# Spatial control of crystal growth of L-phenylalanine by laser ablation

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## 1. Introduction

Control of crystal growth is important in various scientific or industrial processes such as purification, crystalline devises, X-ray crystallography, and so on. Most of studies have focused so far to the control of crystal growth by adjusting environmental parameters such as additive, solvent, and temperature. On the other hand, we have recently reported an innovative approach for promoting protein crystal growth by the direct modification of the local crystal structure utilizing femtosecond laser ablation [1]. The protein crystal with surfaces etched locally by femtosecond laser ablation showed the enhancement of the growth rate. We explained the mechanism based on the laser-induced spiral growth mode, which is energetically advantageous compared to the spontaneous two-dimensional nucleation growth mode. In this study, we apply the laser method to growth control of L-phenylalanine (L-Phe) crystal, which shows several crystal polymorph with different morphology (e.g., plates, needles, etc) depending on solution conditions.

## 2. Experimental

L-Phe powder was completely dissolved in water at 70°C. A portion of L-Phe solution (30 µL) was added and sealed into a custom-made glass chamber and incubated at 45°C on a temperature controlled stage (Supersaturation ratio, $c/c_{sat}$ = 1.1). Micrometer-sized crystals spontaneously appeared in a few minutes in this condition. The generated crystal was directly exposed to a femtosecond laser pulse ($\lambda$ = 800 nm, $\Delta t$ = 120 fs) through 20× objective lens (NA = 0.5). The crystal growth behavior was always monitored with a laser confocal microscopy combined with differential interference contrast microscopy (LCM-DIM).

## 3. Results and discussion

Figure 1 shows the time evolution of change in L-Phe crystal morphology after femtosecond laser irradiation. When a laser pulse (0.03 µJ/pulse) was shot to the crystal edge, the growth rate toward the irradiated side was clearly enhanced (Figure 1a-c). On the other hand, the crystal thickening was induced with the laser irradiation to the center of the crystal surface (0.06 µJ/pulse), while the lateral growth of the crystal remained almost isotropic (Figure 1d-f). To gain more quantitative insights into the crystal growth mechanism, the changes in length, width, and height of the target crystal are plotted as function of the irradiation time. It is obvious that the growth rates in length and height were increased by approximately 2 and 7 times, respectively, after the laser irradiation. This clearly indicates that the femtosecond laser irradiation can induce anisotropic crystal growth of L-Phe. We consider that the mechanism of the laser-induced crystal growth is attributed to the change in crystal growth mode triggered by femtosecond laser ablation. In fact, no such anisotropic crystal growth enhancement was observed when the energy of the input laser was below the ablation threshold (~ 0.02 µJ/pulse). In addition, the LCM-DIM revealed that many crystalline steps were generated from the irradiated spot of crystal. In the presentation, we will show the more detailed dynamics of the laser-induced crystal growth and the high potential of laser ablation method for the control of crystal morphology and polymorph.

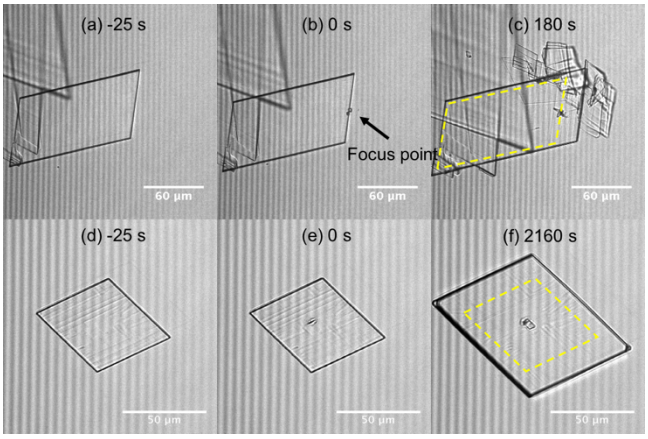


Figure 1. Bright field images of L-Phe crystal growth behavior. A single femtosecond laser pulse was shot to the edge (a-c) or the center of the crystals (d-f) at $t$ = 0 s. The yellow dotted lines represent the contour of the crystal before the laser irradiation.

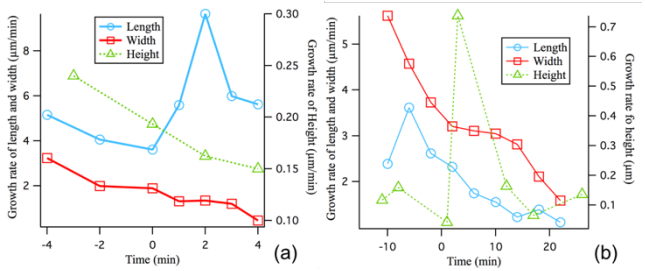


Figure 2. Growth rate in length, width and height of the laser irradiated crystal of Figure 1. The left and right panel correspond Figure 1a-c and Figure 1d-f, respectively.

## Reference

[1] T. Tominaga, M. Maruyama, H. Y. Yoshikawa et al., Nature Photonics. **10** (2016) 723.