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Effect of solvents on the preparation of lithium aluminate by sol–gel method

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Abstract

γ-Lithium aluminate was prepared by sol–gel method using lithium methoxide and aluminum-*sec*-butoxide precursors in *i*-propanol, *n*- and *tert*-butanol. Clear gels could be obtained due to the addition of ethylacetoacetate and the dried solids were calcined at 550 and 900 °C. The resulting solids were characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), thermogravimetric analysis/differential thermal analysis (TGA/DTA). γ-Lithium aluminate with the highest purity was obtained with *t*-butanol solvent and $LiAl_5O_8$ was the second major phase.

1. Introduction

Lithium aluminate, γ-LiAlO$_2$, has gained attention for its potential use as irradiation blanket for nuclear fusion reactors. It can also be used as ceramic carrier material in molten carbonate fuel cell due to its high mechanical and thermal stability [1,2]. These potential usages make the synthesis of the highest purity γ-LiAlO$_2$ an important issue. The synthesis of pure γ-LiAlO$_2$ by a modified sol–gel method is an alternative route to the conventional solid-state reaction [3].

Lithium aluminate has three allotropic forms and they are named α-, β-, and γ-LiAlO$_2$ with hexagonal, monoclinic and tetragonal structures, respectively. γ-LiAlO$_2$ is the most stable form and α-, β-LiAlO$_2$ phases transform to γ-LiAlO$_2$ at elevated temperatures [3]. In the synthesis of γ-LiAlO$_2$, calcination above 1000 °C is considered to be ''high temperature calcination'' and below this threshold it is regarded to be ''low temperature calcination'' [9]. Preparation of lithium aluminate by the conventional solid-state fusion method, which requires the high calcination temperatures necessary for

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the solid-state reactions of lithium salt and aluminate, was reported in earlier works [4–7]. Recently, γ-LiAlO$_2$ was also prepared by fusion and sol–gel methods [8], and it was found that the structural, morphological, and thermal properties of lithium aluminate depended strongly on the preparation method. The effect of heat treatment on the structure of the lithium aluminate was also studied [9] and it was found that after calcinations above 750 °C although both γ-LiAlO$_2$ and LiAl$_5$O$_8$ phases existed when it was prepared by sol precipitation, but pure γ-LiAlO$_2$ could be obtained at this temperature with sol–gel method [9]. Thus, we focused on sol–gel method to improve the purity of γ-LiAlO$_2$. In this study, the effects of employment of different alcohols, *i*-propanol, *n*-butanol and *t*-butanol from lithium methoxide and aluminum-*sec*-butoxide in the presence of ligand aid, ethylacetoacetate, were investigated.

2. Experimental

2.1. Preparation of lithium aluminate by sol–gel method

The reagents used in this study were products of Merck AG and they were used without further purification. Equimolar amounts of lithium methoxide and aluminum-*sec*-butoxide were utilized as precursors, and synthesis grade solvents, such as, *i*-propanol (*i*-Pr), *i*-butanol (*i*-But) and *t*-butanol (*t*-But), were used in preparations. Ethylacetoacetate (Eaa) was also used in all mixtures as ligand aid to improve gelation and prevent early precipitation [10,11].

Lithium-methoxide (0.05 mol), Al-*sec*-butoxide (0.05 mol) and ethylacetoacetate (0.025 mol) were mixed with 50 ml of alcohol solvent. Li:Al:Eaa molar ratios of 1:1:0.5, respectively, were kept constant. 50 ml of water was added to start gelation. A scheme for the sol–gel preparation is illustrated in Fig. 1. Clear gels were obtained in 2 days at room temperature and resulting gels were dried at
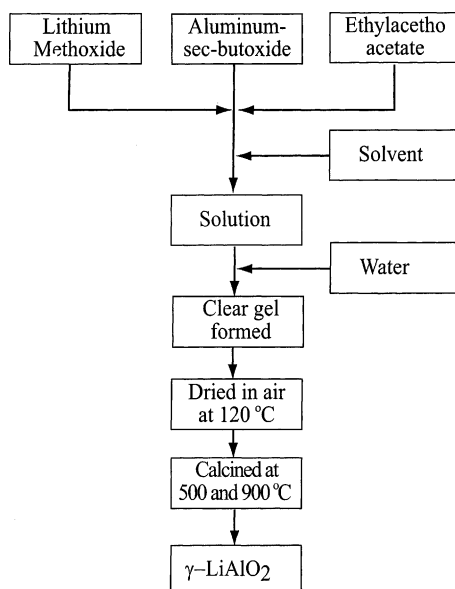

Fig. 1. The preparation scheme for γ-lithium aluminate by sol–gel method.

120 °C under air flow for 8 h. The obtained powders were calcined at 550 and 900 °C. The powders were fluffy and easily crushable fine particles.

2.2. Characterization

X-ray diffractograms were obtained in a Shimadzu X-ray diffractometer (XRD), using ($\lambda = 1.5404$ Å) Cu Kα radiation. TGA analysis was performed in a Shimadzu 50 instrument. A heating rate of 10 °C/min up to 1100 °C was applied under air flow of 100 ml/min. DTA analysis was performed in a Linseis instrument (L62) and α-Al$_2$O$_3$ was used as reference. Samples in DTA analysis were heated from room temperature to 1200 °C with a heating rate of 10 °C/min under air flow of 100 ml/min. Infrared spectra were obtained in a Mattson 1000 Fourier transform infrared spectrophotometer. KBr discs were used in the transmission mode. Morphology of calcined samples was determined by a JEOL JSM 5600 scanning electron microscope at 10 kV.

3. Results and discussion

Crystal phases of the dried powders calcined at 550 °C, prepared with different solvents, are shown in Fig. 2. The predominant phases were LiAl$_2$(OH)$_7$·H$_2$O (JCPDS/31-704) and LiOH·H$_2$O (JCPDS/25-486). Peaks of these two phases were comparatively sharper in t-butanol than those for the other two solvents. γ-LiAlO$_2$ was not yet present in large quantities at this low calcination temperature. X-ray diffractograms of dried powders calcined at 900 °C are shown in Fig. 3. In the diffractograms, the predominant phase was γ-LiAlO$_2$ (JCPDS/38-1464). LiAl$_5$O$_8$ (JCPDS/38-1425) was also present as second phase. γ-LiAlO$_2$ peaks were sharper and more intense in t-butanol solvent than those for the other two solvents. It is worth mentioning that in all solvent systems, minor amounts of LiAl$_2$(OH)$_7$·H$_2$O remained at 900 °C. Kwon and Park [3] also reported that LiAl$_2$(OH)$_7$·H$_2$O did not disappear even at 1000 °C. In the gels obtained with these solvent systems, γ-LiAlO$_2$ was
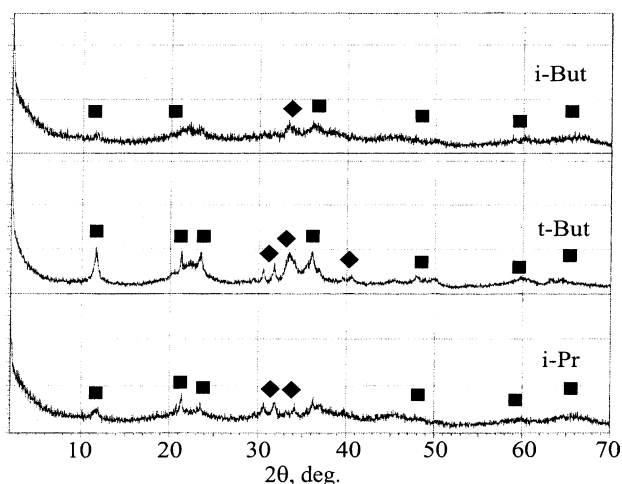
Fig. 2. XRD diagrams of samples calcined at 550 °C (■, LiAl$_2$(OH)$_7$·H$_2$O; ◆, LiOH·H$_2$O).
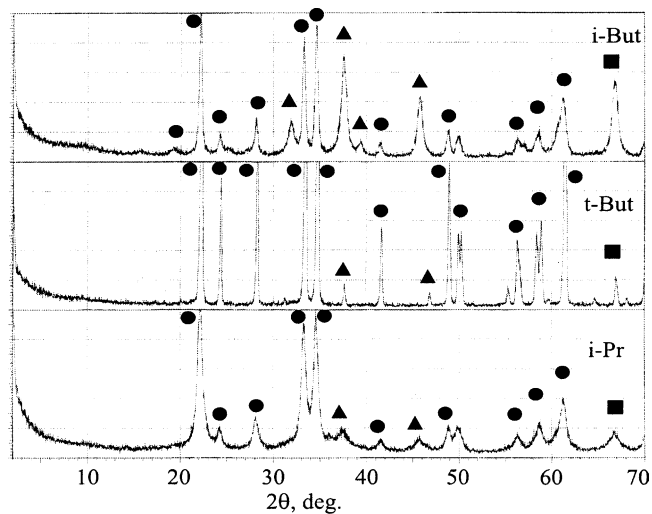
Fig. 3. XRD diagrams of samples calcined at 900 °C ($\bullet$, γ-LiAlO$_2$; $\blacktriangle$, LiAl$_5$O$_8$; $\blacksquare$, LiAl$_2$(OH)$_7 \cdot$H$_2$O).
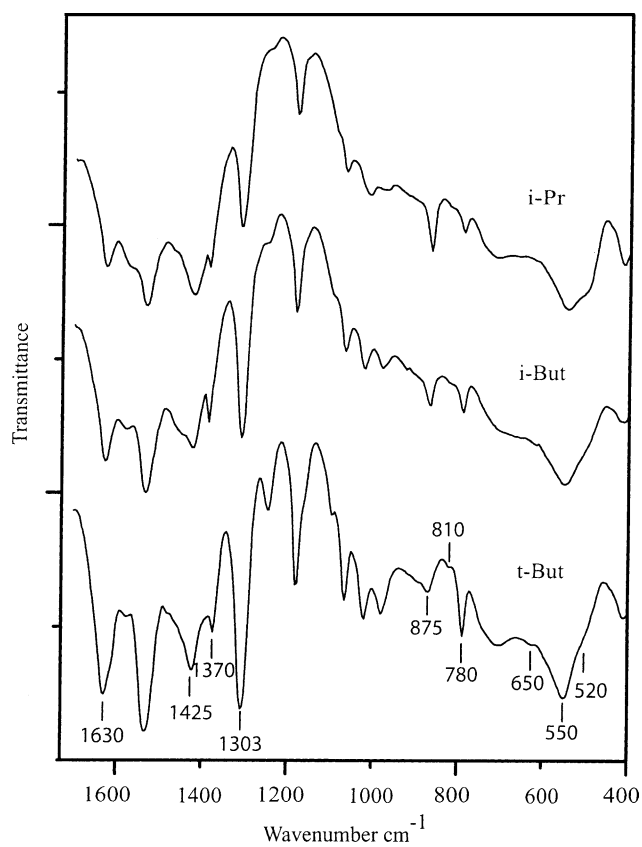

Fig. 4. FT-IR spectra of air-dried samples at 120 °C.
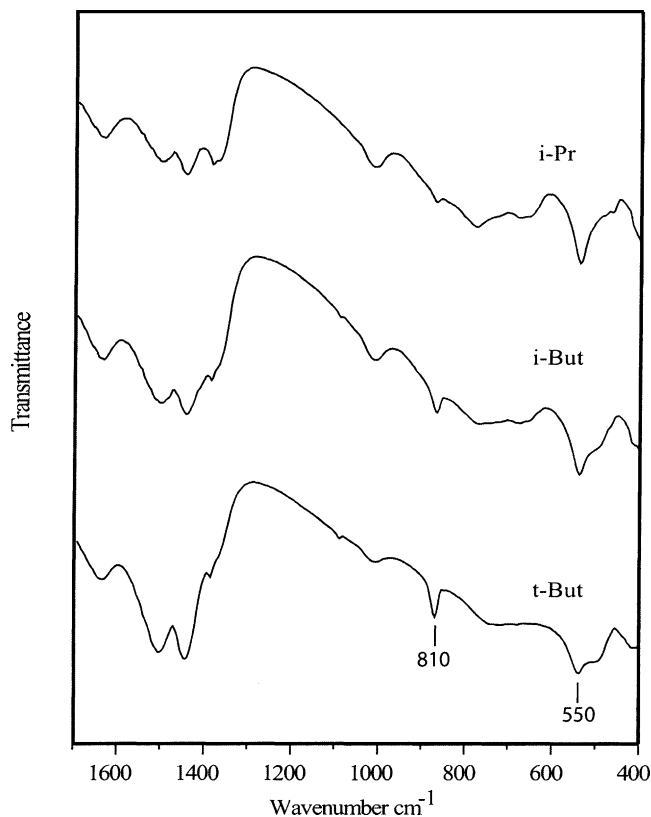
Fig. 5. FT-IR spectra of samples calcined at 550 °C.

predominant phase. $LiAl_5O_8$ and $LiAl_2(OH)_7 \cdot H_2O$ phases were detected in appreciably less quantities in t-butanol than those in the other two solvents. Furthermore, better crystallinity was obtained at 900 °C with t-butanol.

Fig. 4 shows the infrared spectra of samples dried at 120 °C. Peaks at 550 and 780 cm^{-1} are due to the vibrations of AlO_6 and the $LiO_6 + AlO_6$ combination, respectively, [9,12,13] and 1370, 1425 and small shoulder at 1475 cm^{-1} are all due to Al-sec-butoxide [14]. Band at 1630 cm^{-1} is due to hydroxyl formation. Peaks at 875 and 1303 cm^{-1} are due to Eaa ligand formation [14]. Infrared spectra of samples calcined at 550 °C are shown in Fig. 5. Bands at 810, 650 and 550 cm^{-1} indicate the presence of γ-$LiAlO_2$ and $LiAl_5O_8$ phases. Although γ-$LiAlO_2$ and $LiAl_5O_8$ phases were not detected at this low calcination temperature, FTIR analysis clearly shows their presence. Bands showing the presence of organic residues are not visible at this temperature. This is in line with the findings from TG analysis since weight loss due to the removal of organics was finished before 550 °C. Fig. 6 depicts infrared spectra of samples calcined at 900 °C. Infrared spectra of γ-$LiAlO_2$ and $LiAl_5O_8$ phases were well defined in samples with strong bands at 810, 650 and 550 cm^{-1} and weak bands at 520 and 450 cm^{-1} for the samples calcined at 900 °C. Bands appearing at 610 and 680 cm^{-1} refer to $LiAl_5O_8$ phase [9,12,13]. Peaks at 810 and 650, 550 cm^{-1}, characteristic of γ-$LiAlO_2$ phase, were sharper for samples prepared with t-butanol solvent than those with other two solvents. This was an indication of that higher
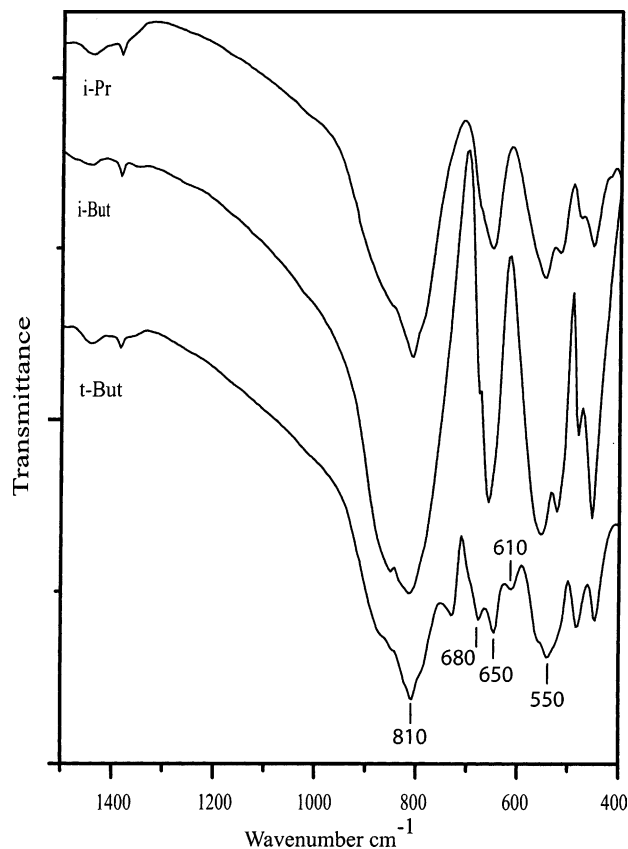
Fig. 6. FT-IR spectra of samples calcined at 900 °C.

purity γ-LiAlO$_2$ was produced when t-butanol was used as solvent. This result was also in line with the XRD results of this study.

The SEM images of samples calcined at 900 °C were shown in Fig. 7. None of the particles showed edges and well-defined crystals of γ-LiAlO$_2$ but the sample prepared with t-butanol was partially faceted, although irregularly shaped, possibly corresponding to tetragonal γ-LiAlO$_2$, as reported by Valenzuela et al. [8]. With i-propanol and i-butanol, the samples showed more rounded corners. Also, the samples showed a distribution of particle sizes.

Thermal behavior of the gels prepared with different solvents was studied by TGA and DTA. TGA and DTA curves are, respectively, shown in Figs. 8 and 9. Slight weight losses observed at about 100 °C in Fig. 8 are attributed to the dehydration of samples. There is no corresponding endothermic peak at the same temperatures in DTA curves given in Fig. 9. Two endothermic peaks seen in the DTA curves were attributed to the reactions between components as well as organic residue pyrolysis. There were two successive weight losses observed around 200–255 °C and 255–550 °C in TGA curves as shown in Fig. 8. Temperatures of two successive weight losses in TG analysis did not coincide with the temperatures of major endothermic peaks observed in DTA. In all alcohol systems, weight losses stopped before 550 °C. Overall weight losses were around 55% for alcohol systems. One interesting feature of the DTA curves
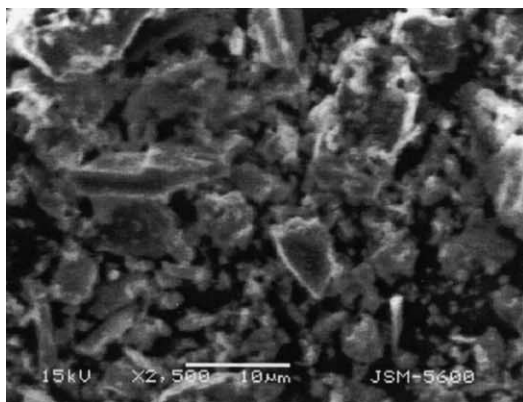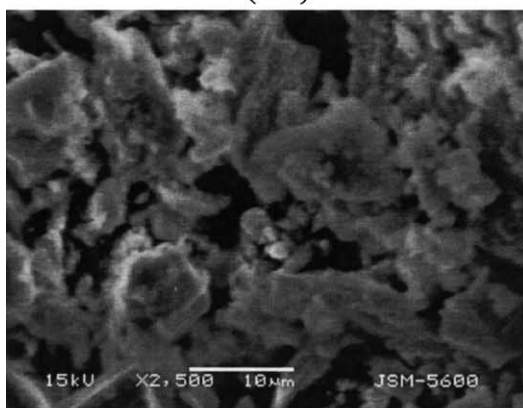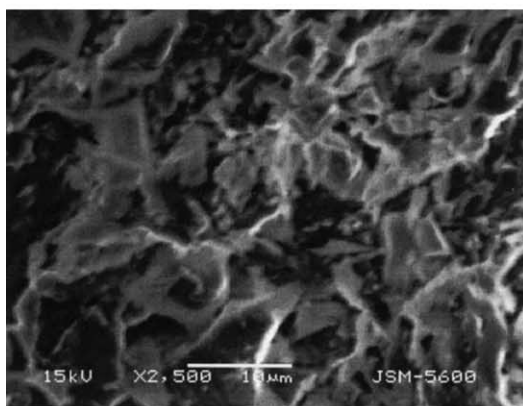
Fig. 7. The SEM images of *i*-Pr, *i*-But, and *t*-But samples calcined at 900 °C.
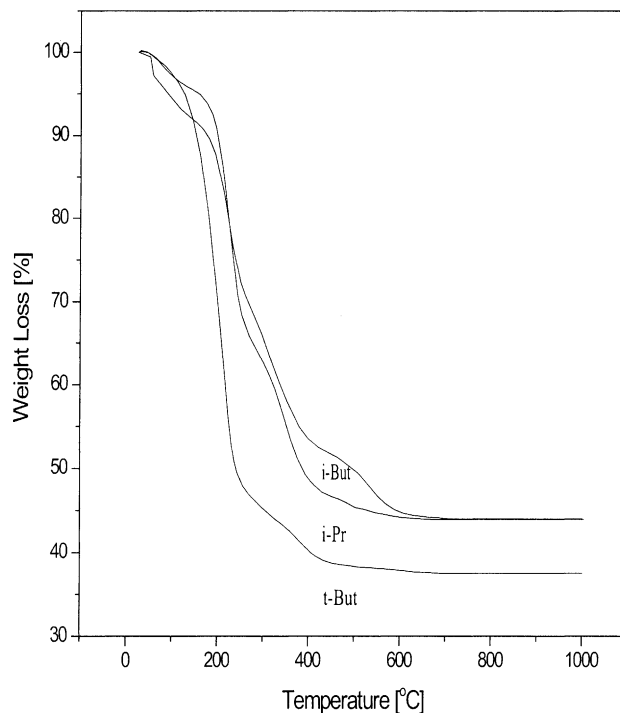
Fig. 8. TGA curves of samples prepared with different solvents.

on changing the solvent from *t*-butanol to *i*-butanol and to *i*-propanol, is the shift in the first and second endothermic peaks (~270–355 °C and 408–432 °C) to comparatively higher temperatures as shown in Fig. 9. Similar shifts in the onset and end temperatures of weight losses in TGA curves were observed. Furthermore, in all samples there was a small endothermic peak near 700 °C in DTA curves. Since no preceding α or β-lithium alumina could be detected from X-ray diffractograms of samples calcined at 550 °C (see Fig. 2), this peak should not be due to α or β-lithium aluminas' phase change to γ-LiAlO$_2$ and it is more reasonable to consider this endothermic peak as an indication of direct formation of γ-LiAlO$_2$ phase. In line with our findings, Kwon and Park [3] reported that this peak was related to the direct formation of gamma lithium aluminate in the sol–gel method and lithium salt and alumina precursor systems. They confirmed γ-LiAlO$_2$ phase formation from X-ray diffractograms of samples obtained after calcinations near 700 °C. On the other hand, Turner et al. [15] reported no such peak.

Kwon and Park [3] reported that when butoxide–butoxide was mixed with methanol or ethanol instead of butanol due to alcohol–alkoxide exchange, the dried gel did not disintegrate easily to give fine homogeneous powders, whereas butoxide–butoxide system led itself to fine homogeneous powders. However, in this study, with a mixed system (lithium methoxide and aluminum-*sec*-butoxide) and various alcohols as solvents, highly pure and crystalline gamma lithium aluminate was produced. With the help of ethylacetoacetate as ligand aid, homogeneous gels were produced. It can be argued that alcohol–alkoxide exchange reaction occurred during gelation resulted in poorer dispersion with *i*-butanol and *i*-propanol and consequently this led to less pure crystals. Thus, it is important to avoid this type of exchanges. It has been shown here that, with the help of ligand aid such as ethylacetoacetate, poor distribution of sol–gel precursors can be avoided.
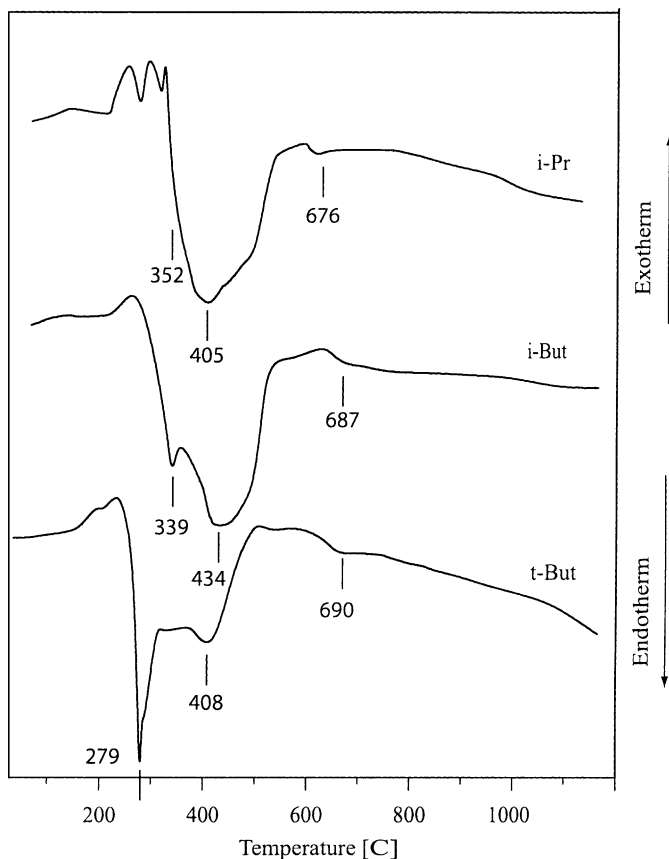
Fig. 9. DTA curves of samples prepared with different solvents.

4. Conclusions

This work showed that the crystallinity and purity of γ-LiAlO$_2$ was depended on the solvent used. Ligand aid such as ethylacetoacetate led to the better gelation of reagents by the sol–gel method and hence higher purity γ-LiAlO$_2$ was produced. Major intermediates leading to the formation of γ-LiAlO$_2$ were LiOH·H$_2$O and LiAl$_2$(OH)$_7$·H$_2$O. Lithium methoxide–aluminum-*sec*-butoxide and *t*-butanol system resulted in γ-LiAlO$_2$ of the highest crystallinity among the solvents studied. Some minor amounts of LiAl$_5$O$_8$ were also present in all solvents.

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