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Ionic Conductivity Studies and Phase Analysis of the Na_2BeSiO_4–$Na_2BeSi_2O_6$ System*

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Compositions along the Na_2BeSiO_4–$Na_2BeSi_2O_6$ join in the Na_2O–BeO–SiO_2 system were prepared by solid state reaction and investigated by means of X-ray powder diffraction and ionic conductivity measurements. Phase stabilities were studied by investigation of quenched samples from 975 to 1335 K. Two phases were observed: an orthorhombic solid solution phase, $Na_xBe_{x/2}Si_{2-x/2}O_4$, e.g., $1.80 \le x \le 2.00$, apparently isotypic with $KGaO_2$ and the high-temperature modification of Na_2ZnSiO_4. The cell parameters for the Na_2BeSiO_4 obtained are $a = 9.861 \pm 2$ Å, $b = 13.875 \pm 2$ Å, and $c = 4.911 \pm 1$ Å. The powder pattern of $Na_2BeSi_2O_6$ was indexed with an orthorhombic cell, $a = 21.096 \pm 3$ Å, $b = 6.870 \pm 1$ Å, and $c = 21.142 \pm 4$ Å, and the phase found to be isotypic with the mineral beryllium-chkalovite. The ionic conductivity for the $Na_xBe_{x/2}Si_{2-x/2}O_4$ composites, $1.33 \le x \le 2.00$, were determined using ac impedance measurements. The conductivity at 600 K increases with decreasing Na content and shows a maximum at $x = 1.80$ (the compositional limit for the solid solution phase); 4.9×10^{-3} $[\Omega\ \mathrm{cm}]^{-1}$ with $E_a = 0.48$ eV. The data are compared with the results obtained in previous studies of the analogous systems Na_2ZnSiO_4–$Na_2ZnSi_2O_6$ and Na_2ZnGeO_4–$Na_2ZnGe_2O_6$.

Introduction

During recent years considerable effort has been put into the design of solid electrolyte materials possessing framework structures. These structures contain cavities and pathways, in one, two, or three dimensions, suitable for migration of ions such as sodium. As pointed out by Goodenough *et al.* (*1*), three essentially different types of oxide-based framework structures can be envisaged, namely, those formed from various arrays of corner- and/or edge-shared tetrahedra and octahedra, respectively, or by a combination of both. The geometry of the framework structure furthermore must be such that the potential barrier between two partially occupied lattice sites of the mobile ion is low.

Following these ideas outlined by Goodenough, we have investigated a number of compounds with stuffed silica structures. In these structures the mode of linking of the tetrahedra is retained, but some of the Si^{4+} ions are replaced by Me^{3+} or Me^{2+} ions and alkali-metal ions are accommodated in the cavities to maintain electrical neutrality. The cavities in the high-temperature modifications (HTm) of tridymite and cris-

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tobalite are large enough for alkali-metal ions such as sodium and potassium while only Li^+ ions can reside in the voids of the high-quartz structure due to size restrictions.

Compounds in systems such as Na_2O–Me_nO_m–$SiO(GeO_2)$, with Me = Mg, Zn, Al, and Ga, frequently have cristobalite or cristobalite-related structures. The ionic conductivity of such sodium conductors have recently been reviewed and discussed in terms of framework relaxation, vacancy content, and effect of the size of the framework constituent cations (see Ref. (*2*)).

The best sodium conductors with cristobalite or cristobalite-related structure are found in the Na_2ZnSiO_4–$Na_2ZnSi_2O_6$ system (*3*). The stoichiometry along this join may be written as $Na_xZn_{x/2}Si_{2-x}O_4$ with $1.33 \leq x \leq 2.00$. The ionic conductivity shows a substantial compositional dependence with a maximum of $1 \cdot 10^{-2}$ $(\Omega\ cm)^{-1}$ at 600 K for $x \approx 1.85$. The phase with this composition is isostructural with the HTm of Na_2Zn SiO_4, called C-type below.

The corresponding germanates and various compounds based on chemical substitutions in Na_2ZnSiO_4, e.g., replacement of some of the Si^{4+} ions by P^{5+} ions or some of the Zn^{2+} ions by Ga^{3+} ions, have also been investigated (*4, 5*). The best conductors in these systems were found to possess C-type structure. However, all compositions did exhibit higher activation energies than the one observed for $Na_{1.85}Zn_{0.925}Si_{1.075}O_4$. One possible reason for this might be that the size of the "bottlenecks" is almost nearly optimum size in the $[(Zn,Si)O_4]$ framework.

Among the best conductors with C-type structure, $Na_{1.85}Zn_{0.925}Si_{1.075}O_4$ has the smallest cell volume per formula unit. In order to investigate to what extent the sodium ion mobility responds to a decrease in size of the framework constituting cations we have investigated the $Na_xBe_{x/2}Si_{2-x/2}O_4$ system, with $1.33 \leq x \leq 2.00$. The results of the phase analysis and ionic conductivity measurements are presented below and are compared with previous findings.

Experimental

Appropriate amounts of $BeCO_3 \cdot nBe(OH)_2$, SiO_2, and water-free Na_2CO_3 (all p.a. grade reagents) were mixed and thoroughly ground. The starting composition of the beryllium compound was determined thermogravimetrically in a Mettler TA 12TG-DTA unit. This unit was also used in the differential thermogravimetric analysis (DTA) studies. The $Na_xBe_{x/2}Si_{2-x/2}O_4$ mixtures were gradually preheated up to 1075 K and held at this temperature for 3 hr. The samples were then reground and compacted into cylindrical pellets, then fired for 12 hr at 1225 K for samples with $x > 1.5$ and at 1175 K for those with lower x values. This procedure was then repeated twice. The completion of the reaction was checked by weight and by examination of X-ray powder diffraction patterns.

The phase analysis was made on samples quenched from elevated temperatures. A part of the synthesized material was placed in Pt ampoules and held at different temperatures, ranging from 975 to 1335 K, for various lengths of time (half an hour at 1335 K, several hours at 975 K). The annealing was stopped by dropping the ampoules into a mercury bath beneath the vertical tube furnace used.

The samples were characterized by their X-ray powder patterns recorded with $CuK\alpha_1$ radiation in a Guinier–Hägg focusing camera, using Si as internal standard. The intensities and positions of the reflections on the films were evaluated with a film-scanning system constructed at this institute (*6*). The cell parameters were calculated with the PIRUM computer program (*7*).

The ionic conductivities of the material were determined by analyzing the ac response measured with an impedance spectrometer in the frequency range 1 Hz–50 MHz. The set-up and the measuring technique are described in Ref. (*8*). The measurements were made on cylindrical disks of the material, sintered for 12 hr at the temperature of synthesis. Ion-blocking electrodes were applied by evaporating gold onto both sides of the disk.

Results

Phase Analysis

The X-ray powder pattern of Na_2BeSiO_4 could be indexed on the basis of an orthorhombic unit cell with a = 9.861 Å, b = 13.875 Å, and c = 4.911 Å and the compound is apparently isostructural with the HTm of Na_2ZnSiO_4 (C-type). The diffraction data are given in Table Ia.

The powder pattern of $Na_2BeSi_2O_6$, which corresponds to x = 1.33 in $Na_xBe_{x/2}Si_{2-x/2}O_4$, was indexable with use of a larger orthorhombic cell with a = 21.096 Å, b = 6.870 Å, and c = 21.142 Å. The diffraction data, given in Table Ib, are in good agreement with the data reported by Simonov *et al.* (*9*) for the mineral chkalovite (data given in Table Ic).

As seen in Tables Ia and Ib the d values of the characteristic reflections of Na_2BeSiO_4 and $Na_2BeSi_2O_6$ are almost the same. This fact makes the determination of solid solution ranges less straightforward. However, for $x \leq 1.75$ the X-ray patterns did contain reflections specific to $Na_2BeSi_2O_6$, and inspection of $\sin^2\theta$ values unique to the Na_2BeSiO_4 phase revealed a constancy in $\sin^2\theta$ values for $1.75 \geq x \geq 1.33$. Thus the solid solution range seems to be $1.80 \leq x \leq 2.00$ in $Na_xBe_{x/2}Si_{2-x/2}O_4$. The powder patterns of these compounds could be indexed as originating from a C-type structure and the cell parameters obtained are given in Table II. A similar examination of the unique reflections of the chkalovite phase leads to the conclusion that $1.33 < x < 1.80$ is a two-phase region.

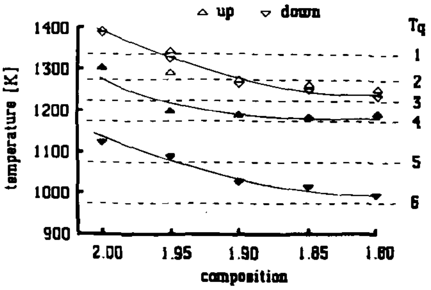

FIG. 1. DTA data plotted against composition. △, endothermic peaks on heating; ▽, exothermic peaks on cooling. Horizontal dashed lines show the different temperatures from which the corresponding compositions $Na_xBe_{x/2}Si_{2-x/2}O_4$ were quenched.

A preliminary DTA investigation of materials possessing C-type structure revealed two reversible phase transitions (see Fig. 1). The transition temperatures were found to decrease with decreasing sodium content. Upon heating, the low-temperature transformation occurs in the temperature region 1200–1300 K, depending on composition, and the high-temperature transition occurs at 1300–1400 K. Upon cooling the former transition occurs at substantially lower temperatures (150–200 K lower) while the hysteresis effect is found to be much less for the high-temperature transition (~10 K). In one of the samples, x = 1.95, a third peak is observed upon heating but not on cooling.

The powder patterns of all quenched samples (the T_q used are indicated in Fig. 1) with $1.80 \leq x \leq 2.00$ indicated C-type structure. Thus it was not possible to quench-in any of the high-temperature modifications.

Conductivity Measurements

The temperature variation of the ionic conductivity was determined for the materials by measuring the conductivity at seven temperatures between 440 and 675 K and was found to give reproducible data

TABLE I

OBSERVED AND CALCULATED *d* VALUES, INTENSITIES, AND INDICES FOR (a) Na_2BeSiO_4 ($x = 2.00$) THIS WORK, (b) $Na_2BeSi_2O_6$ ($x = 1.33$) THIS WORK, (c) THE POWDER DIFFRACTION PATTERN GENERATED FROM STRUCTURAL DATA OF $Na_2BeSi_2O_6$ GIVEN IN REF. (*9*), AND (d) THAT GENERATED FROM THE STRUCTURAL DATA OF Na_2BeSiO_4 GIVEN IN REF. (*11*)

a				b			c			d		
d_{obs} (Å)	d_{calc} (Å)	I/I_0	*hkl*	d_{obs} (Å)	I/I_0	*hkl*	d_{calc} (Å)	I/I_0	*hkl*	d_{calc} (Å)	I/I_0	*hkl*
							7.48	1	202			
										5.73	15	011
				5.280	11	004(400)	5.30	19	004(400)	4.97	3	002
4.024	4.019	17	220	4.030	72	313	4.04	100	313	4.96	27	100
4.008	4.009	7	021							4.05	34	012/110
				3.730	3	404	3.74	3	404	3.75	1	$11\bar{1}/111$
				3.540	7	(115)511	3.56	2	115	3.51	25	$020/10\bar{2}$
3.478	3.480	11	201				3.55	7	511			
3.469	3.469	3	040									
	3.375		211									
3.376		3										
	3.373		230									
				3.330	30	602	3.34	32	(206)602	3.31	1	021
				3.260	38	022(220)	3.27	42	022(220)	3.14	12	$11\bar{2}/112$
							3.21	1	315(513)	2.99	1	013
							3.13	1	222	2.87	32	022/120
2.780	2.781	9	231	2.780	51	224(422)	2.78	41	(224)422	2.75	3	$12\bar{1}/121$
							2.75	3	117			
				2.740	8	(117)515	2.74	4	(515)711			
				2.640	13	008	2.65	13	008(800)	2.56	4	$11\bar{3}/113$
				2.570	10	317	2.58	9	317(713)	2.483	100	004
2.466	2.465	55	400	2.489	100	606	2.494	84	606	2.482	68	$12\bar{2}/122$
2.456	2.457	100	241	2.460	62	206	2.462	42	026/620	2.480	61	200
	2.456		002									
	2.418		250/012							2.409	1	023
2.417	2.416	2	051	2.392	4	622	2.397	2	(226)/622			
2.352	2.352	33	331							2.341	1	014
	2.349		112							2.338	7	210
2.347	2.347	22	151							2.278	4	031
				2.312	8	517(715)	2.316	6	(517)715	2.276	3	$21\bar{1}/211$
	2.254		122							2.220	5	$10\bar{4}/104$
2.252	2.252	6	610	2.229	8	426	2.233	6	426(624)	2.219	6	$20\bar{2}/202$
2.176	2.176	6	411/430				2.215	1	199(911)	2.167	2	$12\bar{3}/123$
2.169	2.170	10	251							2.117	13	$11\bar{4}/114$
	2.169		032	2.116	6	913	2.120	4	(319)913	2.116	3	$21\bar{2}/212$
2.145	2.146	3	341									
2.099	2.100	15	421									
	2.096		222									
2.095	2.094	34	260	2.081	15	333	2.084	9	333			
				2.073	4	2010	2.074	4	2010(1002)	2.070	41	$13\bar{1}/131$
							2.059	9	228			
				2.054	26	228	2.055	9	822			
							2.019	8	626	2.027	1	024
2.010	2.010	6	440	2.016	14	626						
							2.008	3	135			
							2.007	5	531			
2.004	2.004	7	042	2.004	11	531						

TABLE II

CELL PARAMETERS AND CELL VOLUME OF $Na_xBe_{x/2}Si_{2-x/2}O_4$

x	a (Å)	b (Å)	c (Å)	Volume (Å³)
2.00	9.861(2)	13.875(2)	4.911(1)	672.05
1.95	9.866(2)	13.884(3)	4.909(2)	672.45
1.90	9.864(1)	13.910(2)	4.920(1)	675.06
1.85	9.857(6)	13.924(4)	4.906(2)	673.28
1.80	9.826(9)	13.945(3)	4.922(2)	674.43

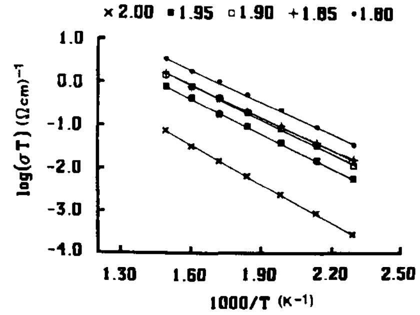

FIG. 2. Arrhenius plot of log (σT) versus 1000/T for compositions $Na_xBe_{x/2}Si_{2-x/2}O_4$ and $1.80 \leq x \leq 2.00$.

upon cycling. At each temperature the frequency dependence of the complex impedance was recorded and the conductivities were calculated from semicircle intercepts in the complex impedance plots. The conductivities were found to follow Arrhenius behavior, $\log(\sigma T) = \log(\sigma_0) - E_a/kT$ as seen in Fig. 2. The values of E_a, $\log(\sigma_0)$, and $\log(\sigma T)$ derived at 600 K are given in Table III. Previous results for the zinc silicates and the zinc germanates are also listed for comparison.

The conductivity at 600 K increases from 7.5×10^{-5} to 4.9×10^{-3} $(\Omega\ \text{cm})^{-1}$ as x decreases from 2.00 to 1.80 with a corresponding decrease in activation energy from 0.62 to 0.48 eV. The corresponding $\log(\sigma_0)$ values show no compositional de-

TABLE III

CONDUCTIVITY DATA FOR $Na_xM_{x/2}M'_{2-x/2}O_4$ with (M, M') = (Be, Si), (Zn, Si), AND (Zn, Ge), RESPECTIVELY

	Beryllium silicate				Zinc silicate				Zinc germanate			
x	E_a (eV)	$\log(\sigma_0)$ (K/Ω cm)	σ_{600} (1/Ω cm)	Phases present	E_a (eV)	$\log(\sigma_0)$ (K/Ω cm)	σ_{600} (1/Ω cm)	Phases present	E_a (eV)	$\log(\sigma_0)$ (K/Ω cm)	σ_{600} (1/Ω cm)	Phases present
2.00	0.62	3.51	7.5E-5	C	0.73	4.60	3.8E-4	A	0.68	4.31	1.5E-4	A
1.975					0.66	4.60	4.6E-4	A	0.65	4.09	1.6E-4	A
1.95	0.53	3.92	1.0E-3	C	0.58	4.40	1.2E-3	A	0.68	4.63	2.7E-4	A
1.90	0.52	4.13	2.0E-3	C	0.53	4.70	5.7E-3	B′	0.66	4.49	2.9E-4	A
1.85	0.49	3.83	2.1E-3	C	0.49	4.90	2.1E-2	C	0.54	4.47	2.8E-3	C
1.80	0.48	4.18	4.9E-3	C					0.55	4.42	2.3E-3	C
1.75	0.44	3.62	4.8E-3	C + Ck	0.50	4.70	1.2E-2	C	0.52	4.11	2.3E-3	C + D
1.70	0.45	3.68	3.2E-3	C + Ck					0.55	4.45	2.1E-3	C + D
1.65	0.48	4.11	4.3E-3	C + Ck	0.52	4.60	7.1E-3	K				
1.625					0.51	4.40	5.4E-3	K				
1.60	0.51	4.02	2.1E-3	C + Ck					0.59	4.09	4.5E-4	C + D
1.575					0.63	4.90	1.5E-3	K				
1.55	0.54	3.84	7.8E-4	C + Ck	0.60	5.00	3.2E-3	K				
1.50	0.47	3.84	2.8E-3	C + Ck					0.62	3.36	5.9E-5	C + D
1.45					0.46	4.00	1.6E-4	M + C				
1.40	0.66	3.32	1.7E-5	C + Ck	0.68	3.50	2.0E-5	M + C	0.75	2.53	5.9E-7	C + D
1.35					0.70	2.50	1.4E-6	M + C				
1.33	0.65	3.74	6.2E-5	Ck					0.87	2.74	8.9E-8	D

Note. The activation energy E_a has an estimated error of ±0.02 and $\log(\sigma_0)$ ±0.2. The σ_{600} column tabulates the conductivity at 600 K. The phases present are A- and C-type as in this paper; B′-type (powder pattern very similar to C), see Ref. (*3*); D-type is zinc chkalovite (*4*); K-type is a cubic phase (*3*); M-type is a monoclinic phase (*3*); and Ck-type is the beryllium chkalovite phase obtained in this work.

pendence, except possibly on going from $x = 2.00$ to 1.95. The material is monophasic (C-type) in this composition range.

In the two-phase region $1.33 < x < 1.80$, the conductivity and σ_0 decrease and E_a increases with decreasing x. It is, however, notable that the sample with $x = 1.75$ shows a conductivity of the same order of magnitude as the best monophasic material.

Discussion

As described above Na_2BeSiO_4 gives a C-type powder pattern, which could be indexed on the basis of an orthorhombic cell with $a = 9.861$ Å, $b = 13.875$ Å, and $c = 4.911$ Å. However, Plakhov *et al.* (*10, 11*) have investigated hydrothermally prepared single crystals of Na_2BeSiO_4 and found the structure to be monoclinic with the cell parameters, $a = 7.022$ Å, $b = 9.933$ Å, $c = 4.968$ Å, and $\gamma = 90.03°$. Although the Na^+, Si^{4+}, and Be^{2+} ions are tetrahedrally coordinated, this structure is not cristobalite related since the BeO_4 tetrahedra have common edges pairwise and thus form Be_2O_6 building blocks. The calculated powder diffraction pattern given in Table Id for this monoclinic structure has been calculated from the structural data given by Plakhov *et al.* (*11*). Although the monoclinic cell is related to ours ($a_{\mathrm{orth}} \approx b_{\mathrm{mon}}$, $b_{\mathrm{orth}} \approx 2a_{\mathrm{mon}}$, $c_{\mathrm{orth}} \approx c_{\mathrm{mon}}$, and $\gamma_{\mathrm{orth}} \approx \gamma_{\mathrm{mon}}$), the powder patterns are quite different, as seen in Tables Ia and Id. Thus we conclude that two different modifications of Na_2BeSiO_4 exist, one with a structure isotypic $KGaO_2$ (*12*) and the other with a monoclinic modification. The former is obtained by a solid state reaction, the latter by hydrothermal synthesis.

Na_2ZnSiO_4 and Na_2ZnGeO_4 can be prepared by solid state reaction as well as hydrothermally. Na_2ZnSiO_4 and Na_2ZnGeO_4, prepared by solid state reactions and quenched from low temperatures, showed powder patterns (*3, 4*) which were found to be identical to those derived from the structural data given in Refs. (*13, 14*). The crystals used in the latter investigations were hydrothermally prepared. Phases yielding this type of powder pattern will be regarded as isotypic and denoted as A-type phases below.

The structure of the low-temperature modification (LTm) of Na_2ZnSiO_4 can be described as a framework of $[(Zn,Si)O_4]$ formed by corner-sharing $(Zn,Si)O_4$ tetrahedra with Na^+ ions residing within the voids and can be topologically derived from either the wurtzite structure or the ideal high-temperature cristobalite structure. It derives from the hexagonal ZnS structure, by an ordered replacement, or cross-substitution of the cations, accompanied by a distortion of the hexagonal close packing of the anions (*15, 16*). Alternatively the structure can be derived from the ideal cristobalite structure by concerted rotations of the corner-sharing framework tetrahedra with the Na^+ ions located in the cavities of a collapsed cristobalite framework (*17*).

The powder pattern of Na_2ZnSiO_4 quenched from higher temperatures ($T_q >$ 1350 K) could be indexed on the basis of an orthorhombic cell with $a = 10.482$ Å, $b = 14.345$ Å, and $c = 5.242$ Å (*3*). The diffraction data indicate that HTm Na_2ZnSiO_4 is isotypic with $KGaO_2$, which has been shown to have a cristobalite derivative structure (*12*). Phases yielding this type of powder pattern will be regarded as being C-type.

The $Na_xZn_{x/2}Si_{2-x/2}O_4$ and $Na_xZn_{x/2}Ge_{2-x/2}O_4$ systems yielded C-type powder patterns when the samples had been quenched not only from higher temperatures but also from lower temperatures when the Na content was small. This shows that the stability of the C-type structure relative to the A-type modification in these materials increases with increasing temperature and decreasing Na content (see Table III) and could be interpreted as a stabilization of the A-type structure primarily by the bonding of Na^+ ions, rather than by the ions constituting the framework. However, in the $Na_xBe_{x/2}Si_{2-x/2}O_4$ system no A-type modification is observed. The C-type powder patterns are thus obtained for compositions $1.80 \leq x \leq 2.00$ quenched within the temperature interval 975 to 1335 K. The stability of the C-type structure is thus also increased relative to A-type by a decrease of the average size of the framework cations.

The ionic conductivity varies considerably with x in the $Na_xBe_{x/2}Si_{2-x/2}O_4$ system. As x decreases from 2.00 the conductivity increases and shows a maximum at $x \approx 1.80$; it then decreases with further decrease in x. The same kind of compositional dependence was observed in the zinc silicate and zinc germanate systems (*3, 4*); see Table III. In all three systems the best conductors were found at $x \approx 1.80$–1.85, with pellet materials having C-type structure. Furthermore the activation energies for conduction are almost the same, $E_a \approx 0.5$ eV, for these compounds. It is noted that the activation energies of beryllium silicate samples are lower than those of corresponding compositions in the zinc silicate and zinc germanate systems with A-type structure. It is also noted that the $\log(\sigma_0)$ values are almost constant within the homogenity range of each system and that E_a decreases smoothly with decreasing x values, in spite of the fact that in the zinc silicate and zinc germanate systems both A-type and C-type structure phases were encountered (see Table III).

TABLE IV

CONDUCTIVITY AND STRUCTURAL DATA FOR $Na_{1.80}Be_{0.90}Si_{1.10}O_4$ (Be, Si), $Na_{1.85}Zn_{0.925}Si_{1.075}O_4$ (Zn, Si), AND $Na_{1.80}Zn_{0.90}Ge_{1.10}O_4$ (Zn, Ge) C-TYPE MATERIAL TOGETHER WITH THE *b*/*a* AXIAL RATIO

Compound	E_a (eV)	$\log(\sigma_0)$ (K/Ω cm)	σ_{600} (1/Ω cm)	V (Å^3)	*b*/*a*
Be, Si ($x = 1.80$)	0.48	4.18	4.9E-3	674.4	1.407
Zn, Si ($x = 1.85$)	0.49	4.90	2.1E-2	793.4	1.377
Zn, Ge ($x = 1.80$)	0.55	4.42	2.3E-3	839.5	1.385

O'Keeffe and Hyde (*17*) have shown that a large number of structures, among them the A-type structure, may be derived from the cristobalite structure by regular concerted rotation of SiO_4 tetrahedra around their 4-axes. For each type of rotation, the degree of distortion relative to high-cristobalite structure can be designated by a rotation angle. (A rotation of 45° implies that cristobalite structure is transformed to wurtzite structure.) From the point of view of ionic conductivity, an undistorted high-cristobalite structure would have large cavities interconnected by hexagonal bottlenecks which are large compared to the ionic radius of Na^+. Compounds based on $NaAl SiO_4$, which have this type of structure, are also found to be poorer ionic conductors (*1, 18, 19*). When the cristobalite structure is distorted, however, the size of the cavities and interconnecting faces decreases with increasing rotation angle of the tetrahedra. According to O'Keeffe and Hyde (*17*) the angle $\Psi = \cos^{-1}(a^2/2bc)$ can be used as a measure of the framework relaxation for A-type structure. The Ψ values found for the low-temperature phases of Na_2ZnSiO_4 and Na_2ZnGeO_4 are 29.9 and 29.6°, respectively, implying that the two networks are collapsed to similar degrees. Accordingly, these compounds are found to be better conductors than those based on $NaAlSiO_4$. Unfortunately there is no simple relation between Ψ and the lattice parameters of the C-type structure; we are thus constrained to use other properties, for instance, the *b*/*a* ratio, as a measure of the collapse of the framework. As seen in Table IV the best conductors in the three systems exhibit similar *b*/*a* ratios.

Assuming the framework relaxation to be similar, it is somewhat puzzling to find almost equal conductivity values for the best conductors in the three systems, although their cell volumes are quite different (see Table IV). Thus the dimensional changes associated with the exchange of framework cations apparently do not greatly affect conductivity. This idea is presently under investigation, in connection with studies of the $Na_{1.80}Be_{0.90-x}Zn_xSi_{1.10}O_4$ system with $0 \leq x \leq 0.9$. The conduction mechanism, however, can, be expected to be a cooperative process. The sodium arrangement in C-type structure, i.e., existing intermediate sites and the site occupancy of the sodium ions, may accordingly influence the conductivity to a higher degree than does the framework size determined by the cations. This conclusion is in agreement with the observation that the best conductors, in the various systems studied by us, are generally those with the lowest sodium content per formula unit.

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