

Synthesis of high purity γ -lithium aluminate by freeze drying

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ABSTRACT

γ -LiAlO₂ plate-like nanostructures have been synthesized by lyophilization of a gel precursor prepared by coprecipitation process. Aqueous solutions of Al(NO₃)₃·9H₂O and LiNO₃ were used as precursors, and NaOH was used as precipitant agent. After freeze-drying, the samples were calcined at several temperatures for characterization. The lyophilization process allowed the preparation of γ -LiAlO₂ phase at 750 °C, which remained stable until temperatures about 1150 °C, without the formation of other undesired phases as LiAl₅O₈. Copyright © 2016 VBRI Press.

Keywords: γ -LiAlO₂; coprecipitation; freeze-drying; TEM.

Introduction

LiAlO₂ is a potential candidate to be employed in the area of energy production, such as tritium breeding material in fusion reactors [1-2], polymeric composites [3], and matrix of molten carbonate fuel cells (MCFC) [4]. LiAlO₂ can be prepared in different crystalline phases, α -LiAlO₂, β -LiAlO₂ and γ -LiAlO₂, which depend on the synthesis route and the heating temperature. Each phase can be used in specific devices or systems, according to their morphology and texture. The γ -phase is obtained at high temperatures and is desirable in applications that require materials with thermal stability. Different synthesis routes have been used to prepare lithium aluminates [3-17], as solid state method based on the mixture of Li and Al oxides or carbonates, sol-gel method, coprecipitation, among others. Each process has advantage and disadvantage, but the main problem related to the preparation of pure-phase γ -LiAlO₂ consists in the lithium loss during the washing processes, due to the high solubility of lithium ions in water [15], and during calcination above of 900 °C, by evaporation of lithium [10]. The lithium loss affects the stoichiometry of the material, leading to the formation of undesirable phases as LiAl₅O₈ [14-16]. The sol-gel process is more efficient than other methods due to the higher homogeneity of their precursors and because the washing step is not necessary. However, this process does not avoid the loss of lithium at high temperatures [14]. The coprecipitation method has been also used due to the low cost of the precursors [13, 14], although the lithium loss occurs during the washing process by leaching, and during the thermal treatment at high temperatures. To avoid these problems, several drying routes have been used to prepare pure phases of lithium aluminate.

In this work, freeze drying was used as the drying process to obtain pure γ -LiAlO₂, eliminating steps of

washing of the precipitate and avoiding the loss of lithium by leaching. Excess of lithium salt was used to compensate the elimination of lithium by sublimation during the calcination process.

Material and methods

LiAlO₂ was obtained by mixing aqueous solutions containing Al(NO₃)₃·9H₂O (*Synth*) and LiNO₃ (*Synth*), with molar ratio of Al:Li = 1:7. It was used an excess of LiNO₃ to maintain the stoichiometry of the material after calcination. The mixture was kept under stirring at 80 °C, and after 1 h an aqueous solution of NaOH (*Sigma*) was added in the reaction, producing a white and gelatinous precipitate. The precipitate was centrifuged, the supernatant containing synthesis waste was discarded, and then, the resulting gel was dipped in liquid nitrogen. The frozen solution was introduced in the freeze-dryer (Labconco freezezone 1L), and maintained at -50 °C and 5 microns Hg for 12 h. The fine white powder produced was separated in aliquots and heated between 550 and 1150 °C for 3 hour. The powder was pressed and heated at 1300 °C for morphologic characterization.

The crystalline phases of the samples were identified by X-ray diffraction (Shimadzu XRD 6000 diffractometer using CuK α radiation) and by infrared spectroscopy (Perkin-Elmer) using anhydrous KBr tablets. The heating behavior of the samples was verified by TGA-DTA analyses (DTA-TG Apparatus, SHIMADZU DTG-60H) from room temperature to 1200 °C at 10 °C/min using a N₂ flow of 110 mL/min. The sample morphologies were observed in a scanning electron microscope (SEM) Quanta 200 FEG – FEI and in a transmission electron microscope (TEM) TECNAI G2 SPIRIT- FEI with an acceleration voltage of 120 KV. The textural characteristics of the

samples were determined by N₂ adsorption in a Quantachrome Autosorb, using the BET method.

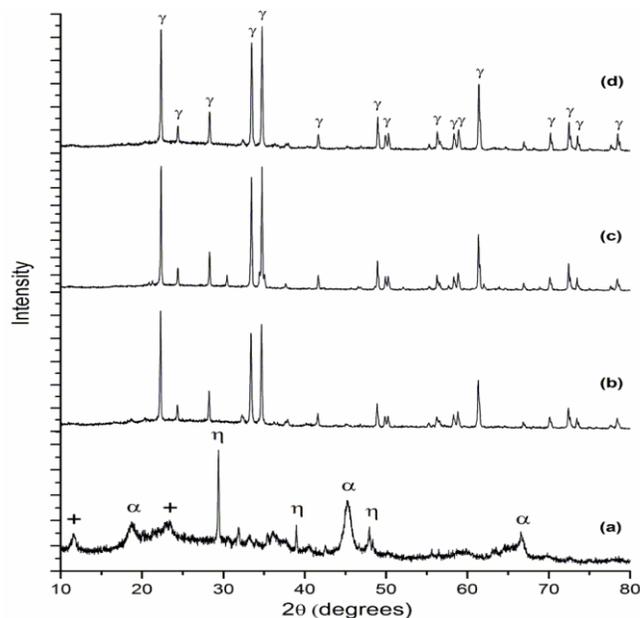


Fig. 1. XRD patterns of the sample calcined at (a) 550, (b) 750, (c) 950 and (d) 1150 °C. η , +, α and γ symbols correspond to NaNO₃, LiAl₂(OH)₇·2H₂O, α -LiAlO₂ and γ -LiAlO₂ phases. π symbol corresponds to unidentified impurities.

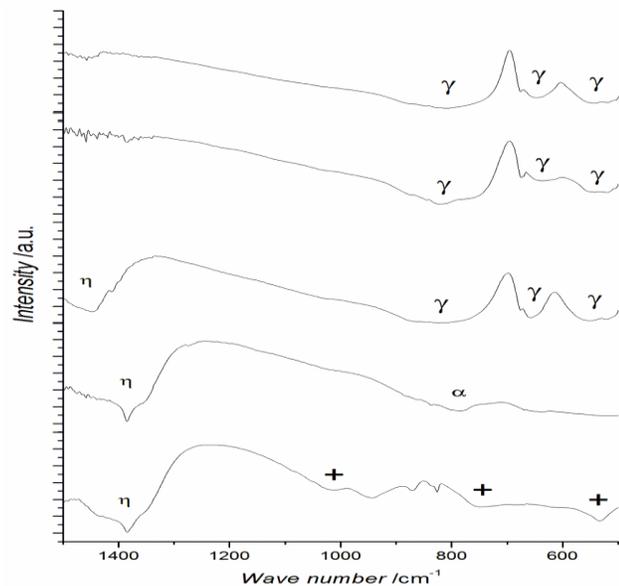


Fig. 2. FTIR spectrum of the sample (a) as-freeze dried and calcined at (b) 550, (c) 750, (d) 950 and (e) 1150 °C. η , +, α and γ symbols correspond to the phases NaNO₃, LiAl₂(OH)₇·2H₂O, α -LiAlO₂ and γ -LiAlO₂.

Results and discussion

Crystalline phases of the powders calcined at 550, 750, 950 and 1150 °C are shown in **Fig. 1**. Peaks related to NaNO₃, formed by reaction between NaOH and LiNO₃ at temperatures below 550 °C, are observed in **Fig. 1(a)**. Peaks related to α -LiAlO₂ and LiAl₂(OH)₇·2H₂O phases are also observed in this temperature, and are according to literature [6, 10, 12]. **Fig. 1(b)** shows the formation of the crystalline phase of γ -LiAlO₂ at 750 °C, showing that the freeze-drying process causes the formation of this phase at lower

temperatures than those shown by some authors. Kwon *et al.* [13] obtained pure γ -LiAlO₂ phase at 850 °C using three different synthesis methods: citrate process, Pechini process and PVA-assisted process. Khomane and co-workers [11] obtained pure γ -LiAlO₂ at 950 °C by coprecipitation method, using Tween 80 as surfactant. The γ -LiAlO₂ phase also was obtained at 950 °C by citrate-based sol-gel method using Li and Al nitrates, citric acid and ammonium hydroxide (NH₄OH). Oksuzomer *et al.* [18], obtained pure gamma phase at 900 °C using sol-gel method. **Fig. 1(c, d)** shows that the material is stable after calcination at 950 and 1150 °C, maintaining only the γ -phase. This result is very relevant, because the γ phase has been formed at ~750 °C and the stoichiometry was preserved at high temperatures of calcination without the formation of undesired phases as LiAl₅O₈. Some authors prepared γ -LiAlO₂, using several synthesis routes, where were observed the presence of the LiAl₅O₈ phase in materials calcined at temperatures above 1000 °C [11-13].

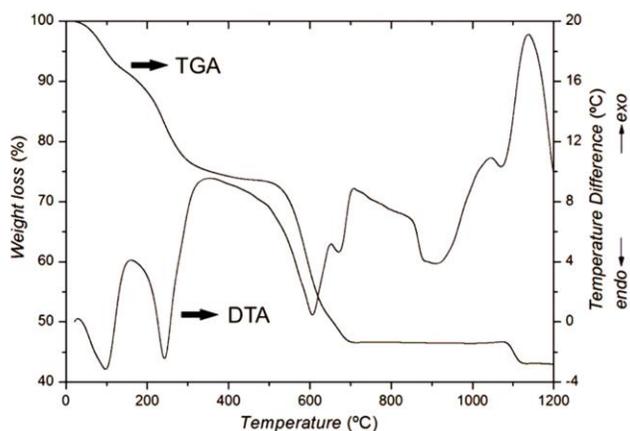


Fig. 3. TGA and DTA curves obtained for the sample as-freeze-dried.

Fig. 2 shows IR spectra of the samples freeze-dried and treated at various temperatures. All the bands are large due to the nanometric dimension of the crystallites. A NO₃⁻ band is observed in the spectrum of the as-prepared material (**Fig. 2a**) indicating the NaNO₃ presence [13]. LiAl₂(OH)₇·2H₂O bands [14] were also found and corroborates XRD results. **Fig. 2(b)**, related to material freeze dried and calcined at 550 °C, shows bands associated to NO₃⁻ and α -LiAlO₂ phases, confirmed by the vibrations of AlO₆ and the LiO₆ + AlO₆ combination, respectively [19]. **Fig. 2(c)** shows γ -LiAlO₂ bands (810, 660 and 525 cm⁻¹) attributed to the AlO₄-LiO₄ vibrations and the stretching vibration of AlO₄ tetrahedron, indicating the α → γ -LiAlO₂ phase conversion between 550 and 750 °C as observed in XRD results. A band related to the decomposition products of NaNO₃ (Na₂O) is observed in this temperature between 1420 and 1440 cm⁻¹. Bands related to pure γ -LiAlO₂ were observed at 950 and 1150 °C (**Fig. 2(d, e)**), accompanied by traces of Na₂O, corroborating XRD results.

Fig. 3 shows TGA-DTA curves of the material freeze-dried. In the range of 25-300 °C approximately, there are weight loss of about 25 % related to loss of water adsorbed in the particle surface [6] (97 °C), dehydroxylation

processes of phase $\text{LiAl}_2(\text{OH})_7 \cdot 2\text{H}_2\text{O}$ and elimination of water molecules in the pore channels [6] (242 °C). Between 300 and 700 °C a weight loss of about 30 % could be assigned to NaNO_3 decomposition. The weight loss between 1080 and 1120 °C (about 3 %) can be attributed to decomposition and/or vaporization of Na_2O and/or Li_2O . Infrared spectroscopy measurements (Fig. 2) corroborate these results.

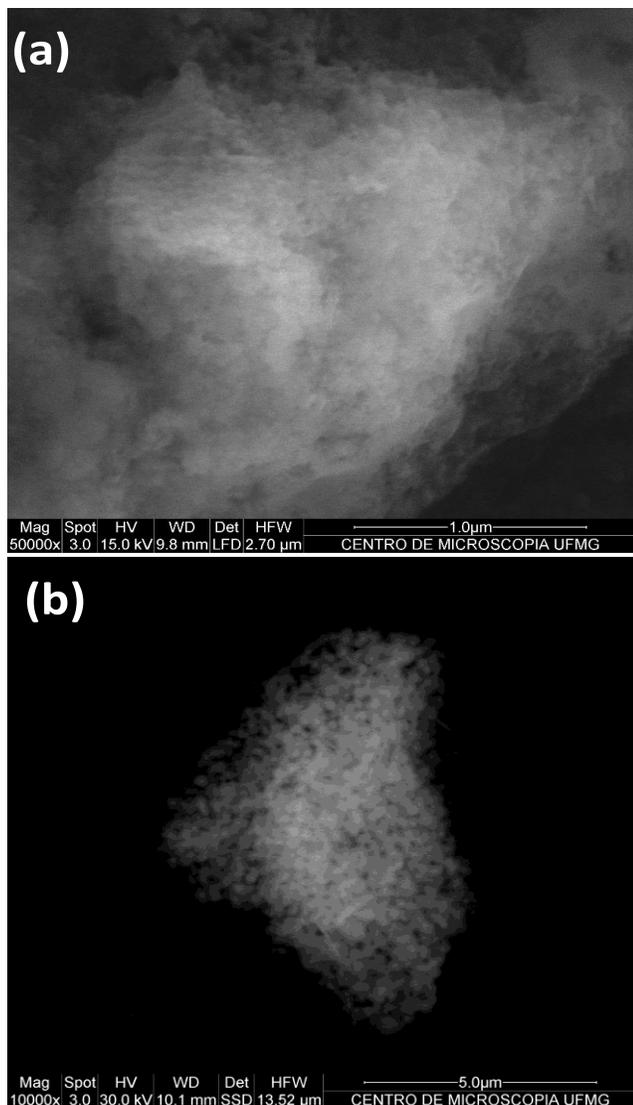


Fig. 4. SEM micrograph of the as-lyophilized sample (a) and SEM micrograph of the sample calcined at 950 °C (b).

The material as-lyophilized, shown in Fig. 4(a), is formed by nanoparticles with diameters of 30 ± 5 nm are arranged as plate-like (lamellar structure), whose morphology is characteristic of lyophilized oxide materials. The nanoparticle size increases with the increasing in the temperature reaching diameter between 170 and 330 nm at 950 °C (Fig. 4b). Each particle is an agglomerate of plate-like structures formed by primary nanoparticles, as observed by TEM images in Fig. 5a. The growth rate increases with the calcination temperature and the particles reach average diameters of 2 microns at 1150 °C (Fig. 5b). A phenomenon observed during the characterization of the plate-like nanostructures was their disintegration due to

electron beam, giving rise to nanoparticles, confirming that the plates are formed by the primary nanoparticles. This disintegration may be related to the sublimation of lithium due to beam energy.

Table 1. Values of Specific Surface Area, Average Particle Size and C constant.

Temperature (°C)	A_{BET} (m^2g^{-1})	Average particle size (nm)	C
550	25	92	295
750	27	85	29
950	10	230	137
1150	1	2000	11

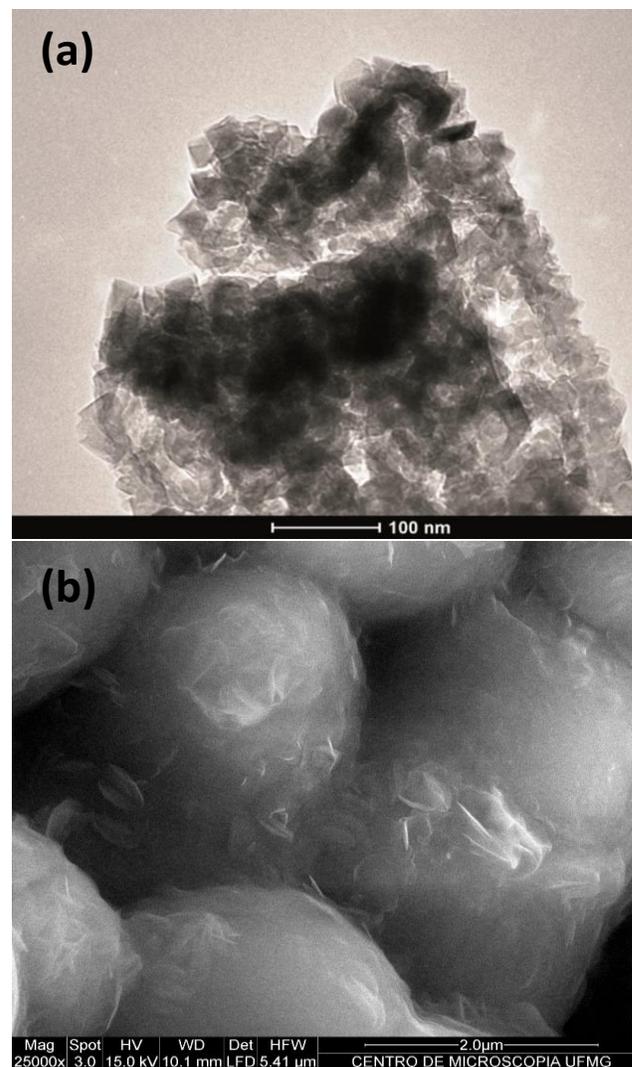


Fig. 5. (a) TEM micrographs of sample calcined at 950 °C, (b) SEM micrograph of the sample calcined at 1150 °C.

Fig. 6 shows the adsorption-desorption isotherms of the samples treated between 550 and 1150 °C and Table 1 the values of the specific surface area. All isotherms have hysteresis without saturation, with characteristic of nanoparticulate material arranged in plate-like nanostructures [20], corroborating results of electron microscopy. The C constant of the samples heated up to 950 °C had acceptable values (between 30 and 300) according literature [20].

At 1150 °C, the C constant became very low, due to the diminishing of interaction forces between the sample and the gas due to densification of the material. The values obtained in this temperature are not reliable. Samples heated at 550 and 750 °C had specific surface area about 25 m²g⁻¹, that diminish to 10 m²g⁻¹ for materials calcined at 950 °C. The average particle size measured by this technique is in accordance with SEM results.

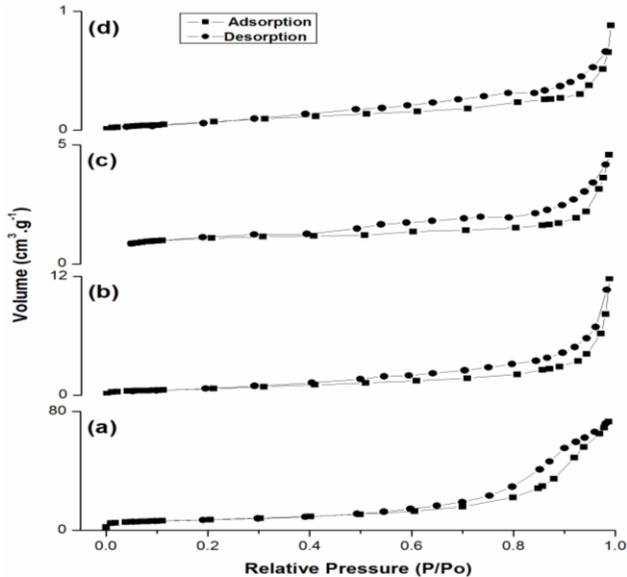


Fig. 6. Adsorption-desorption curves of the LiAlO₂ heated at (a) 550 °C, (b) 750 °C, (c) 950 °C, (d) 1150 °C.

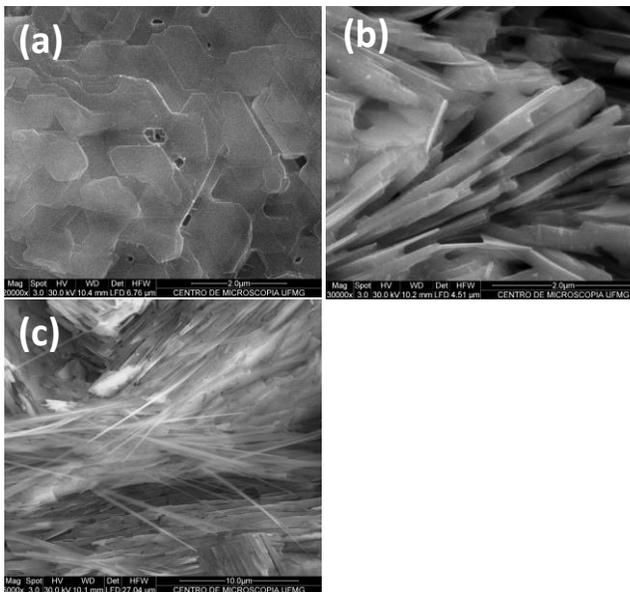


Fig. 7. (a) SEM micrograph of the sample pressed and heated at 1150 °C for 2 h, (b) SEM micrograph of sample pressed and heated at 1300 °C for 2 h, and (c) SEM micrograph of sample pressed and heated at 1350 °C for 2 h.

In preliminary tests, the powder calcined at 950 °C was pressed and heated at 1150 °C (Fig. 7a), 1300 °C (Fig. 7b), and 1350 °C (Fig. 7c) for 2 h. The samples showed lamellar growth during this process, which allows a better ionic conduction, according literature.

Conclusion

γ -LiAlO₂ phase of high purity was prepared by coprecipitation, using freeze-drying as drying method. The $\alpha \rightarrow \gamma$ -LiAlO₂ phase transition occurred before of 750 °C and the gamma phase of high purity remained at temperatures between 950 and 1150 °C without the presence of other phases. The particulate material presented plate-like nanostructures, whose size increased until 1350 °C. The sintered samples also presented lamellar morphology.

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