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The Crystal Structure and Twinning Laws of the Orthorhombic Modification of Na_2BeSiO_4

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The crystal structure of the solid electrolyte Na_2BeSiO_4 has been determined and refined both at 295 and 623 K using crystal diffraction data from a sixfold twin collected with Mo$K\alpha$. The structural relations between the twin components have been elucidated. The structure is orthorhombic with the space group symmetry $Pca2_1$. The unit cell contains eight formula units of Na_2BeSiO_4, and the lattice parameters are $a = 9.861(2)$, $b = 4.911(1)$, $c = 13.875(3)$ Å, and $V = 671.9$ Å^3. The refinement yielded $R_{\mathrm{wiso}} = 0.068$ and $R_{\mathrm{wan}} = 0.053$ for the data collected at 295 K (2504 reflections with $I > 3\sigma_I$), and $R_{\mathrm{wiso}} = 0.059$ and $R_{\mathrm{wan}} = 0.034$ for the 623 K data set (2468 reflections with $I > 3\sigma_I$). The structure can be described as a cristobalite-related framework structure with chains of alternating BeO_4 and SiO_4 corner-sharing tetrahedra. The Na atoms are found at four different positions in the cavities formed by the tetrahedra. Possible conduction pathways have been deduced.

Introduction

Previous studies of the ionic conductivity in systems such as Na_2O–Me_nO_m–$SiO_2(GeO_2)$, with Me = Be, Mg, Zn, Al, and Ga, have shown that the phases isotypic with the high-temperature modification of Na_2ZnSiO_4, denoted type C phase below, possess good ionic conductivity (see Ref. (*1*) and references therein). In the $Na_xBe_{x/2}Si_{2-x/2}O_4$ system the compositional region of this phase is $1.80 \leq x \leq 2.00$. The structures of several of these phases, including Na_2BeSiO_4, have been outlined from powder diffractometer data evaluated by the Rietveld technique (*2, 3*). The basic structure $A_2MeMe'O_4$ has been found to be related to the cristobalite structure and has an orthorhombic unit cell related to the ideal cristobalite structure axis (a_c) by $a \approx a_c\sqrt{2}$, $b \approx a_c/\sqrt{2}$, and $c \approx 2a_c$. The A atoms are located in the cavities formed by the corner-sharing MeO_4 and $Me'O_4$ tetrahedra. The refinement showed the space group to be $Pca2_1$. The number of parameters to be refined with all atoms in the 4(*a*) positions of the $Pca2_1$ space group is 47. The final refinements did not converge, but yielded oscillating positional parameters. The number of parameters to be refined could, however, be reduced by linking pairs of atom coordinates according to x_1, y_1, z_1

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and x_1, $1/2 + y_1$, $1/2 - z_1$. This linking, corresponding to an incorporation of a glide reflection plane along the *b*-axis and perpendicular to the *c*-axis, reduced the number of variables from 47 to 24, which was sufficient for convergence. Structurally, the added constraints imply that the structure determined is geometrically averaged, since by this method, for instance, differently sized MeO_4 and $Me'O_4$ tetrahedra become equivalent.

In this article we report a structure determination of the orthorhombic modification of Na_2BeSiO_4 with data from a crystal consisting of six twin partners. The structural relation between the six partners is given. X-ray diffractometer data were collected at two temperatures, 295 and 623 K. The structures thus obtained are discussed in relation to the one obtained by the Rietveld technique and in relation to the ionic conductivity mechanism of Na_2BeSiO_4.

The structure of hydrothermally prepared Na_2BeSiO_4 has previously been determined by Plakhov *et al.* (*4*) to be of monoclinic symmetry, and the differences between these modifications will be discussed briefly.

Experimental

A powder sample of Na_2BeSiO_4 was prepared by reacting an appropriate mixture of BeO, SiO_2, and Na_2CO_3. The mixture was first decarbonated by gradual heat treatment up to 1075 K and was then held there for 3 hr. The sample was reground, pressed into tablets, and fired at 1225 K for 12 hr. This procedure was repeated twice. No crystals large enough for single crystal X-ray structure determination were obtained in this way, however.

The crystals used in this study were grown in a melt containing excess Na_2SiO_3. The melt was cooled at a rate of 1 K per minute to ~1423 K, reheated to a temperature slightly above the melting temperature (~1523 K), and cooled again. The reaction product was then treated with water, and the insoluble part was found to consist mainly of crystals of Na_2BeSiO_4. About 20 crystals were studied by examining photographs from a Weissenberg camera, and all of them were found to be twinned in the same manner as the one used in this study. The latter had a tetrahedral shape with a maximum diameter of 0.1 mm.

X-ray powder photographs of a number of crushed and powdered Na_2BeSiO_4 crystals and of the polycrystalline material were recorded with a Guinier–Hägg-type focusing camera, using monocromatized $CuK\alpha_1$ radiation. Si was used as internal standard, and the photographs were evaluated with a computer-controlled film scanning system (*5*).

Various single crystal X-ray diffraction methods were used in connection with the elucidation of the twinning laws, including Laue, Weissenberg, and single-crystal diffractometry techniques. The primary X-ray diffractometer data set was recorded with a STOE/AED2 diffractometer, using $MoK\alpha$ radiation. The final set of data used for the structural analysis was obtained with an automatic Nonius CAD-4F diffractometer equipped with a graphite monochromator and a furnace which allowed data collection at elevated temperatures. $MoK\alpha$ radiation was used and ω-scanning at variable rates was applied.

The unit cell parameters assumed in the data collection were refined by least-squares fitting of the 2θ values of 25 reflections and were found to be $a = 13.898(3)$, $b = 13.900(3)$, $c = 13.886(3)$ Å, and $\alpha = \beta = \gamma = 90.02(2)°$ for the room temperature data set, and $a = 13.984(3)$, $b = 13.988(3)$, $c = 13.972(3)$ Å for the data set collected at 623 K. The intensities of all reflections within a hemisphere of reciprocal space were measured for $-18 \leq h \leq 18$, $-18 \leq k \leq 18$, $l \geq 0$, and $\sin \theta/\lambda \leq 0.7$ Å^{-1}, yielding totally 2504 reflections with $I_{hkl} > 3\sigma(I)$ at 295 K

TABLE I

EXPERIMENTAL AND CRYSTAL DATA

Formula		Na_2BeSiO_4	
Formula weight (g/mole)		147.08	
Space group		$Pca2_1$	
Temperature (K)	295(2)		623(2)
Unit cell dimensions			
Twin lattice			
a (Å)	13.898(3)		13.984(3)
b (Å)	13.900(3)		13.988(3)
c (Å)	13.886(6)		13.972(3)
Single crystal component	[a]		[b]
a (Å)	9.861(2)		9.866(2)
b (Å)	4.911(1)		4.945(1)
c (Å)	13.875(3)		13.972(3)
V (Å^3)	671.9		682.6
Formula units per unit cell		8	
Calculated density (g/cm^3)	2.92		2.88
Radiation		Mo$K\alpha$	
Wavelenth (Å)		0.7103	
Crystal shape		Tetrahedral	
Crystal size (mm)		0.1	
Diffractometer		ENRAF–Nonius CAD-4	
Determination of unit cell			
No. of reflections used		25	
Θ-range		16–22	
Intensity data collection			
Maximum sin Θ/λ (Å^{-1})		0.7	
Range of h, k, and l		$-18 - 18$, $-18 - 18$, $0 - 18$ HKL in twin lattice	
Standard reflections		1	
Intensity instability		<4%	
Internal R-value	0.046		0.042
No. of measured reflections		22,853	
No. of observed reflections	2504		2468
Criterion for significance		$I_{HKL} > 3\sigma(I)$	
Absorbtion correction			
Linear absorbtion coefficient (cm)$^{-1}$		6.9	
Transmission factor range		0.94–0.97	
Structure refinement			
Minimization of		$\sum w(\lvert F_{obsd}\rvert^2 - \lvert F_{calcd}\rvert^2)^2$	
Anisotropic thermal parameters		Na, Si, O	
Isotropic thermal parameters		Be	
No. of refined parameters		134	
Weighting scheme		$(\sigma(F))^{-2}$	
Final R	0.049		0.048
Final R_w	0.053		0.034
Final R_w for all reflections	0.053		0.034
Final $(F_{obsd} - F_{calcd}/\sigma)_{max}$	0.93		0.90
Final $\Delta\rho_{min}$ and $\Delta\rho_{max}$ (Å^3)		-0.6 and 0.6	

[a] Determined from powder data.

[b] Transformed from twice lattice by matrix (1/2 1/2 0, 1/4 − 1/4 0, 0 0 1).

and 2468 at 623 K. The preliminary structure determination was performed with the SHELX-76 set of programs (*6*). The final refinement of the positional and thermal parameters was based on all 2504 (295 K) and 2468 (623 K) reflections, using the REMOS-85 (*7*) and the INCRYS (*8*) programs, respectively. The REMOS-85, originally developed for the refinement of modulated structures, provides a possibility for refining crystal structures using diffraction data obtained from twinned crystals. Crystal data and experimental parameters are displayed in Table I.

Results

1. Derivation of Twinning Laws

The X-ray powder patterns of the *powder* sample, and of a number of *crystals* of Na_2BeSiO_4 prepared as described above, could be indexed with an orthorhombic unit cell with $a = 9.861(2)$, $b = 4.911(1)$, and $c = 13.875(3)$ Å. Reflections with $(h0l)$; $h \neq 2n$ and $(0kl)$; $l \neq 2n$ are systematically absent which, together with the assumption that the Na_2BeSiO_4 framework is of the cristobalite type, suggested the space group $Pca2_1$. It became immediately obvious that the single crystal and powder data were inconsistent. Thus all the reflections of the single crystal X-ray diffraction pattern could be uniquely indexed assuming a cubic unit cell with $a \sim 13.9$ Å. The cubic cell is related to the orthorhombic one through $a_{\text{cub}} = c_{\text{orth}}$, $b_{\text{cub}} = a_{\text{orth}} + 2b_{\text{orth}}$, and $c_{\text{cub}} = a_{\text{orth}} - 2b_{\text{orth}}$ as illustrated in Fig. 1. Careful inspection of the complete X-ray data set for Na_2BeSiO_4, with special emphasis on the profiles of the reflections and on the extinction laws not inherent with the space group $Pca2_1$, showed that the cubic reciprocal lattice is generated by pseudo-merohedral twinning in agreement with the Friedel theory (*9, 10*). Twinning should occur in accordance with the reticular pseudo-merohedry, implying that any symmetry element of the pseudo-cubic ($m3m$) twin lattice that is not a symmetry element of Laue class (mmm) of the partner may serve as a twinning element.

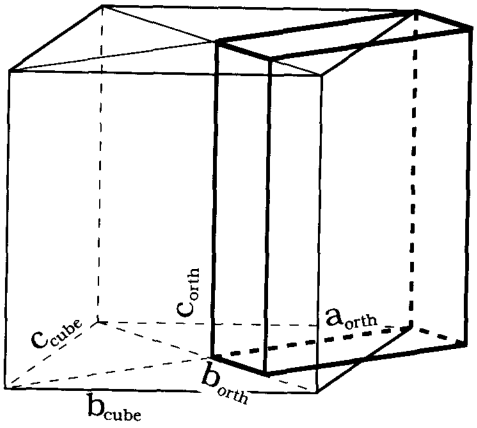

FIG. 1. Relations between the metrics of the twin lattice ($a_{\text{cube}} = b_{\text{cube}} = c_{\text{cube}}$) and the metrics of the single-crystal twinning partner (a_{orth}, b_{orth}, c_{orth}).

Thus, the pseudo-cubic pattern observed experimentally may be considered as being composed of superpositions of six different patterns from orthorhombic single-crystal twin partners, each having lattice parameters equal to those determined from the X-ray powder data. The indices of all the experimental reflections HKL in such twin lattices are obtained from reflections $h_ik_il_i$ ($i = 1$–6) of the orthorhombic partners. Vice versa, the $h_ik_il_i$ indices of each single-crystal component may be represented in terms of the HKL of the twin lattice, as given in Table II.

Single crystal components 1, 2, 3 and 4, 5, 6 are mutually related to each other by 120° rotations around the [201] direction. In the Friedel notation, this is the so-called pseudo-hexagonal twinning by reticular merohedry with twin index four. The pseudo-tetragonal twinning follows from the tetragonal pseudo-symmetry of the double orthorhombic unit cell. Such a unit cell is obtained from the initial one by the matrix transformation (100/002/010). Single

TABLE II

RELATIONS OF CUBIC AND ORTHORHOMBIC INDICES

$H = l_1$ $K = h_1 + 2k_1$ $L = h_1 - 2k_1$	$H = h_2 - 2k_2$ $K = l_2$ $L = h_2 + 2k_2$	$H = h_3 + 2k_3$ $K = h_3 - 2k_3$ $L = l_3$
$H = l_4$ $K = h_4 + 2k_4$ $L = -h_4 + 2k_4$	$H = -h_5 + 2k_5$ $K = l_5$ $L = h_5 + 2k_5$	$H = h_6 + 2k_6$ $K = -h_6 + 2k_6$ $L = l_6$
$h_1 = 1/2(K) + 1/2(L)$ $k_1 = 1/4(K) - 1/4(L)$ $l_1 = H$	$h_2 = 1/2(H) + 1/2(L)$ $k_2 = -1/4(H) + 1/4(L)$ $l_2 = K$	$h_3 = 1/2(H) + 1/2(K)$ $k_3 = 1/4(H) - 1/4(K)$ $l_3 = L$
$h_4 = 1/2(K) - 1/2(L)$ $k_4 = 1/4(K) + 1/4(L)$ $l_4 = H$	$h_5 = -1/2(H) + 1/2(L)$ $k_5 = 1/4(H) + 1/4(L)$ $l_5 = K$	$h_6 = 1/2(H) - 1/2(K)$ $k_6 = 1/4(H) + 1/4(K)$ $l_6 = L$

Note. Indices expressed as orthorhombic partner reflections $h_ik_il_i$ (i = 1–6) derived from the experimentally observed twinned crystal reflections HKL, and vice versa.

crystal components are related by mutual rotation through 90° around the [001] direction. This is a pseudo-tetragonal twinning by reticular merohedry with twin index two. The pseudo-tetragonal twin law transforms component 1 into 4, component 2 into 5, and component 3 into 6. In accordance with the twin laws considered above, the Miller indices of each of the 2504 experimentally observed reflections with $I_{HKL} > 3\sigma(I)$ satisfy at least one of the following conditions:

1. $K + L = 2n$ H no conditions $K - L = 4n$
2. $H + L = 2n$ K no conditions $L - H = 4n$
3. $H + K = 2n$ L no conditions $H - K = 4n$
4. $K - L = 2n$ H no conditions $K + L = 4n$
5. $L - H = 2n$ K no conditions $H + L = 4n$
6. $H - K = 2n$ L no conditions $H + K = 4n$

Only 414 reflections could be uniquely indexed; i.e., each satisfied only one of the six conditions given above, while 1089 reflections satisfied all six conditions. The 414 uniquely indexed reflections originate from different components of the crystal. Since the scattering volume of each of the six partners is very small, the intensities of most of the uniquely indexed reflections only slightly exceed the minimum set by the 3σ criterion. Due to this fact, it was not possible to refine the cell parameters using only data originating from one single-crystal component. Thus we have used the orthorhombic cell parameters obtained from powder diffraction data in the calculations described below.

2. *Structure Refinement*

The space group was determined from the reflections that could be indexed within the framework of one single-crystal component with a = 9.861(2), b = 4.911(1), and c = 13.875(3) Å. Due to the twinning laws given above, systematic absences could only be determined for ($h0l$) reflections. The observed rules for allowed reflections ($h0l$; $h = 2n$) thus only permitted determination of one-third of the characteristic symmetry elements of the orthorhombic space group, namely *P-a-*. The other two symmetry elements could not be determined, due to overlapping of (0*kl*) and (*hk*0) reflections caused by the twinning. Thus we used the acentric monoclinic space group $C_s^2 = Pa$ for the preliminary structure determination. The analysis of the complete and partial Patterson functions (*11*) obtained with use of this space group made it possible to determine the cation framework of the structure and, on the basis of the analysis of electron density maps, the anion positions could be outlined. At this stage of the investigation it was established, by scrutinizing the obtained structure model, that the structure is characterized by the orthorhombic space group $C_{2v}^5 = Pca2_1$.

The final refinement of the positional and thermal parameters was performed with all 2504 (295 K) and 2468 (623 K) reflections of the twin lattice, using the REMOS-85 (*7*) and INCRYS (*8*) programs, respectively. The twinning operations were set by the equations given in Table II. Each of the six possible twin partners $h_ik_il_i$ (i = 1–6) was written in terms of the *HKL* indices of the twinned lattice. The least-squares refinement in the isotropic and anisotropic approximations yielded the following reliability factors: $R_{\text{iso}} = 0.064$, $R_{\text{wiso}} = 0.068$ and $R_{\text{an}} = 0.049$, $R_{\text{wan}} = 0.053$, at 295 K and $R_{\text{iso}} = 0.061$, $R_{\text{wiso}} = 0.059$ and $R_{\text{an}} = 0.048$, $R_{\text{wan}} = 0.034$ at 623 K. The final positional and thermal parameters for Na_2BeSiO_4 at 295 and 623 K are given in Tables III and IV. In Table V the anisotropic temperature factors are given. Selected interatomic distances are given in Table VI. The volume of the crystal under consideration, V, is equal to the sum of the volume v_i of each of the six parameters ($V = \Sigma v_i = 1$) and v_i are proportional to the coefficient of reduction of the $Fh_ik_il_i$ of these partners to general scale factor and are found to be $v_1 = 0.17$, $v_2 = 0.11$, $v_3 = 0.30$, $v_4 = 0.08$, $v_5 = 0.16$, and $v_6 = 0.18$.

TABLE III

ATOMIC COORDINATES OBTAINED AT 295 K

	x a = 9.861 Å	y b = 4.911 Å	z c = 13.875 Å	B_{iso} (Å^2)
Be1	0.2464(19)	0.9954(52)	0.4449(22)	0.4 (fix)
Be2	0.0314(13)	0.5206(36)	0.6928(19)	0.4 (fix)
Si1	0.0122(5)	0.0281(8)	0.8184(5)	0.71(4)
Si2	0.2297(3)	0.5144(11)	0.0739(–)	0.28(2)
Na1	0.0045(7)	0.5187(15)	0.9496(7)	2.07(8)
Na2	0.0080(6)	0.0147(15)	0.5664(6)	1.52(8)
Na3	0.2265(7)	0.5334(14)	0.3226(7)	2.16(7)
Na4	0.2352(6)	0.0347(15)	0.1925(8)	2.10(9)
O1	0.1705(11)	0.0831(24)	0.8512(9)	1.80(6)
O2	0.1725(10)	0.5965(21)	0.6639(8)	0.88(9)
O3	0.1946(9)	0.2852(22)	0.5060(8)	1.01(11)
O4	0.1932(10)	0.7674(20)	0.0068(9)	1.16(8)
O5	0.0876(12)	0.8772(25)	0.4065(9)	1.56(6)
O6	0.0918(10)	0.3859(20)	0.1157(8)	0.69(8)
O7	0.0118(11)	0.7999(19)	0.2209(8)	1.10(7)
O8	0.0120(10)	0.3008(8)	0.2980(9)	0.88(8)

Note. The unit cell axes and the isotropic temperature factors are also given. Standard deviations are given within parentheses.

TABLE IV

ATOMIC COORDINATES OBTAINED AT 623 K

	x a = 9.886 Å	y b = 4.945 Å	z c = 13.972 Å	B_{eq} (Å^2)
Be1	0.2453(24)	0.9921(33)	0.4446(14)	0.5 (fix)
Be2	0.0299(16)	0.5214(28)	0.6926(11)	0.5 (fix)
Si1	0.0163(6)	0.0271(11)	0.8234(—)	0.80(6)
Si2	0.2332(8)	0.5162(14)	0.0739(5)	0.50(9)
Na1	0.0099(14)	0.5044(22)	0.9493(9)	2.27(18)
Na2	0.0052(12)	0.0240(18)	0.5703(11)	2.50(18)
Na3	0.2321(16)	0.5280(22)	0.3248(14)	4.13(26)
Na4	0.2331(15)	0.0306(26)	0.1955(14)	4.24(29)
O1	0.1663(16)	0.0721(24)	0.8546(13)	1.00(30)
O2	0.1719(21)	0.6213(28)	0.6643(15)	2.37(42)
O3	0.2016(19)	0.2767(23)	0.5128(14)	2.25(38)
O4	0.1937(23)	0.7695(24)	0.0159(13)	1.25(30)
O5	0.0834(23)	0.8985(30)	0.4117(13)	1.75(34)
O6	0.0999(17)	0.3795(23)	0.1241(12)	1.03(21)
O7	0.0045(15)	0.8015(23)	0.2255(11)	1.13(19)
O8	0.0175(21)	0.3061(22)	0.3029(11)	1.49(27)

Note. The unit cell axes and the equivalent isotropic temperature factors given. $B_{\text{eq}} = 8\pi^2(\mu_1^2 + \mu_2^2 + \mu_3^2)/3$, where μ_i is the amplitude of the ith principal axis of the ellipsoid. Standard deviations are given within parentheses.

3. *Description of the Na_2BeSiO_4 Structure*

The structure can be described as made up of chains of alternating BeO_4 and SiO_4 corner-sharing tetrahedra which run parallel to the *a*-axis as seen in Fig. 2. Each SiO_4

TABLE V

Anisotropic Temperature Factors at 623 K

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Si1	0.0010(3)	0.0076(10)	0.0016(2)	−0.0003(6)	−0.0002(3)	−0.0011(10)
Si2	0.0014(6)	0.0054(10)	0.0006(3)	−0.0017(10)	−0.0001(3)	−0.0009(4)
Na1	0.0078(8)	0.0189(11)	0.0025(4)	−0.0080(10)	−0.0023(4)	0.0009(3)
Na2	0.0074(10)	0.0276(40)	0.0024(2)	−0.0024(4)	−0.0024(7)	0.0008(4)
Na3	0.0128(11)	0.0368(7)	0.0048(8)	0.0041(8)	0.0024(4)	−0.0096(15)
Na4	0.0111(16)	0.0545(32)	0.0039(4)	−0.0023(6)	0.0028(10)	0.0022(12)
O1	0.0051(6)	0.0057(10)	0.0005(3)	0.0007(3)	0.0010(3)	−0.0010(4)
O2	0.0049(10)	0.0342(4)	0.0024(6)	−0.0001(4)	−0.0001(4)	−0.0019(7)
O3	0.0072(12)	0.0193(14)	0.0026(8)	−0.0003(4)	0.0015(7)	−0.0006(4)
O4	0.0017(7)	0.0092(10)	0.0029(7)	−0.0011(7)	0.0018(7)	0.0008(3)
O5	0.0027(10)	0.0231(11)	0.0025(7)	0.0006(3)	−0.0009(6)	0.0020(3)
O6	0.0037(11)	0.0126(40)	0.0005(4)	−0.0034(8)	−0.0007(5)	−0.0022(4)
O7	0.0045(7)	0.0098(11)	0.0009(4)	0.0037(9)	0.0009(5)	−0.0007(5)
O8	0.0035(15)	0.0081(11)	0.0030(4)	0.0025(10)	−0.0003(3)	−0.0016(8)

Note. The Be atoms are held fixed at $B_{\mathrm{iso}} = 0.5$. The complete temperature factor is given by the expression $\exp -(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)$. Standard deviations are given within parentheses.

tetrahedron is thus surrounded by four BeO_4 tetrahedra. The cristobalite-related framework formed in this way contains cavities, and the sodium atoms are located inside these cavities. The cavities are interconnected via "windows" so as to form tunnels running through the structure. As seen in Fig. 2, two types of tunnels exist, one with almost rhombic windows and one with triangle-shaped windows. Four differ-

TABLE VI

Interatomic Distances

Be1	O4	1.53(3)	1.60(3)	Be2	O2	1.50(2)	1.54(3)
	O1	1.60(3)	1.58(3)		O7	1.68(2)	1.70(2)
	O3	1.73(3)	1.75(2)		O6	1.68(2)	1.67(2)
	O5	1.75(2)	1.73(3)		O8	1.76(3)	1.82(2)
Si1	O7	1.61(1)	1.62(2)	Si2	O4	1.59(1)	1.54(2)
	O5	1.64(1)	1.62(2)		O6	1.61(1)	1.64(2)
	O1	1.65(1)	1.56(2)		O2	1.63(1)	1.66(2)
	O8	1.66(1)	1.71(1)		O3	1.65(1)	1.60(2)
Na1	O5	2.23(1)	2.26(2)	Na2	O6	2.30(1)	2.37(2)
	O8	2.29(2)	2.27(2)		O7	2.34(1)	2.37(2)
	O3	2.32(1)	2.52(2)		O4	2.40(1)	2.34(2)
	O4	2.36(1)	2.43(2)		O3	2.42(1)	2.45(2)
	O6	2.55(1)	2.67(2)		O5	2.45(2)	2.43(2)
	O1	3.02(1)	2.95(2)		O2	2.95(1)	2.90(2)
Na3	O8	2.43(1)	2.41(2)	Na4	O2	2.37(1)	2.27(2)
	O2	2.44(1)	2.48(3)		O1	2.40(2)	2.44(3)
	O1	2.47(1)	2.50(2)		O6	2.47(1)	2.39(2)
	O5	2.47(1)	2.64(2)		O7	2.52(1)	2.56(2)

Note. Calculated for atoms within the first coordination sphere around Be, Si, and Na atoms given in angstroms. The sixth oxygen atom has also been incorporated for Na1 and Na2. Estimated standard deviations are given within parentheses.

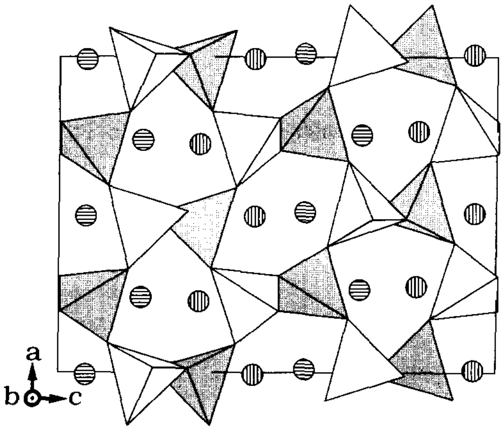

FIG. 2. The Na_2BeSiO_4 structure projected on (010). The shaded tetrahedra contain Si atoms, while the other ones contain Be atoms. The central atoms of the tetrahedra in the chains parallel to the a-axis are located at $y \sim 1/2$ in one chain and at $y \sim 0$ in adjacent chains. The horizontally and vertically striped circles show the Na atoms at heights y ~0 and ~1/2, respectively.

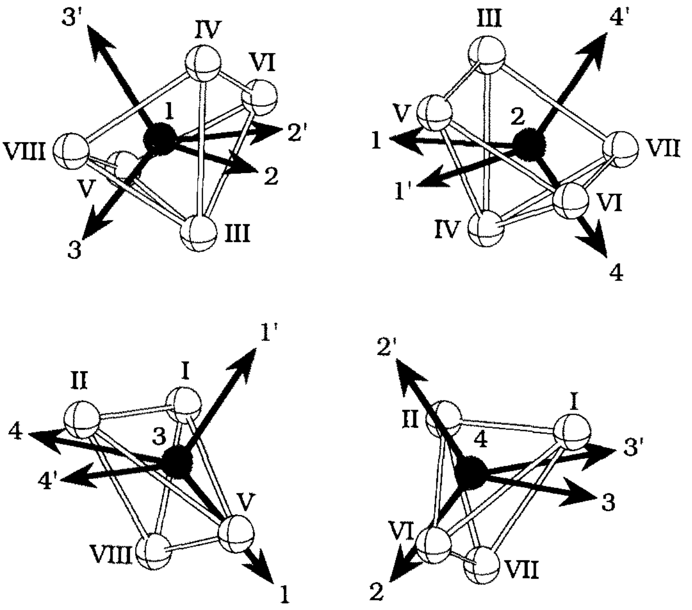

FIG. 3. Coordination polyhedra of oxygen atoms around sodium atoms. The labeling of the oxygen and sodium atoms is in accordance with the numbering in Table III.

ent sodium positions are observed. The Na(1) and Na(2) ions are found in the rhombic tunnels, while Na(3) and Na(4) are found in the other tunnel; and all four are located at levels ~0 and ~1/2 in the *b*-axis direction. The Na(1) and Na(2) ions are coordinated to five oxygen ions, while Na(3) and Na(4) are four-coordinated as seen in Fig. 3. The sodium ions are also seen to form a diamond-net subarray with Na–Na distances around 3 Å.

Discussion

The refinement based on the data set obtained at 623 K showed that Na_2BeSiO_4 has the same structure at 623 and 295 K. Thus one does not observe any change in the configuration of the BeO_4 and SiO_4 tetrahedra or in the coordination of oxygen ions around the Na ions. Due to the thermal expansion of the lattice, the interatomic distances are found to be larger at 623 K which ought to facilitate the mobility of the Na ions.

A comparison of the structure described here with the one obtained by the Rietveld technique from the X-ray powder pattern shows that the present determination is much more accurate, yielding quite reasonable Be–O, Si–O, and Na–O distances. However, the present investigation also confirms that the average structure model derived from the powder data is reasonably good.

In this connection it should be emphasized that the structure of the orthorhombic Na_2BeSiO_4 differs substantially from that of the hydrothermally prepared monoclinic one, determined by Plakhov *et al.* (*4*). The most important difference is that the orthorhombic structure is cristobalite-related, while in the monoclinic Na_2BeSiO_4, Be_2O_6-groups and SiO_4 tetrahedra form a two-dimensional network and these networks are interconnected by Na–O octahedra.

We have previously found relatively high ionic conductivity values for compositions $Na_xMe_{x/2}Me'_{2-x/2}O_4$, with Me = Zn, Be, Ga; Me' = Si and Ge, and $1.80 \leq x \leq 2.00$, all isotypic with the orthorhombic modification of Na_2BeSiO_4. A substantial increase in conductivity with decreasing x-value has been observed, and it can be noted that the $\log(\sigma_0)$-values are almost constant within the homogeneity range while E_a decreases smoothly with decreasing x. In order to conduct, the Na ions have to migrate from one position to another. This implies that the Na(3) and Na(4) ions have to pass through one of the four triangular windows formed by the oxygen ions surrounding the ions, i.e., the faces of the tetrahedron. In the case of the Na(1) and Na(2) ions, one additional rectangular window is formed, i.e., the basal plane of a pyramid, together with four triangles. If one assumes that this window is circular and that the oxygens are perfect spheres of radius 1.24 Å (*12*), the radius of this circular hole can be calculated and is called residual radius (r_j) below. Here we restrict ourselves to calculating r_j-values for windows facing toward the position of another Na ion, see Fig. 3. Due to the prevailing symmetry, it is sufficient to calculate the r_j-values for the pathways Na(1) to Na(2,2′) and to Na(3,3′), Na(4) to Na(2,2′) and to Na(3,3′), where, e.g., Na(2) is located at $y \sim 0$ and Na(2′) at $y \sim 1$. These values are listed in Table VII.

If the oxygen and the sodium ions are assumed to be rigid spheres, it can be deduced from Table VI that the ionic radii of the sodium ions are in the range 1.0–1.2 Å, based on 1.24 Å oxygen radius (*12*). In this connection it can be noted that the Shannon–Prewitt radius for four-coordinated Na^+ ions is 0.99 Å (*13*). To the extent that the r_j-value of a window has to be 1 Å or larger in order to allow sodium ions to pass, there are, according to the data presented in Table VII, no possibilities for the sodium

TABLE VII

RESIDUAL RADII

	LO	295 K	623 K	EO	295 K	623 K
		(Å)			(Å)	
Na1 → Na2	III-IV-VIII	0.84	0.89	III-IV-V	0.75	0.76
	III-IV-VI	0.75	0.80	III-IV-VII	0.91	0.89
Na1 → Na2′	III-V-VI	0.79	0.90	III-V-VI-VII	1.13	1.11
	IV-V-VI-VIII	1.04	1.13	IV-V-VI	0.83	0.83
Na1 → Na3	III-V-VIII	0.70	0.77	I-V-VIII	1.08	1.18
Na1 → Na3′	IV-V-VI-VIII	1.04	1.13	I-II-V	1.22	1.31
Na4 → Na2	II-VI-VII	1.05	0.99	IV-VI-VII	0.75	0.75
	I-VI-VII^a	1.00	1.01	II-V-VI-VII	1.13	1.11
Na4 → Na2′	I-II-VI	1.18	1.12	II-V-VI-VII	1.13	1.11
Na4 → Na3	I-VI-VII	1.00	1.01	I-II-VIII	0.87	0.92
	I-II-VI	1.18	1.12			
Na4 → Na3′	I-II-VII	0.85	0.87	I-II-V	1.23	1.31
				II-V-VII	1.05	1.07

Note. Residual radii, r_j/Å, calculated from the triangular or rectangular windows, which a migrating sodium atom must go through upon leaving (LO) a site and entering (EO) a neighboring site. The window-forming oxygens, given in roman numbers, are in agreement with the numbers given in Fig. 3. The estimated standard deviation of r_j-values are 0.01 Å. The conduction pathway indicated by *a* in the table implies the use of intermediate tetrahedral positions (see text).

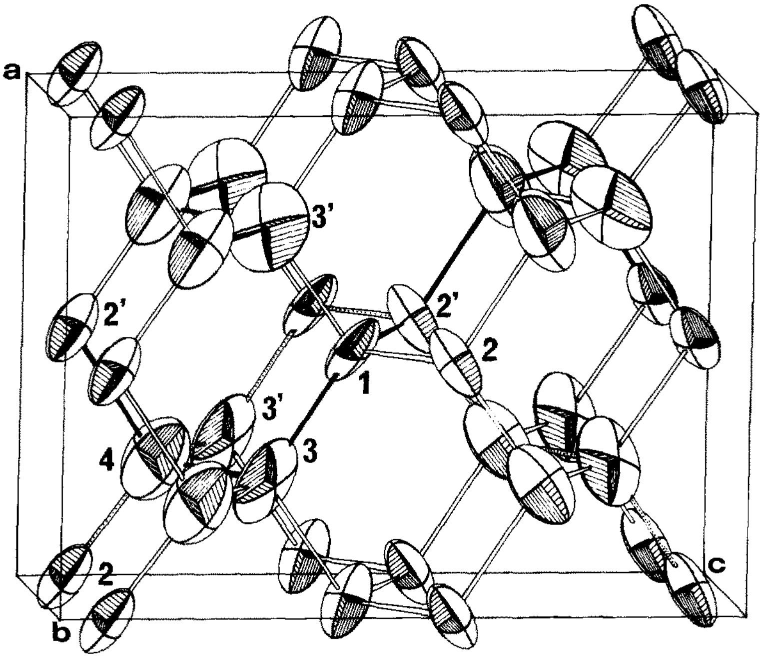

FIG. 4. Thermal vibration ellipsoids for sodium atoms at 623 K. The four crystallographically different sodium atom positions are labeled in accordance with those given in Table IV. The black connecting lines illustrate the conduction pathway for the Na^+ ions as deduced from the various r_j-values (see text). The dotted lines show the pathway suggested by the orientations of the thermal vibration ellipsoids. The latter model seems to favor direct transition between the Na(2) and Na(4) positions, but according to the r_j-value calculation such a transition is not possible (see text).

ions to propagate through the structure via direct jumps from one sodium position to another. However, the anisotropic temperature factors given in Table V clearly show that neither the sodium or the oxygen ions are rigid spheres. Thus, assuming that a sodium ion might pass through windows with r_j-values of about 0.9 Å, the data in Table VII suggest the conducting pathway illustrated in Fig. 4 by the bold connecting lines. In addition to this, pathway migration between the Na(3) and Na(4) positions along the *b*-axis seems possible.

The thermal vibration ellipsoids for the sodium atoms at 623 K are also shown in Fig. 4. The elongation of the ellipsoids may be interpreted as the direction of migration (dotted line in Fig. 4). The sodium conduction pathway deduced from the elongation of the ellipsoids and the one derived from the r_j-values are similar, but there are also differences. Thus the ellipsoid elongation suggests a direct transition between Na(2) and Na(4) positions but the r_j-value (0.75 Å) seems to prevent such a pathway. However, as shown in Table VII, the sodium ions at the Na(2) positions might reach the Na(4) positions via intermediate sites.

In conclusion, both the thermal vibration ellipsoids and the calculated r_j-values seem to indicate that there are several pathways for the sodium ions to migrate through the structure.

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