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PREPARATION AND DEHYDRATION BEHAVIOUR OF THOMSONITE WITH IDEAL CHEMICAL COMPOSITION

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Thomsonite with ideal chemical composition and with an ordered framework structure was synthesised hydrothermally from zeolite Na-A, which was ground to X-ray amorphous, with 0.05 mol dm^{-3} $CaCl_2$ solution at 200°C. The dehydration behaviour of the prepared thomsonite was examined by TG-DTA. It was revealed that thomsonite lost most of zeolitic water below 450°C in three steps at about 180°, 340° and 390°C. The peak profiles of the two higher-temperature endotherms were sharp and similar, and the weight loss at each step was approximately equal.

Keywords: dehydration and preparation of thomsonite, ^{29}Si and ^{27}Al NMR, TG-DTA

Introduction

Thomsonite is a member of the zeolite mineral group, the ideal chemical formula of which is $Na_4Ca_8(Al_{20}Si_{20}O_{80})\cdot 24H_2O$, i.e., the Si/Al ratio of the framework is 1.0 and the M/D ratio (M: monovalent cation, D: divalent cation) is 0.5 [1]. However, in natural thomsonites the Si/Al ratio varies from 1.0 to 1.3 and the Na/Ca ratio from 0.4 to 4.0 ([2], Fig. 1). Natural thomsonite with ideal chemical composition and with an ordered framework structure is rare, and therefore thermal dehydration curves show some diversity. Preparation of thomsonite with ideal chemical composition would thus enable determination of the 'real'

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dehydration characteristics. Many workers have tried to synthesise thomsonite. Synthesis using $CaO{\cdot}Al_2O_3{\cdot}SiO_2$ gels as starting materials was first reported by Barrer and Denny [3]. This synthesis required a temperature of 225° or 245°C and a SiO_2:Al_2O_3 ratio of 34 or 41; the products were sodium-free but similar to the thomsonite structure. Juan and Lo [4] prepared thomsonite from solid solutions between Ab_0An_{100} and $Ab_{30}An_{70}$ in the albite– anorthite– H_2O system. Wirsching [5] synthesised thomsonite from nepheline in $CaCl_2$ solution in an open hydrothermal system.

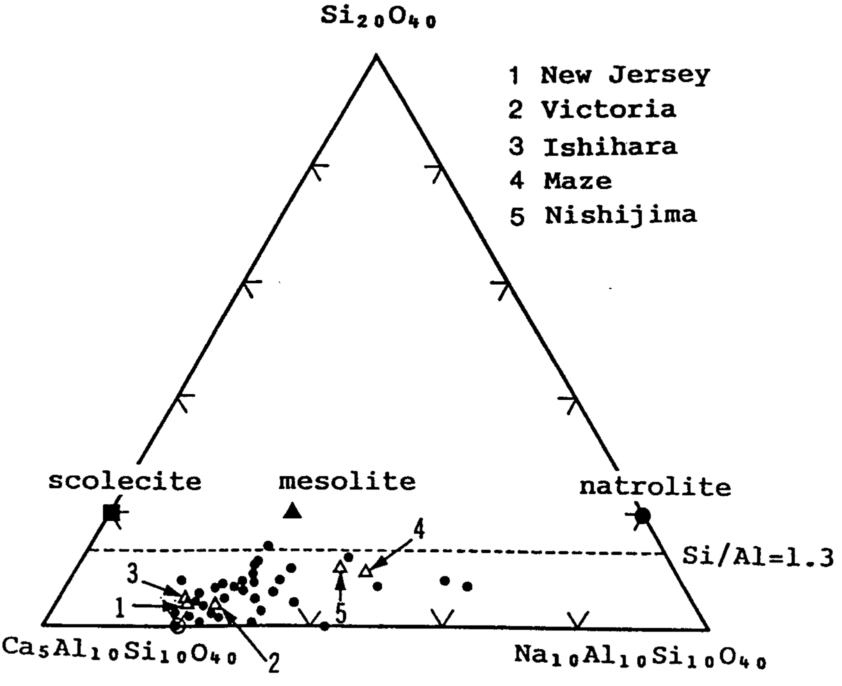

Fig. 1 Triangular plots representing the chemical compositions of five thomsonites together with data reported by Wise and Tschernich [2]. Open circle shows the ideal composition of thomsonite

In this investigation, thomsonite with ideal chemical composition was prepared from synthetic zeolite Na-A, previously ground to the X-ray amorphous state, under hydrothermal conditions. The dehydration behaviour of this thomsonite was examined by TG-DTA.

Experimental

Natural samples

Five natural thomsonite from: (1) West Paterson, New Jersey, U.S.A., (2) Flinders, Victoria, Australia, (3) Ishihara, Saga Pref., Japan, (4) Maze, Nishi-kanbara, Niigata Pref., Japan, and (5) Nishijima, Minami-koma, Yamanashi Pref., Japan, were used for comparison with synthetic products. All except the Ishihara sample occur as colourless or white prismatic crystals 1–5 mm in length. The Ishihara sample, which is covered by brown X-ray amorphous Fe-rich material, occurs as botryoidal spheres about 0.7 mm in diameter and contains minor analcime impurity.

Preparation of thomsonite

The starting material was synthetic zeolite Na-A made by Nippon Chemical Industry Co., Ltd., with the chemical formula $Na_{12.90}Si_{11.96}Al_{11.75}O_{48}\cdot 25.20H_2O$. This was ground to the X-ray amorphous state using a vibrating sample mill for 30 minutes. Hydrothermal experiments were run in a Morey-type bomb, containing a 15 ml Teflon bottle. Initially, 300 mg of ground Na-A was placed in the Teflon bottle, and then 12 ml of 0.05 mol dm^{-3} $CaCl_2$ solution adjusted to pH = 7.5–8.5, was added. After the suspension was stirred and dispersed with an ultrasonic vibrator, the bottle was sealed. The mixtures were hydrothermally treated at 200°C for 10–30 days.

The products were then separated from the solutions through a 0.45 μm micropore filter (Fuji Film Co., Ltd.), and washed with hot distilled water until no chlorine was detected. Finally, the products were dried at 60°C.

Analytical methods

TG-DTA curves were recorded for each 15 mg sample with a Rigaku Thermoflex TAS100 at a heating rate of 10 deg/min in static air. The sample was covered with 5 mg of calcined alumina. X-ray powder diffraction was carried out with a Rigaku Geigerflex RAD-IR using graphite monochromatized CuK_α radiation (40 kV, 20 mA). The unit-cell parameters of each sample were calculated from selected peak data corrected by using reflection data of an internal standard (silicon powder, NBS #640). This calculation was performed by the least-square programme RSLC-3, a programme in the Computer Center, University of Tokyo.

Chemical analysis was carried out using an energy dispersive spectrometer (Link Co., Ltd., type QX200J) installed in a scanning electron microscope (JEOL Co., Ltd., type JXM5400). The measurement conditions of the microanalyzer were an accelerating voltage of 15 kV and a beam current of 4.00×10^{-10} A. The water content was obtained from the weight loss between room temperature and

Table 1 Chemical compositions and unit-cell parameters of natural thomsonites

	(1)	(2)	(3)	(4)	(5)
SiO_2	38.92	39.47	39.34	42.59	43.06
Al_2O_3	30.44	30.67	30.03	29.79	29.74
Fe_2O_3	0.00	0.00	1.96	0.00	0.00
MgO	0.00	0.00	0.00	0.00	0.00
CaO	14.41	13.04	12.68	8.06	8.69
Na_2O	4.35	4.28	3.54	8.70	8.07
K_2O	0.00	0.00	0.28	0.06	0.09
H_2O	11.89	12.54	12.17	10.81	10.36
Total	100.01	100.00	100.00	100.01	100.01
		Structural formula based on 80 oxygens			
Si	20.58	20.87	20.89	21.99	22.10
Al	18.97	19.11	18.80	18.13	17.98
Fe	0.00	0.00	0.87	0.00	0.00
Mg	0.00	0.00	0.00	0.00	0.00
Ca	8.16	7.39	7.21	4.46	4.79
Na	4.46	4.39	3.65	8.71	8.03
K	0.00	0.00	0.19	0.04	0.06
H_2O	20.97	22.12	21.56	18.61	17.73
E%	-8.35	+0.09	+7.67	+2.61	+1.94
Si/Al	1.08	1.09	1.11	1.21	1.23
M/D	0.55	0.59	0.53	1.96	1.69
a/Å	13.065(5)	13.066(7)	13.072(7)	13.062(5)	13.068(6)
b/Å	13.081(8)	13.09 (1)	13.090(7)	13.086(8)	13.09 (1)
c/Å	13.201(7)	13.21 (1)	13.20 (2)	13.202(8)	13.205(9)

Note:

$$E\%(\text{balance error}) = \frac{(\mathrm{Al}+\mathrm{Fe})-(\mathrm{Na}+\mathrm{K}+2\mathrm{Ca})}{(\mathrm{Na}+\mathrm{K}+2\mathrm{Ca})}\times 100$$

$$M/D = \frac{\text{number of monovalent exchangeable cation}}{\text{number of divalent exchangeable cation}}$$

(1) West Paterson, New Jersey, U.S.A.
(2) Flinders, Victoria, Australia
(3) Ishihara, Saga Pref., Japan
(4) Maze, Nishi-kanbara, Niigata Pref., Japan
(5) Nishijima, Minami-koma, Yamanashi Pref., Japan

1000°C. Measured values of the elements, except H_2O, were corrected by the ZAF correction method. The balance error,

$$E\%=[(\mathrm{Al}+\mathrm{Fe}) -(\mathrm{Na}+\mathrm{K})-2\mathrm{x}\ (\mathrm{Ca}+\mathrm{Mg})]/[(\mathrm{Na}+\mathrm{K})+2\mathrm{x}(\mathrm{Ca}+\mathrm{Mg})]\times 100$$

was used to check the reliability of the chemical analysis [1].

Cross-polarized ^{29}Si and ^{27}Al MAS NMR spectra were recorded with a JEOL JNM-GSX400 instrument at 79.30 Hz and 104.05 Hz, respectively. Chemical shifts were calibrated with respect to TMN for ^{29}Si NMR spectra and to $Al(NO_3)_3$ for ^{27}Al NMR.

Results and discussion

Natural thomsonites

Chemical composition and unit-cell parameters

Chemical compositions and unit-cell parameters of the five natural thomsonites are given in Table 1. Figure 1 shows the triangular plots of chemical compositions of the five thomsonites together with the data reported by Wise and Tschernich [2]. Two thomsonites, Maze and Nishijima, have high values for both Si/Al ratio and M/D ratio. Compared with these two thomsonites, the chemical compositions of the other three minerals, especially of Ishihara sample, are close to that of the ideal thomsonite. The cell parameters of the five samples are similar, irrespective of their different chemical compositions.

TG-DTA curves

Figure 2 shows the TG-DTA curves of five natural thomsonites. In these curves, the endothermic peaks and weight losses below 450°C are due to dehydration. The sharp, small endotherm at about 510°C is caused by dehydroxylation. This is followed by destruction of the framework structure [6]. The TG-DTA curves vary between among the samples, depending on chemical composition. The DTA curves of the Maze and Nishijima thomsonites, with the higher Si/Al and M/D ratios, show a sharp, large endothermic peak at about 330°C. The Ishihara thomsonite with nearly ideal chemical composition loses most of its zeolitic water in three steps at 174°, 323° and 391°C. The weight loss at each step is approximately equal: out of 21.56 water molecules (Table 1, (3)), 6.3, 5.8 and 6.3 water molecules are lost successively. This suggests that the dehydration behaviour of Ishihara thomsonite corresponds to that of thomsonite, of idel composition.

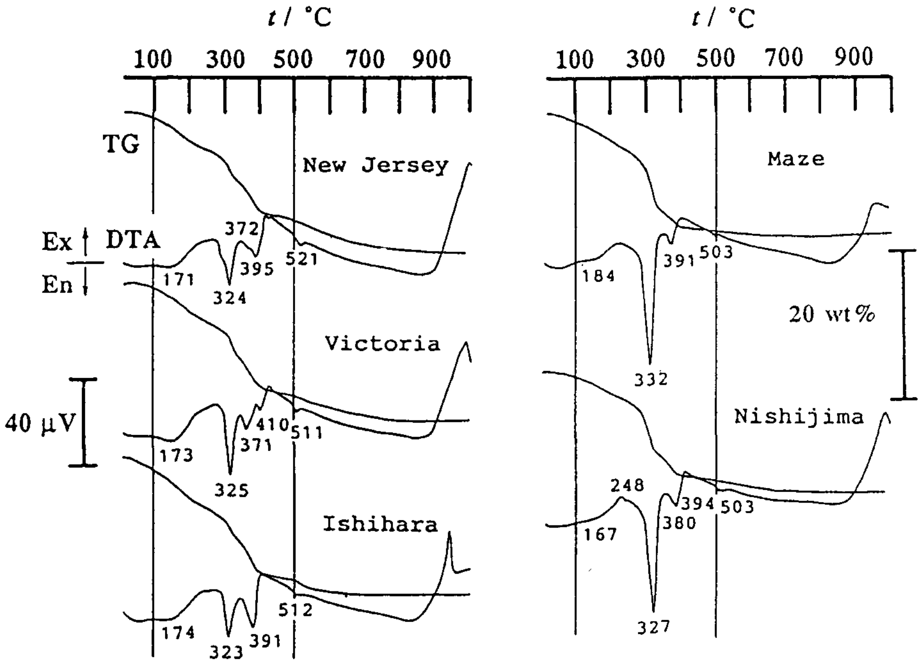

Fig. 2 TG-DTA curves of natural thomsonites

^{29}Si and ^{27}Al MAS NMR spectra

Figure 3 shows the ^{29}Si and ^{27}Al MAS NMR spectra of three thomsonites from New Jersey, Victoria and Ishihara, with the lower Si/Al and lower M/D ratio. In the ^{27}Al MAS NMR spectra of these three thomsonites, all of the peaks are attributed to tetrahedral Al. In the ^{29}Si MAS NMR spectra, two peaks at about –82 and –84 ppm are assigned to Si(4Al) units and one at about –88 ppm to Si(3Al) units [7]. Both peaks of Si(4Al) are broadened owing to the presence of three types of crystallographically non-equivalent Si sites [8]. The ideal thomsonite has a Si/Al ratis of unity and its ^{29}Si MAS NMR spectrum should show a single peak of Si(4Al) units [9]. However, these three thomsonites have both Si(4Al) and Si(3Al) units, indicating the existence of disordered (Si, Al)-distribution in their framework structures.

In addition to these peaks assigned to Si(4Al) and Si(3Al) units, a peak at about –95 ppm in the spectra of two thomsonites from Maze and Nishijima, with higher Si/Al ratio, is observed (Fig. 4). Lippmaa *et al.* [9] reported that in the ^{29}Si MAS NMR spectrum of natrolite two peaks occur at –84.7 and –95.4 ppm, due to Si(3Al) and Si(2Al) units respectively. This suggests that the latter two samples contain natrolite as an impurity, or alternatively that domains of a natrolite-type structure exist in the thomsonite crystal. Assuming that the thomsonites with the higher Si/Al ratios contain the natrolite-type structure, the endotherm at about 330°C on the TG-DTA curves of the Maze and Nishijima samples could be assigned to dehydration of this component.

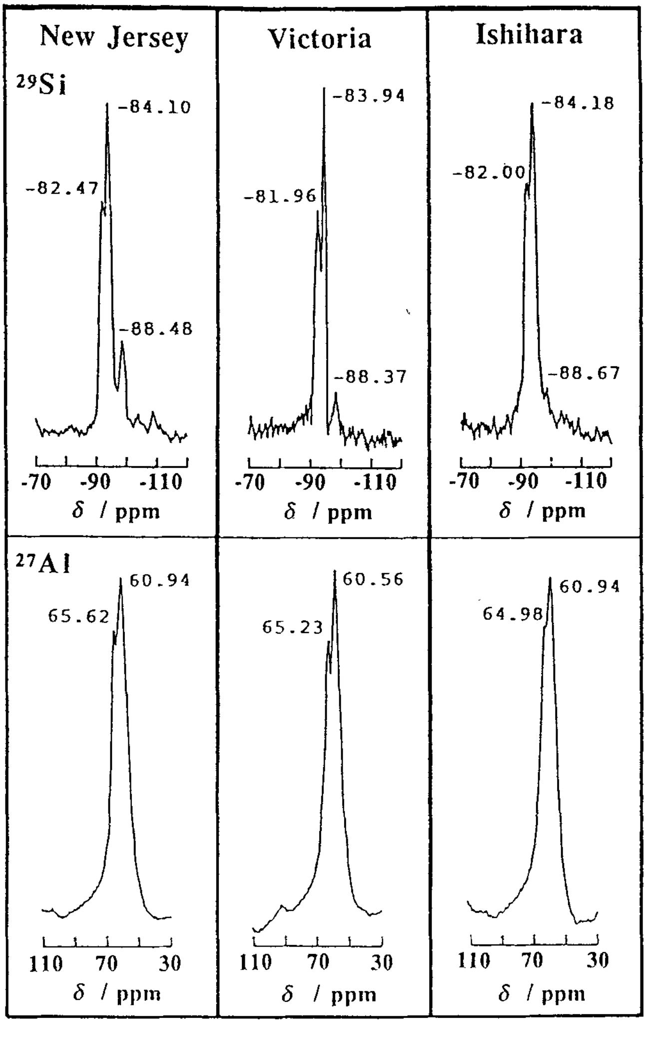

Fig. 3 ^{29}Si and ^{27}Al MAS NMR spectra of three natural thomsonites with the lower Si/Al ratios

These results suggest that the existence of a disordered (Si, Al)-distribution in the framework, and/or of natrolite-type domains having a higher Si/Al ratio, leads

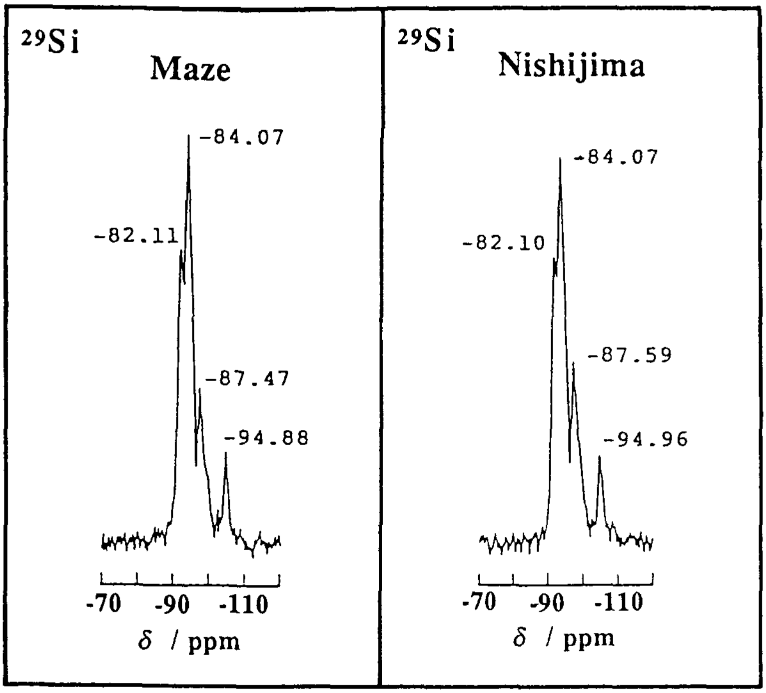

Fig. 4 ^{29}Si MAS NMR spectra of natural thomsonites with the higher Si/Al ratios

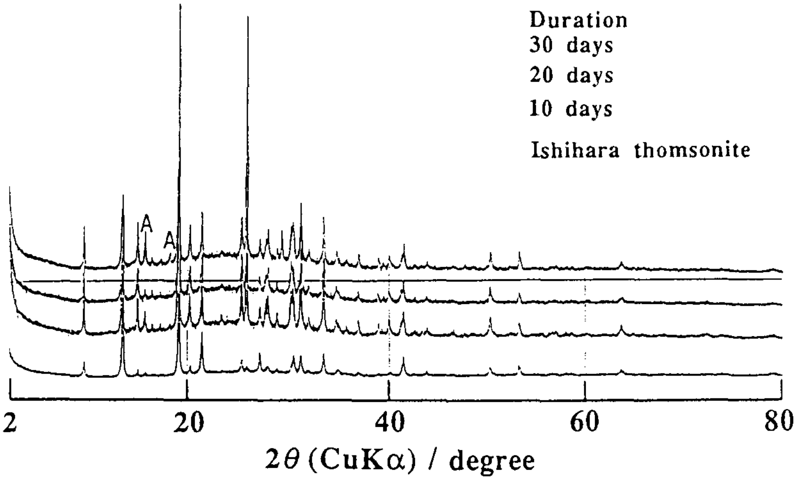

Fig. 5 X-ray diffraction patterns of the hydrothermal products and Ishihara thomsonite. A: analcime reflection

to different distributions of water molecules in the thomsonite crystal, thus explaining the variation in behaviour.

Table 2 X-ray powder diffraction data for the 30-day hydrothermal product and Ishihara thomsonite

	Hydrothermal product		Ishihara thomsonite	
h k l	*d* / Å	I/I_0	*d* / Å	I/I_0
1 1 0	9.167	19	9.302	13
0 2 0	6.520	45	6.577	79
0 1 2	5.882	39	5.921	15
1 1 2	5.368	8	5.390	3
2 2 0	4.612	92	4.640	100
2 1 2	4.367	44	4.390	18
1 3 0, 3 1 0	4.122	39	4.146	54
2 2 2			3.796	3
1 3 2, 3 1 2	3.494	54	3.510	33
0 4 0	3.263	18	3.280	25
0 1 4	3.194	32	3.203	16
3 2 2	3.168	42	3.184	24
3 3 0			3.090	4
0 2 4, 2 0 4	2.941	53	2.947	26
4 2 0	2.922	69	2.929	30
4 1 2	2.851	100	2.863	54
3 3 2	2.786	16	2.798	8
2 4 2	2.668	72	2.679	51
1 3 4, 3 1 4	2.575	19	2.581	10
5 1 0			2.565	8
4 3 2	2.425	25	2.433	11
4 4 0			2.313	4
2 5 2			2.287	4
3 3 4	2.249	26	2.254	10
2 4 4, 4 2 4	2.186	26		
6 0 0	2.172	25	2.180	31
3 5 2, 5 3 2	2.118	7	2.126	6
0 2 6			2.089	3
6 2 0	2.061	11	2.067	7

Synthetic thomsonite

XRD and EM data

Figure 5 shows the X-ray diffraction patterns of the hydrothermal products from three different run durations together with that of the Ishihara thomsonite. In this hydrothermal treatment, products having a well crystallized thomsonite-like structure were obtained, although each product contained a minor amount of analcime. X-ray diffraction data for the 30-day product and the Ishihara sample are given in Table 2.

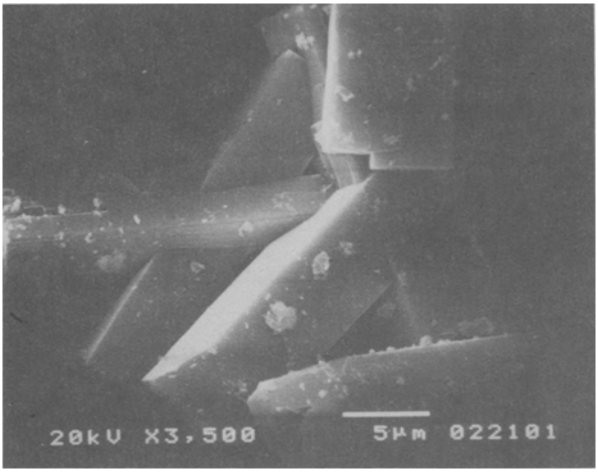

Fig. 6 Scanning electron micrograph of the hydrothermal product treated for 30 days

Figure 6 shows a scanning electron micrograph of this product, in which well-formed, prismatic crystals more than 10 µm in length are observed. These are similar to the typical idiomorphic form of common thomsonite.

Chemical composition and unit-cell parameters

Table 3 shows the chemical composition and formula of the hydrothermal product treated for 30 days. Its chemical formula is close to the ideal formula of thomsonite. Assuming that the symmetry of the product treated for 30 days is orthorhombic, its unit-cell parameters were determined as a= 13.036(5) Å, b = 13.046(7) Å, c = 13.197(4) Å. The a and b parameters are obviously smaller than those of the natural thomsonites given in Table 1.

Table 3 Chemical composition and formula of the hydrothermal product treated for 30 days

		Structural formula based on 80 oxygens	
SiO_2	37.32	Si	19.76
Al_2O_3	32.43	Al	20.24
Fe_2O_3	0.00	Fe	0.00
MgO	0.00	Mg	0.00
CaO	14.11	Ca	8.00
Na_2O	4.13	Na	4.24
K_2O	0.00	K	0.00
H_2O	12.01	H_2O	21.23
Total	100.01		
		$E\%$	–0.05
		Si/Al	0.98
		M/D	0.53

Note:

$$E\%(\text{balance error}) = \frac{(\text{Al}+\text{Fe})-(\text{Na}+\text{K}+2\text{Ca})}{(\text{Na}+\text{K}+2\text{Ca})} \times 100$$

$$M/D = \frac{\text{number of monovalent exchangeable cation}}{\text{number of divalent exchangeable cation}}$$

^{29}Si and ^{27}Al MAS NMR spectra

Figure 7 shows the ^{29}Si and ^{27}Al MAS NMR spectra of the hydrothermal products. In the ^{29}Si MAS NMR spectra, only two peaks at about –82 and –84 ppm assigned to Si(4Al) units were observed initially, but with incresing run duration a third peak appeared between the above two peaks. These three Si(4Al) peaks are consistent with the presence of three types of crystallographycally non-equivalent Si sites [8]. In the ^{27}Al MAS NMR spectra of the products, all of the peaks can be attributed to tetrahedral Al as in the case of natural thomsonite. This suggests that the structure of the hydrothermal thomsonite has nearly identical (Si, Al)-distributions.

TG-DTA curves

Figure 8 shows the DTA curves for the synthetic thomsonites and the Ishihara sample. The synthetic samples lose most zeolitic water in three steps below 450°C at about 180°, 340° and 390°C. Peak profiles of the two higher-temperature endotherms are sharp and similar, and weight losses at each step are approximately equal, i.e. 6.9, 5.6 and 6.1 water molecules. The dehydration behaviour of the synthetic thomsonite is similar to that of the Ishihara sample with nearly ideal chemical composition.

According to single-crystal structure analysis by neutron diffractometry, there are four independent water molecule sites in thomsonite [8]. On the basis of this

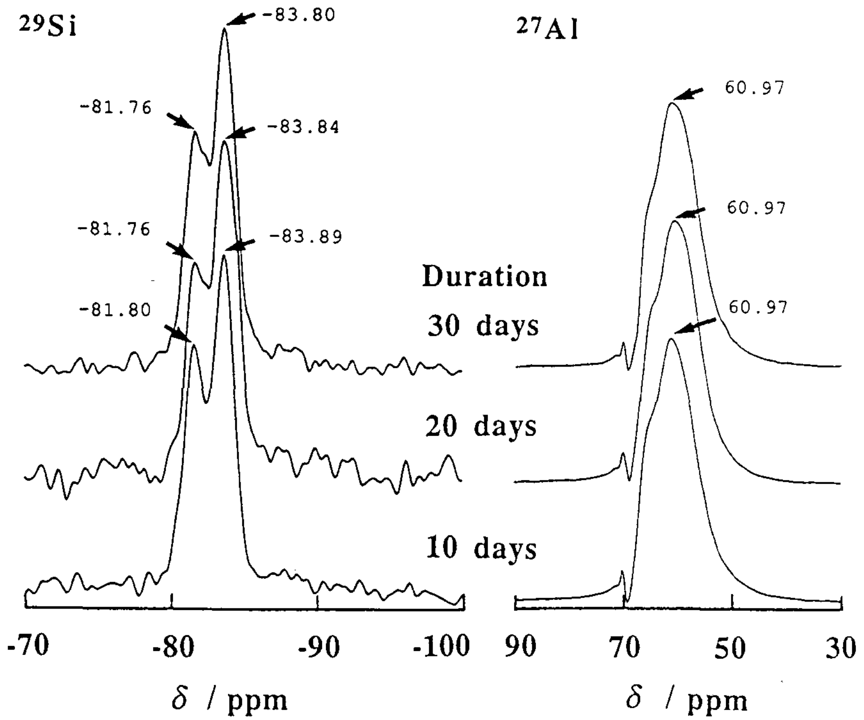

Fig. 7 ^{29}Si and ^{27}Al MAS NMR spectra of the hydrothermal products

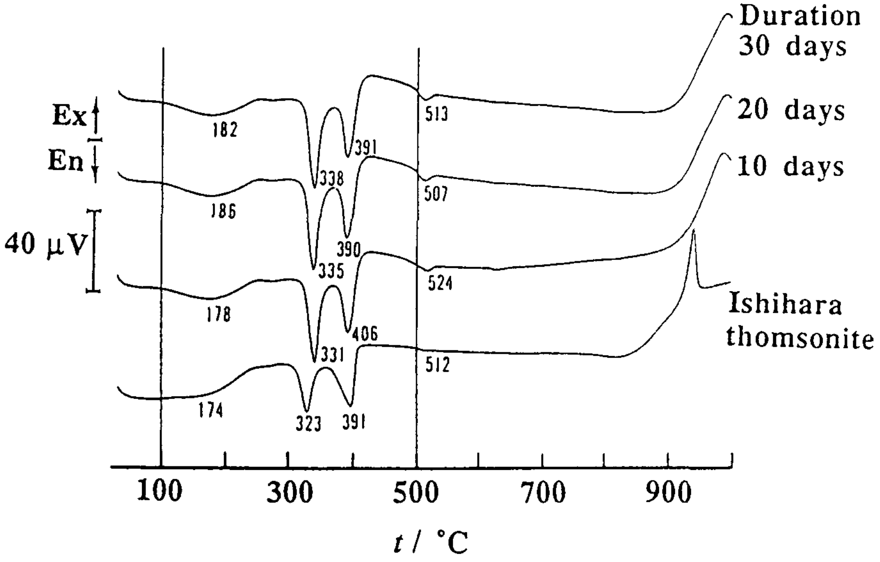

Fig. 8 DTA curves of the hydrothermal products and Ishihara thomsonite

model, the dehydration of thomsonite can be explained. About a quarter of the twenty-four water molecules in the channel are lost up to 250°C at the first step. Following this, half the water molecules in the eight oxygen-ring are eliminated during the second and third steps at about 325°and 390°C. The remaining water and/or hydroxyls are lost at higher temperature.

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Zusammenfassung — Aus Zeolith Na-A, welches mittels einer 0,05 molaren $CaCl_2$-Lösung bei 200°C röntgenographisch amorph gemahlen wurde, stellte man auf hydrothermischem Wege Thomsonit mit idealer chemischer Zusammensetzung und mit einer geordneten Gitterstruktur her. Das Dehydratationsverhalten des hergestellten Thomsonits wurde mittels TG/DTA untersucht. Es wurde gezeigt, daß Thomsonit unter 450°C, in drei Schritten: bei 180°, 340° und bei 390°C einen Großteil Zeolith-Wasser verliert. Die Peakverläufe der zwei Endothermen bei höheren Temperaturen sind scharf und ähneln sich und der Gewichtsverlust ist bei jedem Schritt etwa gleich.