

Synthesis and thermal behavior of the dawsonite-type solid solution $K_{1-x}(NH_4)_xAl(OH)_2CO_3$

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Received 25 August 2004; received in revised form 3 February 2005; accepted 3 February 2005

Available online 17 March 2005

Abstract

This paper reported the hydrothermal synthesis and thermal behavior of a novel kind of dawsonite-type solid solution $K_{1-x}(NH_4)_xAl(OH)_2CO_3$ ($x=0.2-0.93$). The effects of NH_4^+/K^+ molar ratio in the starting reactants and the hydrothermal reaction time on the composition of $K_{1-x}(NH_4)_xAl(OH)_2CO_3$ were investigated. In addition, the influence of the composition on the thermal stability of the solid solution was studied by DTA/TG analyses. It was indicated that compound $K_{0.44}(NH_4)_{0.56}Al(OH)_2CO_3$ ($x=0.56$) is the most thermally stable one among all the dawsonite type solid solutions. Furthermore, $K\text{-}\beta\text{-}Al_2O_3$, a solid state K^+ ion conductor was prepared by calcining $K_{0.19}(NH_4)_{0.81}Al(OH)_2CO_3$ at 1250 °C.

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Keywords: Thermal properties; Hydrothermal; Solid solution; Dawsonite

1. Introduction

Dawsonite is a mineral of formula $MAl(OH)_2CO_3$ ($M=Na, K, NH_4$) named after the Canadian geologist, Dawson. The mineral was first obtained synthetically by Bader [1] and later by Besson et al. [2]. $NaAl(OH)_2CO_3$ and $KAl(OH)_2CO_3$ were also synthesized by hydrothermal method in our previous work [3]. All dawsonites are double hydroxyl carbonates of aluminum [4] and exhibit well-known behaviors 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 consisting of aluminum element and they produce CO_2 and H_2O after thermal decomposition [6–9]. It should be pointed out that although there has been much work on the application of dawsonite-type compounds up

to date, few work was carried out systematically on the synthetic chemistry and thermal stability of such materials.

The space group of both $KAl(OH)_2CO_3$ and $NH_4Al(OH)_2CO_3$ has been determined as C_{mcm} . Such a structure is body-centered and composed of chain structures with distorted $MO_4(OH)_4$ ($M=K$ or NH_4^+) and $AlO_2(OH)_4$ octahedron and carbonate groups [4,10]. Since there is only small difference between the radius of K^+ (133 pm) and NH_4^+ (143 pm) ions, it is very possible that NH_4^+ would enter the lattice of $KAl(OH)_2CO_3$ when both cations co-exist in one reaction system which was described in our previous work [3], then, a new kind of solid solution with formula $K_{1-x}(NH_4)_xAl(OH)_2CO_3$ would be formed. In this paper, we will investigate the preparation of the solid solution of $K_{1-x}(NH_4)_xAl(OH)_2CO_3$ by hydrothermal method and the effect of the composition of starting materials and hydrothermal reaction conditions on their thermal stability. Moreover, the possibility to use the potassium and aluminum containing solid solutions for the preparation of $K\text{-}\beta\text{-}Al_2O_3$, a K^+ fast ion conductor, applied in many

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fields and normally prepared by traditional solid state reaction [11–13] will be reported.

2. Experimental

2.1. Synthesis

In a typical reaction, an appropriate amount of $\text{Al}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (0.005 mol dissolved in 25 ml H_2O) was mixed with supersaturated KHCO_3 solution very slowly with gentle release of CO_2 . A suspension of reaction system was formed in a Teflon-liner autoclave which was filled with deionized water up to 75% of the total volume. Then an amount of NH_4NO_3 powder with the molar ratio of NH_4^+/K^+ 0.05, 0.1, 0.2, 0.5, 0.8 and 1.0 was added to the autoclave respectively in order to adjust the composition of the products. The autoclave was maintained at 120 °C for different periods. The products were all centrifugated, repeatedly washed with deionized water and ethanol, and dried at 60 °C in air for 24 h.

2.2. Characterizations

X-ray diffraction patterns were acquired from a Rigaku D/MAX-III powder diffractometer with nickel-filtered $\text{Cu K}\alpha$ ($\lambda = 1.5418 \text{ \AA}$) source. The scan rate was 10 °C/min and the step size was 0.02°. The contents of K and Al in each product were assayed with ICP spectrophotometer of model Vista AX ICP-AES. Thermal analyses were carried out under N_2 (the flow rate is 50 ml/min) using differential thermal analysis (DTA) and thermogravimetric analysis (TG) on a ZRY-1P thermal analyzer (SHANGPING, China); the DTA and TG profiles were recorded at a heating rate of 10 °C/min. All the samples for thermal analysis were powdered to particles with a diameter of 73 μm by using a 200 mesh sieve. The mass of the testing sample was about 15 mg.

3. Results and discussion

3.1. Phase analysis

Fig. 1 showed XRD spectra of the products hydrothermally synthesized with different molar ratio of NH_4^+/K^+ in comparison with the pristine dawsonites, i.e., $\text{NH}_4\text{Al}(\text{OH})_2\text{CO}_3$ and $\text{KAl}(\text{OH})_2\text{CO}_3$. It was observed that all compounds displayed similar diffraction patterns, with only some shift of the diffraction peaks of $\text{KAl}(\text{OH})_2\text{CO}_3$ or $\text{NH}_4\text{Al}(\text{OH})_2\text{CO}_3$. Therefore, it is reasonably expected that the phase of the solid solution $\text{K}_{1-x}(\text{NH}_4)_x\text{Al}(\text{OH})_2\text{CO}_3$ has been formed over a wide range of NH_4^+/K^+ molar ratio. Random distribution of NH_4^+ ion in the lattice of $\text{KAl}(\text{OH})_2\text{CO}_3$ formed the solid solution phase whose unit cell parameters are related to the contents of K^+ and NH_4^+ ions in the lattice.

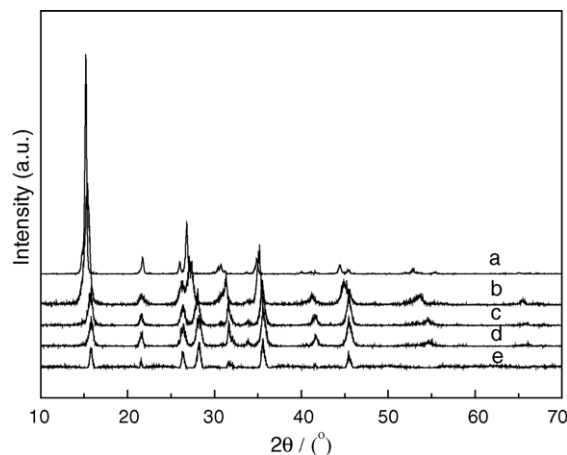
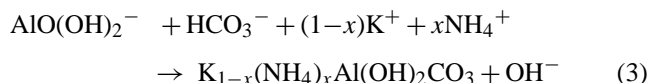
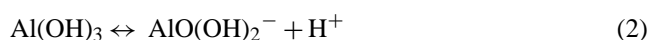
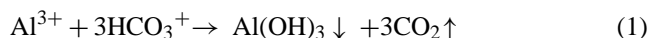


Fig. 1. XRD patterns for the products synthesized from reactants with different molar ratio of NH_4^+/K^+ : (a) pure $\text{NH}_4\text{Al}(\text{OH})_2\text{CO}_3$, (b) 0.01, (c) 0.1, (d) 1.0, and (e) pure $\text{KAl}(\text{OH})_2\text{CO}_3$.

The chemical formula of the solid solutions obtained at different conditions were calculated from ICP and thermogravimetric analysis and listed in Tables 1 and 2. It was seen that the NH_4^+/K^+ molar ratio of the reaction system has great effect on the composition of $\text{K}_{1-x}(\text{NH}_4)_x\text{Al}(\text{OH})_2\text{CO}_3$ solid solution. The x value increased from 0.20 to 0.71 correspondingly when the ratio of NH_4^+/K^+ increased from 0.05 to 1. In addition, as seen from Table 2, the longer the reaction time, the more the content of NH_4^+ is. The x value increased from 0.71 to 0.93 with the extension of the reaction time when the ratio of NH_4^+/K^+ was fixed at 1.0.

Based on our previous investigation on dawsonites with single cation [11], the following chemical reactions were expected in the hydrothermal reaction system:



According to Eq. (3), the composition of the solid solution will be the result of competition between K^+ and NH_4^+ ions in the reaction system during their combination with $\text{AlO}(\text{OH})_2^-$ ions. As a result, the change in NH_4^+/K^+ molar ratio led to different composition of the solid solutions.

3.2. Thermal behaviors

3.2.1. The influence of the composition of reactants

As known, the composition of the solid solution has great effect on the thermal stability of a material. According to Hernandez's work [10], the thermal evolution of $\text{KAl}(\text{OH})_2\text{CO}_3$ and $\text{NH}_4\text{Al}(\text{OH})_2\text{CO}_3$ can be expressed by the following

Table 1

The composition of the solid solutions synthesized from reactants with different NH_4^+/K^+ molar ratio

Sample	K (wt.%)	Al (wt.%)	x value	Chemical formulae
Daw-0.05 ^a	19.72	17.10	0.20	$\text{K}_{0.80}(\text{NH}_4)_{0.20}\text{Al}(\text{OH})_2\text{CO}_3$
Daw-0.1	15.48	17.81	0.40	$\text{K}_{0.60}(\text{NH}_4)_{0.40}\text{Al}(\text{OH})_2\text{CO}_3$
Daw-0.2	11.58	18.21	0.56	$\text{K}_{0.44}(\text{NH}_4)_{0.56}\text{Al}(\text{OH})_2\text{CO}_3$
Daw-0.5	9.80	18.10	0.61	$\text{K}_{0.39}(\text{NH}_4)_{0.61}\text{Al}(\text{OH})_2\text{CO}_3$
Daw-0.8	9.00	18.48	0.66	$\text{K}_{0.34}(\text{NH}_4)_{0.66}\text{Al}(\text{OH})_2\text{CO}_3$
Daw-1	7.56	18.23	0.71	$\text{K}_{0.29}(\text{NH}_4)_{0.71}\text{Al}(\text{OH})_2\text{CO}_3$

^a Daw- r : the obtained samples were labeled Daw- r , where r is the molar ratio of NH_4^+/K^+ in reactants.

Table 2

The composition of the solid solutions synthesized for different reaction time^a

Reaction time (h)	K (wt.%)	Al (wt.%)	x value	Chemical formulae
4	7.56	18.23	0.71	$\text{K}_{0.29}(\text{NH}_4)_{0.71}\text{Al}(\text{OH})_2\text{CO}_3$
8	6.24	18.66	0.67	$\text{K}_{0.23}(\text{NH}_4)_{0.77}\text{Al}(\text{OH})_2\text{CO}_3$
24	5.14	18.88	0.81	$\text{K}_{0.19}(\text{NH}_4)_{0.81}\text{Al}(\text{OH})_2\text{CO}_3$
96	1.88	19.35	0.93	$\text{K}_{0.07}(\text{NH}_4)_{0.93}\text{Al}(\text{OH})_2\text{CO}_3$

^a The molar ratio NH_4^+/K^+ of the reactants was fixed to 1.

schemes while they were decomposed separately:

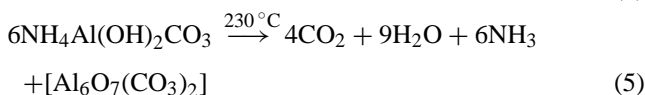
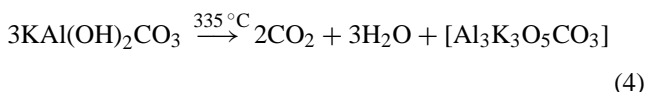
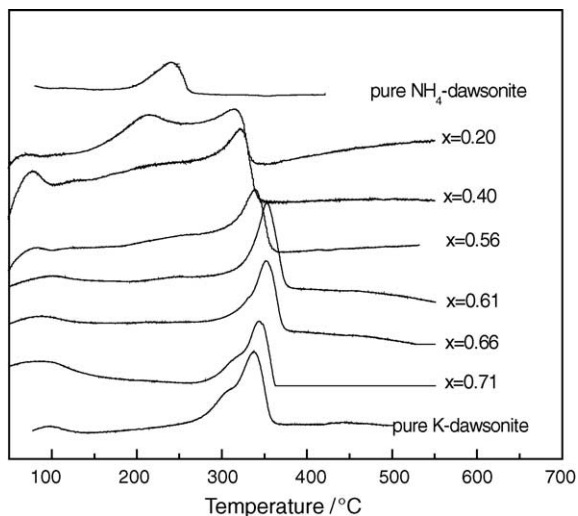


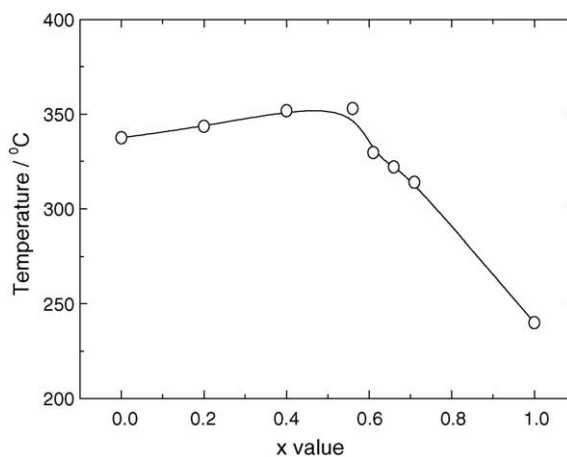
Fig. 2 showed the DTA profiles of a series of $\text{K}_{1-x}(\text{NH}_4)_x\text{Al}(\text{OH})_2\text{CO}_3$ solid solutions and Fig. 3 showed the relationship between the endothermic peak temperature and the x value. It was observed that the endothermic peaks located at ~ 335 and 230°C for pristine $\text{KAl}(\text{OH})_2\text{CO}_3$ ($x=0$) and $\text{NH}_4\text{Al}(\text{OH})_2\text{CO}_3$ ($x=1$), respectively, which was consistent with the results in [10]. For the other samples, the temperature of the endothermic peaks changed with x . The peak temperature rose with the increasing of x until it was up to 0.2. The highest temperature of endothermic peak

Fig. 2. DTA traces of the $\text{K}_{1-x}(\text{NH}_4)_x\text{Al}(\text{OH})_2\text{CO}_3$ solid solutions with different compositions.

appeared at about 352.9°C in $\text{K}_{0.44}(\text{NH}_4)_{0.56}\text{Al}(\text{OH})_2\text{CO}_3$ synthesized with the ratio of NH_4^+/K^+ at 0.2. After then, the peak temperature began to drop with the increase of x and a second endothermic peak appeared at the same time. When x was up to 0.71, the two endothermic peaks of $\text{K}_{0.29}(\text{NH}_4)_{0.71}\text{Al}(\text{OH})_2\text{CO}_3$ were located at 310 and $\sim 220^\circ\text{C}$, respectively, which were all lower than the temperatures at which the pristine dawsonites decomposed.

Fig. 4 illustrated the TG profiles of the solid solutions synthesized with different starting materials. It was shown that the total weight loss increased linearly from 33.2% to 55.8% with the increase of x , which was ascribed to the increase of the content of NH_4^+ in the solid solutions, leading to more NH_3 gas released when decomposed at the same temperature.

According to the results of the DTA and TG profiles, it would be suggested that the structure of $\text{KAl}(\text{OH})_2\text{CO}_3$ was stabilized by appropriate substitution of K^+ with NH_4^+ . Because of difference in ion radii, the distortion of lattice would take place when NH_4^+ replaced K^+ . Thus, the thermal

Fig. 3. The relationship between endothermic peak temperature and x value of $\text{K}_{1-x}(\text{NH}_4)_x\text{Al}(\text{OH})_2\text{CO}_3$.

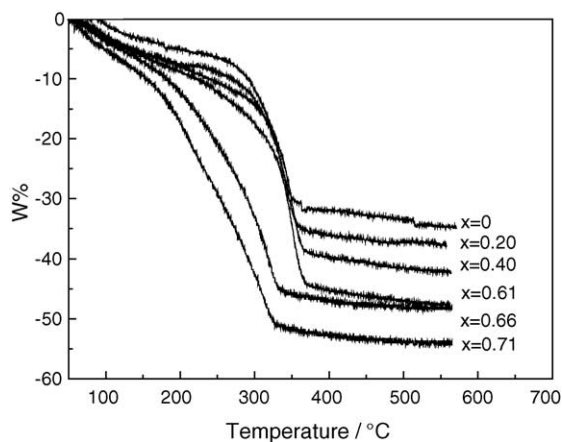


Fig. 4. TG traces of the $K_{1-x}(NH_4)_xAl(OH)_2CO_3$ solid solutions with different composition.

stability of product was improved by forming solid solution of $K_{1-x}(NH_4)_xAl(OH)_2CO_3$ when x was less than 0.56. However, further increase of the NH_4^+ content ($x > 0.56$) in $KAl(OH)_2CO_3$ would lead to too strong distortion of lattice and therefore degraded the thermal stability of the solid solution.

3.2.2. The influence of the reaction time

Further research work was made on the thermal behavior of solid solutions synthesized for different reaction periods while the NH_4^+/K^+ molar ratio of the reaction systems was fixed at 1.0. The DTA and TG profiles were shown in Figs. 5 and 6, respectively. As expected from their chemical composition listed in Table 2, similar thermal events should be appeared in the temperature ranging from r.t. to 600 °C. The endothermic effects below 100 °C were ascribed to the removal of physisorbed water of the solid solutions. As found, two endothermic peaks were recorded for all the four samples. The first peak at 220, 234, 239 and 255 °C for the reaction time

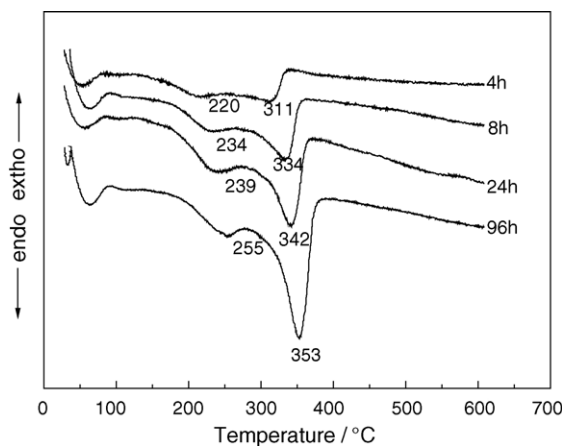


Fig. 5. DTA traces of the solid solutions synthesized for different reaction time with fixed NH_4^+/K^+ molar ratio in the reactants.

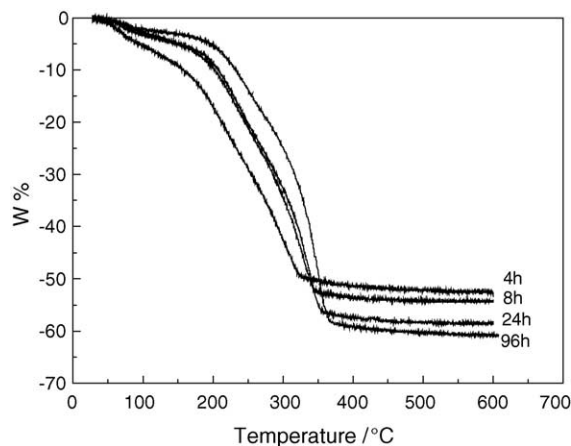


Fig. 6. TG traces of the solid solutions synthesized for different reaction time with fixed NH_4^+/K^+ molar ratio in the reactants.

of 4, 8, 24, and 96 h respectively would be attributed to the release of NH_3 from the solid solutions and the second one at 311, 334, 342 and 353 °C respectively would be to the decomposition of the remained potassium containing dawsonite. In addition, as shown in Fig. 6, the weight loss of the solid solution increased with the extension of the reaction time, which agreed with the increase of the NH_4^+ content in the products.

It was noticeable that the thermal stability of the above four solid solutions enhanced with the increase in x (all x values here were larger than 0.56), which was ambivalent to the conclusion obtained from Figs. 2–4. The improvement of the thermal stability of the products would be ascribed to the enlarged grain size of $K_{1-x}(NH_4)_xAl(OH)_2CO_3$ synthesized with extended reaction time. From Fig. 7 we could obtain the FWHM value of the four samples, i.e., 0.947, 0.941, 0.695 and 0.614, corresponding to the reaction time 4, 8, 24, and 96 h, respectively, which implied enlarged grain size with the extension of reaction time according to Sherrer formula.

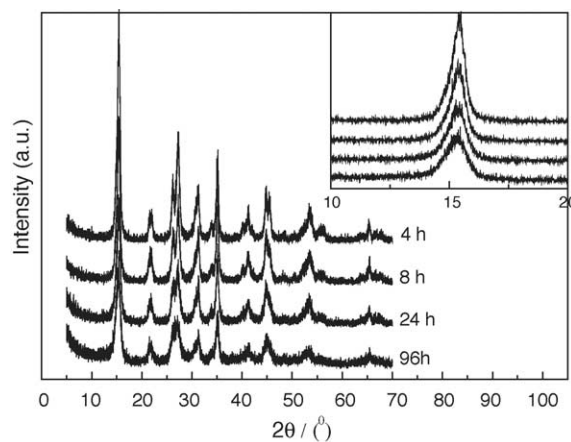


Fig. 7. XRD patterns for the solid solutions synthesized for different reaction time with fixed NH_4^+/K^+ molar ratio in the reactants.

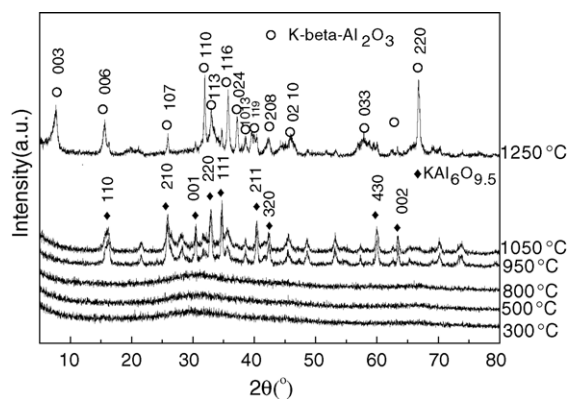


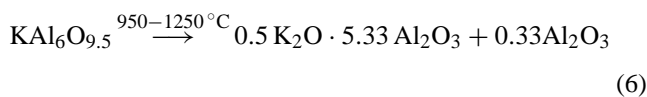
Fig. 8. Phase evolution of the $K_{0.19}(NH_4)_{0.81}Al(OH)_2CO_3$ during thermal decomposition.

Moreover, the extension of reaction time might also be helpful to reduce the defects in the products obtained, which could also to some extent improve their thermal stability.

3.3. Thermal decomposition products

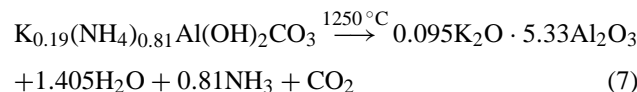
It was found from Table 2 that $K_{0.19}(NH_4)_{0.81}Al(OH)_2CO_3$ has a comparable K/Al molar ratio with $K_2O \cdot 5.33Al_2O_3$, or K-beta-alumina. Therefore, it is possible to obtain the fast K^+ conductive material by the decomposition of $K_{0.19}(NH_4)_{0.81}Al(OH)_2CO_3$ at an appropriate temperature. Fig. 8 showed the phase evolution on calcining $K_{0.19}(NH_4)_{0.81}Al(OH)_2CO_3$. It was found that the decomposition process of this solid solution is quite different from that of the pristine dawsonites, which was precisely reported in [10], that is, $KAlO_2$ or Al_2O_3 was formed while the potassium or ammonium dawsonites were heated at 600 and 700 °C, respectively. In our work, no any such phases were observed until the heating temperature was up to 850 °C. As demonstrated in Fig. 8, there were wholly amorphous compounds yielded when the calcination temperature is lower than 850 °C. The formation of such amorphous products was attributed to the slow release of NH_3 and CO_2 gases during the decomposition. Further rising temperature would cause very complicated solid-state reaction. As shown, in addition to potassium aluminates, i.e., $KAl_6O_{9.5}$ (JCPDS 47-0321), some phases difficult to be indexed were found from the sample decomposed at 950 and 1050 °C. Well crystallized $K_2O \cdot 5.33Al_2O_3$ (JCPDS 77-2314) was obtained while the calcining temperature was raised to 1250 °C.

On the basis of the experimental and calculated results, the formation of the $K_2O \cdot 5.33Al_2O_3$ from $KAl_6O_{9.5}$ could be expressed as



Furthermore, the overall transformation from K- NH_4 -dawsonite solid solution to K-beta- Al_2O_3 can be

schematically shown as



The extra Al_2O_3 might react with other unindexable potassium rich phases to form $K_2O \cdot 5.33Al_2O_3$. As shown in Fig. 8, nearly pure K- β - Al_2O_3 powders were obtained from the decomposition of $K_{0.19}(NH_4)_{0.81}Al(OH)_2CO_3$. Although the crystallinity of the products was to be improved, a new route to synthesize K- β - Al_2O_3 powder, a kind of K^+ ion conductor, but normally prepared by traditional solid state reactions method was identified.

4. Conclusions

Formation of the solid solution $K_{1-x}(NH_4)_xAl(OH)_2CO_3$ has been achieved via a hydrothermal method. The solid solution with x from 0.2 to 0.93 was obtained by changing the NH_4^+/K^+ molar ratio in the hydrothermal reaction system and the reaction time. The thermal stability of $K_{1-x}(NH_4)_xAl(OH)_2CO_3$ was enhanced with the increase in x value when x is lower than 0.56, and then debased with the further increase in x . Extending hydrothermal reaction time improved the thermal stability of the solid solutions. K- β - Al_2O_3 powder could be obtained by calcining $K_{0.19}(NH_4)_{0.81}Al(OH)_2CO_3$ powder at 1250 °C.

Acknowledgements

We are thankful for financial support from National Natural Science Foundation of China (No. 20071033).

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