JOURNAL OF SOLID STATE CHEMISTRY 118, 62–65 (1995)

Structure and Ionic Conductivity of Na_2BeGeO_4

J. Grins

Department of Inorganic Chemistry, Arrhenius Laboratory, Stockholm University, S-106 91 Stockholm, Sweden

Received October 21, 1994; in revised form January 10, 1995; accepted January 11, 1995

The crystal structure of Na_2BeGeO_4 has been determined from Cu$K\alpha_1$ powder diffractometer data and refined by the Rietveld technique to $R_F = 0.047$. It is monoclinic, $a = 7.2155(4)$, $b = 5.0214(3)$, $c = 10.1380(6)$ Å, $\beta = 90.289(5)°$, space group $P2_1/c$, $z = 2$, and is isostructural with monoclinic Na_2BeSiO_4. The structure exhibits $BeGeO_4^{2-}$ layers formed by binuclear Be_2O_6 groups, containing two edge-sharing BeO_4 tetrahedra, which in turn are interconnected by GeO_4 tetrahedra. The Na atoms are located between the $BeGeO_4^{2-}$ layers and are octahedrally coordinated by oxygen atoms. The ionic conductivity of Na_2BeGeO_4 was determined by impedance measurements and found to be 6.7×10^{-6} $(\Omega\ cm)^{-1}$ at 773 K with an activation energy of $E_a = 0.82$ eV.

INTRODUCTION

We have previously investigated the ionic conductivity properties of a number of systems of sodium-ion-conducting silicates and germanates (1, 2). Among good ionic conductors, exhibiting conductivities in the range 1×10^{-3}–1×10^{-2} $(\Omega\ cm)^{-1}$ at 575 K, are the compounds $Na_xM'_{x/2}M''_{2-x/2}O_4$ with $2.0 \geq x \geq 1.8$ and $M'M'' =$ BeSi; ZnSi; ZnGe. The best ionic conductors in these systems are found at compositions $Na_{1.8}M'_{0.9}M''_{1.1}O_4$ (i.e., $x = 1.8$) and are isotypic with the orthorhombic high-temperature modification of Na_2ZnSiO_4. The structure is related to cristobalite, with a framework of corner-sharing SiO_4 and ZnO_4 tetrahedra and Na atoms in cavities formed by the tetrahedra.

The compound Na_2BeSiO_4 adopts this structure type when prepared by solid state reaction (3, 4). Hydrothermally prepared Na_2BeSiO_4, however, crystallizes with a monoclinic layer structure. The structure has been determined by Plakhov and co-workers (5, 6), using single crystals.

The compound Na_2BeGeO_4 was synthesized in order to compare its ionic conductivity properties with those of previously studied compounds possessing cristobalite-related structures. The X-ray powder pattern of Na_2BeGeO_4 was found not to be cristobalite-related, however, but similar to the one generated for the hydrothermally prepared modification of Na_2BeSiO_4. The structure and solid electrolyte properties of Na_2BeGeO_4 have not been previously reported and an investigation of its structure and properties was therefore carried out, the results of which are reported here.

EXPERIMENTAL

Samples of Na_2BeGeO_4 were synthesized by solid state reaction using dried Na_2CO_3, $BeCO_3$, and GeO_2. The composition of the $BeCO_3$ was checked thermogravimetrically. Appropriate amounts of the starting materials were mixed and ground under hexane. The mixture was pelletized, gradually heated to 1175 K, and held there for 15 hr. The sample was then reground, pelletized, and fired at 1175 K for 2 days, with one intermediate regrinding.

Powder X-ray diffraction data were collected in symmetric transmission mode with a STOE STADI/P diffractometer using Cu$K\alpha_1$ radiation. The step-length was 0.02° and the 2θ range 10–110° was covered.

The ionic conductivity was determined by means of impedance measurements, using an apparatus setup constructed at this institute (7). The samples used were 1–2-mm-thick disks with a diameter of 6 mm, sintered at 1175 K for 15 hr. Blocking electrodes were applied by evaporating gold onto the disks.

STRUCTURE DETERMINATION AND REFINEMENT

The powder pattern of Na_2BeGeO_4 was observed to be similar to a generated pattern for monoclinic Na_2BeSiO_4. The cell dimensions $a = 7.2155(4)$, $b = 5.0214(3)$, $c = 10.1380(6)$ Å, and $\beta = 90.289(5)°$ were obtained from Guinier–Hägg data, using Si as an internal standard and using 72 reflections for $2\theta \leq 69°$. The films were measured by means of a computer-controlled microdensitometer (8). The indexed powder pattern is given in Table 1 for the first 20 observed lines.

The structure was refined using a local version of the DBW3.2S Rietveld refinement program (9) and 503 theoretical reflections in the 2θ range 10–110°. Starting coordinates were taken from the monoclinic Na_2BeSiO_4 structure (6).

In the final refinement a total of 42 parameters, including

0022-4596/95 $12.00

TABLE 1
Powder X-Ray Diffraction Pattern Of Na_2BeGeO_4

h	k	l	$2\theta_{obs}$	$\Delta 2\theta$	d_{obs} (Å)	I/I_0 (%)
1	0	0	12.253	−0.004	7.22	11
0	0	2	17.480	−0.001	5.07	14
0	1	1	19.715	0.002	4.499	11
−1	0	2	21.362	0.007	4.156	34
1	0	2	21.453	−0.004	4.139	38
1	1	0	21.512	−0.031	4.127	85
−1	1	1	23.278	0.023	3.818	57
1	1	1		−0.025		
2	0	0	24.654	−0.002	3.608	37
0	1	2	24.928	−0.012	3.569	44
1	1	2	27.915	−0.001	3.194	28
−2	0	2	30.336	0.024	2.944	8
2	0	2	30.463	0.003	2.932	38
−2	1	1	31.734	0.004	2.817	47
0	1	3	31.886	−0.009	2.804	25
−1	1	3	34.251	0.013	2.616	1
−2	1	2	35.294	0.002	2.541	37
0	0	4	35.383	−0.004	2.535	72
0	2	0	35.724	−0.010	2.511	100
0	2	1	36.851	0.000	2.4371	56
3	0	0	37.366	0.007	2.4047	40

Note. $\Delta 2\theta = 2\theta_{obs} - 2\theta_{calc}$. $\lambda = 1.5406$ Å. Intensity values originate from diffractometer data. Cell figure-of-merit $M_{20} = 60$, $F_{20} = 92$ (0.0091, 24).

24 positional parameters, were refined. Collective atomic displacement parameters were used for the Na and O atoms. An empirical absorption correction $\exp(-\mu R \sin \theta)$ was applied, with refined $\mu R = 1.3(2)$. The correlation coefficients between the parameter μR and the atomic displacement parameters for the Na, Ge, and O atoms were 0.88, 0.98, and 0.86, respectively. The final atomic coordinates are given in Table 2. Because of serial correlation, indicated by a Durbin–Watson D-value of 0.94, the esd's obtained in the refinement are multiplied by 1.73 (10). The agreement between calculated and observed

TABLE 2
Atomic Coordinates for Na_2BeGeO_4

Atom	x	y	z	B (Å^2)
Na1	0.001(1)	0.793(1)	0.110(1)	1.7(2)
Na2	0.260(1)	0.816(1)	0.363(1)	1.7(2)
Be	0.493(3)	0.831(5)	0.082(2)	1.1(5)
Ge	0.7205(4)	0.8440(4)	0.3398(2)	0.8(2)
O1	0.949(1)	0.762(2)	0.373(1)	0.6(2)
O2	0.685(1)	0.782(2)	0.171(1)	0.6(2)
O3	0.545(1)	0.679(2)	0.428(1)	0.6(2)
O4	0.316(1)	0.691(2)	0.125(1)	0.6(2)

Note. Monoclinic, $a = 7.2155(4)$, $b = 5.0214(3)$, $c = 10.1380(6)$ Å, $\beta = 90.289(5)°$, $z = 2$, $P2_1/c$.

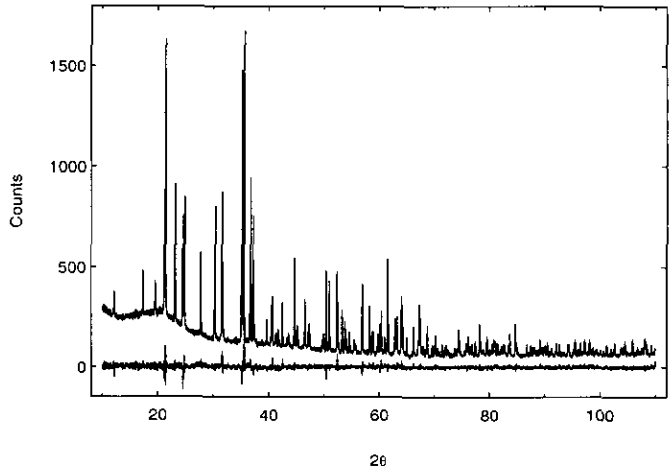

FIG. 1. Observed and difference intensity powder diffraction patterns of Na_2BeGeO_4.

intensities is shown in Fig. 1. The corresponding R values are $R_p = 4.7$, $R_{wp} = 6.0$, $R_I = 6.6$, and $R_F = 4.7\%$.

DESCRIPTION OF THE STRUCTURE

The structure is illustrated in Fig. 2. It exhibits $BeGeO_4^{2-}$ layers, parallel with the yz plane, which contain Be_2O_6 groups formed by two edge-sharing BeO_4 tetrahedra. Each oxygen in a Be_2O_6 group is shared with one GeO_4 tetrahedra. All Be atoms are at $x \approx \frac{1}{2}$ while half of the Ge atoms are at $x \approx \frac{1}{4}$ and the other half at $x \approx \frac{3}{4}$. The GeO_4 tetrahedra have one terminal oxygen which is not shared with any Be_2O_6 group. These terminal oxygens, at $x \approx 0$, point alternately up and down from the middle of the $BeGeO_4^{2-}$ layer at $x \approx \frac{1}{2}$. Selected bond distances are given in Table 3. The average Be–O and Ge–O distances are 1.65 and 1.76 Å, respectively. The shortest O–O distance is found for O3–O3, 2.41(2) Å, with the edge shared between two BeO_4 tetrahedra.

Both Na atoms are coordinated by an irregular octahedron of oxygens, with Na–O distances ranging from 2.26(1) to 2.73(1) Å. The Na1 atoms are found at $x \approx 0$. The equatorial oxygens of the Na1–O_6 octahedra in the yx plane are the terminal oxygens of GeO_4 tetrahedra and the two remaining ones, at $x \approx 0.3$ and 0.7, are the unshared oxygens in a Be_2O_6 group. The Na1–O_6 octahedra share all four equatorial edges with surrounding octahedra. The Na2 atoms are found at $x \approx \frac{1}{4}$ and $\frac{3}{4}$. The equatorial oxygens in the Na2–O_6 octahedra are the unshared oxygens in three surrounding Be_2O_6 groups. One of the two remaining oxygens is a terminal oxygen of a GeO_4 tetrahedra and the other is a shared oxygen of a Be_2O_6 group. Two of the Na–O distances are, for both Na atoms, somewhat longer than the other four and the Na–O coordination polyhedra may alternatively be described as a distorted

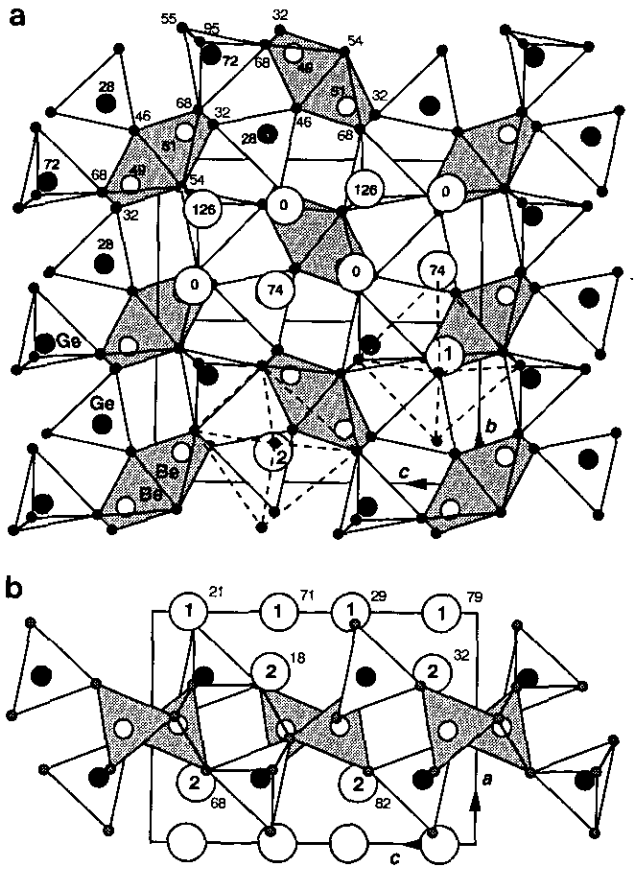

FIG. 2. The structure of Na_2BeGeO_4 projected on (a) the yz plane and (b) the xz plane. Shaded tetrahedra contain Be atoms and unshaded tetrahedra contain Ge atoms. The Be and Ge atom positions are illustrated by medium-sized unfilled and shaded circles, respectively, and the Na atom positions are represented by larger unfilled circles. The crystallographically distinct Na atoms are numbered in accordance with Table 2. The smaller numbers represent the coordinates of the drawn atoms in % along the axis not lying in the projection plane. The broken lines in (a) illustrate the octahedral coordination of the Na atoms.

tetrahedra (5). The structure can, in its tetrahedral aspect, be idealized as a hexagonal close-packed oxide structure with all the cations occupying tetrahedral sites.

Calculation of the empirical bond valences (11) from the structural data gives the following bond–valence sums: Na1 +1.01, Na2 +1.09, Be + 2.03, Ge +3.85, O1 −1.89, O2 −1.93, O3 −2.14, O4 −2.02.

TABLE 3
Bond Distances (Å) in Na_2BeGeO_4

Be–O4	1.53(3)	Ge–O1	1.73(1)	Be–Be	2.38(5)
O3	1.61(3)	O2	1.76(1)		
O2	1.67(3)	O3	1.76(1)		
O3	1.77(3)	O4	1.80(1)		
Na1–O4	2.34(1)	Na2–O1	2.26(1)		
O2	2.37(1)	O3	2.27(1)		
O1	2.39(1)	O2	2.40(1)		
O1	2.45(1)	O4	2.53(1)		
O1	2.70(1)	O4	2.69(1)		
O1	2.70(1)	O2	2.73(1)		

IONIC CONDUCTIVITY

The frequency dependence of the impedance was measured at five temperatures between 573 and 773 K in 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 impedance plots.

The conductivity shows an Arrhenius-type behavior, i.e., obeying the relation $\ln(\sigma T) = \ln(\sigma_0) - E_a/kT$, as seen in Fig. 3. The activation energy and prefactor obtained are $E_a = 0.82$ eV and $\log(\sigma_0) = 3.03$ $(\Omega\ \text{cm/K})^{-1}$. The conductivities at 573 and 773 K are 1.3×10^{-7} and 6.7×10^{-1} $(\Omega\ \text{cm})^{-1}$, respectively.

CONCLUDING REMARKS

The structure of Na_2BeGeO_4 is isostructural with the monoclinic modification of Na_2BeSiO_4, obtained by hydrothermal synthesis (5, 6). The atomic coordinates for Na_2BeSiO_4 in Ref. (6) are given on the basis of the space group setting $P2_1/c11$, with the a axis unique, and of a unit cell with $a = 4.960$, $b = 7.022$, $c = 9.933$ Å, and $\alpha = 90.03°$. A transformation of the cell to the setting used here for Na_2BeGeO_4 yields a β angle of 89.97° for Na_2BeSiO_4, compared with 90.289(5)° for Na_2BeGeO_4. When synthesized by solid state reaction, Na_2BeSiO_4 adopts an orthorhombic cristobalite-related structure (3, 4). Further modifications of Na_2BeSiO_4 may exist at

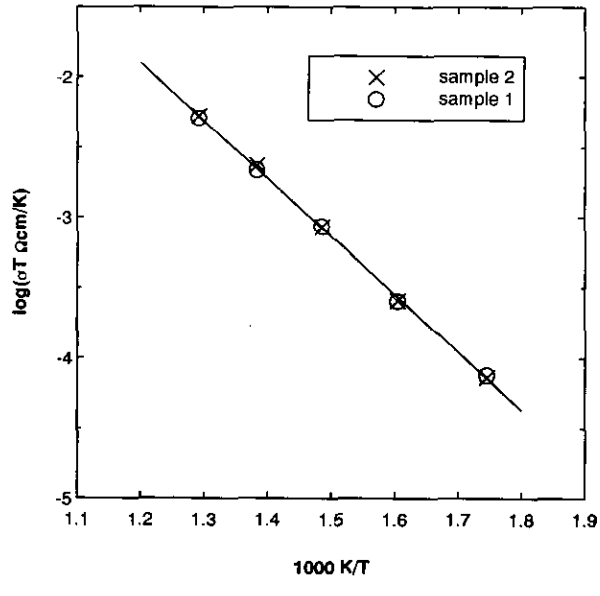

FIG. 3. Conductivity Arrhenius plot.

higher temperatures, as indicated by two endothermic peaks in DTA heating runs at ≈1300 K and ≈1400 K before melting (12).

The ionic conductivity for Na_2BeGeO_4 is found to be modest and lower than that for orthorhombic Na_2BeSiO_4, 7.5×10^{-5} $(\Omega\ \text{cm})^{-1}$ at 575 K (12).

ACKNOWLEDGMENTS

The author thanks Professor M. Nygren for support and valuable discussions. This work has been financially supported by the Swedish Natural Science Research Council.

REFERENCES

1. S. Frostäng, J. Grins, and M. Nygren, *Chem. Scr.* **28,** 107 (1988).
2. J. Grins, S. Frostäng, and M. Nygren, *Mater. Res. Soc. Symp. Proc.* **210,** 657 (1991).
3. S. Frostäng, J. Grins, D. Louër, and P-E. Werner, *Solid State Ionics* **31,** 131 (1988).
4. B. Maksimov, R. Tamazyan, M. I. Sirota, S. Frostäng, J. Grins, and M. Nygren, *J. Solid State Chem.* **86,** 64 (1990).
5. G. F. Plakhov, M. A. Simonov, and N. V. Belov, *Sov. Phys. Dokl. Engl. Transl.* **19**(9), 556 (1975).
6. G. F. Plakhov and N. V. Belov, *Sov. Phys. Crystallogr.* **24**(6), 674 (1979).
7. T. Hörlin, *Chem. Scr.* **25,** 270 (1985).
8. K-E. Johansson, T. Palm, and P-E. Werner, *J. Phys. E* **13,** 1289 (1980).
9. D. B. Wiles, A. Sakthivel, and R. A. Young, "Users 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.
10. J-F. Berár and P. Lelann, *J. Appl. Crystallogr.* **24,** 1 (1991).
11. I. D. Brown and D. Altermatt, *Acta Crystallogr. Sect. B* **41,** 244 (1985).
12. S. Frostäng, J. Grins, and M. Nygren, *J. Solid State Chem.* **72,** 92 (1988).