Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of Solid State Chemistry 177 (2004) 849–855

JOURNAL OF SOLID STATE CHEMISTRY

http://elsevier.com/locate/jssc

Hydrothermal synthesis and thermodynamic analysis of dawsonite-type compounds

Xiangfeng Zhang, Zhaoyin Wen,* Zhonghua Gu, Xiaohe Xu, and Zuxiang Lin

Shanghai Institute of Ceramics, Chinese Academy of Sciences, 1295 Ding Xi Road, Shanghai 200050, People's Republic of China

Received 9 September 2003; received in revised form 16 September 2003; accepted 23 September 2003

Abstract

Dawsonite-type compounds of formula $M\mathrm{Al(OH)_2CO_3}$ (M = Na,K,NH_4) were hydrothermally synthesized. The influences of the composition of starting materials, reaction temperature, acidity of the reaction medium on the formation, morphology and particle size of $M\mathrm{Al(OH)_2CO_3}$ powders were systematically investigated. The experiment results show that increase in the amount of $M\mathrm{HCO_3}$ favors the formation of $M\mathrm{Al(OH)_2CO_3}$ phase with more slender particle morphology. The higher the reaction temperature, the grosser the particle is. It was also demonstrated that the particle size of the $M\mathrm{Al(OH)_2CO_3}$ phase are most uniform when the pH value of reaction system is 10.3 for sodium dawsonite and potassium dawsonite, but it is 9.79 for that of ammonium dawsonite. The thermodynamics of the formation of dawsonite-type compounds have also been analyzed in details.

Keywords: Dawsonite; Hydrothermal syntheses; Thermodynamics

1. Introduction

Dawsonite is a mineral of formula $M\mathrm{Al(OH)_2CO_3}$ (M = Na,K,NH_4) named after the Canadian geologist, Dawson. The mineral was first obtained synthetically by Bader [1] and later by Besson et al. [2]. Potassium and other dawsonites have also been synthesized afterwards [3]. Dawsonite-type compounds include three kinds of compound: i.e., $\mathrm{NaAl(OH)_2CO_3}$, $K\mathrm{Al(OH)_2CO_3}$ and $\mathrm{NH_4Al(OH)_2CO_3}$, which are abbreviated as Na-D,K-D and NH_4-D respectively after sodium dawsonite, potassium dawsonite and ammonium dawsonite. All dawsonites are double carbonato aluminum and a monovalent cation [4] and exhibit a well-known behavior of antacids and fire retardants [5]. In addition, they are often employed in the preparation of new ceramic materials made of alumina because dawsonite-type compounds consist of aluminum element and they produce CO_2 and H_2O after thermal decomposition. For example, Mary Giannos et al. [6] prepared gamma-alumina with a surface area as high as 145 m^2/g by calcinning ammonium dawsonite at 1000°C. Ji-Guang Li et al. [7] synthesized Mg–Al spinel powder via precipitation using ammonium dawsonite hydrate as precursor. Homogeneous, spherical α-alumina particles with 0.2 μm diameter were obtained by firing the NH_4-D with a crystallite size of 5 nm in Koichi Hayashi's research group [8]. Beta-alumina powder was obtained by calcinning the precursors composed of dawsonite and ammonium dawsonite at lower temperature previously in our laboratory [9].

Up to now, there are some literatures on the syntheses of dawsonite compounds. For example, in Ref. [4] NH_4-D as a new aluminum compound was first synthesized by adding an ammonium aluminum sulfate (AA) solution to an ammonium hydrogen carbonate (AHC) solution in 1975. It was founded that the lower concentration of AA, higher reaction temperature and larger concentration of AHC were benefit to the formation of NH_4-D. In 1990 Hayashi et al. [8] discussed the effects of pH of the AHC aqueous solution and reaction temperature on the formation of NH_4-D. It was shown that NH_4^+, $\mathrm{AlO(OH)_2^-}$ and HCO_3^- species in AHC and AA aqueous were necessary to form NH_4-D by the master variable technique of ionic equilibrium. About the structure of dawsonite, Iga and Kato et al. [10] found that the crystal structure of NH_4-D which is composed of chain structure with Al–O(OH) octahedral is base-centered.

---

*Corresponding author. Fax: +86-21-62513903.
E-mail address: zywen@mail.sic.ac.cn (Z. Wen).

0022-4596/$ - see front matter © 2003 Elsevier Inc. All rights reserved.
doi:10.1016/j.jssc.2003.09.019

Although dawsonite-type compounds are very promising in many fields, there are still no detailed reports on their syntheses law so far and there is little work on its thermodynamic analysis either. In order to contribute new date to the knowledge of this type of compounds, three dawsonite compounds, i.e., Na-D, K-D, NH_4-D, have been synthesized by using hydrothermal method and thermodynamic analysis has also been carried out in this work.

2. Experimental

The hydrothermal synthesis of dawsonite-type compounds was carried out in a stainless steel autoclave with a Teflon liner under autogenous pressure. The $Al(OH)_3$ suspension freshly precipitated by the addition of $AlCl_3$ solution (2 mol/L) to $NH_3 \cdot H_2O$ solution (25%) was used as the aluminum source for the synthesis of dawsonites. The typical synthesis procedures are described in details as follows: first, a given amount of $Al(OH)_3$ suspension was added to the supersaturated MHCO$_3$ solution in an autoclave (ca. 45 cm^3 in capacity), stirred vigorously when a 10 M solution of MOH was added slowly until a certain pH obtained, then the autoclave was sealed and kept at 80–180°C for 2–72 h. Finally, the product was washed to remove excess M^+ ions with distilled water and ethanol and dried at 60°C.

The X-ray powder diffraction patterns were acquired from a Rigaku D/MAX-III A powder diffractometer with nickel-filtered Cu$K\alpha$ ($\lambda = 1.5418$ Å) source. The microstructure of potassium dawsonite was obtained with a JEM-2010 transmission electron micrograph.

3. Results and discussion

3.1. Effects of hydrothermal conditions on the synthesis of dawsonite-type compounds

3.1.1. Crystallization temperature

The effect of crystallization temperature on the hydrothermal synthesis of dawsonite-type compounds was drawn according to the phase analysis of the products obtained at different temperatures ranging from 80°C to 180°C at fixed pH, $KHCO_3$/Al and reaction time of 9.5,16,and 24 h, respectively. The X-ray powder diffraction patterns of these products are shown in Fig. 1 ([4] and JCPDS Card No. 21-979). It can be found from Fig. 1 that the reactants transformed completely to potassium dawsonite at 120°C. However, small amount of $Al(OH)_3$ was remained in the products at a lower temperature, e.g., 80°C. The XRD patterns also indicated that the crystallinity of $KAl(OH)_2CO_3$ improved when reaction temperature increased. Fig. 2 shows the TEM image of products obtained at different temperatures. It can be observed that the particles of powder products are dispersive with needle like morphology. Differences in particle size are shown in the microstructure photographs. It can be found that increase in reaction temperature leads to a bigger particle size.

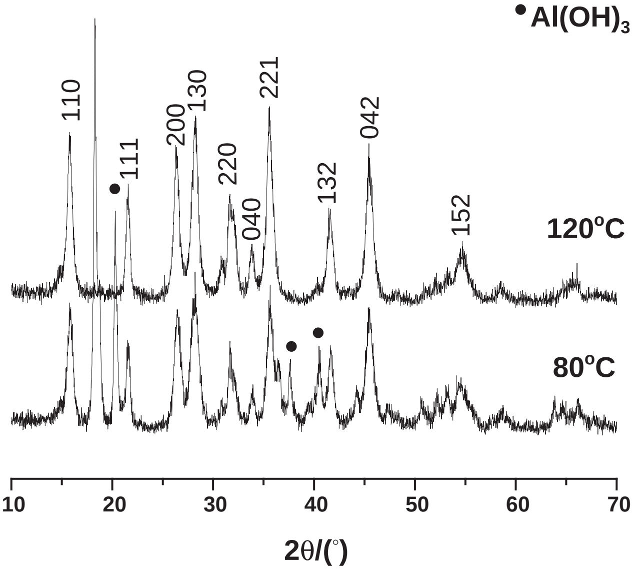

Fig. 1. XRD spectra of the K-D powders synthesized at various temperatures

It is well known that the growth and recrystallization speed of $KAl(OH)_2CO_3$ particles in hydrothermal system can be enhanced when the reaction temperature increase. However, immoderately high temperature results in overgrown particles. Consequently, it can be drawn out on the basis of XRD and TEM results that the most suitable temperature for $KAl(OH)_2CO_3$ synthesis is 120°C.

3.1.2. MHCO$_3$/Al ratio

In order to investigate the influence of the molar ratio of MHCO$_3$/Al on the reaction processes and formation mechanisms of dawsonite-type compounds, we selected a hydrothermal reaction system for $NH_4Al(OH)_2CO_3$ with the fixed crystallization temperature, pH, and the time of 120°C, 9.5 and 24 h, respectively.

The XRD diffraction patterns for the $NH_4Al(OH)_2CO_3$ samples obtained at different NH_4HCO_3/Al ratios were shown in Fig. 3 (JCPDS Card No. 76-1923). It can be seen that pure $NH_4Al(OH)_2CO_3$ was obtained when the ratio of NH_4HCO_3/Al is higher than 16, while mixture of diaspore and $NH_4Al(OH)_2CO_3$ was obtained when the ratio is lower than 8, which indicates that superfluous MHCO$_3$ is requisite to the formation of single dawsonite phase. The reason for this result will be explained in this paper

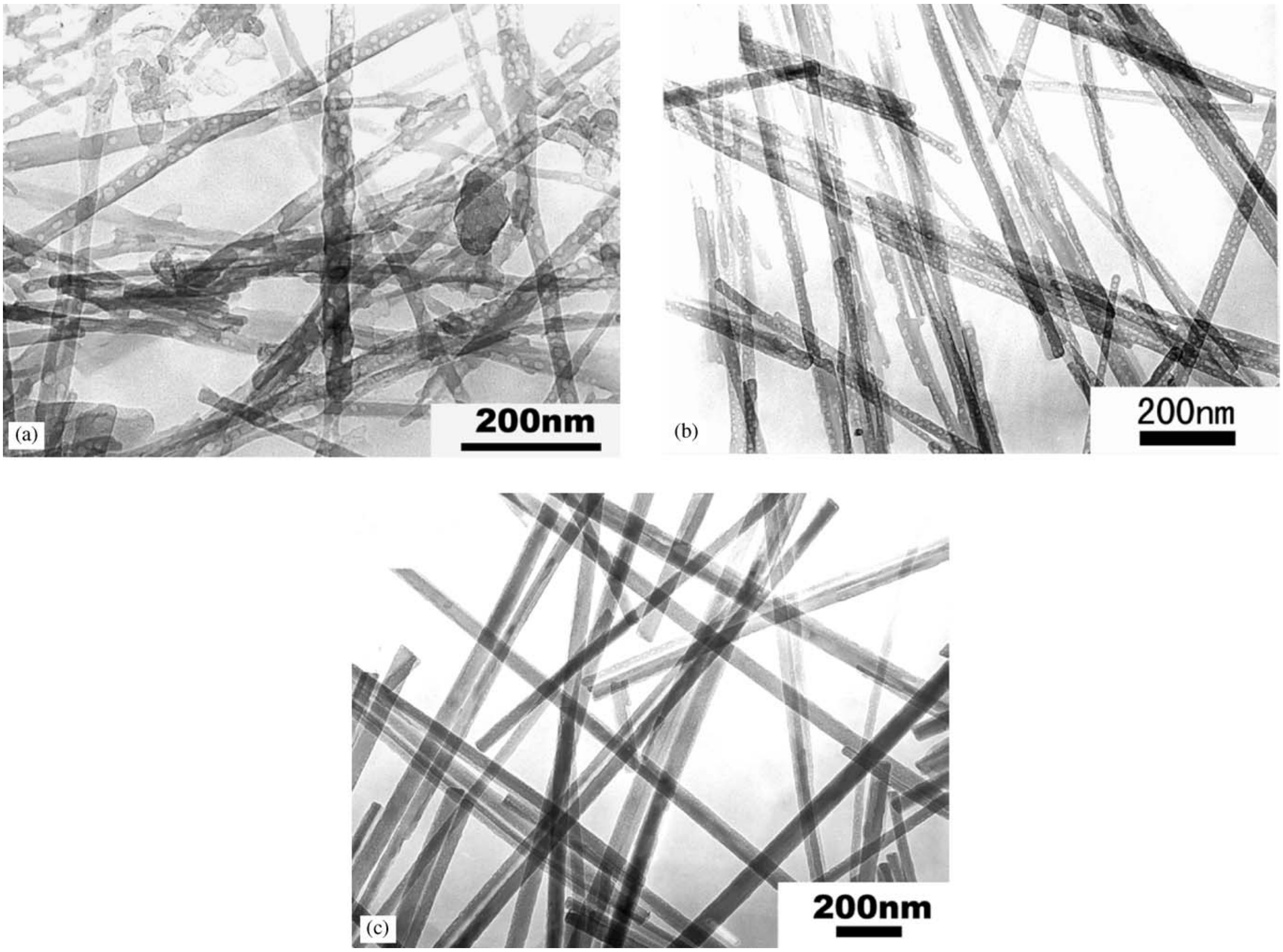

Fig. 2. TEM photographs of the K-D powders synthesized from various temperatures (a) (80°C), (b) (120°C), (c) (180°C).

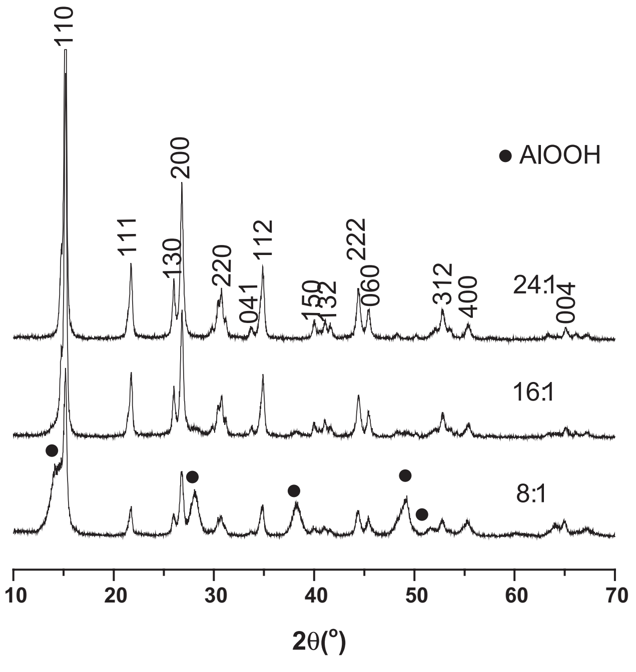

Fig. 3. XRD spectra of the powders synthesized at various molar ratios of NH_4HCO_3/Al.

later. Fig. 4 exhibited the TEM photos of $KAl(OH)_2CO_3$ hydrothermally synthesized at various molar ratio of $KHCO_3$/Al. It can be seen that the increase in the ratio led to smaller particle size, and when the ratio reached 24, the minimum diameter of 15 nm of the needle-like particle was obtained (Fig. 4(c)). As a result, the addition of excessive $MHCO_3$ is important to produce dawsonite-type compounds with smaller particle size.

3.1.3. pH of hydrothermal reaction system

Influence of pH on the preparation of dawsonite-type compounds were observed on a reaction system with the crystallization temperature, the ratio of $NaHCO_3$/Al and reaction time fixed at 120°C, 16 and 24 h, respectively.

Fig. 5 shows the relationship between the intensity of (110) reflection which is a representative of the crystallinity of $NaAl(OH)_2CO_3$, and pH values of the reaction system. It can be drawn according to the fitted curve that the crystallinity of $NaAl(OH)_2CO_3$ powder increased with the increase in pH firstly, reached the

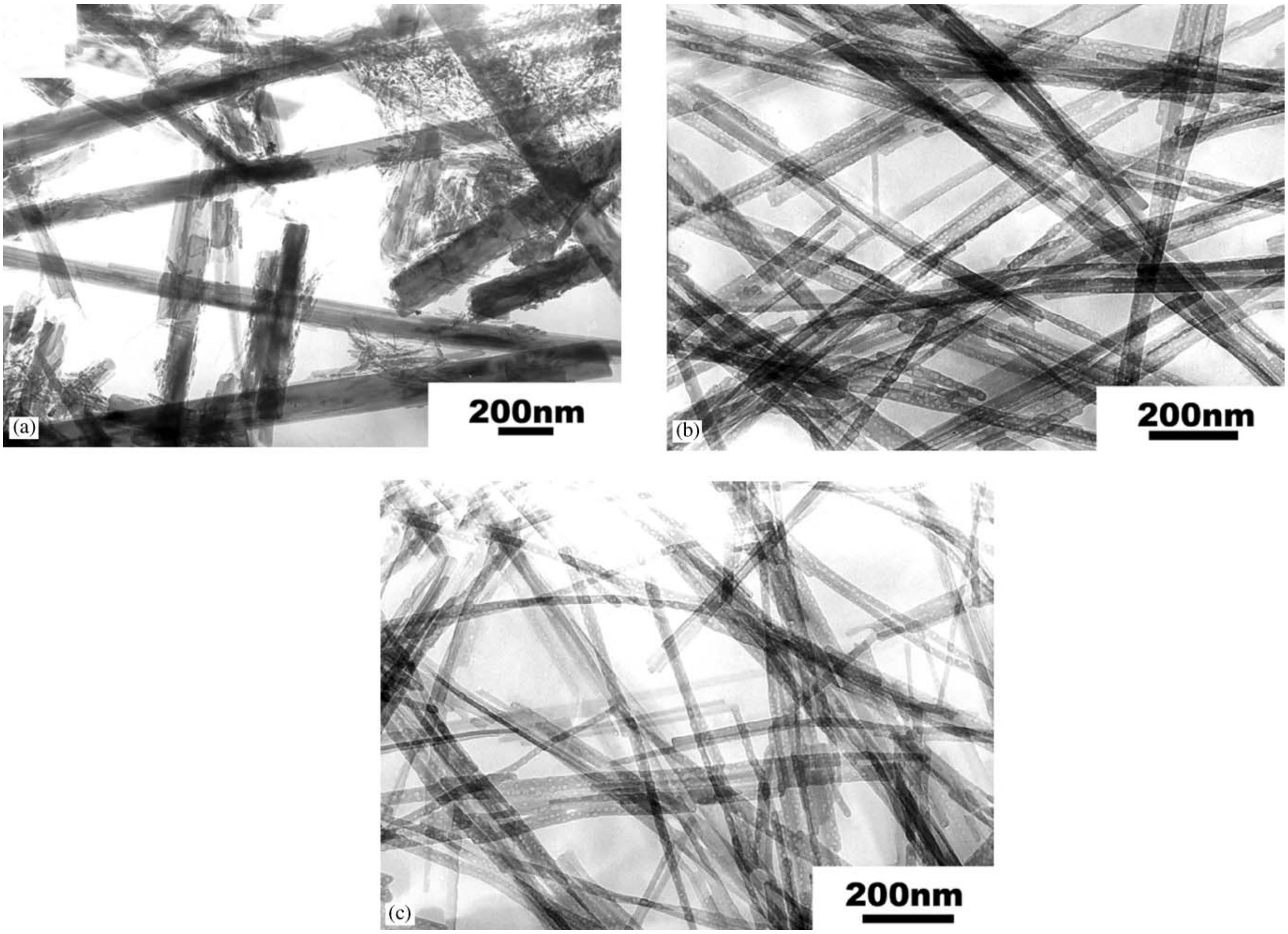

Fig. 4. TEM photographs of the K-D powders hydrothermal synthesized at various molar ratio of $KHCO_3$ to $Al(OH)_3$, (a) 8:1 (b) 16:1 (c) 24:1.

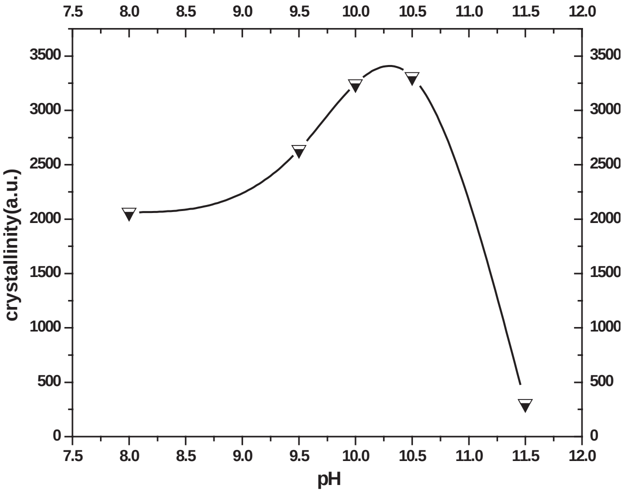

Fig. 5. Plot of the crystallinity of Na-D against pH of solution.

maximum at pH of 10.3, and then decreased with further increase of pH. Therefore it is believed that most favorable pH for $NaAl(OH)_2CO_3$ formation is 10.3. Further discussion will be made in next segment.

3.2. Thermodynamic analyses of hydrothermal synthesis

The formation of dawsonite-type compounds in this hydrothermal solution can be expressed by the following scheme:

$$Al(OH)_3 + MHCO_3 \xrightarrow{K_{Mp}} MAl(OH)_2CO_3.$$

In this hydrothermal aqueous system there are many ionic species, such as Al^{3+}, $Al(OH)_4^-$, $[(OH)_3Al–O–Al(OH)_3]^{2-}$ and $AlO(OH)_2^-$ et al., and $AlO(OH)_2^-$ is considered as the main form of aluminum element in the solution [8,11–13]. Therefore the ionic reaction can be expressed as

$$HCO_3^- + AlO(OH)_2^- + M^+ \xrightarrow{K_{ip}} MAl(OH)_2CO_3$$

and the corresponding concentration product is

$$K_{ip} = [HCO_3^-][AlO(OH)_2^-][M^+]. \quad (1)$$

There are some other possible reactions happened in the system and their corresponding equilibrium constants are as follows:

$$Al(OH)_3 \underset{K_1}{\rightleftharpoons} H^+ + AlO(OH)_2^-$$

$$K_1 = [H^+][AlO(OH)_2^-], \tag{2}$$

$$H_2O \underset{K_2}{\rightleftharpoons} H^+ + OH^-$$

$$K_2 = [H^+][OH^-], \tag{3}$$

$$H_2CO_3 \underset{K_3}{\rightleftharpoons} H^+ + HCO_3^-$$

$$K_3 = \frac{[H^+][HCO_3^-]}{[H_2CO_3]}, \tag{4}$$

$$HCO_3^- \underset{K_4}{\rightleftharpoons} H^+ + CO_3^{2-}$$

$$K_4 = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]}. \tag{5}$$

In the solution of NH_4HCO_3, the following reaction is also involved [14]

$$NH_4^+ \underset{K_5}{\rightleftharpoons} NH_3 + H^+$$

and the equilibrium constant is given by

$$K_5 = \frac{[NH_3]\,[H^+]}{[NH_4^+]} \tag{6}$$

let

$$[H_2CO_3] + [HCO_3^-] + [CO_3^{2-}] = C_V. \tag{7}$$

From Eq. (4), (5) and (7), the concentration of HCO_3^- is give by

$$[HCO_3^-] = C_V K_3[H^+]/([H^+]^2 + K_3[H^+] + K_3K_4) \tag{8}$$

let

$$[NH_4^+] + [NH_3] = C_{V1}. \tag{9}$$

From Eq. (6) and (9), the concentration of NH_4^+ is give by

$$[NH_4^+] = C_{V1}[H^+]/(K_5 + [H^+]). \tag{10}$$

$KHCO_3$ and $NaHCO_3$ are both strong base salt of weak acid; however NH_4HCO_3 is weak base salt of weak acid. As a result, their thermodynamic analyses are different. For the hydrothermal systems with $KHCO_3$ or $NaHCO_3$, the concentration product of dawsonite can be obtained from Eqs. (1), (2) and Eq. (8) as

$$K_{mp} = \frac{K_1K_3C_MC_V}{([H^+]^2 + K_3[H^+] + K_3K_4)}, \tag{11}$$

where K_{mp} is the concentration product of sodium dawsonite or potassium dawsonite; C_M is the concentration of K^+ or Na^+.

For ammonium dawsonite the concentration product derived from Eqs. (2), (7) and Eq. (10) is given as the following equation:

$$K_{(N\text{-}D)p} = \frac{K_1K_3C_VC_{V1}}{(1 + (K_5/[H^+]))([H^+]^2 + K_3[H^+] + K_3K_4)}, \tag{12}$$

where $K_{(N\text{-}D)p}$ represents the concentration product of ammonium dawsonite.

We can therefore analyze the effects of pH, temperature, MHCO$_3$/Al ratio on the dawsonite formation according to Eqs. (11) and (12) as follows.

3.2.1. Effect of pH of hydrothermal system

3.2.1.1. For K-D and Na-D systems.

The relationship of pH on $[H^+]$ is given by

$$pH = -lg^{[H]} \Rightarrow [H^+] = 10^{-pH}$$

thus Eq. (11) becomes

$$K_{mp} = \frac{K_1K_3C_MC_V}{(10^{-2pH} + K_3 10^{-pH} + K_3K_4)}, \tag{13}$$

where C_V and C_M have nothing to do with pH, therefore the product of $K_1K_3C_VC_M$ equals to constant C, and Eq. (13) becomes:

$$K_{mp} = \frac{C}{(10^{-2pH} + K_3 10^{-pH} + K_3K_4)} \tag{14}$$

The pH range for $Al(OH)_3$ to exist in aqueous solution is from 3.2 to 10.8 [15]. Within this range, the dependence of pH on the concentration product can be drawn as Fig. 6. Differentiation of Eq. (13) with pH yields Fig. 7, demonstrating the relationship between acceleration of K_{mp} and pH.

From these two curves it can be seen that as pH increases the product of concentration will increase slowly first, and then increases quickly from the pH of

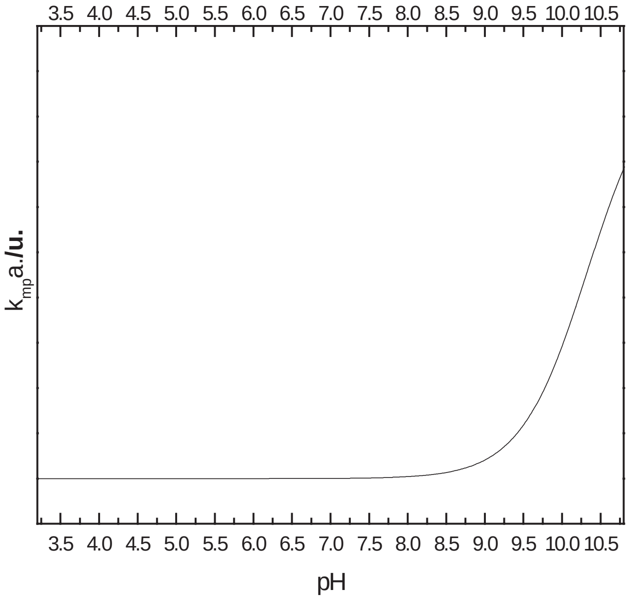

Fig. 6. K_{mp} as a function of pH.

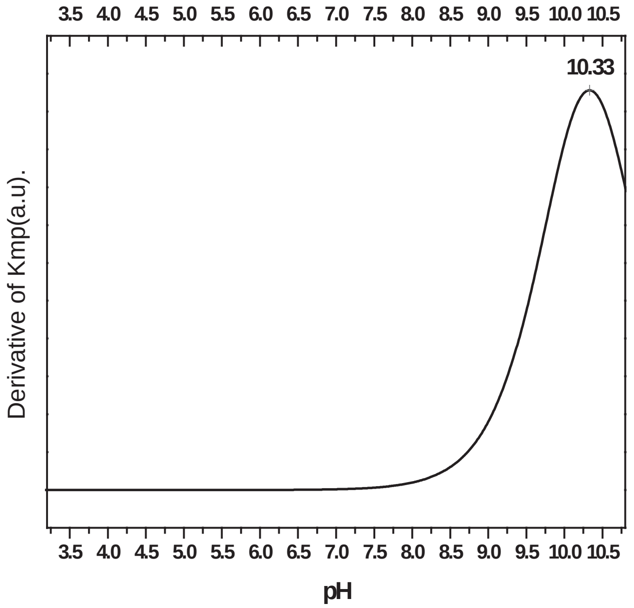

Fig. 7. Derivative of K_{mp} as a function of pH.

about 8.0. There is a maximum of concentration product when pH equals to 10.8. Consequently, the increase of pH will be benefit to the reaction, which is accorded with the experiment result stated earlier. Fig. 7 shows that a maximum of derivative of K_{mp} is obtained at 10.33. It is known that there is a maximum of crystallinity of dawsonite powder synthesized in hydrothermal system with fixed pH of 10.3. Thus it can be seen that the derivative of K_{mp} is relative to the crystallinity of dawsonite powder. Therefore, the most favorable acidity for K-D and Na-D preparation is thermodynamically and experimentally proved to be 10.3.

Furthermore, in the hydrothermal reaction system, the increase of crystallinity of dawsonites could be attributed to the transformation of $\mathrm{Al(OH)_3}$ to $\mathrm{AlO(OH)_2^-}$ and the formation of $\mathrm{HCO_3^-}$. At lower pH, concentration of $\mathrm{AlO(OH)_2^-}$ increases with the increasing pH, which facilitates the formation of dawsonite. However at higher pH the concentration of $\mathrm{AlO(OH)_2^-}$ increases continuously, but it favors $\mathrm{CO_3^{2-}}$ rather than $\mathrm{HCO_3^-}$, the concentration of $\mathrm{HCO_3^-}$ therefore decreases. As a result, the most favorable pH, i.e., 10.3 would occur for the crystallinity of dawsonite. Similar explanation could also be contributed to the occurrence of a maximum in Fig. 5.

3.2.1.2. *For NH$_4$-D systems.*

The dependence on acidity of solution for the $\mathrm{NH_4}$-D systems can be expressed as

$$K_{(\text{N-D})\text{p}} = \frac{C}{(1 + K_5 10^{\text{pH}})(10^{-2\text{pH}} + K_3 10^{-\text{pH}} + K_3 K_4)} \tag{15}$$

the range of pH is also from 3.2 to 10.8.

Fig. 8 shows the relationship between the concentration product of $\mathrm{NH_4}$-D and pH of the hydrothermal reaction system. It can be seen that the concentration product of $\mathrm{NH_4}$-D increases until the basicity is above 9.79; and then it begins to decrease with the falling of pH. Hence it favors the growth of ammonium dawsonite crystal when pH increases in the regime of 3.2–9.79; when basicity continues to increase, the growth velocity will slow down. The optimum basicity for the growth of $\mathrm{NH_4Al(OH)_2CO_3}$ is about 9.79.

3.2.2. *Effect of reaction temperature*

3.2.2.1. *For K-D and Na-D system.*

Within the hydrothermal synthesis temperature range of this work, all the three kinds of bicarbonates decompose. For K-D and Na-D reaction system, the ionic concentration related to $M\mathrm{HCO_3}$ can be expressed as follows:

$$[M^+] = \mathrm{C}_M = an/V, \tag{16}$$

$$C_V = \frac{an}{2V} + K_{\mathrm{CO_2}} P_{\mathrm{CO_2}}, \tag{17}$$

$$P_{\mathrm{CO_2}} V' = \frac{n\mathrm{RT}}{2} \Rightarrow P_{\mathrm{CO_2}} = \frac{n\mathrm{RT}}{2V'} \xrightarrow{V'=(1-b)V} \frac{n\mathrm{RT}}{2(1-b)V},$$

$$\mathrm{C}_V = \frac{an}{2V} + \frac{nK_{\mathrm{CO_2}}\mathrm{RT}}{2(1-b)V} = n/2V\left(a + \frac{K_{\mathrm{CO_2}}\mathrm{RT}}{(1-b)}\right) \tag{18}$$

thus the dependence of K_{mp} on the reaction temperature can be given from Eqs. (1), (16), (18) and (8):

$$K_{\mathrm{mp}} = \frac{an^2 K_1 K_3}{([\mathrm{H}^+]^2 + K_3[\mathrm{H}^+] + K_3 K_4)V^2}\left(\frac{a}{2} + \frac{K_{\mathrm{CO_2}}\mathrm{RT}}{2(1-b)}\right), \tag{19}$$

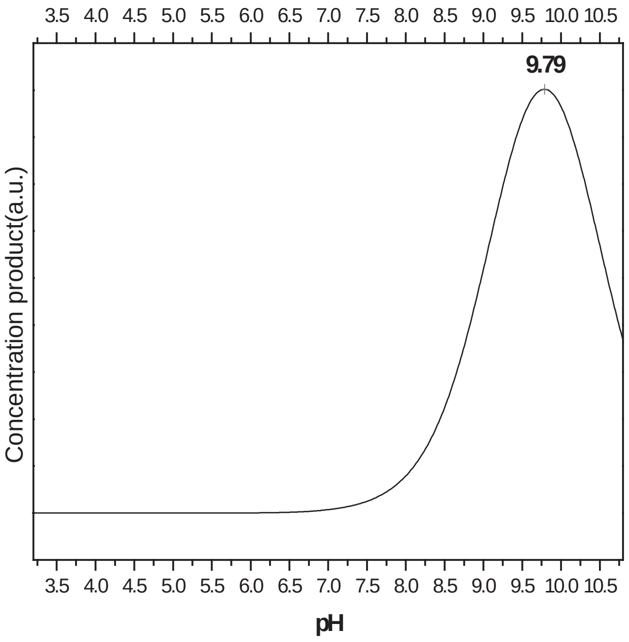

Fig. 8. Dependence of concentration product of $\mathrm{NH_4Al(OH)_2CO_3}$ on pH.

where n is the molar weight of $M\mathrm{HCO_3}$, a is the fraction of $M_2\mathrm{CO_3}$ dissolved in the solution, b is the filling factor, $K_{\mathrm{CO_2}}$ is the Henry constant, $P_{\mathrm{CO_2}}$ is the $\mathrm{CO_2}$ partial pressure in the hydrothermal system.

3.2.2.2. For NH_4-D system. The dependence on temperature can also be derived for the hydrothermal synthesis of ammonium dawsonite. From Eqs. (20), (21) and Eq. (12), temperature dependence of $\mathrm{K_{(N\text{-}D)P}}$ is expressed as Eq. (22):

$$C_{V1} = K_{\mathrm{NH_3}} P_{\mathrm{NH_3}}, \tag{20}$$

$$C_V = K_{\mathrm{CO_2}} P_{\mathrm{CO_2}}, \tag{21}$$

$$K_{(\mathrm{N\text{-}D})\mathrm{P}} = \frac{K_1 K_3 K_{\mathrm{NH_3}} K_{\mathrm{CO_2}} (n\mathrm{RT})^2}{(bV)^2(1+(K_5/[\mathrm{H}^+]))([\mathrm{H}^+]^2 + K_3[\mathrm{H}^+] + K_3K_4)}. \tag{22}$$

As known, K_1, K_3, K_4 and K_5 are all temperature dependent. When the temperature increases, K_1 becomes larger, but K_3, K_4 and, K_5 turn smaller. Moreover, higher concentration of $\mathrm{AlO(OH)_2^-}$ and $\mathrm{HCO_3^-}$ favors the dawsonite formation. The increase in reaction temperature raises $\mathrm{AlO(OH)_2^-}$ concentration, but it decreases the $\mathrm{HCO_3^-}$ concentration. So possible optimal temperatures are expected for K_{mp} and $K_{(\mathrm{D\text{-}N})\mathrm{p}}$.

In our work, the influence of reaction temperature in the crystallite size of dawsonites has been carried out in the temperature ranging from 80°C to 180°C. The results showed that crystallinity of dawsonite compounds increases with the increase in temperature. However, maximum crystallinity size has not been found within the above temperature range. Further investigation outside the temperature range of this paper is underway.

3.2.3. Effect of the molar fraction of MHCO$_3$

Eqs. (19) and (22) are the equations describing molar fraction of $M\mathrm{HCO_3}$ dependence of concentration product when reaction time and pH are fixed. As the molar fraction of both the hydrothermal systems of $M\mathrm{HCO_3}$ increase, the concentration will increase too. As a result, increase in the molar fraction of $M\mathrm{HCO_3}$ could promote the growth of dawsonite-type compounds.

4. Conclusions

Three kinds of dawsonite compound have been hydrothermally synthesized under different conditions. It is concluded that increase in the molar ratio of $M\mathrm{HCO_3/Al(OH)_3}$ of reactants will be benefit to the growth of dawsonite crystals. But augment of the reaction temperature will produce powder with large particle size. The most favorable pH values for dawsonite preparation are obtained experimentally and theoretically, they are 10.3 for sodium dawsonite and potassium dawsonite, and 9.79 for ammonium dawsonite, respectively.

Acknowledgments

We are thankful for financial the support from NSFC (No. 20071033).

References

[1] E. Bader, Neues Jahrb Mineral. Geol. Palaeontol. Abh. Abt. A. 74 (1938) 449–455.

[2] H. Besson, S. Caillere, S. Henin, R. Prost, C. R. Acad. Sci. Ser. D. 277 (1973) 261–270.

[3] S.L. Hem, J.L. White, US Pat. (1975) 3911090.

[4] T. Iga, S. Kato, Yogyo-Kyokai-Shi. 86 (11) (1978) 509–512.

[5] C.J. Serna, J.l. White, S.L. Hem, J. Pharm. Sci. 67 (1978) 324–331.

[6] M. Giannos, M. Hoang, T.W. Turney, Chem. Lett. (1998) 793–799.

[7] J.G. Li, T. Ikegami, J. Eur. Ceram. Soc. 21 (2001) 139–145.

[8] K. Hayashi, S. Toyota, et al., J. Ceram. Soc. Jpn. 98 (5) (1990) 444–449.

[9] Z.Y. Wen, J.H. Yang, Z.X. Lin, D.L. Jiang, in: B. Chowdari, et al. (Ed.), Solid State Ionics: Materials and Devices, World Scientific, Singapore, New Jersey, London, Hong Kong, Vol. 79, 2000.

[10] T. Iga, S. Kato, Yogyo-Kyokai-Shi. 86 (11) (1978) 509–512.

[11] N. Mizutani, Bull. Ceram. Soc. Jpn. 16 (1981) 774–780.

[12] J.W. Akitt, W. Gessner, M. Weinberger, Magn. Reson Chem. 26 (1988) 1047–1050.

[13] M. Weinberger, M. Schneider, D. Mueller, W. Gessner, Z. Anorg. Allg. Chem. 621 (1995) 679–684.

[14] M.F. Zhang, C.L. Kong, Inorganic Chemistry, College Education Press, Beijing, 1983.

[15] Q.C. Gu, Newly Edited Chemical Manual, 1st Edition, Jiangsu Education Press, Jiang su, 1998, pp. 1026.