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HYDROTHERMAL SYNTHESIS OF SMECTITE FROM DICKITE

KYOUNG-WON RYU[1], YOUNG-NAM JANG[2], SOO-CHUN CHAE[2], IN-KOOK BAE[2] AND SANG-HOON CHOI[1]

[1] Department of Earth and Environmental Sciences, Chungbuk University, Cheongju 361-763, Korea
[2] Korea Institute of Geoscience and Mineral Resources, Minerals and Materials Processing Division, Daejeon 305-350, Korea

Abstract—Dioctahedral smectite was prepared hydrothermally from dickite [$Al_2Si_2O_5(OH)_4$] as a starting material by autoclaving in a closed stainless steel vessel with variable temperature, pressure, time and pH conditions. Highly crystalline smectite can be obtained at 290ºC under a pressure of 69 bar for 48 h. The pH of the solution was an important factor and should be maintained at 10 to 11 for the successful formation of smectite. Characterization by X-ray powder diffraction, scanning electron microscopy, infrared spectroscopy, thermogravimetric analysis, differential thermal analysis and the Greene-Kelly test showed that the smectite synthesized was Na-beidellite, mostly because of the heat treatment of the starting material and the stoichiometric batch composition.

Key Words—Beidellite, Greene-Kelly Test, Hydrothermal Synthesis, Smectite.

INTRODUCTION

Smectite is one of the most important groups of phyllosilicate minerals and can be used for a variety of industrial purposes because of its physicochemical properties such as swelling in water, the formation of gel and colloid, and its ability to incorporate organic and inorganic complexes. It has a variety of applications in ceramics, nanocomposite materials, oil drilling, waste isolation, and in the paper industry.

To avoid the problems inherent in the use of natural smectite, the hydrothermal synthesis of pure smectite has been studied (Tsunashima *et al.*, 1975; Goh and Huang, 1986; Torii and Iwasaki 1986, 1987; Plee *et al.*, 1987; Kloprogge *et al.*, 1990; Kawano and Tomita, 1995; Vogels *et al.*, 1997; Tomita and Kawano, 2004).

Trioctahedral saponite and hectorite are already produced at the industrial scale but there has been little research into the synthesis of dioctahedral smectites such as beidellite and montmorillonite (Torii, 1985; Sanji *et al.*, 1988; Iwasaki, 1989; Kloprogge *et al.*, 1999). The starting materials used for hydrothermal synthesis include gel, glass and other aluminosilicate minerals, and high-purity chemical reagents. According to Kloprogge (1993), Na-beidellite cannot be synthesized from X-ray amorphous materials or chemicals below a temperature of 300ºC and 1 kbar of pressure. As dioctahedral smectite is similar to dickite in terms of its crystal-chemical characteristics, in the present study the experimental formation of smectite from dickite at relatively low-temperature hydrothermal conditions has been investigated.

* E-mail address of corresponding author:
crystal@rock25t.kigam.re.kr
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EXPERIMENTAL

The starting material for the synthesis was dickite from Sungsan-mine, Hae-Nam, Korea. All the chemicals used are of reagent grade, *i.e.* Na_2CO_3 (Tedia Company, Inc.), SiO_2 (Merck, Kieselgel 60) and NaOH (DC chemical Co.).

The chemical composition of the starting material was determined by X-ray fluorescence (XRF) as shown in Table 1. From X-ray diffraction (XRD) analysis, the sample was found to consist mainly of dickite, including a small amount of quartz (Figure 1). Dickite was crushed in a Jet-mill to grains that would pass through a <320 mesh sieve, and used as the starting material without further separation processes. The experiments were carried out in cold-seal type stainless steel vessel (with a capacity of ~1 L).

The agitation speed was fixed at 180 rpm. To regulate temperature within ±1ºC, a Rex-P100 automatic thermo-controller was used and two CA-type thermocouples were installed inside the autoclave and near the heater. Approximately 80% of the vessel was filled with the solution.

The product was analyzed by XRD (graphite-monochromated CuKα radiation on an X'pert MPD X-ray diffractometer, Phillips Co.). The d_{001} spacing of the synthesized smectite was measured for a randomly oriented sample. The location and magnitude of layer charge were studied by the Greene-Kelly test and glycolation. The morphology of the synthetic smectites was observed using scanning electron microscopy (SEM: LEO 1455VP and JSM-5410).

Infrared (IR) absorption spectra were obtained on powdered samples in KBr tablets using a Travel-IR spectroscope (SensIR Technologies), and thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were performed using the DTA-50 and TGA-50 devices of TA 50WSI (Shimadzu) at a heating rate of 10ºC/min for the synthesized smectite.

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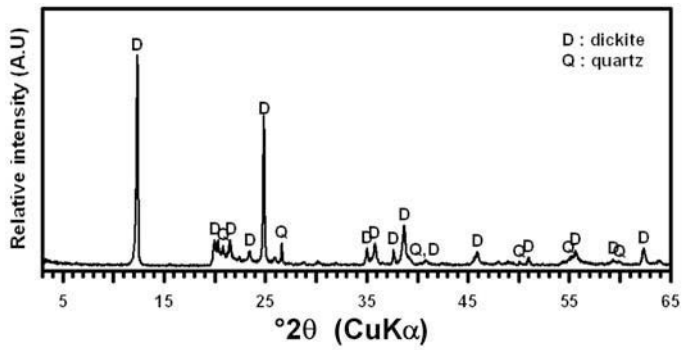


Figure 1. XRD patterns of dickite.

RESULTS AND DISCUSSION

Effect of activation

A possible reaction mechanism for the transformation of the dickite to smectite is as follows:

$$2.35\ Al_2Si_2O_7 + 0.35\ Na_2O + 2.6\ SiO_2 + nH_2O = Na_{0.7}Al_{4.7}Si_{7.3}O_{20}(OH)_4 \cdot nH_2O \quad (1)$$

Additional Na_2O and SiO_2 are needed for the forward reaction so Na_2CO_3 (0.35 moles) and X-ray amorphous SiO_2 (2.6 moles) were added for the stoichiometry based on Na-0.7 beidellite.

As heating dickite is expected to facilitate its transformation to smectite, 20 g of the dickite were heated at 800ºC for 4 h with 1.2 g of Na_2CO_3. Analysis by XRD showed that dickite became metadickite after the heat treatment (Figure 2a). The chemical composition of the dehydroxylated dickite is shown in Table 1.

To detect the effect of activation, starting materials were prepared based on equation 1. The mixture of dehydroxylated dickite, silica gel and distilled water was kept for 1 day under atmospheric conditions to stabilize the alkalinity of the solution. The experimental conditions: temperature, pressure, reaction time and the alkalinity were fixed at 290ºC, 69 bar, 48 h and pH 10.0, respectively.

The heat treatment affected the result of the synthesis experiment. The XRD analysis of the synthetic products showed that smectite was formed. The activated sample produced is more crystalline than the precursor samples and chemical reagents (Figure 2). Tomita *et al*. (1994) reported that Mg ions play an important role in the formation of octahedral sheets but in this experiment the addition of Mg did not have a detectable effect on the formation of smectite.

That cavities and so called 'curled habits' in the synthetic products were observed, using SEM, between the dense and thick grains (Figure 3).

Effects of temperature, time and pressure

The results of hydrothermal synthesis at temperatures of 250, 270 and 290ºC are shown in Figure 4. The pH and the reaction time were fixed at 10 and 48 h,

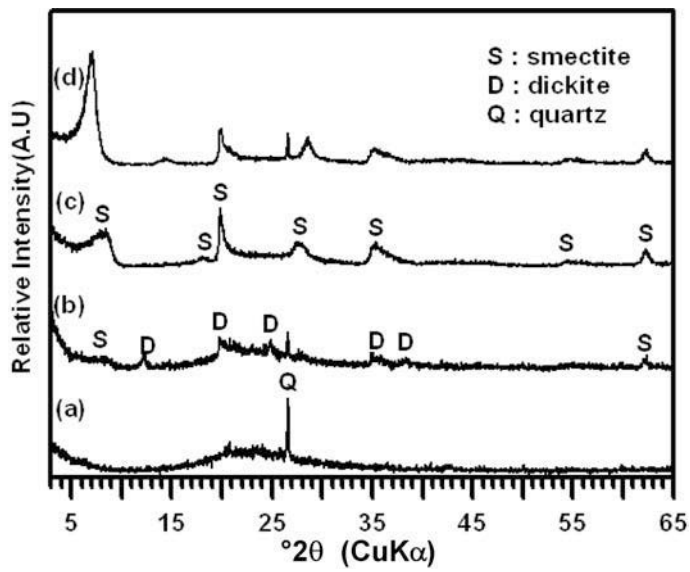


Figure 2. XRD patterns of activated dickite and smectite: (a) activated dickite; (b) synthetic product from inactivated dickite; (c) smectite from chemical reagents; and (d) smectite from activated sample.

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Table 1. Chemical compositions (wt.%) of natural (1) and activated (2) dickite.

	SiO_2	Al_2O_3	Fe_2O_3	MgO	K_2O	Na_2O	MnO	TiO_2	P_2O_5	*LOI	Total
(1)	49.46	37.53	0.52	0.02	0.20	0.1	0.02	0.08	0.16	12.25	100.24
(2)	49.75	40.60	0.03	0.01	0.01	7.89	0.01	0.09	0.17	0.48	99.04

	SiO_2	Al_2O_3	Fe_2O_3	MgO	K_2O	Na_2O	MnO	TiO_2	P_2O_5	*LOI	Total
(1)	49.46	37.53	0.52	0.02	0.20	0.1	0.02	0.08	0.16	12.25	100.24
(2)	49.75	40.60	0.03	0.01	0.01	7.89	0.01	0.09	0.17	0.48	99.04

* LOI: loss on ignition

respectively. At 250ºC, under a pressure of ~39–69 bar, the reaction was not feasible (Figure 4a). At 270ºC, under a pressure of 49 bar, weak 001 and 004 peaks of smectite appeared (Figure 4b). At 290ºC, under a pressure of 59 bar, good crystals of smectite were formed (Figure 4c). These results indicate that the reaction temperature is a more significant factor in the formation of Na-type smectite than reaction pressure.

The reaction time was varied from 36 to 96 h at a fixed temperature of 290ºC. Highly crystalline smectite had been synthesized after 48 h, and longer exposure times did not improve the crystallinity significantly after that time.

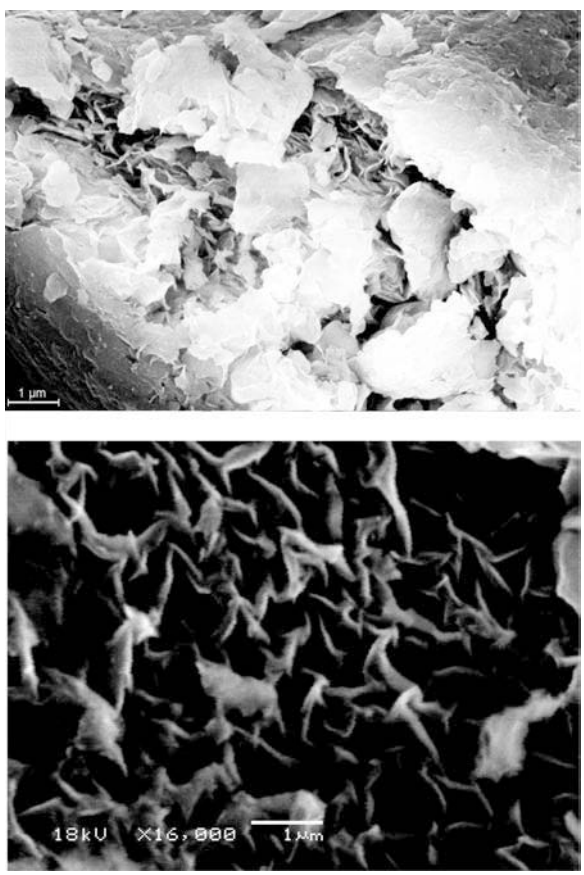


Figure 3. SEM images of smectite synthesized at 290ºC.

In the preparation of kaolinite from chemical reagents, the formation of an octahedral sheet containing Al is critical (De Kimpe, 1975). In the synthesis of smectite, the formation of the octahedral sheet is also an important feature (Nemecz, 1981). Hydrothermal synthesis of beidellite from aluminosilicate gel has been carried out and it was reported that the most crystalline beidellite was obtained at a temperature of 350ºC, pressure of 1 kbar and a reaction period of 5 days (Kloprogge *et al*., 1990).

In our experiment, smectite was formed easily at a relatively lower temperature and pressure, from dehydroxylated dickite. This may be due to the octahedral sheet in the dickite crystal structure. The results from this study were comparable to other studies, *e.g.* Plee *et al.* (1987), Schutz *et al.* (1987), Eberl and Hower (1977) and Kloprogge *et al.* (1990).

Effect of pH

Smectite can be formed under acidic, neutral and basic conditions (Kloprogge *et al.*, 1999), *e.g.* beidellite synthesized from zeolite shows good crystallinity at pH 4 (Komarneni and Breval, 1985), and saponite can be synthesized from talc at pH 10 (Bae *et al.*, 2003). The formation and crystallinity of Na-beidellite depend on the pH of the solution. In conditions of weak alkalinity, the formation of the tetrahedral AlO_4^- ion is favored and the formation of beidellite was promoted (Frank-Kamenetskii, 1973a, 1973b). Beidellite of good crystallinity was formed in a solution with an initial pH of 10 (Kloprogge *et al.*, 1990). This study also confirmed that the initial pH of solution is an important factor in the formation of beidellite. At pH 10, smectite was well crystallized (Figure 5b). However, at pH 9, the 001 reflection appeared rather broad and weak, some of the dickite was re-crystallized, and an unknown phase was also formed (Figure 5c). At pH 7 and 12, the beidellite formed was less crystalline and at pH 12 the 100 reflection became strongly abnormal (Figure 5a,d). After the reaction, the pH of the solution decreased to ~6–7, presumably due to the release of H^+ ions during the reaction.

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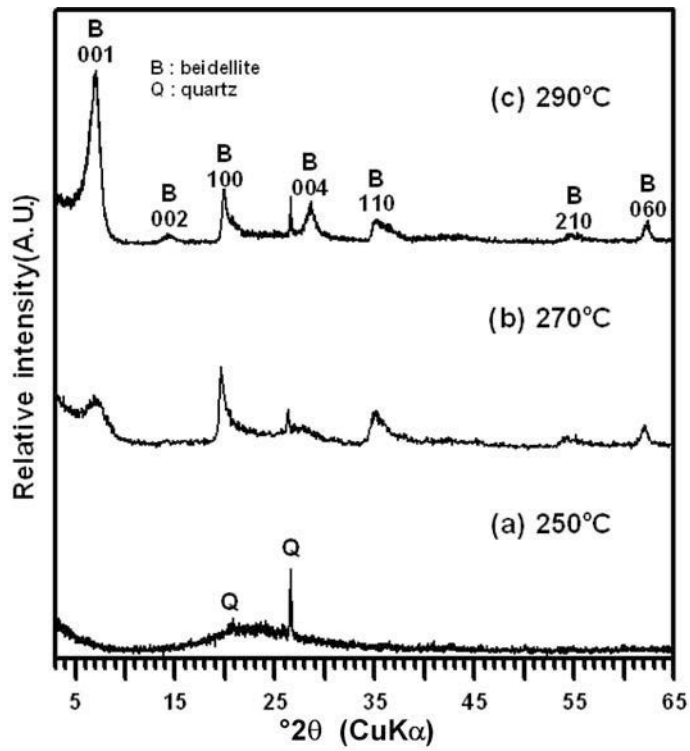


Figure 4. XRD patterns of synthetic products at different temperatures.

PROPERTIES OF THE SYNTHETIC SMECTITE

The di- or trioctahedral nature of smectite was determined by the *d* value of the 060 reflection of an unoriented sample. Generally, a d_{060} value of 1.53–1.55 Å indicates a trioctahedral smectite, whereas a spacing of 1.48–1.50 Å indicates a dioctahedral smectite (Brown and Brindley, 1980). The smectite synthesized in this study clearly showed the dioctahedral nature, *i.e.* d_{060} value of 1.49 Å and the d_{001} value of 12.2 Å (Figure 4).

The magnitude of layer charge of smectite is determined by ethylene glycol treatment and the Greene-Kelly Li test, used to distinguish beidellite

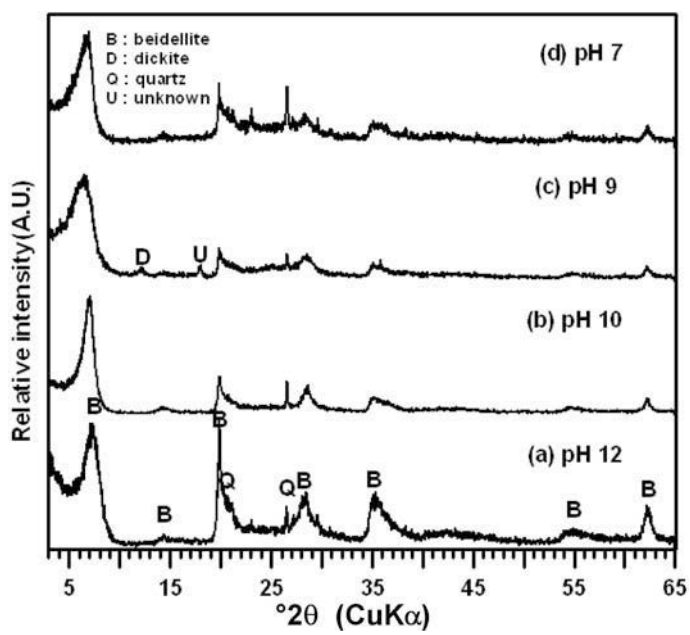


Figure 5. XRD patterns of smectite synthesized at different pH values.

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from montmorillonite (Schultz, 1969). From the sample synthesized in this study, an oriented slide was prepared. The results of XRD showed a d_{001} value of 12.2 Å, which increased to 16.4 Å after glycolation, corresponding to the value of 16.7 Å for the natural beidellite (MacEwan and Wilson, 1980).

After saturation with Li and heating at 300ºC for 12 h, the sample showed a d_{001} basal spacing of 10.9 Å, but re-expanded to 17.4 Å after glycolation (Figure 6). This indicated that the phase is beidellite, which has a negative layer charge because of tetrahedral substitution of Si^{4+} by Al^{3+}. This has no affect on the basal spacing. There is octahedral isomorphous substitution of montmorillonite, resulting in the migration of Li^{+} from the interlayer position to vacant octahedral sites, with a consequent neutralization of the negative charge (Kloprogge *et al.*, 1990).

The IR spectrum of the 2-day reaction product exhibited the following absorption bands: Al–O–H stretching vibrations at 3672, 3650 and 3620 cm^{-1}; a H–O–H stretching vibration at 3432 cm^{-1}; a Si–O–Si stretching vibration at 1030 cm^{-1} and $Si–O–Al^{IV}$ bending vibrations at 542 cm^{-1} and 480 cm^{-1}. Al–O–H bending vibrations at 818 and 770 cm^{-1} were observed in particular in pure beidellite (corresponding to the muscovite vibration band: Nadeau *et al.*, 1985). All of these are characteristic absorptions of dioctahedral smectite (Stubican and Roy, 1961; Farmer, 1974). A synthetic beidellite, produced from aluminosilicate gel at 350ºC, displayed a similar spectrum (Kloprogge *et al.*, 1990). Montmorillonite has an Al–O–H bending vibration band at 915 cm^{-1}, whereas in beidellite this band is at 930 cm^{-1} (Figure 7).

The results of DTA and TGA of synthetic Na-beidellite are shown in Figure 8. The principal features of the Na-beidellite (TGA, DTA) curve are well resolved. During heating, 11 wt.% of adsorbed water was lost at 147ºC. The DTA curve shows a low-temperature endothermic peak at 116.5ºC and two dehydroxylation endothermic peaks at 482ºC and 685ºC. In the literature, some beidellites have double dehydroxylation peaks because of more hydroxyl content than is ideal. Alternatively, the double dehydroxylation may not be equivalent to the OH groups in the Al octahedral sheet and in the Si tetrahedral sheet substituted by Al (Kloprogge *et al.*, 1990). In the range 147–733ºC, an additional 5 wt.% loss can be ascribed to the loss of OH groups. Hence, Na-beidellite synthesized in this study contains ~16 wt.% of water.

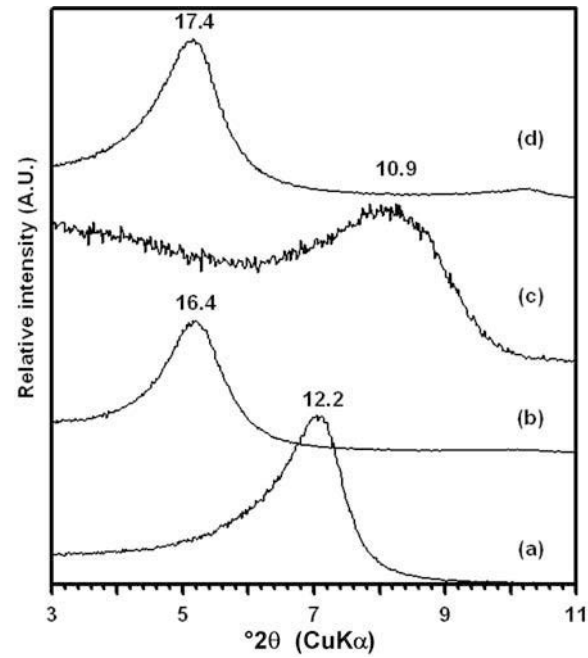


Figure 6. Variation of 001 basal spacing of synthetic Na-beidellite: (a) oriented; (b) after treatment with ethylene glycol; (c) heat treated at 300ºC after Li saturation; (d) after the Greene-Kelly test method.

The two peaks at 993ºC and 1061ºC in the DTA curve are probably due to the breakdown of anhydrous Na-beidellite to a non-crystalline phase (Grim and Bradley, 1940; Bradley and Grim, 1951; Greene-Kelly, 1957).

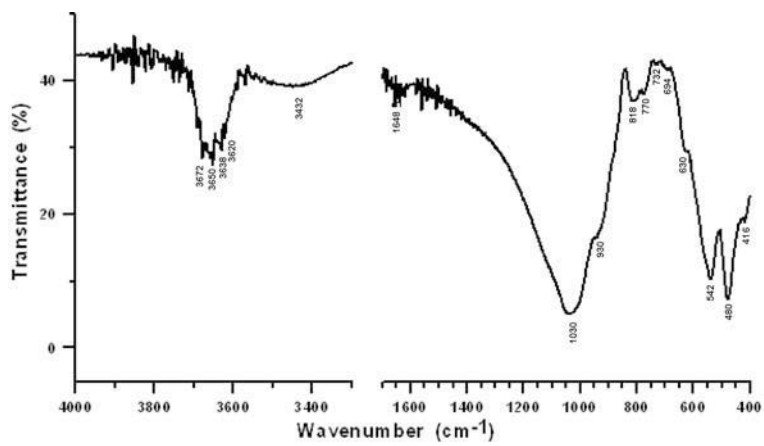


Figure 7. IR spectrum of beidellite synthesized at 290ºC.

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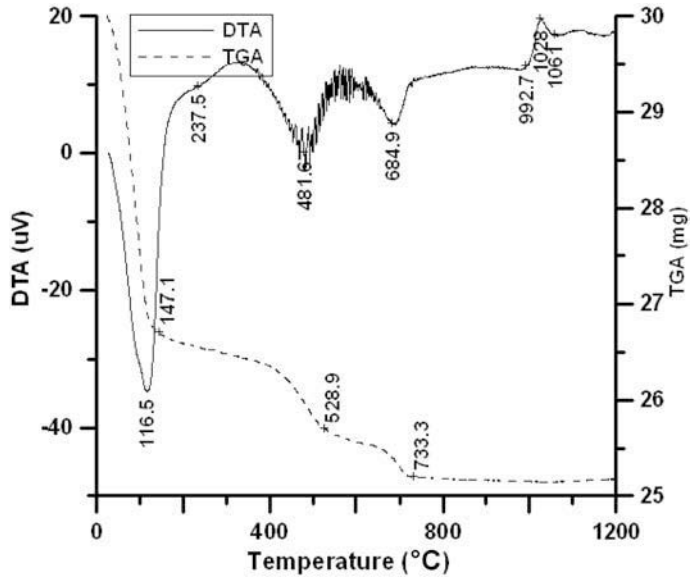


Figure 8. Thermogravimetric analysis and differential thermal analysis of beidellite synthesized at 290ºC.

CONCLUSIONS

Dioctahedral smectite was synthesized successfully with a stoichiometric composition of $Na_{0.7}Al_{4.7}Si_{7.3}O_{20}(OH)_4 \cdot nH_2O$. The following can be concluded. (1) The crystallization of smectite took place in alkaline conditions and by heating the starting material at 800ºC for 4 h. (2) Smectite with good crystallinity was synthesized hydrothermally at 290ºC for 48 h under a pressure of 69 bar. The batch composition was found to be stoichiometric. (3) The reaction temperature and time were directly proportional to the crystallinity of the synthetic phase. (4) As a result of ethylene-glycol treatment and the Greene-Kelly test, the phase synthesized was identified as a 12 Å Na-beidellite. A SEM study reveals that the smectite showed typical scalloped features. (5) The IR spectroscopy showed that the synthetic product was pure Na-beidellite. The absorption band at ~3672–3620 cm^{-1} due to an OH-stretching vibration and the broad bands at 3432 cm^{-1} and 1648 cm^{-1} are attributed to interlayer water and sorbed water, respectively. (6) Synthetic Na-beidellite contains ~16 wt.% water. Double hydroxylation peaks were observed at 482ºC and 685ºC. At 1028ºC the remaining solid recrystallized to other phases.

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