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## 論文の内容の要旨

In this thesis, we have demonstrated control of crystal morphology and polymorphism of L-Phe by laser ablation.

In chapter 1, the purpose of this study, together with scientific history and principles of laser ablation and crystallization, are summarized.

In chapter 2, we have firstly confirmed that effects of laser pulse durations (nanosecond to femtosecond) on laser ablation of crystals. When laser pulse durations were focus to crystal surface, femtosecond laser ablation showed a tiny etching area, while, as pulse duration increasing to picosecond and nanosecond, ejected fragments and clear crystal disruption were observed. From AFM image, it clearly proved that femtosecond laser ablation generated a flat and smooth hole smaller than diffraction limit, which can be well-explained by multi-photon absorption and photomechanical process. In the picosecond and nanosecond laser ablation, photothermal process caused larger fused etching area was presented with surround protrusion, which easily leads to polycrystallization. The results of laser ablation of as-grown crystals well agree with it, which perform the single crystal growth and polycrystallization in femtosecond and nanosecond case, respectively. In short, femtosecond laser ablation showed greater advantage for promoting single crystal growth without protrusion and poly-crystallization among the laser pulse durations. As a result, we utilized a femtosecond laser pulse as light source to the spatial control of crystal experiment. Anisotropic crystal growth was observed with the vertical and horizontal direction when laser was shoot to center face and side face. It is explained by generation of energetically advantageous growth modes, which clearly showed spiral growth pattern in LCM-DIM images. A spiral growth pattern was generated and propagated to outside from the etching, and it finally dominated the crystal surface. Therefore, this study also confirmed femtosecond laser ablation generated a dislocation for generation of energetically favored spiral growth. At last, we succeed in preparation of L-Phe bulky crystal by promoting normal growth at center face of crystal via femtosecond laser ablation, which cannot be achieved by conventional method.

In chapter 3, we have confirmed that femtosecond laser irradiation also shows the high potential for controlling crystal polymorph via cooperative effect of laser ablation and laser trapping. When femtosecond laser was introduced to an air/solution interface of unsaturated solution, plate-like anhydrous poly-crystals were formed at laser focus. This behavior was ascribed to effect of laser trapping. During the irradiation, generation of supercontinuum and bubble well explained that femtosecond laser trapping induced concentration increasing; thus, it occasionally triggers the formation of plate-like anhydrous poly-crystals at the focus in unsaturated solution by cooperative effect of laser trapping and laser ablation. Following the crystal nucleation, continuous laser irradiation caused laser ablation of crystal, leading to formation of whisker-like monohydrate crystal. Furthermore, we also succeed in formation of plate-like anhydrous crystal by irradiated focused femtosecond laser to the bottom of glass chamber where fully filled by spontaneously generated whisker-like crystals. These bidirectional polymorph conversions were presented by the presence of laser ablation. By shooting the femtosecond laser pulses to the crystal surface, cavitation bubble induced concentration increasing result in precipitation of another crystal polymorph on the surface of bubble. The polymorphic conversion can be interpreted by the conventional nucleation rate theory, where the thermodynamically meta-stable form is preferentially at high SS value and vice Versa. To conclude, laser ablation shows not only control of crystal growth but also control of nucleation resulting in different crystal morphology and polymorphism.

My research described in this thesis was carried out under the double doctoral degree program between Saitama University and National Chiao Tung University. A part of my research that was mainly done at National Chiao Tung University was described as Appendix with the title of Laser trapping controlled polymorphism of L-Phe. Here, it shows that formation of plate-like crystal can be induced by laser trapping in unsaturated solution, which is metastable form under room temperature. Second, whisker-like crystal and plate-like crystal were preferentially precipitated by focusing the circularly polarized laser and linearly polarized laser, respectively. These results also reveal its various possibility of laser in application of crystallization field.

Finally, from this thesis, we could say that we succeed in controlling the crystallization process via laser ablation, which is different from the conventional crystallization methods such as tuning the environmental conditions. Various size, shape and crystal structure can be generated by tuning laser parameters; thus, it is very promising to produce of functional crystals, which cannot simply generate by conventional crystallization methods, via laser ablation. We are looking forward this study can open new generation of crystallization fields.

# 論文の審査結果の要旨

本学位論文は、レーザーアブレーションという光技術を用いて、有機結晶の形状と多形を制御する手法論の開発とその詳細なメカニズムに関する研究について述べられている。第１章に研究背景、第２章と第３章に研究成果、第４章で結論が述べられ、英語で作成されている。以下の学位論文の内容の概略を英語で述べる。

In chapter 1, the purpose of this study, together with scientific history and principles of laser ablation and crystallization, are summarized.

In chapter 2, to clarify the appropriate laser condition for controlling the shape of single crystals with minimized damage, the dependence of pulse duration on laser ablation and crystal growth of L-phenylalanine (L-Phe) was systematically investigated. By using a laser system with tunable pulse durations from fs to nanosecond (ns), this study revealed that fs laser ablation can offer nanometer-sized, sharp etching of which diameter was smaller than the diffraction limit. By utilizing such nano-processing via fs laser ablation for promoting the growth of a targeted crystal face, this study clearly demonstrated the preparation of a bulky crystal of L-Phe, which are difficult to be obtained by conventional crystallization methods.

In chapter 3, this study demonstrated bidirectional polymorphic conversion of L-phenylalanine by focused femtosecond laser irradiation, which can work as laser ablation and laser trapping. When the femtosecond laser beam was focused at an air/solution interface of its unsaturated solution, plate-like anhydrous crystals are generated from the laser focus. This crystal nucleation was realized by local concentration increase achieved by femtosecond laser trapping, which is the first demonstration of femtosecond laser trapping-induced crystallization. Furthermore, whisker-like monohydrate crystals were produced by the followed laser ablation on the surface of the plate-like crystals. On the other hand, when a femtosecond laser was focused to whisker-like monohydrate crystals, plate-like crystals were formed, meaning that an unstable phase can be produced from a stable phase. The dynamics and mechanism of the bidirectional polymorphic conversion was explained from the viewpoint of the nucleation rate theory considering solution concentration around the surface of laser ablation-induced cavitation bubbles. From this result, this study concludes that cooperative effect with laser trapping and laser ablation is promising in controlling of nucleation stage.

In conclusion, this study mentions that laser ablation techniques is very prospective in crystallization field. In the stage of crystal growth, femtosecond laser ablation acts as a trigger for promotion of growth of target crystal face. Thus, desired crystal morphology (size and shape) can be achieved. In the stage of nucleation, laser ablation also acts as a tool for increasing local solution concentration. As the results, different crystal polymorph can be nucleated based on the different supersaturation value. Thus we can expect that the laser ablation techniques will be widely applied to various scientific and industrial fields.

以上のように申請者は、レーザーアブレーションを駆使することで、バルク結晶の作製や、安定相から準安定相への誘導などに成功し、従来法とは全く異なる新しい結晶化制御アプローチを開拓した。これらの研究成果は、レーザーという外部刺激を用いて結晶化を能動的に制御する革新的手法論を提示するものであり、

分子構造解析や創薬など、結晶化が関わる様々な基礎研究・産業分野に大きな波及効果をもたらすことが期待できる。

なお申請者は、埼玉大学と国立交通大学（台湾）とのダブルディグリープログラムの学生であり、本学位論文の第２章は埼玉大学をメインとして実施した研究、第３章は埼玉大学と国立交通大学の双方で実施した研究に関するものである。第２章の内容は、アメリカ化学会の論文誌（J. Phys. Chem. C）に筆頭著者論文として出版され、同雑誌の Supplementary Cover Art にも選ばれている。さらに、第３章の内容は、筆頭著者論文が Jpn. J. Appl. Phys. 誌に受理されている。また、本学位論文の Appendix には、国立交通大学を主として得られた研究成果がまとめられており、これは筆頭著者論文１報と共著論文１報として発表されている。

以上の理由から本論文は、埼玉大学から博士の学位を授与するために質・量とも十分なものであり、合格という結論に至った。