

Determination of the Substructure of $\text{Na}_2\text{ZnSi}_2\text{O}_6$, Synthesised in the Solid State

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The substructure of $\text{Na}_2\text{ZnSi}_2\text{O}_6$, synthesised in the solid state, has been determined from $\text{CuK}\alpha_1$ powder diffractometer data, using direct methods. It was refined by the Rietveld method to $R_F=9.9\%$ in the space group $C2/c$, with 14 positional parameters and a subcell with $a=6.176(1)$, $b=9.413(1)$, $c=9.790(1)$ Å and $\beta=93.7(1)^\circ$. The structure contains SiO_3^{2-} chains along [001], which are interconnected by ZnO_4 tetrahedra. Electron diffraction patterns showed that the true cell is primitive and has a tripled a -axis.

The compound $\text{Na}_2\text{ZnSi}_2\text{O}_6$ was identified by Holland and Segnit in a phase study of the $\text{Na}_2\text{O}-\text{ZnO}-\text{SiO}_2$ system¹. Unindexed powder diffraction data (JCPDS no. 20–1181) and some optical data, indicating a monoclinic symmetry, were given, and the compound was found to melt incongruently at 860 °C. It was subsequently encountered in a study of the ionic conductivity properties of sodium zinc silicates in the compositional region $\text{Na}_2\text{ZnSiO}_4-\text{Na}_2\text{ZnSi}_2\text{O}_6$.² It is a moderate Na^+ ion conductor with an activation energy of 0.64(2) eV and $\sigma=4.7 \times 10^{-6}$ S cm^{-1} at 325 °C. Its powder pattern could be indexed with a monoclinic unit cell with $a=9.790(1)$, $b=9.413(1)$, $c=12.351(1)$ Å, $\beta=93.7(1)^\circ$, $V=1135.8$ Å³ and a figure-of-merit $M(20)=20$ (JCPDS no. 37–410). The pattern did not agree with a calculated pattern for the reported structure of hydrothermally synthesised $\text{Na}_2\text{ZnSi}_2\text{O}_6$ (zinc chkalovite).³ The present study consists of a determination of the substructure of $\text{Na}_2\text{ZnSi}_2\text{O}_6$ obtained by solid-state synthesis.

Experimental

A sample of $\text{Na}_2\text{ZnSi}_2\text{O}_6$ was prepared by heat treatment of a mixture of corresponding amounts of analytical grade Na_2CO_3 , ZnO and SiO_2 at 750 °C for 8 days in air, with three intervening regrindings. The initial heating was made in steps in order to expel CO_2 slowly and prereact the sample.

Powder X-ray diffraction data were collected on a STOE STADI/P diffractometer, using monochromated $\text{CuK}\alpha_1$ radiation and a small linear-position sensitive detector covering 4.6° in 2θ . Data were recorded both for a sintered sample in reflection mode and for a powder

sample in symmetric transmission mode. The step-length was 0.02°, and the 2θ -range 10–130° was covered.

Electron diffraction patterns were recorded with a Jeol JEM-2000 FX-II transmission electron microscope. Differential thermal analysis was performed with a Setaram TAG 24 analyzer, operated in air with a heating rate of 10 °C min^{-1} .

Structure determination and refinement

The recorded X-ray diffractometer data for the prepared $\text{Na}_2\text{ZnSi}_2\text{O}_6$ agreed well with the previous Guinier–Hägg data,² with the difference that an additional number of very weak reflections could be observed. Differential thermal analysis revealed no phase transitions up to the melting point of the compound, which was determined to be 850 °C, in good agreement with the preceding report.

An examination of the powder pattern showed that all reflections except those with relative intensities less than ca. 3% can be indexed with an A -centered cell with half the c -axis of the original cell given above. An interchange of axes yields the conventional C -centered cell with $a=6.176(1)$, $b=9.413(1)$, $c=9.790(1)$ Å, $\beta=93.7(1)^\circ$ and $V=567.9$ Å³. No further systematic reflection absences could be reliably ascertained, which indicated $C2$, Cm and $C2/m$ as possible space groups for this cell.

Observed integrated intensities were extracted from the reflection mode data and converted into $|F|^2$ values by the program ALLHKL.⁴ The data set obtained was used with the direct-methods package SIRPOW.⁹¹⁵ to derive a partial structure of $\text{Na}_2\text{ZnSi}_2\text{O}_6$ in space group $C2$ ($Z=4$). The structural parameters generated by

SIRPOW.91 were then refined, using a local version of the DBW3.2S Rietveld program,⁶ yielding⁷ $R_F=7.3\%$ and a goodness-of-fit⁷ $S=5.8$ for 30 positional parameters and 347 theoretical reflections in the 2θ range $10\text{--}100^\circ$.

An inspection of the derived partial structure showed that the preferable space group symmetry is $C2/c$, and not $C2$. The presence of a glide plane along the c -axis was subsequently confirmed by electron diffraction (see below). Furthermore, the intensity statistics calculated by SIRPOW.91 strongly indicated a centrosymmetric structure. A total of 30 parameters were used in the final refinement in $C2/c$, including 14 positional parameters and a collective temperature factor for O atoms. The 2θ range $10\text{--}100^\circ$, containing 325 theoretical reflections, was used. The refinement yielded $R_F=9.9\%$ and $S=6.0$. A list of obtained atomic coordinates is given in Table 1. Because of serial correlation, the estimated standard deviations in the refinement are multiplied by 5.1.⁸ Figure 1 shows the fit between the observed and calculated patterns.

Practically equivalent atomic positions, and with similar estimated standard deviations, were obtained in a corresponding refinement using the transmission mode data. The refinement yielded $R_F=12.2\%$ and $S=2.2$. The substantially smaller S value in the transmission case

Table 1. Atomic coordinates for $\text{Na}_2\text{ZnSi}_2\text{O}_6$; space group $C2/c$; $a=6.176(1)\text{ \AA}$, $b=9.413(1)\text{ \AA}$, $c=9.790(1)\text{ \AA}$, $\beta=93.7(1)^\circ$ and $Z=4$.

Atom	Site	x	y	z	$B/\text{\AA}^2$
Zn	4e	0	0.715(2)	1/4	0.3(3)
Si	8f	0.145(4)	0.997(3)	0.634(2)	2.4(7)
Na	8f	0.547(5)	0.180(3)	0.592(3)	3.2(9)
O1	4a	0	0	0	5(1)
O2	4e	0	0.065(8)	1/4	5(1)
O3	8f	0.148(8)	0.607(6)	0.386(5)	5(1)
O4	8f	0.197(8)	0.151(6)	0.670(6)	5(1)

could be ascribed to a better fit obtained between observed and calculated peak positions. The reflection-mode data provided, on the other hand, considerably higher peak intensities.

Several shortcomings were evident for the $C2/c$ model. The corresponding interatomic distances, although on the whole reasonable, show some unsatisfactory variations. Secondly, the unit cell used could not account for the weak reflections in the powder pattern. Some of these could be indexed with the originally used larger primitive cell with a *doubled a-axis* (JCPDS no. 37-410, see above), while others could not. A fraction of these reflections could at this stage also possibly originate from unidentified impurity phases.

Electron diffraction patterns were therefore recorded in a transmission electron microscope in order to determine the correct unit cell and existing reflection absences. The study revealed that (i) the cell is primitive and not C -centered, (ii) that the a axis is *three times* longer than assumed and (iii) that the structure contains a c glide plane. A re-examination of the powder pattern showed that all observed reflections, including weak ones, could be accounted for by this larger cell.

The possible space groups for the larger primitive cell with a tripled a -axis are Pc and $P2_1/c$. Refinements of a model with three similar structure parts stacked along $[100]$ in a cell with $a=18.528\text{ \AA}$ did, predictably, not converge, owing to the large number of positional parameters; 198 in Pc and 99 in $P2_1/c$. An expanded part of the diffraction pattern corresponding to a refinement in Pc is shown in Fig. 2 (reflection-mode data). The figure shows that the weaker superstructure reflections can be accounted for, both with respect to their positions and to their intensities, by the structural model used, although reliable atomic coordinates could not be obtained. The S value for the refinement was 2.2 and the S value for a corresponding refinement using transmission data 0.9.

The average structure of the subcell with $a=6.176\text{ \AA}$

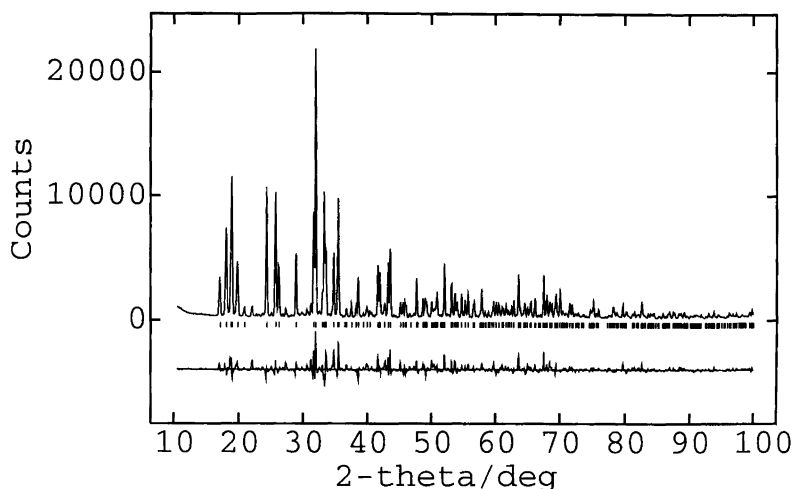


Fig. 1. Observed and difference intensity powder diffraction patterns of $\text{Na}_2\text{ZnSi}_2\text{O}_6$ for the refinement of the substructure in $C2/c$ (reflection-mode data).

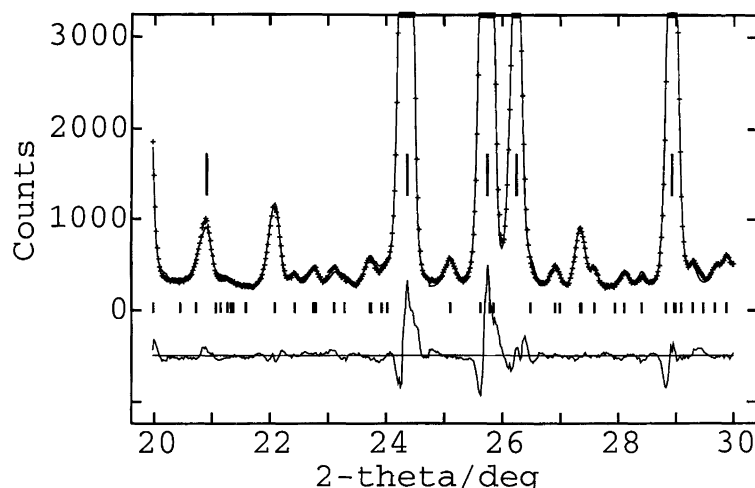


Fig. 2. An expanded part of the observed (crosses), calculated (full line) and difference intensity powder diffraction patterns of $\text{Na}_2\text{ZnSi}_2\text{O}_6$ for a non-converging refinement in Pc and with $a = 18.528 \text{ \AA}$ (reflection-mode data). The sub-cell ($a = 6.176 \text{ \AA}$) reflections are indicated by extended markers.

may also be described in the two space groups Pc and $P2_1/c$. Corresponding refinements using the reflection-mode data yielded $R_F = 6.5\%$, $S = 4.9$ for Pc and $R_F = 8.2\%$, $S = 5.5$ for $P2_1/c$. No substantial changes in the orientation of structural elements could, however, be observed in these refinements, compared with the refinement in $C2/c$. The relatively small decrease in residuals achieved by making the subcell primitive, thereby approximately doubling the number of positional parameters, does therefore in our opinion not yield a better description of the subcell structure than using a C -centered cell. It may also be mentioned here that refinements, corresponding to those discussed above and yielding essentially the same results, were also performed using the program package GSAS.⁹

Structure description and discussion

The partial crystal structure model is illustrated in Fig. 3, and corresponding selected interatomic distances given in Table 2. Following the Liebau¹⁰ classification for silicates, it is a mono-polysilicate that contains unbranched single vierer [001] chains (of corner-sharing SiO_4 tetrahedra). The formula may accordingly be written as $\text{Na}_4\text{Zn}_2\{\mathbf{uB}, 1^1_\infty\}[\text{Si}_4\text{O}_{12}]$. The Zn atoms are in ZnO_4 tetrahedra which interconnect three SiO_3^{2-} chains. Two oxygens in each ZnO_4 tetrahedron are shared with two SiO_4 tetrahedra in one adjacent SiO_3^{2-} chain, and the remaining two oxygens each with one SiO_4 tetrahedron in one adjacent SiO_3^{2-} chain. The Na atoms are irregularly coordinated by up to nine oxygens at distances from 2.25(6) to 3.44(3) \AA .

The interatomic distances obtained correspond to an average structure and can hence not be considered strictly correct. The obtained average distances for Si–O and Zn–O, 1.58 and 1.91 \AA , respectively, compare favourably with corresponding expected distances of ca. 1.62¹⁰ and

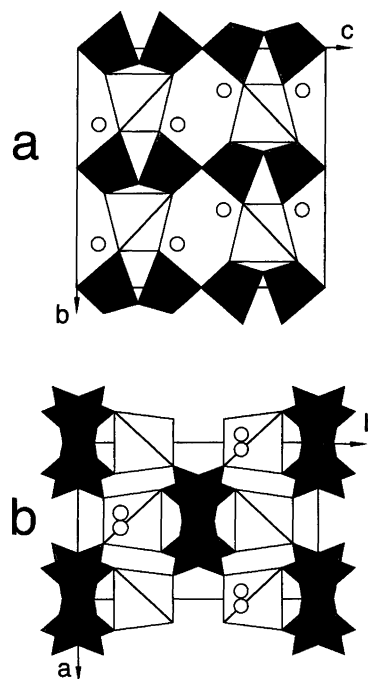


Fig. 3. The structure of $\text{Na}_2\text{ZnSi}_2\text{O}_6$ projected (a) along $[-100]$ and (b) along $[00-1]$. The shaded tetrahedra contain Si atoms and the unshaded tetrahedra Zn atoms. The Na atom positions are shown by open circles.

1.98 \AA .¹¹ The obtained average Na–O distance is, however, somewhat longer than expected,¹¹ irrespective of the choice of coordination number for the Na atom. The expected value for a six-coordinated Na atom is ca. 2.40 \AA , and the obtained average distance to the first six oxygens is 2.66 \AA .

The structure may be compared with the structure of hydrothermally synthesised $\text{Na}_2\text{ZnSi}_2\text{O}_6$ (zink chkalovite), which has been determined from single crystals,

Table 2. Bond distances (in Å) in Na₂ZnSi₂O₆.

Zn-O3	2 × 1.87(5)	Na-O3	2.25(6)
Zn-O4	2 × 1.95(5)	Na-O4	2.35(6)
Mean	1.91	Na-O4	2.75(6)
		Na-O3	2.76(6)
Si-O4	1.53(6)	Na-O2	2.89(7)
Si-O1	1.54(2)	Na-O3	2.97(6)
Si-O2	1.60(4)	Na-O1	3.15(3)
Si-O3	1.63(6)	Na-O4	3.30(6)
Mean	1.58	Na-O1	3.44(3)
		Mean	2.87

using film data obtained with unfiltered Mo radiation, and refined to a residual $R_{hkl} = 12.9\%$.³ It crystallises in space group *Fdd2* with a unit cell with $a = 21.503(5)$, $b = 7.120(2)$ and $c = 7.400(2)$ Å. The X-ray density, 3.09 g cm^{-3} , is nearly identical to that observed for the modification synthesised in the solid state, 3.08 g cm^{-3} . The structure of zinc chkalovite, illustrated in Fig. 4, contains unbranched single zweier SiO₃²⁻ chains, along [011] and [01-1], which are interconnected by ZnO₄ tetrahedra. Each ZnO₄ tetrahedron connects to four SiO₃²⁻ chains, however, instead of three as in the solid-state preparation. The Na atoms are five-coordinated at distances from 2.23 to 2.58 Å, with an average of 2.46 Å. The SiO₃²⁻ chains may be characterised by a stretching factor $f_s = I_{\text{chain}}/(2.7P)$, where I_{chain} = the identity period of the chain and P = the periodicity of the chain.¹⁰ The SiO₃²⁻ chains in zinc chkalovite are found to be stretched, with $f_s = 0.95$, to a similar extent as those in the solid-state preparation, $f_s = 0.91$.

The structure also shows similarities with that of K₂ZnGe₂O₆,¹² which crystallises in space group *C222*₁ with $a = 9.7904(4)$, $b = 6.3612(2)$, $c = 10.8078(4)$ Å. The structure contains comparable GeO₃²⁻ chains along [001], interconnected by ZnO₄ tetrahedra. The structure part of K₂ZnGe₂O₆ with $-1/4 \leq z \leq 1/4$ matches well with that of Na₂ZnSi₂O₆ (solid-state) with $0 \leq z \leq 1/2$. These parts are, however, connected differently in the

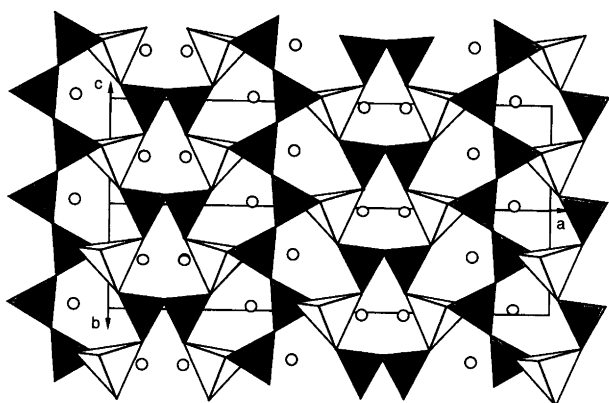


Fig. 4. The structure of hydrothermally synthesised Na₂ZnSi₂O₆ (zinc chkalovite) projected along [0-1-1]. The shaded tetrahedra contain Si atoms and the unshaded tetrahedra Zn atoms. The Na atom positions are shown by open circles.

two structures; by a [010] two-fold axis for K₂ZnGe₂O₆ and a [010] glide plane along the *c*-axis for Na₂ZnSi₂O₆.

It is not uncommon to find that different structure modifications are obtained for compounds synthesised by solid-state and by hydrothermal reaction. For example, the solid-state synthesis Na₂BeSiO₄ crystallises with an orthorhombic cristobalite-related structure,¹³ while a layered monoclinic structure is obtained via hydrothermal synthesis.¹⁴ The powder pattern for Na₂BeSi₂O₆¹⁵ (solid-state) agrees well with a calculated pattern for the corresponding mineral chkalovite.¹⁶ Solid-state synthesis Na₂ZnGe₂O₆ gives a powder pattern that can be indexed on the basis of an orthorhombic cell with $a = 21.761(1)$, $b = 7.365(1)$, $c = 7.646(1)$ Å,¹⁷ which indicates a structure related to zinc chkalovite. The powder pattern contains, however, a number of reflections incompatible with the space group *Fdd2*, which indicates structural differences.

The previous study² indicates that the solid-state synthesis Na₂ZnSi₂O₆ may exhibit a small homogeneity range according with the substitution $2\text{Na}^+ + \text{Zn}^{2+} \leftrightarrow \text{Si}^{4+}$, in analogy with that exhibited by Na₂ZnSiO₄. Further studies are, however, necessary to determine this. We have experienced no evidence for sodium losses occurring at the comparatively low synthesis temperatures employed. The sample used in the present study should therefore have a composition very close to the nominal one.

The derived structure model for Na₂ZnSi₂O₆ (solid-state) is one of an average structure, obtained by using a *C*-centered subcell. A speculative cause for a superstructure with a tripled *a*-axis is that the ZnSi₂O₆²⁻ framework may be forced to distort slightly in order to achieve a more suitable oxygen environment for the Na atoms. A reliable structure refinement using the larger cell could, however, not be carried out on the basis of the present X-ray powder data, due to the large number of positional parameters to be determined. It would thus seem probable that single-crystal data are necessary for an accurate determination of the atom positions in the larger cell.

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References

- Holland, A. E. and Segnit, E. R. *Aust. J. Chem.* 19 (1966) 911.
- Grins, J., *Solid State Ionics* 7 (1982) 157.
- Belokoneva, E. L., Egorov-Tismenko, Yu. K., Simonov, M. A. and Belov, N. V. *Sov. Phys.—Crystallogr.* 14 (1970) 918.
- Pawley, G. S. *J. Appl. Crystallogr.* 14 (1981) 357.
- Cascarano, G., Favia, L. and Giacovazzo, C. *J. Appl. Crystallogr.* 25 (1992) 310.
- Wiles, D. B., Sakthivel, A. and Young, R. A. *User's Guide to Program DBW3.2S for Rietveld Analysis of X-Ray and*

- Neutron Powder Diffraction Data Patterns (Version 8804)*, School of Physics, Georgia Institute of Technology, Atlanta 1985.
7. Young, R. A., Ed. *The Rietveld Method, IUCr Monographs on Crystallography 5*, p.22, Oxford University Press, Oxford 1993.
 8. Berár, J.-F. and Lelann, P. *J. Appl. Crystallogr.* 24 (1991) 1.
 9. Larson, A. C. and Von Dreele, R. B., Los Alamos National Laboratory Report No. LA-UR-86-748, 1987 Los Alamos.
 10. Liebau, F. *Structural Chemistry of Silicates*, Springer-Verlag, Berlin 1985.
 11. Shannon, R. D. *Acta Crystallogr. Sect. A* 32 (1976) 751.
 12. Grins, J. and Werner, P-E. *Acta Chem. Scand.* 43 (1989) 11.
 13. Maksimov, B., Tamazyán, R., Sirota, M. I., Frostäng, S., Grins, J. and Nygren, M. *J. Solid State Chem.* 86 (1990) 64.
 14. Plakhov, G. F., Simonov, M. A. and Belov, N. V. *Sov. Phys. Dokl.* 19 (1975) 556.
 15. Frostäng, S., Grins, J. and Nygren, M. *J. Solid State Chem.* 72 (1988) 92.
 16. Simonov, M. A., Egorov-Tismenko, Yu. K. and Belov, N. V. *Sov. Phys. Dokl.* 20 (1976) 805.
 17. Grins, J. and Nygren, M. *Solid State Ionics* 9/10 (1983) 869.

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