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Isomorphous Substitution of Fe in Sodalite and Its Electric Characterization

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Experiment on isomorphous substitution of Al by Fe in sodalite framework was carried out using dry way method at 800-900℃ in nitrogen atmosphere. The substitution of Fe was possible up to 25 mole% with some deviation of symmetry in sodalite cage. The cubic unit cell parameter increased with increasing Fe content. It showed ionic semiconducting property, especially the highest conductivity and the lowest activation energy in 10 mole% Fe-substituted sodalite which could behave as a superionic conductor at above 400℃. When more Fe was introduced into sodalite the electronic conductivity was improved at high temperature. But the relative electronic contribution was found to be lower compared with ionic contribution at high temperature. In infrared spectra some major absorption bands of sodalite shifted to lower wave numbers due to heavier Fe atoms substitution in Al lattice sites.

Introduction

The structure of sodalite ($Na_8Al_6Si_6O_{24}Cl_2$) is known to be cubic p$\bar{4}$3m[1]. As shown in Figure 1(b) its unit cell consists of 14-hedron with eight 6-rings and six 4-rings where Si and Al tetrahedra are linked together alternately. It is called a cubooctahedron or sodalite unit cell. The cubooctahedron is the basis for the structure of sodalite in Figure 1(a) which is obtained by directly connecting such 14-hedra through sharing of the 4-membered rings. The free diameter of a sodalite unit is about 6.6 Å[2]. Here the free distance means the distance between diagonally opposite points of polyhedra which is not impinged upon by the oxygen atom linings. The channel networks in sodalite allow 3-dimensional diffusion of all guest molecules small enough to enter the main cavities. The guest molecules and framework oxygens are not hard spheres and the lattice oxygens are also in the state of vibration with breathing frequencies.

In a previous study it has been reported that the elements of Be, B, Fe, Cr, P, and Mg can replace other elements such as Al and Si in tectosilicates[3]. The substitution of Al by Fe in the ZSM-5 framework has also been established[4-6]. In another study Szostak and Thomas were the first to synthesize a condensed phase zeolite, sodalite with significant quantities of iron in the framework ($SiO_2/Fe_2O_3=6\text{-}30$)[7].

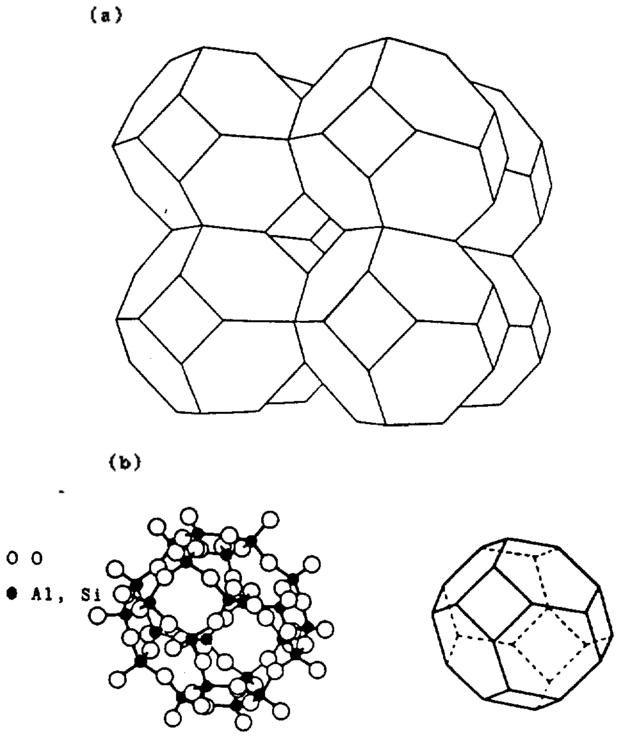

Figure 1. (a) The stacking of 14-hedra of sodalite structure, (b) Sodalite unit.

In tectosilicates trivalent aluminum has inert valence electrons. On the other hand, trivalent iron has $3d^5$ electrons which might show good electronic characters. In an effort to elucidate the role of Al site substitution by Fe on the electronic properties of sodalite, a study was undertaken to prepare the samples by dry way synthetic method in high temperature condition. Because salts are relatively non-volatile and high melting, dry way synthesis of salt-bearing tectosilicates can be expected from salt melt and silica, alumina, and alkali. Sodalite has open structure and thus the mobility

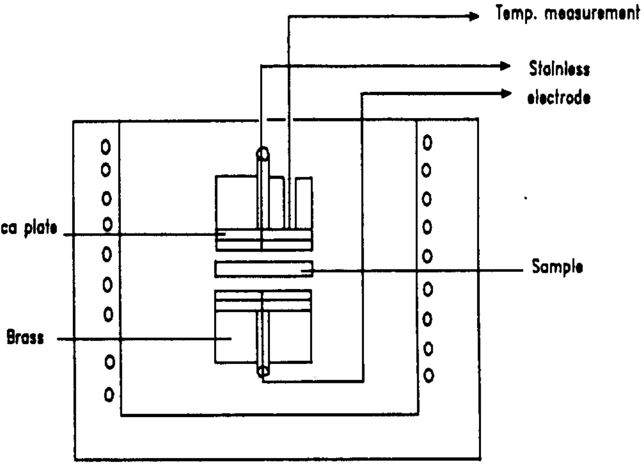

Figure 2. Sample holder.

of the cations can be expected. The possibility as an ionic conductor of the sodalite phase was also studied.

Experimental

Starting materials Na_2CO_3 (Aldrich, 99.95-100.05%), Al_2O_3 (Aldrich, 99.8%), Fe_2O_3 (Aldrich, 99+%), and SiO_2 (Hayashi, GR level) were mixed in proper stoichiometric proportion. They were fired in a predried nitrogen atmosphere at 800-900℃ (900℃ for 0 mole% and 5 mole% substitution of Fe; and 850℃ for 10 mole% and 15 mole% substitution of Fe; and 800℃ for 20 mole% and 25 mole% substitution of Fe) for 36 hours. To insure that the reactions were complete the products were reground and reheated at the same temperatures while the reactions were in progress. X-ray powder diffraction patterns of the products were obtained with a Shimadzu XD-3A diffractometer using Cu $K\alpha_1$ radiation ($\lambda = 1.5405$ Å). Cell parameters were determined by a least-squares refinement of the reflections using a computer program which corrects for the systematic errors of the measurement.

With a JASCO A-200 spectrometer infrared spectra of the products were obtained to see the effects of the vibration of the substitutes.

For the measurement of conductivity, about 0.5 g of powder sample was mixed with about 0.04-0.05 g of recrystallized naphthalene. Naphthalene acts as a binder. The mixture was loaded into die and the pellet was made using a compressor. The disc-shaped pellet produced was then heated at 250℃ for one hour to drive off naphthalene, followed by sintering at the reaction temperature for one hour. Then the pellet was coated with thin layer of gold for electrode using vacuum deposition.

Figure 2 shows the sample holder used for the measurement. Chromel-alumel thermocouple was used for checking the temperature of the sample which was placed between two stainless discs. Once the sample was introduced into the furnace, the conductivities were measured at the varying temperatures in a predried nitrogen atmosphere. The conductivity set-up is shown in Figure 3. As can be seen in the figure, the sample is placed in series with a known resistor. The voltage across the entire circuit and the voltage across the sample were measured by an oscilloscope. Voltage pulses of 0.8 V in magnitude, a pulse width 100 μsec and pulse duration time 500 μsec were utilized. The instruments used here were PG 1990 Pulse Generator of ED Engineering Company and Trio Oscilloscope CS-1040. For the dc measurement 0.5 V from a constant source was applied. Also two-terminal ac measurement was performed at 5 Hz-13 MHz and at 0.1 V by using Hewlett-Packard 4192 LCR Meter.

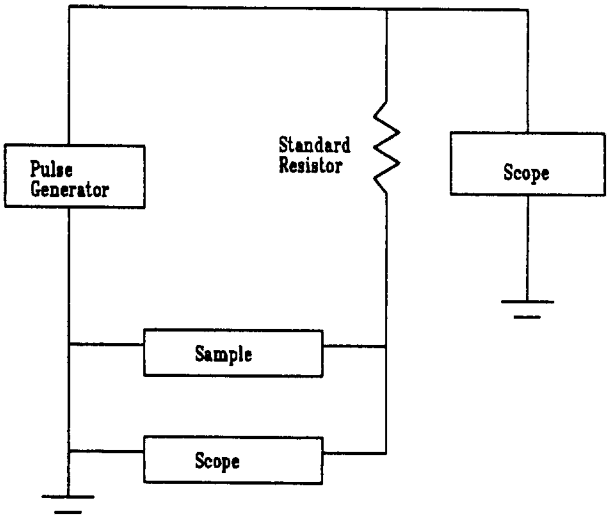

Figure 3. Set-up for conductivity measurement.

Results and Discussion

Figure 4 indicates X-ray diffraction patterns of the sodalite phase depending on Fe substitution in Al sites. Sodalite is known to be cubic with cell parameter $a = 8.878$ Å. But the X-ray pattern in Figure 4 exhibits the occurrence of superstructure. The order of this structure extends over two cages, as if one cage and its inclusion affected the arrangement in its neighbor[8]. The sodalite peaks were then indexed on a cubic with twice the usual sodalite parameter, *i.e.*, $a = 17.755$ Å. As more irons are introduced into Al sites the lines (444) and (660) are split indicating a disturbance of symmetry in sodalite cage. The cell parameters of each samples are listed in Table 1. With increasing iron species in the structure the cell volume increases by the fact that the ionic radius of tetrahedral Fe^{3+} (0.49 Å) is larger than that of Al^{3+} (0.39 Å).

Figure 5 shows the variation in conductivity with increasing Fe content. The results were obtained by pulse method at six different temperatures. The conductivity includes both ionic and electronic contributions. As can be seen in the figure Fe 10 mole% sodalite brings about an exceptional result compared with others. The conductivity measured by pulse and dc method and electronic contribution (%) in each sample is listed in Table 2. The electronic conductivites are almost constant up to the 360℃ and then begin to increase at above that temperature. The electronic contribution is almost 100% up to 200℃, which means that sodium mobile ions do not get enough activation energy below 200℃. At above 200℃ the ionic conductivities begin to increase but the electronic conductivities are still constant. So, the relative electronic contributions come to decrease as the temperature

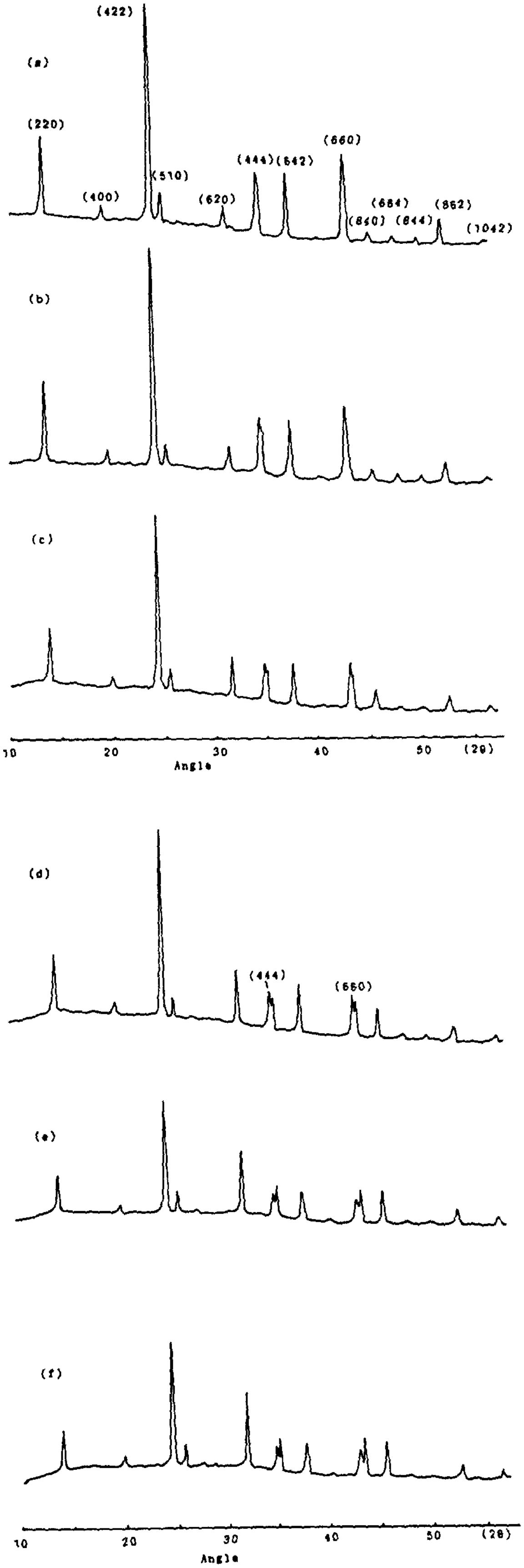

Figure 4. X-ray patterns of (a) sodalite, (b) Fe 5 mol%, (c) Fe 10 mole%, (d) Fe 15 mole%, (e) Fe 20 mole%, and (f) Fe 25 mole%-substituted sodalite.

Table 1. Unit Cell Parameters for $Na_8Al_{6-x}Fe_xSi_6O_{24}Cl_2$

x (mole%)	a (Å)
0.0 (0 mole%)	17.755
0.3 (5 mole%)	17.761
0.6 (10 mole%)	17.769
0.9 (15 mole%)	17.782
1.2 (20 mole%)	17.807
1.5 (25 mole%)	17.815

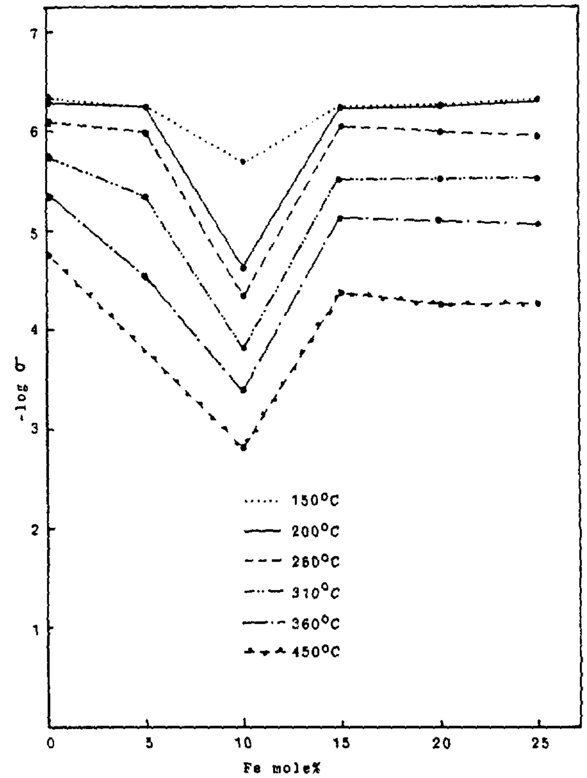

Figure 5. $-\log \sigma$ versus Fe-sodalite.

increases. Thus it can be said that these materials show ionic semiconducting properties. Especially Fe 10 mole% sodalite belongs to a superionic conductor at above 400℃ because its conductivity is in the order of 10^{-3} $(\Omega \cdot cm)^{-1}$ and the electronic contribution is less than 1%. The exceptional behavior of Fe 10 mole% sodalite can be interpreted as follows:

"Each sodalite unit contains one Cl at the center tetrahedrally coordinated 2.73 Å to four Na displaced inwards from four of the eight 6-rings. Each Na is bonded tetrahedrally to one Na neighbor and is strongly distorted such that the other three framework oxygens are more than 3 Å from Na. This distortion results from the Na being pulled 1 Å into the sodalite unit by the Cl from the mean plane of the 6-ring[9]." So the mobile Na ions are in flexible positions not in fixed positions. Once irons are introduced into the structure and then the volume of unit cell increases, the mobility of Na ion may also increae. On the contrary, the flexibility of Na ion might be limited due to the occupancy of larger Fe ions in space of the cage. It is expected that

Table 2. Conductivity (pulse and dc method) and Electronoic Contribution (unit: $\Omega^{-1}cm^{-1}$)

Fe (mole%)		150℃	200℃	260℃	310℃	360℃	450℃
0	pulse	4.5×10^{-7}	4.8×10^{-7}	8.0×10^{-7}	1.8×10^{-6}	4.4×10^{-6}	1.7×10^{-5}
	dc	4.5×10^{-7}	4.6×10^{-7}	4.5×10^{-7}	4.6×10^{-7}	4.8×10^{-7}	6.0×10^{-7}
	elec. contr.	100%	96%	56%	26%	11%	4%
5	pulse	5.5×10^{-7}	5.5×10^{-7}	1.0×10^{-6}	1.8×10^{-6}	4.7×10^{-6}	2.8×10^{-5}
	dc	5.5×10^{-7}	5.5×10^{-7}	5.5×10^{-7}	5.6×10^{-7}	5.5×10^{-7}	1.0×10^{-6}
	elec. contr.	100%	100%	55%	31%	12%	4%
10	pulse	2.0×10^{-6}	9.0×10^{-6}	4.5×10^{-5}	1.5×10^{-4}	4.1×10^{-4}	1.5×10^{-3}
	dc	8.0×10^{-7}	9.0×10^{-7}	4.0×10^{-6}	4.4×10^{-6}	9.0×10^{-6}	1.4×10^{-5}
	elec. contr.	40%	10%	9%	3%	2%	1%
15	pulse	5.5×10^{-7}	5.5×10^{-7}	9.0×10^{-7}	3.0×10^{-6}	7.7×10^{-6}	4.2×10^{-5}
	dc	5.0×10^{-7}	5.0×10^{-7}	5.0×10^{-7}	5.0×10^{-7}	5.0×10^{-7}	1.0×10^{-6}
	elec. contr.	91%	91%	56%	17%	6%	2%
20	pulse	5.1×10^{-7}	5.1×10^{-7}	1.0×10^{-6}	3.0×10^{-6}	8.0×10^{-6}	5.5×10^{-5}
	dc	5.1×10^{-7}	5.1×10^{-7}	5.2×10^{-7}	5.4×10^{-7}	5.5×10^{-7}	1.3×10^{-6}
	elec. contr.	100%	100%	52%	18%	7%	2%
25	pulse	4.5×10^{-7}	4.5×10^{-7}	1.1×10^{-6}	2.9×10^{-6}	8.7×10^{-6}	5.3×10^{-5}
	dc	4.5×10^{-7}	4.5×10^{-7}	4.7×10^{-7}	4.8×10^{-7}	7.0×10^{-7}	3.5×10^{-6}
	elec. contr.	100%	100%	43%	17%	8%	7%

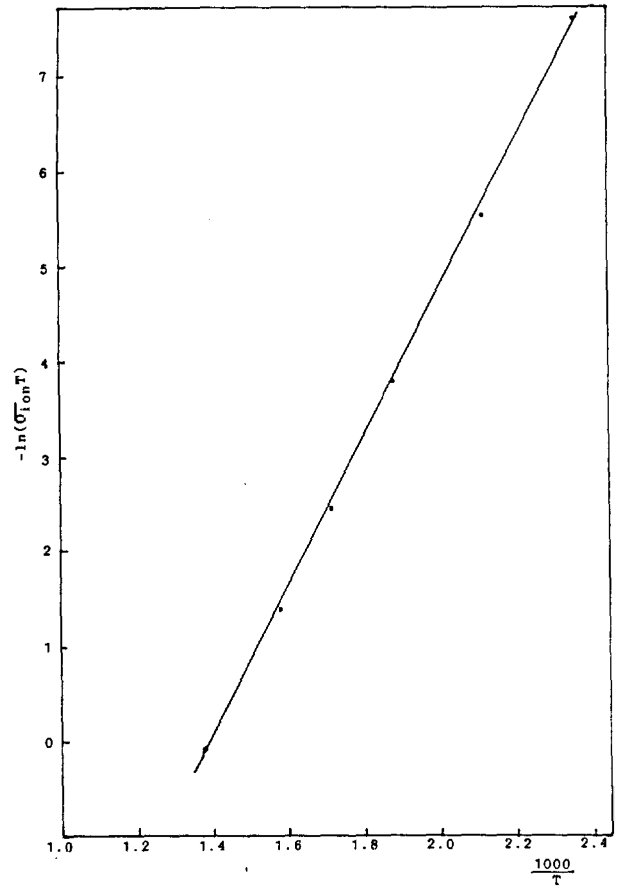

Figure 6. $-\ln(\sigma_{ion}T)$ versus $1000/T$ for Fe 10 mole% sodalite.

these two opposite factors result in maximum flexibility of Na ions when 10 mole% of Al ions are replaced by Fe ions. Figure 6 is Arrhenius plot of the ionic conductivity as a function of temperature for the same system.

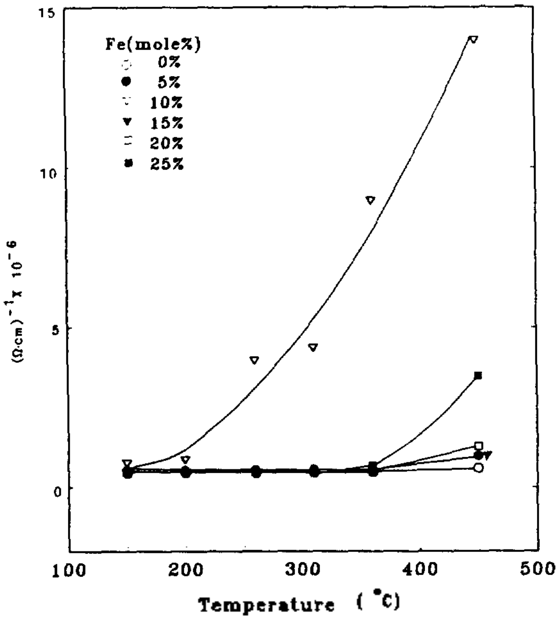

Figure 7. Electronic conductivity versus temperature.

The ionic property and activation energy estimated in the same way are described in Table 3. The activation energies of Na β-alumina and nasicon ($Na_{1+x}Zr_2P_{3-x}O_{12}$ where $x=0.4$-2.8) are known to be 3.7 kcal/mol and 5.5-7.4 kcal/mol.

It has been mentioned that the electronic conductivity increases at above 360℃ and the degree of increment somewhat depends on the Fe content, that is, higher conductivity in highter Fe content. But the values are quite low resulting in 10^{-6} $(\Omega\cdot cm)^{-1}$ order at 450℃ except for Fe 10 mole%

Table 3. Ionic Conductivity and Activation Energy for Fe-Substituted Sodalite

Fe	Ionic conductivity $(\Omega\cdot cm)^{-1}$						Act. *E*
(mole%)	150℃	200℃	260℃	310℃	360℃	450℃	(kcal/mol)
0	0	2.0×10^{-8}	3.5×10^{-7}	1.3×10^{-6}	1.9×10^{-6}	1.6×10^{-5}	19.2
5	0	0	4.5×10^{-7}	1.2×10^{-6}	4.2×10^{-6}	2.7×10^{-5}	17.9
10	1.2×10^{-6}	8.1×10^{-6}	4.1×10^{-5}	1.5×10^{-4}	4.0×10^{-4}	1.5×10^{-3}	15.5
15	5.0×10^{-8}	5.0×10^{-8}	4.0×10^{-7}	2.5×10^{-6}	7.2×10^{-6}	4.1×10^{-5}	19.5
20	0	0	4.8×10^{-7}	2.5×10^{-6}	7.5×10^{-6}	5.4×10^{-5}	20.0
25	0	0	6.3×10^{-7}	2.4×10^{-6}	8.0×10^{-6}	5.0×10^{-5}	18.8

Table 4. Impedance, Conductance, and Conductivity by ac method

Fe	320℃			450℃		
(mole%)	*Z* (kΩ)	*G* (μs)	$\sigma\,(\Omega\cdot cm)^{-1}$	*Z* (kΩ)	*G* (μs)	$\sigma\,(\Omega\cdot cm)^{-1}$
0				22.5	44.0	2.0×10^{-5}
5	237.0	4.1	2.2×10^{-6}	16.0	62.0	3.3×10^{-5}
10	3.4	294.0	1.8×10^{-4}	0.4	2520.0	1.6×10^{-3}
15	127.0	7.9	3.5×10^{-6}	9.2	108.0	5.1×10^{-5}
20	130.0	7.6	4.1×10^{-6}	6.9	144.0	7.7×10^{-5}
25	165.0	6.1	2.9×10^{-6}	7.7	129.0	6.2×10^{-5}

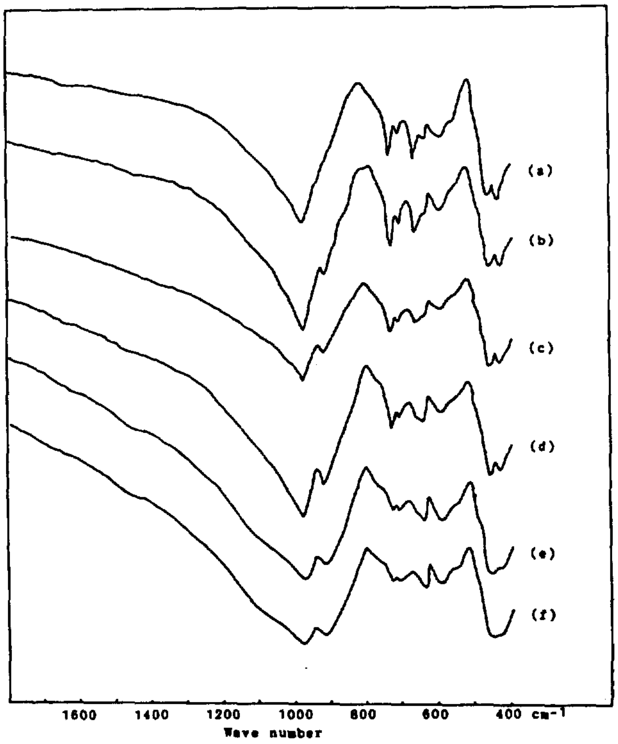

Figure 8. IR spectra of (a) sodalite, (b) Fe 5 mole%, (c) Fe 10 mole%, (d) Fe 15 mole%, (e) Fe 20 mole%, and (f) Fe 25 mole%-substituted sodalite.

sample. Fe^{3+} has $3d^5$ electrons compared with Al^{3+} containing filled valence electrons and so more Fe^{3+} concentration can induce higher conductivity. In addition, the difference of electronegativity between Fe-O is lower than that between Al-O. Thus the degree of the ionic character will be less in Fe-O, which cause the band gap to decrease[10]. However, the overlap of *d* orbital between Fe^{3+} ion and other Fe^{3+} ion appears to be very poor because they are not neighbor and the *d* orbitals of the first transition atoms usually do not spread out as far as possible. Exceptional electronic conductivity is also found in Fe 10 mole% sodalite (Figure 7). In the system it increases from 200℃ and the values are higher than those of other systems. This may be attributed to the fact that maximum mobility of Na ion can change the surrounding conditions which influence the energy gap of Fe ion toward improving the conductivity.

AC measurements were carried out in the range of 5 Hz-13 MHz at different temperatures. Table 4 shows the impedance (Z), conductance (G) of each system and conductivity was estimated from the resistance ($R=GZ^2$) when the susceptance (B) is zreo. These results quite agree with those of the pulse method.

Figure 8 is infrared spectra of the sodalite and Fe-substituted sodalite phases. Strong peak at 980 cm^{-1} indicates the T-O (T=Si, Al) stretching vibration. Part of the peak shifts to lower wave number at 920 cm^{-1} as the heavier Fe replaces Al in the lattice framework. The shift to lower wave number can also be observed partly at 730 cm^{-1} and 640 cm^{-1} owing to Si-O-Fe vibration from at 738 cm^{-1} and 670 cm^{-1} corresponding to Al-O-Si vibration[11]. The peaks appear around 450 cm^{-1} due to deformation vibration of the cage and decrease of the peak intensity at 435 cm^{-1} is caused by the decrease of Al concentration.

In conclusion, isomorphous substitution of Fe in sodalite was possible and the Na^+ ion in the framework could behave as mobile ion causing the ionic conductivity. When more Fe was introduced into the sodalite framework the semiconducting property was somewhat improved at above 400℃ due to the factors that the lower ionic character in Fe-O than in Al-O bond and the overlap of *d* orbital between transition metal ions.

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Free Energy of Ion Hydration

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The influence of temperature and pressure on the free energy of the ion hydration has been considered. The ion radii measured by conductometric method and the saturated dielectric constant cited from other works were used to calculate the free energy in the hydration shell. The Born equation was modified in order to fit in our model. In our model, the environment of ion consists of three regions. The innermost one is the hydration shell in which water is immobilized and electrostricted, the middle one is the one which contains less ordered waters than the bulk medium, and the outermost one is the bulk water which is under the influence of the electric field of ion. Our results for the free energy of ion hydration were compared with those of other attempts. Especially, ΔG_{hyd} of Li^+ ion is considerably too negative in this study at given temperature, comparing with those of other attempts. But ΔG_{hyd} of other ions coincides with each other.

Introduction

The solvation properties of electrolytes in aqueous solution are important in solution chemistry. Especially the ion hydration plays an important role in chemical and biochemical processes. The Born model[1] for the free energy of ion hydration forms the basis for a continuum approach.[2] The free energy of ion hydration is the reversible work required to charge a conducting hard sphere of radius r, embedded in a polarizable fluid with the relative dielectric constant ε_r at constant temperature and pressure and is expressed as

$$\Delta G = \frac{N_A (Ze)^2}{8\pi\,\varepsilon_o r}\ (1 - 1/\varepsilon_r) \qquad (1)$$

Where, N_A, Ze, and ε_o are the Avogadro number, the charge of the ion, and the dielectric constant of vacuum, respectively. As it was shown by Born approximation, the free energy of ion hydration depends upon two parameters, the ionic radius r and the relative dielectric constants ε_r of the fluid. Quantitatively speaking, the Born model is rather crude, due to the hard sphere assumption for the ionic solute and the treatment of the solvent as a continuous dielectric medium. According to this model, the free energies of hydration of not only the positively charged ions but negatively charged ones turn out to be the same when the same values of radii are used. However, such results are highly questionable since the surrounding patterns of water molecules around positive ion and negative one are quite different. Better result may be obtained, if the effective radii of hydrated ion and the dielectric constant of water in regions vicinal to the ion (due to dielectric saturation) are obtained. In fact, because of this, Born equation has been modified by a number of authors.[3-11]

In this paper, we have used the effective hydrated ionic radii obtained from our experimental results[12] and the saturated dielectric constant cited from other works[9,13] in order to calculate the free energies of ion hydration in the hydration shell and outside of it as well. We have modified the Born equation for the electrostatic free energy of the ion hydration using the effective hydrated ionic radii and the saturated dielectric constants.

Model

The hydration-shell model deduced from our experiment resembles that of the Frank and Wen.[14] In their (or our) model, the environment of ion consists of three regions. The innermost one is the hydration shell in which the water is