不飽和微小液滴中での光圧捕捉結晶化による$NaClO_3$準安定相制御
"Freezing" of $NaClO_3$ Metastable Crystalline State by Optical Trapping in Unsaturated Microdroplet

*新家 寛正[1]、杉山 輝樹[2,3]、宮本 克彦[1]、尾松 孝茂[1]
*Hiromasa Niinomi[1], Teruki Sugiyama[2,3], Katsuhiko Miyamoto[1], Takashige Omatsu[1]

1. 千葉大学大学院工学研究院、2. 台湾国立交通大学、3. 奈良先端科学技術大学
1. Graduate School of Engineering, Chiba University, 2. National Chiao Tung University, 3. Nara Institute of Science and Technology

Control of the metastable single crystal in crystallization from a solution has importance on the purpose of fundamental research to precisely explore crystal structure of an unprecedented phase and mechanisms of its polymorphic transformation or non-classical nucleation pathway intermediated by metastable precursors during mineral formation process. The essence and difficulty of metastable phase control in spontaneous crystallization lies on how crystallization conditions fulfill two requirements in a relationship of trade off: (1) High supersaturation state sufficient to induce nucleation of the target metastable phase (2) Low supersaturation state enough to suppress undesired nucleation of the stable phase during the growth of the target crystal. Crystallization from a microdroplet has been known as a potential method to stably grow a metastable crystal because its small volume enough for solute molecule to diffuse to a mother crystal that appeared in the microdroplet suppresses an undesired additional stable phase nucleation.[1] However, the microdroplet method has a limitation to achieve low supersaturation state in the period from the primary nucleation to early stage of crystal growth as long as the onset of the nucleation relies on spontaneous nucleation. Here, we demonstrate that optical trapping-induced crystallization,[2] in which optical trapping of crystalline clusters induces crystal nucleation from unsaturated solution, can overcome the limitation of the microdroplet method.

We used sodium chlorate ($NaClO_3$) as a target compound. Crystallization of $NaClO_3$ from an aqueous solution exhibits two kinds of polymorphs: monoclinic metastable phase and cubic stable. The solubility of the metastable phase is about 1.6 times higher than that of the stable phase.[3] An aqueous solution of $NaClO_3$ saturated at 22˚C was sprayed to the cover glass using a commercially available spray container. This procedure allowed us to produce hemispherical microdroplets of the $NaClO_3$ solution on the cover glass. The hemispherical microdroplets were confined in an enclosed crystal growth cell [Figure 1 (a) right]. The mother solution is unsaturated state with respect to the metastable phase. A system for optical trapping-induced crystallization was constructed by introducing circularly polarized green laser (532 nm) to an inverted polarized light microscope equipped with a 60× objective lens [Figure 1(a) left]. A circularly polarized light focused by the objective lens was irradiated to the air/$NaClO_3$ microdroplet interface to induce nucleation. We observed crystallization dynamics induced in-situ using the polarized light inverted microscope and a CCD camera.

We have achieved to crystallize $NaClO_3$ metastable single crystal by optical trapping-induced crystallization despite the microdroplet is unsaturated state after the onset of the laser irradiation to the air/solution interface [Figure 1 (b) (left) (i)-(vii)]. On the other hand, the crystal started to dissolve when the laser irradiation was stopped [Figure 1 (b) (left) (viii)-(x)]. The dissolution turned to growth when we restarted the laser irradiation again, namely, we achieved reversible metastable phase control without polymorphic transformation. This crystal growth dynamics shows that laser irradiation causes the change of the magnitude relationship between chemical potentials of the solution phase and the crystalline phase in the microdroplet. Our method achieved to "freeze" a kinetic pathway of crystal formation intermediated by a metastable phase, being useful for precise analysis a short-lived unprecedented phase. Our method shed a light on complete polymorph control.

[1] Teshima et al. , CrystEngComm 15, 9874-9877 (2013)
[2] Sugiyama et al., Acc. Chem. Res. 45(11), 1946-1954 (2012)
[3] Niinomi et al., Cryst. Growth Des., 13(12), 5188-5192 (2013)

キーワード：準安定相、光学捕捉、微小液滴
Keywords: Metastable phase , Optical trapping, Microdroplet