# Depositing $Li_{7-x}La_3Zr_{2-x}Ta_xO_{12}$ (LLZTO) Thin Films Using Pulse Laser Deposition

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## 1 Abstract

Recently, lithium-ion batteries became of a great interest in industry due to their high energy density and reasonable price. Garnet-type electrolytes (e.g., LLZTO) can be of great contribution to these batteries due to their outstanding properties. In this research, LLZTO thin film was deposited using Pulse Laser Deposition (PLD) technique, which is based on physical vapor deposition. An LLZTO pellet (target for PLD) was re-grinded and a new pellet was produced, using uniaxial dry pressing followed by sintering and X-ray Diffraction (XRD) analysis. The LLZTO film was deposited on a stainless-steel substrate at 500 °C for 40 min . The oxygen partial pressure was 75 mTorr with an energy of 452 mJ. The XRD of the target/pellet before PLD was generally good and matched with literature. After the PLD, generally LLZTO was not deposited. However, it is still cannot be concluded that LLZTO was not deposited, as the peaks between angles 40° to 60° match with the original LLZTO target, so it may be that the peaks of stainless-steel and LLZTO on stainless-steel had interfered. However, this needs more investigation and evaluation in order to give a final conclusion.

## 2 Introduction

Recently, lithium-ion batteries became of a great interest in industry due to their high energy density and reasonable price. Garnet-type electrolytes (e.g., LLZTO) can be of great contribution to these batteries due to their outstanding properties. However, current liquid LIBs have many problems including the risk of electrolyte leakage [10] and flammability [2]. For future solid-state LIBs, LLZTO is one of the candidates. Lithium lanthanum zirconium tantalum oxide ($Li_{7-x}La_3Zr_{2-x}Ta_xO_{12}$ ) (LLZTO) is an enhanced version of lithium lanthanum zirconium oxide ($Li_7La_3Zr_2O_{12}$) (LLZO). LLZO is a ceramic material, specifically, garnet-type that has lithium-ion conductivity that can reach to $10^{-4}$ S/cm, or higher at room temperature. Also, it is considered to has high thermal and chemical stability interface with Li metal. It can be one of the promising electrodes due to its energy density, electrochemical stability, high temperature stability, and being safe [9]. LLZO has cubic crystal structure, but tetragonal crystal structure can also occur which is not quite helpful, as it has lower conductivity (lower by two orders of magnitude) compared to the cubic structure. The formation of the tetragonal structure can be avoided using high sintering temperatures and durations. However, due to the lithium volatility (at high temperatures), pores may develop, which will decrease the conductivity. In this case, an applicable solution can be substituting amounts of Tantalum (Ta), which then will be ($Li_{7-x}La_3Zr_{2-x}Ta_xO_{12}$) (LLZTO), can help with obtaining a cubic structure [10]. In this case, the Ta atoms will occupy some of the Zr sites [4].

Synthesizing LLZTO can be a bit challenging, as using a normal solid-state reaction requires high sintering temperature which lead to the same problem faced in LLZO (results in a porous material, that may have lower conductivity). Recently, various studies have shown that the use of Sol-gel method can be a good synthesis method due to its various advantages, like high purity, high stoichiometry controllability, and the low processing temperature [10].

Using a large solid sample will not be useful and applicable for the real-world application, as the world and industries are now moving to use small objects, like phones, laptops, solar panels, etc. Therefore, a large LLZTO will not add much to this field. This research will focus on depositing a LLZTO thin film that then can be used in Lithium-ion batteries for the different applications. Also, thin films are considered to have better properties compared to the bulk, this can be due to the differences in morphology, structure (heterostructure will develop by using this technique), and composition [6]. As well as, thin films can cober large areas (contact area). The synthesis of this thin film will be done using a Pulsed Laser Deposition (PLD) machine. PLD is based on physical vapor deposition (PVD) technique, inside an ultra-high vacuum chamber, a beam of laser will strike the sample, where LLZTO will be vaporized as plasma plume and then deposited as a thin film (in micro-meter thickness) on a substrate (see Figure 1 [1]). Further, X-ray Diffraction (XRD) analysis will be used to make sure that it is the desired material and structure. Such to ensure that it has a cubic structure, determine phases present, and check for any impurities that may exist.

Also, a Scanning Electron Microscope (SEM) with Energy-dispersive Spectroscopy (EDS) (SEM/EDS) was used to determine the composition of the sample/pellet or target used. In SEM/EDS, an beam of electron is directed to hit sample. When it hits the sample, some electrons from the inner shells of the different atoms will be knocked off which will result in leaving holes behind them (positively charged). These holes will attract electrons from their outer shells to fill those vacancies. As these electrons move from on shell to another, X-ray will be emitted, with each element has its own characteristic X-ray. These X-rays will be detected and analyzed to determine the composition of each element in a compound/material [8].

Moreover, Atomic Force Microscope (AFM) is characterization technique that is used for substrate. The AFM was used to check and investigate the

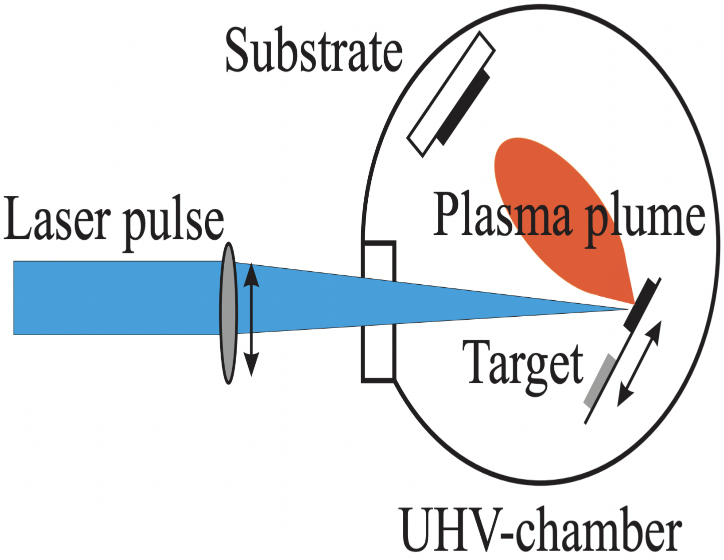

Figure 1: A schematic illustration of how does Pulse Laser Deposition works [1]

substrate's topography and see how flat and clean it is before depositing LLZTO film. A sharp tip that is normally piezoelectric go through the surface of the sample (non-contact mode) in a raster pattern. Then the observed/measured data will be converted into an image [5]. There are different substrates that can be used/tried for LLZTO deposition, this includes copper foil, stainless steel, silicon, $Al_2O_3$, etc. Also, Saccoccio et al. [6], had successfully deposited LLZTO on an MgO substrate. However, in this research, due to the given materials and situation, it is expected that the deposition may be bit challenging and may not work well from the first time. Therefore, for a beginning, a stainless steel substrate will be used. A stainless steel substrate was the first candidate due to its availability and low cost (compared to MgO for example). Also, comparing copper foil with stainless steel, stainless has higher melting temperature which can be great in case of high temperatures needed for the PLD. If it did not work well, other substrates will be examined. As of using stainless steel as substrate, it will be risky to put the substrate in AFM, as it can break the tip. Therefore, the stainless steel substrate did not go through the AFM scanning. Instead, it was only cleaned with methanol and acetone.

In general, it is expected that the deposition will be quite challenging and different substrates and deposition conditions will need to be tried. However, it is believed that the deposition can work well after trying different conditions and analyzing and looking closely to the results. Also, there are some other possible errors/challenges that may appear, including, being unable to have a good sample after dry pressing (this will need to be done multiple times to get a perfect sample), as it is expected that the pellets will break quickly as they are brittle and fragile. Also, the laser in the LLZTO deposition may need be adjusted multiple times to ensure perfect alignment.

## 3 Procedure

In this research, for better use of time, the Sol-gel method wast not used to produce a new LLZTO sample. As the main aim of this research is to successfully deposit a LLZTO thin film and characterize it. Instead, an old broken LLZTO sample has been re-used for this study, where the sample went through grinding to form a powder. Then, it was dry pressed at 20 Tlb for 70 min. However, the pellet broke due to some human errors, like lack of care when removing the pellet out of the die, and lack of experience. Then, the broken pellet was re-grinded to powder, and another pellet was produced. The second time, the pressure used in the dry pressing machine was 19 Tlb (decreased to 16.5 Tlb through the period of pressing) for 65 min. After the second attempt, the pellet worked well and it went to the next step, sintering to allow more and even elements diffusion, eliminate impurities, and make the sample/target denser. The pellet was placed in a alumina crucible and covered with another alumina crucible, and then sintered at 900 °C for 3 hours with 5 °C/min. Due to Li volatility, the sintering temperature/time was designed carefully to avoid any Li losses in sintering. Further, the pellet was covered with tiny bits of LLZTO powder to compensate for any possible losses of Li during the sinetring process. These sintering conditions were chosen based on literature experiments and results, then the appropriate conditions were chosen to best fit the conditions of the pellet used in this research. After sintering, the sample/pellet had broke from the middle (almost divided into two layers), so the sample needed to be re-grinded again a new pellet was produced. Before re-grinding the pellet, it went through X-ray Diffraction (XRD) to check if there are any changes in the crystal structure, purity, and phases. After that, the broken pellet was re-grinded and a new pellet was produced using another dry pressing machine (another machine was used due to some machine difficulties on the previous machine) with a pressure of 20 Tlb (dropped to zero by the end of the pressing period) for 65 min. Following that, the pellet was sintered (second sintering) and held at 600 °C and held there for 4 hours and then allowed to cool in the furnace. Then, an XRD measurement has been taken. After that, the pellet went through SEM/EDS to determine the content of the elements inside, but mainly it was done to help with determining and identifying the new additional phases that appeared after the second sintering. The SEM/EDS scan did not give very clear data about the pellet composition. Also, Li is a light element that is normally cannot be detected in normal SEM/EDS. Unfortunately, when the pellet was removed/detached from the SEM/EDS holder, the pellet had accidentally broken again (as the pellet was held there using carbon tape which is very sticky). Therefore, the pellet was re-grinded again and another pellet was produced. A pressure of 20 Tlb was for 60 min (by the end of the 60 min, the pressure had dropped to approximately 17.9 Tlb). Then, it went through sintering (third sintering), the pellet was heated to 600 °C and held there for 4 hours, followed by XRD measurement. After confirming that it is the right material and structure, using XRD, the pellet had been polished using sand paper (P400) with methanol only (as acetone is a bit strong). After polishing, the pellet was placed on a hot plate at 300 °C for 5 min. Along with this, a stainless steel substrate has been chosen as the substrate for the LLZTO deposition. The stainless steel substrate has been cleaned using methanol and acetone. Next, the pellet/target was placed in a Pulsed Laser Deposition (PLD) machine where the thin film will be deposited. As what was done in Saccoccio et al. group [6], an oxygen pressure of 75 mTorr was used, and the deposition temperature was 500 °C. The oxygen pressure was to slow down the plume which can possibly produce a better deposited film quality. The background pressure was $5.10 \times 10^{-5}$ Torr. Normally, an surface layer of $LiCO_3$ will form when LLZTO is exposed to air, so before the actual deposition, the LLZTO target was first cleaned with laser while it was in the chamber to remove the $LiCO_3$ layer. The energy was 452 mJ.

All XRD scans that were used had the Cu K-$\alpha$ A radiation $\lambda = 1.5418$ Å, except for the pre-sintered sample and the first sintered sample, which had $\lambda = 1.540562$ Å.

After successfully getting the deposited film, which is the main challenge and the purpose of this research, the film will go through XRD for analysis and make sure that the LLZTO was deposited right and as desired. Finally, after ensuring we have the right LLZTO film, it can go through further characterization, like measuring conductivity and other properties.

# 4 Results and Discussion

For the XRD results, Orgin Pro was used to create the graphs and analyse. From Figure 1, before sintering the sample's XRD was quite good and matches with literature, Figure 2 [10]. Yoon et al., have made LLZTO using Sol-gel method, despite the differences in the preparation method, they got the same material, LLZTO. However, it can be seen that there are some additional peaks and a lot of noise compared to that in Figure 2. These additional peaks and noise can be tied back to the fact that an old sample/pellet has been re-used. The old pellet was previously used in PLD and was stored in different places, which make it likely that the pellet got contaminated. In general, the peaks matched and it can be concluded and confirmed that the pellet is LLZTO.

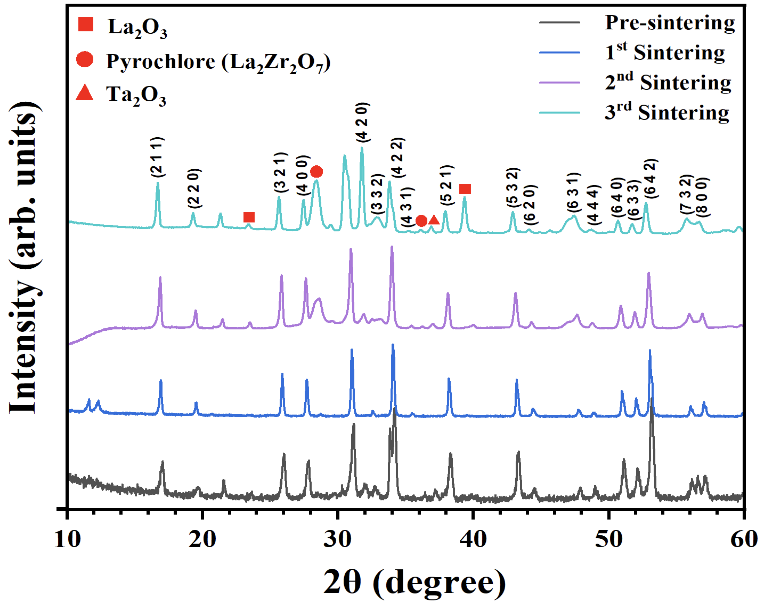

Figure 2: XRD graphs of the LLZTO sample through the different cases

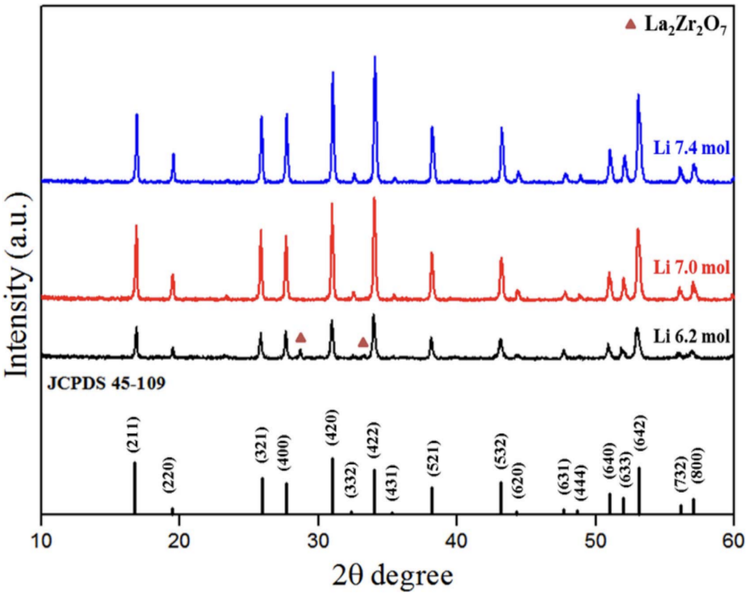

Figure 3: XRD graphs of LLZTO for different Li content [10]

The XRD graph for the pellet after sintering, Figure 1, looked more precise. It can be seen that the peaks had became thinner and more accurate. Unlike before sintering, after sintering had all the peaks matching perfectly with literature (Figure 2) [10]. This can be tied back to the fact that sintering increases density, and it also may reduced the impurities which explains the less noise in the XRD graph after sintering. The two additional peaks shown at the beginning of the after sintering XRD graph (indicated by a blue circle on the top of them) were from the clay used to hold pellet. When the pellet was placed in the XRD machine for analysis, the pellet was held with clay that contained minerals and may also had other contamination. This was later proved and confirmed by measuring the XRD of the clay by itself. Furthermore, according to Yoon et al. [10], based on their XRD analysis, they concluded that the crystal structure of the shown XRD graph, specifically Li 7.4 mol, is cubic, this can also be applied to the LLZTO pellet used in this research based on the perfect match between the XRD graphs in Figure 1 and Figure 2. Moreover, from Figure 1 and Figure 2, it can be seen that the peaks after sintering matched the best with the Li content of 7.4 mol. This can also show that the pellet in this research has 7.4 mol of Li. However, after the second sintering (see Figure 1), additional peaks had appeared which were tied back to other phases that appeared. These additional peaks has been approximated and identified to be pyrochlore ($La_2Zr_2O_7$), $La_2O_3$ and $Ta_2O_3$ (red shapes shown in Figure 1) [10, 3, 7, 11] (shown in Figure 1). These additional peaks were quite expected, as due to the high volatility of Li, Li tend to leave the sample which will result in having Li deficient sample. Also, these particular peaks were expected and were reasonable, as they are part of the pellet's composition. Further, Yoon et al. [10], mentioned that they also had additional peaks between the diffraction angles of 23° to 40° and they might corresponded to $La_2O_3$ and $Ta_2O_3$. Also, they mentioned and showed in the XRD measurement that they had pyrochlore ($La_2Zr_2O_7$) phases (shown in Figure 2). The same thing occurred after the third sintering, but with the disappearance of some peaks and the appearance of new other peaks. This was also reasonable, as after the third sintering, the sample was exposed to high temperature for the third time now which means more Li loss. Unlike the first sintering, the second and third sintering looked more like the Li deficient graph ( Li 6.2 mol) from Yoon et al. experiment [10]. Which is as stated above, this was expected, as the Li tend to escape the sample at high temperatures.

Figure 4 shows the XRD measurement of a the stainless steel substrate before and after the pulse laser deposition of LLZTO. It can be seen that the peaks of the substrate before LLZTO deposition are quite the same as the peaks of the substrate itself (before deposition). This can mean that the deposition did not work well, or actually there was not any LLZTO deposition. However, It can be seen that there is a difference in the intensity of the peaks between the angles 40° to 60°. At the same time, those peaks almost match with the LLZTO's XRD itself (Figure 2). Therefore, this may mean that there was a small LLZTO deposition, and the there was an interference between the peaks of the stainless steel substrate and the LLZTO peaks. Nevertheless, more testing and investigation needs to be done in order get a clear and final conclusion (like X-ray Photoelectron Spectroscopy (XPS) which helps in analyzing the surface). Also, an XRD of a stainless-steel substrate before and after exposing into PLD temperature will also need to be compared. As it is needed to checked if there will be any changes in the peaks before and after PLD heating. Figure 5 shows the stainless steel substrate before and after PLD.

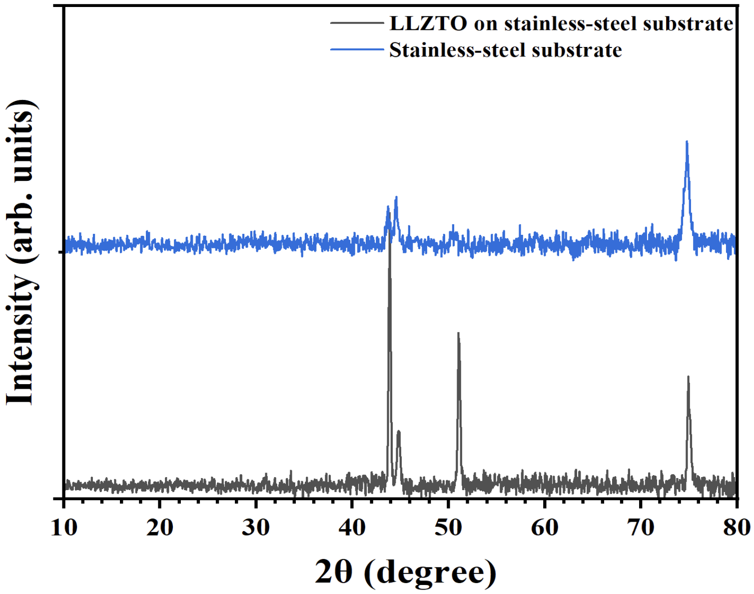

Figure 4: XRD graph of the stainless steel substrate before Pulse Laser Deposition (PLD) and the XRD of the stainless steel substrate by itself

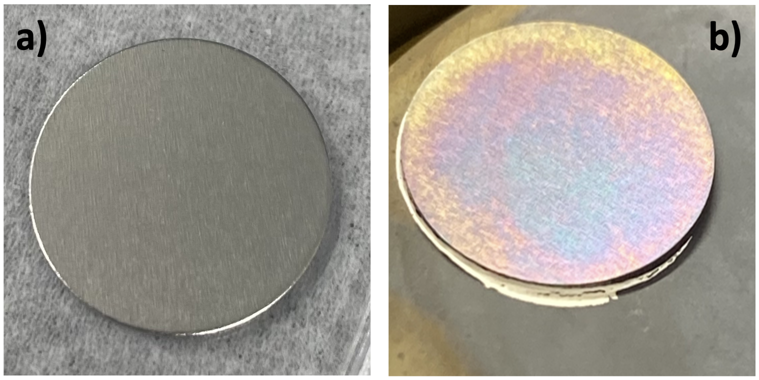

Figure 5: Stainless steel substrate a) before and b) after Pulse Laser Deposition (PLD)

# 5 Conclusion

In conclusion, $Li_{7-x}La_3Zr_{2-x}Ta_xO_{12}$ (LLZTO) can be a good candidate for solid-state lithium ion batteries (LIBs). After re-synthesizing (making a pelle followed by sintering and X-ray Diffraction analysis (XRD)) an old LLZTO target, Pule Laser Deposition (PLD) was used to deposit LLZTO on a stainless steel substrate. As expected, high temperatures during sintering resulted in losing Li, as Li tend to escape the sample due to its high volatility. Therefore, phases may be affected. Also, the final Li content can be said to be 6.2 mol, based on literature. The overall LLZTO deposition did not work quite well. However, there were some peaks between the angles 40° to 60° that almost matched with the original LLZTO target's XRD. These peaks can also be an interference between the the stainless-steel substrate XRD and the LLZTO XRD, but more investigation needs to be done in order to get better a conclusion.

# 6 Future Work

The stainless steel substrate after PLD (LLZTO may been deposited on it) will go through more investigation using X-ray Photoelectron Spectroscopy (XPS) and XRD. Also, examining different substrates will take place, like MgO, Al2O3, Cu foil, etc. Moreover, trying different deposition conditions, manipulating temperature, pressure, deposition period, etc. Characterizing the LLZTO thin film and its properties and working to deposit epitaxial thin films of LLZTO.

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