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Effect of precursors on the morphology of lithium aluminate prepared by hydrothermal treatment

SANG WOON KWON
KALIMER Development Team, Korea Atomic Energy Research Institute,
150 Dukjin-dong Yusong-gu, Taejon 305-353, South Korea

SEUNG BIN PARK*
Department of Chemical Engineering, Korea Advanced Institute of Science & Technology,
373-1 Kusong-dong Yusong-gu, Taejon 305-701, South Korea
E-mail: sbpark@hanbit.kaist.ac.kr

Hydrothermal treatment method was proposed to prepare pure $LiAlO_2$ with fibrous crystal morphology and the effect of precursors on the morphology of lithium aluminate was investigated. Lithium butoxide-aluminum butoxide system gave mostly rod-like β-$LiAlO_2$ crystal. As the length of alkoxy group decreases, the fraction of plate shape crystals was increased and boehmite was dominant crystal phase. Needle-shape β-$LiAlO_2$ was produced from lithium nitrate-aluminum butoxide-sodium hydroxide system with the mole ratio of 6 : 1 : 3, respectively. β-$LiAlO_2$ prepared by hydrothermal treatment was transformed to γ-$LiAlO_2$ at 750–850°C. The specific surface area of γ-$LiAlO_2$ powders was above 10 m^2/g.

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1. Introduction

Lithium aluminate, $LiAlO_2$, is a potential candidate for tritium breeder of fusion reactor or electrolyte matrix of molten carbonate fuel cell due to its chemical and thermal stability as well as low radiation damage problem [1–5]. Three allotropic forms of $LiAlO_2$ are known: α-, β-, and γ-$LiAlO_2$, which are hexagonal, monoclinic, and tetragonal structures, respectively. γ-$LiAlO_2$ is the most stable polymorph and α- or β-$LiAlO_2$ is transformed to γ-$LiAlO_2$ at elevated temperature.

There are basically two methods to prepare lithium aluminate. One is a solid state reaction method [3, 4, 6] and the other is a wet chemical method such as sol-gel process [1, 7, 8]. The sol-gel method has advantages over the solid state reaction method in intimate mixing of reactants, high purity, high surface area of the product particles, and low processing temperature [9, 10].

The morphology control of ceramic particle is important because the morphology of the ceramic particle affect the characteristics of the final product. However, the optimum morphology of the lithium aluminate particle is yet to be determined for long-term fuel cell application and fusion reactor breeder material [4]. Long rod shaped or fibrous lithium aluminate forming a fine porous structure is especially desirable for strengthening the matrix of molten carbonate fuel cell [11].

Only a few methods of preparing fibrous lithium aluminate are proposed. The method by drawing from a melt is difficult to maintain the lithium and aluminum ratio during heating at high temperature. The method by filling a micromold fiber with a mixture of lithium and aluminum precursors and burning out the micromold was reported [12]. But impurities such as binder, plasticizer were added during mixing of precursors and high temperature was needed for burning the micromold. Needle shape β-$LiAlO_2$ was obtained by the solid state reaction between lithium hydroxide and alumina in alkali hydroxide [11, 13].

Hydrothermal preparation has been used to make fine powders. The starting materials are metal powders or chips, gel, solutions, solids, and oxides [4]. Kutty *et al.* prepared $CaTiO_3$ fine powders by the hydrothermal method and claimed that the temperature of preparation was reduced and the reactivity of the materials was enhanced [14]. Hydrothermal treatment method has advantages in reducing the processing temperature and yielding nearly site-ordered phase and producing fine crystalline powders [15].

In this paper, we proposed a hydrothermal method to prepare pure $LiAlO_2$ with fibrous crystal morphology and examine the effect of various combinations of lithium and aluminum precursors on the morphology.

2. Experimental procedure

2.1. Preparation of samples for hydrothermal treatment

Table I is a list of reagents used in this experiment. All reagents were used without further purification except alcohols from which moisture was removed by molecular sieve 3A. Table II shows a list of stoichiometric samples by varying the combination of lithium

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[*] Author to whom all correspondence should be addressed.

TABLE I Reagents used for the preparation of hydrothermal treatment samples

Reagents	Formula	Contents	Manufacturors
Lithium Methoxide	$Li(OCH_3)$	98(%)	Aldrich
Aluminum Methoxide	$Al(OCH_3)_3$	99.9	High Purity Chem
Lithium Ethoxide	$Li(OC_2H_5)$	95	Aldrich
Aluminum Ethoxide	$Al(OC_2H_5)_3$	97	Aldrich
Lithium Isopropoxide	$(CH_3)_2CHOLi$	95	Aldrich
Aluminium Isopropoxide	$[(CH_3)_2CHO]_3Al$	99.99+	Aldrich
Aluminium sec-Butoxide	$[C_2H_5CH(CH_3)O]_3Al$	97	Aldrich
Lithium Nitrate	$LiNO_3$	EP	Junsei Chem
Aluminum Nitrate, Enneahydrate	$Al(NO_3)_3 \cdot 9H_2O$	EP	Junsei Chem
Lithium Hydroxide, Monohydrate	$LiOH \cdot H_2O$	GR	Junsei Chem
Methanol	CH_3OH	99.8	Merck
Ethanol	C_2H_5OH	99.9	Hayman LTD
Isopropanol	$(CH_3)_2CHOH$	99.5+	Aldrich
Sec-Butanol	$CH_3CH(OH)CH_2CH_3$	99+	Merck

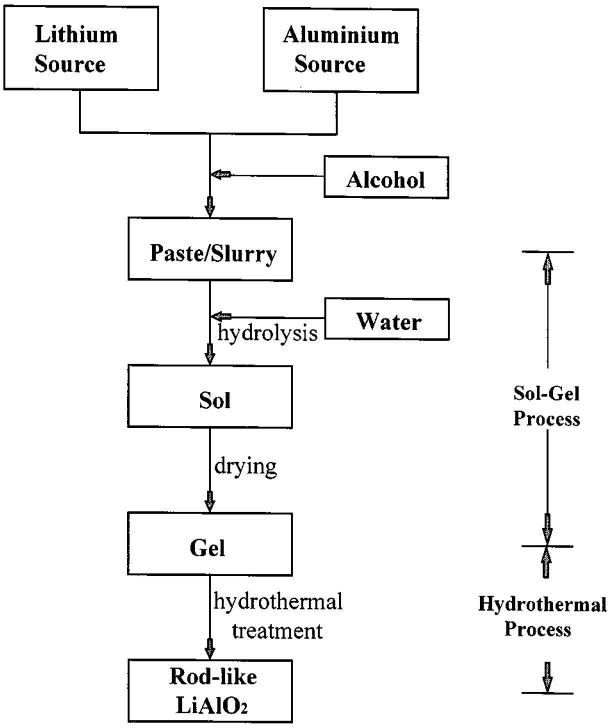

Figure 1 Flow chart of lithium aluminate fabrication route from lithium alkoxide/salt-aluminum alkoxide systems via hydrothermal treatment.

and aluminum precursors. In the first four samples, lithium alkoxide and aluminum alkoxide were mixed in the corresponding alcohol. The rest of three samples were made from either salt-salt or salt-alkoxide system.

The procedures for preparing lithium aluminate by stoichiometric mixing were summarized in Fig. 1. For each alkoxide-alkoxide system, lithium and aluminum alkoxides, 0.05 moles of each, were mixed with 100 ml of alcohol in a 3-neck flask. This mixture was stirred with a magnetic stirrer near at the boiling point of each alcohol. Lithium and aluminum alkoxides were mixed in the corresponding alcohol to avoid the possible exchange reaction between the alcohol and alkoxide group. All handling of alkoxides was carried out under argon gas to avoid moisture and carbon dioxide. Alkoxide-alkoxide mixture was hydrolyzed by five times of excess pure water to complete the reaction in two hours after mixing of alkoxides near at the boiling point of each alcohol. Hydrolysis product was gelled in an electric oven at 60 °C under air atmosphere.

Lithium nitrate or hydroxide and aluminum sec-butoxide were used as the salt-alkoxide system. Aluminum sec-butoxide diluted in butanol was hydrolyzed by aqueous lithium salt solution. A clear mixture of lithium nitrate and aqueous aluminum nitrate solution were used for the salt-salt system and treated hydrothermally as solution state.

In the nonstoichiometric samples listed in Table III, ratio of lithium precursor, aluminum precursor, and sodium hydroxide was 60, 10, and 30 mole %, respectively. For lithium nitrate-aluminum butoxide-sodium hydroxide systems, lithium salt, aluminum butoxide, sodium hydroxide were dissolved in water/butanol, butanol, and water, respectively, in separate beakers. Aluminum butoxide solution were mixed with aqueous lithium salt solution for one hour by stirring with a magnetic stirrer and hydrolyzed to form sol. When sodium hydroxide solution was added, the sol was destabilized and phase separation was occurred due to precipitation. The resulting slurry solution were well stirred and dried in an electric oven to reduce the volume. Another lithium nitrate-aluminum butoxide-sodium hydroxide samples were prepared. Lithium nitrate was dissolved in butanol instead of water, which was mixed

TABLE II Results after hydrothermal treatment of lithium alkoxide/salt-aluminum alkoxide/salt systems

			Hydrothermal treatment results	
Li precursor	Al precursor	Solvent (alcohol)	Crystal shape	Crystal phase
Methoxide	Methoxide	Methanol	Thin round platelet	β-$LiAlO_2$ + boehmite
Ethoxide	Ethoxide	Ethanol	Platelet major, rod minor	β-$LiAlO_2$ + boehmite
Iso-propoxide	Iso-propoxide	Iso-propanol	Rod shape major, plate minor	β-$LiAlO_2$ + boehmite
Sec-butoxide	Sec-butoxide	Sec-butanol	Rod shape	β-$LiAlO_2$
$LiNO_3$	Sec-butoxide	Sec-butanol	Platelet	Boehmite
LiOH dissolved in water	Sec-butoxide dissolved in sec-butanol		Rod shape	β-$LiAlO_2$
$LiNO_3$ dissolved in water	$Al(NO_3)_3$ dissolved in water		Rod shape	Boehmite

TABLE III Results after hydrothermal treatment of lithium salt-aluminum butoxide-sodium hydroxide systems

Li precursor	Al precursor	Additive	Mole ratio	Hydrothermal treatment results: Morphology	Hydrothermal treatment results: Crystal phase
$LiNO_3$ dissolved in butanol	Butoxide dissolved in butanol	NaOH	6 : 1 : 3	Rod shape	β-$LiAlO_2$
$LiNO_3$ dissolved in water	Butoxide dissolved in butanol	NaOH	6 : 1 : 3	Needle shape	β-$LiAlO_2$
$LiNO_3$ dissolved in water	Butoxide dissolved in butanol	NaOH	6 : 1 : 3	Rectangular column	β-$LiAlO_2$

with aluminum butoxide solutions, and the mixed solution was hydrolyzed by aqueous sodium hydroxide solution.

2.2. Hydrothermal treatment

Hydrothermal treatment for each sample was carried out in an autoclave at 250 °C. The autoclave was constructed with Teflon-lined stainless steel and the chamber volume of the reactor was 175 ml. Pyrex beaker filled with the sample is placed into the autoclave vessel. The pure water of 7 ml was poured into the outside the beaker as a hydrothermal medium. The autoclave was heated in an electric furnace at the rate of 3°C/min. Holding 24 hours after reaching at 250°C, the autoclave was quenched and opened. Product was washed with pure water and filtered several times and then dried in an oven. The dried powders were heated in alumina crucible under air atmosphere to examine the morphology and crystal phase change after heating.

The prepared particles were characterized with Scanning Electron Microscopy (Philips, model 535M), X-ray diffractometry (Rigaku, D/Max-RB), and BET surface area measurement (Quantachrome, Autosorb-6).

3. Results and discussion

3.1. Reaction between lithium alkoxide and aluminum alkoxide

For the stoichiometric mixing of lithium and aluminum precursors, alkoxide-alkoxide, salt-alkoxide, and salt-salt systems were used. Four types of alkoxide-alkoxide systems were applied to prepare samples for the hydrothermal treatment. The alkoxide-alkoxide systems have an advantage of high purity.

Lithium isopropoxide and aluminum isopropoxide were only slightly soluble in isopropanol, respectively. When they were mixed in isopropanol, alkoxide powder particles were observed in the reactor at first, but they reacted in alcohol and formed new paste-like light yellowish material. No particular matter was observed in the reactor after the reaction and this newly formed material was dissolved clearly in ethanol. So the system can be hydrolyzed at paste-like state (not slurry state) or at solution state after dissolved in ethanol. A same phenomenon was observed in the lithium butoxide-aluminum butoxide system. When the two precursors were mixed in butanol, similar material was formed.

Turner *et al.* reported that the mixture of lithium alkoxide and aluminum alkoxide were hydrolyzed only at slurry state since the alkoxides are solid and not dissolved in alcohol [7]. It is probable that they did not find the reaction between the lithium alkoxide and aluminum alkoxide because their concentration was as high as 30% solid by weight.

Alkoxide-alkoxide reaction was not observed in the lithium ethoxide-aluminum ethoxide or lithium methoxide-aluminum methoxide system. Each alkoxide did not dissolved in alcohol, and alkoxide particles were maintained after mixing of the lithium alkoxide and the aluminum alkoxide. In conclusion, lithium alkoxide and aluminum alkoxide longer than C3 react each other in alcohol to form paste-like new material. C3 and C4 alkoxides have lower degree of polymerization because they have relatively long organic group and the molecular association is decreased [16]. Therefore, lithium alkoxide and aluminum alkoxide of C3 or C4 react easily each other. The light yellowish paste-like material is considered as a double metal alkoxide.

3.2. Effect of precursors on the morphology

Each mixture of alkoxides was hydrolyzed (at slurry state for methoxide-methoxide or ethoxide-ethoxide, paste-like state for propoxide-propoxide, butoxide-butoxide) and gelled. The gel samples were treated hydrothermally and the products were examined by SEM and XRD.

Morphology of the dried gel is shown in Fig. 2a. After hydrothermal treatment of the gel, the methoxide-methoxide system gave thin rectangular platelet (about 3×3 μm) and the ethoxide-ethoxide system gave platelet including some rod shape crystals as shown in Fig. 2b and c, respectively.

In Fig. 3a, which is from the propoxide-propoxide system, the rod-like and plate like particles are observed. In Fig. 3b, which is from the butoxide-butoxide system, mostly rod-like particles are observed. We concluded that the longer alkoxide group (C4) gives the rod shape crystal after hydrothermal treatment, whereas platelet was major from the gel of C2-C2 or C1-C1 alkoxides. Therefore, the butoxide-butoxide system is favorable for the preparation of fibrous lithium aluminate. But further study is needed to increase the aspect ratio.

Crystal phase of the hydrothermal product was a mixture of β-$LiAlO_2$ and boehmite. The fraction of β-$LiAlO_2$ depends on the length of alkoxy group. Crystal phase of butoxide system is mainly β-$LiAlO_2$ and the fraction of boehmite increased as the length of alkoxy group decreased as shown in the XRD spectra (Fig. 4).

Hydrothermal crystal growth makes the surface area reduced. The surface area of dried gel after heating

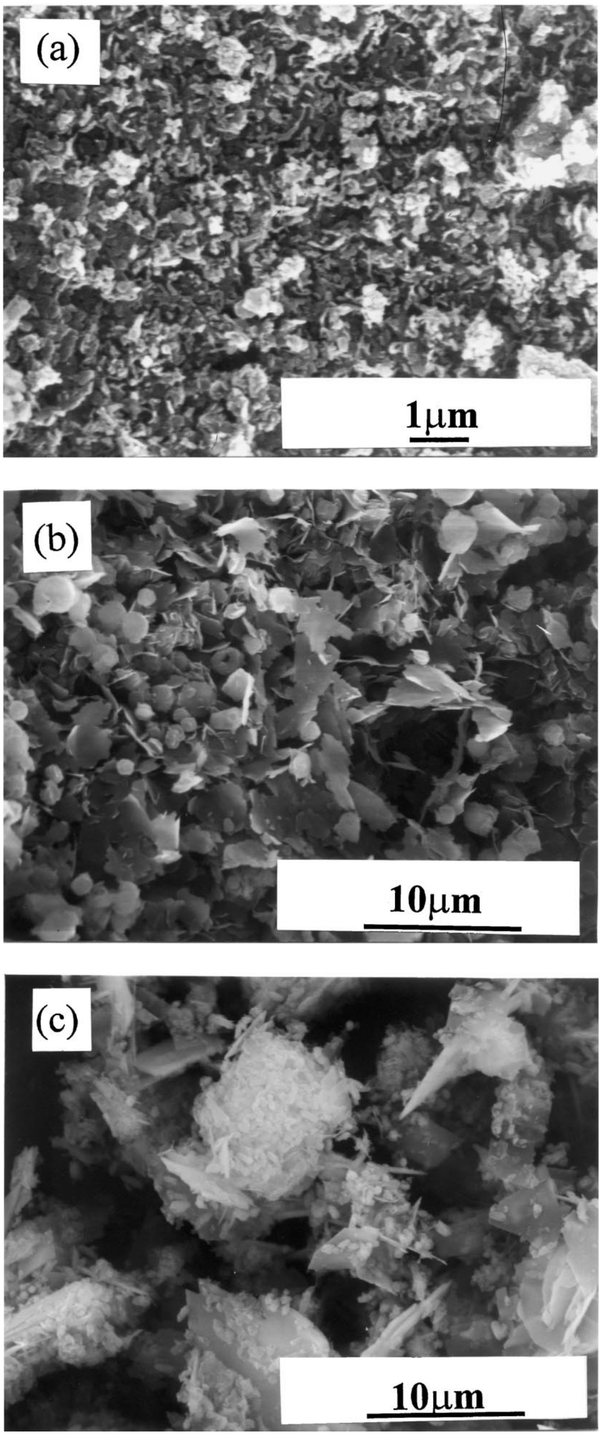

Figure 2 SEM photographs of (a) the dried gel and the hydrothermal products from the precursor systems of (b) lithium methoxide-aluminum methoxide and (c) lithium ethoxide-aluminum ethoxide.

at 250°C was above 100 m^2/g. It decreased to 15 m^2/g after hydrothermal treatment at 250°C. The prepared β-$LiAlO_2$ was transformed to γ-$LiAlO_2$ at about 850°C.

The paste-like material produced from the reaction of the lithium and aluminum alkoxides was dissolved in ethanol and this clear solution was hydrolyzed and gelled. After the hydrothermal treatment, thin platelet crystal was produced as shown in Fig. 3c and a mixture of boehmite and β-$LiAlO_2$ was obtained. This result is similar to the ethoxide-ethoxide system. This is probably caused by the alcohol-alkoxide exchange reaction. Therefore, it is important to use the corresponding alcohol as a solvent.

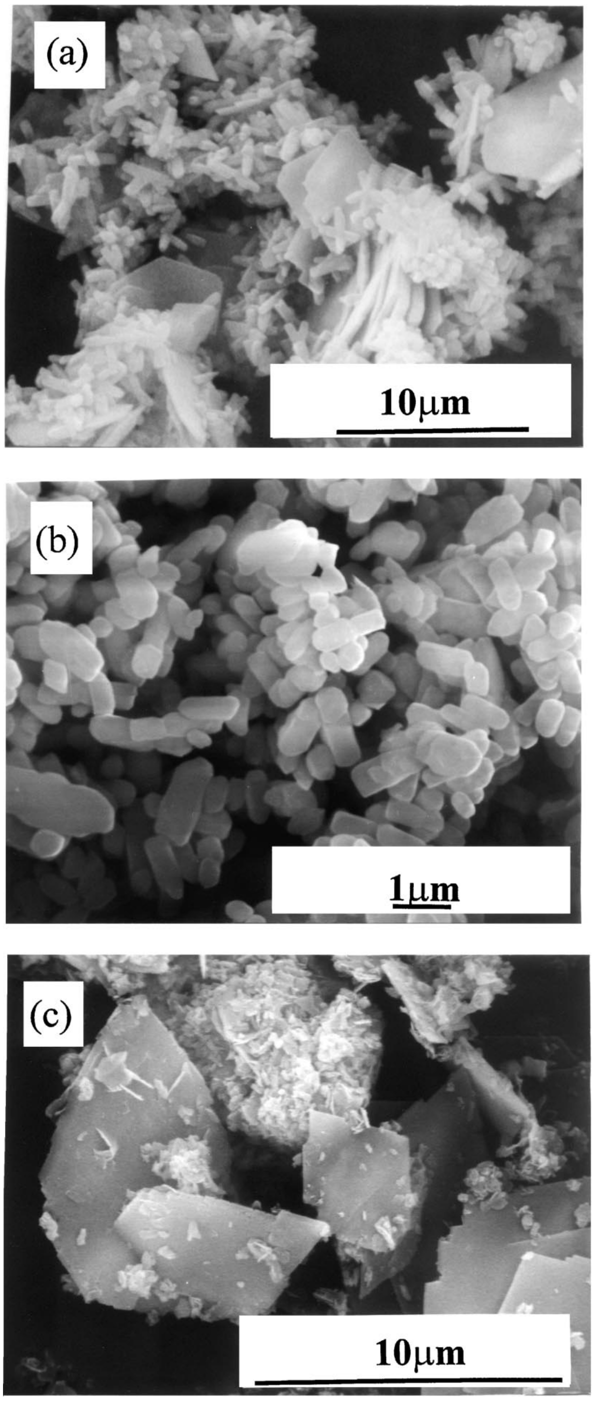

Figure 3 SEM photographs of the hydrothermal products from the precursor systems of (a) lithium isopropoxide-aluminum isopropoxide, (b) lithium secbutoxide-aluminum secbutoxide, and (c) lithium secbutoxide-aluminum secbutoxide (ethanol treated).

The effect of replacing water with alcohol outside the sample beaker in the vessel of hydrothermal treatment was examined. As shown in Fig. 5, thin round platelet shaped crystal was obtained from the alcohol treated sample. Effect of hydrothermal treatment time on crystal growth was examined. There was no difference in the aspect ratio when hydrothermal time was varied from 3 to 72 hours. Therefore, the crystal growth of lithium aluminate is considered to be completed in 3 hours.

Lithium salt-aluminum alkoxide, lithium salt-aluminum salt systems were hydrothermally treated. The lithium nitrate-aluminum butoxide system gave

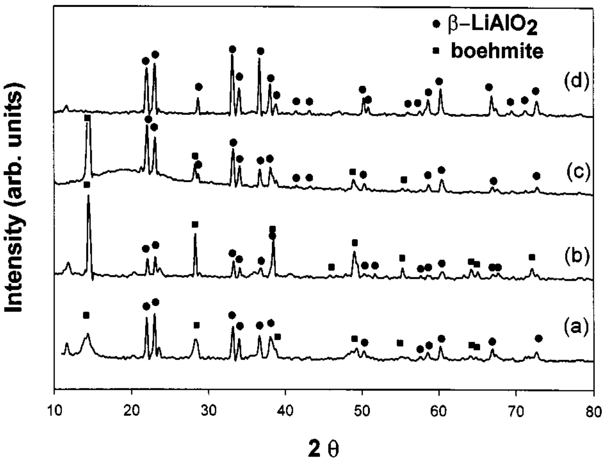

Figure 4 XRD patterns of the particles prepared by hydrothermal treatment of the alkoxide-alkoxide systems: (a) lithium methoxide-aluminum methoxide, (b) lithium ethoxide-aluminum ethoxide, (c) lithium isopropoxide-aluminum isopropoxide, and (d) lithium secbutoxide-aluminum secbutoxide.

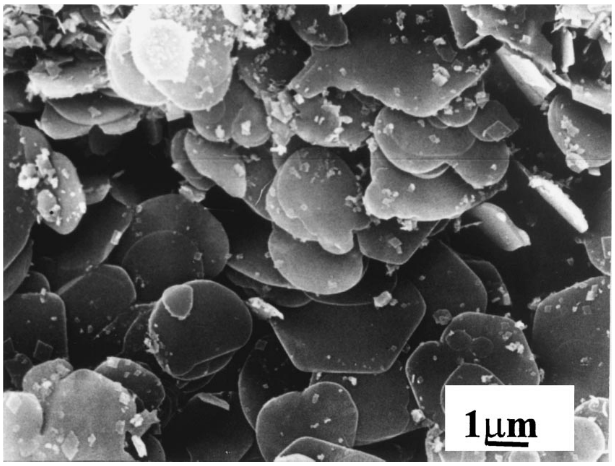

Figure 5 SEM photographs of particles treated with butanol.

platelet, the lithium hydroxide-aluminum butoxide gave short rod shape crystal, and the lithium nitrate-aluminum nitrate system gave long but thin plate shape crystal. The results are summarized in Table II.

Fig. 6 represents XRD pattern of hydrothermal product of the salt-alkoxide and the salt-salt systems. Both the lithium nitrate-aluminum butoxide and lithium nitrate-aluminum nitrate systems gave boehmite. β-$LiAlO_2$ was produced from the lithium hydroxide-aluminum butoxide system, however the aspect ratio and homogeneity of the particles are inferior to the lithium butoxide-aluminum butoxide system. Therefore, the salt-alkoxide and salt-salt systems are not favorable for preparing the rod shape lithium aluminate by hydrothermal treatment.

Among the stoichiometric mixing samples tested in this study, the butoxide-butoxide system is considered as the best precursor system for the preparation of fibrous $LiAlO_2$. Even though the aspect ratio of the particles is very low, the alkoxide-alkoxide system is still attractive since starting materials are pure alkoxides and no additive was needed. Further study is needed to increase the aspect ratio.

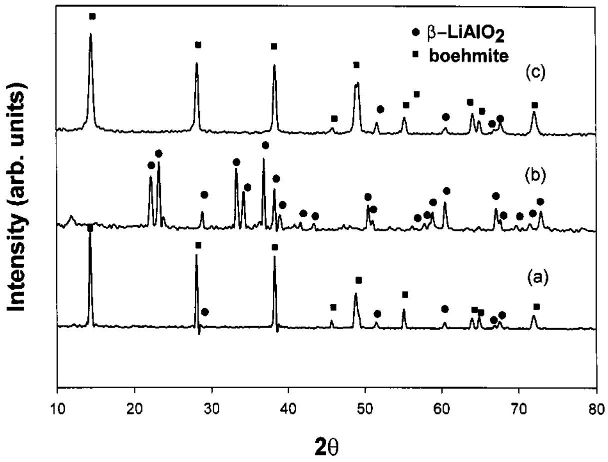

Figure 6 XRD patterns of the particles prepared by hydrothermal treatment of lithium salt-aluminum alkoxide/salt systems: (a) lithium nitrate-aluminum secbutoxide, (b) lithium hydroxide-aluminum secbutoxide, and (c) lithium nitrate-aluminum nitrate.

3.3. Effect of sodium hydroxide and excess lithium

Watanabe *et al.* [11, 17–19] prepared the needle shape lithium aluminate crystal by heating a mixture of LiOH, Al_2O_3, and NaOH. The ratio of LiOH, Al_2O_3, and NaOH was 40–60, 10, and 30–50 mole %, respectively. In our study, a modification of their preparation method was tried with the wet chemical method. Lithium salt, aluminum alkoxide, and sodium hydroxide were mixed and hydrothermally treated. The mole ratio of each component was 6 : 1 : 3. Lithium alkoxide-aluminum salt-sodium hydroxide or lithium salt- aluminum salt-sodium hydroxide systems were not suitable for the hydrothermal sample because of some problems such as mixing.

Three types of starting materials were hydrothermally treated [lithium nitrate (dissolved in butanol before mixing)-aluminum butoxide, lithium nitrate (dissolved in water before mixing)-aluminum butoxide, and lithium nitrate-aluminum nitrate systems]. Sodium hydroxide was added after mixing of each lithium and aluminum precursors.

The results after hydrothermal treatment of these nonstoichiometric precursor systems are summarized in Table III. As shown in Fig. 7, needle shape β-$LiAlO_2$ particles with length about 0.6–1.2 μm, and diameter about 0.1 μm were produced from the lithium nitrate (dissolved in water)-aluminum butoxide-sodium hydroxide system. But when lithium nitrate was dissolved in butanol, aspect ratio of product particles were reduced even though the same precursors were used. The lithium nitrate-aluminum nitrate-sodium hydroxide system gave short rectangular column shape. Fig. 8, XRD spectra, shows that β-$LiAlO_2$ is obtained from all the three precursor systems. Therefore the lithium nitrate (dissolved in water)-aluminum butoxide-sodium hydroxide system is the best precursor system for hydrothermal treatment among the above three systems.

Even though the aspect ratio of the products obtained in this work is a little less than that obtained by the solid state reaction method [17], wet chemical and

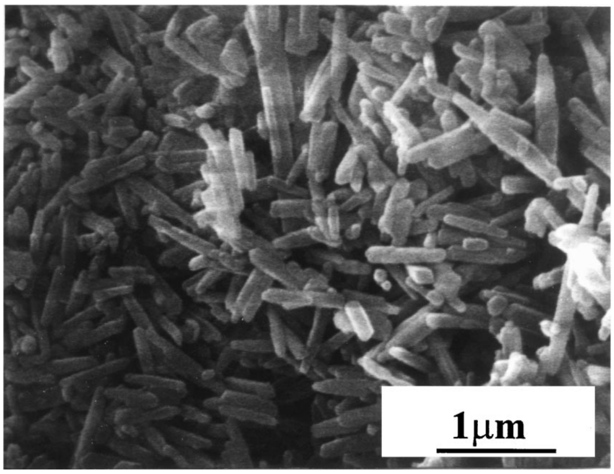

Figure 7 SEM photograph of hydrothermal product from the lithium nitrate (dissolved in water)-aluminum secbutoxide-sodium hydroxide system.

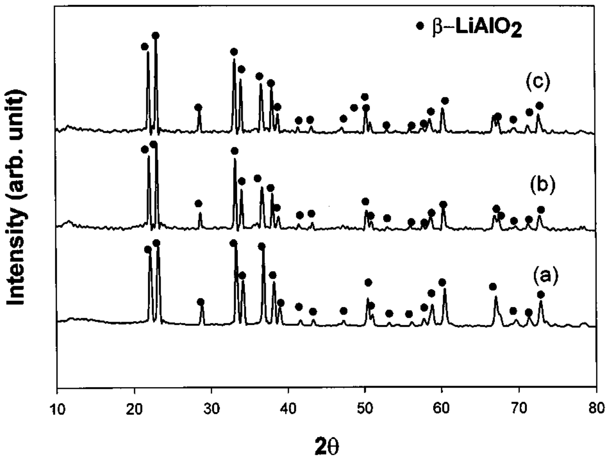

Figure 8 XRD patterns of the particles prepared by hydrothermal treatment of lithium salt-aluminum alkoxide/ salt-sodium hydroxide systems (mole ratio 6 : 1 : 3): (a) lithium nitrate (dissolved in water)-aluminum secbutoxide-sodium hydroxide, (b) lithium nitrate (dissolved in butanol)-aluminum secbutoxide-sodium hydroxide, and (c) lithium nitrate-aluminum nitrate-sodium hydroxide.

hydrothermal method have advantages such as homogeneous mixing and low processing temperature.

The specific surface area of the needle shape powders was 16 m^2/g and it is similar to the specific surface area of lithium aluminate prepared by the solid state reaction method of Watanabe *et al.* [17]. β-$LiAlO_2$ prepared by hydrothermal treatment was transformed to γ-$LiAlO_2$ at about 750°C.

4. Conclusions

Various precursor systems were tested to investigate the effect of the precursors on the morphology of lithium aluminate after hydrothermal treatment. Different crystal shapes were obtained from the various precursor systems after hydrothermal treatment.

The crystal shape and phase were dependent on the length of alkoxy groups of alkoxide precursors. The lithium butoxide-aluminum butoxide and lithium propoxide-aluminum propoxide systems gave rod-like lithium aluminate crystal, whereas the lithium ethoxide-aluminum ethoxide and lithium methoxide-aluminum methoxide systems gave mainly plate shape. β-$LiAlO_2$ was produced from the lithium butoxide-aluminum butoxide system, but a mixture of β-$LiAlO_2$ and boehmite was produced from the other alkoxide-alkoxide systems. The salt-alkoxide and salt-salt systems were not suitable for the hydrothermal treatment samples. Needle shape β-$LiAlO_2$ was produced by the hydrothermal treatment of the lithium nitrate-aluminum butoxide-sodium hydroxide system with the mole ratio of 6 : 1 : 3.

Two types of the precursor systems, lithium butoxide-aluminum butoxide and lithium nitrate-aluminum butoxide-sodium hydroxide, are recommended as candidates for fibrous $LiAlO_2$ preparation by the hydrothermal treatment. β-$LiAlO_2$ prepared by the hydrothermal treatment was transformed to γ-$LiAlO_2$ at 750–850°C. The specific surface area of γ-$LiAlO_2$ powders was above 10 m^2/g.

References

1. S. I. HIRANO, T. HAYASHI and T. TOMOYUKI, *J. Amer. Ceram. Soc.* **70** (1987) 171.
2. C. ALVANI, S. CASADIO and A. BAUGH, *Fusion Technology* **10** (1986) 106.
3. J. BECERRIL, P. BOSCH and S. BULBULIAN, *J. Nucl. Mater (Letter to the Editors)* **185** (1991) 304.
4. K. KINOSHITA, J. W. SIM and J. P. ACKERMAN, *Mat. Res. Bull.* **13** (1978) 445.
5. L. M. PAETSCH, J. D. DOYON and M. FAROOQUE, in Proceedings of the 3rd Symposium on Carbonate Fuel Cell Technology, May 1993, edited by D. Shores, H. Maru, I. Uchida and J. R. Selman (The Electrochemical Society, NJ, 1993) p. 89.
6. K. KINOSHITA, J. W. SIM and G. H. KUCERA, *Mat. Res. Bull.* **14** (1979) 1357.
7. C. W. TURNER, B. C. CLATWORTHY and A. H. Y. GIN, *Adv. Ceram.* **25** (1989) 141.
8. J. M. JUNG and S. B. PARK, *J. Mater. Sci. Lett* 15 (1996) 2012.
9. R. C. ANDERSON and W. J. THOMSON, *Adv. Ceram.* **27** (1994) 13.
10. Y. C. KANG, S. B. PARK and S. W. KWON, *J. Colloid and Interface Science* **182** (1996) 59.
11. A. WATANABE, Y. TAKEUCHI and G. SAEKI, *J. Amer. Ceram. Soc.* **70** (1987) C-268.
12. C. C. FAIN, G. M. LOWE, T. N. FRIANEZA-KULLBERG and D. P. McDONALD, Patent WO 94/03409, February 17 (1994).
13. G. SAEKI and A. WATANABE, *J. Ceram. Soc. Japan* **100** (1992) 1421.
14. T. R. N. KUTTY and R. VIVEKANDAN, *Materials Letter* **5** (1987) 79.
15. S. KOMARNENI, R. ROY, E. BREVAL, M. OLLINEN and Y. SUWA, *Adv. Ceram. Materials* **1** (1986) 87.
16. F. CHAPUT, J. P. BOILOT and A. BEAUGER, *J. Amer. Ceram. Soc.* **73** (1990) 942.
17. A. WATANABE, Y. TAKEUCHI and G. SAEKI, *ibid.* **73** (1990) 3094.
18. G. SAEKI, H. TAKAHASHI and A. WATANABE, *J. Ceram. Soc. Japan* **104** (1996) 221.
19. G. SAEKI and A. WATANABE, *ibid.* **101** (1993) 593.

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