

The phase relationship of Na⁺-beta-aluminas synthesized by a sol-gel process in the ternary system Na₂O-Al₂O₃-Li₂O

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Na⁺-β"-alumina was synthesized by a sol-gel process in the ternary system Li₂O-Na₂O-Al₂O₃. In order to research the phase formation of Na⁺-β"-alumina by varying the composition and calcination temperature in the range of pH 1-9, the sodium concentration was varied within the molar ratio range, [Na₂O] : [Al₂O₃] = 1 : 4-1 : 8, and the calcination temperature was varied between 1100-1500 °C. The phase fraction of Na⁺-β"-alumina indicated a tendency to increase continually to 1500 °C. It was shown that up to about 88% in the molar ratio of [Na₂O] : [Al₂O₃] = 1 : 5, the transient eutectic liquid in the Li₂O-Na₂O-Al₂O₃ system at about 1460 °C promoted the transformation of β-alumina to β"-alumina at higher temperatures. The average particle size of the synthesized powder was 300-500 nm.

Key words: Na⁺-β"-alumina, Sol-Gel process, Sodium/Sulfur battery.

Introduction

The sodium sulfur battery has been, since its development in the 1980s, one of the most promising candidates for energy storage applications. It works based on the electrochemical reaction between sodium and sulfur and the formation of sodium polysulfide and exhibits a high power and energy density, temperature stability, and furthermore low cost because of its abundant low cost raw materials and suitability for high volume mass production. The battery is composed of a sodium anode, sulfur cathode and Na⁺-β"-alumina as electrolyte and separator simultaneously [1-3]. Na⁺-β"-alumina is a superionic conductor of Na⁺ ions and has the highest level of ionic conductivity among ceramic materials. It has been used as a solid electrolyte in a sodium sulfur battery and as an electrode in an alkali metal thermoelectric converter (AMTEC). Applications of this material are being extended mainly to sensors and proton conductors by exchanging Na⁺ ions with other conductive ions such as Ag⁺, NH₄⁺, H₃O⁺, etc. There are two parent phases: designated β-alumina and β"-alumina. The β-alumina phase has the theoretical formula Na₂O·11Al₂O₃, or NaAl₁₁O₁₇ [4, 5], and the β"-alumina phase has the formula Na₂O·5Al₂O₃, or NaAl₅O₈ [6]. According to the Na₂O-Al₂O₃ phase diagram proposed by Fally *et al.* [7], the β + β" phases coexist in a region corresponding to the formula Na₂O·nAl₂O₃ (5.33 ≤ n ≤ 8.5). The crystalline structure of β"-alumina is a rhombohedral structure with an R3m space group with lattice constants of 'a' = 5.614 and 'c' = 33.85 Å. Generally, its 'a' axis is similar to that of the β-

alumina structure, but the length of its 'c' axis is 1.5 times longer and the concentration of alkaline ions on the conduction plane is higher. Therefore, β"-alumina shows much higher ionic conductivity [8, 9].

Conventional methods of synthesizing β- and β"-alumina suffer from two major shortcomings: (a) inclusion of impurities during ball milling giving rise to significant loss in electrical conductivity and a reduced ionic transport number of the solid electrolyte, and (b) loss of sodium oxide as well as grain growth during high-temperature sintering, leading to a higher resistance and poor mechanical strength [10]. In order to overcome these problems, novel methods such as sol-gel processing, solution spray-drying, freeze-drying, co-precipitation etc. are being developed as alternatives to a solid state reaction.

The sol-gel method for producing ceramics is an emerging route that has high promise. Preparation of β"-alumina by this method would have the following advantages over the conventional powder route: (a) being a solution method, molecular-level mixing of reactant species is ensured, which results in a high degree of homogeneity, (b) it yields high-surface-area powders, which can be sintered at lower temperatures compared with conventional procedures and (c) it gives relatively high purity products because of the absence of grinding and milling steps. In this study, Na⁺-β"-aluminas were synthesized by a sol-gel process, using aluminum nitrate nonahydrate and sodium hydroxide as precursors. The phase fraction and particle size distribution of Na⁺-β"-aluminas according to varying composition, calcination temperature, and solution pH were studied.

Experimental

Na⁺-β"-aluminas were synthesized by a sol-gel process

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in the ternary system Na₂O-Al₂O₃-Li₂O in which the Li₂O content is fixed at 0.4 w/o. Aluminum nitrate nonahydrate (Al(NO₃)₃·9H₂O) and sodium hydroxide (NaOH) were used as starting materials for the alumina and sodium oxide source, respectively. Lithium carbonate (Li₂CO₃) and ethyl alcohol (C₂H₅OH) were used as a stabilizer and dispersing agent, respectively, and deionized water was used as the solvent. Appropriate amounts of aluminum nitrate nonahydrate, sodium hydroxide, lithium carbonate, and ethyl alcohol were dissolved in deionized water. The mixture was pH-controlled by ammonia water (NH₄OH) in the range of 1–9 at 80 °C, and the pH controlled mixture was aged for one day at 25 °C. Then the mixture was oven-dried for one day at 90 °C, and calcined at 1200 °C for 2 h. In order to analyze the phase fraction of β''-alumina according to varying composition and calcination temperature in the range of pH 1–9, the sodium concentration was varied within the molar ratio range, [Na₂O] : [Al₂O₃] = 1 : 4–1 : 8, and the calcination temperature was changed at 1100–1500 °C. Fig. 1 shows the procedure of the sol-gel process used in this study.

The microstructure and particle size were determined by a scanning electron microscope (SEM ; Model JSM-6380, JEOL, JAPAN) and particle size analyzer (PSA; Brookhaven Instruments Co.). Phase compositions of calcined samples were measured by a X-ray diffractometer (D/max 2200, Rigaku, Japan). The relative amounts of phases were determined by calculating the line intensities of well-separated peaks of each phase using the following equations [11, 12]. :

$$\% \text{ of } \alpha = \frac{f(\alpha)}{f(\alpha) + f(\beta) + f(\beta'')} \times 100 \quad (1)$$

$$\% \text{ of } \beta = \frac{f(\beta)}{f(\alpha) + f(\beta) + f(\beta'')} \times 100 \quad (2)$$

$$\% \text{ of } \beta'' = \frac{f(\beta'')}{f(\alpha) + f(\beta) + f(\beta'')} \times 100 \quad (3)$$

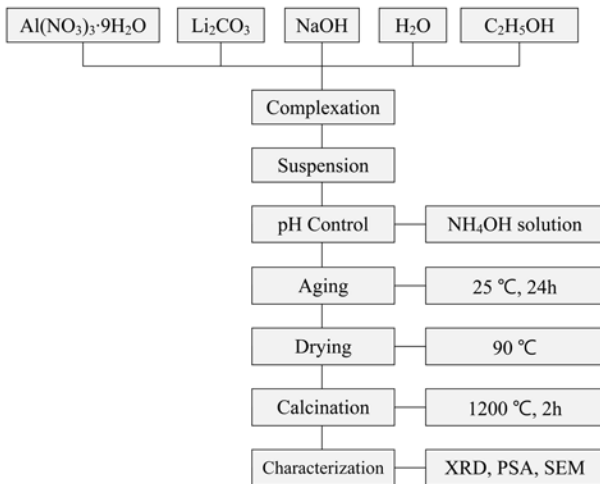


Fig. 1. Schematic diagram of the procedure of the sol-gel process used in this study.

$$f(\alpha) = \frac{1}{2} \left\{ I_{\alpha(104)} \times \frac{10}{9} + I_{\alpha(113)} \right\} \quad (4)$$

$$f(\beta) = \frac{1}{3} \left\{ I_{\beta(012)} \times \frac{10}{3} + I_{\beta(026)} \times \frac{10}{3.5} + I_{\beta(017)} \times \frac{10}{5.5} \right\} \quad (5)$$

$$f(\beta'') = \frac{1}{2} \left\{ I_{\beta''(011)} \times \frac{10}{4} + I_{\beta''(2010)} \times \frac{10}{8} \right\} \quad (6)$$

Where, $I_{\alpha(104)}, \alpha(113)$ = X-ray intensities of (104), (113) planes of the α-alumina phase

$I_{\beta(012), \beta(026), \beta(017)}$ = X-ray intensities of (012), (026), (017) planes of the β-alumina phase

$I_{\beta''(011), \beta''(2010)}$ = X-ray intensities of (011), (2010) planes of the β''-alumina phase

Results and Discussion

Fig. 2 shows schematic structures of β-alumina and β''-alumina, which contains a tightly packed spinel block and loosely arranged conduction slab where the sodium ions can conduct rapidly. Three spinel blocks are contained in each β''-alumina unit cell, while β-alumina has two spinel blocks per unit cell. β''-alumina has a higher sodium content in the conduction slab than β-alumina, and therefore is more conductive than β-alumina.

During the sol-gel process used in this study, the following reactions occurred. :

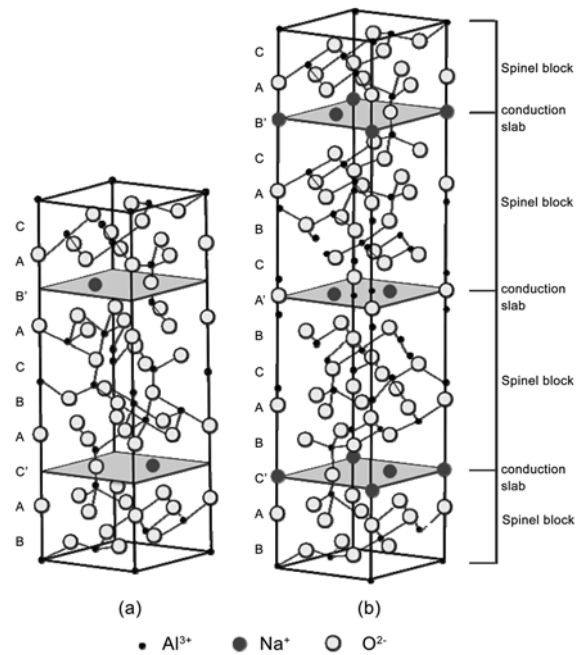
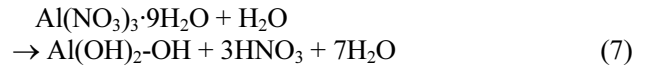
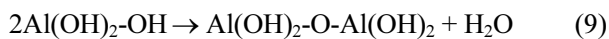
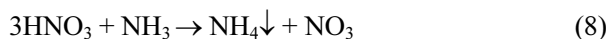


Fig. 2. Perspective drawings of the idealized structures of (a) β-alumina (b) β''-alumina [8, 9].



When aluminum nitrate nonahydrate was dissolved in the deionized water, the solution became acidic because of the formation of nitric acid by the hydrolysis of aluminum nitrate nonahydrate. The nitric acid that forms acts as an acid catalyst and participates in the hydrolysis and condensation reactions of the different aluminum nitrate nonahydrates. When an ammonia solution is added to the solution of aluminum nitrate nonahydrate and deionized water, ammonium (NH_4) forms as a white precipitate. Ammonium was dissolved in the reaction system by stirring, and its ionized proton participates in the condensation reaction.

In order to study the phase fraction according to varying the composition in the range of pH 1-9, the calcination temperature was fixed at 1200 °C, and the sodium concentration was varied within the molar ratio range of $[\text{Na}_2\text{O}] : [\text{Al}_2\text{O}_3] = 1 : 4-1 : 8$. The schematic results are shown in Fig. 3. In the molar ratio $[\text{Na}_2\text{O}] : [\text{Al}_2\text{O}_3] = 1 : 8$, part of a α -alumina phase was observed, and the phase fraction of β'' -alumina was less than in other compositions, because it was a Na_2O -deficient composition. In all compositions,

generally, the phase fraction of β'' -alumina was highest at pH 1 and pH 9, showing values between 50 and 60%.

Also, the phase fraction of β'' -alumina largely depended on the calcination temperature. The results in terms of the calcination temperature are shown Fig. 4. The sodium concentration was varied within the molar ratio range, $[\text{Na}_2\text{O}] : [\text{Al}_2\text{O}_3] = 1 : 4-1 : 6$, and the calcination temperature was changed at 1100-1500 °C. Fig. 4 shows that, in all compositions, the phase fraction of β'' -alumina was highest at 1500 °C.

Fig. 5 shows the β'' -alumina fraction at pH 1, pH 5, and pH 9 at each composition, and indicates a tendency of the β'' -alumina fraction to rapidly increase at 1500 °C.

Fig. 6 shows the XRD patterns of synthesized powders according to calcination temperatures of 1100-1500 °C at pH 1, pH 5, and pH 9 at the molar ratio $[\text{Na}_2\text{O}] : [\text{Al}_2\text{O}_3] = 1 : 5$. All XRD patterns of synthesized powders appeared similar in shape, and the growth of the (0111), (2010) plane corresponding to β'' -alumina phase was observed with rising temperature. This is explained by the transformation of β -alumina to β'' -alumina, a type of transformation of β'' -alumina that is a distinctive feature in Li_2CO_3 -stabilized systems.

It has been reported that β'' -alumina densifies in a few minutes, and such rapid densification is attributed to the ternary transient eutectic liquids that form at 1460-1470 °C

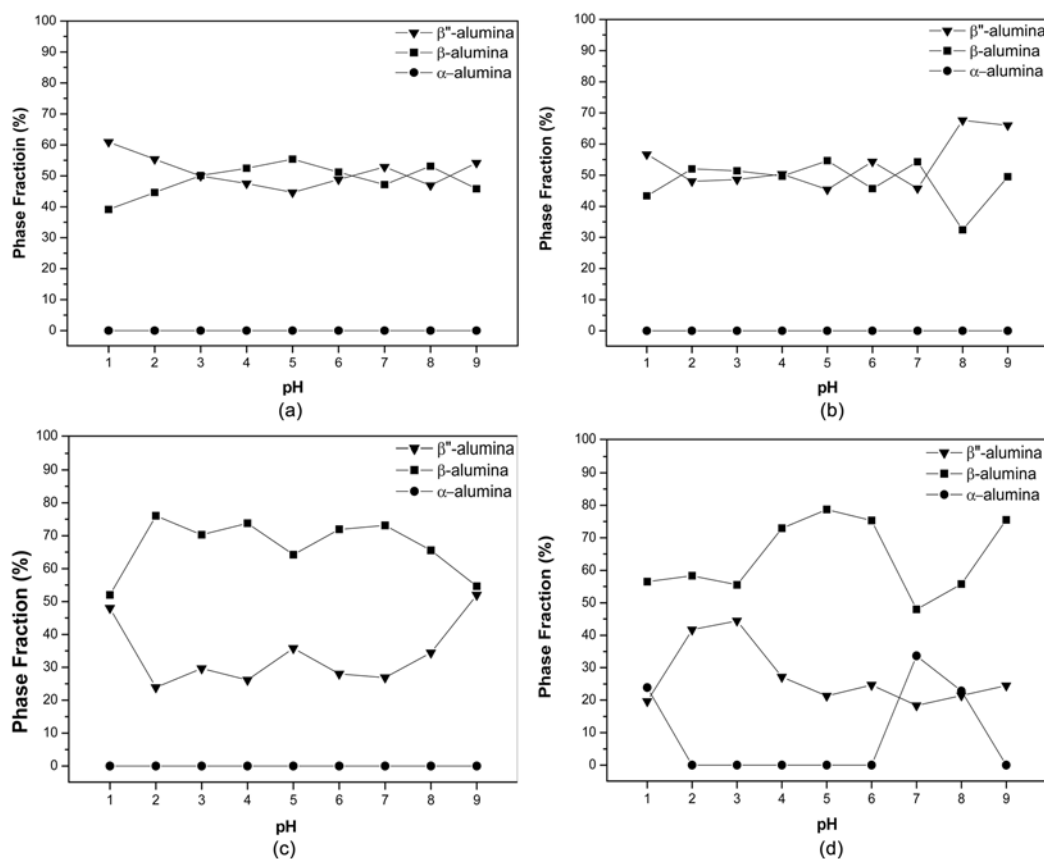


Fig. 3. Phase fraction of calcined powders according to varying the composition; the molar ratio $[\text{Na}_2\text{O}] : [\text{Al}_2\text{O}_3] =$ (a) 1 : 4 (b) 1 : 5 (c) 1 : 6 and (d) 1 : 8, calcined at 1200 °C.

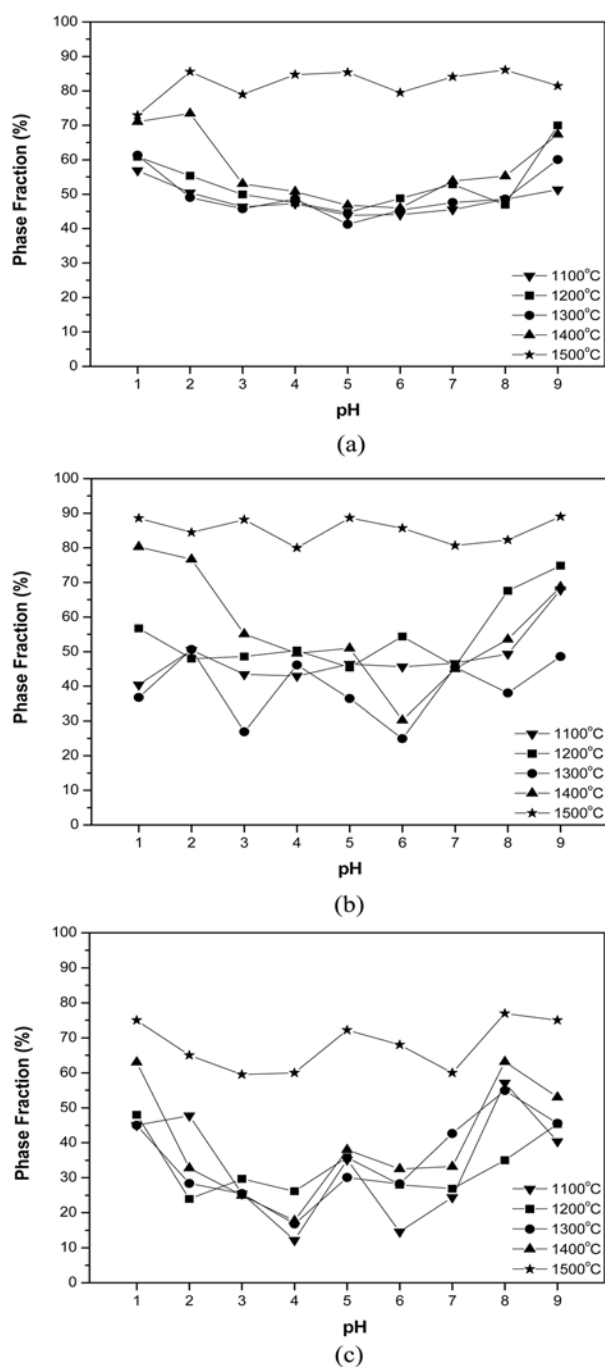


Fig. 4. Phase fraction of β'' -alumina according to the calcination temperature; the molar ratio $[\text{Na}_2\text{O}] : [\text{Al}_2\text{O}_3] =$ (a) 1 : 4 (b) 1 : 5 and (c) 1 : 6.

in the $\text{LiAlO}_2\text{-NaAlO}_2\text{-Al}_2\text{O}_3$ system [13]. Even though compositions used in this study are not exactly in accordance with the eutectic composition in the $\text{LiAlO}_2\text{-NaAlO}_2\text{-Al}_2\text{O}_3$ system, it is well-known that eutectics do not form exactly at the eutectic composition. Eutectics can be formed in regions of local inhomogeneity and have hardly been observed in micrographs because the transient eutectic liquid has a high solid solubility, and it disappears after complete homogenization caused by a diffusional process [14].

Stabilization of β'' -alumina is basically the substitution

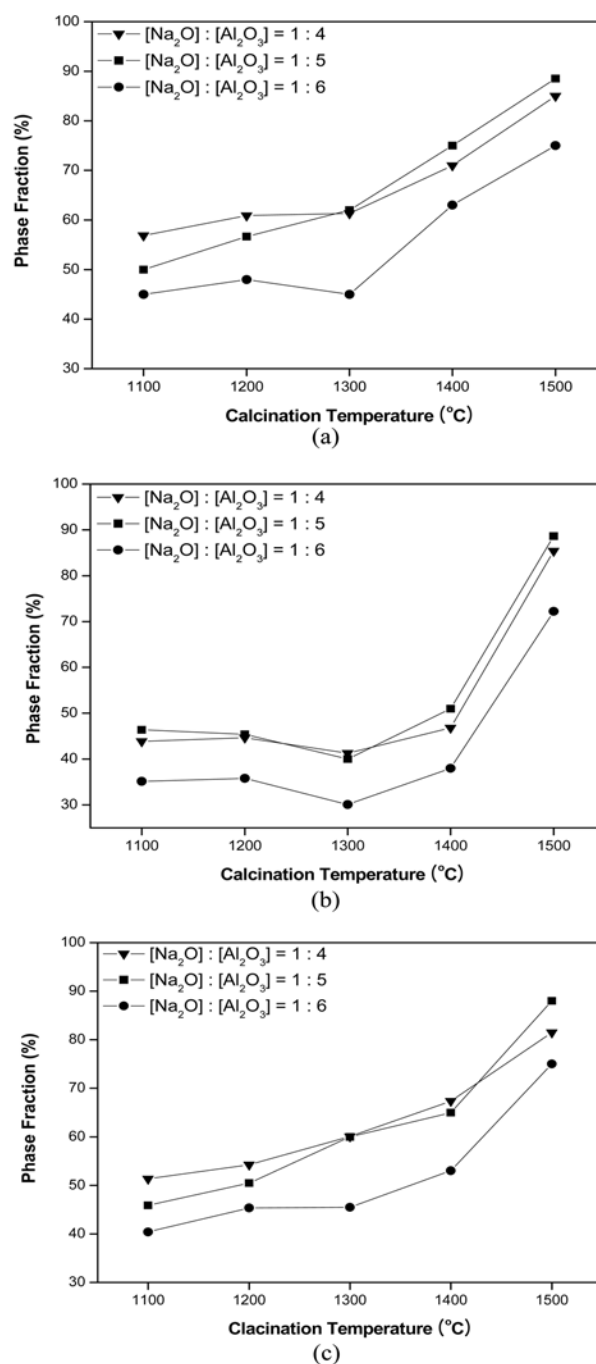


Fig. 5. Phase fraction of β'' -alumina at (a) pH 1 (b) pH 5 and (c) pH 9 according to the calcination temperature.

of the Al^{3+} ions by the stabilizing cations, and the compensating Li^+ ions substitute octahedral Al^{3+} ions in the spinel block [15, 16]. Thus, it can be thought that the β'' -alumina phase formation is mainly controlled by the diffusion of stabilizing ions. The ternary eutectic liquid is expected to be the fast path for diffusion, enhancing the transformation of β -alumina to β'' -alumina.

Fig. 7 shows the particle size of synthesized powders at molar ratios of $[\text{Na}_2\text{O}] : [\text{Al}_2\text{O}_3] = 1 : 4$ – $1 : 8$, at a calcination temperature at 1200 °C. The largest particle size, about

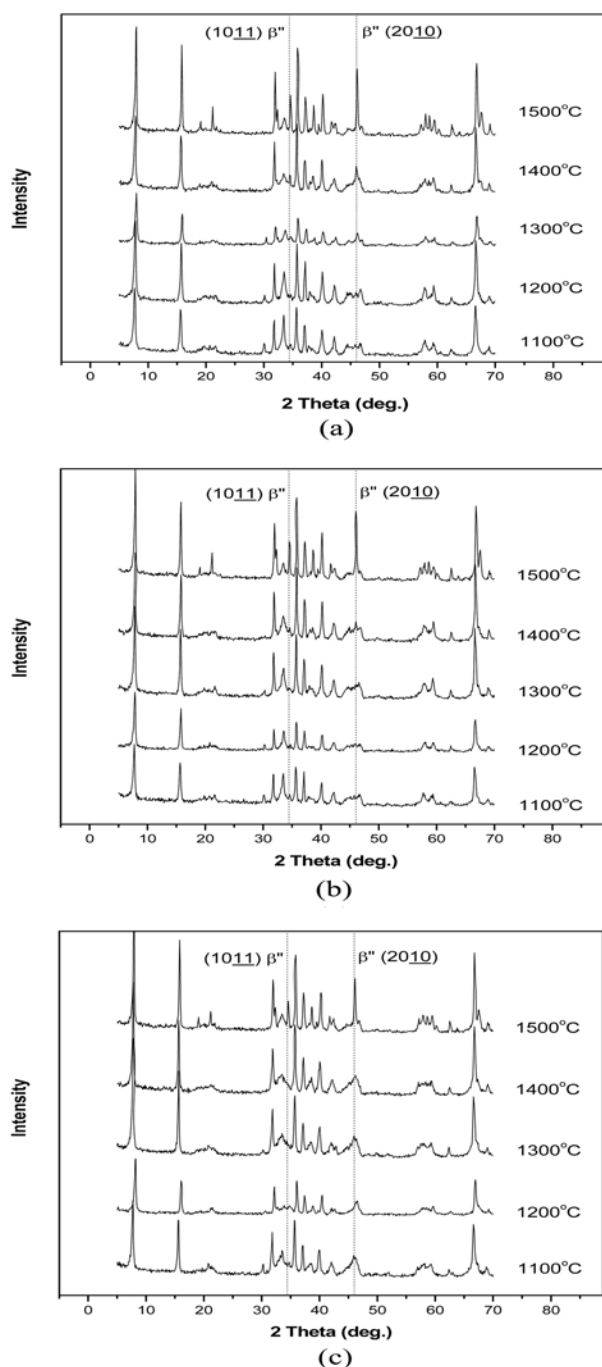


Fig. 6. X-ray diffraction patterns according to calcination temperature of calcined powders at (a) pH 1 (b) pH 5 and (c) pH 9; herein the molar ratio was $[\text{Na}_2\text{O}] : [\text{Al}_2\text{O}_3] = 1 : 5$.

870 nm, was observed at pH 1 in the molar ratio $[\text{Na}_2\text{O}] : [\text{Al}_2\text{O}_3] = 1 : 5$. The mean particle size was about 400 nm. The particle size of the synthesized powders was smallest in pH 3-4 and pH 8-9, because of the solubility of aluminum hydroxide ($\text{Al}(\text{OH})_3$), as shown in Fig. 8, which shows the solubility curve of $\text{Al}(\text{OH})_3$. The solubility curve of aluminum hydroxide has a very sudden incline in the ranges of pH 3-4 and pH 8-9, showing that although the change in pH was small, the solution was saturated at once, and quick precipitation occurred. As a result, the initial pre-

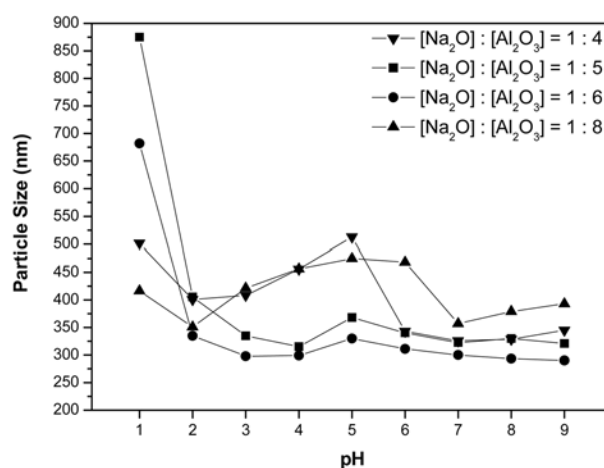


Fig. 7. Particle size of powders calcined at 1200 °C.

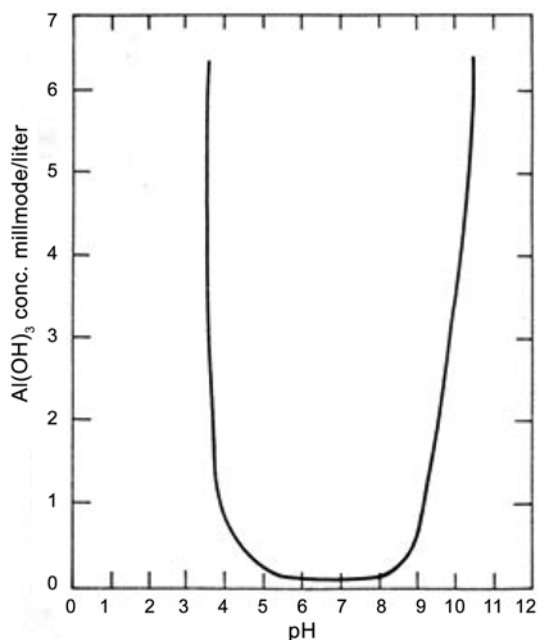


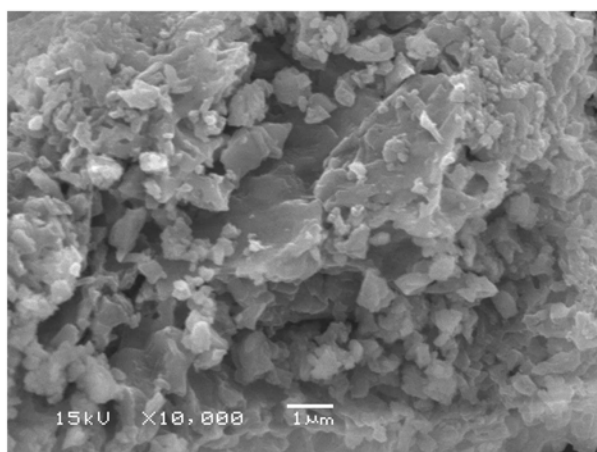
Fig. 8. Solubility of $\text{Al}(\text{OH})_3$ as a function of pH [17].

cipitates were mostly colloid size, with a low degree of crystallinity. Colloidal aluminum hydroxides in the pH ranges 3-4 and pH 8-9 were hydrophilic and solidified easily to the gel, resulting in a small mean particle size.

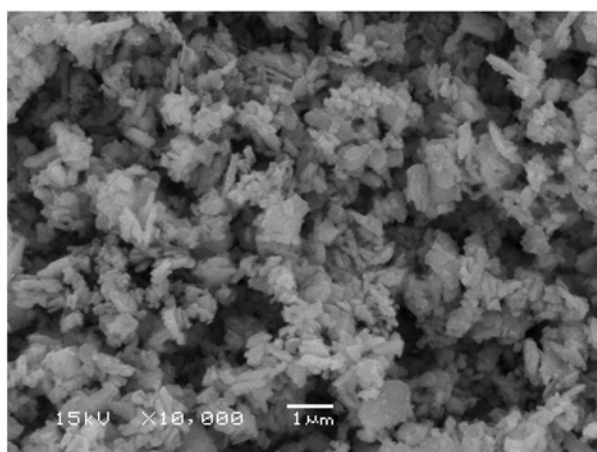
Fig. 9 shows SEM images of powders at pH 1 and pH 9 in the molar ratio $[\text{Na}_2\text{O}] : [\text{Al}_2\text{O}_3] = 1 : 5$ and calcination temperature of 1200 °C. Like the preceding results in Fig. 7, the powder at pH 9 shows a smaller crystalline size than that at pH 1.

Conclusions

In the present study, Na^+ - β'' -alumina was synthesized by a sol-gel process in Li_2O - Na_2O - Al_2O_3 ternary systems. The phase fraction of β'' -alumina according to the solution pH was analyzed to be highest at pH 1 and pH 9 at calcination temperatures of 1100-1500 °C and for most



(a)



(b)

Fig. 9. SEM images of powders at (a) pH 1 (b) pH 9 at the molar ratio [Na₂O] : [Al₂O₃] = 1 : 5, calcined at 1200 °C.

compositions, that is [Na₂O] : [Al₂O₃] = 1 : 4-1 : 8. The β"-alumina phase fraction continually increased with rising temperature. It increased especially rapidly between 1400-1500 °C, which could be explained by the transient eutectic liquid in the Li₂O-Na₂O-Al₂O₃ system promoting the transformation of β-alumina to β"-alumina at those higher temperatures. The mean particle size of synthesized powders

was 300-500 nm, and the powder at pH 1 in the molar ratio [Na₂O] : [Al₂O₃] = 1 : 5 had the largest particle size, about 870 nm. Also, the particle size in the range of pH 3-4 and 8-9 was smaller than other pH ranges. This can be explained by the solubility of aluminum hydroxide, which is intensively affected by pH.

Acknowledgements

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