Fast laser-based sintering of LLZO on Titanium substrate

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The presented work and results are part of the **"LASIBAT - Laser-based in-line sintering of adapted ceramic materials for the manufacturing of solid-state battery cells"** *project.*

Motivation and Scientific Concept

The LASIBAT-project aims to develop an in-line manufacturing process for ceramic cathode and separator layers based on $Li_{6.25}Al_{0.25}La_3Zr_2O_{12}$ (Al-LLZO) for all solid-state batteries (ASSB). By means of screen-printing roughly 20-30 µm thick layers are applied onto a titanium grade 2 substrate. The laser-based sintering process [1, 2] is designed to deposit energy directly into the ceramic particles (see Fig. 1). As laser radiation has a narrow band width (here 440 ± 3.1 nm), the absorptance must be adjusted accordingly. CuO is a suitable electrically nonconductive additive [3] with suitable optical properties. Adding CuO allows heating rates of > 1000 K/s. As high lithium-loss at elevated temperatures and sufficient densification are the main development challenges in the project, Li-excess of 20 mol-% in the form of LiOH is added to prevent LLZO decomposition.

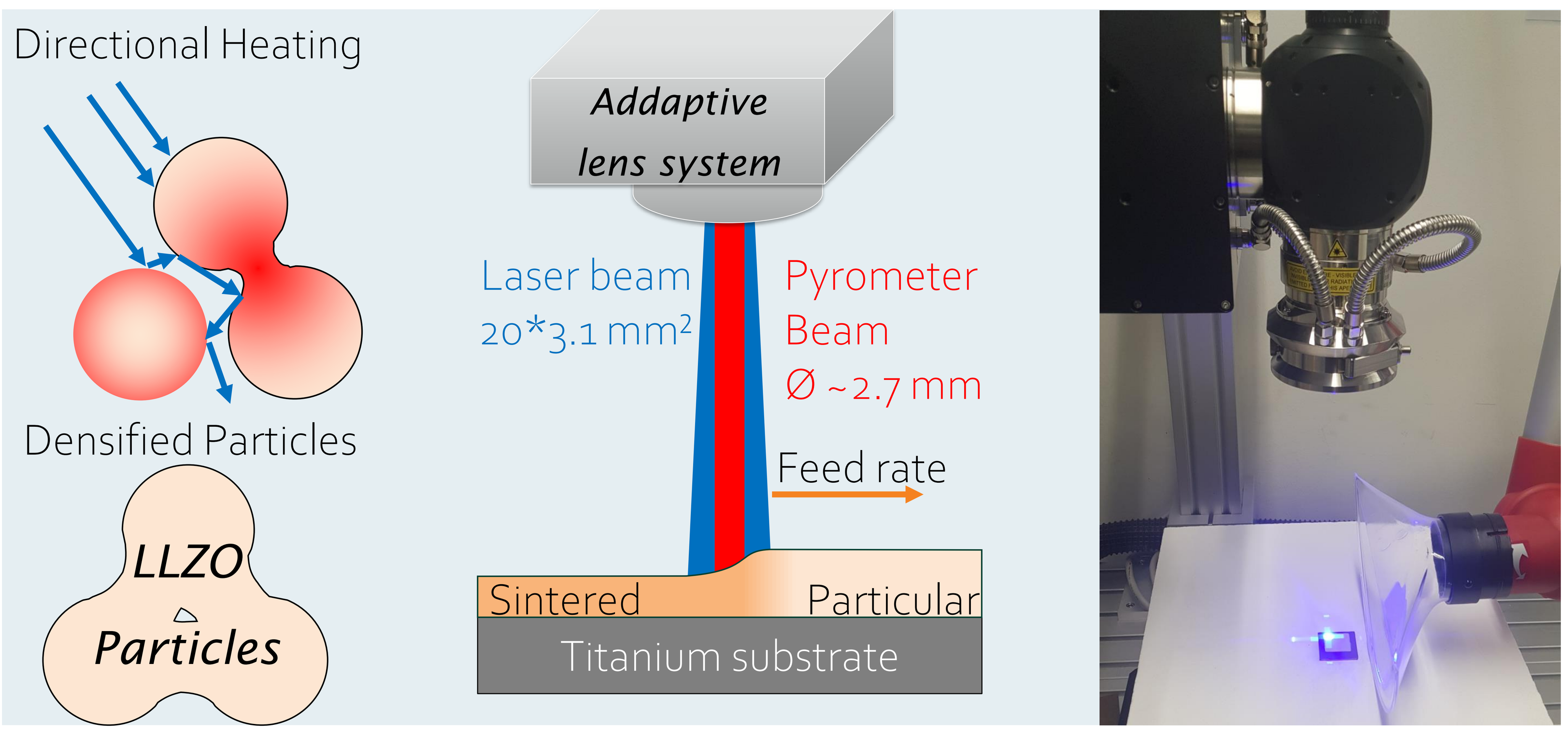

Fig. 1: Schematic concept of energy deposition in particulate LLZO layer and experimental setup. Regulation of laser power by co-axially integrated pyrometer.

Optical properties

Fig. 2 shows the absorptance for LLZO layers of 25 µm thickness with different fractions of CuO from 250-2500 nm.

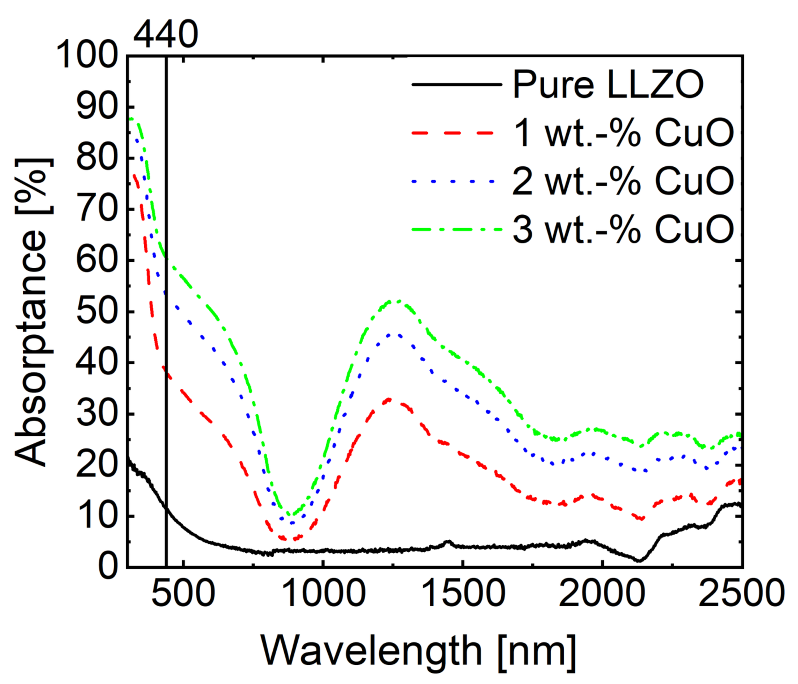

Fig. 1: Absorptance of LLZO layers with varying CuO content.

- Absorptance for 25 µm thick pure Al-LLZO layer ~**5 %** in optical and NIR spectral range
- CuO as electrically nonconductive laser additive
- Increase of absorptance @ 440 nm to **40 %**, **55 %** and **60 %**, for **1**, **2** and **3** wt.-% CuO as additive in screen-printing paste

Scanning Electron Microscopy

The pristine LLZO particles (d50 = ~700 nm) are sharp-edged and densely packed (fig. 3 left). After laser processing, the particles have rounded edges, and a fine and dense grain structure has been formed (fig. 3 right).

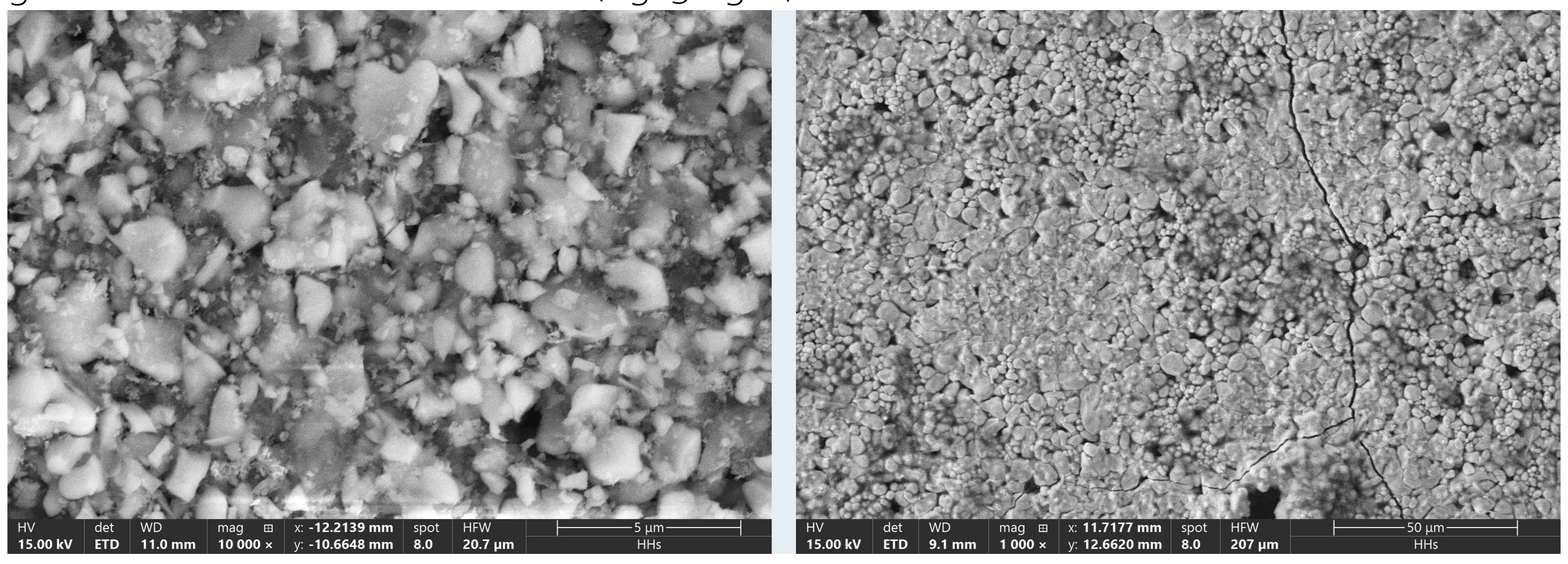

Fig. 3: Left: Unprocessed screen-printed and oven debinded LLZO-layer. Right: Laser-sintered LLZO-layer on titanium grade 2 substrate.

- Laser processing @ 0.25 s interaction time and 1400 °C pyrometer temperature
- Highly densified layer and distinct grain formation
- Residual pores and (most likely) thermally induced cracks in LLZO-layer

X-Ray Diffraction

XRD phase analysis indicates the conservation of cubic LLZO as well as the formation of $La_2Zr_2O_7$ and Li_2ZrO_3 (fig. 4).

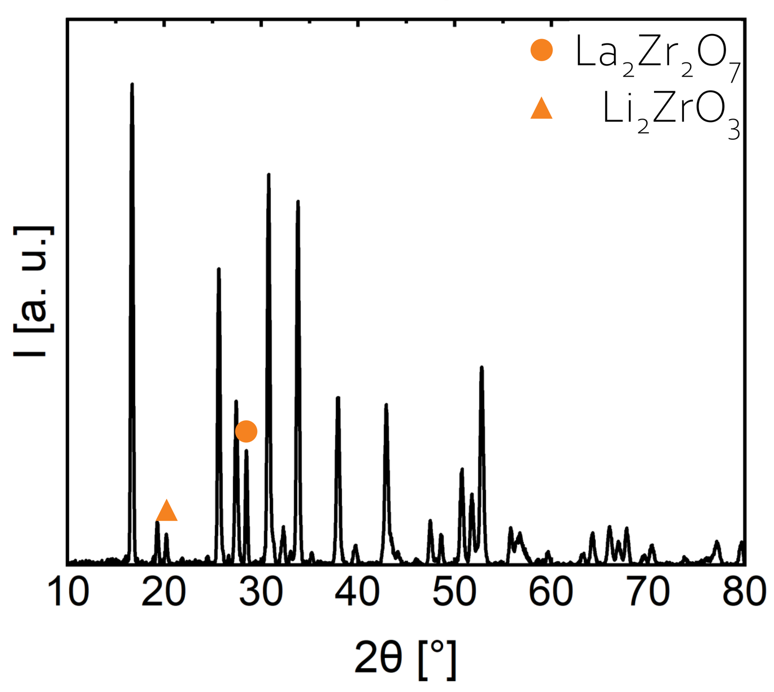

Fig. 3: X-ray diffractogram of laser-sintered LLZO Layer on Ti-substrate.

- LiOH as Li-excess for stabilization of c-LLZO phase
- Observed secondary phases $La_2Zr_2O_7$ [2,2,2] @ 28.6 ° and Li_2ZrO_3 [1,1,0] @ 20.3 ° (more possible)

Conclusion and Outlook

The results demonstrate the feasibility of a first scaled-up in-line capable laser-based sintering process for LLZO with area rates of 240 mm²/s. Further trials to determine Li-ion conductivity, sintering depth and adhesion are pending.

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