Conversion of stable crystals to metastable crystals in a solution during temperature cycling

Hiroyasu Katsuno[1*], Makio Uwaha[2]
*lead presenter: katsuno@lowtem.hokudai.ac.jp
1 Institute of Low Temperature Science, Hokkaido University, Kita-19, Nishi-8, Kita-ku, Sapporo, Hokkaido 060-0819, Japan
2 Science Division, Center for General Education, Aichi Institute of Technology, 1247 Yachigusa, Yakusa-cho, Toyota, Aichi 470-0392, Japan

Among many possible crystal structures, the most stable structure is realized and metastable structures disappear in equilibrium. An exceptional case is chiral crystals which have two stable structures that are thermodynamically equivalent. In the case of chiral crystals, both left- and right-handed crystals exist in equilibrium. In 2005, Viedma showed the conversion of a racemic mixture of chiral sodium chlorate crystals into homochiral crystals (chirality conversion) by grinding crystals in a solution [1]. The result suggests that a metastable state is realized by grinding crystals. The chirality conversion of chiral crystals is also seen with a periodic temperature change (temperature cycling: TC) of a solution with crystals [2,3]. In addition, a numerical study showed the possibility of conversion of stable crystals to metastable crystals (crystal phase conversion) with grinding [4]. We theoretically investigated the possibility of the crystal phase conversion by TC using a generalized Becker-Döring model which includes cluster incorporation.

Figure 1 shows the crystal mass distribution during TC. The initial mass difference of crystals is about 5%. The minority stable phase crystals disappear and only the majority metastable phase crystals remain. From analysis of the masses in a single period, we find that the mass difference increases at high temperature duration. The majority crystals yield more clusters than the minority at high temperature. Large amount of the majority clusters provide the large supersaturation which promotes incorporation of clusters into crystals leading to mall net dissolution. At low temperature, both crystals grow by coalescence with abundant clusters and monomers in much the same way. By repeating this process, the phase conversion of crystals is accomplished.

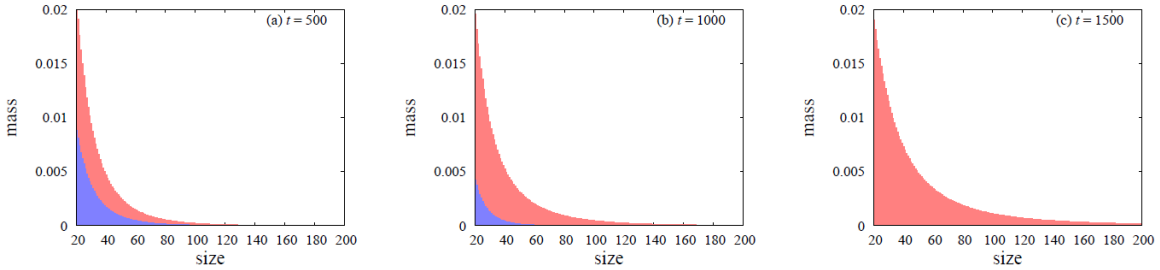

Fig1. The crystal mass distribution at (a) t=500, (b) t=1000, and (c) t=1500. Red (light gray) and blue (dark gray) areas represent the masses of metastable crystals and stable crystals.

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