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Hydrothermal synthesis of $K_4Nb_6O_{17}$

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A new approach for the synthesis of $K_4Nb_6O_{17}\cdot 3H_2O$ by hydrothermal method was examined using different alkaline solutions such as Nb_2O_5-KOH-NaOH-H_2O, Nb_2O_5-KOH-NH_4OH-H_2O and Nb_2O_5-KOH-H_2O. $K_4Nb_6O_{17}\cdot 3H_2O$ was formed as single phase in Nb_2O_5-KOH-H_2O system in the region of KOH concentration 1.0–1.5 m and temperature 220–285 °C. $KNbO_3$ was also formed as single phase in 3.0 m KOH solutions above 250 °C. Addition of methanol was useful to decrease the particle size and increase the specific surface area of $K_4Nb_6O_{17}\cdot 3H_2O$.

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1. Introduction

In the K_2O-Nb_2O_5 system, many kinds of compounds with various crystal structures containing layered [1–2] and tunnel structures [3–5] have been synthesized and their various physico-chemical properties such as ferroelectric property, ionic conductivity and photocatalytic property, have been investigated. Among the various potassium niobates, $K_4Nb_6O_{17}$ is one of the most interesting compound for its unique layered crystal structure, ion exchange property and photocatalytic property. The structure consists of sheets made of two planes of NbO_6 octahedra linked with one-half of the K atoms [6, 7]. This potassium ion is easily exchanged by other metal ion or colloidal oxide sol to produce nanocomposites consisting of Nb_6O_{17} host layer and nanoscale particles incorported in the interlayer [8]. Presently, $K_4Nb_6O_{17}$ nanocomposites attract a great deal of attention as photocatalysts. For example, $K_4Nb_6O_{17}$ loaded Ni or NiO in the layer is reported to show excellent photocatalytic activity for the decomposition of water into hydrogen and oxygen [9–12]. $H_4Nb_6O_{17}$ intercalated CdS-ZnS and Fe_2O_3 was reported to be capable of hydrogen evolution under visible light irradiation in the presence of various sacrificial donors and that intercalated TiO_2 with Pt was also known to manifest pure water cleavage into hydrogen and oxygen without a sacrificial donor under band gap irradiation [13, 14].

In spite of variety of wide application of $K_4Nb_6O_{17}$, the synthesis of $K_4Nb_6O_{17}$ is a few to name, viz conventional solid state and flux method. These methods employ Nb_2O_5 and K_2CO_3 or K_2O as raw materials and are not suitable to control the particle size and morphology of products. In this point of view hydrothermal synthesis is a promising method. In this study, therefore, a series of experiments was carried out to investigate the synthesis of $K_4Nb_6O_{17}$ under hydrothermal conditions. Moreover the effect of addition of alcohol was also examined to control the morphology of $K_4Nb_6O_{17}$.

2. Experimental

All reagent used were reagent grade and used directly without any further purification. Nb_2O_5 powder used as the starting material was 99.5% purity. The chemical analysis of the potassium hydroxide was as follows: Potassium carbonate (K_2CO_3) $< 1.5\%$, Chloride (Cl) $<$ 0.002%, Phosphate (PO_4) $< 0.001\%$, Sulfate (SO_4) $<$ 0.001% and that of the sodium hydroxide was: Sodium carbonate (Na_2CO_3) $< 1.5\%$, Chloride (Cl) $<$ 0.005%, Phosphate (PO_4) $< 0.001\%$, Sulfate (SO_4) $<$ 0.001%. Water was deionized by the ion exchanger after the distillation.

A typical experimental procedures can be described as follows. Initially 0.14 g of KOH, 0.50 g Nb_2O_5 and 4 g water were put into a tubular 10 cm^3 of autoclave which are made of SUS316 stainless steel, indicating the molar concentrations of KOH and Nb_2O_5 were 0.625 and 0.470 m, respectively where m is mol(kg-solvent)$^{-1}$. Namely, the K/Nb atomic ratio initially added was 2/3 which corresponds to that of $K_4Nb_6O_{17}$. Additional KOH, NaOH and NH_3 were put to control the basicity of the solution. In some series of experiment, methanol was also added in order to examine the effect of addition of alcohol on the morphology of the product. When methanol was added, total volume of the solution was kept constant as 4 cm^3. Except for the experiments above 285 °C, the polytetrafluoroethylene (Teflon®) cup was placed inside the autoclave to prevent further corrosion. After sealing the autoclave, the autoclave was set into a KNO_3-$LiNO_3$ molten salt bath at the desired temperature. During the reaction period, the autoclave was kept at an autogeneous saturation vapor pressure of the solution. After maintaining at the desired temperature for 24 h, the autoclave was taken out from molten salt bath, cooled immediately by forced air. The product was separated from the solution by centrifuge, then rinsed with pure water, and finally dried in an oven to remove the absorbed water at 105 °C for 12 h.

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The products were identified by X-ray powder diffraction (Shimadzu diffract meter XD-D1). The thermal property of products was examined by TG-DTA analysis (Rigaku TAS-200).

3. Results and discussion

3.1. Nb_2O_5-KOH-NH_4OH-H_2O system

Hydrothermal treatment of the mixtures consisting 0.470 m Nb_2O_5, 0.625 m KOH and various concentrations of NH_3 was carried out at 285 °C. When NH_3 concentration was less than 15 m, both Nb_2O_5 and $K_4Nb_6O_{17}\cdot 3H_2O$ were identified by XRD, while only $K_4Nb_6O_{17}\cdot 3H_2O$ was identified above 15 m NH_3. Fig. 1a shows the XRD pattern of the product in 0.470 m Nb_2O_5-0.625 m KOH-15 m NH_3 mixed solution at 285 °C for 24 h. All XRD peaks could be identified as $K_4Nb_6O_{17}\cdot 3H_2O$. XRD peaks indexed (0k0), however, completely vanished after the calcination at 1000 °C as shown in Fig. 1b, although pure $K_4Nb_6O_{17}$ is stable even at 1200 °C and easily form $K_4Nb_6O_{17}\cdot 3H_2O$ by adsorbing moisture in air. It was found that 5 mol % of K^+ was replaced by NH_4^+ by chemical analysis. Therefore, it was suspected that the partial replacement of K^+ with NH_4^+ might degrade the thermal stability of $K_4Nb_6O_{17}$.

3.2. Nb_2O_5-KOH-NaOH-H_2O system

Fig. 2 shows XRD patterns of the products by the hydrothermal reactions of the solutions containing 0.470 m Nb_2O_5, 0.625 m KOH and 0.2–1.0 m NaOH at 285 °C for 24 h. XRD peaks corresponding to $K_4Nb_6O_{17}\cdot 3H_2O$ were observed together with that of sharp (003) peak of $NaNbO_3$ at NaOH concentrations of 0.2 and 0.25 m. When the NaOH concentration was 0.5 and 0.6 m, peaks of $K_4Nb_6O_{17}\cdot 3H_2O$ disappeared clearly, whereas those of $KNbO_3$ were observed together with those of $NaNbO_3$. Finally, only the peaks of $KNbO_3$ were observed at 1.0 m. These results suggested that NaOH promotes the formation of $K_4Nb_6O_{17}\cdot 3H_2O$ and $KNbO_3$, but it is difficult to form $K_4Nb_6O_{17}\cdot 3H_2O$ as single phase in Nb_2O_5-KOH-NaOH-H_2O system.

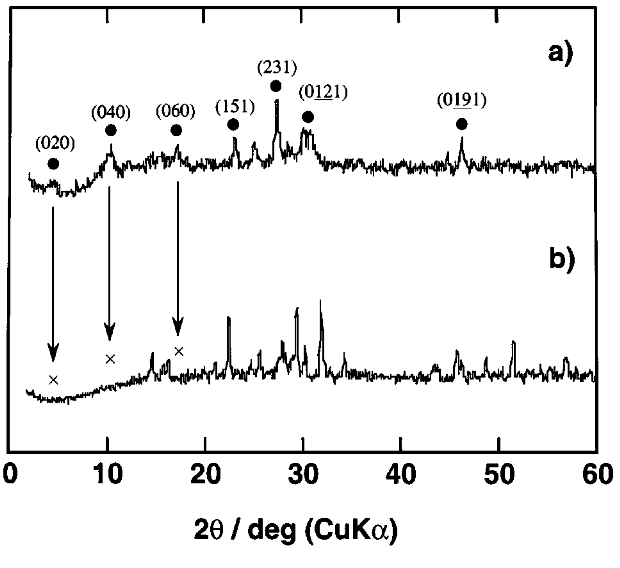


Figure 1 XRD patterns of products synthesized (a) by the hydrothermal treatment of 0.470 m Nb_2O_5-0.625 m KOH-15 m NH_3 at 285 °C and by calcination of (b) at 1000 °C (●: $K_4Nb_6O_{17}\cdot 3H_2O$).

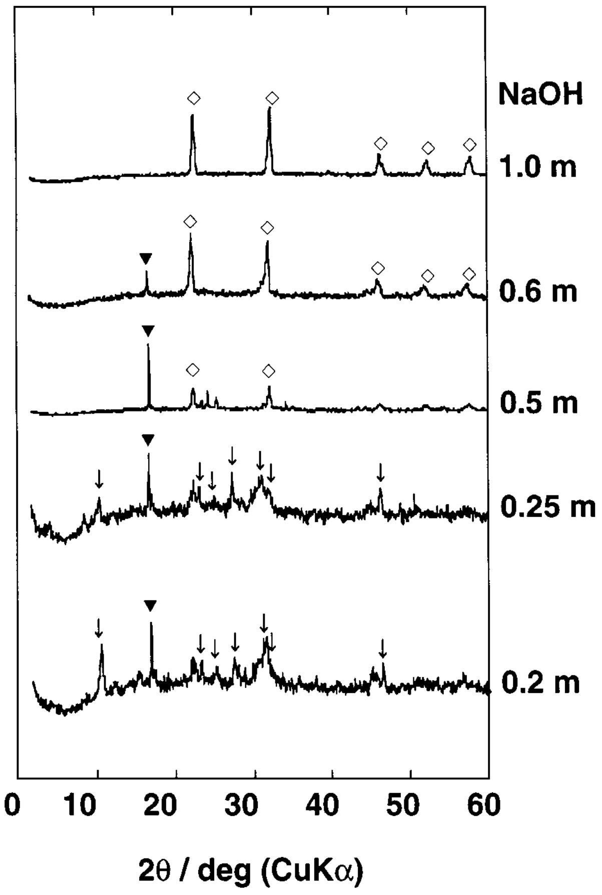


Figure 2 XRD patterns of products synthesized by the hydrothermal treatment of the mixtures containing 0.470 m Nb_2O_5, 0.625 m KOH and 0.2–1.0 m NaOH at 285 °C for 24 h (↓: $K_4Nb_6O_{17}\cdot 3H_2O$, ▼: $NaNbO_3$, ◇: $KNbO_3$).

3.3. Nb_2O_5-KOH-H_2O system

Fig. 3 shows XRD patterns of the products by the hydrothermal reactions of the solutions containing 0.470 m Nb_2O_5 and 0.5–3.5 m KOH at 285 °C for 24 h. In 0.5 m KOH solution, Nb_2O_5 was left intact and no product was found. In 1.0 and 2.5 m KOH solutions, peaks corresponding to Nb_2O_5 completely disappeared and all peaks could be identified as $K_4Nb_6O_{17}\cdot 3H_2O$. On the other hand, the peaks corresponding to $KNbO_3$ appeared in 3.0 m KOH solution and those corresponding to only $KNbO_3$ were observed in 3.5 m KOH solution. By and large, KOH-H_2O system seemed to be adequate to produce single phase of $K_4Nb_6O_{17}\cdot 3H_2O$ and/or $KNbO_3$.

Stability of each potassium niobium oxide at different KOH concentrations and temperatures was investigated in more detail. Fig. 4 shows the formation diagram of powders synthesized for 24 h in Nb_2O_5-KOH-H_2O system. When the temperature was below 175 °C, Nb_2O_5 was left intact, while all products were dissolved in 2.0–3.0 m KOH at 200 °C. $K_4Nb_6O_{17}\cdot 3H_2O$ could be observed in wide region of the KOH concentration from 1.0 to 3.0 m and the temperature from 200 to

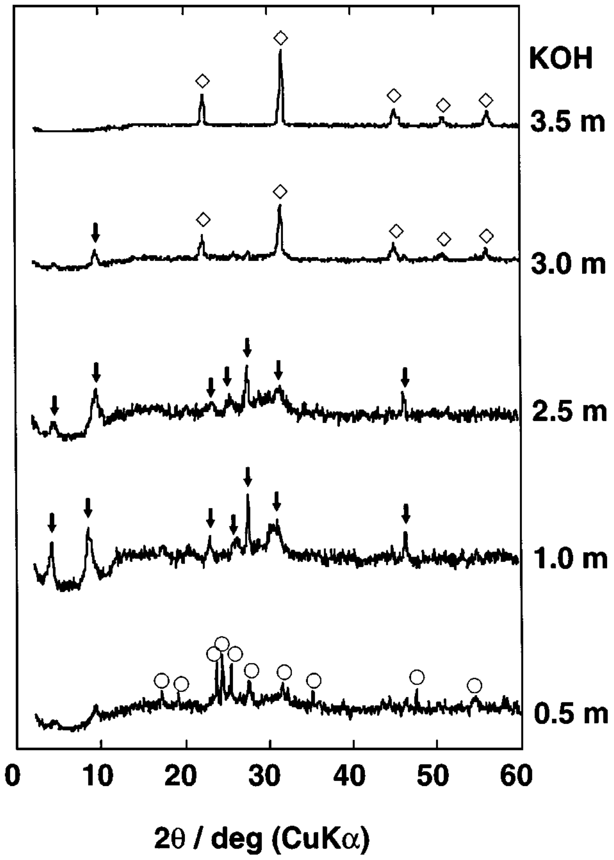


Figure 3 XRD patterns of products synthesized by the hydrothermal treatment of 0.470 m Nb_2O_5 in 0.5–3.5 m KOH at 285 °C for 24 h (○: Nb_2O_5, ↓: $K_4Nb_6O_{17}\cdot3H_2O$, ◇: $KNbO_3$).

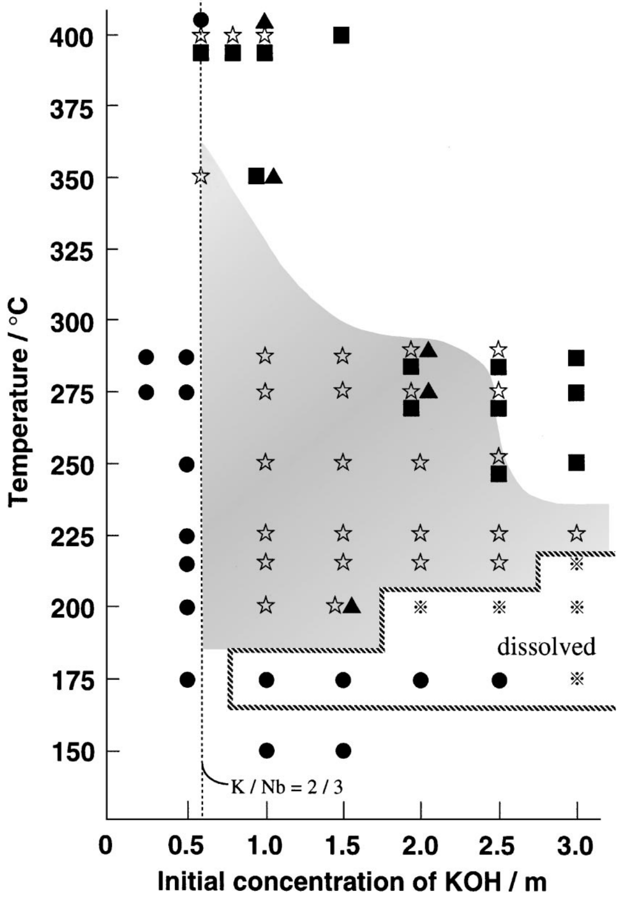


Figure 4 Formation diagram of powders synthesized at various temperatures for 24 h in Nb_2O_5-KOH-H_2O system (●: Nb_2O_5, ☆: $K_4Nb_6O_{17}\cdot3H_2O$, ■: $KNbO_3$, ▲: $K_8Nb_{18}O_{49}$).

350 °C. Synthesis of single phase $K_4Nb_6O_{17}\cdot3H_2O$ was succeeded mainly in the region of KOH concentration from 1.0 to 1.5 m and the temperature from 220 to 285 °C. $KNbO_3$ tended to form at the region relatively high temperature and high KOH concentration. Single phase $KNbO_3$ existed in 3.0 m KOH above 250 °C. $K_8Nb_{18}O_{49}$ was also observed above 285 °C together with $K_4Nb_6O_{17}$ and/ or $KNbO_3$.

3.4. Nb_2O_5-KOH-CH_3OH-H_2O system

It is well known that size and morphology of ceramic powders can be controlled using alcoholic solvent in the hydrothermal synthesis. Generally, organic solutions have lower dielectric constants which result in lower solubility of inorganic material in the solution. Consequently the products would be expected to be smaller. Further, organics solvents possess lower surface tension which result in soft agglomeration of the powders. Fig. 5 shows the formation diagram of powders synthesized in Nb_2O_5-KOH-CH_3OH-H_2O system at 285 °C for 24 h. Here the volume percent of methanol in the solvent was changed from 0 to 100%. Without methanol, $K_4Nb_6O_{17}\cdot3H_2O$ was produced in 1.0 to 1.5 m KOH solutions as already shown in Fig. 4. In these KOH concentration region $K_4Nb_6O_{17}\cdot3H_2O$ existed as a single phase until the volume fraction of methanol of 50%. When the volume fraction of methanol was over 75%, $KNbO_3$ began to form instead of $K_4Nb_6O_{17}\cdot3H_2O$. The decrease of water concentration is considered to promote the formation of $KNbO_3$ according to following equilibrium.

$$K_4Nb_6O_{17} + 2KOH \rightleftarrows 6KNbO_3 + H_2O \qquad (1)$$

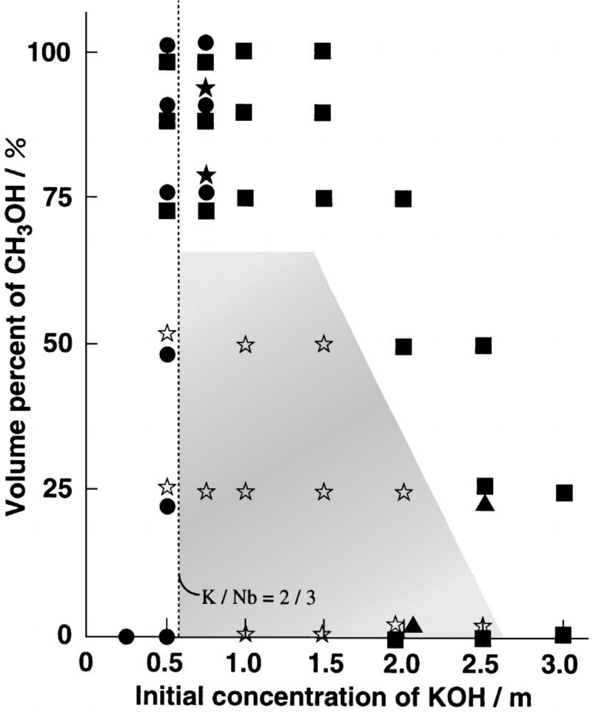
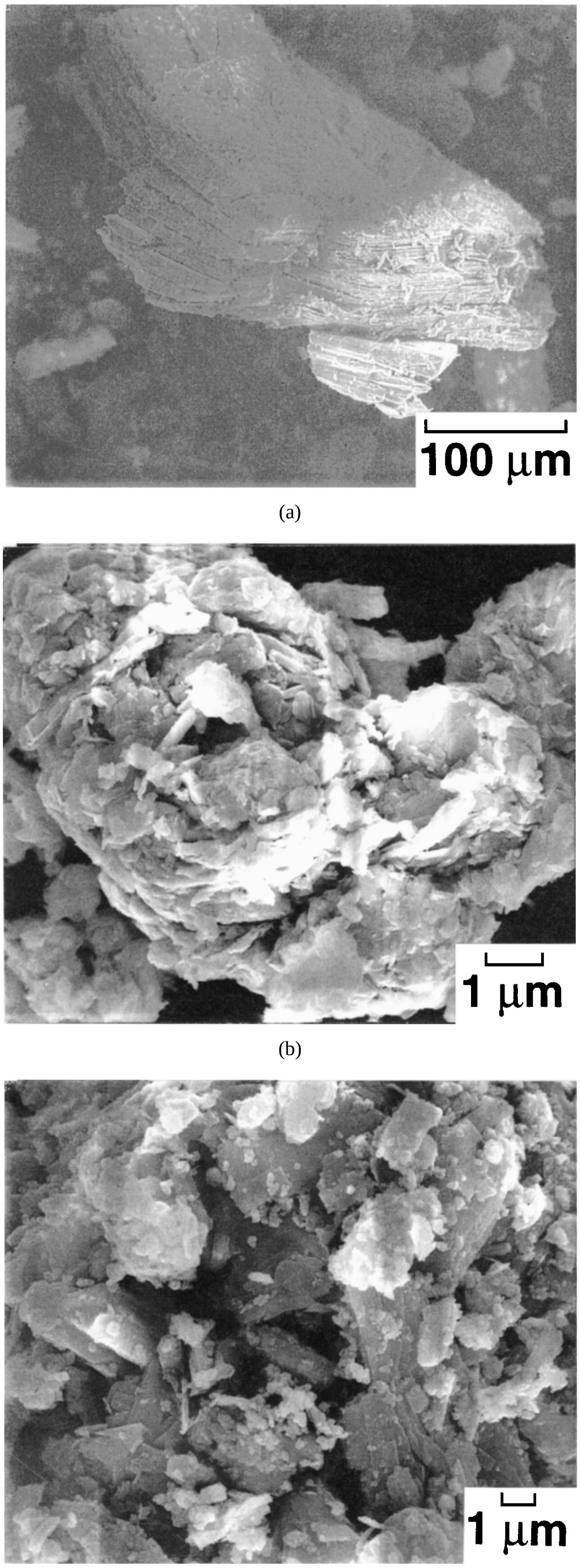


Figure 5 Formation diagram of powders synthesized at 285 °C for 24 h in Nb_2O_5-KOH-H_2O-CH_3OH system (●: Nb_2O_5, ☆: $K_4Nb_6O_{17}\cdot3H_2O$, ★: $K_4Nb_6O_{17}$, ■: $KNbO_3$, ▲: $K_8Nb_{18}O_{49}$).



(a)

(b)

(c)

Figure 6 Scanning electron micrographs of $K_4Nb_6O_{17}{\cdot}3H_2O$ synthesized by (a) solid state reaction at 1200 °C for 2 h (b) hydrothermal reaction in 1.0 m KOH solution at 285 °C for 24 h (c) hydrothermal reaction with 50 vol % of methanol.

TABLE I BET specific surface areas of $K_4Nb_6O_{17}{\cdot}3H_2O$ prepared by (a) solid state reaction and hydrothermal reactions in 1.0 m KOH solution (b) without and (c) with 50 vol % methanol

Sample	Specific surface area (m^2g^{-1})
Solid state reaction	6.6
Hydrothermal reaction without methanol	12.5
Hydrothermal reaction with methanol	23.8

The effect of addition of methanol on the particle size and morphology was investigated by SEM. Fig. 6 shows the scanning electron micrographs of $K_4Nb_6O_{17}{\cdot}3H_2O$ synthesized by (a) conventional solid state reaction at 1200 °C for 2 h (b) hydrothermal reaction in 1.0 m KOH solution at 285 °C for 24 h (c) hydrothermal reaction with 50 vol % of methanol. An obvious fact can be seen that the particle size synthesized by hydrothermal method is almost ten times smaller than that synthesized by solid state reaction. In case hydrothermal method, both powders consisted of platelet particles, but the powder prepared in 50 vol % methanol contained much smaller primary particles than that in water.

BET surface areas of $K_4Nb_6O_{17}{\cdot}3H_2O$ synthesized in 1.0 m KOH solution at 285 °C for 24 h with and without 50 vol % of methanol are shown in Table I together with that prepared by conventional solid state reaction at 1200 °C using Nb_2O_5 and K_2CO_3. The order of BET surface area of the samples prepared by hydrothermal method with and without methanol were four and two times larger than that prepared by solid state reaction, indicating that hydrothermal synthesis is useful to increase the surface area of $K_4Nb_6O_{17}{\cdot}3H_2O$ especially when methanol is coexisting in the solvent.

4. Conclusions

From the results of tests described, the following conclusions may be drawn:

1. Nb_2O_5-KOH-H_2O system was useful to produce single phase of $K_4Nb_6O_{17}{\cdot}3H_2O$ and/or $KNbO_3$.
2. Single phase $K_4Nb_6O_{17}{\cdot}3H_2O$ succeeded to be produced in Nb_2O_5-KOH-H_2O system mainly at the region of KOH concentration from 0.9 to 1.4 m and the temperature from 220 to 285 °C, whereas single phase $KNbO_3$ was formed in 3.0 m KOH above 250 °C.
3. By adding methanol in the solvent $K_4Nb_6O_{17}{\cdot}3H_2O$ with smaller particle size and larger BET surface area was obtained.

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