

## Promotion of crystal growth rate in aqueous solution by direct contact with gas corona discharge

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A new technique to promote crystal growth in aqueous solution using gas plasma is proposed. In this method, short-lived radical species produced in solution which is contacted with gas corona discharge play a role to increase chemical potential of inorganic solute. In an experimental examination, single crystal of KDP was grown in a supersaturated solution which receives oxygen ions and radicals from adjacent corona discharge in air. KDP crystal has two unique growth faces (100) and (101), and the growth rates of both faces were increased considerably by generating the corona discharge. The both growth rates with and without corona discharge were well converged by one function based on chemical potential supersaturation. This result revealed that the solution in contact with gas corona discharge has a larger capacity of chemical potential than that without the discharge. Short-lived species induced by gas corona discharge are considered to be anti-solvents to cause this effect. The crystal growth process proposed here is considered to be an excellent method in terms of low impurity inclusion because such short-lived species do not remain in the final crystal products and solution.

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### Introduction

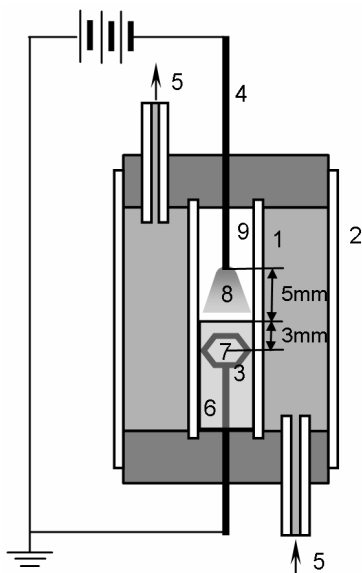
This article proposes a novel application of gas discharge technology to crystal growth process. Nowadays, there are a considerable number of researches to use gas discharge to some industrial applications such as plasma chemical deposition [1], surface modification [2], gas purification [3-5], and water purification [6-12]. To achieve these processes, highly-reactive gas radicals induced by reactions of accelerated electrons with gas molecules are important. Among them, water purification using gas discharge [8-12] is noteworthy because this process utilizes such gas radical species to produce aqueous short-lived species. In this report, we suggest these discharge-induced aqueous species can be used as anti-solvents to promote crystal growth processes.

Crystal growth is controlled by supersaturation in solution in nature. There are two common methods to generate supersaturation. One is to concentrate solute by evaporation, and another is to lower the solution temperature below the saturated level. In addition to these methods, alternative one is to admix anti-solvents or solutes into the solution as third components. The addition of these third components play a role to change activity of all species in the solution, resulting in changing solubility of solutes. However, these third additives are concerned to be remaining impurities in solute crystals, and are in many cases not desired in industrial processes. Here, it should be recognized that if short-lived additives can be continuously supplied to solution, such species can be clean third components.

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This report shows an experimental evidence that corona discharge in air above KDP (potassium dihydrogenphosphate) aqueous solution, which produce short-lived species, can increase the activity of solute, resulting in the promotion of KDP crystal growth rate.



**Fig. 1** Temperature controlled growth cell with corona discharge in gas phase: 1 inner glass tube (ID=20mm), 2 outer glass tube (OD=40mm), 3 platinum anode pole, 4 platinum cathode pole, 5 cooling water, 6 KDP solution, 7 KDP crystal (5mm size), 8 corona discharge in air, 9 air.

## Experimental

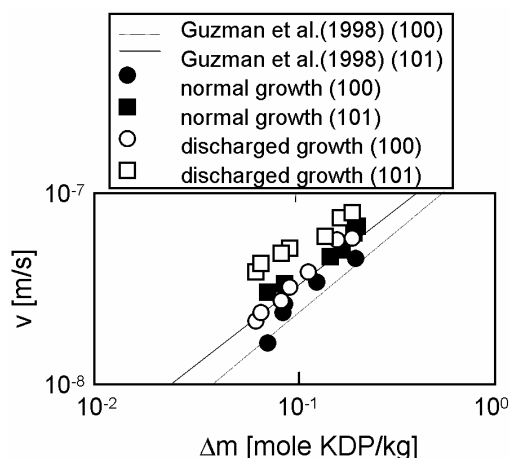
Growth experiment was performed at 313 K in a small batch cell. Figure 1 shows the illustrative apparatus for this growth experiment. The reactor consists of two Pyrex glass tubes coaxially placed. KDP solution was kept in the inner tube, and temperature-controlled water was circulated through the space between inner and outer tubes to stabilize the temperature of the KDP solution. There are two phases inside the inner tube, aqueous phase and gas phase above it. In this experiment, we used ambient air for the gas phase where corona discharge was generated. Two platinum poles (diameter = 1 mm) were provided in the inner tube: One is for anode and another is for cathode. The cathode tip was located above the gas-liquid interface by 5 mm, and the anode mounting a single KDP seed crystal was submerged in KDP supersaturated solution. A high voltage was applied on the cathode and the anode was grounded. The voltage and discharge current to generate corona discharge were fixed at 10 kV and 1mA D.C. respectively. When corona discharge is generated, oxygen ions ( $O^-$ ,  $O_2^-$ ,  $O_3^-$ ) and uncharged radicals (O, OH) produced in humid air [13-15] are supposed to reach the solution surface by electric force and ion wind of a large flow rate of several meters per second [18].

The seed crystals of KDP were obtained at 313 K by natural evaporation, and the seed crystals having typical shape were selected. The initial size (approximately 3mm x 3mm) of the seed crystal was measured before the growth experiment. As a reference to the growth experiment with the corona discharge, a normal growth experiment without the corona discharge was performed for a first step. In this experiment, the seed crystal and KDP solution was kept at the saturated temperature, followed by lowering the cell temperature down to 313 K. After this temperature drop, the seed crystal has been grown for three hours keeping 313 K. The growth rate of KDP crystal was determined by the change from original to final crystal size for three hours. The growth rates were obtained as a function of supersaturation of the solution. For the second step, a growth experiment in contact with gas corona discharge was carried out at the same condition as the first step. The saturated solubility of KDP in water,  $m^*$ , is 2.4617 mole KDP /L at 313 K. The supersaturated solution was prepared with KDP concentration,  $m = \Delta m + m^*$ , where  $\Delta m$  is the amount of supersaturation. The accuracy of the growth rate and supersaturation data are less than 10 % and 1 %, respectively.

## Results and discussion

The supersaturated solution properties such as pH, conductivity, activity and so on in our experiments may be changed by corona discharge. In general, the effect of pH on crystal growth will appear when the inorganic impurity which forms complex exists in the aqueous solution. However, this case should not show the pH effect because such complex cannot be in the aqueous solution. The conductivity cannot be the driving force in crystal growth. The activity of solute may be changed by the generated species by corona discharge. We estimate how much the activity changes in our experiments with respect to the growth rate.

**Fig. 2** Relationship between supersaturation and (100) and (101) face growth rates of KDP crystal at normal and discharged conditions.



The growth rates of two unique faces (100) and (101) of KDP crystal were plotted for the growth with and without corona discharge as a function of concentration supersaturation in Fig. 2. It is well known that the growth rates of (101) face are larger than that of (100) face. The growth without discharge is well corresponded to this common trend. This result was well corresponded to our previous report [19]. Here, it is found that both growth rates of (100) and (101) faces obviously increased when corona discharge is generated. The crystal growth rate  $V$  is commonly expressed by a function of supersaturation  $\Delta m$  with the following empirical definition.

$$V = k (\Delta m)^n \quad (1)$$

where  $k$  and  $n$  are constants, and they are different values for (100) and (101) faces.  $n$  generally ranges from one to two.  $k$  and  $n$  in Eq.(1) also have different values for different operative conditions. Therefore, supersaturation in Eq.(1) should be defined rigorously by chemical potential ( $\mu$ ) as the following formulae,

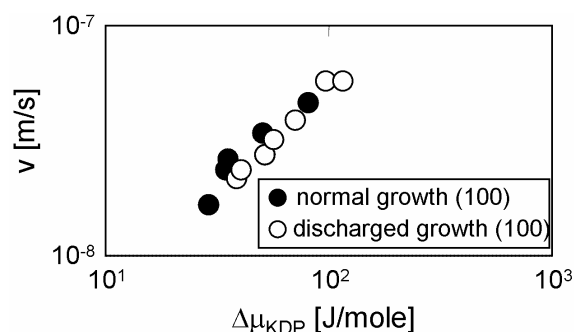
$$V = k_c (\Delta \mu)^{nc} \quad (2).$$

$\Delta \mu = \mu - \mu^*$ , where  $\mu^*$  is chemical potential of KDP in saturated solution. The relationship between chemical potential supersaturation and concentration supersaturation is given by

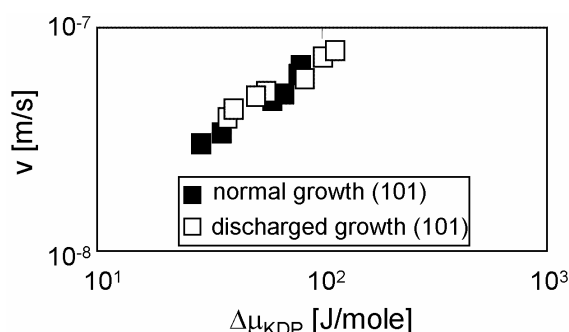
$$\Delta \mu = RT \ln [m/m^* \gamma/\gamma^*] \quad (3).$$

where  $\gamma$  and  $\gamma^*$  are activities of the solute at supersaturated and at saturated concentrations, respectively. Here, the same experimental values of  $m$  and  $\gamma$  in Eq.(3) are adopted for the normal growth and the growth under gas corona discharge. Therefore, it is thought that  $m^*$  and  $\gamma^*$  with corona discharge should be different from those of normal growth. We calculated the chemical potential supersaturation by using electrolyte solution model [20-21], and plotted the growth rates of the faces (100) and (101) as a function of the chemical potential

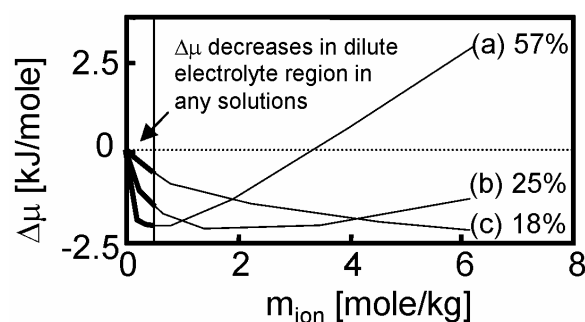
supersaturation in Figs. 3 and 4, respectively. Here,  $k_c$  and  $n_c$  should have the same values for different operative conditions. Assuming that discharge increases 50% of chemical potential supersaturation, the growth rates with and without the discharge of the faces (100) and (101) were well converged by the chemical potential supersaturation.



**Fig. 3** (100) face growth rate as a function of supersaturation defined by chemical potential of KDP.



**Fig. 4** (101) face growth rate as a function of supersaturation defined by chemical potential of KDP.



**Fig. 5** Categorization of chemical potential changes in water as function of molality for typical electrolytes.

This effect is analogical with ‘salting out’ by adding organic solvent to KDP solution as a second salt or an anti-solvent. It is known that corona discharge in air produces short-lived species such as  $O^{\cdot}$ ,  $O_2^{\cdot-}$ ,  $O_3^{\cdot-}$ ,  $O$ ,  $OH$ , and some other ionic and uncharged radicals [13–15]. During the discharge, such ionic species transfer to grounded solution by electric static force, resulting in a steady negative charge current to the anode through the solution. Also uncharged species may reach the solution by agitation by ion wind of velocity of several meters per second [18]. As these short-lived species are extremely unstable, it is expected that these species react with water to produce hydroxyl radical,  $OH$ , in solution [10–12]. The production of  $OH$  radical by direct contact of gas pulsed-corona with water surface was confirmed by the detection in the treated water by trapping the produced  $OH$  using spin trap DMPO with in-situ ESR and fluorescent molecular probe [10]. We consider that the effect of the corona discharge to increase the chemical potential super saturation is caused by the existence of negative charges and aqueous  $OH$  radical in the solution as third components. The species that dissolve in the aqueous solution in our experiments should be discussed. We expect that they are some ions, radicals caused by corona discharge. As for ions species, the mean ion's activity coefficient decreases when small amount of ions dissolved in the aqueous solution according to the Debye-Huckel theory, and results in the decrease of chemical potential as shown in the dilute electrolyte region of Fig. 5. We have researched how the mean ion's activity coefficient of many electrolytes change as function of molality [22, 23], and statistically obtained the percentage of three different types as shown in Fig. 5. The possible species are radicals that do not affect on ion strength in the aqueous solution. The electrolyte solution has been well studied, and activities of ionic species in aqueous solution are considered to be small in general. In other words, affinity of ions to water

is quit well [24] as shown in the dilute electrolytes region of Fig. 5. Therefore, applying static electric field on solution should not be effective to change activities of ions in aqueous solution. Thus, it is expected that promotion of KDP crystal growth rate would not be observed without discharge current even when a high voltage was applied. In our experiment, this insignificance of static electric field on KDP crystal growth was confirmed when the voltage was set at a point slightly lower than corona-discharge breakdown, 9.5 kV.

Since third components often increase activity of solute in solution, there are many conventional processes to add the third components to control the crystal growth rate. However, such processes require additional processes and energy to recover the third component. For crystallization processes, because the third component is in fact an impurity for crystal products, the remaining component is not desired. Contrary to such a conventional method, it is important to recognize that the radical species induced by the corona discharge in the solution are very unstable and disappear in a short time when discharge is stopped. As a result, the radical species turned to be a third component that does not remain after the crystallization process. Therefore, discharge-induced species can be a clean agent to increase chemical potential of inorganic solute in water. We should propose the several applications of corona discharge to make the chemical potential increase in the solution in future.

## Conclusions

It was proposed that crystal growth in aqueous solution can be promoted by the contact of gas corona discharge with the surface of the solution. Experimentally, single crystal of KDP was grown in a supersaturated solution which receives oxygen ions and radicals from corona discharge in air. In this method, short-lived radical species produced in the solution which is contacted with gas corona discharge may play a role to increase chemical potential of inorganic solute. As a result, the growth rates of (100) and (101) faces of KDP crystal was increased considerably by generating the corona discharge. The both growth rates with and without corona discharge were well converged by one function based on chemical potential supersaturation. From this result, it is found that the solution in contact with gas corona discharge has a larger capacity of chemical potential than that without the discharge. It was considered that negative charge current in the solution and the short-lived species induced by the corona discharge, OH radical, play a roll of third component to cause the change of the chemical potential of KDP solute. One important aspect in this process is that the discharge-induced species do not remain after the crystallization process. Thus, the proposed method can be a new clean process for inorganic crystallization.

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