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Sol–Gel Synthesis of Lithium Aluminate

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$LiAlO_2$ was prepared by two sol–gel methods using simultaneous hydrolysis of the reagents: aluminum *sec*-butoxide/lithium methoxide and aluminum *sec*-butoxide/LiOH. The resulting ceramic powders were compared with those prepared by two conventional methods (i.e., solid-state fusion and peroxide). The sol–gel method provided powders with a very high γ-$LiAlO_2$ content after calcining at temperatures as low as 700°C when LiOH was used. The solids were characterized by AAS, DTA, TGA, XRD, and SEM.

I. Introduction

BECAUSE γ-$LiAlO_2$ provides the required thermophysical, chemical, and mechanical stability at high temperature as well as favorable irradiation behavior, it is often recommended as a tritium-breeding blanket in fusion reactors.[1–4]

Control of the microstructure has to be exercised when preparing this ceramic, because the microstructure is important in controlling the rate of tritium release from the blanket.[5] Furthermore, the preparation technique determines the purity of the γ-$LiAlO_2$ obtained,[6] which is important in determining activation products.

The sol–gel preparation method has gained much interest as a means to obtain ceramic materials at low temperatures. This method involves the controlled hydrolysis of an alkoxide, followed by condensation, which, in turn, forms a gel.

The structure of the final material is very sensitive to pH, stability of the reactants, amount of water, refluxing temperature, and impurities.[7–12]

In a previous work,[12] the preparation of $LiAlO_2$ by hydrolysis of lithium and aluminum alkoxides did not lead directly to a precipitate of $LiAlO_2$ but rather to a mixture of LiOH and a lithium dialuminate, which combined to form $LiAlO_2$ through a solid-state reaction at 250°C. This reaction provided the high-temperature γ-$LiAlO_2$ at temperatures as low as 550°C. It seemed, therefore, interesting to prepare $LiAlO_2$ by the sol–gel method, which provides a mixing of reactants as intimate as hydrolysis, but, because a gel is formed, LiOH and lithium dialuminate formation is avoided. The main steps of the sol–gel synthesis technique are hydrolysis and condensation or polymerization.

Therefore, the purpose of this work was to prepare $LiAlO_2$ by the sol–gel method: from aluminum *sec*-butoxide/lithium methoxide and from aluminum *sec*-butoxide/LiOH. These materials were then compared with those obtained by conventional methods and by hydrolysis.[12]

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II. Experimental Procedure

(1) Synthesis of $LiAlO_2$

(A) Sol–Gel Synthesis: The $LiAlO_2$ sol–gel sample was synthesized by dissolving in isopropyl alcohol the required amounts of aluminum *sec*-butoxide (Aldrich Chemical Co., Milwaukee, WI) and lithium methoxide (Aldrich). The alcohol: alkoxides molar ratio was 60. The mixture was stirred under continuous agitation at 70°C and refluxed for 1 h.

The metallic complex solution was hydrolyzed by slow addition of a pH 2 (HNO_3 + water) mixture. The water:alkoxide and acid:alkoxide molar ratios were 30 and 0.2, respectively. The reflux was continued until gelation, and the solvent excess was eliminated by distillation *in vacuo*. The obtained gel was aged for 24 h and dried in a vacuum oven at 110°C for 8 h. The powder was calcined in air flow at 800°C for 4 h and then at 1000°C for 1 h. It has been reported that lithium and aluminum alkoxides hydrolyze simultaneously, forming a metallic complex that, after calcination (600°C), yields $LiAlO_2$.[5,12]

The $LiAlO_2$ sol–gel sample was prepared using aluminum *sec*-butoxide (Aldrich) and LiOH (Merck, Darmstadt, Germany) in equimolar amounts. This sample was synthesized by a procedure similar to the previous one, but the LiOH + water + HNO_3 mixture was added only after the complete dissolution of the aluminum *sec*-butoxide. The overall reaction was completed after 24 h, and a white, pure gel was obtained.

(B) Fusion Synthesis: Equimolar amounts of γ-Al_2O_3 and Li_2CO_3 were mixed in acetone for 30 min. The acetone was evaporated, and the resulting solid was dried at 100°C for 3 h. The powder was calcined at 800°C for 4 h, or at 800°C for 4 h and then at 1000°C for 1 h.

(C) Peroxide Synthesis: Equimolar amounts of γ-Al_2O_3 and Li_2CO_3 were mixed in 20 mL of distilled water. 20 mL of 30% H_2O_2 solution were added to decompose the Li_2CO_3 and to obtain Li_2O_2. The resulting mixture was slightly heated for 5 min. When the reaction began, external heating was stopped, and the solution was stirred until the reaction was finished. The excess water was evaporated, and the solid was dried at 100°C for 3 h. The powder was then calcined at 800°C for 4 h, or at 800°C for 4 h and then at 1000°C for 1 h.

(2) Characterization Techniques

Powder samples were dissolved by the mixed-acid (3:1 HNO_3:H_2SO_4) digestion method and diluted in distilled water. Aliquots of the solution were then analyzed by atomic absorption spectroscopy (AAS) (Model 2380, Perkin Elmer, Norwalk, CT) in an air–acetylene flame mode to determine lithium and in a nitrous oxide–acetylene mode to determine aluminum.

Lithium and aluminum oxides were identified by X-ray diffractometry (XRD) (Model D500, Siemens, Karlsruhe, Germany) coupled to a copper-anode X-ray tube. The K_α wavelength was selected with a diffracted beam monochromator. The relative contents of γ-$LiAlO_2$, $LiAl_5O_8$, and impurities were estimated from the areas under the diffraction peaks. Because no internal standard was introduced, the X-ray absorption for each compound was assumed to be the same.

Table I. Sample Colors

Sample	Temperature (°C)	Gelation time (h)	Color
Aluminum	110	24	Brown
sec-butoxide/	800		White-gray
lithium methoxide	1000		White
Aluminum	110	24	White
sec-butoxide/	800		White
LiOH	1000		White
Fusion	110		Pale yellow
	800		White
	1000		White
Peroxide	110		White
	800		White
	1000		White

The morphology of the crystals constituting the various samples was studied by scanning electron microscopy (SEM) (Model JSM-85CF, JEOL, Tokyo, Japan) equipped with silicon–lithium windows to obtain the images.

Differential thermal and thermogravimetric analyses (DTA and TGA, respectively) were used to determine the water loss and the weight loss at high temperature (Model 92-16.18, SETARAM, Caluire, France).

III. Results and Discussion

(1) $LiAlO_2$ Synthesis

The $LiAlO_2$ was initially a transparent gel by both sol–gel methods. In both cases the synthesis was a "sol–gel" because the initial alkoxide homogeneous solution was transformed to a solid with colloidal properties. The appearances of the samples, as obtained and after heat treatment, are given in Table I. They are compared with the samples obtained by the fusion and peroxide methods.

(2) AAS

The elemental analysis of the various samples is presented in Table II. Samples synthesized by all of the sol–gel methods were lithium enriched.

(3) XRD

Table III summarizes the XRD results. In the aluminum *sec*-butoxide/lithium methoxide and aluminum *sec*-butoxide/LiOH samples treated at 800°C, although the main component was γ-$LiAlO_2$ (77.8% and 69.3%, respectively), a considerable amount of noncrystalline compound was found. A broad peak at small angles and three sharp peaks around d = 4.15 Å, d = 2.91 Å, and d = 2.81 Å correspond to Li_2CO_3, (11.5% and 8.1% respectively), which was probably the result of organic material decomposition or reaction of LiOH with CO_2, as reported by Turner *et al.*[12]

Table II. Elemental Analysis of Samples Treated at 800° and 1000°C

Sample	Temperature (°C)	Lithium: aluminum ratio
Aluminum *sec*-butoxide/	800	1.75
lithium methoxide	1000	1.18
Aluminum *sec*-butoxide/	800	1.19
LiOH	1000	1.09
Fusion	800	0.92
	1000	0.85
Peroxide	800	0.83
	1000	0.82

The amorphous compound disappeared (Table III) when samples were treated at 1000°C. Both samples were fully crystalline, although their composition was not the same. The aluminum *sec*-butoxide/lithium methoxide sample treated at 1000°C was composed of γ-$LiAlO_2$ (94.9%) and α-$LiAlO_2$ (5.1%), but only γ-$LiAlO_2$ was identified in aluminum *sec*-butoxide/LiOH treated at 1000°C. Therefore, at 1000°C, the noncrystalline and crystalline impurities reacted through different mechanisms.

The amount of γ-$LiAlO_2$ in the sample prepared by the fusion method and treated at 800°C was as high as 91.1%, and the noncrystalline compounds, if any, were beyond the XRD detection limit. In this case, the remaining 8.9% was identified as α-$LiAlO_2$. When the sample prepared by the fusion method was calcined at 1000°C, only γ-$LiAlO_2$ was observed, because, at this temperature, α-$LiAlO_2$ produces γ-$LiAlO_2$.[13]

The XRD pattern of the peroxide sample at 800°C showed specific and intense peaks attributed to α-$LiAlO_2$ that faded when the sample was treated at 1000°C (see Table III).

The γ-$LiAlO_2$ content of the sample prepared by the peroxide method increased from 63.2% when treated at 800°C to 89.8% when treated at 1000°C, and the α-$LiAlO_2$ decreased from 31.8% to 10.2%. In this preparation, as in fusion synthesis, at 1000°C, γ-$LiAlO_2$ developed from α-$LiAlO_2$, although not all α-$LiAlO_2$ was transformed.

(4) SEM

Only the sol–gel samples treated at 800°C were studied by SEM (Fig. 1). The micrograph of the aluminum *sec*-butoxide/lithium methoxide sample treated at 800°C shows clear bipyramidal crystals. This shape is different from the elongated faceted crystals reported by Takahashi *et al.*[14] However, small nonfaceted particles (0.5 μm) also were found on these large bipyramidal crystals (~6 μm).

Similar bipyramidal crystals were present in the aluminum *sec*-butoxide/LiOH sample treated at 800°C; however, the shape of the faceted particles was often more complex. Twinning appeared to be a common feature in this material. Small, nonfaceted particles (0.5 μm) also were deposited on the large crystals. In the Fig. 1 micrograph, a large planar crystal, apparently hexagonal, was observed behind the large crystals. Therefore, the morphology of the resulting γ-$LiAlO_2$ crystals seems

Table III. XRD Characterization of Samples

Preparation technique	Preparation temperature (°C)	$LiAlO_2$ (%) α	$LiAlO_2$ (%) γ	Li_2CO_3	Noncrystalline compound (%)
Fusion	800	8.9	91.1		
	1000		100.0		
Peroxide	800	36.8	63.2		
	1000	10.2	89.8		
Sol–gel/	800		69.3	8.1	22.6
hydroxide	1000		100.0		
Sol–gel/	800		77.8	11.5	10.7
methoxide	1000	5.1	94.9		

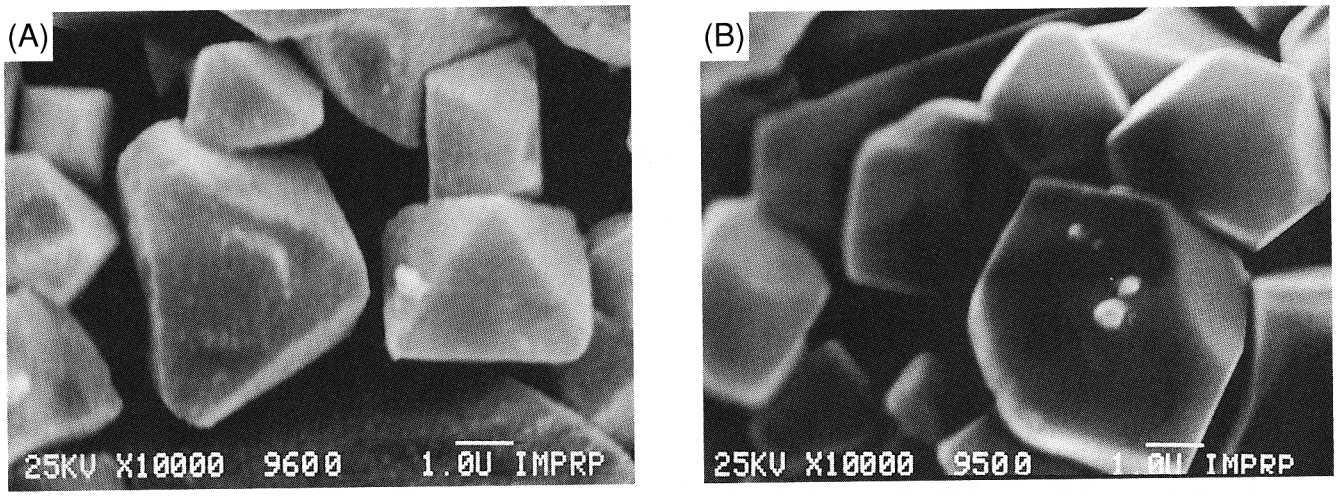

Fig. 1. SEM micrographs of (A) aluminum *sec*-butoxide/lithium methoxide and (B) aluminum *sec*-butoxide/LiOH, both at 800°C.

to depend upon the preparation method (sol–gel) for the samples calcined at 800°C.

(5) DTA and TG Analyses

TGA and DTA curves of the aluminum *sec*-butoxide/lithium methoxide sample are shown in Fig. 2. An important weight loss (17%) was found in the range 150°–600°C. The next weight loss (5%) occurred between 600° and 1000°C. They were attributed to desorption, dehydration, and decomposition of the precursors until crystalline $LiAlO_2$ was obtained. The dehydration and decomposition of mixed aluminum lithium hydrate explained the endothermic peaks at 260° and at 550°C. No weight loss was observed in the range 600°–800°C, and only a small exothermic peak at 610°C and an endothermic peak at 700° were found. Hence, another compound, probably Li_2CO_3, was formed at this temperature range. The last endothermic peak at 900°C was attributed to the thermal treatment decomposition of Li_2CO_3.

The XRD patterns of the aluminum *sec*-butoxide/lithium methoxide preparation calcined for 1 h at 300°, 500°, 700°, and 750°C are compared in Fig. 3. If the sample was treated at a temperature <700°C, the main compound was a microcrystalline compound that may be composed by hydrated LiOH and lithium dialuminate, as reported in Ref. 12. This microcrystalline compound was slowly dehydrated, as shown by the thermal analysis.

However, peaks attributed to γ-$LiAlO_2$, even in the sample treated at 300°C, were found. As the temperature was increased, the amount of microcrystalline compound decreased to produce α-$LiAlO_2$.

Significant changes were observed from the diffractograms of the 500°- and 700°C-treated samples. The decomposition suggested by the thermal analysis is, indeed, accompanied by the crystallization of the microcrystalline compound to γ-$LiAlO_2$, α-$LiAlO_2$, and Li_2CO_3. The broad peaks present in the diffractogram of the aluminum *sec*-butoxide/lithium methoxide sample treated at 700°C implied that the crystallites of α- and γ-$LiAlO_2$ were small, which was not the case for the Li_2CO_3. For the sample treated at 750°C, the composition of the resulting material was very different; the amount of microcrystalline material Li_2CO_3 and α-$LiAlO_2$ decreased significantly, and the main compound was γ-$LiAlO_2$.

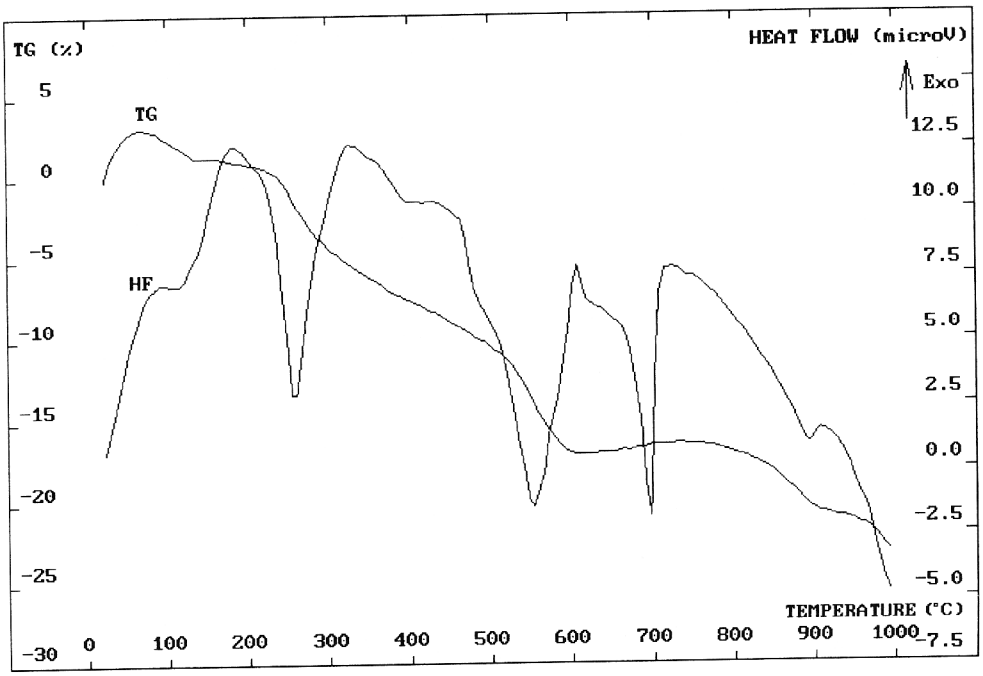

Fig. 2. TGA and DTA curves of the aluminum *sec*-butoxide/lithium methoxide sample.

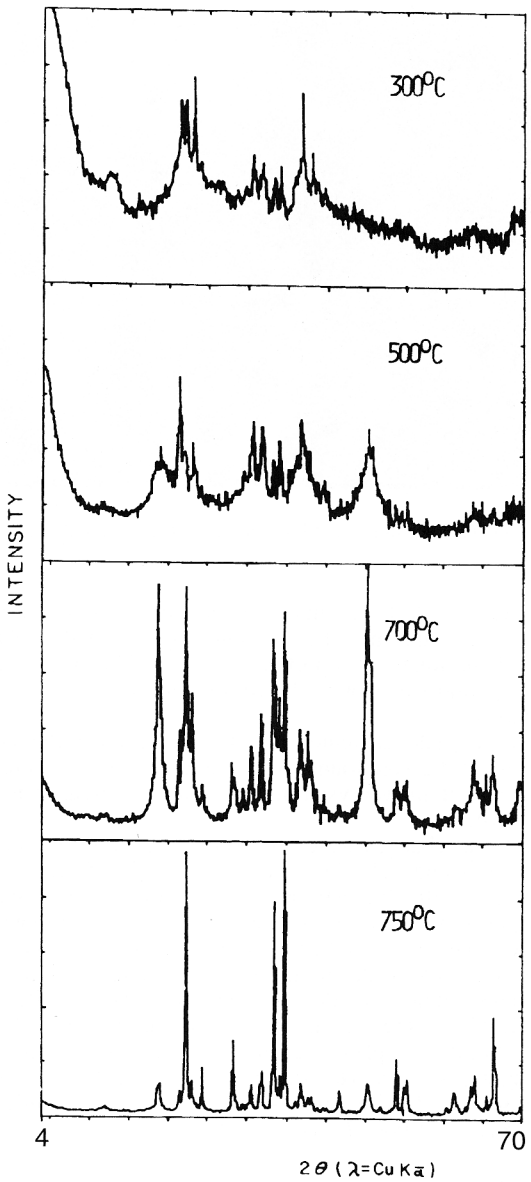

Fig. 3. XRD patterns of the aluminum *sec*-butoxide/lithium methoxide sample treated for 1 h at 300°, 500°, 700°, and 750°C.

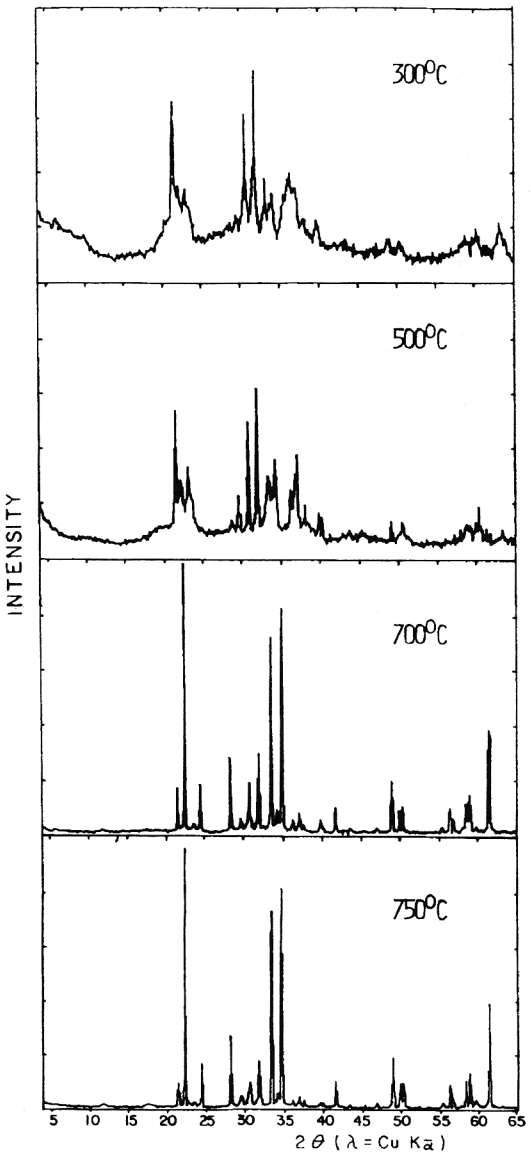

Fig. 5. XRD patterns of the aluminum *sec*-butoxide/LiOH sample treated for 1 h at 300°, 500°, 700°, and 750°C.

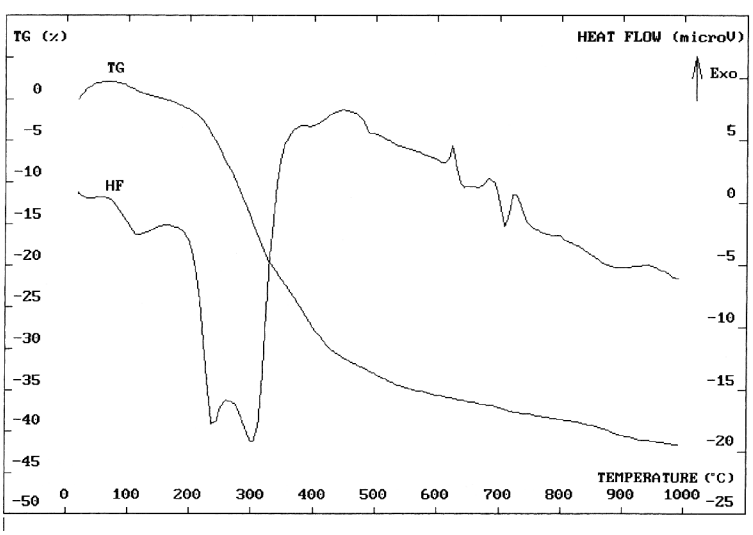

Fig. 4. TGA and DTA curves of the aluminum *sec*-butoxide/LiOH sample.

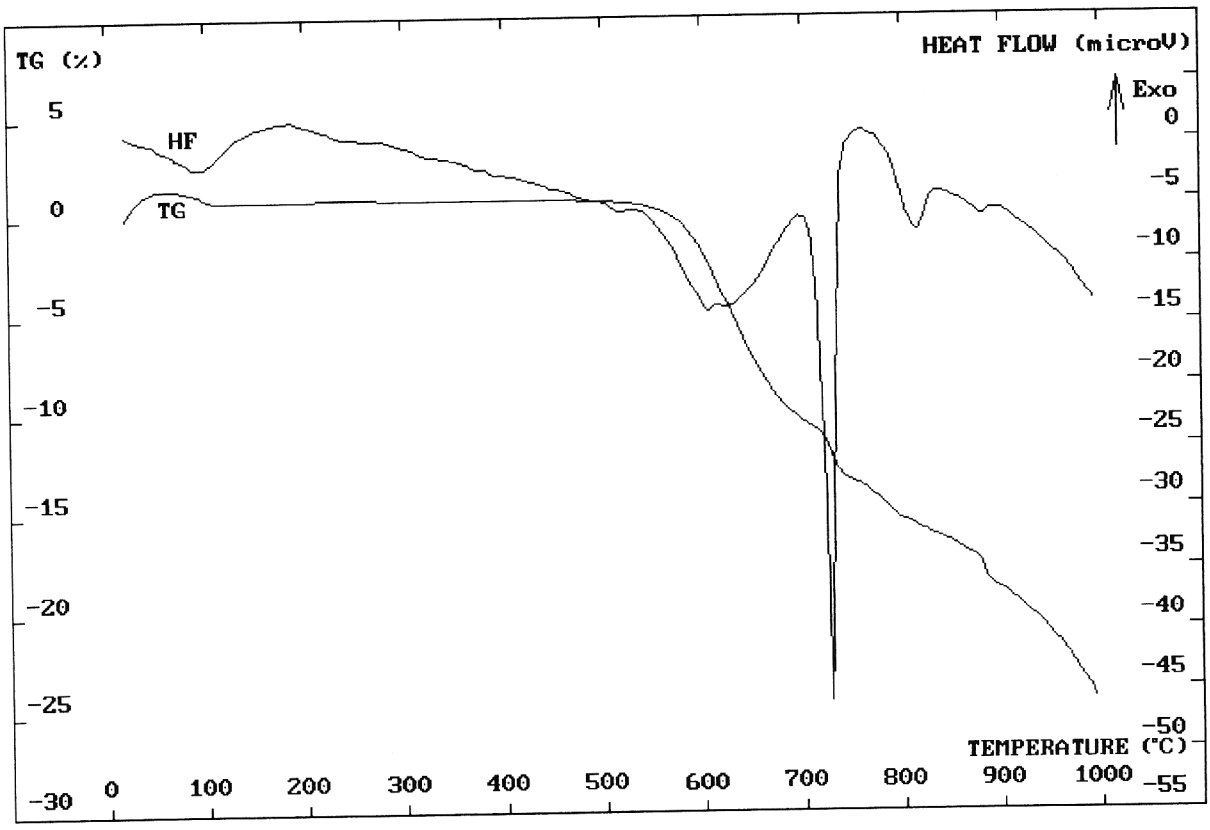

Fig. 6. TGA and DTA curves of the fusion sample.

Figure 4 shows TGA results obtained from the aluminum *sec*-butoxide/LiOH sample. In this sample, aluminum *sec*-butoxide and LiOH were used as reagents; consequently the thermal behavior was slightly different when compared with the aluminum *sec*-butoxide/lithium methoxide sample. The total weight loss (150°–1000°C) was 40%, twice the value found for the aluminum sec-butoxide/lithium methoxide sample. Nevertheless, the dehydration and decomposition of the precursor gel occurred at about the same temperature as in the previous synthesis. The theoretical weight loss was not calculated, because the precise determination of the $LiAlO_2$ precursor was not made. Turner *et al.*[12] reported a weight loss of 40%–44% if the samples were prepared by hydrolysis. Their samples reached constant weight by 600°C. Because no endothermic peaks in the range of 500°–600°C were observed, a different decomposition mechanism to form γ-$LiAlO_2$ was probably followed by, for instance, a dehydroxilation process. Also, the composition of the microcrystalline compound, which reacted between 600° and 700°C, was expected to be different.

Diffractograms of the aluminum *sec*-butoxide/LiOH sample thermally treated for 1 h are presented in Fig. 5. A microcrystalline compound was found in the 300°- and 500°C-treated material, but the γ-$LiAlO_2$ content was much higher than in the corresponding aluminum *sec*-butoxide/lithium methoxide samples. At 700°C, the main compound was γ-$LiAlO_2$, although a small amount of microcrystalline compound and α-$LiAlO_2$ was observed. This feature was an important difference between the aluminum *sec*-butoxide/lithium methoxide and the aluminum *sec*-butoxide/LiOH preparations. After a 750°C heat treatment, the sample was composed mainly of large γ-$LiAlO_2$ crystallites (sharp peaks) and a small amount of α-$LiAlO_2$ and microcrystalline compound. In this case, no Li_2CO_3 was found.

Figure 6 shows the thermal behavior of the γ-$LiAlO_2$ obtained by fusion. The compounds used in this preparation were γ-Al_2O_3 and Li_2CO_3. A large weight loss (24%) was observed in the range 610°–1000°C. As in the aluminum *sec*-butoxide/lithium methoxide sample, a sharp endothermic peak at 610°C was assigned to a dehydroxylation process. A small endothermic peak at 810°C also was present. In this procedure, the temperature at which γ-$LiAlO_2$ was formed was higher than in the other three preparations.

Figure 7 shows the TGA and DTA curves of the sample prepared by the peroxide method. The weight loss, in this case, was 23%, quite similar to the aluminum *sec*-butoxide/lithium methoxide and the fusion preparations. As in the fusion preparation, the most important weight loss was between 600° and 1000°C. Endothermic peaks were found at 720°, 820°, and 920°C.

IV. Conclusions

The sol–gel method provided materials different from those obtained by hydrolysis:[12] the sample prepared from LiOH and aluminum *sec*-butoxide by hydrolysis was amorphous at 600°C, but γ-$LiAlO_2$ was formed at 650°C. If the sample was prepared from the same reactants by the sol–gel method presented in this work at 700°C, the main compound was γ-$LiAlO_2$, although α-$LiAlO_2$ and microcrystalline compounds also were observed.

$LiAlO_2$ could be prepared by the sol–gel method by heating the hydrolysis products from lithium methoxide or LiOH and aluminum *sec*-butoxide. When lithium methoxide was the starting material, Li_2CO_3 was obtained, among other compounds, at 800°C, although the main compound was γ-$LiAlO_2$. If LiOH was used instead, a fairly pure compound (i.e., >80% γ-$LiAlO_2$) was obtained at 750°C. If this sample was treated at 1000°C, only γ-$LiAlO_2$ was obtained.

The conventional methods often used to synthesize γ-$LiAlO_2$ provided pure γ-$LiAlO_2$ by the fusion technique and γ-$LiAlO_2$ + α-$LiAlO_2$ for samples treated at 1000°C. Hence, the main advantage of the sol–gel method was the preparation of γ-$LiAlO_2$ at lower temperatures.

It seemed that, in the sol–gel synthesis, depending on the lithium precursors, the reaction followed different mechanisms, and, therefore, the obtained compounds varied. Furthermore, a

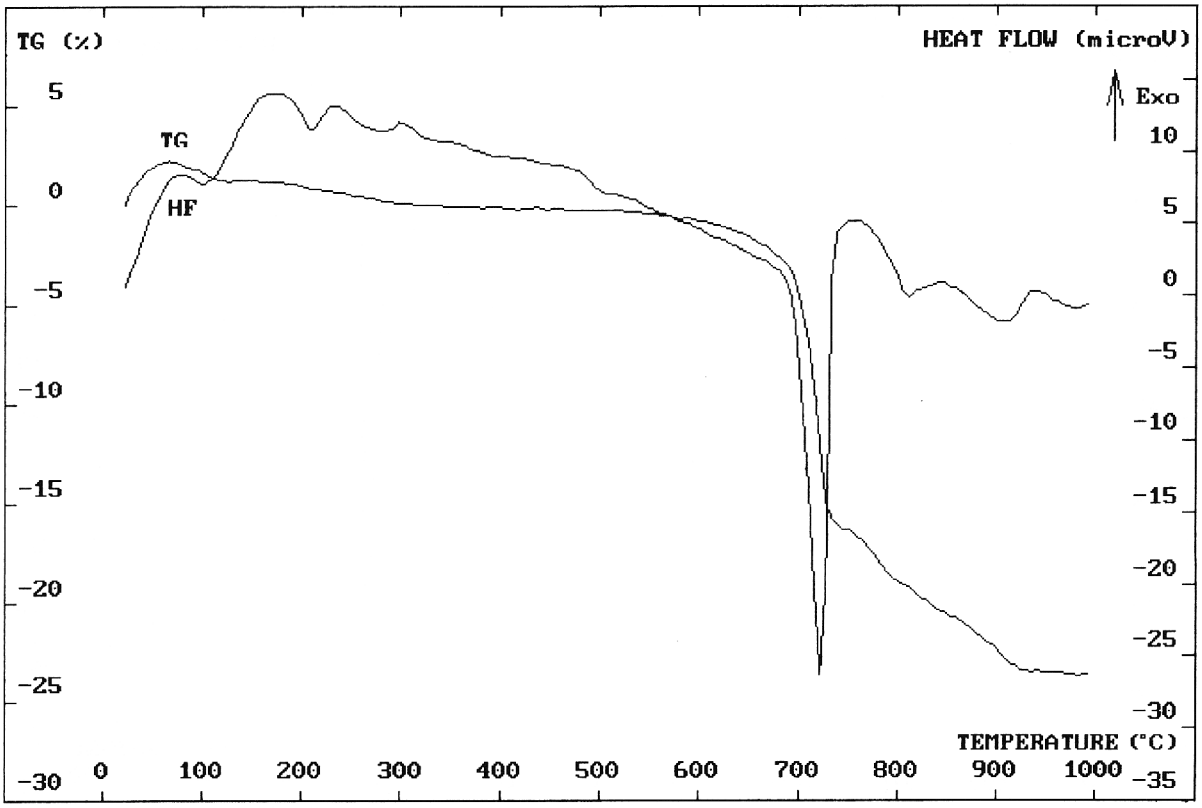

Fig. 7. TGA and DTA curves of the peroxide sample.

mixture of α- and γ-$LiAlO_2$ was produced by synthesis with lithium methoxide as opposed to a relatively pure γ-$LiAlO_2$ when LiOH was used.

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