8_2.8_2$
	Si(4)	3	11	23	46	66	93	145	183	228	272	$4.8_2.8_2$
	Si(1)	4	15	19	45	78	99	146	162	228	318	$4.4.4.4.4.6_2$
	Si(2)	4	15	19	45	78	99	146	162	228	318	$4.4.4.4.4.6_2$
	Ca(2)	6	10	28	43	70	112	129	185	232	371	$4.4.4.4.4.4.6_2.6_2.6_2.6_2.6_2.6_4.8.8_8.\ 8_8$
	Ca(4)	6	10	28	43	70	112	129	185	232	371	$4.4.4.4.4.4.6_2.6_2.6_2.6_2.6_2.6_4.8.8_8.\ 8_8$

the program TOPOS4.0 (Blatov 2012). Therefore, the crystal structures have 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 $\{N_k\}$ ($k = 1,..,n$), 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. The results of the topological analysis can be summarized as follows: (i) Despite the differences in space group symmetry $Na_2Ba_6Si_4O_{15}$ and β-$Na_2Ca_6Si_4O_{15}$ represent the same mixed-framework type, i.e. they are topologically equivalent. (ii) Although α- and β-$Na_2Ca_6Si_4O_{15}$ both are based on kröhnkite-type chains their mixed frameworks are significantly different, i.e. a potential α→β transition requires a larger re-arrangement of the structure and not only small shifts or tilts of the polyhedral units. (iii) The framework within the crystal structure of $K_2Ca_6Si_4O_{15}$ in turn is not topologically equivalent to those observed in the other three phases.

Furthermore, so-called *polyhedral microensembles* or *PME*'s were constructed for β-$Na_2Ca_6Si_4O_{15}$. On the lowest sublevel they are formed for *each* octahedron and tetrahedron in the asymmetric unit by considering all *directly* bonded $[MO_6]$- and $[TO_4]$-groups. They represent a geometrical interpretation of the coordination sequences up to the index $k = 3$. The *PME*'s of the first sublevel observed for the M nodes can be described as follows: each $[MO_6]$-octahedron is immediately linked to six tetrahedra (see Fig. 4a). According to the classification given by Ilyushin and Blatov (2002) based on the calculation of the coordination sequences up to $k = 3$ (including the oxygen atoms) the *PME's* can be denoted as {6,6,18} (for Ca(2) and Ca(4)). For the *PME*'s of the four crystallographically independent tetrahedral T (Si) nodes two groups of ensembles can be distigushed: {4,4,20} (for Si(1) and Si(2)) as well as {4,3,13} (for Si(3) and Si(4)) (see Fig. 4b and c).

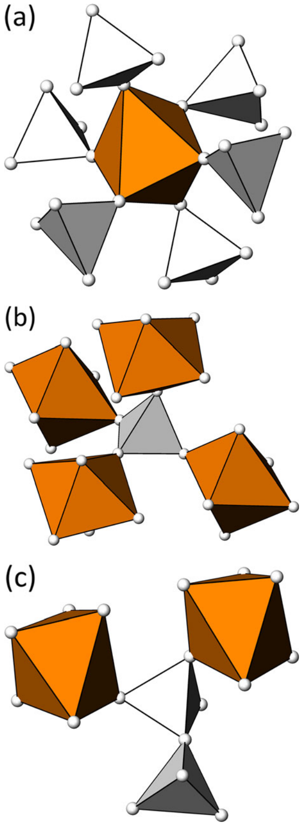

Fig. 4 *PME's* for the M- and the T-nodes in β-$Na_2Ca_6Si_4O_{15}$ drawn in polyhedral representations. (a) {6,6,18} (for Ca(2) and Ca(4)), (b) {4,4,20} (for Si(1) and Si(2)) as well as (c) {4,3,13} (for Si(3) and Si(4))

The similarity between the values of the lattice parameters of $Na_2Ba_6Si_4O_{15}$ and β-$Na_2Ca_6Si_4O_{15}$ as well as the topological equivalence of their mixed frameworks prompted us to look for further structural correlations based on group theoretical considerations. First of all, the space group types of $Na_2Ba_6Si_4O_{15}$ ($P12_1/c1$) and β-$Na_2Ca_6Si_4O_{15}$ ($P1c1$) are in a group-subgroup relationship, i.e. $P1c1$ is a *translationengleiche* subgroup of index 2 of $P12_1/c1$. For a more detailed analysis the program STRUCTURE RELATIONS available via the web site of the Bilbao Crystallographic Server was employed (Tasci et al. 2012). The software is able to find relations between a crystal structure S with space group symmetry H when it can be derived from a virtual or real parent structure in a higher symmetry G using a left coset decomposition of G with respect to H: $G = H + g_2H + \ldots + g_nH$. In the next step the structure S to be tested is compared with the transformed structures g_iS. If the differences between the corresponding pairs of atoms in S and g_iS are below a certain threshold Δ_{max}, a relationship is indicated. In the present case a relation between $Na_2Ba_6Si_4O_{15}$ and β-$Na_2Ca_6Si_4O_{15}$ is suggested if a maximum tolerance of 2 Å for the shifts between corresponding atoms is allowed. Both structures are related according to the following transformation (P,p): a,b,c (0.0041,-¼,-0.0098), i.e. the sequence of the lattice parameters is not changed. However, an origin shift has to be applied. The deviations in Ångstrom between the positions of the corresponding atoms for the different atom types in the $Na_2Ba_6Si_4O_{15}$ and β-$Na_2Ca_6Si_4O_{15}$ structures are as follows: tetrahedrally coordinated cations (spread: 0.158–0.568; average: 0.364), octahedrally coordinated cations (spread: 0.082; average: 0.082), non-framework cations (spread: 0.107 – 0.828; average: 0.356) and oxygen anions (spread: 0.134–1.697; average: 0.601). It is interesting to note, that the largest shift of about 1.7 Å occurs between the bridging oxygen atoms of the $[Si_2O_7]$–dimers. However, the average displacement of all corresponding atoms in both structures is relatively small and has a value of 0.172 Å.

Discussion

As mentioned in the experimental section a pronounced weight loss due to evaporation of Na_2O was observed shifting the bulk composition of the sample away from $Na_2Ca_3Si_2O_8$ located on the tie-line Ca_2SiO_4 – Na_2CaSiO_4. This result is also of importance, because previous synthesis experiments by Maki (1969) and other groups were performed under similar conditions concerning temperature treatment of the samples. Therefore, it can be anticipated that the above mentioned substantial Na_2O losses must have occurred in the older experiments as well. $Na_2Ca_3Si_2O_8$ (starting composition and chemical formula suggested by Maki) and $Na_2Ca_6Si_4O_{15}$ (the composition determined for our crystals) can be related by the following equation: 2 $Na_2Ca_3Si_2O_8$ -> $Na_2Ca_6Si_4O_{15}$ + Na_2O, i.e. the requested change of the bulk composition to produce a

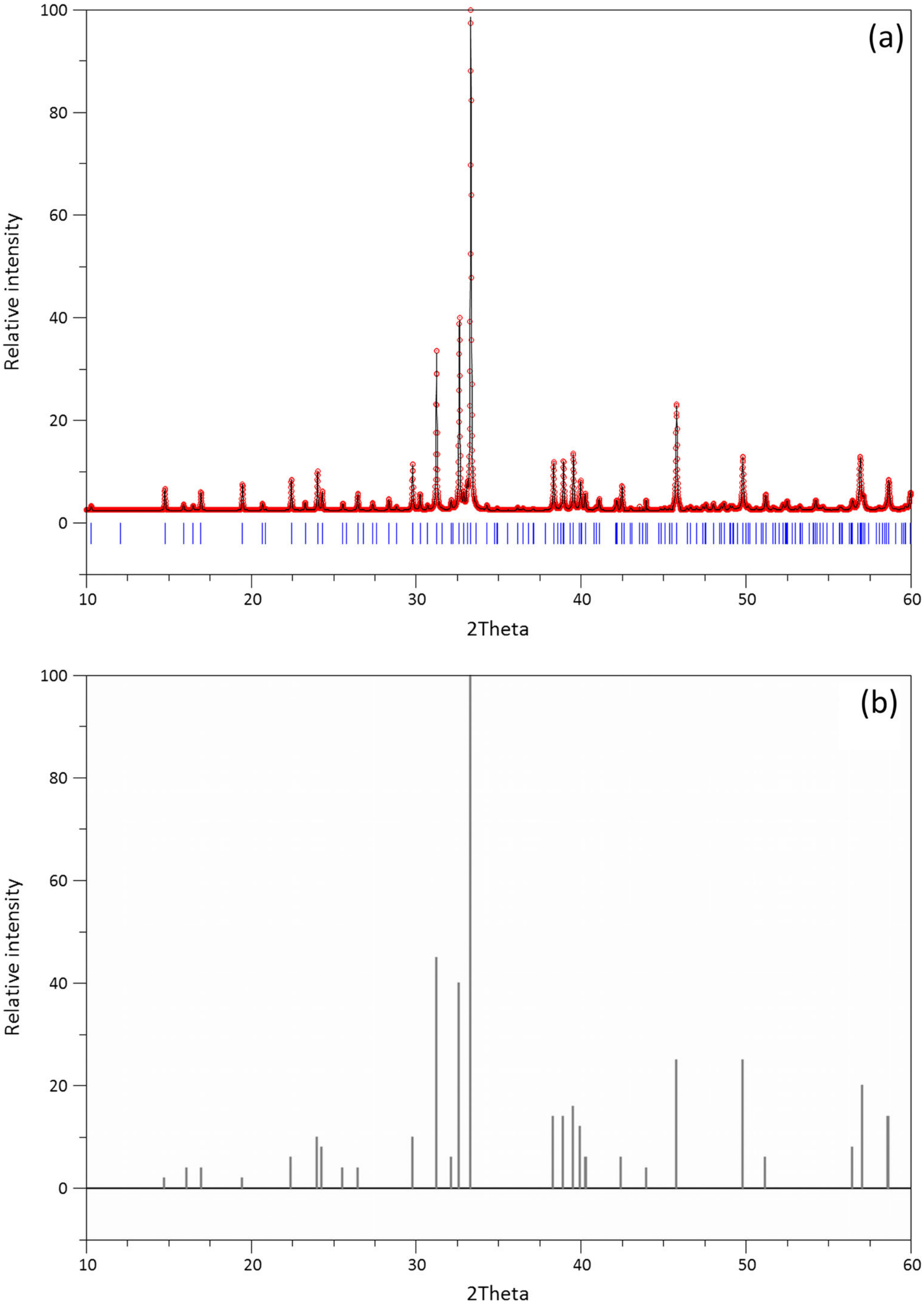

Fig. 5 Comparison between (a) the simulated powder diffraction pattern of β-$Na_2Ca_6Si_4O_{15}$ based on the crystallographic data given in Tables 1 and 2; for the calculations the program FullProf.2 k (Rodriguez-Carvajal 2011) has been employed (λ = 1.54056 Å, Bragg-Brentano geometry, TCH-pseudo Voigt functions) and (b) the experimental powder pattern from PDF-entry no. 00-023-0670 for monoclinic $Na_2Ca_3Si_2O_8$ based on the data reported by Maki (1969)

phase pure $Na_2Ca_6Si_4O_{15}$ sample could be simply induced by partial volatilization of the sodium oxide component. Of course, in case that the Na_2O losses are lower than needed for the reaction to be complete other phases such as Na_2CaSiO_4 or Ca_2SiO_4, for example, have to be present as well.

Furthermore, there is a striking similarity between Maki's postulated monoclinic $Na_2Ca_3Si_2O_8$-phase and β-$Na_2Ca_6Si_4O_{15}$ not only what concerns the unit cell parameters but also what concerns the principle distribution of the relative intensities. The comparison between the calculated powder diffraction pattern of β-$Na_2Ca_6Si_4O_{15}$ and the data for $Na_2Ca_3Si_2O_8$ based on the PDF-entry 00-023-0670 is given in Fig. 5. The remaining small differences could be due to slightly different distributions of the Na/Ca atoms on the non-tetrahedrally coordinated sites, for example. In summary one can say that there are strong indications that monoclinic $Na_2Ca_3Si_2O_8$ is actually misinterpreted β-$Na_2Ca_6Si_4O_{15}$.

This leaves the question whether Maki's triclinic $Na_2Ca_3Si_2O_8$ polymorph may de facto also correspond to a further $Na_2Ca_6Si_4O_{15}$ modification. If so, several very recent publications on the luminescent properties of REE-doped $Na_2Ca_3Si_2O_8$ where phase identification was solely based on the evaluation of powder diffraction patterns using the PDF-entry 00-023-0668 have to be revised (Jin et al. 2015; Fu and Hu 2016).

Finally, we would like to point out that single-crystals of α-$Na_2Ca_6Si_4O_{15}$ were obtained by Armbruster and Röthlisberger (1990) as a by-product in experiments aiming on the synthesis of silicate-germanate melilite-type compounds using NaOH solutions under *hydrothermal* conditions (0.2 GPa, 700 °C). So far, however, this compound has not been mentioned in any of the previous phase equilibrium studies. The results of our investigation demonstrate that at least another polymorph of $Na_2Ca_6Si_4O_{15}$ can be prepared by standard ceramic methods without any application of pressure. This indicates that $Na_2Ca_6Si_4O_{15}$ has a stability field in the system Na_2O-CaO-SiO_2 at ambient pressure and that additional phase analytical studies are necessary to clarify this point. Notably, more than ninety years after the first comprehensive study of Morey and Bowen (1925) this ternary system still holds many surprises.

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