

Synthesis of lithium aluminate by thermal decomposition of a lithium dawsonite-type precursor

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Of all ceramic materials, lithium aluminate has been widely studied and has become a good candidate to be used as both a fusion blanket and as a matrix in molten carbonate fuel cells. On behalf of these lithium aluminate applications, a variety of procedures has been proven to prepare adequate crystalline and pure material. In this study, lithium aluminate was synthesized by thermally decomposing a lithium dawsonite-type precursor using aluminum nitrate and chloride as a starting material. The lithium aluminate was characterized by scanning electron microscopy (SEM) and X-ray diffraction. According to the results the crystalline form, in mixtures of several phases, of the lithium aluminate obtained depends strongly on the thermal treatment.

Key words: lithium aluminate, dawsonite.

Introduction

Lithium aluminate is a ceramic material that has chemical, mechanical, and thermo-physical properties that allow it to be used as a breeder blanket in nuclear fusion reactors [1-3] and as a matrix in molten carbonate fuel cells [4-6]. The lithium aluminate crystal structure may be in either α , β , or γ phases [7, 8]. Mixtures of these polymorphs are common in syntheses performed below 973 K, where α - and γ -LiAlO₂ can coexist; it is at this temperature that its performance as a tritium breeder material has been investigated [9, 10]. The γ -LiAlO₂ phase is the main crystallographic form found at high temperatures; indeed, it possesses a somewhat higher melting point of 1880 K. The transformation of α to γ phase was considered irreversible until some α -LiAlO₂ was synthesized from γ -LiAlO₂ by a dissolution-precipitation process [11].

Synthesis of lithium aluminate has been essentially performed by several methods: in the solid state, by wet chemical, sol-gel, with the use of templates, various precursors, and combustion processes [1-13]. The main product in a solid state reaction is the β -phase; in a wet chemical reaction, the main product is a solid solution of α -LiAlO₂ and γ -LiAlO₂ phases. Research in the improved synthesis of LiAlO₂ continues to develop.

By contrast, dawsonite is a natural sodium mineral, an aluminum hydroxyl carbonate. Dawsonite may be prepared from several precursors, mainly by hydrothermal and hydrolysis processes during the synthesis of cements and aluminas [14-18]. Dawsonite-type compounds and laminar

hydroxycarbonate have been hydrothermally synthesized; their thermal decomposition produces different aluminates [19]. Treatment of the ammonium analogue of the mineral dawsonite with appropriate amounts of barium and lanthanum solutions led to the formation of a layered aluminate structure on subsequent heating [20]. If this mineral is put into contact with alkali solutions, it can selectively accumulate alkali [21]. Also, it is well known that thermal decomposition of dawsonite materials produces spinel powders; the method for preparing sodium aluminate from basic aluminum sulfate (BAS) consists of two steps. In the first step, BAS is transformed into sodium dawsonite [NaAl(OH)₂CO₃] by treating BAS with a sodium carbonate aqueous solution at various temperatures and times [22]. Or, it can be transformed into a layered double hydroxide where there is an interlayer anion. This is synthesized by a hydrothermal process from aluminum-tri-(sec-butoxide) and lithium carbonate. This product has a platy morphology with a distinct hexagonal symmetry, and there is evidence for a superlattice, indicating cation ordering among octahedral sites [23].

In this study, it is proposed that the use of the thermal decomposition of a lithium dawsonite-type precursor prepared from a basic aluminum sulfate and lithium carbonate can be used as a new route for lithium aluminate synthesis.

Experimental

Lithium dawsonite-type compound preparation and thermal treatment

The process consists of three steps:

1) The initial precursor of lithium dawsonite was basic aluminum sulfate (BAS), which was prepared following the sol-gel method of monodisperse microcrystals [24]. Mixed aluminum salt solutions were prepared, 40 ml of

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0.8 mol.l⁻¹ Al₂(SO₄)₃ and 50 ml of 0.8 mol.l⁻¹ Al(NO₃)₃ or AlCl₃ in place of Al(NO₃)₃. For each preparation, 15 ml of the mixed solution was added to 9 ml of 4.8 mol.l⁻¹ NaOH. The gels obtained were heated at 373 K for 4 hours in a stainless steel autoclave. After the aging, the samples were quenched to room temperature in an ice bath, centrifuged, washed with distilled water, and dried at 323 K for 48 hours.

2) In order to obtain lithium dawsonite, 0.2 g BAS was added to a saturated solution of lithium carbonate (0.16 M) and aged over 102 hours. After this time, the solid was filtered, then washed several times with distilled water and finally dried at 373 K. Additionally, a BAS sample was added to a saturated solution of lithium carbonate (0.16 M) and lithium hydroxide (0.16 M) in order to obtain a dawsonite sample with a higher lithium content.

3) The thermal transformation of the lithium dawsonite-type compound into lithium aluminate involved putting the solids under calcination in air at 723, 823, 923, 1023, and 1123 K. For simplicity, samples are designed by D1 to D5 (nitrate precursor) and D6 to D10 (chloride precursor); this indicates that all samples proceed from lithium dawsonite and the consecutive numbers indicate low to higher temperatures. In order to observe the effects of a major content of lithium, a sample was prepared with double the amount of lithium and was then put under calcination at 1123 K.

Material characterization

The thermal behavior of the samples obtained was analyzed in a thermogravimetric analyzer (TA Instruments TGA 51).

Total surface area was calculated using the BET method from N₂ adsorption by the single point method using 30% N₂ balanced with a He gas mixture that was recorded at the temperature of liquid nitrogen in an ISRI RIG-100. The volumetric characterization of the samples studied was made by X-ray diffraction. A Siemens D5000 diffractometer coupled to a copper anode X-ray tube was used to obtain the experimental X-ray diffraction patterns; the wavelength K_α was selected with a diffracted beam monochromator. The X-ray tube was operated at 35 kV and 20 mA. Crystalline compounds were conventionally identified with the JCPDS files.

Superficial characterization of samples was made with scanning electron microscopy (SEM). A Phillips X130 scanning electron microscope was used to determine the sample morphology and the surface topology. To make the materials electrically conductive, all samples were covered with a thin gold film with the use of a Jeol (JFC-1100) fine coat ion sputter.

Results and Discussion

Thermogravimetric and differential thermal analysis

Figs. 1-4 show the thermal behavior of lithium dawsonite obtained; the differentiation method of the derivative was used to compute the rate at which weight loss changes

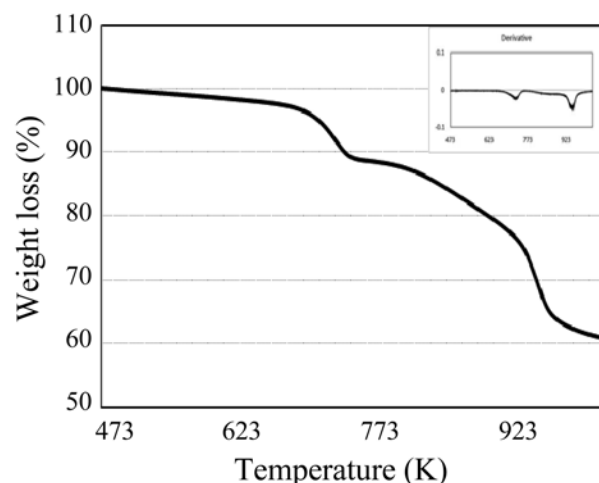


Fig. 1. TGA and its derivative (insert); results of sample D1 synthesis with a nitrate precursor.

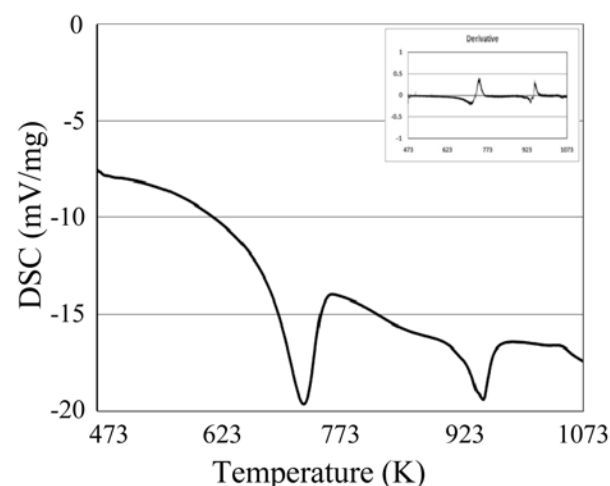


Fig. 2. DSC and its derivative (insert); results of sample D1 synthesis with a nitrate precursor.

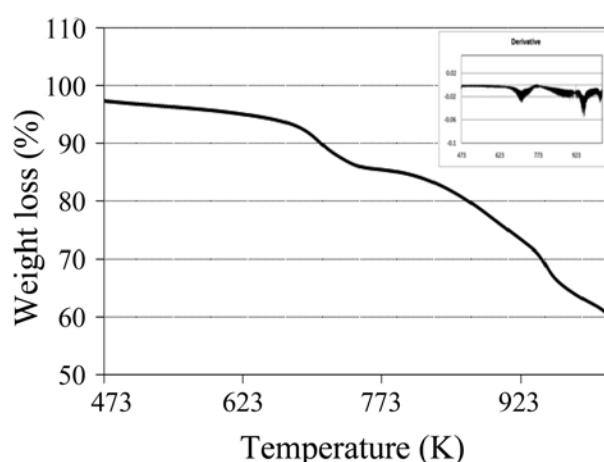


Fig. 3. TGA and its derivative (insert); results of sample D6 synthesis with a chloride precursor.

occurred with respect to changes in the temperature, shown as inserts in Figs. 1-4.

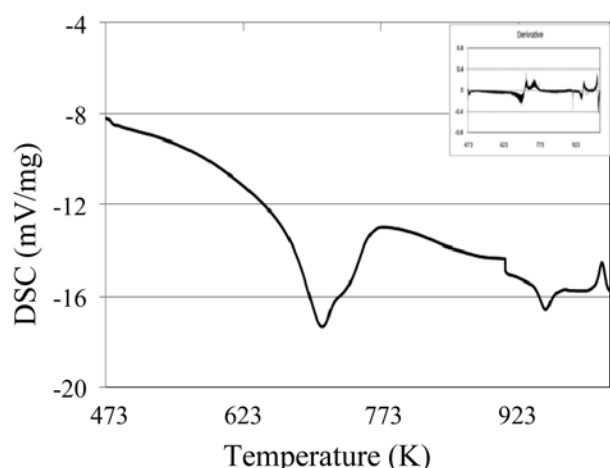


Fig. 4. DSC and its derivative (insert); results of sample D6 synthesis with a chloride precursor.

Two main thermal weight losses at 728 and 948 K are present in the sample that was prepared with the nitrate aluminum precursor (Fig. 1), and are associated with two endothermic peaks that appear in Fig. 2. The first peak has been related to the thermal decomposition of hydroxide layers and a partial decomposition of carbonates, as well as to the conversion of dawsonite to lithium aluminum oxide [3, 15, and 19]. The second peak, which represents an endothermic process, is related to the formation of lithium aluminate. A measured mass loss of 42.5% that is associated with the mineral decomposition agrees well with the expected loss, according to the theoretical formula of dawsonite (43.1%).

The sample with the aluminum chloride precursor presents three weight loss masses (Fig. 3) and is associated with two endothermic processes, centered at 703 and 948 K, and one exothermic process centered at 1013 K (Fig. 4). The first peak shows the contribution of two endothermic processes at 703 and 728 K (Fig. 4, insert); the first occurs at a lower temperature because of the decomposition of hydroxide. The other peak is due to the thermal decomposition of carbonates. The second endothermic process was related to the decomposition of carbonates and the formation of lithium aluminate. The third process at 1013 K, which is exothermic, was related to total carbonates decomposition and the phase transition $\alpha \rightarrow \gamma$ of lithium aluminate.

Specific surface area behavior

Table 1 shows the changes in surface area of the samples

Table 1. Relationship between specific area and temperature

Sample ID	Specific surface area S ($\text{m}^2\cdot\text{g}^{-1}$)	Temperature (K)
D1	33.5	623
D5	86.8	1123
D6	26.2	623
D10	87.8	1123

with respect to calcinations. In both series of samples, an increase in surface area was observed when the samples were put under calcination. The surface area of sample D1 for example, which was synthesized with a nitrate aluminum precursor, increased by 2.5 times when it was put under calcination at 1123 K. A similar phenomenon occurred with sample D6, which was synthesized using an aluminum chloride precursor. Following calcinations, sample D10 showed an increase in surface area by 3.3 times. This effect may occur because BAS particles were disaggregated; during the decomposition of carbonates, CO_2 gas is released.

X-ray diffraction analysis

The X-ray diffraction patterns in Figs. 5 and 6 represent the thermal phase transformation of the lithium dawsonite as the treatment temperature increases. No contribution from a non-crystalline compound was observed in all the studied

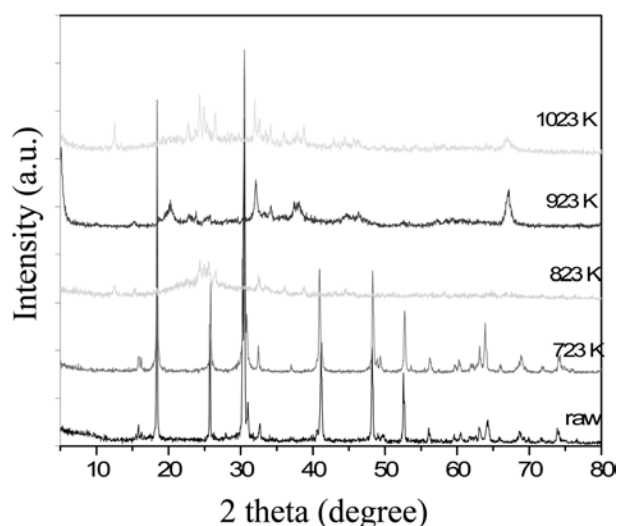


Fig. 5. XRD patterns of the thermal phase transformation of the lithium-type dawsonite as the treatment temperature increases with a nitrate precursor.

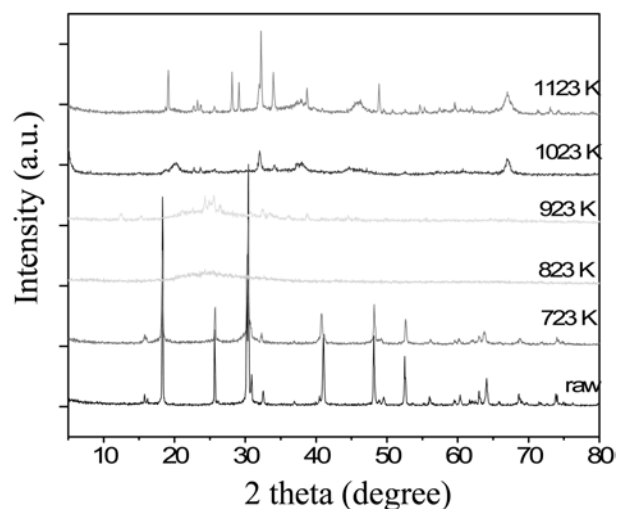


Fig. 6. XRD patterns of the thermal phase transformation of the lithium-type dawsonite as the treatment temperature increases with a chloride precursor.

diffractograms. In both cases, lithium dawsonite-type precursors were obtained as the raw material from direct synthesis, and their correspondence to several dawsonite-type compounds were reported [13-23]. When samples were heated, phase transformation is lost. Non-crystalline or nano-crystalline phases occur at 823 K, and continue through phase transformation with hydroxyl and carbonate decomposition until α - LiAlO_2 and LiAl_5O_8 is obtained (923-1023 K), then a mixture of several aluminum and lithium aluminate compounds is observed at temperatures above 1123 K. The presence of Al_2O_3 and low lithium content compounds indicates that the exchange of lithium from lithium carbonate to aluminum sulfate is incomplete. Very low amounts of α and γ LiAlO_2 were detected; their presence is extremely temperature dependent. More crystallinity can be observed due to doubling the amount of lithium during preparation as shown in Fig. 7.

Morphology analysis by SEM

Scanning electron microscope (SEM) morphology of lithium dawsonite microspheres is shown in Figs. 8(D1) and 9(D6), which suggest that microsphere size, about $3\ \mu\text{m}$, is the same as was expected due to the synthesis of precursors that provide that microstructure [24]. Nevertheless, sample D1 demonstrates a different morphology, one that is faceted with the similar appearance of undefined hexagonal phases, but is uniform in size. The coalescence effect is observed when samples are heated to 723 and 823 K, Figs. 8(D2, D3), 9, (D7, D8), but a disaggregation process begins above 1023 K, Figs. 8 (D5) and 9(D10) with a posterior structure that displays rough surfaces. However, from the microimages of the calcined product, spheres with an average diameter of $3.5\ \mu\text{m}$ can be observed. In the case of the template-assisted synthesis of lithium aluminates [2], rough surfaces are obtained during the calcination

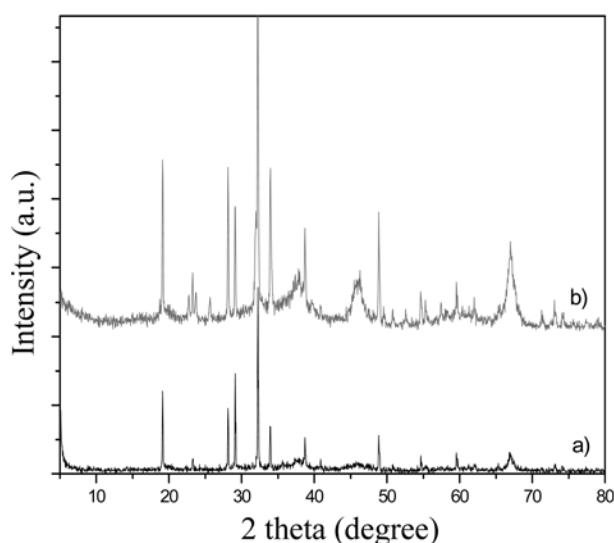


Fig. 7. XRD patterns comparison of the thermal phase transformation of different lithium content a) represents the doubled amount of lithium during preparation under calcination at 1123 K, and b) corresponds to the general content of lithium.

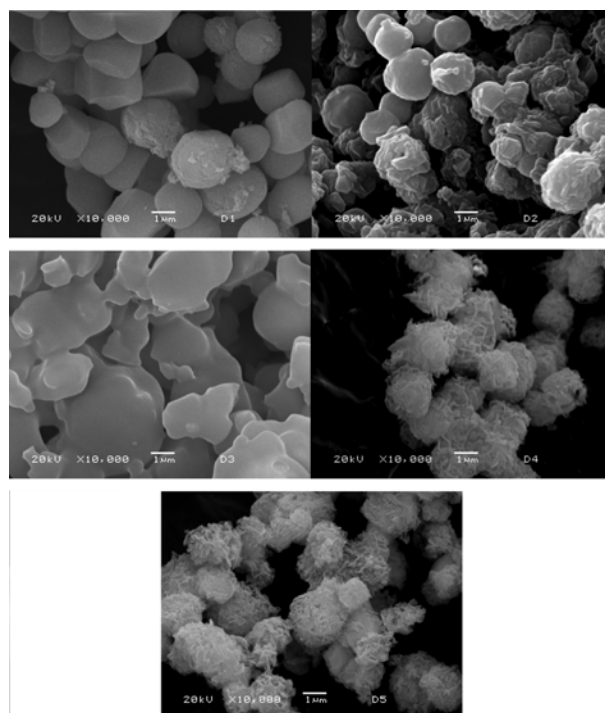


Fig. 8. SEM morphology of lithium type-dawsonite microspheres D1 to D5 for the nitrate precursor.

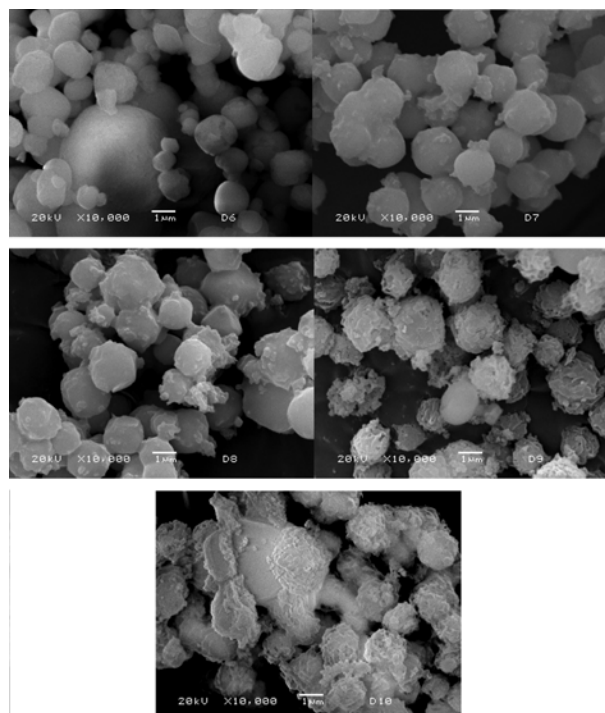


Fig. 9. SEM morphology of lithium type-dawsonite microspheres D6 to D10 for the chloride precursor.

process, where surfactant is eliminated, leaving behind hollow shells. Using a lithium dawsonite precursor, a similar effect is observed for carbonate decomposition; this flaky-branches morphology is similar to that reported by Li and Ng [25].

Results from EDS spectra show that final samples under

calcination (D5 and D10) contain only Al and O. The ratio of Al : O is 1 : 9, which is close to that in LiAlO_2 . Because lithium is difficult to detect by EDS analysis, the content of these structures could be considered to be LiAlO_2 .

Conclusions

The thermal decomposition of lithium dawsonite-type compounds produces solid solutions with several crystalline phases, including $\alpha\text{-LiAlO}_2$ and $\gamma\text{-LiAlO}_2$; the presence of each is temperature dependent. The $\alpha\text{-LiAlO}_2$ is present from 573 to 973 K and reappears at 1473 K, while $\gamma\text{-LiAlO}_2$ only appears at high temperatures: 1173 and 1473 K.

Acknowledgements

The authors acknowledge the assistance of Albina Gutiérrez regarding the specific surface area analysis.

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