

Ordered Distribution of Aluminum Atoms in a Gmelinite Framework

Masanao Kato* and Kenta Takahashi

Research Center for Chemometrics, Toyohashi University of Technology, Toyohashi 441-8580, Japan

Received: November 17, 1999; In Final Form: February 16, 2000

The distribution of Al atoms in the gmelinite framework was examined for three models: (1) the conventional unit cell with no assumption of space group; (2) the conventional unit cell with an assumption of a 3-fold axis at the center of main channels, and (3) the super lattice composed of three unit cells with a 3-fold axis at the center of main channels. The final structural models for the ordered Al distribution in the gmelinite framework is based on model 1, with the noncentrosymmetric space group $P2_1$, which is much lower than the conventional space group $P6_3/mmc$. The estimated ^{29}Si NMR spectrum from the ordered distribution was in excellent agreement with the observed spectrum. The spectrum derived from model 2 was unsuitable to fit the observed spectrum. The spectrum from model 3 resembles the observed spectrum, but the agreement is not as close as between model 1 and the observed spectrum. These results suggest that the configuration derived from model 1 is the most suitable as the ordered Al distribution of gmelinite framework.

Introduction

Recently, we have demonstrated the ordered distribution of Al atoms in the zeolitic frameworks.^{1,2} Although it is widely considered that Al atoms are randomly distributed in most zeolites, Al ordering is reasonable in the zeolitic frameworks from the viewpoint of the XRD measurement, the chemical compositions, and the ^{29}Si NMR study. The ordered distribution, however, has not been examined in most of the zeolites.

Gmelinite is one of the zeolites composed of double 6-rings, and the centric space group $P6_3/mmc$ has been assigned to its framework.^{3,4} All tetrahedron sites (abbreviated as T site hereafter) in the framework are equivalent in this space group, and it has been asserted⁵ that Al atoms are randomly distributed in them. Generally, the XRD measurement tends to assign a symmetry that is too high because Si and Al atoms in a zeolitic framework cannot be discriminated from one another. On the other hand, Ventriglia⁶ reported that gmelinite is piezoelectric. This suggests that the structure of gmelinite has no center of symmetry and that the true symmetry of the framework of gmelinite is lower than $P6_3/mmc$. The lowering of the symmetry may be due to the ordered distribution of Al atoms in the framework. Although the ordering of Al atoms in the gmelinite frameworks has been discussed by Lipmaa et al.,⁷ from ^{29}Si MAS NMR spectrum, the detailed structure has remained unclear until now. In this study, we examined the detailed, ordered distribution of Al atoms in gmelinite and attempted to clarify the piezoelectricity of gmelinite.

Experimental Section

Natural gmelinite from Sarbai, Kazakhstan was purchased from Hori Mineralogy Inc. Its composition, without the extra-framework water molecule, was determined as $\text{Na}_{6.92}\text{Ca}_{0.45}\text{Al}_{7.64}\text{Si}_{16.36}\text{O}_{48}$ by an electron probe microanalyzer (Nikon ESEM-2700 scanning electron microscope equipped with a Horiba EMAX-5770W energy dispersive elemental analyzer). The Al content per unit cell is slightly smaller than the typical value, $\text{Na}_8\text{Al}_8\text{Si}_{16}\text{O}_{48}$, reported by Gottardi and Galli.⁵ No peak, due to the impurity, was observed in the XRD patterns of the

samples (Rigaku RINT 2500). The ^{29}Si MAS NMR spectrum was measured by a Varian Unity-400plus at 79.426 MHz with a spinning rate of 6 kHz, a pulse width of 5.5 μs ($\pi/2$ pulse), and a delayed time of 20 s. The spectrum was obtained by averaging 1000 scans.

Results and Discussion

The process for finding the ordered distribution of Al atoms in a gmelinite framework was described in the previous paper.¹

NMR Spectrum of Gmelinite. Prior to the determination of the ordered distribution of Al atoms in the gmelinite framework, the ^{29}Si MAS NMR spectrum of gmelinite was measured because observed NMR spectrum was used as a criterion to select the candidates of the ordered distribution. The ^{29}Si MAS NMR spectrum of gmelinite is shown in Figure 1a.

The obtained spectrum has clear structure and can be deconvoluted by four Gaussian peaks. The peaks were assigned to $\text{Si}(-\text{OSi})_4(-\text{OAl})_0$, $\text{Si}(-\text{OSi})_3(-\text{OAl})_1$, $\text{Si}(-\text{OSi})_2(-\text{OAl})_2$, $\text{Si}(-\text{OSi})_1(-\text{OAl})_3$, (hereafter abbreviated as $\text{Si}(0\text{Al})$ to $\text{Si}(3\text{Al})$, respectively) from high-magnetic field. The population of $[\text{Si}(n\text{Al})]_s$ (where $4 \geq n \geq 0$) can be calculated from the peak area. The chemical shifts of the peaks and the population of $[\text{Si}(n\text{Al})]_s$ were summarized in Table 1. The Al content per unit cell was determined from NMR spectrum as 7.59, which agreed with the value obtained by EPMA, showing that the Al–O–Al linkage avoidance rule (the Loewenstein's rule) is valid. It should be noticed that the spectrum has no peak corresponding to $\text{Si}(4\text{Al})$. Although a small population was obtained for $[\text{Si}(0\text{Al})]$, it was suggested from the observed population that the populations of $[\text{Si}(n\text{Al})]$, for the typical sample with $[\text{Al}]/\text{u.c.} = 8$, are $[\text{Si}(0\text{Al})] = [\text{Si}(4\text{Al})] = 0$, $[\text{Si}(3\text{Al})] = [\text{Si}(1\text{Al})] = 4$, and $[\text{Si}(2\text{Al})] = 8$ because the Al content of the sample used in the present study was less than the value of eight that was reported for the typical sample.⁵ Therefore, we employed these populations to search the ordered distribution of Al.

Candidates of the Ordered Distribution of Al Atoms in the Gmelinite Framework. Although the framework of gmelinite has been analyzed by the space group $P6_3/mmc$,^{3,4} it is considered that the true symmetry should be lower than the $P6_3/mmc$.

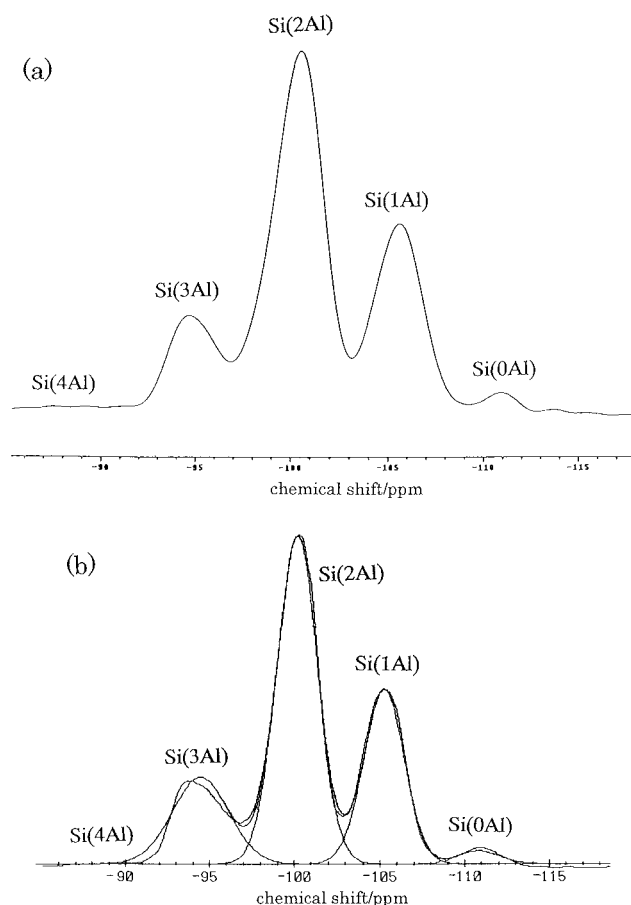


Figure 1. ^{29}Si MAS NMR spectrum of gmelinite. (a) Raw spectrum of MAS NMR of gmelinite, and (b) simulation of the spectrum by four Gaussian components on the basis of the ordered distribution of Al atoms in the framework with partial substitution of Al atoms by Si atoms.

TABLE 1: Assignment of ^{29}Si MAS NMR Spectrum and Populations of $[\text{Si}(n\text{Al})]$ s

	chemical shift /ppm				
	-110.8	-105.2	-100.2	-94.5	nd ^b
assignment	Si(0Al) ^a	Si(1Al)	Si(2Al)	Si(3Al)	Si(4Al)
population of $[\text{Si}(n\text{Al})]$ s	0.45	4.6	8.4	3.0	0.0
suggested population of $[\text{Si}(n\text{Al})]$ s for the typical gmelinite	0	4	8	4	0

^a $\text{Si}(-\text{OSi})_{4-n}(-\text{OAl})_n$ is abbreviated as $\text{Si}(n\text{Al})$. ^b not detected.

mmc value for cases in which the ordered distribution of Al atoms are assumed. Three models of the ordered Al distribution were considered in the present study: (1) the conventional unit cell with no assumption of space group (model I); (2) the same lattice with an assumption of a 3-fold axis at the center of the main channels (model II); and (3) the super lattice composed by three unit cells with a 3-fold axis at the center of the main channels (model III).

In model I, the investigation of the ordered distribution of Al atoms in the framework was started from the space group *P1*, which means no assumption about any symmetry in the lattice. In this case, the connectivity table of the gmelinite framework, which represents the connectivity relation between the T sites in the framework, is 24×24 (Table 2) because the framework of gmelinite contains 24 equivalent positions per

unit cell. The coordinates of the T sites and the sequence of T sites were derived from the equivalent positions of *P6₃/mmc* with an asymmetric unit of (0.442, 0.106, 0.094), based on the *International Tables for Crystallography*, Vol. A.⁸ Because the Al content per unit cell of gmelinite is considered to be eight in the typical samples,⁵ the candidates of the ordered distribution containing eight Al atoms per unit cell were searched under the restriction of the Al—O—Al avoidance rule (the Loewenstein's rule). The total number of candidates was 1260. Of these candidates, only three configurations were obtained as the topologically independent candidates with the populations of $[\text{Si}(n\text{Al})]$ s described above. The locations of Al atoms in the configurations are listed in Table 3 with their space groups. The space group of configuration A and C in Table 3 was *P2*. That of configuration B was *P1*. It is assumed in the present study that the configurations with higher symmetry should be realized as the ordered distribution, and the two candidates with space group *P2* were selected as the model of the ordered distribution.

The final selection of ordered Al distribution from the two candidates, A and C, is based on the comparison of the observed ^{29}Si MAS NMR spectrum with the one calculated from the configurations. The ^{29}Si MAS NMR spectrum can be simulated from the two candidates under the condition that small amounts of Al atoms are substituted by Si atoms because the Al content of the present sample is less than that of the typical value. The population changes of $[\text{Si}(n\text{Al})]$ s by the substitutions are listed in Table 4. Table 4 represents, for example, that the population of $[\text{Si}(0\text{Al})]$ increases unity by the substitution of Al by Si atom at the T_1 or T_2 site. The results of the simulation are summarized in Table 5. It was found from Table 5a that the populations of $[\text{Si}(n\text{Al})]$, based on the configuration A, were in good agreement with the observed values when 0.30 Al atoms at the T_2 , T_{10} , T_{14} , or T_{22} site and 0.06 Al atoms at T_1 or T_{12} sites were substituted by Si atoms. The sum of the square of the differences between the observed and calculated populations of $[\text{Si}(n\text{Al})]$, $\Sigma\Delta_{\text{calc-obs}}^2$ in Table 5, was 0.026. The result of the simulation is illustrated in Figure 1b.

A similar process was applied to configuration C. The minimum value of $\Sigma\Delta_{\text{calc-obs}}^2$ was 0.244 for cases in which 0.12 Al are substituted at T_1 site and 0.24 Al are substituted at T_5 site (Table 5b). The fit to the observed populations of configuration C was not as good as their fit to configuration A. This fact suggests the predominance of configuration A as the ordered distribution.

Configuration A is illustrated in Figure 2a,b. Configuration A includes two types of double 6 rings (D6R) shown in Figure 3. Both types of D6R contain four Al atoms in the framework. Two of the Al atoms are in para positions in the upper and lower 6 rings in the D6R, named para-D6R. In another D6R, two of the Al atoms are located in the meta positions of the T sites (meta-D6R). Configuration A consists of the two layers comprising these D6Rs. The "para-layer" is composed only of para-D6Rs, and the other layer, the "meta-layer", includes only meta-D6Rs. These layers are alternatively stacked, as shown in Figure 2b. It can also be seen that configuration A consists of two columns, the para-column and meta-column, composed of the para- and meta-D6Rs respectively as shown in Figure 2b.

We also investigated other possibilities for the ordered distribution. Model II was considered because the framework structure of gmelinite can be seen to include a 3-fold axis at the center of the main channels. In the model, the candidates were searched under the condition that nine Al atoms per unit

TABLE 2: Connectivity Table of Gmelinite Framework

sites	T1	T2	T3	T4	T5	T6	T7	T8	T9	T10	T11	T12	T13	T14	T15	T16	T17	T18	T19	T20	T21	T22	T23	T24
T1	1							1								1				1				
T2		1					1										1		1	1				
T3			1						1									1	1		1			
T4				1						1			1									1	1	1
T5					1						1			1								1	1	
T6						1						1			1							1		1
T7							1						1		1							1		
T8								1					1	1									1	
T9									1					1										1
T10										1							1	1	1					
T11											1					1				1				
T12												1					1				1			
T13													1					1						
T14														1					1					
T15															1						1			
T16																1						1		
T17																	1							
T18																		1						
T19																			1					
T20																				1				
T21																					1			
T22																						1		
T23																							1	
T24																								1

^aThe sequence of the T sites corresponds to that described by the *International Tables for Crystallography*, Vol. A. An asymmetric unit (0.442, 0.106, 0.094) was chosen

TABLE 3: Three Topologically Independent Configurations of Al Atoms in Gmelinite Framework with [Si(0Al)] = [Si(4Al)] = 0, [Si(1Al)] = [Si(3Al)] = 4, and [Si(2Al)] = 8

notation	sites occupied by Al atoms	space group
A	T ₁ , T ₂ , T ₄ , T ₉ , T ₁₀ , T ₁₂ , T ₁₄ , T ₂₂	P2
B	T ₁ , T ₂ , T ₆ , T ₉ , T ₁₁ , T ₁₄ , T ₁₈ , T ₂₃	P1
C	T ₁ , T ₅ , T ₇ , T ₁₂ , T ₁₃ , T ₁₇ , T ₁₉ , T ₂₄	P2

TABLE 4: Population Changes of [Si(nAl)] by the Substitution of Al Atom with Si Atom

configuration	T-site substituted	$\Delta[\text{Si}(n\text{Al})]$				
		$n = 0$	1	2	3	4
A	T ₁ or T ₁₂	+1	+3	-4	0	0
	T ₂ , T ₁₀ , T ₁₄ or T ₂₂	+1	+1	+2	-3	0
	T ₄ or T ₉	+3	0	-2	0	0
C	T ₁ , T ₁₂ , T ₁₃ or T ₂₄	+1	+4	-4	0	0
	T ₅ , T ₇ , T ₁₇ or T ₁₉	+2	-1	+3	-3	0

cell were distributed in the gmelinite framework with *P3* symmetry. In this case, the connectivity table is Table 6. The number of the independent T site is 8 because of the existence of the 3-fold axis located at the center of the main channel. All of the configurations obtained are listed in Table 7. Only eight configurations are possible under the restriction of Loewenstein's rule. The populations of [Si(*n*Al)] of the candidates were [Si(0Al)] = 3, [Si(1Al)] = 0, [Si(2Al)] = 3, [Si(3Al)] = 6, and [Si(4Al)] = 3 in all configurations. There was no configuration in which [Si(0Al)] = [Si(4Al)] = 0. In these configurations, nine Al atoms are included in the unit cell. A small amount of the Al atoms in the configuration must be substituted by Si atoms because [Al]/u.c. in the natural sample used here was 7.64. The simulated intensities of the NMR spectrum by the substitution never agree with the observed spectra, especially in [Si(0Al)], because the population of [Si(0Al)] always increases with the substitution. This means that model II is not suitable to be the ordered distribution of Al atoms in the framework.

TABLE 5: Simulation of ²⁹Si MAS NMR Spectrum by Substitution of Al Atoms^a

(a) for configuration A							
		[Si(<i>n</i> Al)]					$\Sigma \Delta_{\text{calc-obs}}^2$
substitution		<i>n</i> = 0	1	2	3	4	
0.06 T ₁ + 0.30 T ₂ ^b		0.36	4.48	8.36	3.10	0	0.026
observed values		0.5	4.6	8.4	3.0	0	
$\Delta_{\text{calc-obs}}$		-0.14	-0.12	-0.04	+0.10	0	
(b) for configuration C							
		[Si(<i>n</i> Al)]					$\Sigma \Delta_{\text{calc-obs}}^2$
substitution		<i>n</i> = 0	1	2	3	4	
0.12T ₁ + 0.24T ₅		0.6	4.24	8.24	3.28	0	0.244
observed values		0.5	4.6	8.4	3.0	0	
$\Delta_{\text{calc-obs}}$		0.1	-0.36	-0.16	0.28	0	

^a The 0.36 Al atoms were substituted by Si atoms. The populations of [Si(*n*Al)], calculated from the substitutions indicated by Gothic letter in pattern A are in good agreement with the observed values. ^b (amount of substitution) × (T-site substituted).

Model III was examined as the conquest of disagreement in model II. In model II, the number of Al atoms is restricted as a multiple of 3, and the nearest value to that of the typical sample in the conventional unit cell is 9. In model III, 24 Al atoms were considered, which is the least common multiple of 3 and 8. In this case, the candidates were searched under the condition that 24 Al atoms per unit cell were distributed in the super lattice comprising three unit lattices of the gmelinite framework with a 3-fold axis at the center of the main channels. The connectivity table is shown in Table 8, and the searched candidates are listed in Table 9. The populations of [Si(*n*Al)] in the candidates are [Si(0Al)] = [Si(4Al)] = 0, [Si(1Al)] = [Si(3Al)] = 4, and [Si(2Al)] = 8 per unit cell. Only three configurations satisfy the condition of the populations. On the basis of these configurations, the populations of [Si(*n*Al)] were simulated under the condition that the Al content was 7.64×3 . The population

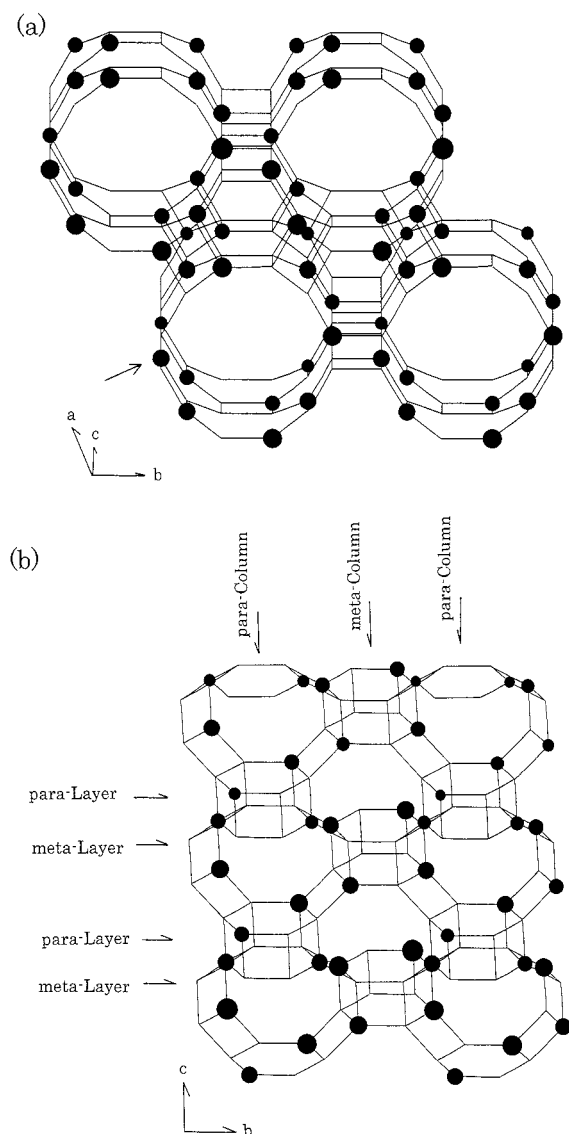


Figure 2. Model of the ordered distribution of Al atoms in the gmelinite framework. Oxygen atoms are omitted for clarity. Closed circle denotes Al atom. (a) Whole view along with c -axis, arrow denotes a 2-fold axis, and (b) layered structure of gmelinite framework projected to bc -plane.

changes from the substitution of Al by Si are summarized in Table 10. It is known from the table that the population changes of $Si(nAl)$ s are equivalent to all configurations. The minimum value of $\Sigma\Delta_{calc-obs}^2$ in Table 11 was 0.27 for cases in which 0.36 Al atoms were substituted by an Si atom at $T_{2,10}$, $T_{2,13}$, $T_{3,7}$, or $T_{3,16}$ in configuration A, at $T_{1,10}$, $T_{1,13}$, $T_{2,7}$, or $T_{2,16}$ in configuration B, or at $T_{1,1}$, $T_{1,22}$, $T_{3,4}$, or $T_{3,19}$ in configuration C. It was found that the agreement of the simulated spectrum with the observed spectrum was not good enough to model I described in Table 5. Moreover, the evidence of super lattice is not observed in the present stage. Consequently, it is also considered that this model should not be the configuration of the ordered distribution of Al atoms in the gmelinite framework.

As a result of the simulation of the NMR spectrum, on the basis of the ordered distribution of Al atoms, the configuration illustrated in Figure 2 is considered to be the most suitable one to the model of the Al ordering in the framework of gmelinite. This configuration has a 2-fold axis in the framework, that is, its space group is $P2$ contrary to the conventional $P6_3/mmc$. Ventriglia⁶ reported that gmelinite is piezoelectric instead of

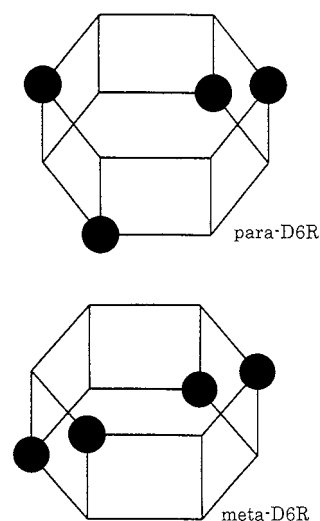


Figure 3. Two D6R components in gmelinite framework, para-D6R and meta-D6R.

TABLE 6: Connectivity Table for Gmelinite Framework, Assuming a 3-Fold Axis at the Center of the Main Channel

sites	T1 ^a	T4	T7	T10	T13	T16	T19	T22
T1			1			1	2	
T2				1	1			2
T3	1				2			1
T4		1				2	1	
T5		1	2				1	
T6	1			2				1
T7	2			1	1			
T8		2	1			1		

^a Notation of T sites in this table correspond to those in Table 2.

TABLE 7: Al Configuration in Gmelinite Framework, Assuming a 3-Fold Axis at the Center of the Main Channel^a

notation	configuration of Al atoms
A	T1, T10, T13
B	T1, T10, T22
C	T1, T13, T22
D	T4, T7, T16
E	T4, T7, T19
F	T4, T16, T19
G	T7, T16, T19
H	T10, T13, T22

^a The populations of all of the configurations are $[Si(0Al)] = 3$, $[Si(1Al)] = 0$, $[Si(2Al)] = 3$, $[Si(3Al)] = 6$, and $[Si(4Al)] = 3$.

the centric space group such as $P6_3/mmc$. This means that the true symmetry of gmelinite is much lower and has no center of symmetry. The true symmetry of gmelinite is considered to be $P2$ for cases in which the ordered distribution of Al atoms is assumed and the space group contains no center of symmetry in the lattice. This demonstrates the piezoelectricity of gmelinite.

The random distribution of Al atoms in the zeolitic frameworks has been discussed by many investigators. High symmetry, such as that found for $P6_3/mmc$ in the gmelinite framework, is based on the randomness. If Al atoms were randomly distributed in the framework, then all possible candidates should exist with the equivalent possibility in the framework, and the populations of $[Si(nAl)]$ s should be the averaged values of the distributions. The averaged populations of 1260 configurations, assuming the random distribution were $[Si(0Al)] = 3.31$, $[Si(1Al)] = 1.68$, $[Si(2Al)] = 4.29$, $[Si(3Al)] = 5.14$, and $[Si(4Al)] = 1.58$. These populations are quite

TABLE 8: Connectivity Table for Gmelinite Framework, Assuming a Super Lattice of Three-Unit Cells and a 3-Fold Axis at the Center of the Main Channel.

Sites	$T_{1,n}^a$								$T_{2,n}$								$T_{3,n}$							
n	1	4	7	10	13	16	19	22	1	4	7	10	13	16	19	22	1	4	7	10	13	16	19	22
$T_{1,1}$			1			1	1							1										
$T_{1,4}$				1	1			1																1
$T_{1,7}$	1				1			1					1											
$T_{1,10}$		1				1	1															1		
$T_{1,13}$			1	1			1											1						
$T_{1,16}$	1				1			1				1												
$T_{1,19}$		1			1	1											1							
$T_{1,22}$			1	1			1				1													
$T_{2,1}$											1		1	1									1	
$T_{2,4}$							1					1			1									
$T_{2,7}$								1					1			1						1		
$T_{2,10}$						1				1				1	1									
$T_{2,13}$			1							1	1				1									
$T_{2,16}$									1			1				1					1			
$T_{2,19}$	1								1			1	1											
$T_{2,22}$						1	1			1			1					1						
$T_{3,1}$							1									1			1		1	1		1
$T_{3,4}$																	1			1				1
$T_{3,7}$					1												1				1			1
$T_{3,10}$												1						1				1	1	
$T_{3,13}$										1								1	1				1	
$T_{3,16}$				1													1			1				1
$T_{3,19}$								1									1			1	1			
$T_{3,22}$			1														1	1			1			

^a $T_{n,m}$ denotes the m th sites in the n th unit cell composing superlattice.

TABLE 9: Al Configurations in Gmelinite Framework, Assuming a Super Lattice of Three-Unit Cells and a 3-Fold Axis at the Center of the Main Channela

notation	configuration of Al atoms
A	$T_{1,1}, T_{1,4}, T_{2,10}, T_{2,13}, T_{2,22}, T_{3,7}, T_{3,16}, T_{3,19}$
B	$T_{1,1}, T_{1,10}, T_{1,13}, T_{2,4}, T_{2,7}, T_{2,16}, T_{3,19}, T_{3,22}$
C	$T_{1,1}, T_{1,10}, T_{1,22}, T_{2,13}, T_{2,16}, T_{3,4}, T_{3,7}, T_{3,19}$

^a The population of $[\text{Si}(0\text{Al})]/\text{U.c.} = [\text{Si}(4\text{Al})]/\text{U.c.} = 0$, $[\text{Si}(1\text{Al})]/\text{U.c.} = [\text{Si}(3\text{Al})]/\text{U.c.} = 4$, and $[\text{Si}(2\text{Al})]/\text{U.c.} = 8$.

TABLE 10: Population Changes of $[\text{Si}(n\text{Al})]$ by the Substitution of Al by Si Atoms in the Super Lattice Structure

configuration	T site substituted by Si atom	$\Delta[\text{Si}(n\text{Al})]$				
		$n = 0$	1	2	3	4
A	$T_{1,1}, T_{1,4}, T_{2,22}, T_{3,19}$	+2	+1	-1	-1	0
	$T_{2,10}, T_{2,13}, T_{3,7}, T_{3,16}$	+1	+2	0	-2	0
B	$T_{1,1}, T_{2,4}, T_{3,19}, T_{3,22}$	+2	+1	-1	-1	0
	$T_{1,10}, T_{1,13}, T_{2,7}, T_{2,16}$	+1	+2	0	-2	0
C	$T_{1,10}, T_{2,13}, T_{2,16}, T_{3,7}$	+2	+1	-1	-1	0
	$T_{1,1}, T_{1,22}, T_{3,4}, T_{3,19}$	+1	+2	0	-2	0

different from the observed populations. Therefore, it is considered that the random distribution of Al atoms in the gmelinite framework should not be assumed.

Recently, we reported the ordered Al distribution in chabazite framework.¹ In a chabazite framework, six or three Al atoms were located in D6Rs. In gmelinite, on the other hand, D6Rs do not contain three or six Al atoms, but instead, they contain four Al atoms. Chabazite and gmelinite belong to the same group, "zeolites with 6 rings", classified by Gottardi and Galli.⁵ These zeolites include double 6 rings in their framework, and the difference between them has simply been regarded as a difference in the manner of linkage of the 6 rings. In such a viewpoint, a random distribution of Al atoms is assumed and,

TABLE 11: Simulation of ^{29}Si MAS NMR Spectrum by Substitution of Al Atoms for Super-lattice Structure. Common Values Were Obtained for Configuration A to C. In This Table, One Example for Configuration A Is Listed

substitution	$[\text{Si}(n\text{Al})]$					$\Sigma \Delta_{\text{calc-obs}}^2$
	$n = 0$	1	2	3	4	
$0.36 \times T_{2,10}$	0.36	4.72	8.00	3.28	0	
observed values	0.5	4.6	8.4	3.0	0	
$\Delta_{\text{calc-obs}}$	-0.14	0.12	-0.4	+0.28	0	0.27

hence, implies that there is no difference in D6Rs in chabazite and gmelinite. From the comparison of the present study with the previous¹ study, however, we found the difference between D6Rs in chabazite and gmelinite. This difference seems to result from the charge compensation of D6R. Galli and Gottardi⁵ reported that the typical composition of natural chabazite and gmelinite is $\text{Ca}_2(\text{Al}_4\text{Si}_8\text{O}_{24}) \cdot 12\text{H}_2\text{O}$ and $\text{Na}_8(\text{Al}_8\text{Si}_{16}\text{O}_{48}) \cdot 22\text{H}_2\text{O}$, respectively. Although the Si/Al ratios are equivalent in both of zeolites, synthesized chabazite with a composition of $K_{17.4}\text{-Al}_{17.4}\text{Si}_{18.6}\text{O}_{72} \cdot 30.2\text{H}_2\text{O}$ has been reported,⁹ and it has been shown that chabazite can contain more Al atoms in the framework, up to $\text{Si}/\text{Al} \approx 1$. Therefore, the maximum number of Al atoms in D6R is six in chabazite.¹ The difference between them is an extra-framework cation, and chabazite and gmelinite contain Ca and Na as an extra-framework cation, respectively. The divalent cation Ca seems to permit the existence of D6Rs with six Al atoms, and it is considered that Ca ion plays a very important role in the synthesis of chabazite, as pointed out by Gottardi and Galli.⁵

In the present study, the ordered Al distribution of gmelinite was determined as configuration A. The structure includes two layers, each composed of two D6Rs. Lipmaa et al.⁷ also discussed the ordered distribution of Al atoms in the gmelinite framework and proposed three models composed of only meta-

or para-D6Rs. The models comprising only meta-D6Rs, as mentioned by Lipmaa et al.,⁷ are omitted in this work because the predicted ²⁹Si NMR spectra cannot agree with the observed one. They proposed another model, composed of para-D6R, that can be compared with configuration C in the present study, but they ignored the population of [Si(3Al)] in their model. Because the NMR spectrum of gmelinite explicitly shows the existence of Si(3Al) in the framework ([Si(3Al)] = 4), their model may not be suitable for the model of ordered distribution of Al atoms in the gmelinite framework. It is considered, however, that configuration C was also not realized in the sample used here for the reason mentioned above, but in the proposed model, both meta- and para-D6Rs are included in the framework as the components of gmelinite framework.

In the XRD measurement, high-symmetry *P*₆₃/*mmc* has been assigned to gmelinite. However, the proposed symmetry is much lower. This discrepancy results from the existence of topologically equivalent Al distribution. For example, configuration (T₂, T₃, T₆, T₈, T₁₁, T₁₂, T₁₃, T₂₄) is topologically the same as configuration (T₁, T₂, T₄, T₉, T₁₀, T₁₂, T₁₄, T₂₂) proposed in the present paper. This corresponds to a 2 π /3 rotation of the 12 membered rings. There are 12 topologically equivalent configurations. It is considered that a number of small domains composed of one of these configurations appear in gmelinite crystal with the same possibility, and then, the occupation factors of the Al atom are apparently equivalent at all T sites. This may be the reason for the apparent randomness of Al distribution in the framework in the XRD measurement.

Conclusion

The ordered distribution of Al atoms in the framework of gmelinite was examined. Very high-symmetry *P*₆₃/*mmc* has

conventionally been assigned to its framework, and random distribution of Al atoms has been assumed. In this paper, we propose the ordered distribution of Al atoms in the framework with space group *P*2, in which only a 2-fold axis exists in the unit cell.

The simulated spectrum of the ²⁹Si MAS NMR was in excellent agreement with the observed one.

It was found from the distribution that gmelinite framework is composed of two D6Rs, designated para- and meta-D6R. Each D6R contains four Al atoms, each with different topology. These D6Rs are different from those in chabazite framework. This means that the Al distribution is fundamentally different between them, although they belong to the same group in zeolite classification.

It was shown that the random distribution of Al atoms is not realized in the gmelinite framework.

References and Notes

- (1) Takaishi, T.; Kato, M. *Zeolites* **1995**, *15*, 689.
- (2) Takaishi, T.; Itabashi, K.; Kato, M. *Zeolites* **1995**, *15*, 21.
- (3) Fisher, K. *Neues Jahrb. Mineral. Monatsh.* **1966**, 1.
- (4) Galli, E.; Passaglia, E.; Zanazzi, P. F. *Neues Jahrb. Mineral. Monatsh.* **1982**, 145.
- (5) Gottardi, G.; Galli, E. *Natural Zeolites*; Springer-Verlag: Berlin, 1985; Chapter 4.
- (6) Ventligria, U. *Rend. Soc. Miner. Ital.* **1953**, *9*, 268.
- (7) Lipmaa, E.; Mägi, M.; Samson, A.; Tarmak, M.; Engelhardt, G. *J. Am. Chem. Soc.* **1981**, *103*, 4992.
- (8) Hahn, T. *International Tables for Crystallography*, Vol. A, 4th ed.; Kluwer Academic Publishers: Dordrecht, 1995.
- (9) Barrer, R. M.; Klinowski, J. *J. Chem. Soc., Faraday Trans. 1* **1972**, *68*, 1956.