

Refinement of synthetic guanine crystals for fast diamagnetic rotation

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(Abstract)

Synthetic guanine crystals, with the same magnetic controllable reflection property as a biogenic guanine crystal from fish scales, were prepared using a classical Ostwald ripening method for crude crystals, from the aqueous sodium hydroxide solution of a commercially available synthesized guanine powder. The resulting synthetic guanine crystals with an average size of several tens of micrometers were in the same crystal system as the biogenic guanine crystals under measurement by X-ray diffraction (XRD). However, XRD patterns of water-floating crystals showed that the correlation between the growing direction and reflecting surface in the synthetic crystals is different

27 from that in the biogenic crystals. Therefore, the synthetic crystals were ground by an agate mortar
28 for refinement of its optical and magnetic-orientation characters. As a result, we realized a fast-
29 magnetic orientation against the vertical field, which is related to the magnetic control of light
30 reflection, the same as the biogenic guanine crystal behavior.

31

32 **I. INTRODUCTION**

33 Guanine, which is a simple molecule with a molecular weight of only 151, is one of the most
34 important molecules for the manipulation of light in living system [1-8]. There is a possibility that
35 the use of guanine crystals may lead to a novel micro optical device with a higher ordered function,
36 such as an artificial iridosome or a material exhibiting structural color. Recently, we reported that
37 biogenic guanine crystals can be used as micro optical devices that can control the reflection
38 characteristics by using the external magnetic field response accompanied by the anisotropy of the
39 diamagnetic susceptibility of guanine crystals [5, 9-11]. For example, the reflection property of
40 guanine crystal can be switched through applying or removing a magnetic field by using the
41 perpendicular magnetic orientation character, as shown in Fig. 1(b) [9]. However, guanine crystals
42 that can be used as magnetic switchable reflectors can only be collected from living creatures, such
43 as fish, because the shape and size of synthetic guanine crystals prepared using an artificial method
44 are much poorer than those of biogenic crystals. A notable reason for the difficulty in the preparation
45 of synthetic guanine crystals by an artificial method is the low water-solubility [12]. Several groups
46 have succeeded in recrystallizing synthetic guanine under basic aqueous solution, because the
47 solubility can be increased by using the acid-dissociation equilibrium of a guanine molecule [12-14].
48 The resulting synthetic guanine crystals have the same crystal structure as that of biogenic guanine
49 crystals, but these external shapes are insufficient for use in magnetic switching optical devices, as
50 described above. It is not necessary to make identical crystals as the biogenic crystals, but an external
51 shape that provides reflection and perpendicular magnetic rotation is required for the creation of a
52 magnetic switchable micro optical device.

53 In this study, we have optimized the conditions to prepare a synthetic guanine crystal with an
54 external shape that provides reflection and perpendicular magnetic rotation similar to the magnetic
55 orientation in a biogenic crystal [9]. Synthetic guanine crystals were first prepared from a basic
56 aqueous solution at pH 13 and were ripened by using a classical Ostwald ripening method. Next, the
57 crystallographic information regarding the correlation between growing direction and reflecting
58 surface of the ripened synthetic guanine crystal were estimated using X-ray diffraction (XRD)
59 measurements of the water-floating crystals. Finally, crystal grinding was applied to the synthetic
60 guanine crystal for refinement towards our purpose.

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62 **II. Method**

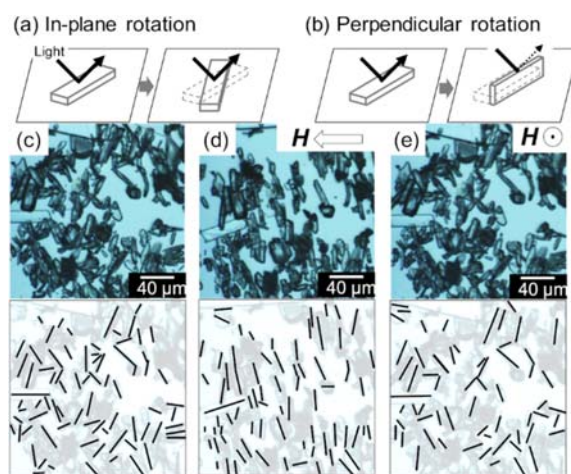
63 Crystallization from synthesized high-grade guanine (077-01692, Fujifilm Wako, Japan) was
64 performed according to our previously reported procedure [11]. The synthesized guanine (12.6 g) was
65 dissolved in an aqueous solution of sodium hydroxide (1 L) with a pH of 13 at the boiling point, and
66 crude crystals were obtained after cooling to ambient temperature with a cooling rate of 10 °C/day.
67 The temperature of the dispersion containing the crude crystals was heated again to *ca.* 100 °C for
68 growth of the crystals. After ripening for several weeks, the ripened guanine crystals were collected
69 by filtration after cooling to room temperature. The resulting crystals were washed with
70 water/methanol and dried *in vacuo*, and then were used as the “synthetic guanine crystals” for the
71 following measurements. Characterization of the shape of the synthetic crystal was performed by
72 optical microscopy. Crystallographic information of the crystals, which were dried or floating in water,
73 was obtained by using an XRD analysis.

74 After checking the general character of the synthetic guanine crystals without further modification,
75 the synthetic guanine crystals were gently ground on an agate mortar in a lateral stretch manner by
76 using an agate pestle for half-an-hour to improve its external shape of the synthetic crystal. Drastic
77 changes were observed from the results of XRD and magnetic orientation, as described in the next
78 section.

79

80 III. Results and Discussion

81 The crude crystals with an average size of 10 μm were boiled at *ca.* 100 $^{\circ}\text{C}$ in an aqueous sodium
82 hydroxide solution at pH 13 to increase the crystal size in a classical Ostwald ripening condition over
83 one week. The size of the resulting guanine crystal was significantly larger than that before ripening.
84 Although the major external formation of the crystal was rod-like, which was the same as the
85 previously reported synthetic crystals [12-14], plate-like crystals showing interference fringes, which
86 are a sign of high-quality crystals without cracks, were also obtained (Fig. 1(c)).



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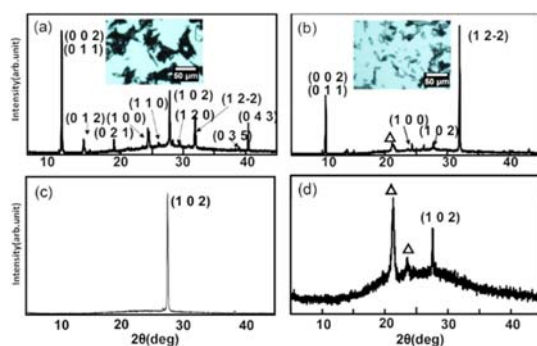
88 **Figure 1.** Schematic illustration of rotation manner of crystals under a magnetic field: (a) In-plane
89 rotation and (b) perpendicular rotation. Rotation direction depends on the sample and direction of the
90 external magnetic field. Optical microscopy images of synthetic guanine crystals (top) and images
91 indicating the orienting direction of the long axis of the crystals (bottom): (c) Before applying a
92 magnetic field, (d) after applying a horizontal magnetic field of 130 mT, and (e) after applying a
93 vertical magnetic field of 150 mT by using permanent magnets.

94

95 For XRD measurements, two types of samples were prepared for both the synthetic guanine
96 crystal and the biogenic guanine crystal from the scales of a goldfish [5]. Here, we defined two types
97 of samples depending on preparation **methods** before the XRD measurements: The type I sample is
98 dried crystals obtained after drying the water dispersion of crystals on the surface of a flat glass plate,
99 and the Type II sample is floating crystals in a water droplet on the surface of the glass plate covered
100 with a wrap film. XRD measurement of the crystals floating in water (Type II) was possible by
101 irradiating X-rays from above the water surface. The plots of XRD patterns of the two types of

102 samples of the synthetic and biogenic crystals are shown in Fig. 2. All clear XRD peaks could be
103 assigned to the crystal in the anhydrous guanine-phase [3,15], which proved that the synthetic guanine
104 crystals belonged to the same crystal structure as the biogenic crystals. This agreement was also
105 confirmed by Fourier-transform infrared spectroscopy. As a feature of the synthetic crystals, the
106 intensity corresponding to the $(12\bar{2})$ plane became large and dominated along with the $(002)/(011)$
107 plane, which could not be distinguished because their peak positions overlapped, in contrast to the
108 biogenic crystals [4]. These results suggested that the synthesized crystals grew with a preferential
109 orientation that resulted in flat $(12\bar{2})$ and $(002)/(011)$ planes.

110 The difference between the XRD patterns were observed depending on the presence of water
111 (Fig. 2(a) and (b)) in the case of the synthetic crystals, whereas the two patterns were matched in the
112 case of the biogenic crystals and only the peak from (102) was observed (Fig. 2(c) and (d)). The
113 biogenic crystals exhibited an elongated hexagonal plate having a smooth broad surface of the (102)
114 plane and the averaged size was $20\ \mu\text{m}\times 5\ \mu\text{m}\times 100\ \text{nm}$ (thickness). Such a plate-formed guanine
115 crystal was aligned so that the (102) plane was parallel to the water surface because the crystals could
116 float in water because of its extremely thin structure. Therefore, even when the floating biogenic
117 crystals were dried, the (102) plane was stacked parallel to the substrate surface, as was observed
118 from XRD. However, the synthetic crystals mainly exhibited a rectangular shape with a larger
119 thickness compared with the biogenic crystals. The dried synthetic crystals in the Type I samples
120 should be stacked so that the plane orientation of the crystal faces adopt various directions after drying
121 to exhibit many XRD peaks that originate from the resulting randomness (Fig. 2(a) inset). However,
122 in the case of the floating synthetic crystal in the Type II sample, the crystals tended to float in water
123 with a flat surface facing up (Fig. 2(b) inset).



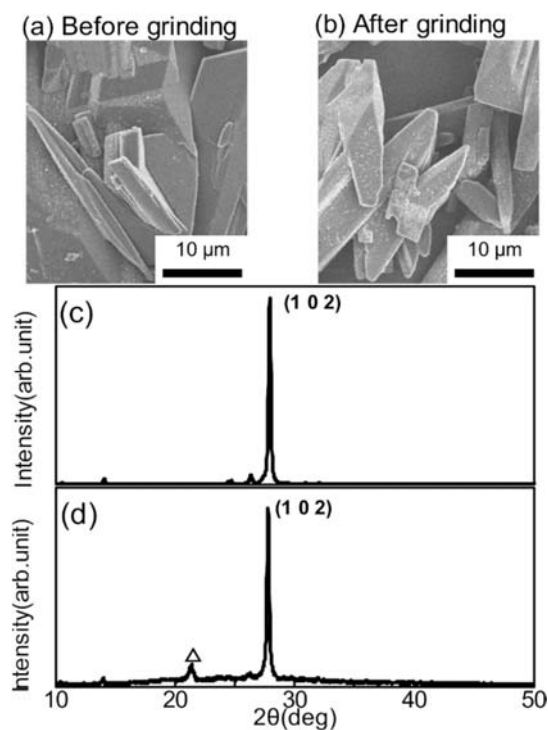
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125 **Figure 2.** Diagrams of XRD patterns of (a) dried (Type I) and (b) water-floating (Type II) synthetic
 126 guanine crystals, and of (c) dried (Type I) and (d) water-floating (Type II) biogenic guanine crystals.
 127 The diffraction peaks marked by open triangles (Δ) arise from the wrap used to mount the sample.
 128 Optical microscopy images are shown as insets in (a) and (b), respectively.

129

130 The magnetic orientation experiments of the synthetic guanine crystals dispersed in water by
 131 using a permanent magnet were conducted. The optical microscopy images of the crystals under a
 132 horizontal magnetic field of 130 mT and vertical magnetic field of 150 mT are shown in Fig. 1(b) and
 133 (c), respectively. The $(12\bar{2})$ plane and $(002)/(011)$ plane made angles of 55.8° and $61.7^\circ/76.0^\circ$ with
 134 the (102) plane, which meant that the (102) plane was arranged inclined to the upper surface of the
 135 crystals. When a horizontal magnetic field was applied, the synthetic crystals rotated and turned the
 136 longitudinal direction of the crystal towards 90° from the field direction, which supported the growth
 137 of the crystal planes that was discussed above. It should be noted that a quick horizontal rotation can
 138 be realized in synthetic guanine crystals. This is because that the (102) plane layered with a large
 139 thickness has a high diamagnetic anisotropy energy, and therefore a large torque is generated to make
 140 the (102) plane parallel to the magnetic field, while the biogenic guanine crystal is in a thin layer with
 141 a thickness of *ca.* 100 nm. However, a magnetic response is not observed in most synthetic crystals
 142 under a vertical field of 150 mT. The synthetic crystals exhibited the same magnetic orientation as
 143 the biogenic crystals reported previously; however, their frequency was not large. It was proposed
 144 that the reason for the poor magnetic response of the synthetic crystals to the vertical field compared
 145 with the biogenic crystals is caused by the difference in the correlation between the external shape
 146 and the molecular alignment in the crystal [2]. Such a difference should result in a different magnetic
 147 field response from the biologic crystals.

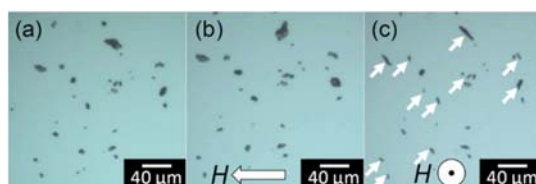
148 To improve the magnetic response of the synthetic crystals through the refinement of its external
149 shape, the synthetic guanine crystals were ground by using an agate mortar to obtain cracked crystals,
150 because several synthetic crystals immediately after the ripening had bundled together, as shown in
151 Fig. 1. It was surprisingly obvious that the (102) peak became dominant and no remarkable peaks of
152 the other planes were observed in the XRD measurements (Fig. 3(c), and see also Fig. 2(a) for a
153 comparison). Moreover, the XRD pattern of the ground crystal did not change after floating the crystal
154 in water (Fig. 3(d)), which was the same trend as the biogenic guanine, as shown in Fig. 2(c) and (d).
155 These results indicated that the synthetic guanine crystal could be cleaved along the (102) plane after
156 physical grinding and its general crystal structure was maintained, even if the crystals were exposed
157 to violent conditions such as a mechanical grinding. Through the notable toughness of the synthetic
158 crystal, the shape of the crystal could be optimized to a flat thin plate after physical grinding, which
159 was close to the shape of the biogenic guanine crystal.



160 **Figure 3.** SEM image of crystal (a) before and (b) after mechanical grinding. XRD patterns of (c)
161 dried ground synthetic guanine crystal, which is the same sample shown in Fig. 3(b), and (d) ground
162 crystal floating in water (Type II sample). The diffraction peak marked by open triangle (Δ) arises
163 from the wrap used to mount the sample.
164

165

166 The magnetic orientation behavior of the ground synthetic crystals is shown in Fig. 4. The
167 longitudinal direction of the ground guanine crystal did not clearly orient along the horizontal
168 magnetic field (Fig. 4(b)) compared with the crystal before grinding shown in Fig. 1(d), probably
169 because the *b*-axis (1st easy axis) direction of the ground guanine crystal in the (102) plane became
170 irrelevant to the isotropic external shape of the crystal. In contrast, many ground crystals were
171 oriented perpendicular to the field and gravity under a vertical magnetic field (Fig. 4(c)). The behavior
172 against the vertical field, which is related to the magnetic control of light reflection, was the same as
173 the biogenic guanine crystal behavior.



174 **Figure 4** Optical microscopy images of a ground synthetic guanine crystal (a) before applying a
175 magnetic field, (b) after applying a horizontal magnetic field of 130 mT, and (c) after applying a
176 vertical magnetic field of 150 mT by using permanent magnets. Sectional area of crystals marked by
177 white arrows decreased under the vertical magnetic field by perpendicular rotation as shown in Fig.
178 1(a).
179
180

181

182 IV. CONCLUSIONS

183 Here, we prepared a synthetic guanine crystal showing a magnetic controllable reflection property
184 similar to biogenic guanine crystals. A classical Ostwald ripening for crude crystals, composed of a
185 synthesized guanine powder, and a mechanical grinding technique were applied to refine the shapes
186 of the resulting synthetic guanine crystal. It is surprising that the crystals with a practical property
187 were obtained with a rough approach, which can be termed as a top-down approach. An optimization
188 of the procedure by modifications of the recrystallization and ripening conditions is currently in
189 progress.

190

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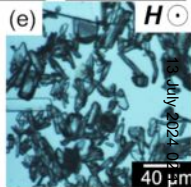
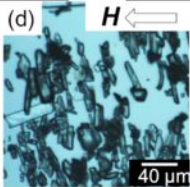
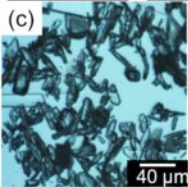
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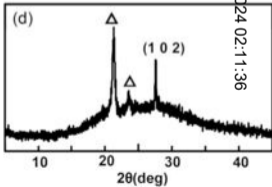
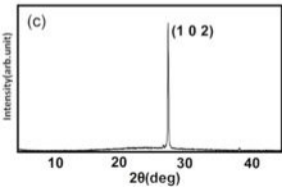
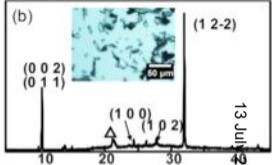
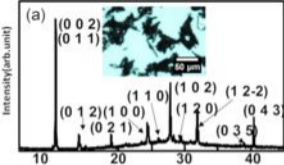
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(a) In-plane rotation



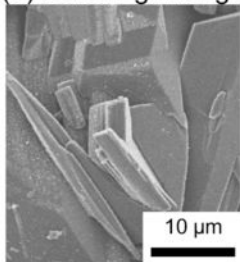
(b) Perpendicular rotation



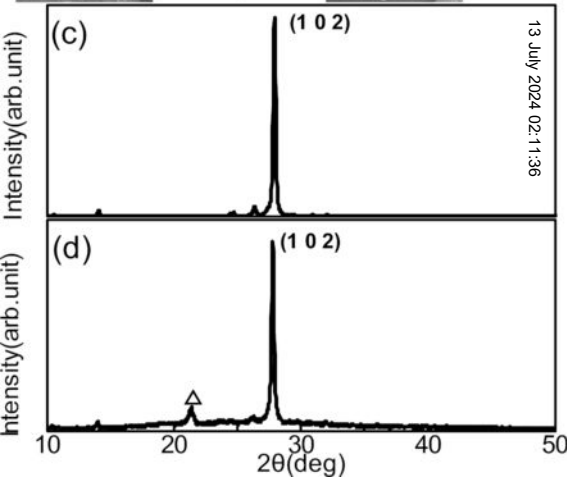
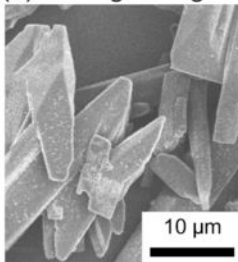


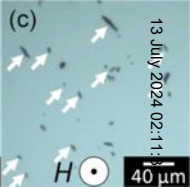
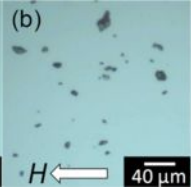
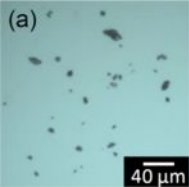
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(a) Before grinding



(b) After grinding





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