Acta Cryst. (1981). B37, 1483–1491

Structure of Magnesium Disodium Silicate Na_2MgSiO_4 and Ionic Conductivity in Tetrahedral Structures

By Werner H. Baur* and Tsutomu Ohta

Department of Geological Sciences, University of Illinois, Chicago, Illinois 60680, *USA*

and Robert D. Shannon

Central Research and Development Department, EI du Pont de Nemours and Co., Wilmington, Delaware 19898, *USA*

(*Received* 28 *May* 1980; *accepted* 27 *January* 1981)

Abstract

The conductivity of Na_2MgSiO_4 is $3{\cdot}0 \times 10^{-3}$ $(\Omega m)^{-1}$ at 573 K. It is the parent compound of a variety of substituted derivatives with ionic conductivities ranging up to 0·48 $(\Omega m)^{-1}$. Na_2MgSiO_4 is isostructural with Na_2ZnSiO_4 and crystallizes in the monoclinic space group Pn with a = 7·015 (2), b = 10·968 (2), c = 5·260 (1) Å, β = 89·97 (1)°, V = 404·7 Å^3, D_x = 2·666 Mg m^{-3}, M_r = 162·392; Z = 4, μ(Mo $K\alpha$) = 0·803 mm^{-1}, μR = 0·14. The crystal studied was a twin of orthorhombic diffraction symmetry. A substructure with b = 5·484 Å is pronounced. Single-crystal diffractometer data of the substructure were refined to R = 0·025 for 2729 F_o. The superstructure refined to R = 0·029 for 3175 F_o. All atoms in Na_2MgSiO_4 are tetrahedrally four-coordinated. The structure can be derived from the hexagonally closest-packed wurtzite structure by replacing the S atoms by O, and the Zn atoms by Na, Mg and Si. The most probable potential pathway for diffusion is in the direction $[\bar{1}01]$ in which there are chains of Na atoms separated by distances of 3·21 and 3·22 Å. In order to move from one site to another, the Na atoms must pass through unoccupied tetrahedral and/or octahedral sites of the framework.

Introduction

Ionic conductivity has received considerable attention in recent years because of the use of ionic conductors in solid-state batteries and fuel cells and because of the intrinsic scientific interest in the properties of these materials (see, for instance, *Solid Electrolytes*, 1978, and literature cited therein). Several compounds related to carnegieite, the cubic high-temperature polymorph of $NaAlSiO_4$, display moderate to good ionic conductivity: $NaAlSiO_4(Na_2O)_{0\cdot25-0\cdot5}$ and $Na_{1\cdot625}Mg_{0\cdot625}Al_{0\cdot375}SiO_4$ (Goodenough, Hong & Kafalas, 1976), $Na_{1+x}Al_{1+x}Si_{1-x}O_4$, with x from 0 to 0·7 (Shannon & Berzins, 1979), and $Na_{2-x}Mg_{1-x}Al_xSiO_4$, $Na_{2-2x}Mg_{1-x}Si_{1+x}O_4$, $Na_{2-x}MgSi_{1-x}P_xO_4$ and $Na_4Mg_2Si_3O_{10}$ (Shannon, 1979). The structures of these compounds are topologically related to the cristobalite type and can be described as stuffed derivatives of cristobalite (Buerger, 1935; O'Keeffe & Hyde, 1976). These compounds have ionic conductivities ranging from $3{\cdot}0 \times 10^{-3}$ to 0·48 $(\Omega m)^{-1}$ at 573 K. Once we know their crystal structures, we can aim at correlating the geometry of the silicate frameworks with the conductivity data. Detailed structural investigations of these compounds are lacking despite some early work based on powder-diffraction data (Barth & Posnjak, 1932; Borchert & Keidel, 1947). As a first step the structure of Na_2MgSiO_4, the parent compound of several of the substituted ionic conductors prepared by Shannon (1979), has been investigated.

Experimental

The specimen of Na_2MgSiO_4 used for the crystal-structure determination was grown hydrothermally by Shannon (1979). Electron microprobe analysis of material from the same batch from which the crystal for the diffraction experiment was selected yielded 36·5 wt% Na_2O, 24·7 wt% MgO, 37·8 wt% SiO_2, with a total of 99·00% (average of three analyses). The respective theoretical values for the composition Na_2MgSiO_4 are 38·2, 24·8 and 37·0 wt%. The only other component identified was H, which contributes according to a semiquantitative ion microprobe analysis, 0·25 wt% H_2O. This value is a lower bound; the actual H_2O content may be up to a factor of two higher. These results indicate a composition of $H_{0\cdot04}Na_{1\cdot90}Mg_{0\cdot99}Si_{1\cdot02}O_4$ for the sample. The microprobe analyses were kindly performed by Ian Steele.

---

* To whom correspondence should be addressed.

0567-7408/81/081483-09$01.00

A sphere with a radius of 0·18 (2) mm was prepared for structure analysis. The unit-cell constants as determined at room temperature by the setting of 15 reflexions on a four-circle X-ray diffractometer were close to those determined by Shannon (1979) from powder-diffraction patterns using a Hägg–Guinier camera. Throughout the course of the work we used the cell constants determined by Shannon (1979) except for the monoclinic angle β which was taken from our determination on the single-crystal X-ray diffractometer. Three-dimensional X-ray diffraction intensities were collected in four octants ($\bar{h}\bar{k}\bar{l}$ and $h\bar{k}\bar{l}$ up to $\sin\theta/\lambda = 1{\cdot}08$ Å^{-1} and in octants hkl and $\bar{h}kl$ up to $\sin\theta/\lambda = 0{\cdot}70$ Å^{-1}) on a computer-controlled four-circle diffractometer using graphite-monochromatized Mo $K\alpha$ radiation ($\lambda = 0{\cdot}71069$ Å). Lorentz–polarization and absorption corrections were applied to the intensity data. For details of data-measuring procedures and for a list of most of the computer programs used in the course of this work, see Baur & Khan (1970). In addition, Meier & Villiger's (1969) distance least-squares program *DLS* and Araki's (1977, 1979) program *TWXLLS* for refining diffraction data from twin crystals were used. The atomic-scattering curves and the dispersion corrections from *International Tables for X-ray Crystallography* (1974) were employed for the structure-factor calculations.

The diffraction pattern of Na_2MgSiO_4 shows a substructure: about 97% of the reflexions with $k = 2n + 1$ have weaker intensities than three times their standard deviations, while only 4% of the intensities of reflexions with $k = 2n$ are smaller than three times their standard deviations and were set to zero intensity. Therefore, the structure with $b = 10{\cdot}968$ Å clearly is a superstructure. Because of the well-known difficulties in solving superstructures, the solution of the structure was attempted first in the substructure with a halved b cell edge.

Solution of the substructure

Shannon (1979) proposed space group $Pmn2_1$ for Na_2MgSiO_4, based on systematic extinctions and on a positive second-harmonic generation (SHG) test. When the complete set of 6625 non-unique reflexions was averaged in orthorhombic symmetry, 2466 unique F_o were obtained, which had an internal R_I value of 0·039, where $R_I = \sum |F - F_{\rm mean}|/\sum F_{\rm mean}$, and F is an individual structure factor, while $F_{\rm mean}$ is averaged over symmetrically equivalent reflexions. For 1282 of the intensities, $F_{\rm mean}$ was found to be smaller than three times its standard deviations. Of the 1184 remaining F_o only 28 were of the $k = 2n + 1$ type, while 1156 were of the $k = 2n$ type. Nine of these violated the extinction condition for the n glide plane: *i.e.*, $h + l = 2n + 1$ for nine of the $h0l$ reflexions. These reflexions were omitted from any further calculations. The fact that the structure could be refined to an R value of 0·0251 assuming the presence of a glide plane (see below) shows that any deviation from this symmetry, if present, is small. A Patterson map calculated with the 1147 remaining structure factors proved impossible to solve in space group $Pmn2_1$. Several ternary structures related to cristobalite, such as β-$NaFeO_2$ (Bertaut & Blum, 1954) crystallize in space group $Pbn2_1$ (O'Keeffe & Hyde, 1976) with cell constants similar to those of Na_2MgSiO_4. Since the $0kl$ reflexions with $k = 4n + 2$ were much weaker than those with $k = 4n$, it seemed that the substructure had almost $Pbn2_1$ symmetry. However, the Patterson map could not be interpreted on the basis of this space group either.

At this point the similarity between Na_2MgSiO_4 and Na_2ZnSiO_4 (Ilyukhin, Nikitin & Belov, 1966; Joubert-Bettan, Lachenal, Bertaut & Parthé, 1969) was noted (Table 1). According to the Russian authors Na_2ZnSiO_4 crystallizes in space group Pn. They determined the structure from three projections with R = 0·15 to 0·18 for an unstated number of structure factors. The French authors found the same space group and refined the structure from 21 multiple powder-diffraction lines to R = 0·15. Both determinations agree in finding tetrahedral coordinations of O atoms around the atoms of Si, Zn and Na.

The complete data set was therefore averaged in monoclinic symmetry resulting in 4423 unique reflexions, with an internal value R_I of 0·041. For 2119 of

Table 1. *Cell constants and hexagonal close-packing parameters of the substructure of* Na_2MgSiO_4, Na_2ZnSiO_4, β-$NaFeO_2$ *and* ZnO

All are in the setting of the substructure of Na_2MgSiO_4.

	a (Å)	b (Å)	c (Å)	β (°)	Thickness of 1 layer in c (Å)	Thickness* of 1 atom in a, b (Å)	1 layer / 1 atom
Na_2MgSiO_4 (*Pn*) (substructure, this work)	7·015	5·484	5·260	89·97	2·630	3·337	0·788
Na_2ZnSiO_4 (*Pn*) (Ilyukhin *et al.*, 1966)	7·02	5·48	5·33	90·33	2·67	3·34	0·799
Na_2ZnSiO_4 (*Pn*) (Joubert-Bettan *et al.*, 1969)	7·02	5·44	5·24	90	2·62	3·33	0·788
β-$NaFeO_2$ ($Pbn2_1$) (Bertaut & Blum, 1954)	7·136	5·672	5·377	90	2·689	3·421	0·786
ZnO ($P6_3mc$) (Swanson & Fuyat, 1953)	6·498	5·627	5·205	90	2·603	3·249	0·801

* $0{\cdot}5\,(a/2 + b/\sqrt{3})$.

these, the intensities were larger than three times their standard deviations. 14 of these violated the extinction condition for an n glide plane and 40 were of the $k = 2n + 1$ type. A least-squares refinement starting with the parameters reported by Joubert-Bettan *et al.* (1969) resulted after seven cycles in an R $(=\sum||F_o| - |F_c||/\sum|F_o|)$ of 0·133 for the remaining 2065 F_o. The number of parameters refined was 31 (1 scale factor, 8 isotropic temperature factors and only 22 positional coordinates because the x and z parameters of one atom had to be kept constant in order to define the origin). A close inspection of the structure factors revealed that the intensity data were collected from a twinned crystal, thus simulating orthorhombic symmetry. The volumes of the two differently oriented twin components must be similar in order to give the appearance of higher symmetry. The reciprocal lattices of the two twin components are overlapping and cannot be resolved within the accuracy achieved by the diffraction experiment, since β is almost a right angle. Potential twin relations are twofold axes parallel to [100] or [001] or mirror planes normal to [100]* or [001]*. In all these cases the diffraction patterns would be identical to each other, assuming that Friedel's Law is obeyed.

The refinement was continued using Araki's (1977, 1979) twin-refinement least-squares program. It was assumed for the computations that we were dealing with a reflexion twin and that the twin plane was a mirror normal to [100]*. The structure-factor calculation before the first cycle, *i.e.* without any refinement of parameters and taking the volumes of the two twin components as equal, immediately gave an R value of 0·072, which is a significant improvement over the value of 0·133 calculated previously without making the assumption of twinning. In six subsequent cycles of refinement with isotropic temperature factors R converged to 0·0391. After a few more cycles of refinement with anisotropic temperature factors the R value was reduced to 0·0251 for 2065 structure factors. Two different absolute configurations of the structure were then checked against a data set in which the Friedel pairs were not averaged (2729 observations). The R value for the adopted configuration was for the expanded data set smaller by 0·0008 (or more than 3%) than for the alternate arrangement. The expanded data set and the chosen absolute configuration were used for all subsequent refinements of the substructure and the superstructure. No attempts were made to investigate the numerous combinations of potential twin laws and configurations.

Since all reciprocal-lattice points of the twin crystals are overlapping, one cannot distinguish between the different twin laws by studying the diffraction pattern. A study of the crystals under the polarizing microscope does not give any indication of macroscopically recognizable twinning. Presumably the twinning is polysynthetic at a level which cannot be resolved by a polarizing microscope. This raises the possibility that β which has been measured to be slightly, but significantly different from a right angle (Table 1), is only an apparent angle. The relative volumes of the twin individuals are, at the end of the refinement, 0·562 (1) and 0·474, which means that one of the twin components has a volume 11% larger than the other. This is close enough to 0·5 to give the diffraction pattern the appearance of orthorhombic symmetry, but sufficiently different to allow the displacement of the maxima of the diffraction peaks to the side of the larger twin component. Taking into account the volume ratio of the twin components, the true value of β could be about 89·42° (or 90·58°). It is interesting that Ilyukhin *et al.* (1966) measured a β value for Na_2ZnSiO_4 of 90·33°. The difference from a right angle is similar in these two cases. However, Joubert-Bettan *et al.* (1969) report β of Na_2ZnSiO_4 to be a right angle.

Attempts to refine the occupancy factors of the cations were inconclusive, and were therefore abandoned. The only conclusion which could be drawn is that the Na(2) site may not be fully occupied. However, the amount of missing Na is not as large as the microprobe analysis would indicate. In ten additional cycles of refinement the R value was reduced to 0·0251 for 72 parameters (1 scale factor, 1 relative volume of one twin component, 22 positional coordinates, 48 anisotropic thermal parameters). The R value was calculated for the apparent structure factors Fa, defined as $Fa = (V_1F_1^2 + V_2F_2^2)^{1/2}$ where $V_1 + V_2 = 1$ and F_1 and F_2 are the structure factors of the separate twin components. The average parameter shift in the final cycle was 0·25 of the estimated standard deviation of the parameters, while the maximum shift to standard deviation ratio was 1·40. The highest peak in the final difference synthesis has a height of 0·7 e Å^{-3} and is located 0·6 Å from the position of the Si atom in the direction of an O atom. Similar peaks are found between the Si position and the other O atoms at distances from 0·5 to 0·8 Å from the Si atom. Analogous peaks were observed by Marumo, Isobe, Saito, Yagi & Akimoto (1974) in γ-Ni_2SiO_4 and by Takeuchi & Kudoh (1977) in pectolite. These authors interpret the peaks as being due to the bonding electrons between the Si and O atoms. Other strong peaks are near the Mg-atom location. The final positional coordinates (general positions x,y,z; $\frac{1}{2} + x$, $-y$, $\frac{1}{2} + z$) are given in Table 3.*

---

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36014 (37 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Solution of the superstructure

While the presence of the reflexions with $k = 2n + 1$ proves that the refined substructure must be a pseudosymmetric structure, there are nevertheless no clues (see Baur, 1977) why the symmetry must be lowered by doubling the b cell constant. No pseudosymmetric statistical occupation of atomic sites which could be separated in the superstructure occurs here. No unusually short distance indicates the necessity to lower the symmetry, since the Na—O, Mg—O and Si—O distances are close to their expected values. The small magnitude of the superstructure reflexions relative to the substructure reflexions (Table 2) shows that the deviations of the superstructure from the substructure ought to be very small, since these relative magnitudes must be approximately proportional to the deviations of the superstructure from the substructure.

Table 2. *Data-set statistics and final R values for substructure and superstructure refinements*

		Superstructure		
	Sub-structure	*Fa* with $k = 2n$	*Fa* with $k = 2n + 1$	All *Fa*
Number of independent Fa_{hkl}	2824	2824	2809	5633
Number of independent $Fa_{hkl} = 0$	95	95	2363	2458
Sigma limit based on I	3	3	$\sqrt{2}$	–
Number of independent Fa_{hkl} used in refinement	2729	2729	446	3175
Mean relative standard deviation	0·029	0·029	0·240	0·0586
Average relative magnitude of Fa_{hkl}	13·78	13·78	1·37	12·04
R for observed Fa_{hkl}	0·0251	0·0247	0·2805	0·0287
$R_w = [\sum w(\lvert Fa_o\rvert - \lvert Fa_c\rvert)^2/\sum wFa_o^2]^{1/2}$ for observed Fa_{hkl}	0·0313	0·0300	0·2785	0·0331

Table 3. *Positional parameters of the substructure* ($\times 10^5$) *and the superstructure* ($\times 10^4$) *of* Na_2MgSiO_4 *and equivalent isotropic temperature factors* ($\times 10^2$) *with e.s.d.'s in parentheses*

	x	y	z	B_{eq} (Å^2)
(*a*) Substructure				
Si	24768 (5)	68748 (4)	00561 (7)	49 (1)
Mg	0	18612 (6)	0	62 (1)
Na(1)	74990 (10)	67180 (10)	98468 (13)	121 (1)
Na(2)	49469 (9)	18565 (9)	98922 (14)	106 (2)
O(1)	71678 (11)	60026 (12)	43548 (17)	83 (2)
O(2)	27791 (11)	71452 (15)	31204 (15)	88 (2)
O(3)	55832 (11)	15553 (14)	42645 (17)	83 (2)
O(4)	93827 (12)	21182 (14)	36245 (16)	86 (2)
(*b*) Superstructure				
Si(*a*)	2480 (1)	3437 (1)	0072 (1)	38 (2)
Mg(*a*)	0	0932 (1)	0	71 (5)
Na(1*a*)	7520 (2)	3359 (1)	9860 (3)	111 (5)
Na(2*a*)	4952 (3)	0933 (1)	9944 (3)	109 (7)
O(1*a*)	7184 (4)	2983 (2)	4403 (4)	111 (8)
O(2*a*)	2774 (3)	3580 (2)	3122 (3)	67 (6)
O(3*a*)	5575 (3)	0778 (2)	4264 (3)	57 (6)
O(4*a*)	9415 (3)	1073 (2)	3665 (4)	74 (7)
Si(*b*)	2489 (2)	8438 (1)	0064 (2)	63 (3)
Mg(*b*)	0019 (1)	5930 (1)	0033 (2)	56 (5)
Na(1*b*)	7497 (3)	8359 (2)	9869 (3)	138 (6)
Na(2*b*)	4962 (3)	5924 (1)	9872 (2)	106 (7)
O(1*b*)	7166 (3)	8013 (2)	4333 (4)	60 (6)
O(2*b*)	2800 (4)	8563 (2)	3138 (3)	117 (9)
O(3*b*)	5610 (4)	5778 (2)	4287 (5)	118 (8)
O(4*b*)	9358 (4)	6044 (2)	3599 (4)	94 (8)

The only remaining possibility is, therefore, that the superstructure is related to an ordering of deficiencies in the Na sites. The sample was prepared hydrothermally and the microprobe analyses indicate a deficiency in Na and the presence of H. The weak IR band at 3450 cm^{-1} which was attributed by Shannon (1979) to absorbed H_2O is, therefore, most likely due to the O—H stretching mode of OH groups.

In order to simulate a superstructure with Na deficiency, the distance least-squares method was used (Meier & Villiger, 1969; Baur, 1977). The positional-parameter set of the substructure was expanded to the superstructure in space group *Pn*. This meant that the number of symmetrically independent atoms was doubled. The structure was simulated by using as input 80 Mg—O, Si—O, Na—O and O—O distances. All coordination tetrahedra were assumed to be regular with Si—O of 1·637, O—O in the polyhedral edges around Si 2·673, Mg—O 1·955, O—O around Mg 3·193, and for three of the four Na sites Na—O 2·304 and O—O around Na 3·762 Å. In one simulation it was assumed that the fourth Na site, namely Na(1*a*) was deficient in Na and therefore had a longer Na(1*a*)—O distance of 2·45 Å and O—O 4·001 Å (model 1), while in a second simulation Na(2*a*) was assumed to be the Na-deficient site with Na(2*a*)—O of 2·38 Å and O—O 3·887 Å (model 2). The weights of the O—O input distances around Mg and Si were taken as 0·07, those of the O—O edges around Na as 0·02, while the Pauling bond strengths of the cation–oxygen bonds were used as weights for the cation–oxygen distances. For further details of the method of computer simulation of crystal structures, see Baur (1977) and references cited therein.

Both simulated models were tested against the X-ray diffraction data. Model 1 refined in fewer cycles and to lower R values than model 2. The final refinement of the superstructure was performed with the data set in which the Friedel pairs were not averaged and where the cutoff limit for the $k = 2n + 1$ type reflexions was taken as $\sqrt{2}$ times sigma (Table 2) in order to have more reflexions which were due only to the superstructure. In 13 refinement cycles with the full data set and 144 variable parameters (1 scale factor, 1 relative volume of one twin component, 46 positional coordinates, 96 anisotropic thermal parameters) the overall R value was reduced to 0·0287. The maximum shift in the final cycle was 1·8 times the e.s.d., even though the average shift/deviation ratio was less than 0·50. This slow convergence is apparently related to strong correlations between some of the parameters of atoms in the two subcells of the superstructure. 11 correlation coefficients are larger than 0·9 and range up to 0·939.

The R value for the superstructure reflexions is high; however, one has to keep in mind that the relative magnitude of the superstructure structure factors is only 10% of the substructure structure factors and that, therefore, their relative error is much larger. In fact, the mean relative standard deviation based on the counting statistics is 24·0% for the 446 Fa_o of the $k = 2n + 1$ type reflexions, while it is 2·9% for the 2729 Fa_o of $k = 2n$ type. The ratio of these numbers is 8·2, while the ratio of the R values for these classes of reflexions is 11·4. Obviously, the R value for the superstructure reflexions is approximately of the correct relative magnitude expected for data of low intensity and high relative standard deviations. This means also that the details of the superstructure are not very precisely defined. The final difference synthesis shows no surprising features. The distribution and the heights of the peaks are similar to the difference synthesis of the substructure. No peak is higher than 0·74 e Å^{-3}. The final positional coordinates are presented in Table 3.*

The average coordinates of the corresponding a and b atoms in the superstructure should coincide with the experimentally determined coordinates of the substructure atoms. In order to make such a comparison meaningfully, one has to relate both structures to a common origin. This was done by setting the mean x and z coordinates of the heaviest atoms, *i.e.* Si(a) and Si(b) as zero, adjusting all other superstructure x and z coordinates to this origin and doubling the numerical values of all y coordinates of the superstructure. The resulting transformed superstructure coordinates agree on the average with the substructure coordinates within one half of the pooled e.s.d.'s of the coordinates. The difference vectors, *i.e.* the distances from the substructure atoms to the corresponding superstructure atoms are on average only 0·016 Å. In other cases where superstructures have been determined, these mean difference vectors are much larger: they are 0·05 Å in the case of $Na_{12}Al_{12}Si_{12}O_{48}.27H_2O$ (zeolite Na*A*) determined by Gramlich & Meier (1971) and 0·4 Å in the case of cubic SiP_2O_7 (Tillmanns, Gebert & Baur, 1973). Because the difference vectors are so small, the superstructure reflexions are very weak.

The most significant differences between the superstructure and the substructure involve the mean distances from Na(1a) and Na(1b) to their coordinating O atoms which are respectively 0·013 Å larger and 0·011 Å smaller than the mean Na(1)–O distance and also the individual Na(a)–O and Na(b)–O distances which range from being 0·05 Å shorter to 0·07 Å longer between the two tetrahedra. These differences and the fact that the mean Na(1)–O distances are larger than the mean Na(2) distances must be related to Na deficiencies in the Na sites. The missing Na atoms have to be replaced by OH groups. The fact that the distance Si(a)–O(1b) is 0·019 Å longer than the mean Si(a)–O distance may indicate partial replacement by OH in the O(1b) site. Because of the small Na deficiency in this sample firm conclusions cannot be drawn. Investigation of Na_2MgSiO_4 derivatives with larger Na deficiencies would be useful.

Description and discussion of the structure

As pointed out by Joubert-Bettan *et al.* (1969), Na_2ZnSiO_4, and therefore also Na_2MgSiO_4, are derivatives of the wurtzite-type structure, the hexagonal polymorph of ZnS. The wurtzite type can be viewed as a hexagonal closest packing of S atoms in which one half of the tetrahedral interstices are occupied by Zn atoms, or *vice versa*, since the Zn atoms are also arranged in a hexagonal close packing.* The space group is $P6_3mc$ with both atoms located at sites of symmetry $3m$ with coordinates of equivalent positions of $\frac{1}{3}\frac{2}{3}z$, $\frac{2}{3}\frac{1}{3}\frac{1}{2}+z$ where $z_{Zn} = 0$ and $z_S \approx 0{\cdot}375 = \frac{3}{8}$ (*Strukturbericht*, 1931). All coordination tetrahedra are oriented the same way. Each atom is surrounded tetrahedrally by four atoms of another kind: one at a distance of zc along the 6_3 axis, and three more at a distance of $[a^2/3 + (\frac{1}{2} - z)^2c^2]^{1/2}$. In addition, there is a further fifth atom of the other kind at a distance of $(1 - z)c$. This fifth atom together with the atoms of the base of the coordination tetrahedron forms the second tetrahedral environment of the hexagonal closest packing. This tetrahedral site, however, is not occupied in wurtzite or its derivative structures because it shares a face with the occupied tetrahedral site and one edge each with three neighboring tetrahedra. Additionally, there are two octahedral sites per unit cell which share three faces with occupied tetrahedral sites, three faces with empty tetrahedral sites and two faces (in the **c** direction) with neighboring octahedral sites.

The replacement of one kind of metal atom by two kinds results in the lowering of symmetry by two mechanisms: the unit cell is enlarged and several symmetry elements are lost. An example is β-$NaFeO_2$ (Bertaut & Blum, 1954; Joubert-Bettan *et al.*, 1969) where Na and Fe occupy in an ordered way the Zn positions of wurtzite, and O replaces S. Replacing the Fe atoms of β-$NaFeO_2$ by Zn and Si in an ordered arrangement as in Na_2ZnSiO_4 (Joubert-Bettan *et al.*, 1969) reduces the symmetry to *Pn*, but a further enlargement of the unit cell is not necessary. The transformation matrix of the larger cell of β-$NaFeO_2$ and Na_2ZnSiO_4 from the wurtzite-type cell is (200/120/001). In Na_2MgSiO_4 all cations can be distributed

---

* See deposition footnote.

* The reference to hexagonal close packing need not imply that there is contact between the anions or between the cations. It is meant as a characterization of the geometry of the array.

in an ordered arrangement within the same size unit cell as in Na_2ZnSiO_4. However, the actual superstructure cell of Na_2MgSiO_4 has a doubled *b* cell edge so that the transformation matrix from the wurtzite type is (200/240/001). The close relationship of all these structures to an ideal hexagonally close packed arrangement is evident from the ratio of the thickness of one atomic layer parallel to **c** to the average thickness of one atom in the **a** and **b** directions (see Table 1; compare also the close-packing parameters of the barium titanates, Tillmanns & Baur, 1970). Ideally, this ratio is 0·816 ($=\sqrt{2/3}$) as can be calculated from the geometry of hexagonal closest packing. The differences in cell volumes between the different compounds are approximately proportional to the third power of the mean radius (Shannon, 1976; Hawthorne, 1978) of their cations.

O'Keeffe & Hyde (1976, 1978) have shown that a wurtzite-type structure can be derived by a rotation of individual tetrahedra and a collapse of a filled cristobalite framework. Consequently, the Na_2MgSiO_4 structure can also be viewed as a framework with composition $MgSiO_4$ and with the topology of cristobalite in which the Na atoms fill additional tetrahedral sites.

The details of the structure of Na_2MgSiO_4 deviate from the ideal hexagonally closest packed arrangement because of the different sizes of the Na, Mg and Si atoms and of their coordination tetrahedra (Table 4). The actual structure is distorted and the individual tetrahedra are tilted relative to the highly symmetrical wurtzite type (Fig. 1). The coordination tetrahedra around the Na atoms are much larger and more distorted than those around the Si and Mg atoms. This distortion allows a fifth O atom to approach closely both Na(1) and Na(2) [2·93 Å for Na(1)—O(1) and 3·00 Å for Na(2)—O(3)]. These fifth O neighbors are located at distances $(1 - z)c$ from the cations as described above for the wurtzite type structure.

Table 4. *Interatomic distances* (Å) *and bond angles* (°)

(*a*) Substructure

Si—O(4)	1·630 (1)	Si—O(1)	1·635 (1)	Na(1)—O(2)	2·313 (1)	Na(1)—O(3)	2·381 (1)
Si—O(2)	1·633 (1)	Si—O(3)	1·637 (1)	Na(1)—O(4)	2·367 (1)	Na(1)—O(1)	2·415 (1)
	Mean	1·634			Mean	2·369	
				Na(1)—O(1)	2·925 (1)		
		O—Si—O				O—Na—O	
O(4)—O(2)	2·649 (1)	108·56 (4)		O(2)—O(4)	3·653 (1)	102·63 (4)	
O(4)—O(1)	2·664 (1)	109·36 (4)		O(2)—O(3)	3·692 (1)	103·69 (4)	
O(4)—O(3)	2·704 (1)	111·70 (4)		O(2)—O(1)	3·730 (1)	104·17 (3)	
O(2)—O(1)	2·662 (1)	109·13 (5)		O(4)—O(3)	4·374 (1)	134·20 (4)	
O(2)—O(3)	2·645 (1)	108·01 (5)		O(4)—O(1)	3·738 (1)	102·84 (4)	
O(1)—O(3)	2·681 (1)	110·03 (4)		O(3)—O(1)	3·834 (1)	106·13 (4)	
Mean	2·668	109·47			3·837	108·94	
Mg—O(2)	1·924 (1)	Mg—O(3)	1·956 (1)	Na(2)—O(2)	2·261 (1)	Na(2)—O(4)	2·314 (1)
Mg—O(1)	1·949 (1)	Mg—O(4)	1·960 (1)	Na(2)—O(1)	2·293 (1)	Na(2)—O(3)	2·349 (1)
	Mean	1·947			Mean	2·304	
				Na(2)—O(3)	2·998 (1)		
		O—Mg—O				O—Na—O	
O(2)—O(1)	3·209 (1)	111·85 (4)		O(2)—O(1)	4·038 (1)	124·89 (4)	
O(2)—O(3)	3·175 (1)	109·81 (4)		O(2)—O(4)	3·631 (1)	105·05 (4)	
O(2)—O(4)	3·133 (1)	107·51 (3)		O(2)—O(3)	3·650 (1)	104·67 (4)	
O(1)—O(3)	3·242 (1)	112·22 (3)		O(1)—O(4)	3·716 (1)	107·53 (4)	
O(1)—O(4)	3·149 (1)	107·34 (4)		O(1)—O(3)	3·770 (1)	108·58 (4)	
O(3)—O(4)	3·166 (1)	107·90 (4)		O(4)—O(3)	3·684 (1)	104·39 (4)	
Mean	3·179	109·44		Mean	3·748	109·19	

(*b*) Superstructure

Si(*a*)—O(4*b*)	1·631 (3)	Si(*b*)—O(4*a*)	1·629 (3)	Na(1*a*)—O(2*b*)	2·303 (2)	Na(1*b*)—O(2*a*)	2·325 (3)
Si(*a*)—O(2*a*)	1·625 (2)	Si(*b*)—O(2*b*)	1·637 (3)	Na(1*a*)—O(4*b*)	2·406 (3)	Na(1*b*)—O(4*a*)	2·338 (3)
Si(*a*)—O(1*b*)	1·652 (3)	Si(*b*)—O(1*a*)	1·611 (3)	Na(1*a*)—O(3*b*)	2·384 (3)	Na(1*b*)—O(3*a*)	2·379 (3)
Si(*a*)—O(3*b*)	1·623 (3)	Si(*b*)—O(3*a*)	1·649 (3)	Na(1*a*)—O(1*a*)	2·436 (3)	Na(1*b*)—O(1*b*)	2·390 (3)
Mean	1·633	Mean	1·632	Mean	2·382	Mean	2·358
				Na(1*a*)—O(1*a*)	2·910 (3)	Na(1*b*)—O(1*b*)	2·946 (3)
Mg(*a*)—O(2*b*)	1·910 (3)	Mg(*b*)—O(2*a*)	1·945 (2)	Na(2*a*)—O(2*b*)	2·280 (3)	Na(2*b*)—O(2*a*)	2·243 (3)
Mg(*a*)—O(1*b*)	1·942 (2)	Mg(*b*)—O(1*a*)	1·959 (3)	Na(2*a*)—O(1*b*)	2·293 (3)	Na(2*b*)—O(1*a*)	2·301 (3)
Mg(*a*)—O(3*a*)	1·957 (2)	Mg(*b*)—O(3*b*)	1·958 (3)	Na(2*a*)—O(4*a*)	2·331 (2)	Na(2*b*)—O(4*b*)	2·299 (3)
Mg(*a*)—O(4*a*)	1·977 (2)	Mg(*b*)—O(4*b*)	1·936 (2)	Na(2*a*)—O(3*a*)	2·320 (3)	Na(2*b*)—O(3*b*)	2·372 (3)
Mean	1·947	Mean	1·950	Mean	2·306	Mean	2·304
				Na(2*a*)—O(3*a*)	3·024 (2)	Na(2*b*)—O(3*b*)	2·977 (3)

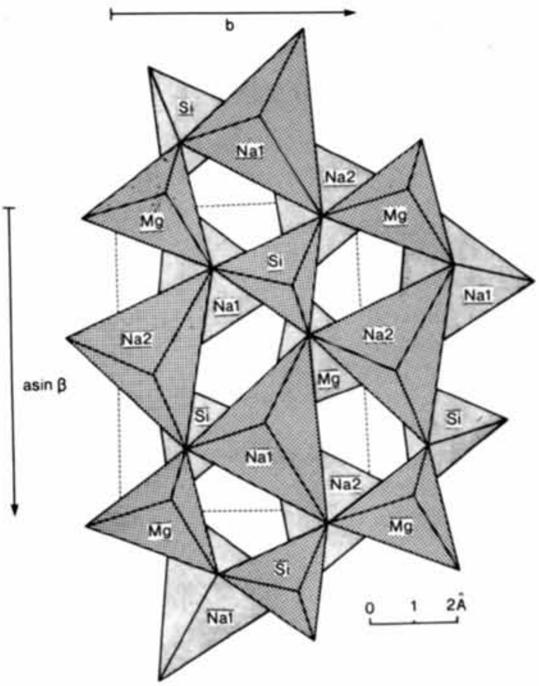

Fig. 1. Na_2MgSiO_4: view parallel to [001] of the substructure. The cations of the top layer of tetrahedra are at a height of z of about 1·0, while the layer below is at a height of z of about 0·5.

Because of the shorter Mg—O(4) and Si—O(2) coordination distances these fifth neighbors are in these cases at much larger distances [3·66 Å for Si—O(2) and 3·39 Å for Mg—O(4)]. None of the coordination tetrahedra share edges or faces with neighboring tetrahedra. All connexions are *via* corner sharing. Each O atom connects four different kinds of tetrahedra with each other.

Conduction of Na ions in other silicate structures proceeds through polyhedra with shared faces. The conduction paths in $Na_5YSi_4O_{12}$ and $Na_4Zr_2Si_3O_{12}$ involve Na in VI, VII and VIII coordinated sites (Chen, Gier & Shannon, 1981; Tranqui, Capponi, Joubert, Shannon & Johnson, 1979). In these compounds the sizes of the openings are somewhat smaller or equal to the size of the Na ion (see Table 5) and the distances between Na sites vary between 1·50 and 4·72 Å with better conductivity generally correlating with openings similar to the size of the Na ion. Conductivity also appears to correlate with Na temperature factors (Table 5).

There must be a conducting pathway in Na_2MgSiO_4 which allows the Na atoms to move from one site to the other. If this were not the case the conductivity of 3×10^{-3} $(\Omega m)^{-1}$ at 573 K would not have been observed. Since the coordination tetrahedra around the Na atoms only share corners with neighboring Na tetrahedra, and since the coordination tetrahedra around the Si and Mg atoms are fully occupied and smaller than the Na tetrahedra, the Na-ion conduction must proceed through the unoccupied tetrahedra and/or octahedra in the structure. There are four each of these sites in the substructure unit cell of Na_2MgSiO_4 and each is surrounded by an equal number of cations and O atoms (Table 6). Considering the sizes of the openings of triangular faces of these polyhedra, the best potential pathway for diffusion is in the direction $[\bar{1}01]$ in which there are Na(1)—Na(2)—Na(1) chains with distances of Na(1)—Na(2) of 3·21 and 3·22 Å. The $[\bar{1}01]$ path involves the following sites: Na(1)→ Oc(2) → Na(2) → Oc(3) → TNa(1) [or Oc(4)] → Na(1).* These sites are connected by triangular faces with openings of respectively 1·80, 1·94, 1·82, 2·00 (or 1·96) and 2·10 (or 2·16) Å. The calculation of openings is made on the assumption that the radius of an O atom is 1·24 Å. The corresponding diameter of the Na atom is about 2·30 Å (see Shannon, 1976, crystal radii). The free diameters of the openings are slightly smaller than they

---

* For definitions of Oc and TNa see Table 6.

Table 5. *Important features of silicate ionic conductors*

Compound	$Na_5YSi_4O_{12}$[a]	$Na_4Zr_2Si_3O_{12}$[b]	$Na_3\square Zr_2Si_2PO_{12}$	Na_2MgSiO_4	$Na_{1.9}\square_{0.1}Mg_{0.9}$-$Al_{0.1}SiO_4$[c]
Shared faces between occupied sites	VII→VIII VI→VII	VI→VIII VIII→VIII	?	None	?
Sizes of openings at room temperature (Å)*	1·92	1·86 2·30	?	1·74–2·16	?
Shortest Na—Na distances (Å)	1·50, 1·60 2·82, 2·87 3·00, 3·35	3·5 4·72	?	3·21–3·26	?
B(Na) at RT (Å^2)	Na(4) 2·5 Na(5) 8·0 Na(6) 2·8	Na(1) 1·4 Na(2) 2·2	?	Na(1) 1·21 Na(2) 1·06	?
σ(573 K), $(\Omega m)^{-1}$	10	3×10^{-2}	20	3×10^{-3}	0·1

References: (*a*) Chen, Gier & Shannon (1981). (*b*) Tranqui, Capponi, Joubert, Shannon & Johnson (1979). (*c*) Shannon (1979).

* Compare with $d(Na^+) = 2.30$ Å.

Table 6. *Approximate positional coordinates of unoccupied octahedral* (Oc) *and tetrahedral sites in the* Na_2MgSiO_4 *substructure and their neighbors and the mean distances to them*

The notation TSi *etc.* refers to tetrahedral sites sharing a basal plane with the Si tetrahedron *etc.*

	x	*y*	*z*	Neighbors	Mean distances (Å) to Cations	O atoms
Oc(1)	0·5	0·5	0·63	2×: O(1),O(2),Si,Na(1)	2·4	2·3
Oc(2)	0·0	0·5	0·63	1×: O(3),O(4),Mg,Na(2)	2·4	2·4
Oc(3)	0·75	0·0	0·63	2×: O(3),O(4),Mg,Na(2)	2·4	2·3
Oc(4)	0·25	0·0	0·63	1×: O(1),O(2),Si,Na(1)	2·4	2·5
TSi	0·25	0·69	0·75	One each of all the atoms in one asymmetric unit	2·1	2·0
TMg	0·0	0·19	0·75		2·1	1·9
TNa(1)	0·75	0·63	0·75		2·1	2·2
TNa(2)	0·5	0·16	0·75		2·1	2·2

are in $Na_5YSi_4O_{12}$ and $Na_4Zr_2Si_3O_{12}$, which have better conductivities than Na_2MgSiO_4 (Table 5).

Other potential pathways for diffusion are in the direction [010] in which there are Na(2)—Na(1)—Na(2) chains with distances of Na(2)—Na(1) of 3·21 and 3·34 Å and in the direction [001] connecting Na(1)—Na(2)—Na(1) chains at distances of 3·22 and 3·26 Å. In the [010] path, the Na atoms would pass through the Oc(2) and Oc(4) sites to which the Na coordination tetrahedra are connected by triangular faces with openings of 1·94, 1·80, 2·16, and 1·74 Å. These are smaller than openings in $Na_5YSi_4O_{12}$ and $Na_4Zr_2Si_3O_{12}$. The [001] path involves the following sites: Na(1) → TNa(1) → Oc(3) → Na(2) → TNa(2) → Oc(4) → Na(1). In this case the diameter of the smallest opening would be only 1·68 Å, thus making this path the least probable.

It seems reasonable to assume that conduction of Na ions in the two compositions, $Na_{2-x}Mg_{1-x}Al_xSiO_4$ and $Na_4MgSi_3O_{10}$, must proceed through continuous channels of face-shared polyhedra. Although we do not know the detailed structure of these two conductors, we believe that the structure of the parent compound, Na_2MgSiO_4, can help us predict the most probable conductivity paths in $Na_4Mg_2Si_3O_{10}$ and $Na_{2-x}Mg_{1-x}Al_xSiO_4$. We assume that in the conductive phases some of these Na sites, unoccupied in Na_2MgSiO_4, must become at least partially occupied. Although it seems unusual for removal of Na ions to result in filling of unoccupied sites, it must be remembered that both $Na_4Mg_2Si_3O_{10}$ and nonstoichiometric Na_2MgSiO_4 have space groups different from Na_2MgSiO_4. This change of space group may reflect the progressive occupation of these sites. The actual paths could be established by studying by X-ray diffraction appropriately substituted Na-deficient derivatives of Na_2MgSiO_4 at elevated temperatures where Na atoms would have a higher probability of being encountered in 'in-between positions'.

We thank Dr T. Araki for providing us with a copy of his computer program *TWXLLS*, Dr I. Steele for the electron and ion microprobe analyses of a sample of Na_2MgSiO_4 and the Computer Center of the University of Illinois for computer time.

Note added in proof: A 30-fold increase in NH content resulted in an increase of one order of magnitude in the ionic conductivity of H-doped Li_3N (Bell, Breitschwerdt & von Alpen, 1981). In view of this observation the hydrogen content of Na_2MgSiO_4 is of interest. To which degree does the conductivity of the oxide-based tetrahedral ionic conductors depend on their H content? Inasmuch as this structure type has many vacant sites (the octahedral positions and the unoccupied tetrahedral sites) it is unlikely that the creation of additional vacancies by H incorporation should change the ionic conductivity in a drastic way. However, it would be prudent to know the H content of samples used for ionic conductivity measurements.

References

Araki, T. (1977). *Am. Crystallogr. Assoc. Program Abstr.* **5**, 68.

Araki, T. (1979). *Am. Crystallogr. Assoc. Program Abstr.* **7**, 36.

Barth, T. F. W. & Posnjak, E. (1932). *Z. Kristallogr.* **81**, 376–385.

Baur, W. H. (1977). *Phys. Chem. Miner.* **2**, 3–20.

Baur, W. H. & Khan, A. A. (1970). *Acta Cryst.* **B26**, 1584–1596.

Bell, M. F., Breitschwerdt, A. & von Alpen, U. (1981). *Mater. Res. Bull.* **16**, 267–272.

Bertaut, F. & Blum, P. (1954). *C. R. Acad. Sci.* **239**, 429–431.

Borchert, W. & Keidel, J. (1947). *Heidelb. Beitr. Mineral. Petrogr.* **1**, 17–30.

Buerger, M. J. (1935). *Z. Kristallogr.* **90**, 186–192.

Chen, H.-Y., Gier, T. E. & Shannon, R. D. (1981). To be published.

Goodenough, J. B., Hong, H. Y.-P. & Kafalas, J. A. (1976). *Mater. Res. Bull.* **11**, 203–220.

Gramlich, V. & Meier, W. M. (1971). *Z. Kristallogr.* **133**, 134–149.

Hawthorne, F. C. (1978). *Acta Cryst.* A**34**, 139–140.

Ilyukhin, V. V., Nikitin, A. V. & Belov, N. V. (1966). *Dokl. Akad. Nauk SSSR*, **171**, 1325–1328 [Engl. trans. (1967). *Sov. Phys. Dokl.* **11**, 1035–1037].

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

Joubert-Bettan, C. A., Lachenal, R., Bertaut, E. F. & Parthe, E. (1969). *J. Solid State Chem.* **1**, 1–5.

Marumo, F., Isobe, M., Saito, Y., Yagi, T. & Akimoto, S. (1974). *Acta Cryst.* B**30**, 1904–1906.

Meier, W. M. & Villiger, H. (1969). *Z. Kristallogr.* **129**, 411–423.

O'Keeffe, M. & Hyde, B. G. (1976). *Acta Cryst.* B**32**, 2923–2936.

O'Keeffe, M. & Hyde, B. G. (1978). *Acta Cryst.* B**34**, 3519–3528.

Shannon, R. D. (1976). *Acta Cryst.* A**32**, 751–767.

Shannon, R. D. (1979). *Phys. Chem. Miner.* **4**, 139–148.

Shannon, R. D. & Berzins, T. (1979). *Mater. Res. Bull.* **14**, 361–367.

Solid Electrolytes (1978). Edited by P. Hagenmuller & W. van Gool. New York: Academic Press.

Strukturbericht 1913–1928 (1931). Vol. 1, pp. 128–129. Leipzig: Akademische Verlagsgesellschaft.

Swanson, H. E. & Fuyat, R. K. (1953). *Natl Bur. Stand.* (*US*) *Circ.* **593**, Vol. II, 25–26.

Takeuchi, Y. & Kudoh, Y. (1977). *Z. Kristallogr.* **146**, 281–292.

Tillmanns, E. & Baur, W. H. (1970). *Acta Cryst.* B**26**, 1645–1654.

Tillmanns, E., Gebert, W. & Baur, W. H. (1973). *J. Solid State Chem.* **7**, 69–84.

Tranqui, D., Capponi, J. J., Joubert, J. C., Shannon, R. D. & Johnson, C. K. (1979). Int. Conf. Fast Ion Transport in Solids – Electrolytes and Electrodes, Lake Geneva, Program and Abstracts, PA-25.

Acta Cryst. (1981). B**37**, 1491–1496

Structural Aspects of the Hexagonal to Orthorhombic Transition in Stoichiometric $BaVS_3$

By M. Ghedira,* J. Chenavas, F. Sayetat and M. Marezio

Laboratoire de Cristallographie, CNRS, 166*X*, 38042 *Grenoble CEDEX, France*

and O. Massenet and J. Mercier

Groupe des Transitions de Phases, 166*X*, 38042 *Grenoble CEDEX, France*

(*Received* 18 *February* 1980; *accepted* 27 *January* 1981)

Abstract

The crystal structure of stoichiometric $BaVS_3$ has been refined at room temperature from single-crystal X-ray data. This compound is hexagonal, space group $P6_3/mmc$ with two molecules per unit cell of dimensions $a = 6{\cdot}7283\ (5)$ and $c = 5{\cdot}6263\ (5)$ Å. The structure has been refined to a final R value of 1·1% for 216 independent reflections. The sulfur and the barium atoms form a slightly distorted hexagonal close-packed network with the vanadium atoms occupying one quarter of the octahedral sites, namely those formed only by sulfur atoms. These vanadium-occupied sulfur octahedra share faces and form infinite chains parallel to the c hexagonal axis. This arrangement makes $BaVS_3$ a 1*D* compound as far as the vanadium atoms are concerned. The average V—S distance is 2·385 (1) Å. The barium atoms are surrounded by 12-sulfur polyhedra, the average Ba—S distance being 3·396 (1) Å. These results are in good agreement with those previously published by Gardner, Vlasse & Wold [*Acta Cryst.* (1969), B**25**, 781–787]. The thermal vibrations of the vanadium atoms are strongly anisotropic. The r.m.s. value in the basal plane is 0·163 (1) Å, whereas that along the c axis is 0·106 (1) Å. This seems to indicate that already in the hexagonal phase the vanadium atoms zig-zag along the c axis, which can be considered as a dynamical distortion of the vanadium sublattice. Single-crystal X-ray data at low temperature show that stoichiometric $BaVS_3$ undergoes a crystallographic phase transition at about 250 K. Since the crystal symmetry becomes orthorhombic, twin formation is observed at the transition. The twinning is by pseudomerohedry. Precession photographs of twin crystals have been fully indexed on an orthorhombic cell of dimensions $a_O \simeq a_H$, $b_O \simeq \sqrt{3}a_H$ and $c_O \simeq c_H$. The possible space

---

* Permanent address: Faculté des Sciences de Monastir, Monastir, Tunisie.

0567-7408/81/081491-06$01.00