



# Thick-films of garnet-type lithium ion conductor prepared by the Aerosol Deposition Method: The role of morphology and annealing treatment on the ionic conductivity



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## HIGHLIGHTS

- Thick films of  $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$  laced with Al and Ta prepared at room temperature.
- Aerosol Deposition following the room temperature impact consolidation mechanism.
- Nano-crystallinity and micro strain in as-deposited films reduce ionic conductivity.
- Decreases of strain and increases of crystallite size through annealing.
- Recovery of ionic conductivity and reduction of activation energy through annealing.

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## ABSTRACT

We fabricated thick films of cubic garnet solid electrolyte  $\text{Al}_y\text{Li}_{7-3y-2z}\text{La}_3\text{Zr}_{2-z}\text{Ta}_z\text{O}_{12}$  (ALLZTO) by the Aerosol Deposition Method (ADM). Due to the room temperature impact consolidation (RTIC) mechanism, the films become dense. A thermal post-treatment of the film revealed the morphological and process-related impact on the ionic conductivity. As-deposited films show a reduced conductivity around  $2 \cdot 10^{-7}$  S/cm. Using electrochemical impedance spectroscopy and high-temperature X-ray diffraction, we found the lattice distortion and nano-crystallinity of the films to be the decisive effect for the conductivity reduction. In our case, post-deposition annealing at 400 °C lead to an increase of the ionic conductivity to  $2 \cdot 10^{-5}$  S/cm. With a beginning of sintering at 600 °C, the conductivity successively increased further, reaching values of  $7 \cdot 10^{-5}$  S/cm.

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## 1. Introduction

Lithium ion batteries play a decisive role in mobile electronic devices and hybrid electric vehicles. While current battery cell systems suffer from unsatisfying specific capacity, all-solid-state rechargeable lithium ion batteries with higher specific capacity could pave the way for electric vehicles in mass markets. This encourages research in the field of solid-state lithium ion conductors. Besides material-related issues like chemical stability and ionic conductivity of the electrolyte component, processing is a main issue. For electrolytes, there is an application-born

requirement of zero-defects. Another safety related issue is good mechanical stability, which increases when the films become thicker, but leads to a higher electrical resistance. With respect to processing technology, it is a quite advanced challenge to overcome these issues. The Aerosol Deposition Method (ADM), which is based on the room temperature impact consolidation (RTIC) of ceramic powders, yields dense films of adequate thickness directly at room temperature from a ceramic powder. A high velocity aerosol jet with  $\mu\text{m}$  to sub- $\mu\text{m}$  ceramic particles is focused on a substrate material where the particles fracture upon impact to nano-crystallites and consolidate due to the hammering of subsequently impacting particles [1,2]. Due to the room temperature conditions during deposition, there is a high degree of freedom in the substrate choice for this process. From this point of view, even temperature sensitive substrates like

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polymers could be used [3].

A quite large variety of materials has been already deposited to thick-films by the ADM and their film properties have been studied [1,4]. Recently it has been shown that aerosol-deposited materials can potentially be applied in the field of gas sensing [5–7] or energy conversion such as solid oxide electrolyte [8], thermoelectric materials [9], as well as optically active materials for solar energy conversion [10]. Most investigations, especially of more fundamental nature, i.e., dedicated to the deposition and consolidation mechanism, have been conducted on alumina [1,2,4,11,12]. Besides, there are already some investigations that deal with AD of materials for battery applications like cathode materials  $\text{LiFePO}_4$  [13–15],  $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$  (NMC) [16], as well as anode materials such as  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  (LTO) [17], silicon [18,19],  $\text{Fe}_2\text{O}_3$  [20] and solid electrolytes like  $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$  (LATP) [21] and  $\text{Li}_{1.5}\text{Al}_{0.5}\text{Ge}_{1.5}(\text{PO}_4)_3$  (LAGP) [22], as well as composites [23]. They assign this effect to the increase in the crystal grain size and to the higher degree in crystallinity caused by sintering.

Further studies deal with the lithium ion conducting oxide ceramic  $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$  (LLZO). Ahn *et al.* demonstrated the possibility to fabricate electrolyte films of cubic LLZO [24]. It is a promising material for all-solid-state battery applications, since LLZO ceramics show a good stability against lithium and provide a high  $\text{Li}^+$ -ion conductivity of approx.  $2\text{--}6 \cdot 10^{-4}$  S/cm [25]. LLZO crystallizes in the garnet-type structure. At room temperature, the highly lithium filled lattice is thermodynamically stable in the tetragonal modification [26], which shows lower bulk ionic conductivity ( $\sigma_{\text{bulk}} \approx 2 \cdot 10^{-6}$  S/cm) [27]. In order to achieve the cubic modification with higher conductivity, doping with  $\text{Al}^{3+}$  leads to a reduction of the number of  $\text{Li}^+$ -ions in the crystal structure (ALLZO,  $\text{Al}_y\text{Li}_{7-3y}\text{La}_3\text{Zr}_2\text{O}_{12}$ ) and to a stabilization of the cubic LLZO [28]. A significant reduction of the activation energy  $E_a$  can be observed for the cubic garnet [29]. The exchange of  $\text{Zr}^{4+}$  by higher valent elements, e.g.  $\text{Nb}^{5+}$  or  $\text{Ta}^{5+}$  leads, due to charge neutrality (LLZTO,  $\text{Li}_{7-z}\text{La}_3\text{Zr}_{2-z}\text{Ta}_z\text{O}_{12}$ ), also to a lower  $\text{Li}^+$  content in the crystal structure and to a stabilization of the cubic phase at room temperature [30]. At the same time, the synthesis temperature for mixed oxide preparation can be reduced to 1000 °C.

First studies by Ahn *et al.* demonstrated that fully cycleable cells of cubic LLZO could be achieved by aerosol deposition, but with reduced ionic conductivity [24]. While LLZO itself appears to be stable against elemental lithium, it shows certain degradation in air [15]. Some studies show instabilities in the presence of humidity or  $\text{CO}_2$  [31,32]. Both can be serious issues, since they can drastically increase the transfer resistance in processed films. Therefore, a trade-off exists between the requirements of mechanical stability (thicker membrane) and of low resistance (thinner membrane). Considering the reduced ionic conductivity of the ceramic-electrolyte system, the thickness should be in the range between 10 and 100  $\mu\text{m}$  to achieve an optimum.

In this study, we pick up first results on AD of LLZO and investigate in detail the conductivity of AD-processed films and how it is influenced by film morphology. We process Al and Ta-doped cubic lithium garnet (ALLZTO) and analyze resulting films with respect to conductivity and morphology. Furthermore, we shed light on the effect of a thermal post-processing on the film properties. Usually conductivity measurements are conducted on pellets that were sintered at higher temperatures, e.g. 1100 °C. Since we just use a single temperatures step of 900 °C for powder calcination, we dedicate in a first step to the crystallographic properties of such powders with two different amounts of Al- and Ta- doping.

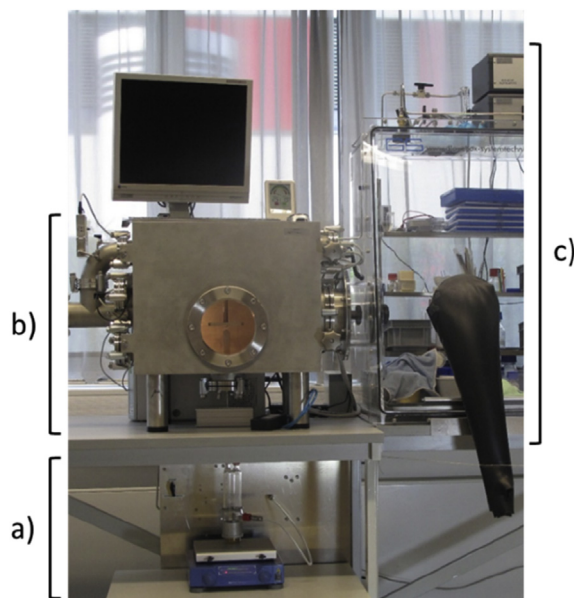
## 2. Experimental section

### 2.1. Powder synthesis

The LLZO garnet-type powder were synthesized by a mixed oxide route. The initial oxides were mixed stoichiometrically with an excess of  $\text{Li}_2\text{CO}_3$  of 10 w.-%. Al ( $\text{Al}_2\text{O}_3$ ) and Ta ( $\text{Ta}_2\text{O}_5$ ) was added to achieve the favored cubic modification with enhanced ionic conductivity [28,30,33]. In this study, we used two lots of garnet powders with two different amounts of Al and Ta as dopants. Prior to deposition, the powders were examined by XRD to verify the effect of the Al and Ta on the content of the desired cubic garnet phase. Films for XRD analysis were produced from  $\text{Li}_{7-3y-z}\text{Al}_y\text{La}_3\text{Zr}_{2-z}\text{Ta}_z\text{O}_{12}$  (ALLZTO) with Al content ( $y = 0.4$ ) and Ta content ( $z = 0.5$ ), and films for conductivity measurements were produced with  $y = 0.2$  and  $z = 0.3$ . The mixtures were calcined at 900 °C in air for 6 h in a Au crucible. In order to achieve  $\mu\text{m}$  to sub- $\mu\text{m}$  particle size after calcination, the powders were treated by high energy ball milling in cyclohexane, using a planetary ball mill with zirconia jars and balls (10 mm balls, 255 rpm, 2 h) and dried in various steps with a final step at 500 °C for 2 h in air.

### 2.2. Aerosol deposition experiments

For film preparation, we used the custom-built AD apparatus as shown in Fig. 1. The general principles as well as a detailed description of the process can be found in our former publications [4,8]. In order to prevent certain deterioration of the ALLZTO films in the presence of moisture during storage and characterization, the films were directly transferred to a flanged glovebox (GS Glovebox Systemtechnik GmbH, Germany) after deposition. A description of the AD device and the process can be found in former publications [4,11,12]. For deposition, we used a slit nozzle with an orifice of  $10 \times 0.5 \text{ mm}^2$  and  $\text{N}_2$  serving as a carrier gas with an overall gas flow of 4 ltr/min. The substrate passes over the nozzle with a speed of 2 mm/s. The nozzle-distance to the substrate was set to 5 mm.



**Fig. 1.** AD apparatus with a) aerosol generation unit, b) deposition chamber and c) flanged glove box for sample transfer in inert gas, preparation and electrical characterization.

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