Acta Cryst. (1990). B**46**, 736–739

Structure and Ionic Conductivity of Decasodium Tetraberyllotetrasilicate, $Na_{10}Be_4Si_4O_{17}$

By L. Eriksson, S. Frostäng and J. Grins

Departments of Structural and Inorganic Chemistry, Arrhenius Laboratory, University of Stockholm, S-106 91 Stockholm, Sweden

(*Received* 18 *April* 1990; *accepted* 3 *July* 1990)

Abstract

In connection with an investigation of ionic conductors in the Na_2O–BeO–SiO_2 system, the compound $Na_{10}Be_4Si_4O_{17}$ has been synthesized and single crystals obtained by cooling a melt containing an excess of Na_2CO_3. $Na_{10}Be_4Si_4O_{17}$ crystallizes in the cubic space group $P\bar{4}3m$ with $a = 7{\cdot}2811\,(3)$ Å, $V = 386{\cdot}00\,(3)$ Å^3, $D_x = 2{\cdot}797$ g cm^{-3}, $Z = 1$ and $M_r = 650{\cdot}28$. The crystal structure was solved from three-dimensional single-crystal X-ray diffraction data obtained with Cu $K\alpha$ radiation, $\lambda = 1{\cdot}5418$ Å, $\mu = 74{\cdot}6$ cm^{-1}, $F(000) = 318$, $T = 293\,(1)$ K, and was refined to $R = 0{\cdot}033$ for 96 unique observed reflexions. The structure exhibits separate $Be_4Si_4O_{17}$ units formed by corner-sharing BeO_4 and SiO_4 tetrahedra. In each $Be_4Si_4O_{17}$ unit a central O atom is common to four BeO_4 tetrahedra. The SiO_4 tetrahedra share three of their O corner atoms with separate BeO_4 tetrahedra, and they have one free apex O atom pointing outwards from the unit. The Na atoms are located on three crystallographically different sites between the $Be_4Si_4O_{17}$ units. Mean bond distances for Si—O and Be—O are 1·637 and 1·650 Å, respectively. The ionic conductivity of $Na_{10}Be_4Si_4O_{17}$ has been determined by impedance measurements and found to be $1{\cdot}0\,(1) \times 10^{-2}$ S m^{-1} at 600 (1) K, with an activation energy E_a of $1{\cdot}04\,(3) \times 10^{-19}$ J. The JCPDS File No. for $Na_{10}Be_4Si_4O_{17}$ is 41-1500.

Introduction

During recent years we have studied the solid electrolyte properties of several sodium-ion conducting silicate and germanate systems (Frostäng, Grins & Nygren, 1988*a*). In connection with an investigation of ionic conductors in the Na_2O–BeO–SiO_2 system, the compound $Na_{10}Be_4Si_4O_{17}$ has been synthesized and its crystal structure determined. The ionic conductivity of $Na_{10}Be_4Si_4O_{17}$ has been determined and is compared below with the conductivities of previously studied phases in the Na_2O–BeO–SiO_2 system.

Experimental

Synthesis

Polycrystalline $Na_{10}Be_4Si_4O_{17}$ was synthesized by solid-state reaction in air, using dried Na_2CO_3, BeO and SiO_2 as starting materials. As alternative starting materials, Na_2CO_3 and pre-synthesized Na_2BeSiO_4 could be used. A ground mixture of stoichiometric amounts of the starting materials was slowly heated up to 1225 K and held at this temperature for 1 h. The sample was re-ground and fired at 1225 K for 15 h. The chemical formula $Na_{10}Be_4Si_4O_{17}$ was arrived at from inspection of Guinier–Hägg films of preparations along the join between Na_2BeSiO_4 and Na_2O, and subsequently confirmed by the single-crystal X-ray data. Single crystals of $Na_{10}Be_4Si_4O_{17}$ were obtained by cooling a melt of approximate composition $Na_2BeSiO_4.20Na_2CO_3$ at a rate of 2 K h^{-1} from 1155 to 1075 K. The excess Na_2CO_3 was removed by dissolving in boiling water.

Powder data

Powder diffraction photographs were recorded with a Guinier–Hägg-type camera at 293 K, using Cu $K\alpha_1$ radiation, $\lambda = 1{\cdot}5406$ Å, and Si as internal standard. The films were measured by means of a computer-controlled microdensitometer (Johansson, Palm & Werner, 1980). The indexed powder pattern yielded the cubic cell edge $a = 7{\cdot}2813\,(3)$ Å.*

Structure determination

The single-crystal X-ray diffraction data were collected with a Stoe/AED2 diffractometer. The experimental conditions are listed in Table 1. The data were corrected for background, polarization, Lorentz and absorption effects. The unit-cell parameter was

---

* Lists of structure factors and powder diffraction data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53340 (17 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

0108-7681/90/060736-04$03.00

Table 1. *Experimental conditions for the structure determination of* $Na_{10}Be_4Si_4O_{17}$

Crystal shape	Cubic
Crystal size	0·04 × 0·04 × 0·04 mm
Intensity data collection	
Maximum $\sin(\theta)/\lambda$	0·587 Å^{-1}
Range of h, k and l	$0 < h < 8$, $0 < k < 8$, $0 < l < 8$ data merged
Standard reflections	3
Intensity instability	< 3·5%
Internal R value	3·3%
No. of measured reflexions	412
No. of observed reflexions	393
No. of unique reflexions	104
No. of observed unique reflexions	96
Criterion for significance	$I > 3\sigma(I)$
Absorption correction	Numerical integration
Linear absorption coefficient	74·6 cm^{-1}
Transmission-factor range	0·75–0·79
Structure refinement	
Minimization of	$\sum w(\Delta F)^2$
Isotropic thermal parameters	Na, Be, Si and O
Number of refined parameters	15
Weighting scheme	$w = 1{\cdot}1043/[\sigma^2(\lvert F\rvert)]$
Final R	0·033
wR	0·031
wR for all reflexions	0·032
Goodness of fit	1·0
$(\Delta/\sigma)_{max}$	0·002
$\Delta\rho_{min}$ and $\Delta\rho_{max}$	−0·164 and +0·132 e Å^{-3}

Table 2. *Fractional coordinates and isotropic thermal parameters* (× 10^4)

	Wyckoff position	x	y	z	U_{iso}(Å^2)
Si	4(e)	2201 (3)	2201 (3)	2201 (3)	93 (8)
Be	4(e)	8688 (16)	8688 (16)	8688 (16)	181 (48)
Na(1)	4(e)	6589 (5)	6589 (5)	6589 (5)	168 (16)
Na(2)	3(d)	$\frac{1}{2}$	0	0	173 (19)
Na(3)	3(c)	0	$\frac{1}{2}$	$\frac{1}{2}$	245 (18)
O(1)	12(i)	2612 (4)	2612 (4)	9 (8)	102 (10)
O(2)	4(e)	3464 (8)	3464 (8)	3464 (8)	147 (28)
O(3)	1(a)	0	0	0	104 (48)

determined from six reflexions in the range $73° \leq 2\theta \leq 76°$, yielding $a = 7{\cdot}2811\ (3)$ Å, a value which agrees well with that obtained from Guinier–Hägg powder data. Since there were no systematically absent reflexions, there are only five possible cubic space groups, *viz.* $P23$ (No. 195) and four of its supergroups.

The structure was solved by the Patterson method in the least symmetric of these space groups, $P23$, using *SHELXS*86 (Sheldrick, 1986). The structural refinements were performed by means of the *SHELX*76 program package (Sheldrick, 1976), with atomic X-ray scattering factors for neutral atoms from *International Tables for X-ray Crystallography* (1974, Vol. IV). Inspection of some of the refined atomic positions in space group $P23$ indicated that a better description of the structure could be obtained with the space group $P\bar{4}3m$ (No. 215). The observed Laue symmetry of the diffraction data, $m\bar{3}m$, vindicated this conclusion. Subsequent refinements in $P\bar{4}3m$ yielded significantly lower R and wR values than the corresponding initial refinements in $P23$. In order to keep the overdetermination above five, the refinements were made with use of only isotropic thermal parameters. The final atomic coordinates and isotropic thermal parameters are given in Table 2.*

Structure description

The structure exhibits isolated $Be_4Si_4O_{17}$ units with centers at the origin of the unit cell. The $Be_4Si_4O_{17}$ unit is formed by corner-sharing BeO_4 and SiO_4 tetrahedra, as illustrated in Fig. 1. Four BeO_4 tetrahedra share a common corner O atom at the center of the unit. The four SiO_4 tetrahedra share three of their corner O atoms with BeO_4 tetrahedra, and have one free apex O atom. A selection of bond distances and angles is given in Table 3.

The Na atoms occupy three crystallographically different sites between the $Be_4Si_4O_{17}$ units. The four Na(1) atoms occupy positions on the space diagonals of the unit cell. They are coordinated by six O atoms forming a distorted octahedron: three O(1) atoms at a distance of 2·276 (7) Å and three O(2) atoms at a distance of 2·622 (8) Å. The three Na(2) atoms occupy mid-edge positions in the unit cell. They are coordinated by eight O(1) atoms at a distance 2·5768 (2) Å, forming a tetragonal prism. The three Na(3) atoms occupy face-center positions in the unit

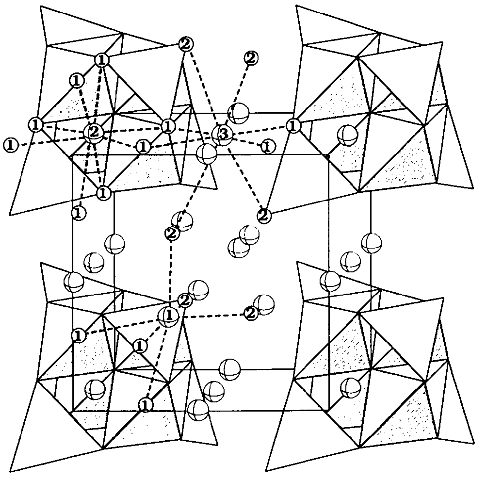

Fig. 1. An illustration of the $Na_{10}Be_4Si_4O_{17}$ structure. Shaded tetrahedra contain Be atoms and unshaded tetrahedra Si atoms. The oxygen coordination around the Na atoms is illustrated by the dashed lines, and the crystallographically different Na and O atoms are numbered in accordance with Table 2.

---

* See deposition footnote.

Table 3. *Representative bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

SiO_4 tetrahedron		BeO_4 tetrahedron	
Si—O(2)	1·592 (11)	Be—O(3)	1·654 (20)
Si—O(1) 3 ×	1·652 (6)	Be—O(1) 3 ×	1·648 (8)
O(1)—O(1^{i}) 2 ×	2·680 (9)	O(1)—O(1^{ii}) 2 ×	2·698 (9)
O(1)—O(2)	2·664 (10)	O(1)—O(3)	2·689 (4)
O(1)—Si—O(1^{i})	108·5 (6)	O(1^{iii})—Be—O(1^{iv})	109·9 (8)
O(1)—Si—O(2)	110·4 (4)	O(3)—Be—O(1)	109·1 (7)
Na—O polyhedra			
Na(1)—O(2) 3 ×	2·277 (7)	Na(3)—O(1) 4 ×	2·459 (4)
Na(1)—O(1) 3 ×	2·622 (8)	Na(3)—O(2) 4 ×	2·977 (1)
Na(2)—O(1) 8 ×	2·5768 (2)		
Na—Na distances			
Na(1)—Na(3) 3 ×	2·9741 (2)	Na(2)—Na(3) 6 ×	3·6405 (2)
Na(1)—Na(1^{v}) 3 ×	3·273 (8)	Na(2)—Na(1) 4 ×	3·698 (4)
Na(3)—Na(1) 4 ×	2·9741 (2)		
Na(3)—Na(2) 4 ×	3·6405 (2)		

Symmetry code: (i) y, z, x; (ii) $-z, x, -y$; (iii) $1-x, 1-y, 1+z$; (iv) $1-y, 1+z, 1-x$; (v) $-y, -x, z$.

cell. They are situated in a planar four-coordination of O(1) atoms at a distance of 2·460 (4) Å. Four next-nearest-neighbour O(2) atoms are, however, found at a distance of 2·977 (1) Å, forming an elongated tetrahedron around the Na(3) atoms.

Ionic conductivity measurements

The ionic conductivity of $Na_{10}Be_4Si_4O_{17}$ was determined by means of impedance measurements using an apparatus setup constructed at this institute (Hörlin, 1985). The samples used were 1–2 mm thick sintered disks with a diameter of 6 mm. The frequency dependence of the impedance was measured at six different temperatures between 478 and 625 K in a series of heating–cooling cycles. Reproducible data were obtained in consecutive cycles. The ionic conductivity was calculated from the intercept of the semicircular arc obtained in complex impendance plots.

The conductivity shows an Arrhenius-type behavior, obeying the relation $\ln(\sigma T) = \ln(\sigma_0) - E_a/kT$, as seen in Fig. 2. The activation energy and prefactor obtained are $E_a = 1{\cdot}04\,(3) \times 10^{-19}$ J and $\log(\sigma_0) = 6{\cdot}3\,(2)$ S m^{-1} K^{-1}, respectively. The conductivity at 600 (1) K is 1·0 (1) × 10^{-2} S m^{-1}.

Discussion

The mean Si—O and Be—O bond lengths, 1·637 (30) and 1·650 (3) Å, are in good agreement with those found in similar compounds, *e.g.* 1·635 and 1·647 Å in γ-Li_2BeSiO_4 (Howie & West, 1974), and 1·63 and 1·65 Å in orthorhombic Na_2BeSiO_4 (Maksimov, Tamazyan, Sirota, Frostäng, Grins & Nygren, 1990). The corresponding root-mean-square deviations (r.m.s.d.'s) for the bond lengths are 0·026 and 0·003 Å for $Na_{10}Be_4Si_4O_{17}$, 0·007 and 0·013 Å for γ-Li_2BeSiO_4 and 0·023 and 0·093 Å for orthorhombic Na_2BeSiO_4, respectively. A mean value for Be—O bond lengths in BeO_4 tetrahedra has been given as 1·636 Å (Ross, 1964). The mean Si—O bond length for tetrahedrally coordinated Si in silicates was found to be 1·62 Å (Liebau, 1985).

A calculation of empirical bond valences (Brown & Altermatt, 1985) from the structural data gives bond-valence sums of 1·94 for Be, 3·88 for Si and 1·16, 0·99 and 0·85 for Na(1), Na(2) and Na(3) respectively. The values are in fair agreement with the expected formal charges of the metal atoms, showing also that the average bond distances are acceptable.

In the crystal structures of γ-Li_2BeSiO_4 and orthorhombic Na_2BeSiO_4 the BeO_4 and SiO_4 tetrahedra share corners, with each O atom common to one BeO_4 and one SiO_4 tetrahedron, whereby cristobalite-type frameworks are formed. The $Na_{10}Be_4Si_4O_{17}$ structure, in contrast, exhibits separate $Be_4Si_4O_{17}$ units with a central O atom common to four BeO_4 tetrahedra. Similar types of corner-sharing arrangements of four BeO_4 tetrahedra are found in the structures of swedenborgite, $NaBe_4SbO_7$ (Aminoff, 1933), and beryllium acetate, $Be_4O(CH_3CO_2)_6$ (Tulinsky & Worthington, 1959). The $Be_4Si_4O_{17}$ unit in itself has however, to our knowledge, not been observed in other crystal structures.

The ionic conductivity of $Na_{10}Be_4Si_4O_{17}$ can be compared with the conductivities of previously investigated phases in the Na_2O–BeO–SiO_2 system: $Na_xBe_{x/2}Si_{2-x/2}O_4$ with $2{\cdot}0 \geq x \geq 1{\cdot}8$ and $Na_2BeSi_2O_6$ (Frostäng, Grins & Nygren, 1988*b*). [The conductivity values given in the paper referenced above should be corrected by a multiplication factor of about 1/ln(10).]) The solid-solution phase $Na_xBe_{x/2}Si_{2-x/2}O_4$ possesses a filled cristobalite-type

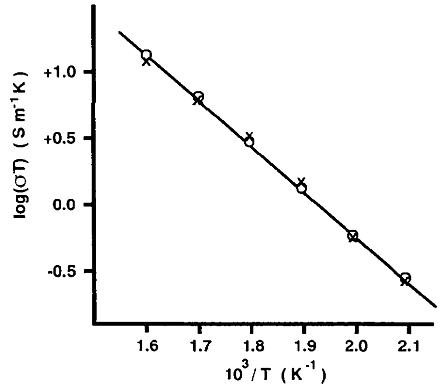

Fig. 2. Conductivity data for $Na_{10}Be_4Si_4O_{17}$.

structure and exhibits a composition-dependent ionic conductivity which increases, at 600 K, from 3·4 × 10^{-3} S m^{-1} for $x = 2{\cdot}0$, Na_2BeSiO_4, to 2·3 × 10^{-1} S m^{-1} for $x = 1{\cdot}8$, $Na_{1\cdot8}Be_{0\cdot9}Si_{1\cdot1}O_4$. The increase in conductivity with decreasing x is paralleled by a decreasing occupancy of Na-atom sites. The compound $Na_2BeSi_2O_6$ is found to be isostructural with the beryllium mineral chkalovite (Simonov, Egorov-Tismenko & Belov, 1976), with a filled cristobalite-type structure, and shows a conductivity value of 2·8 × 10^{-3} S m^{-1} at 600 K.

The conductivity of $Na_{10}Be_4Si_4O_{17}$ at 600 K is thus considerably lower than that of the best conductor, $Na_{1\cdot8}Be_{0\cdot9}Si_{1\cdot1}O_4$, but is of the same magnitude as those found for Na_2BeSiO_4 and $Na_2BeSi_2O_6$. The rather limited conductivity in $Na_{10}Be_4Si_4O_{17}$ may be understood as caused by the full occupancy of Na-atom sites and the denseness of the Na-atom arrangement. The migration of an Na atom can be expected to require a high activation energy, since it probably involves severe displacements of neighbouring Na atoms from their equilibrium positions and possibly displacements of the rigid $Be_4Si_4O_{17}$ units.

The conductivity may possibly be increased by introducing vacancies on the Na-atom sites by substituting *e.g.* Mg^{2+} for Na^+. Preparative work is in progress to investigate this possibility.

The authors wish to thank Professors M. Nygren and R. Norrestam for valuable discussions and great interest in this work. This investigation has received financial support from the Swedish Natural Science Research Council.

References

AMINOFF, G. (1933). *K. Sven. Vetenskapsakad. Handl.* **11**(4), 1–13.
BROWN, I. D. & ALTERMATT, D. (1985). *Acta Cryst.* **B41**, 244–247.
FROSTÄNG, S., GRINS, J. & NYGREN, M. (1988*a*). *Chem. Scr.* **28**, 107–110.
FROSTÄNG, S., GRINS, J. & NYGREN, M. (1988*b*). *J. Solid State Chem.* **72**, 92–99.
HÖRLIN, T. (1985). *Chem. Scr.* **25**, 270–279.
HOWIE, R. A. & WEST, A. R. (1974). *Acta Cryst.* **B30**, 2434–2437.
JOHANSSON, K.-E., PALM, T. & WERNER, P.-E. (1980). *J. Phys. E*, **13**, 1289–1291.
LIEBAU, F. (1985). *Structural Chemistry of Silicates*. Berlin: Springer Verlag.
MAKSIMOV, B., TAMAZYAN, R., SIROTA, M. I., FROSTÄNG, S., GRINS, J. & NYGREN, M. (1990). *J. Solid State Chem.* **86**, 64–74.
ROSS, M. (1964). *US Geol. Surv. Prof. Pap.* No. 468.
SHELDRICK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
SHELDRICK, G. M. (1986). *SHELXS86*. Program for the solution of crystal structures. Univ. of Göttingen, Federal Republic of Germany.
SIMONOV, M. A., EGOROV-TISMENKO, YU. K. & BELOV, N. V. (1976). *Sov. Phys. Dokl.* **20**, 805–807.
TULINSKY, A. & WORTHINGTON, C. R. (1959). *Acta Cryst.* **12**, 626–634.

Acta Cryst. (1990). **B46**, 739–742

Single-Crystal Neutron Diffraction Studies of MnF_2 as a Function of Temperature: the Effect of Magnetostriction

BY W. JAUCH

Hahn-Meitner-Institut, Glienicker Str. 100, *D*-1000 *Berlin* 39, *Federal Republic of Germany*

G. J. MCINTYRE

Institut Laue–Langevin, 156*X*, 38042 *Grenoble CEDEX*, *France*

AND A. J. SCHULTZ

Chemistry and Materials Science Divisions, *Argonne National Laboratory*, *Argonne*, *Illinois* 60439, *USA*

(*Received* 13 *March* 1990; *accepted* 13 *July* 1990)

Abstract

MnF_2 has been investigated at 295, 60 and 15 K by monochromatic neutron diffraction in order to determine the effect of antiferromagnetic order on the fluorine nuclear positional parameter. An internal displacement of 2·0 (3) × 10^{-3} Å is found between 295 and 15 K which is in excellent agreement with the result obtained from single-crystal time-of-flight neutron diffraction. At 15 K there is a significant difference between the neutron and γ-ray refined positional parameters.

Introduction

The influence of antiferromagnetic order on the fluorine position in MnF_2 has been the subject of

0108-7681/90/060739-04$03.00