



# Sintering Mechanisms of High-Performance Garnet-type Solid Electrolyte Densified by Spark Plasma Sintering



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## ABSTRACT

Garnet-type solid electrolyte  $\text{Li}_{6.5}\text{La}_3\text{Zr}_{1.5}\text{Ta}_{0.5}\text{O}_{12}$  (LLZT) was densified by using a spark plasma sintering (SPS) technique. Formation of impurities in the obtained pellets was studied in detail. It is revealed that impurities are strongly related to the SPS process: electrolysis of LLZT and electromigration of graphite. The electrolysis results in  $\text{La}_2\text{Zr}_2\text{O}_7$  on anode of the SPS process, which is accompanied by reduction of  $\text{Li}_2\text{CO}_3$  to amorphous carbon on cathode. The electrolysis on SPS could be successfully suppressed by employing LLZT powder without  $\text{Li}_2\text{CO}_3$ . When these impurities were removed, pellets obtained by SPS exhibited electrochemical performance comparable with those densified by other methods total ionic conductivity of  $6.9 \times 10^{-4} \text{ S cm}^{-1}$  at 298 K and short-circuit prevention up to  $100 \mu\text{A cm}^{-2}$  on dc polarization. The results confirm great advantage of SPS on manufacturing the dense garnet-type solid electrolytes: a low-temperature (900–1100 °C) and short-sintering-time process (10 min).

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## 1. Introduction

All solid-state batteries (ASSBs) have attracted great interests due to their potential application to large-scale energy storage devices [1–3]. Potential advantages of ASSBs are larger energy density, higher safety and higher reliability in comparison with conventional lithium ion batteries. Solid electrolytes are the key materials of ASSBs, and a wide variety of researches have been conducted from development of high ionic conductors [4–12] to interfacial phenomena [1,13–19]. During the last decade, much attention has been paid to a group of lithium ion conductors, originally explored by Weppner's group [6–8]. These solid electrolytes have crystal structure that is similar to that of garnet, and exhibit a general formula  $\text{Li}_x\text{B}_y\text{C}_z\text{O}_{12}$  ( $B = \text{Ca, Sr, Ba, La}$ ;  $C = \text{Zr, Nb, Ta, etc.}$  [9]). Especially,  $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$  (LLZ) (with partial substitution of Li by Al and/or Zr by Nb, Ta) has attracted interests due to their relatively high ionic conductivity of  $> 10^{-4} \text{ S cm}^{-1}$  at room temperature. In comparison with sulfide-based solid electrolytes (ionic conductivity:  $> 10^{-2} \text{ S cm}^{-1}$  at room temperature) [10–12], lithium ionic conductivity of the garnet-type solid electrolytes may be still low for their practical application.

However, the garnet-type solid electrolytes wouldn't produce toxic materials on exposure to air, which is an important issue on their application to large-scale energy storage systems. The most attractive feature of garnet-type solid electrolytes is their superb electrochemical stability, which may realize lithium metal anode to expand energy density of ASSBs.

When lithium metal is used as an anode of ASSBs, it is important to prepare dense solid electrolytes without through-holes. It is reported that short-circuit occurs during galvanostatic lithium deposition even for solid electrolytes with relative density higher than 90% [20–25]. The short-circuit is supposed to be caused by the deposited lithium growing through voids among grains [24]. To obtain well-sintered garnet-type solid electrolytes by conventional sintering processes, generally high temperature ( $> 1200 \text{ °C}$ ) and long sintering time ( $> 30 \text{ h}$ ) are required. Even if hot press is employed, high temperature is necessary. Such high-temperature processes (and long duration time) often result in decomposition of solid electrolytes and loss of Li.

Spark plasma sintering (SPS), which is also known as field assisted sintering technique (FAST) or pulsed electric current sintering (PECS), is one of techniques to sinter materials with assistance of uniaxial pressure and pulsed electric current [26–28]. The current through specimens and/or die generates large local joule heat to facilitate sintering of particles. Baek et al. reported fabrication of sintered  $\text{Li}_{7-x}\text{La}_3\text{Zr}_{2-x}\text{Ta}_x\text{O}_{12}$  (LLZT) by SPS [26]. They

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reported ionic conductivity of the obtained LLZT was comparable to specimens prepared by conventional sintering processes in spite of rather low process temperature (900–1100 °C) and very short process time (10 min). Zhang, et al. prepared a highly dense pellet of Al-doped LLZ (relative density: 99.8%) by SPS at 1150 °C for 10 min [27]. In these report, impurity ( $\text{La}_2\text{Zr}_2\text{O}_7$ ) was formed after SPS, which increased with increasing process temperature of SPS. The mechanism of the impurity formation is not revealed yet, and further detailed studies are required to see whether SPS is a useful process or not.

In this work, local structure of LLZT pellets prepared by SPS was investigated in detail, especially with respect to the formation of impurity. Further, lithium ionic conductivity and short-circuit prevention were also examined to study the possibility of practical application of SPS-prepared LLZT to ASSBs.

## 2. Experimental

### 2.1. Preparation of LLZT Pellets

LLZT powder was synthesized by solid-state reaction using  $\text{LiOH}\cdot\text{H}_2\text{O}$  (Kishida Chemical Co. Ltd., 99.0%),  $\text{La}_2\text{O}_3$  (Kishida Chemical Co. Ltd, 99.99%),  $\text{ZrO}_2$  (Kishida Chemical Co. Ltd., 99.9%) and  $\text{Ta}_2\text{O}_5$  (Wako Pure Chemical Industries Ltd., 99.9%).  $\text{LiOH}\cdot\text{H}_2\text{O}$  and  $\text{La}_2\text{O}_3$  were heated at 200 °C and 800 °C, respectively, in advance to remove water and  $\text{CO}_2$ . Excess  $\text{LiOH}$  was added by 10% to compensate loss of Li by volatilization during the following calcination. The starting powder was mixed using a planetary ball-mill using  $\text{ZrO}_2$  balls ( $\phi 3$  mm) and a  $\text{ZrO}_2$  pot with a rotation rate of 300 rpm for 1 hour. Then, the mixed powder was calcined in aluminum crucible for 900 °C for 12 hours. At this calcination temperature, Al contamination from the crucible was not confirmed. SPS was conducted on a CSP-I-02121 (SS Alloy Co Ltd.) using graphite die and punches (diameter 10 mm). Graphite sheets were inserted between powder and the graphite mold for facile demolding after SPS.

SPS was carried out under vacuum (initial chamber pressure was below 10 Pa), dc pulse current was applied to control the temperature, which was monitored on outer surface of the graphite die using a thermo-couple. Specimens were heated with a ramp rate of 50 °C/min toward a target temperature (900–1100 °C), and held at the target temperature for 10 min. Then, the samples were cooled inside the chamber. During the sintering, a constant uniaxial pressure (12.5–50 MPa) was applied. The

obtained pellets were typically 10 mm in diameter and 1 mm in thickness (after the graphite sheets were removed).

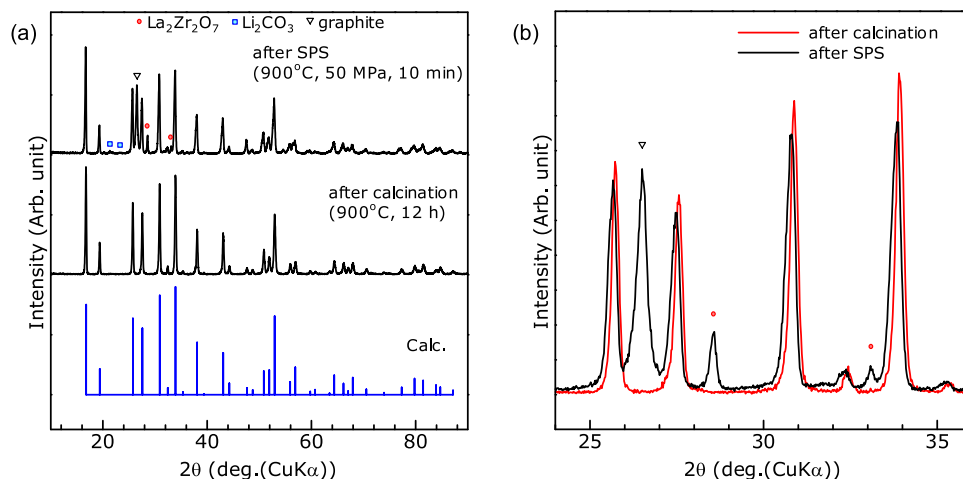
As the garnet-type solid electrolytes are sensitive to moisture and  $\text{CO}_2$  [29,30], the LLZT powder and pellets were stored in vacuum-desiccators to minimize the formation of surface impurities. Typical exposure time to air was less than 1 hour. To investigate the influence of  $\text{H}_2\text{O}$  and  $\text{CO}_2$  (resulting in  $\text{Li}_2\text{CO}_3$  on the surface of LLZT particles) on SPS,  $\text{Li}_2\text{CO}_3$ -free LLZT powder and pellets were prepared by modifying the preparation process as follows. First,  $\text{LiOH}\cdot\text{H}_2\text{O}$ ,  $\text{ZrO}_2$  and  $\text{Ta}_2\text{O}_5$  were vacuum-dried at 200 °C in a glass-tube oven, which was directly transferred into an Ar-filled glovebox.  $\text{La}_2\text{O}_3$  was pre-heated at 800 °C in dry oxygen gas using a furnace connected to the glovebox. Next, the starting materials were mixed in the glovebox, and then, the powder was calcined at 900 °C for 12 h in dry oxygen gas using the furnace connected to the glovebox. Then, the calcined LLZT powder was put into a graphite die and sealed in the glovebox, and transferred into the SPS chamber. Finally, after SPS, the pellets were taken out of the die and stored in the glovebox.

### 2.2. Characterization

Crystalline structures of calcined and sintered LLZT were investigated by X-ray diffraction (XRD) on SmartLab (Rigaku Corp.,  $\text{CuK}\alpha$ , 45 kV, 200 mA) equipped with a parallelized incident beam. Soller slits (5°) for both incident and diffracted beams and a parallel slit analyzer (0.5°) were used. An incident slit and two receiver slits were 1.0 mm and 0.4 mm in width, respectively. A graphite monochromator was placed in front of a scintillation counter to suppress fluorescent X-ray. Diffraction was recorded every 0.02° step by  $2\theta/\theta$  scan with a scan rate of 2.0°/min. For detailed structural analysis, step-scan was employed with an accumulation time of 10 sec at each angle. The structure refinement was conducted by Rietveld method using RIETAN-FP [31].

Density of pellets was obtained using the dimensions and weight of pellets. The relative density was calculated by comparing the geometric density with the density estimated from lattice constant ( $5.36 \text{ g cm}^{-3}$ ).

Morphology of surface and fractural cross-section of sintered pellets were observed by field-emission scanning electron microscope (FE-SEM) on a JSM-7500F (JEOL Ltd.). Distribution of elements was confirmed by energy dispersive spectroscopy (EDS) attached on FE-SEM.



**Fig. 1.** XRD profiles of  $\text{Li}_{6.5}\text{La}_3\text{Zr}_{1.5}\text{Ta}_{0.5}\text{O}_{12}$  prepared in this study. (a) (Top) A pellet sintered by SPS at 900 °C for 10 min under 50 MPa., (middle) powder after calcination, and (bottom) a calculated profile for comparison. (b) Expanded profiles of after calcination and after SPS.

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