

Hydrothermal Syntheses of Na-Magadiite and Na-Kenyaite in the Presence of Carbonate

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In order to synthesize well-crystallized Na-magadiite and Na-kenyaite as a single phase in a short reaction time, the amorphous silica was hydrothermally reacted with the alkali solution of NaOH-Na₂CO₃ in the temperature range of 150 to 180 °C. From a suspension containing SiO₂ and NaOH-Na₂CO₃ with the molar ratios of SiO₂/(NaOH+Na₂CO₃) = 5 and H₂O/(NaOH+Na₂CO₃) = 100, magadiite was formed after 24 hours of reaction at 150 °C. On the other hand, kenyaite was formed with magadiite or quartz simultaneously in 48-96 hours of reaction at 160 or 170 °C. In the molar ratios of SiO₂/(NaOH+Na₂CO₃) = 5-10, H₂O/(NaOH+Na₂CO₃) = 100, and SiO₂/(NaOH+Na₂CO₃) = 3, H₂O/(NaOH+Na₂CO₃) = 150-200, well-crystallized kenyaite was purely synthesized. In the higher molar ratios of Si/Na [SiO₂/(NaOH+Na₂CO₃) = 20 and H₂O/(NaOH+Na₂CO₃) = 200], kenyaite can be directly synthesized from amorphous silica without the formation of magadiite as an intermediate. These results indicate that the composition of reactant is one of the important factors in the formation of kenyaite. In spite of the similarity of XRD pattern, the morphology of kenyaite represents diverse shapes.

Introduction

In recent years, the syntheses of layered silicates such as magadiite (Na₂Si₁₄O₂₉·9H₂O), kenyaite (Na₂Si₂₂O₄₅·10H₂O), and makatite (Na₂Si₄O₉·5H₂O) have growing interests due to their catalytic, absorptive, and ion-exchange properties.^{1,2} They also have a characteristic of being free of aluminum unlike zeolite or clay, and exhibit the acid-resistant property and the thermal stability. Recently, the preparation of molecular sieve from silica pillaring through interlayer of these materials was studied by a few researchers.³⁻¹⁰

Magadiite and kenyaite were primarily found by Eugster¹¹ in the lake beds of the lake Magadi in Kenya. Afterward, other occurrences of these have been continuously reported in various regions.^{12,13} Most of these deposits were found in sodium carbonate-rich alkaline lake waters. Also they have been successfully synthesized under a hydrothermal condition. Their basic structures are composed of duplicated SiO₄ tetrahedral sheets and are similar to clay minerals with no aluminum.^{14,15}

Lagaly and Beneke¹⁶ discussed the preparation of Na-magadiite in a hydrothermal system at 100 °C for 4 weeks of reaction. More recently, Muraishi¹⁶ synthesized K-magadiite at 100-180 °C for 2-5 days of reaction in KOH solution containing various amount of NaCl. Kosuge *et al.*¹⁷ synthesized Na-magadiite at 170 °C for 18 hours of reaction in the presence of organic solvent. However, the preparation of kenyaite was rarely reported. Beneke and Lagaly¹⁸ indicated that the formation of kenyaite at 100 °C required several months. At higher temperature, the reaction time in the formation of kenyaite is much decreased, but quartz was formed simultaneously. More recently, Fletcher and Bibby¹⁹ preliminarily investigated the effects of anions on the formation of kenyaite.

The objective of this work is to synthesize pure and well-crystallized Na-magadiite and Na-kenyaite under the carbon-

ate system in a short reaction time. We report here the effects related to the compositions of reactants, reaction time, and temperature on the preparation of Na-kenyaite and Na-magadiite in the sodium carbonate system.

Experimental

Na-magadiite and Na-kenyaite were prepared by the reaction of SiO₂-NaOH-Na₂CO₃ system under hydrothermal conditions. Materials used were silica gel (Wakogel Q-63) and NaOH and Na₂CO₃ of analytical reagent grades. Experiments were carried out in a stainless steel autoclave without stirring in the various reaction times and molar ratios of reactants at 150-180 °C under autogenous pressure. The molar ratio of NaOH to Na₂CO₃ is fixed to 1/2 in all cases. The compositions of reactants and reaction conditions are shown in Table 1.

The products were filtered, and washed with deionized water in order to remove excess NaOH or Na₂CO₃, and then dried at 40 °C. Identification of samples was carried out by X-ray powder diffraction (Rigaku Rotaflex diffractometers equipped with CuK_α radiation) and Scanning Electron Microscopes (Jeol, JSM-840A). The chemical compositions of synthetic magadiite and kenyaite were determined by Energy Dispersive X-ray Spectrometer (Link System AN10000-85S) and TGA. EDS analysis was carried out using electron beam with the sample of carbon-coated pellet. For the quantitative analyses of silica and sodium, quartz and sodium chloride were used as references. Thermogravimetric analyses were performed in air on a Dupont 9900 thermogravimetric analyzer.

Results and Discussion

Table 1 shows reaction conditions and the results of XRD for the samples synthesized. The results were selected among about 100 experimental runs. Figure 1 shows the development of crystalline magadiite with reaction time at 150

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Table 1. Representative Runs to Synthesize Magadiite and Kenyaite from SiO₂, NaOH, Na₂CO₃ and H₂O Suspensions

Run No.	Temp. (°C)	Time (hr)	Molar ratio of starting materials		Product ^a
			SiO ₂ /B ^c	H ₂ O/B ^c	
1	150	72	3	100	M
2	160	72	3	100	M
3	150	48	3	150	M
4	150	72	3	150	M>K
5	150	96	3	150	M>K
6	160	48	3	150	M>K
7	160	72	3	150	K<Q
8	170	24	3	150	M>K
9	170	72	3	150	Q
10	150	72	3	200	K
11	150	96	3	200	K
12	160	72	3	200	K
13	160	96	3	200	K>Q
14	170	72	3	200	K<Q
15	170	96	3	200	Q
16	150	10	5	100	A,M
17	150	24	5	100	M
18	150	48	5	100	M
19	150	72	5	100	M
20	150	96	5	100	M
21	160	48	5	100	M>K
22	160	72	5	100	K
23	160	96	5	100	K>Q
24	170	24	5	100	M
25	170	41	5	100	M>K
26	170	50	5	100	M<K
27	170	55	5	100	K
28	170	60	5	100	K>Q
29	170	72	5	100	K>Q
30	160	72	10	100	K
31	180	48	20	200	A,K
32	180	64	20	200	A,K
33	180	96	20	200	K

^cB=NaOH+Na₂CO₃ (Molar ratio of NaOH to Na₂CO₃ is 1/2).

^aM=Na-magadiite, K=Na-kenyaite, A=amorphous silica, Q=α-quartz, M>K means that the amount of Na-magadiite is more than that of Na-kenyaite.

^c in the reactant compositions of SiO₂/(NaOH+Na₂CO₃)=5 and H₂O/(NaOH+Na₂CO₃)=100. The XRD pattern of synthetic magadiite exhibited 00 ℓ X-ray reflections of film sample corresponding to a basal spacing of 15.9 Å. The peak positions for synthetic magadiite agree well with values reported previously^{3,5,11} for synthetic and natural magadiite. Pure magadiite was obtained after 24 hours of reaction, and then the intensity of peak increases as the reaction time increases from 24 to 72 hours.

Magadiite is directly synthesized from amorphous form of silica, and the pure magadiite can be synthesized easily

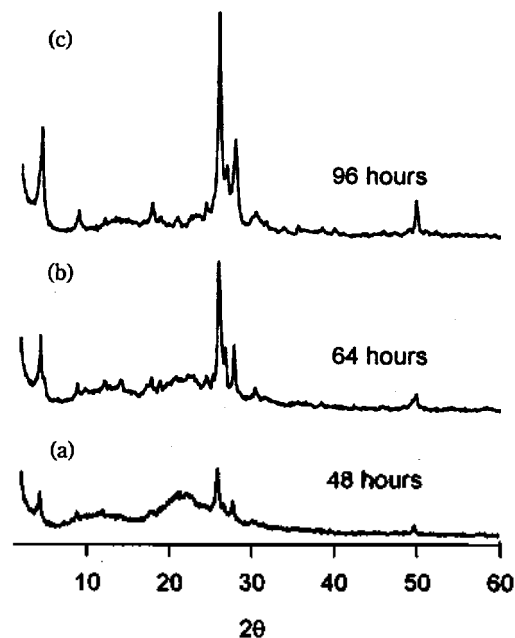


Figure 1. XRD patterns of synthetic magadiites at 150 °C according to reaction time. Reactants molar ratio: SiO₂/(NaOH+Na₂CO₃)=5, H₂O/(NaOH+Na₂CO₃)=100.

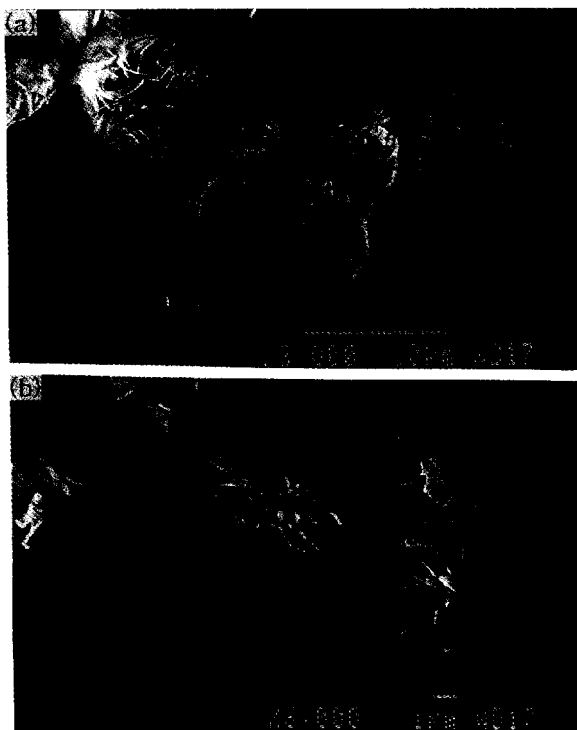


Figure 2. Scanning electron micrographs of synthetic samples at 150 °C according to reaction time. Reactants molar ratio: SiO₂/(NaOH+Na₂CO₃)=5, H₂O/(NaOH+Na₂CO₃)=100. (a) 24 hours (b) 96 hours.

by adjusting reaction time and temperature. Figure 2 shows the scanning electron micrographs of the synthetic magadiite. The morphology of magadiite doesn't change in the range

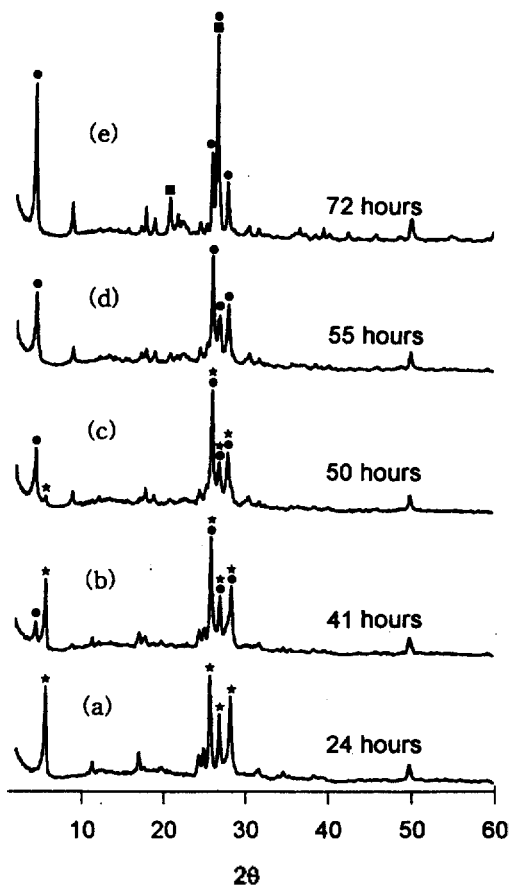


Figure 3. XRD patterns of synthetic samples at 170 °C according to reaction time. Reactants molar ratio: $\text{SiO}_2/(\text{NaOH}+\text{Na}_2\text{CO}_3)=5$, $\text{H}_2\text{O}/(\text{NaOH}+\text{Na}_2\text{CO}_3)=100$. \star : magadiite, \bullet : kenyaite, \blacksquare : quartz.

of reaction time between 24 and 72 hours. From the results of XRD and SEM, magadiite can be synthesized in a wide range of reaction time. After 96 hours of reaction, the morphology of magadiite changes from a rosettes-like shape to a broken rosettes-like shape.

Figure 3 shows XRD patterns of synthetic samples at 170 °C at the fixed reactant compositions of $\text{SiO}_2/(\text{NaOH}+\text{Na}_2\text{CO}_3)=5$ and $\text{H}_2\text{O}/(\text{NaOH}+\text{Na}_2\text{CO}_3)=100$ for the different reaction time. As reaction time increases from 24 to 72 hours, magadiite was transformed into kenyaite, and then kenyaite was transformed to quartz. Beneke and Lagaly¹⁸ suggested that at 100 °C, amorphous silica was transformed into magadiite, and then to kenyaite. Above 100 °C, the rate of kenyaite formation is much increased, and the rate of quartz formation is increased simultaneously. After 55 hours, pure-crystallized kenyaite was formed. The XRD pattern of synthetic kenyaite exhibited 001 X-ray reflections of film sample corresponding to a basal spacing of 20.3 Å. The peak positions for synthetic kenyaite agree with values reported previously^{17,18} for synthetic kenyaite. After 72 hours of reaction, however, quartz phase appears. This result indicates that it is very difficult to obtain pure kenyaite by controlling reaction time because pure kenyaite can be synthesized at short range of reaction time.

The phase transformations from magadiite to kenyaite are

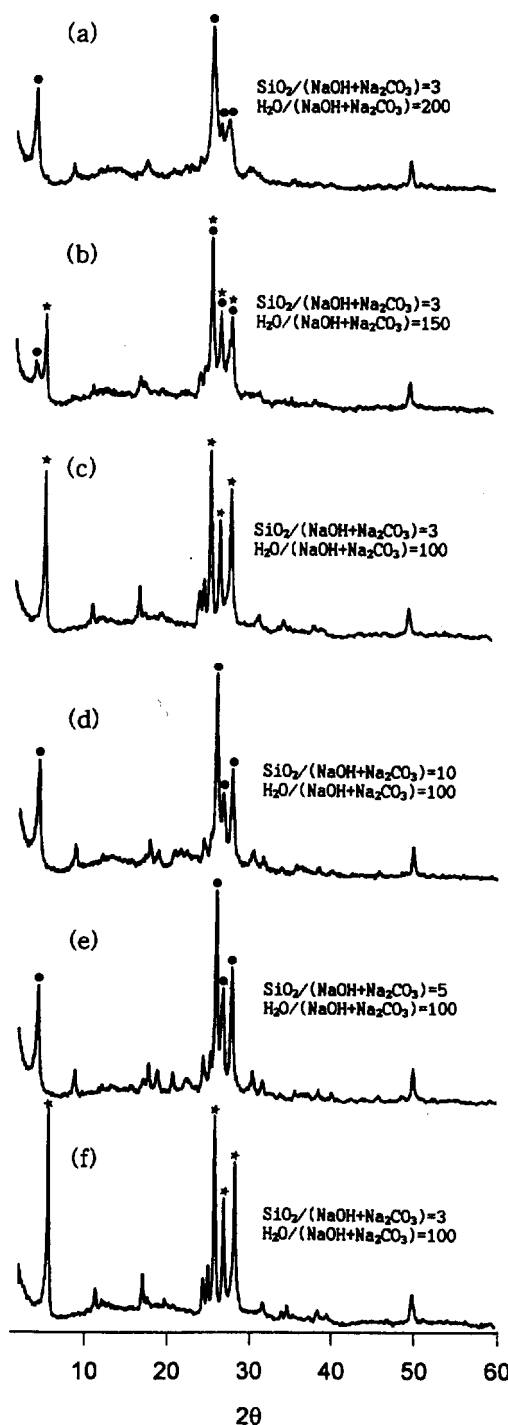


Figure 4. XRD patterns of synthetic samples at 150 °C, 72 hours (a), (b), (c) and 160 °C, 72 hours (d), (e), (f) according to reactants compositions. \star : magadiite, \bullet : kenyaite, \blacksquare : quartz.

also observed at different reaction temperatures. Figure 1(c), Figure 4(e), and Figure 3(e) show the phase transformation with reaction temperature. In spite of temperature difference of 10 °C, the phase transformation occurs abruptly. Therefore, the results suggest that temperature can be a main factor in the formation of magadiite and kenyaite. In summary, it is easy to synthesize the pure well-crystallized magadiite in the range of 150–170 °C for 18–72 hours in the reactant com-

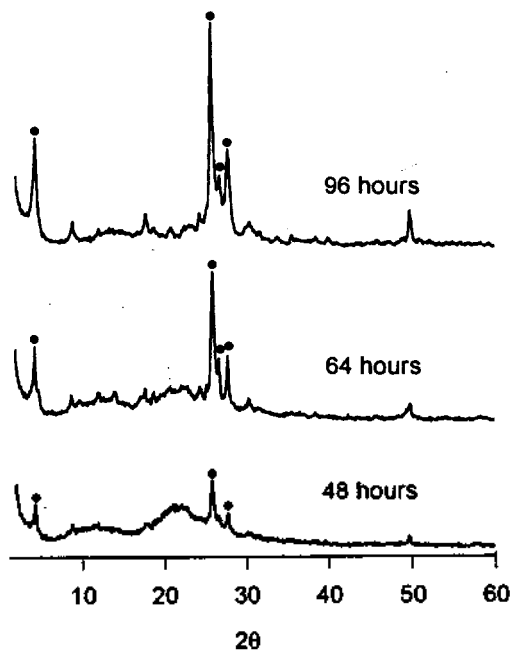


Figure 5. XRD patterns of synthetic samples at 180 °C according to reaction time. Reactants molar ratio: $\text{SiO}_2/(\text{NaOH} + \text{Na}_2\text{CO}_3) = 20$, $\text{H}_2\text{O}/(\text{NaOH} + \text{Na}_2\text{CO}_3) = 200$.

positions of $\text{SiO}_2/(\text{NaOH} + \text{Na}_2\text{CO}_3) = 5$ and $\text{H}_2\text{O}/(\text{NaOH} + \text{Na}_2\text{CO}_3) = 100$. However, it is difficult to obtain the pure well-crystallized kenyaite. Not only the life time of kenyaite was very short under this composition but also quartz was formed simultaneously. Preparation of quartz-free kenyaite requires special compositions of reactants.

Figure 4 shows XRD patterns of synthetic samples obtained at the reaction conditions of 150 °C-72 hours and 160 °C-72 hours, with different reactant compositions. As the molar ratio of $\text{H}_2\text{O}/(\text{NaOH} + \text{Na}_2\text{CO}_3)$ increases from 100 to 200, magadiite phase is transformed to kenyaite phase. The higher molar ratio of $\text{H}_2\text{O}/\text{Na}$ tends to promote the formation of kenyaite. In the reactant compositions of $\text{SiO}_2/(\text{NaOH} + \text{Na}_2\text{CO}_3) = 5-10$ and $\text{H}_2\text{O}/(\text{NaOH} + \text{Na}_2\text{CO}_3) = 100$, well-crystalline kenyaite was easily obtained at 160 °C. From these results, the amount of silica appears to influence the types of the silicate formed. The higher molar ratio of Si/Na accelerate the formation of kenyaite. Silica is first dissolved in alkali solution at elevated temperature, and then the nucleation of layered silicate occurs gradually. Therefore, the ratio of Si/Na dissolved in the solution is a very important factor in the formation of layered silicate. Also, the higher content of silica in the composition of starting materials may cause a large ratio of Si/Na dissolved in the solution. These conditions could accelerate the nucleation of kenyaite which has a large ratio of Si/Na. Whereas, if the ratio of Si/Na dissolved in the solution is large enough, kenyaite is capable of forming directly from amorphous silica without the formation of magadiite as an intermediate.

Figure 5 shows XRD patterns of synthetic samples obtained at 180 °C in the higher molar ratio of Si/Na [$\text{SiO}_2/(\text{NaOH} + \text{Na}_2\text{CO}_3) = 20$ and $\text{H}_2\text{O}/(\text{NaOH} + \text{Na}_2\text{CO}_3) = 200$] with reaction time. Kenyaite can be directly synthesized from



Figure 6. Scanning electron micrographs of synthetic kenyaite. (a) 150 °C, 72 hours, $\text{SiO}_2/(\text{NaOH} + \text{Na}_2\text{CO}_3) = 3$, $\text{H}_2\text{O}/(\text{NaOH} + \text{Na}_2\text{CO}_3) = 200$. (b) 160 °C, 72 hours, $\text{SiO}_2/(\text{NaOH} + \text{Na}_2\text{CO}_3) = 3$, $\text{H}_2\text{O}/(\text{NaOH} + \text{Na}_2\text{CO}_3) = 200$. (c) 160 °C, 72 hours, $\text{SiO}_2/(\text{NaOH} + \text{Na}_2\text{CO}_3) = 5$, $\text{H}_2\text{O}/(\text{NaOH} + \text{Na}_2\text{CO}_3) = 100$.

amorphous silica, and magadiite was not observed as an intermediate. The higher molar ratio of Si/Na and the direct synthesis without an intermediate could take advantage of obtaining pure kenyaite in the industrial point of view.

Figure 6 shows diverse types of scanning electron micrographs of kenyaite. The shape of kenyaite is very similar to that of magadiite. There are three types of kenyaite which are spherical aggregates of the plates (Figure 6 (a)), loosely packed plates (Figure 6 (b)), and open aggregates of plates (Figure 6 (c)). As reaction time increases, the morphology is transformed from spherical aggregates of the plates to loosely packed plates. More extension of reaction time results in the formation of broken plates and quartz.

The chemical compositions of Na-magadiite and Na-kenyaite were obtained by TGA and EDS analyses for silica and sodium. TGA and EDS data obtained from Na-magadiite and

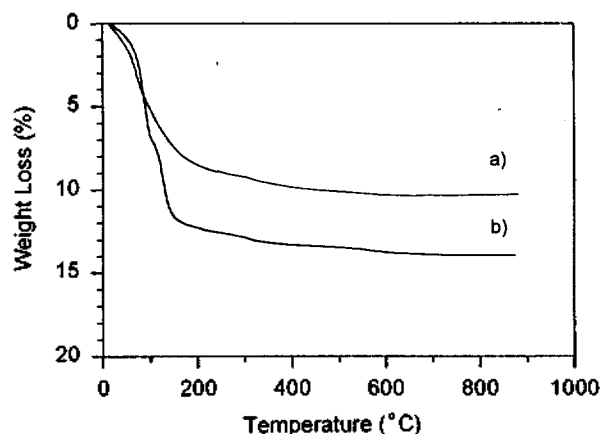


Figure 7. Thermogravimetric analyses of (a) Na-magadiite. (b) Na-kenyaite.

Table 2. Compositions of Synthetic Magadiite and Kenyaite

Sample	Weight percent			Atomic ratios		
	Na ₂ O	SiO ₂	H ₂ O	Na	Si	H ₂ O
Synthetic Na-magadiite	6.4	83.9	9.6	2.06	14	5.35
Synthetic Na-kenyaite	4.4	82.7	12.9	2.06	20	10.43
Synthetic Na-magadiite (Grace <i>et al.</i> ²¹)	6.3	87.0	8.1	1.96	14	4.35

Na-kenyaite are illustrated in Figure 7 and Table 2. The weight losses from Na-magadiite and Na-kenyaite are coincident with an associated endotherm on a DTA scan from dehydration. The weight losses below 300 °C are attributed to dehydration, while those above 300 °C are presumably from the water losses *via* condensation of the silanol groups to form siloxane bonds.²⁰ The water loss, sodium, and silica content give an approximate unit cell composition of Na_{2.06}-Si₁₄O_{29.03}·5.35 H₂O, which compares well with that of Grace *et al.*²¹ (The degree of hydration can be different due to sample treatments.) The unit cell composition of Na-kenyaite deduced from TGA and the analyses of sodium and silica is Na_{2.06}Si₂₀O_{41.03}·10.43 H₂O, which compares favorably with approximate composition of Na₂Si₂₀O₄₁·10 H₂O supported by the early work of Beneke and Lagaly.¹⁰

Conclusions

In the suspension of SiO₂, NaOH and Na₂CO₃, the effects of the compositions of reactants, reaction time, and temperature on the formation of Na-magadiite and Na-kenyaite were investigated. Magadiite was easily synthesized after a short reaction time of 24 hours at various compositions of reactants and reaction temperatures. In the molar ratios of SiO₂/(NaOH+Na₂CO₃)=5 and H₂O/(NaOH+Na₂CO₃)=100, kenyaite was formed with magadiite or quartz simultaneously

in reaction time of 48-96 hours at 160 °C or 170 °C. In the molar ratios of SiO₂/(NaOH+Na₂CO₃)=5-10, H₂O/(NaOH+Na₂CO₃)=100, and SiO₂/(NaOH+Na₂CO₃)=3, H₂O/(NaOH+Na₂CO₃)=150-200, well-crystallized kenyaite were purely synthesized. In the higher molar ratio of Si/Na [SiO₂/(NaOH+Na₂CO₃)=20 and H₂O/(NaOH+Na₂CO₃)=200], kenyaite can be directly synthesized from amorphous silica without the formation of magadiite as an intermediate. The higher content of silica in the composition of starting materials may cause a large ratio of Si/Na dissolved in the solution. These conditions could accelerate the nucleation of kenyaite which has a large ratio of Si/Na. These results indicate that the composition of reactant is one of important factors in the formation of kenyaite. In spite of the similarity of XRD pattern, the morphology of kenyaite represents diverse shapes.

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