Na$_2$Si$_3$O$_7$: An incommensurate structure with crenel-type modulation functions, refined from a twinned crystal*

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Abstract

The structure of metastable, incommensurately modulated Na$_2$Si$_3$O$_7$ has been determined from single crystal X-ray diffraction data. In contrast to previous investigations which stated that the compound crystallises orthorhombic, this study shows that the compound is monoclinic with a pseudo orthorhombic cell and is affected by twinning. The structure is described in the (3+1)-dimensional superspace. Crenel-type modulation functions are used to account for an aperiodic sequence of enantiomorph oriented zweiwer single chains of silicate tetrahedra. The modulation mainly affects one of the two symmetrically independent tetrahedral chains, which are connected to build up [Si$_3$O$_7$]$^{2-}$ layers. Sodium cations are coordinated by five oxygen ligands and provide linkage between adjacent tetrahedral sheets. Distortions of the silicate tetrahedra and crystal chemical relationships of the title compound to sodium and lithium di- and metasilicates are discussed in detail.

1 Introduction

The system Na$_2$O-SiO$_2$ and the phase relationships between the crystalline and vitreous sodium silicates have been the subject of many investigations (Williamson & Glasser 1965, Williamson & Glasser 1966, Hoffmann & Scheel 1969, Shahid & Glasser 1971, Scherer & Uhlmann 1975, Mogensen & Christensen 1981, Neilson & Weinberg 1984, Zaitsev, Shelkova, Lyakishev & Mogutnov 1999, Meshalkin & Kaplun 2003). This is mainly due to the fact that these compounds are of considerable importance in materials science: Sodium silicates are basic constituents of the synthesis of glasses and ceramics. However, crystalline phases such as Na$_2$Si$_3$O$_5$ have been studied because of their high ion-exchange capacity and selectivity (Wolf & Schwieger 1979) as well as their two-dimensional sodium diffusion and conductivity (Heinemann & Frischat 1990). A review of industrial uses with an emphasis on applications as builders in washing powders can be found in the article of Rieck (1996). From a crystal chemists point of view it is interesting to note that the existence of several sodium silicates has been known for more than forty years, although their crystal structures remained to be solved. For example, only very recently a detailed structural study on Na$_6$Si$_8$O$_{19}$ has been reported.

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(Krüger, Kahlenberg & Kaindl 2005). An important reason for the problems with the structural characterisations can be definitely attributed to the fact that many of the SiO$_2$-rich phases reported in the literature are metastable compounds and consequently of low quality for X-ray diffraction. One of the phases belonging to this class of materials is sodium trisilicate, Na$_2$O · 3SiO$_2$. Williamson & Glasser (1966) prepared Na$_2$Si$_3$O$_7$ single crystals from the devitrification of glasses with > 67 Mol.% SiO$_2$ at temperatures of about 923K and reported an orthorhombic $C$-centred unit cell of $a$=20.6, $b$=6.50, $c$=4.90 Å. A subsequent structural study of Jamieson (1967) on these crystals revealed that the diffraction pattern was much more complex involving additional satellite reflections with non-integral indices. Focusing on the strong main reflections a preliminary structural model for Na$_2$Si$_3$O$_7$ was sketched in space group $Cmc_2_1$. However, due to an unacceptable final $R$ index of about 0.18 in combination with extremely high atomic displacement parameters for some of the oxygen atoms no atomic coordinates were reported. On the other hand, Na$_2$Si$_3$O$_7$ can occur in a second modification. It is known, that sodium trisilicate prepared from the careful dehydration of Na$_2$Si$_3$O$_7$ · H$_2$O at 713K adopts an interrupted framework structure with three- and four-connected [SiO$_4$]-tetrahedra with a ratio of $Q^3$: $Q^4$ = 2:1 (Kahlenberg, Marler, Muñoz Acevedo & Patarin 2002). Furthermore, a high-pressure modification of Na$_2$Si$_3$O$_7$ has also been described (Fleet & Henderson 1995) and crystallises in a monoclinic framework structure containing diothosilicate [Si$_2$O$_7$] groups as well as isolated [SiO$_6$] octahedra. A discussion on polymorphism of [Si$_3$O$_7$] anions in layered silicates was published by Pushcharovsky & Belov (1978). The present investigation was aimed to investigate the apparently modulated structure of Na$_2$Si$_3$O$_7$ in more detail and to clarify structural relationships with other known silicates.

2 Experimental details

Single crystals of Na$_2$Si$_3$O$_7$ were grown by isothermal aging of a glass of stoichiometric composition. The glass was prepared by mixing the analysis grade chemicals Na$_2$CO$_3$ and SiO$_2$ (fine grained quartz) in a molar ratio of 1.3. The mixture was homogenised in an agate mortar, subsequently filled in a platinum crucible. The reagents were high temperature treated at 1773K for 1h in a resistance-heated furnace, followed by quenching to room conditions. The obtained glass was used as starting material for devitrification by static heat-treatment at 873K. Single crystals were found in samples heated for 48h. They were generally of bad optical quality and their X-ray diffraction patterns were also of poor quality. In order to achieve crystals of better characteristics devitrification experiments at 873K were performed up to 34 days. Unfortunately, even after this long heat treatment the crystal quality did not significantly increase. Nevertheless, a platy shaped crystal from this experiment was selected by optical criteria using a polarising microscope and mounted on a glass fibre for single crystal X-ray diffraction experiments. Further details of the data collection are summarised in Table 2. A re-investigation of the same crystals 14 months after the data collection (stored at room conditions), showed that the compound is not stable. The crystals decomposed to an amorphous material, which showed no significant diffraction intensities.

3 Refinement

As already pointed out by Jamieson (1967), the diffraction pattern of Na$_2$Si$_3$O$_7$ shows two types of reflections: The first type, strong Bragg reflections, can be indexed with a monoclinic $C$-centred lattice. The monoclinic angle is approximately 90° implying high orthorhombic pseudosymmetry (see Tab. 2). The second type are generally weaker satellite reflections, which can be indexed with an incommensurate vector $q$ of $(0, \beta, 0)$ with $\beta = 0.562(2)$. The refinement of the cell parameters and the wave vector $q$, as well as the data reduction was carried out using the software provided by STOE & Cie GmbH (2005). The internal $R$ value for the main reflections in the Laue group 12/m1 is 0.06, whereas $R_{int}$ for the other settings $(2/m1, 112/m)$ as well as for $2/m2/m2/m$ is about 0.14-0.16. The analysis of systematic absent reflections points to $Cc$ or $C2/c$ as possible space groups of the average structure. In fact, the structure could be solved in $C2/c$ using direct methods (Altomare, Burla, Camalli, Cascarano, Giacovazzo, Guagliardi, Moliterni, Polidori & Spagna 1997) and was consecu-
### Table 1: Crystal data and experimental details

<table>
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<th>Crystal data</th>
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<tr>
<td>Chemical Formula</td>
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<tr>
<td>M</td>
<td>242.2</td>
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<tr>
<td>Superspace group</td>
<td>$C2/c(0/0/3)$s0</td>
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<td>20.416(6)</td>
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<td>$b$(Å)</td>
<td>6.4987(15)</td>
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<td>$c$(Å)</td>
<td>4.9294(19)</td>
</tr>
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<td>90.26(3)</td>
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<tr>
<td>$V$(Å³)</td>
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<tr>
<td>$D_{calc}$(Mg m$^{-3}$)</td>
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<td>$\mu$(mm$^{-1}$)</td>
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</tr>
<tr>
<td>No. of obs. reflections (main; sat)</td>
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<td>Reflection ranges</td>
<td>$-25 \leq h \leq 25; -8 \leq k \leq 8; -6 \leq l \leq 4; -1 \leq m \leq 1$</td>
</tr>
</tbody>
</table>

| Refinement                                        |                  |
| Refl. used in ref. (all; main; sat)               | 1914; 685; 1229  |
| $\theta_{max}$(°)                                 | 26.71            |
| Parameters refined                                | 157              |
| Refinement on                                     | F                |
| $R_{int}$                                         | 0.082            |
| $S$                                               | 2.30             |
| $R$ (all; main; sat)                              | 0.112; 0.070; 0.164|
| $R_w$ (all; main; sat)                            | 0.065; 0.051; 0.092|
| Weighting scheme                                  | based on $\sigma$; $w = 1/(\sigma^2(F) + (0.01F)^2)$ |
| $(\Delta/\sigma)_{max}$                          | 0.0004           |
| $\Delta \rho_{max}$: $\Delta \rho_{min}$(eÅ$^{-3}$) | 1.07; -0.80      |

Computer programs used: Stoe X-Area (STOE & Cie GmbH 2005), Jana2000 (Petříček, Dušek & Palatinus 2000), structural graphics were prepared using DRAWxtl (Finger, Kroeker & Toby 2005).
tively refined to a weighted $R$ value of 0.32. The orthorhombic pseudosymmetry of the lattice suggested additional twinning. The difference of $0.26^\circ$ between the monoclinic angle $\beta$ and $90^\circ$ should lead to a splitting of the reflections with higher indices ($h$ or $l$), if twinning is present. In reconstructed sections of the reciprocal space the reflections with higher $l$ indices show an elongation along the $a$-direction, suggesting a mirror plane perpendicular to the $a$ axis as twin element. The theoretical distance between the split diffraction spots (for the highest observed index $l = 6$) is about 0.011Å$^{-1}$, alternatively 0.23, given in units of the index $h$. According to the small distances, the diffraction spots were not separated during the integration, leading to completely overlapped reflections. In fact, the refinement could be significantly improved ($R_w = 0.18$) by introducing one of the additional orthorhombic symmetry elements as twin operator (we chose the mirror plane perpendicular to the $a$ axis). The twin volume fraction of individual II obtained in the final refinement is 0.330(3). The introduction of anisotropic displacement parameters for all atoms led to a final $R_w$ value of 0.07 for the average structure.

For the satellite reflections an additional extinction rule for reflections $0k0m$ with $m \neq 2n$ is observed, suggesting the superspace symmetry element $\mathbf{s}_2$. The only $(3+1)$-dimensional superspace group in compliance with this condition is $C2'/c(030)s0$, which is an alternative setting of superspace group $B2'/b(00\mathbf{t})s0$ (No. 15.3) as listed in Janssen, Janner, Looijenga-Vos & de Wolff (1995). By choosing the $\mathbf{q}$-vector within the first Brillouin-zone $\{0, 1 - \beta, 0\}$, i.e. assigning the satellites to the main reflections extinct by the $C$-lattice the equivalent superspace group $X2'/c(030)s0$ with a centring vector of $(\frac{1}{2}, \frac{1}{2}, 0, \frac{1}{2})$ could be used. In order to stay conform with the cell chosen by Jamieson (1967) we decided to use the description in $C2'/c(030)s0$.

The refinement of the modulated structure was carried out using first order satellite reflections only, as the average $I/\sigma(I)$ ratio of the second order satellites was less than 1.4.

To describe the four-dimensional structure two crenel functions (Petřiček, van der Lee & Evain 1995) to define the occupational modulation of the atoms Si2 and O3 were employed. These atoms correspond to split atom positions in the three-dimensional average structure, where two distinct orientations of one [SiO$_4$] tetrahedra are realised. In the four-dimensional description the two split atom positions of the ‘crenel atoms’ Si2 and O3, respectively, are linked by the superspace symmetry element $\mathbf{s}_2$ and are phase shifted by $\tau = 1/2$. To ensure that for all physical space sections only the atoms belonging to one of the two alternative tetrahedral positions are present, the phases of Si2 and O3 have to be restricted according to the following equation:

$$\ell^0_4(O3) = \ell^0_4(Si2)$$

For the same reason, the widths of the crenel functions, expressed via the parameter $\Delta$, also have to be set equal. Since these parameters did not refine to values significantly different from 0.5, they were fixed at this value. Values of $\Delta$ differing from 0.5 would lead to physically unacceptable situations: values larger than 0.5 would cause the existence of cells with two fully occupied sites, whereas $\Delta < 0.5$ would leave some cells unoccupied.

The only positional parameter of the ‘crenel atoms’, which was refined additionally with a harmonic modulation function was $x_1$ of Si2. Other positional modulations could only be refined by introducing an orthogonalisation procedure (Petřiček et al. 1995) for the atoms Si2 and O3, respectively. Without the orthogonalisation extremely large correlations between the coordinates of the atoms and the displacive modulation functions occurred. However, the refinement of more positional waves for Si2 and O3 did not significantly improve the refinement. Therefore the orthogonalisation method was not included in the final model.

For the remaining atoms all positional parameters, as well as anisotropic displacement parameters, were refined with first order harmonic modulation functions.

4 Structure and modulations

As already shown by Jamieson (1967) Na$_2$Si$_2$O$_7$ is composed of layers of composition [Si$_3$O$_7$]$^{2-}$ which are arranged parallel to the $b$, $c$-plane and stacked along the $a$ direction (Fig. 4). Between the layers sodium cations (green in the figures) are located to compensate for the charge. Each layer is built up by two independent tetrahedral chains running along $c$. The periodicity of these chains is
two, therefore they are called zweier single chains (Liebau 1985). The silicate tetrahedra of the central chain (red in the figures) is $Q^4$ connected (via all four corners), the outer chain (blue in the figures) has a lower connectedness of three. Each individual chain comprises only one symmetrically independent tetrahedra.

As can be seen in Fig. 4 the $Q^4$ chain is disordered in the average structure. The oxygen atom (O4) connecting to the outer chains is fixed at one position, but the central silicon (Si2) and the oxygen atom connecting along the chain direction (O3) are occupying two positions with occupancy factors of 0.5. To show the distinct positions of the Si2 atom the central chain in Fig. 4 is kept transparent. The two resulting orientations of the central chain are enantiomorphic and can arbitrarily be called left- (L) and right-oriented (R).

The crenel modulation functions describing the positions of the Si2 and O3 atom in the modulated structure are indicated in the the $x_3 - x_4$ sections (Fig. 4 and 4, respectively) of the electron density maps as obtained from the the final refinement.

The two corresponding orientations of the tetrahedra are periodically alternating in the (3+1)-dimensional structure, whereas in three-dimensional physical space an aperiodic sequence of these two orientations is present within one layer. A similar incommensurately modulated sequence of tetrahedral chains was recently described by Krüger & Kahlenberg (2005) in the Brownmillerite-type compound Ca$_2$Fe$_5$O$_5$ at high temperatures. In the structure presented here, the basic sequence of the orientation of the central chain in physical space is alternating. After seven or eight alternations, RR or LL-pairs of equally oriented chains follow. A fragment of such a sequence could be: R-L-R-L-R-L-R-L-R-L-R-L-R-R-L. A two-dimensional physical space section (at $t = 0$) of the four-dimensional $F_{\text{obs}}$-map intersecting at $x_1 = 0.25$ (see Fig. 4) exhibits such a sequence of chains within one layer. This section cuts the central chains of one layer almost exactly at the coordinates of Si2 and O3. RR or LL pairs require the physical space section to cut the internal dimension close to the ‘jumps’ in the crenel functions. Due to a partial overlapping of the electron densities in these areas, the second orientation of the chain can be seen (although weaker) in the t-map at $3 < x_2 < 5$.

The distances from Si2 to the tetrahedrally coordinating oxygen atoms are shown in Fig. 4, for the $t$-range of 0 to 0.5 (corresponding to the width of the crenel function). The curves show the modulated distances, the constant lines of the same colour show the unmodulated distances between the atoms. For the two O4 atoms the unmodulated distances are quite short: 1.548(4) and 1.566(4) Å for O4 ($x, y, z$) and O4 ($-x, y, 1/2-z$), respectively. The averaged distances as obtained from the modulated structure show larger values of 1.594(7) and 1.589(8) Å. Consequently, the modulation relaxes the Si2-tetrahedra (hereafter called T2). This effect can also be seen in the bond valence sum (Brown & Altermatt 1985) of Si2, the unmodulated value of which is 4.45(10), yet the value averaged over the modulated structure is 4.28(10).

The mean quadratic elongation ($\lambda_{\text{tet}}$) and the tetrahedral angle variance $\sigma^2_{\theta(\text{tet})}$ as defined by Robinson, Gibbs & Ribbe (1971) were calculated in dependence of $t$ for the coordination tetrahedra of both silicon atoms using Mathematica (Wolfram Research, Inc. 2003). $t$-dependent values of $\lambda_{\text{tet}}$, $\sigma^2_{\theta(\text{tet})}$, as found by Robinson et al. (1971) for a large number of rock-forming silicates. This is understandable if one takes into account that the displacive modulations affecting the T2 tetrahedra in this case are fairly simple: though all three fractional coordinates of O4 are affected by displacive modulation, O3 has no positional modulation at all and only one fractional coordinate ($x$) of Si2 is modulated.

The other tetrahedra (around Si1, hereafter called T1), which is affected by displacive modulation only, also shows a relaxation of the bond
Figure 1: The layers viewed parallel to the direction of the chain. The red polyhedra represent the disordered central chain, the blue ones the outer chains. Green spheres depict sodium atoms.

Figure 2: View parallel to the stacking direction of the sheets. Two distinct positions of the disordered central chain (red) are represented. Black spheres represent Si2 atoms, green spheres sodium atoms. One layer in the $x$-range of 0.2-0.8 is shown.
Figure 3: The crenel modulation function of the Si2 atom. $x_3 - x_4$ map, intersecting the four-dimensional $F_{\text{obs}}$ Fourier synthesis at $x_1 = 0$, $x_2 = 0.136$. Contour lines from 3 to 30 eÅ$^{-3}$ in intervals of 3 eÅ$^{-3}$. The map is summed up in $x_1$ and $x_2$ in a range of 0.5Å.

Figure 4: The crenel modulation function of the O3 atom. $x_3 - x_4$ map, intersecting the four-dimensional $F_{\text{obs}}$ Fourier synthesis at $x_1 = 0$, $x_2 = -0.0607$. Contour lines from 2 to 10 eÅ$^{-3}$ in intervals of 2 eÅ$^{-3}$. The map is summed up in $x_1$ and $x_2$ in a range of 0.5Å.
Figure 5: Physical space map $(x_2 - x_3)$ at $t = 0$, $x_1 = 0.25$ calculated from four-dimensional $F_{obs}$-Fourier synthesis. Incommensurately modulated sequence of right-(R) and left-handed (L) tetrahedral chains can be seen. Positions of Si2 and O3 are indicated.
Figure 6: Modulated and unmodulated Si2-O distances.

Figure 7: Distortion of Si1 and Si2 tetrahedra. Mean quadratic elongation plotted versus tetrahedral angle variance. Numbers next to the curves represent $t$-values.

Figure 8: Modulated and unmodulated Si1-O distances.
valence sum due to the modulation. The unmodulated bond valence sum is 4.14(10), the averaged value for the modulated structure is 4.07(10). A corresponding \( t \)-dependent plot can be found in the supplementary material. The Si1 exhibits one short non-bridging bond to O2 [average 1.575(7) \( \text{\AA} \)]. Strong modulated distances are those to O1 (1/2 - x, 1/2 - y, z) and O1 (1/2 - x, 1/2 + y, 1/2 - z), which show fluctuations from 1.603(8)-1.723(8) and 1.583(7)-1.665(7) \( \text{\AA} \), respectively. The bond distance of more than 1.72 \( \text{\AA} \) seems to be quite large, but a plot of all distances regarding Si1 (Fig. 4) shows, that the maximum (at \( t \approx 0 \)) in the Si1-O1 (1/2 - x, 1/2 - y, -z) bond distance has to compensate for the other bonds, which exhibit minima at the same \( t \). The fifth curve in Fig. 4 (denoted by \( l_0 \)) represents the Si-O distance of an ideal tetrahedra of the same volume. This distance is used as a reference value in the calculation of the mean quadratic elongation. In the \( t \)-interval between 0.28 and 0.69 the \( (\lambda_T^1) \) parameter of T1 becomes smaller than one, which is caused by the minima of three bond lengths in this interval. The maximum of the tetrahedral angle variance is 26.4 at \( t = 0 \). The distortion plot of T1 exhibits an ‘egg-shaped’ outline and does not show any linear correlation between \( (\lambda_T^1) \) and \( \sigma^2_{\theta(T^1)} \). All involved atoms (of T1) are modulated in all directions, therefore the O-O distances and O-T1-O angle functions are represented by higher order harmonic functions and do not show correlations.

A look at the environment of the sodium atom reveals a 5-fold coordination by oxygen. All coordinating oxygen atoms belong to outer tetrahedral chains (i.e. chains limiting the tetrahedral layer). Four of the oxygen atoms form part of one tetrahedral layer, a fifth one (O2) connects to a neighbouring layer (Fig. 4). The coordination polyhedra can be described as a trigonal bipyramid, where, in general, the equatorial coordinating oxygen atoms are located at shorter distances than the axial oxygens. The variation of bond distances as observed in the modulated structures is given in Fig. 4. The extrema of the bond valence sum of the sodium atom are 0.94(8) and 1.09(8), the average value is 1.01(8). Additional \( t \)-dependent plots of Na-O distances and the bond valence sum can be found in the supplementary material.

5 Discussion
A structural comparison of Na\(_2\)Si\(_3\)O\(_7\) with sodium metasilicate Na\(_2\)SiO\(_3\) (McDonald & Cruickshank 1967) and sodium disilicate \( \alpha \)-Na\(_2\)Si\(_2\)O\(_5\) (Pant & Cruickshank 1968) was already realised by Jamieson (1967). The main results are the increasing condensation of the chains (with increasing SiO\(_2\) content), as well as the fact, that the coordination of the sodium atoms remains essentially the same in the different compounds [compare Fig. 3 in (Jamieson 1967)].

Until now, only three other compounds, which may possibly exhibit a similar [Si\(_3\)O\(_7\)]\(^{2-}\) silicate layer have been discovered: Na\(_2\)Cu(Si\(_3\)O\(_7\))\(_2\)-5H\(_2\)O, a hydrated compound derived by acid leaching (H\(_2\)Si\(_3\)O\(_7\)), and Li\(_2\)Si\(_3\)O\(_7\). For the sodium copper silicate an orthorhombic cell is given, determined by single crystal diffraction: \( a = 25.542(18), b = 13.065(10), c = 9.877(8)\text{\AA} \) (Hubert, Jordan, Guth & Kalt 1977). The second compound was investigated by IR-spectroscopy and powder diffraction techniques and considered to be of the same structural type, although the authors did not give any cell parameters (Guth, Hubert, Jordan, Kalt, Perati & Wey 1977). By inspecting the cell of the copper compound it is obvious, that the doubling of the \( c \) parameter (relative to the cell of Na\(_2\)Si\(_3\)O\(_7\)) would cause a doubling of the chain periodicity from two to four. The doubling of the \( b \)-lattice parameter, on the other hand, could be an evidence for a well ordered alternating sequence of L and R chains in the layer.

The third compound, Li\(_2\)Si\(_3\)O\(_7\), was first described by West & Glasser (1970) and later studied by Morozova, Gutkina & Shmatok (1972) and Kalinina, Maslenikov & Filipovich (1975). West & Glasser (1970) postulated a structure, similar to Na\(_2\)Si\(_3\)O\(_7\) without giving further structural details. A detailed structural study on this compound is currently under progress in our laboratory.

Examples for the effect of substituting lithium for sodium can be seen in the d- and metasilicates. For lithium disilicate, for example, two modifications are known: a stable form described by Liebau (1961) and a metastable one (Smith, Howie & West 1990). Both structures contain tetrahedrally coordinated lithium located between the disilicate layers, whereas the configuration and arrangement of the strongly folded layers is different.
Figure 9: The coordination scheme of the sodium atom in the average structure. The two outer tetrahedral chains (blue) belong to the closest neighbouring layer. One of the coordinating oxygen atoms (O2) belongs to the next \([\text{Si}_3\text{O}_7]\) layer. Distances corresponding to the modulated structure are shown.

[see Fig. 1(a,b) in (Smith et al. 1990)]. In the \(\alpha\)-\(\text{Na}_2\text{Si}_2\text{O}_5\) (Pant & Cruickshank 1968) the silicate layers are basically the same as in the metastable lithium disilicate. The coordination of the sodium anions is five-fold, as in \(\text{Na}_2\text{Si}_3\text{O}_7\).

In the metasilicates the differences in the anion coordination are comparable: Sodium is fivefold coordinated in \(\text{Na}_2\text{Si}_3\text{O}_5\) (McDonald & Cruickshank 1967), while lithium is tetrahedrally coordinated in \(\text{Li}_2\text{Si}_3\text{O}_5\) (Hesse 1977). The orientation of the tetrahedral chains is the same in both compounds. Investigations of West (1976) in the system \(\text{Na}_{2-x}\text{SiO}_3-\text{Li}_x\text{SiO}_3\) revealed a limited solid solubility. Samples with \(x = 1\) showed a six-fold supercell along \(a\). Further studies carried out by West (1977) confirmed the existence of a modulated structure. Later a detailed transmission electron microscopy study on the incommensurate phase in the range \(0.86 \leq x \leq 1.02\) was carried out by Withers, Thompson & Hyde (1989), who chose the same setting as Hesse (1977) for \(\text{Li}_2\text{SiO}_3\) (\(\text{Cmc}_2_1\)). According to the observed reflection conditions for the satellite reflections they proposed the superspace group \(\text{Cmc}_2_1(0/30)s0\) [which is another setting of \(\text{A}_2\text{ma}(00\gamma)0s0\) as listed as No. 36.8 in (Janssen et al. 1995)]. Interestingly, the orientation of the modulation wavevector is essentially the same as in modulated \(\text{Na}_2\text{Si}_3\text{O}_7\) i. e. both perpendicular to the direction of the chains and to the stacking direction of the layers (in metasilicates defined by layers of Li or Na). Furthermore, the intrinsic phase shift \(\tau = \frac{1}{2}\) is common in both phases. Withers et al. (1989) suggest an antiphase relationship of the Li and Na occupation of symmetry related sites. More detailed comparison of these two modulated structures requires a complete superspace embedded structural model for the sodium-lithium metasilicate, which is not available at the moment. Future investigations should also concentrate on the question of solid solubility in the systems \(\text{Na}_2\text{Si}_3\text{O}_7-\text{Li}_2\text{Si}_3\text{O}_7\) and \(\text{Na}_2\text{Si}_3\text{O}_7-\text{Li}_2\text{Si}_3\text{O}_5\), respectively, and the corresponding structural consequences.

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References


A Supplementary Material

Figure 10: Bond valence sum of Si1. The constant line represents the unmodulated value, the averaged value is lower at 4.07(10).

Figure 11: Modulated O-Si1-O bonding angles. Constant lines represent unmodulated angles.
Figure 12: Modulated O-O bonding angles in Si1 tetrahedra.

Figure 13: Modulated volume of Si1 tetrahedra.

Figure 14: Quadratic elongation of Si1 tetrahedra.
Figure 15: Tetrahedral angle variance of Si1 tetrahedra.

Figure 16: Bond valence sum of Si2. The constant line represents the unmodulated value, the averaged value is lower at 4.28(10).

Figure 17: Modulated O-Si2-O bonding angles. Constant lines represent unmodulated angles.
Figure 18: Modulated O-O bonding angles in Si2 tetrahedra.

Figure 19: Modulated volume of Si2 tetrahedra.

Figure 20: Quadratic elongation of Si2 tetrahedra.
Figure 21: Tetrahedral angle variance of Si2 tetrahedra.

Figure 22: Bond valence sum of the sodium atom Na1. The constant line represents the unmodulated value, the averaged value is at 1.01(8).

Figure 23: Modulated Na1-O distances. Constant lines represent unmodulated distances.