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Effect of precursors on the preparation of lithium aluminate

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Abstract

Gamma lithium aluminate, which is a tritium breeding material proposed for use in fusion reactors, was prepared via a sol–gel method or a solid state reaction method and the effect of precursors on the crystallinity was studied. In the sol–gel method, the lithium butoxide–aluminum butoxide system gave pure gamma lithium aluminate. Lithium salt–aluminum butoxide systems result in high purity but a slightly higher temperature was needed. The γ-phase was preceded by the α- or β-phase in lithium salt–alumina precursor systems, whereas γ-lithium aluminate was directly developed in lithium alkoxide–aluminum alkoxide precursor systems and lithium salt–aluminum butoxide precursor systems. Among the precursor systems tested in this study, lithium butoxide–aluminum butoxide system was most favorable in the formation of phase pure γ-$LiAlO_2$. © 1997 Elsevier Science B.V.

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1. Introduction

Lithium aluminate, $LiAlO_2$, is a potential tritium breeder for a nuclear fusion reactor due to its chemical and thermal stability as well as low radiation damage problem [1–6]. Three allotropic forms of $LiAlO_2$ are known: α-, β- and γ-$LiAlO_2$, which are hexagonal, monoclinic and tetragonal structures, respectively. The most stable polymorph is γ-$LiAlO_2$. The α- or β-$LiAlO_2$ phases transform to γ-$LiAlO_2$ at elevated temperatures.

There are basically two methods to prepare multi-component oxide powder. One is a solid state reaction method and the other is a wet chemical method such as the sol–gel process. The solid state reaction method is generally based on the mixing of fine powders. Preparation of lithium aluminate by the solid state reaction method was reported by many research groups [3,4,6–10]. In most of the solid state reaction methods, mixtures of lithium salt and alumina are heated in air at a high temperature to form γ-$LiAlO_2$. Kullberg et al. studied the preparation of γ-$LiAlO_2$ using different lithium salts and a high specific surface area alumina [8]. Kinoshita et al. prepared γ-$LiAlO_2$ by reaction of alumina with mixtures of alkali carbonates or with alkali hydroxides [7]. Becerril et al. obtained γ-$LiAlO_2$ including small amounts of $LiAl_5O_8$ by heating a mixture of Li_2CO_3 and alumina powder at 1000°C [3]. One of the common conclusions of these reports was that the γ-phase of lithium aluminate was preceded by the α- or β-phase and purity of the γ-$LiAlO_2$ was relatively low. Moreover, a high temperature was needed to develop γ-$LiAlO_2$.

The sol–gel method has advantages over the solid state reaction method in intimate mixing of reactants, high purity and low processing temperature [10,11]. Despite these advantages, there are few reports on the preparation of lithium aluminate by the sol–gel process [1,12,13] and

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no systematic investigation of the precursor effect on the properties of the final product was attempted.

In the present study, the effects of precursors were investigated for the preparation of phase pure gamma lithium aluminate in order to select an optimum precursor system.

2. Experimental

Six types of precursor systems, summarized in Table 1, were used to prepare lithium aluminate by the sol–gel method. Three kinds of starting materials were also used to prepare lithium aluminate by the solid state reaction method. Most of the reagents used in this study are products of the Aldrich Chemical Company and High Purity Chemicals (Japan). All reagents were used without further purification except alcohols from which moisture was removed by a molecular sieve (Type 3A). Four types of lithium alkoxide and aluminum alkoxide were used for alkoxide–alkoxide systems as shown in Table 1. Lithium hydroxide or lithium nitrate and aluminum butoxide were used for salt–alkoxide systems.

The procedure for preparing lithium aluminate by the sol–gel process is summarized in Fig. 1. For the alkoxide–alkoxide system, lithium and aluminum alkoxides, 0.05 mol of each, were mixed with 100 ml of alcohol in a three-neck flask. This mixture was stirred with a magnetic stirrer near the boiling point of each alcohol. Lithium and aluminum alkoxides were mixed in their 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 mixtures were hydrolyzed by a five times excess of deionized pure water to complete the reaction in 2 h after mixing of the alkoxides. The hydrolysis product was gelled at room temperature and dried at 105°C in an electric oven. In salt–alkoxide systems, diluted aluminum sec-butoxide in butanol was hydrolyzed by aqueous lithium salt solutions. Other procedures were the same as for alkoxide–alkoxide systems.

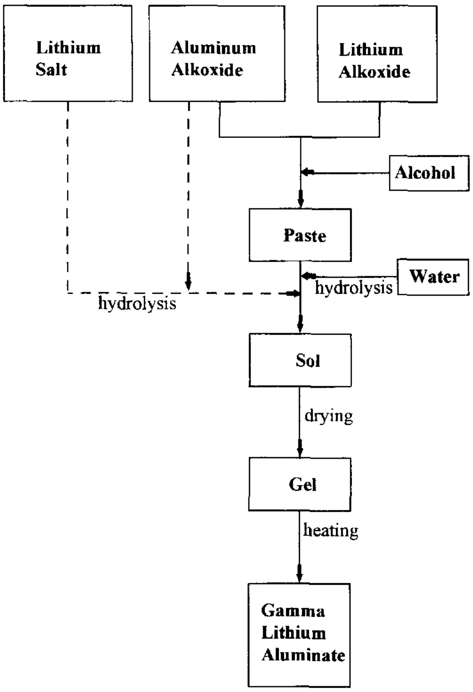

Fig. 1. Preparation procedure for gamma lithium aluminate by sol–gel method.

In the solid state reaction method, lithium hydroxide, nitrate or carbonate and alumina (~ 150 mesh, 155 m^2/g of the BET surface area) were used as starting materials. Lithium hydroxide and nitrate were used as aqueous solutions and lithium carbonate was used as a suspension in water because of its low solubility in water. Lithium containing solutions were mixed with alumina at 70°C in a rotary vacuum evaporator. The resulting samples were transferred to a petri dish and dried in an electric oven at

Table 1
Precursor systems used for the preparation of lithium aluminate

Lithium source	Aluminum source	Preparation method
Lithium methoxide	aluminum methoxide	sol–gel method
Lithium ethoxide	aluminum ethoxide	sol–gel method
Lithium isopropoxide	aluminum isopropoxide	sol–gel method
Lithium secbutoxide	aluminum secbutoxide	sol–gel method
Lithium hydroxide	aluminum secbutoxide	sol–gel method
Lithium nitrate	aluminum secbutoxide	sol–gel method
Lithium hydroxide	aluminum secbutoxide	sol–gel method
Lithium hydroxide	alumina	solid state reaction method
Lithium nitrate	alumina	solid state reaction method
Lithium carbonate	alumina	solid state reaction method

105°C to compare crystal phases with the dried gel samples.

The heating behavior of dried gel or lithium salt–alumina mixtures was investigated by DTA and XRD. The samples were heated on DTA at 10°C/min in an air flow of 100 ml/min and cooled down to room temperature when the desired temperature was reached. Crystal phases of the resulting samples were examined. The prepared particles were characterized with X-ray diffractometry (Rigaku, D/Max-RB), differential thermal analysis (TA Instrument, SDT2960), infrared spectrometry (Perkin Elmer, 1725X) and BET surface area measurement (Quantachrome, Autosorb-6).

3. Results and discussion

3.1. Preparation of gamma lithium aluminate by sol–gel method

Gamma lithium aluminate powders were prepared by the sol–gel method. Four kinds of lithium alkoxide–aluminum alkoxide precursor systems and two kinds of lithium salt–aluminum butoxide precursor systems were used as starting materials for the sol–gel process as shown in Table 1. Only a few researchers have used alkoxides as starting materials for the preparation of lithium aluminate [1,12,13]. Since all the alkoxides except aluminum butoxide are solid and only slightly soluble in the corresponding alcohol, it is difficult to mix lithium alkoxide and aluminum alkoxide at the molecular level during the sol–gel process.

Kwon and Park have reported the reaction between lithium alkoxide and aluminum alkoxide [14]. In propoxide–propoxide or butoxide–butoxide precursor systems, lithium alkoxide and aluminum alkoxide react with each other to form new light yellowish material in the corresponding alcohol, but there was no reaction in methoxide–methoxide or ethoxide–ethoxide systems. The reaction products were considered as double metal alkoxides. Each precursor system was hydrolyzed as slurries for the methoxide–methoxide and ethoxide–ethoxide systems and as paste material (product of reaction between lithium alkoxide and aluminum alkoxide) for the propoxide–propoxide and butoxide–butoxide systems. The gellation time for the butoxide–butoxide system was much longer than that for the methoxide–methoxide system. The dried gel from the butoxide–butoxide system was easily disintegrated to form fine homogeneous powders, whereas hard crushing is needed in the methoxide–methoxide or ethoxide–ethoxide system. When the butoxide–butoxide system was mixed in methanol or ethanol instead of butanol, the dried gel was not easily disintegrated.

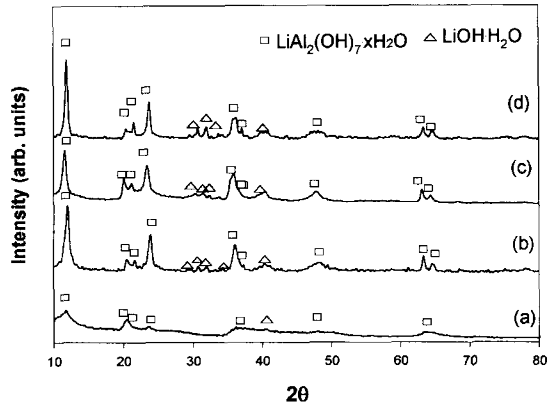

Fig. 2. XRD patterns of gel prepared from (a) lithium methoxide–aluminum methoxide, (b) lithium ethoxide–aluminum ethoxide, (c) lithium propoxide–aluminum propoxide, and (d) lithium butoxide–aluminum butoxide systems.

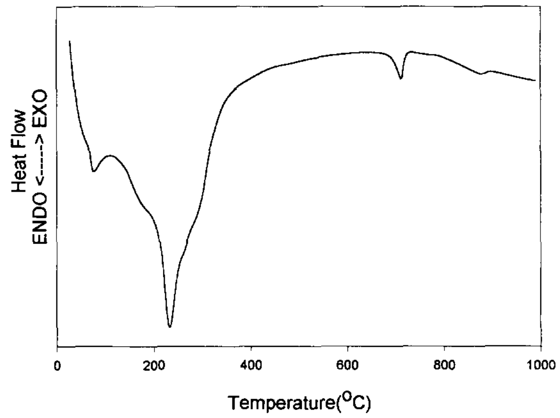

Fig. 3. DTA curve of gel prepared from lithium butoxide–aluminum butoxide system in an air flow of 100 ml/min.

Thermal behavior of the gel prepared from each precursor system was studied by DTA and XRD. Gel samples were heated at a rate of 10°C/min in air atmosphere and cooled down to room temperature when the desired temperature was reached. Crystal phases of gels from four precursor systems were a mixture of $LiOH \cdot xH_2O$ and $LiAl_2(OH)_7 \cdot xH_2O$ as shown in Fig. 2. According to the results of Turner et al., the gel was composed of LiOH and lithium dialuminate [12]. However, Hirano et al. reported that the crystal phase present in the gel was beta lithium aluminate [1]. Fig. 3 is a DTA curve of gel prepared from the butoxide–butoxide system. There is a small endothermic peak at about 700°C. It was found that this peak was related to gamma lithium aluminate formation, which was confirmed by XRD at temperatures near the peak. Similar DTA curves were obtained from all four types of alkoxide–alkoxide precursor systems. Thermal analyses were carried out by Turner et al. [12] and Hirano et al. [1], but no such peak was reported.

Fig. 4 represents the crystal phase change of the gel

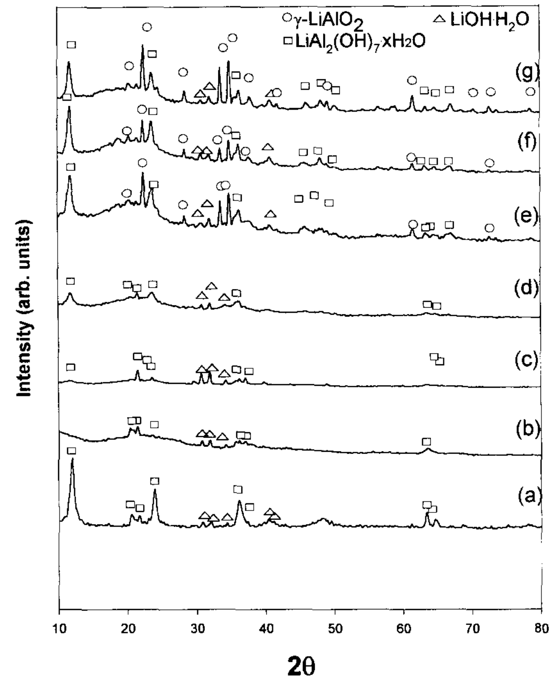

Fig. 4. XRD patterns of gel prepared from a lithium ethoxide–aluminum ethoxide system (heated at (a) 105°C, (b) 250°C, (c) 400°C, (d) 650°C, (e) 750°C, (f) 850°C and (g) 1000°C).

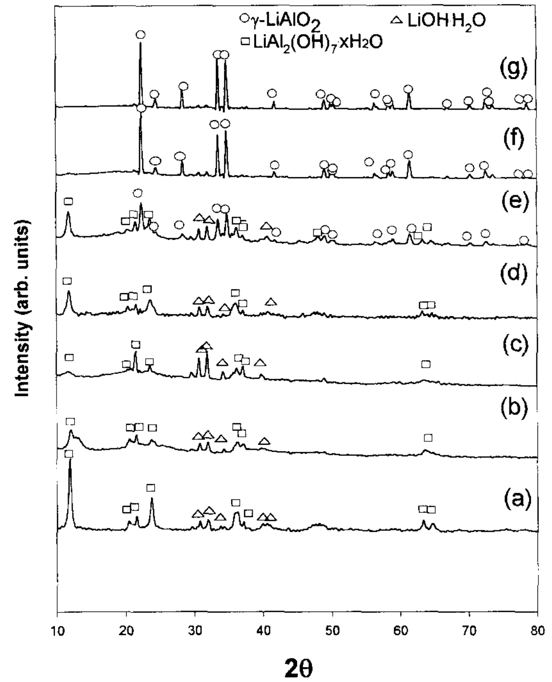

Fig. 5. XRD patterns of gel prepared from a lithium butoxide–aluminum butoxide system (heated at (a) 105°C, (b) 250°C, (c) 400°C, (d) 650°C, (e) 750°C, (f) 850°C and (g) 1000°C).

sample prepared from the ethoxide–ethoxide system at various temperatures. At about 750°C, gamma lithium aluminate has begun to be developed. This gamma lithium aluminate was formed by the reaction of $\mathrm{LiOH} \cdot x\mathrm{H_2O}$ and $\mathrm{LiAl_2(OH)_7} \cdot x\mathrm{H_2O}$. Gamma lithium aluminate formation was kept over 1000°C.

Fig. 5 represents the crystal phase change of the gel sample prepared from the butoxide–butoxide system. Gamma lithium aluminate was developed at a similar temperature as for the ethoxide–ethoxide system, but the reaction was completed at about 850°C as in Fig. 5. The crystal phase formed at 850°C was also confirmed by IR as shown in Fig. 6. Pure gamma lithium aluminate was obtained from the precursor system with large alkoxy groups at low temperature.

Fig. 7 shows XRD patterns of lithium aluminate prepared by heating gel samples from four precursor systems up to 1000°C. At 1000°C, pure gamma lithium aluminate was obtained from the butoxide–butoxide system, but there were still $\mathrm{LiOH} \cdot x\mathrm{H_2O}$ or $\mathrm{LiAl_2(OH)_7} \cdot x\mathrm{H_2O}$ peaks in the methoxide–methoxide and ethoxide–ethoxide systems. These peaks disappeared at temperatures higher than 1200°C. It is interesting to note that the crystal phase of the gels from all four systems were the same, but the phase purity was dependent on the size of alkoxy group in the precursor. No difference in the DTA curve and XRD pattern was observed when the ambient gas was switched from air to nitrogen.

Hirano et al. [1] prepared crystalline $\beta\text{-LiAlO}_2$ by controlled hydrolysis of refluxed alcoholic solution of lithium ethoxide and aluminum ethoxide. Turner et al. [12] reported that $\beta\text{-LiAlO}_2$ was produced when aluminum isopropoxide was a starting material, whereas $\gamma\text{-LiAlO}_2$

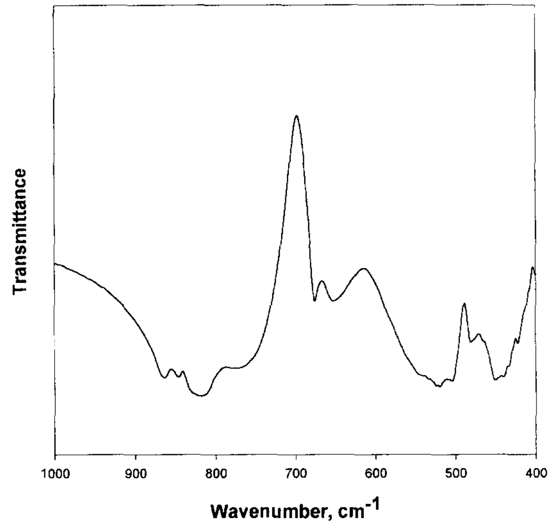

Fig. 6. IR spectra of lithium aluminate prepared from lithium butoxide–aluminum butoxide system.

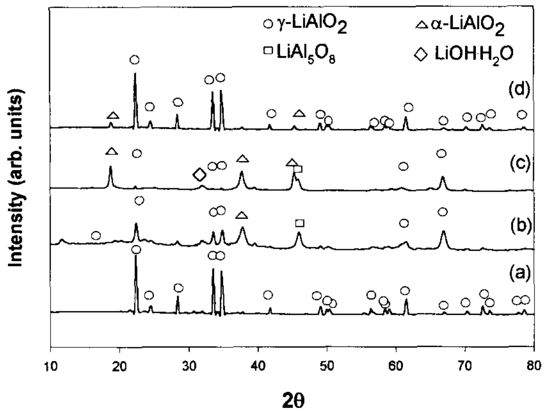

Fig. 7. XRD patterns of lithium aluminate prepared by heating of gel up to 1000°C on DTA from (a) lithium methoxide–aluminum methoxide, (b) lithium ethoxide–aluminum ethoxide, (c) lithium propoxide–aluminum propoxide and (d) lithium butoxide–aluminum butoxide systems.

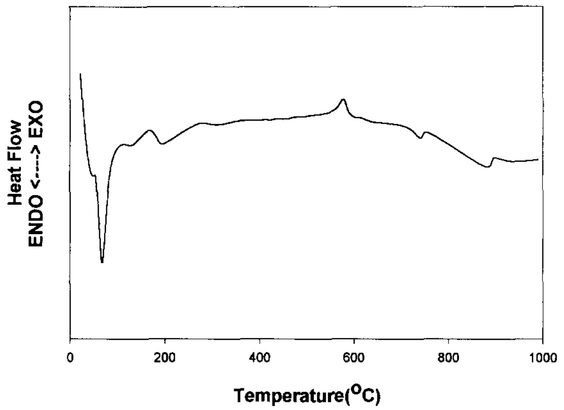

Fig. 9. DTA curve of gel prepared by hydrolysis of lithium butoxide–aluminum butoxide system with $R = 2$ in air flow of 100 ml/min.

was produced for preparations starting with aluminum n-butoxide. In this study, γ-LiAlO$_2$ was produced without going through the β-phase even when aluminum ethoxide was used as aluminum source. The reason is not clear and further work is necessary to elucidate the difference.

The effect of solvent on the properties of lithium aluminate powder was investigated. The reaction product from the butoxide–butoxide system was dissolved in ethanol and hydrolyzed. The resulting gel was heated up to 1000°C. Crystal phases of the product (Fig. 8b) were compared with that of the ethoxide–ethoxide system (Fig. 8a) and the butoxide–butoxide system without ethanol treatment (Fig. 8c). As shown in Fig. 8, crystal phases of the product from the butoxide–butoxide system with ethanol treatment (Fig. 8b) were very similar to the crystal phases of the product from the ethoxide–ethoxide system (Fig. 8a). In these two samples, LiOH · xH$_2$O and LiAl$_2$(OH)$_7$ · xH$_2$O did not disappear, even at 1000°C. The result indicates that alcohol–alkoxide exchange reactions occur and it is important to use the corresponding alcohol to the alkoxide to avoid the exchange reaction. This result is similar to the result reported by Kwon and Park [14]. They found that the crystal shape and phase of the butoxide–butoxide system after hydrothermal treatment of the gel were very similar to those of the ethoxide–ethoxide system, when the reaction product from the butoxide–butoxide system was dissolved in ethanol before hydrolysis.

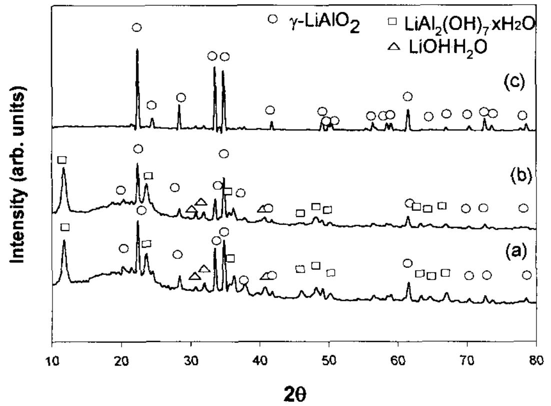

Fig. 8. Comparison of XRD patterns of lithium aluminate prepared from (a) lithium ethoxide–aluminum ethoxide system, (b) lithium butoxide–aluminum butoxide system treated in ethanol and (c) lithium butoxide–aluminum butoxide system.

The effect of excess water was studied by varying the R from 2 to 8, where R is defined by the ratio of amount of water added divided by the stoichiometric amount of water. When $R = 2$, an exothermic peak was observed on the DTA curve of the resulting gel at about 600°C as shown in Fig. 9. The peak was probably caused by the decomposition of alkoxides which were not reacted during the hydrolysis step. The remaining alkoxides in the gel have a negative effect on the phase purity of the final product. When $R = 4$–6, there was no evidence that alkoxide remained in the gel. When $R = 8$, it was difficult to obtain a stable sol and it took a long time for gellation. Therefore, $R = 4$–6 is suitable for the hydrolysis of the mixture of lithium alkoxide and aluminum alkoxide.

Lithium butoxide and aluminum butoxide were hydrolyzed separately, then mixed together. The resulting gel was heated and the crystal phase was compared with the product obtained from the premixed alkoxides of lithium and aluminum. Phase pure gamma lithium aluminate was also observed and no difference in XRD was found as shown in Fig. 10. Even though lithium butoxide and aluminum butoxide were hydrolyzed separately, then mixed together, the crystal phase of lithium aluminate was purer than that of lithium aluminate prepared from premixed alkoxide systems with smaller alkoxy groups. This implies

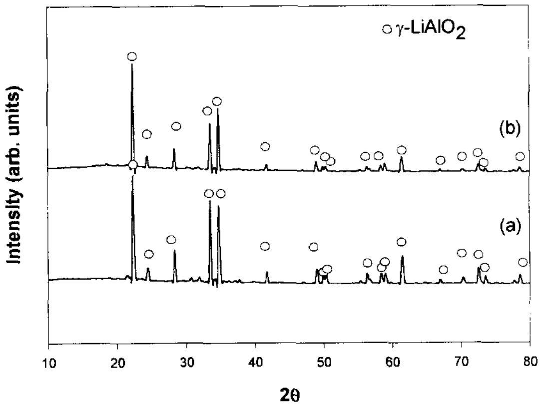

Fig. 10. Comparison of XRD patterns of lithium aluminate prepared from a lithium butoxide–aluminum butoxide. (a) Hydrolysis of the premixed alkoxides and (b) mixing of separately hydrolyzed alkoxide.

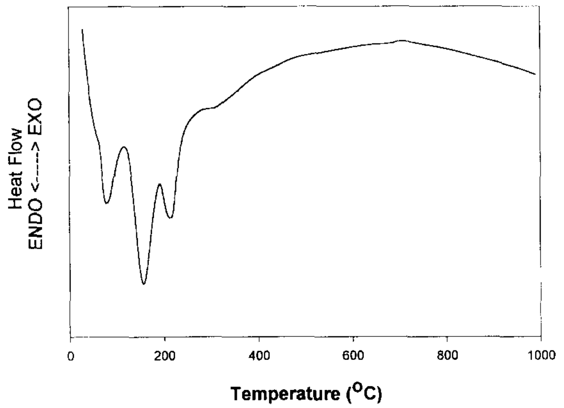

Fig. 12. DTA curve of lithium hydroxide–alumina mixture in air flows of 100 ml/min.

that the formation of double metal alkoxide is not essential for the phase pure lithium aluminate. However, this hypothesis should be tested further.

Since alkoxides of group I or II elements are generally solid, non-volatile and most of them have low solubility, it is difficult to obtain pure alkoxides[15]. In an attempt to solve this problem, the possibility of using salt–alkoxide precursors was tested. Lithium hydroxide–aluminum butoxide and lithium nitrate–aluminum butoxide systems were used as the starting material for the sol–gel process. Fig. 11 represents the XRD patterns of lithium aluminate prepared from lithium salts–aluminum butoxide systems. Comparing these XRD patterns with those from the butoxide–butoxide system, the crystallinity appears to be a little lower at the same temperature, but phase purity is the same as that in the butoxide–butoxide system. Lithium salt–aluminum butoxide systems are also attractive along with butoxide–butoxide system.

In conclusion, lithium butoxide–aluminum butoxide is the best precursor system for the preparation of phase pure gamma lithium aluminate.

3.2. Comparison with solid state reaction method

Lithium aluminate was prepared from three lithium salt–alumina precursor systems by a solid state reaction method to compare with the sol–gel process. At 105°C, lithium hydroxide–alumina or lithium carbonate–alumina systems give a mixture of $LiOH \cdot xH_2O$ and $LiAl_2(OH)_7 \cdot xH_2O$, which are the same crystal phases as the gel prepared from alkoxide–alkoxide, whereas the lithium nitrate–alumina system gives an amorphous product. The preparation route to gamma lithium aluminate from each lithium salt–alumina precursor was examined by DTA and

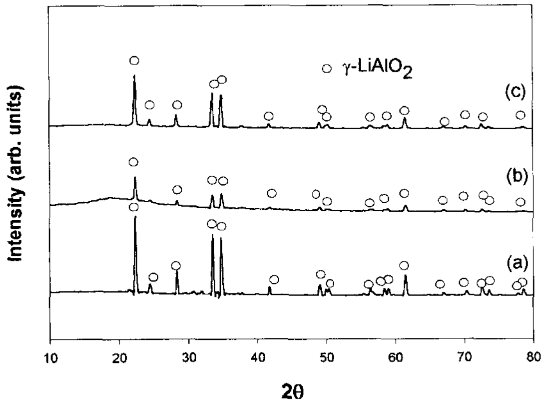

Fig. 11. Comparison of XRD patterns of lithium aluminate prepared from (a) lithium butoxide–aluminum butoxide, (b) lithium hydroxide–aluminum butoxide and (c) lithium nitrate–aluminum butoxide systems.

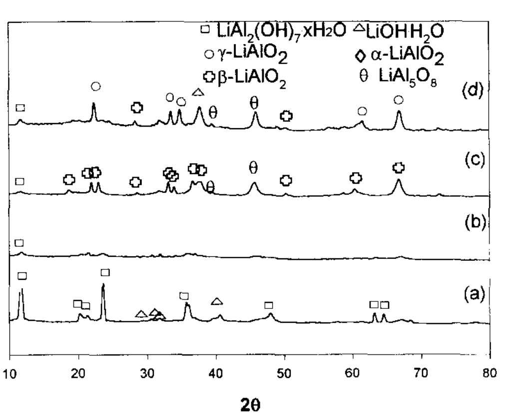

Fig. 13. XRD patterns of gel prepared from a lithium hydroxide–alumina system (heated at (a) 105°C, (b) 550°C, (c) 800°C and (d) 1000°C).

Table 2
A summary of gamma lithium aluminate formation routes

Precursor system	γ-LiAlO$_2$ formation route	Preparation method
Lithium hydroxide + alumina	$LiOH \cdot H_2O + LiAl_2(OH)_7 \cdot xH_2O \rightarrow$ amorphous $\rightarrow \beta$-LiAlO$_2 \rightarrow \gamma$-LiAlO$_2$	solid state reaction method
Lithium nitrate + alumina	amorphous $\rightarrow \alpha$-LiAlO$_2 \rightarrow \gamma$-LiAlO$_2$	solid state reaction method
Lithium carbonate + alumina	$LiOH \cdot H_2O + LiAl_2(OH)_7 \cdot xH_2O \rightarrow$ amorphous $\rightarrow \alpha$-LiAlO$_2 \rightarrow \gamma$-LiAlO$_2$	solid state reaction method
Lithium alkoxide + aluminum alkoxide	$LiOH \cdot H_2O + LiAl_2(OH)_7 \cdot xH_2O \rightarrow \gamma$-LiAlO$_2$	sol–gel method
Lithium salt + aluminum alkoxide	$LiOH \cdot H_2O + LiAl_2(OH)_7 \cdot xH_2O \rightarrow \gamma$-LiAlO$_2$	sol–gel method

XRD. Fig. 12 shows the DTA curve of the sample prepared from the lithium hydroxide–alumina system. There is no peak corresponding to the formation of gamma lithium aluminate, which was found in the alkoxide–alkoxide precursors. The peak was absent in all the precursor systems in the solid state reaction method.

Fig. 13 shows the XRD patterns of powders prepared from the lithium hydroxide–alumina system. The crystal phase at 105°C is a mixture of $LiOH \cdot xH_2O$ and $LiAl_2(OH)_7 \cdot xH_2O$ and as the temperature increases, the peak intensity of the two compounds decreases and an amorphous phase is formed at 500°C. At 800°C, beta lithium aluminate is formed and it is transformed to the gamma phase at about 1000°C. The preparation routes to gamma lithium aluminate from each precursor system are summarized in Table 2. The γ-phase was preceded by the α- or β-phase in lithium salt-alumina precursor systems, whereas γ-lithium aluminate was directly developed in lithium alkoxide–aluminum alkoxide precursor systems or lithium salt–aluminum butoxide systems. Fig. 14 shows XRD patterns of samples from the lithium salt–alumina systems heated up to 1000°C. γ-lithium aluminate was not phase pure and crystallinity was low in comparison with the butoxide–butoxide system. Better crystallinity was obtained at a higher temperature. From the above results, it is obvious that the solid state reaction method starting from lithium salt–alumina systems is not favorable to prepare phase pure γ-lithium aluminate.

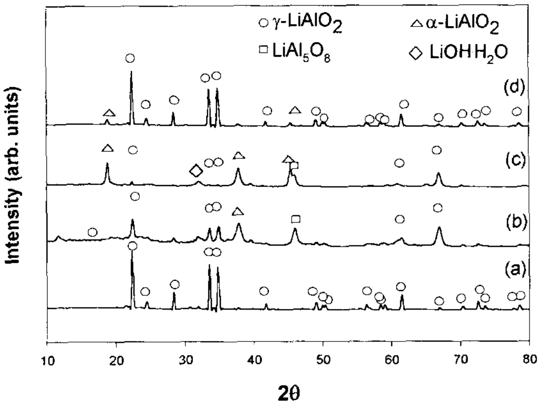

Fig. 14. XRD patterns of lithium aluminate prepared from (a) lithium butoxide–aluminum butoxide, (b) lithium hydroxide–alumina, (c) lithium nitrate–alumina and (d) lithium carbonate–alumina systems.

4. Conclusions

Various precursor systems were used to investigate the precursor effect on the preparation of gamma lithium aluminate.

Gels prepared from all lithium alkoxide–aluminum alkoxide systems were a mixture of $LiOH \cdot xH_2O$ and $LiAl_2(OH)_7 \cdot xH_2O$. When the gels were heated, gamma lithium aluminate began to form at about 700°C. The temperature at which gamma lithium aluminate was completely formed was lowered as the size of alkoxy group became larger. The alcohol–alkoxide exchange reaction was appreciable, so the alcohol corresponding to the alkoxide should be used. The dried gel was easily disintegrated to form homogeneous fine powders when butanol was used for the route. In the case of the lithium salt–aluminum butoxide systems, phase pure gamma phase was obtained but the crystallinity was lower than that for the lithium butoxide–aluminum butoxide system. In the solid state reaction method, high temperature was needed to obtain gamma lithium aluminate and the phase purity was low.

The γ-phase was preceded by the α- or β-phase in lithium salt–alumina precursor systems, whereas γ-lithium aluminate was directly developed in alkoxide–alkoxide precursor systems or salt–alkoxide systems. Among the precursor systems tested in this study, the lithium butoxide–aluminum butoxide system was most favorable for the preparation of phase pure γ-LiAlO$_2$.

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