The Study of $Li_{7-x}La_3Zr_{2-x}Ta_xO_{12}$ (LLZTO) Thin Films Using Pulse Laser Deposition (PLD)

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July 9, 2022

1 Introduction

Lithium lanthanum zirconium oxide ($Li_7La_3Zr_2O_{12}$) (LLZO) is a ceramic material, specifically, garnet-type. LLZO 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 [3]. 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 [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 [4].

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 [2]. 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.

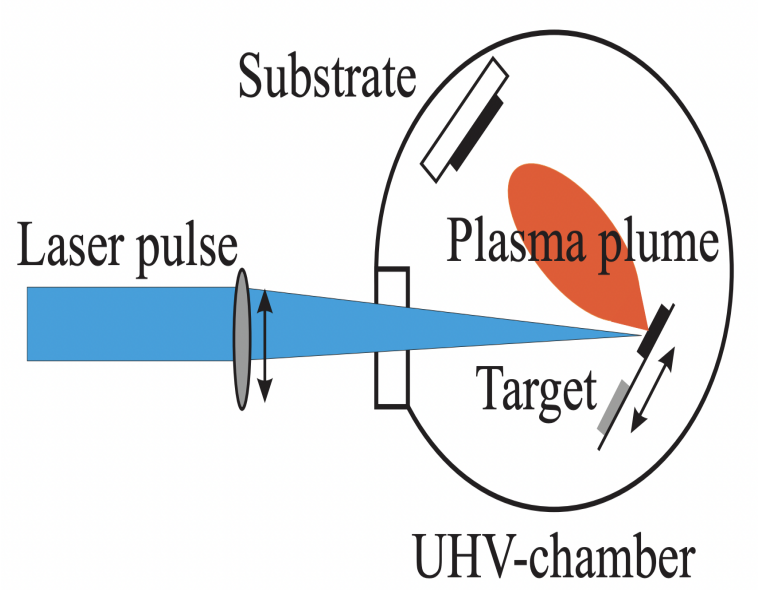

Figure 1: A schematic illustration of how does Pulse Laser Deposition works [1]

In general, it is expected that the deposition will work well. However, there are some 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 substrate that the LLZTO film will be deposited on will not be appropriate (different substrates need to be used and examined), and the laser in the LLZTO deposition may need be adjusted multiple times to ensure perfect alignment.

2 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 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, broken pellet was re-grinded and a new pellet was produced using the dry pressing machine with a pressure of 20 Tlb (dropped to zero by the end of the pressing period) for 65 min.

After confirming that it is the right material and structure, using XRD, the sample/target will be placed in a Pulsed Laser Deposition (PLD) machine where the thin film will be deposited. Again, 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.

3 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 [4]. 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 peals matched and it can be concluded and confirmed that the pellet is LLZTO.

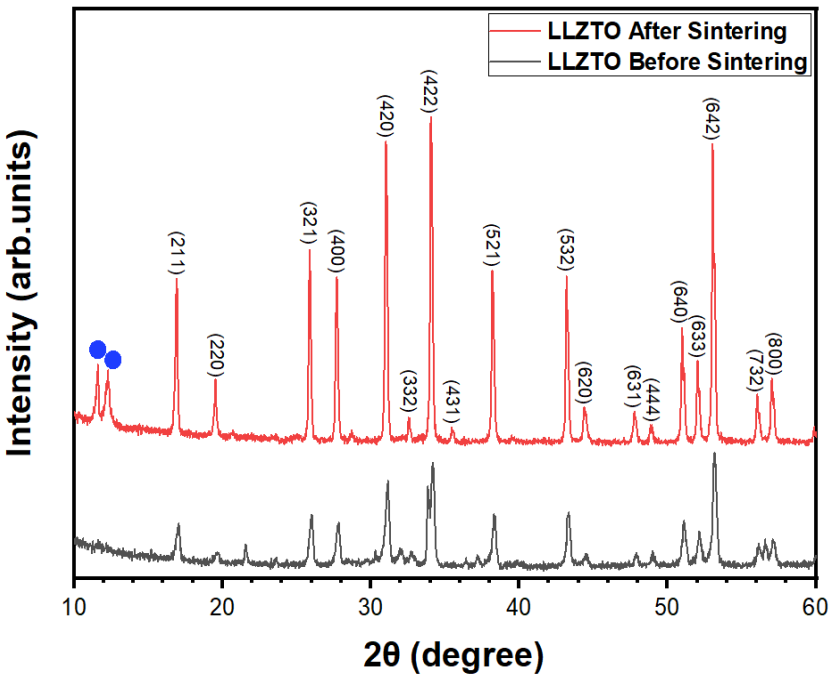

Figure 2: XRD graphs of LLZTO before and after sintering

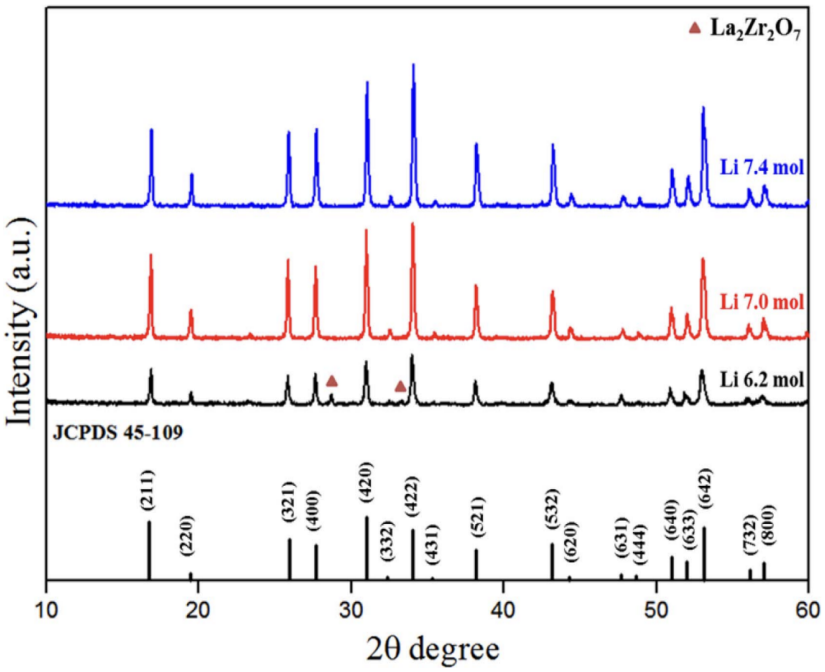

Figure 3: XRD graphs of LLZTO for different Li content [4]

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) [4]. 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. [4], 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.

References

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