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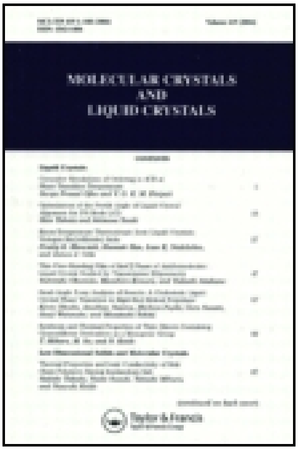

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Mechanism of Surface Crystal Formation on Naf Mother Crystal for Nano-Technology

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MECHANISM OF SURFACE CRYSTAL FORMATION ON NaF MOTHER CRYSTAL FOR NANO-TECHNOLOGY

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An investigation of mechanism that the surface crystals forming on the mother crystal of NaF in the course of the solution crystallization was attempted by using the additive molecules and excess species of reactants (NaOH and NH_4F*) in NaF crystallization. Based on the mechanism, it was supposed that the surface crystal formation was dictated by the interfacial supersaturation on the crystal, which was determined the bulk diffusion and surface integration of the molecular growth process. As the surface integration was inhibited or the bulk diffusion was facilitated, the interfacial supersaturation was improved, the surface crystal formation. Thereby, the population of the surface crystal was found to increase as increasing the reactant concentration and agitation speed, which promoted the bulk diffusion. Similarly, as surface integration was retarded by the ionic additives of NaOH,* NH_4F *and KCl, the surface crystal formation was facilitated due to the interfacial supersaturation increased. However, it was found that the surface crystal formation was suppressed by the* NH_4OH *was added in the crystallization because of relaxation effect of* NH_4OH *on compact adsorption of NaOH on the crystals. Those experimental results of additives and excess species effects were consistent with the mechanism of the surface crystal formation.*

Keywords: crystallization; ionic additives; NaF crystal; surface crystal formation

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1. INTRODUCTION

In addition to twinning and dislocation, the surface crystal formation on the mother crystal frequently frustrates the production of crystal required for study of crystal structure and design of electronic devices. Although it is a great concern in crystalline material processing, controlling the surface crystal formation has hardly been achieved, yet.

Liu *et al.* [1] have observed the small crystals growing on and with the mother crystal during the crystallization of barium sulfate, attributing the surface crystal formation on the mother crystal via surface nucleation at a low supersaturation. The surface crystal formation on the mother crystal has also been reported by Denk and Botsaris [2] in sodium chlorate crystallization, where the surface nucleation is driven by the supersaturation gradient related to the mother crystal. The crystal growth requires the concentration gradient to drive the solute molecules from the bulk to the crystal lattice. As a result, the interfacial supersaturation on the crystal surface is developed, leading to the surface nucleation as well as the crystal growth at the same time. Thereby, the surface crystal formation is promoted as increasing the driving force of the supersaturation gradient. Tai *et al.* [3,4] have investigated operating factors influencing on the surface nucleation. Especially, in the agitated suspension, the surface nucleation is promoted by the turbulent shear and crystal collision because they stimulate the formation of crystal embryos on the mother crystal. Kim and Kim [5] have suggested a mechanism to depict the surface crystal formation on the mother crystal and compared with experimental results.

In the production of crystal, the additive is sometimes adopted to control the crystal morphology via modification of the crystal growth process on molecular level. As the additive molecules are adsorbed on the crystal surface, the supersaturation gradient around the crystal is changed to reduce the crystal growth. In addition, the crystal shape varies as the additive molecules are preferentially adsorbed in certain crystal faces. Thus, the morphological change are reported by Frondel [6], Nielsen [7] and Jung *et al.* [8] in the crystallization of sodium chloride, adipic acid and calcium carbonate, respectively. From above studies it could be indicated that the modification of crystal growth and morphology by the additives reflects the change of the interfacial supersaturation influencing on the surface nucleation.

Thereby, in the present study, the investigation of the mechanism of the surface crystal formation is attempted using the crystallization conditions, which might modify elementary steps of the mechanism, the such as reactant concentration, agitation speed, ionic additives.

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2. EXPERIMENT

NaF crystallization in the single-jet semi-batch reactor was driven by the reaction of NH_4F (ACS grade, Fluka, Swiss) and NaOH (ACS grade, Fluka, Swiss). The aqueous reactants of the NH_4F and NaOH was prepared with highly purified water and their concentrations were measured with conductivity meter. To remove solid impurities in the reactant solution they were filtered with microfilter having 0.1 μm pore diameter (MFS Cellulose Nitrate, Whatman, Japan) prior to storage in feed tank.

Initially, as shown in Figure 1, the reactor was half-filled with the one reactant solution and the other reactant solution was fed into the reactor by Master flex pump. The flow rate of feeding solution was monitored by floating flow meter and the fluctuation in the feed flow rate was eliminated by running the feed pump at high speed and using bypass valve to adjust the feed flow rate. The feeding of the reactant solution was stopped after the solution in the reactor reached the final working volume of the reactor. The feed flow rate was fixed at 0.15 ml/s to suppress the simultaneous primary

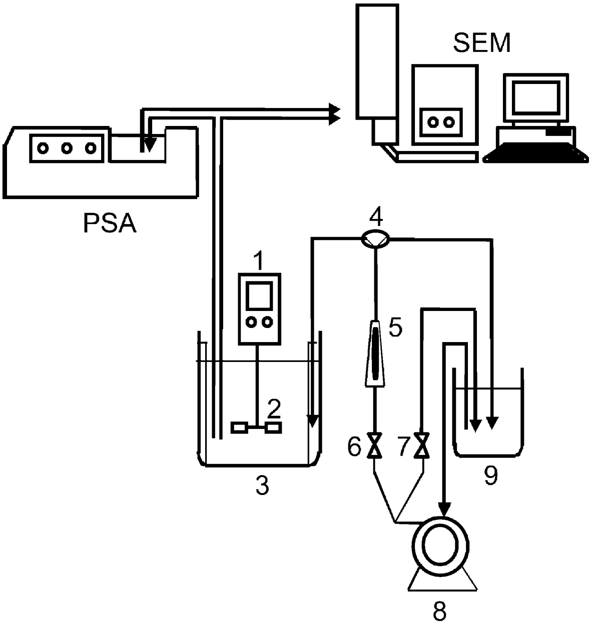

FIGURE 1 Schematic diagram of experimental apparatus. 1. agitator, 2. impeller, 3. rushton reactor, 4. 3-way valve, 5. flow meter, 6. control valve, 7. by-pass valve, 8. pump, 9. feed reservoir.

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nucleation in the bulk solution. The reactant concentrations of NH_4F and NaOH were varied on the base of the stoichiometric reaction condition at the end of the feeding. Excess conditions of NaOH and NH_4F were provided by applying higher reactant concentration of one species than the other, and allowing to playing a role of additive on the crystallization. Other ionic additives, KCl (ACS grade, Fluka, Swiss) and NH_4OH (ACS grade, Fluka, Swiss) were applied to examine the mechanism of surface crystal formation on mother crystal.

The standard Rushton-type reactor was used for experiment. The reactor was made of the lucid acrylic plastic having a working volume of 0.8 liter. To agitate the solution the six paddle turbine was placed at one third of the working height of the reactor in center. The agitation speed was varied from 500 to 1800 rpm (model BDC 1850, Cafroma, Canada). The turbine was made of the stainless steel and was finely polished, washed with HCl and then rinsed with distilled water to minimize the effect of heterogeneous surface on the NaF crystallization. To facilitate the power dissipation in the agitated solution the four baffles were placed on the reactor wall with 90° angles between each other.

At the end of the crystallization a sample of product suspension in the reactor was taken to analyze the number of surface crystals and morphology of NaF. The sample suspension was quickly filtered with vacuum and then the crystals were re-dispersed in pure methanol. To measure the crystal size distribution a particle size analyzer (Mastersizer/E, Malvern, UK) was used. To investigate the influence of the crystallization conditions on the surface crystal formation a scanning electron microscope (Leica, Stereoscan 440, Germany) was employed. The crystal system and lattice of NaF were studied with XRD (M18XHF, Mac Science, Japan).

3. RESULTS AND DISCUSSION

By injecting a reactant into the reactor, NaF crystallization was initiated after the supersaturation of NaF reached at a level to induce a spontaneous primary nucleation in the bulk phase. Then, the clear solution was turned into turbid one due to the generation of huge numbers of tiny crystals, resulting in the rapid drop of the supersaturation. After this primary induction, the supersaturation remained at a low level, which was below for the primary nucleation, as any increase in the supersaturation due to the reaction is consumed for the growth of the crystals generated during the primary induction [9]. Accordingly, the crystallization became then predominantly dictated by secondary nucleation of the mother crystals and molecular crystal growth, as supported by Kim and Kim [5]. In the present study, a low feed flow rate (0.15 ml/s) was applied in an attempt to guarantee such a low supersaturation level in the crystallization of NaF. In addition, as comparing with the equilibrium concentration of NaF (1.0 mol/l in water), the reactant concentration ranged from 1.75–3.75 mol/l allowed to support that the supersaturation level after the initial primary induction was low enough to suppress a further primary nucleation during the crystallization.

As shown in Figure 2, NaF crystals produced by the crystallization appeared as small crystals formed on the mother crystal, depending on the reactant concentration, agitation speed, additives of NaOH, NH_4F, KCl and NH_4OH. According to Kim and Kim [5], the small crystals on the mother crystal were suggested as surface crystals formed by the secondary nucleation, which was predominantly dictated by the interfacial supersaturation on the mother crystal [2,4]. In the present study, it was assumed that the interfacial supersaturation depended on crystallization conditions of reactant concentration and agitation speed, resulting in varying the surface crystal formation, as depicted in Figure 3. In general, the crystal growth is achieved via the transport of solute molecules from the bulk to the crystal surface, which is regarded as bulk diffusion, and the following lattice integration of the solute molecules on the crystal, which is regarded as surface integration [4]. As a result, the interfacial supersaturation on the crystal, which driving the surface integration, is built up. If enhancing the bulk diffusion it causes the increase of interfacial supersaturation and, if facilitating the surface integration it results in the reduction of interfacial supersaturation. Thereby, the higher population of the surface crystals on the mother crystals was found at the higher reactant concentration because the higher reactant concentration generated the higher bulk supersaturation inducing the higher interfacial supersaturation. Also, since the turbulent fluid induced by the agitation reduced the boundary layer resistance for the mass transfer, resulting in the promotion of the bulk diffusion, the increase of the interfacial supersaturation arose from the increase of the agitation speed. In addition, the agitation stimulated the surface crystal formation by the contact energy between the turbulently moving crystals in the suspension [3].

The mechanism of the surface crystal formation on the mother crystal was examined by using ionic additives of NaOH and NH_4F (excessive species of reactants), which might be involved in the crystal growth process during the crystallization. As shown in Figures 4(a) and (b), the population of the surface crystals increased as increasing the additive concentrations of excess species, NaOH and NH_4F. Here, the population of surface crystal was defined the numbers of the surface crystals formed on a single mother crystal. Via the adsorption of additives of NaOH and NH_4F on the mother crystal, the surface integration process of the crystal growth was retarded and the interfacial supersaturation was enhanced. Thereby, as increasing the additive concentration of excess species, the population of the surface

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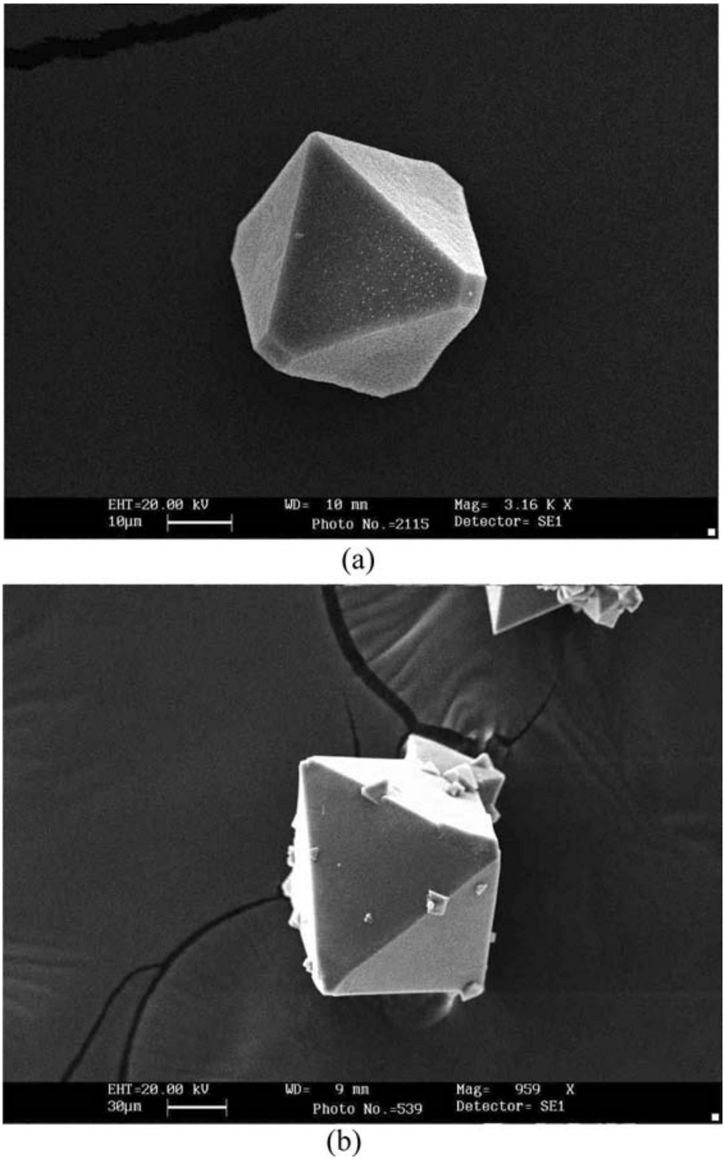

FIGURE 2 Typical morphologies of NaF crystals produced under various crystallization conditions. (a) 1.75 mol/l of reactant concentration and 700 rpm of agitation, (b) 3.75 mol/l of reactant concentration and 1200 rpm of agitation, (c) 1.75 mol/l of reactant concentration and 1200 rpm of agitation, (d) 1.75 mol/l of reactant concentration, 700 rpm of agitation and excess NH_4F of 3.0 mol/l, (e) 1.75 mol/l of reactant concentration, 700 rpm of agitation and excess NaOH of 3.0 mol/l and (f) 1.75 mol/l of reactant concentration, 700 rpm of agitation, excess NH_4F of 1.0 mol/l and KCl of 3.0 mol/l.

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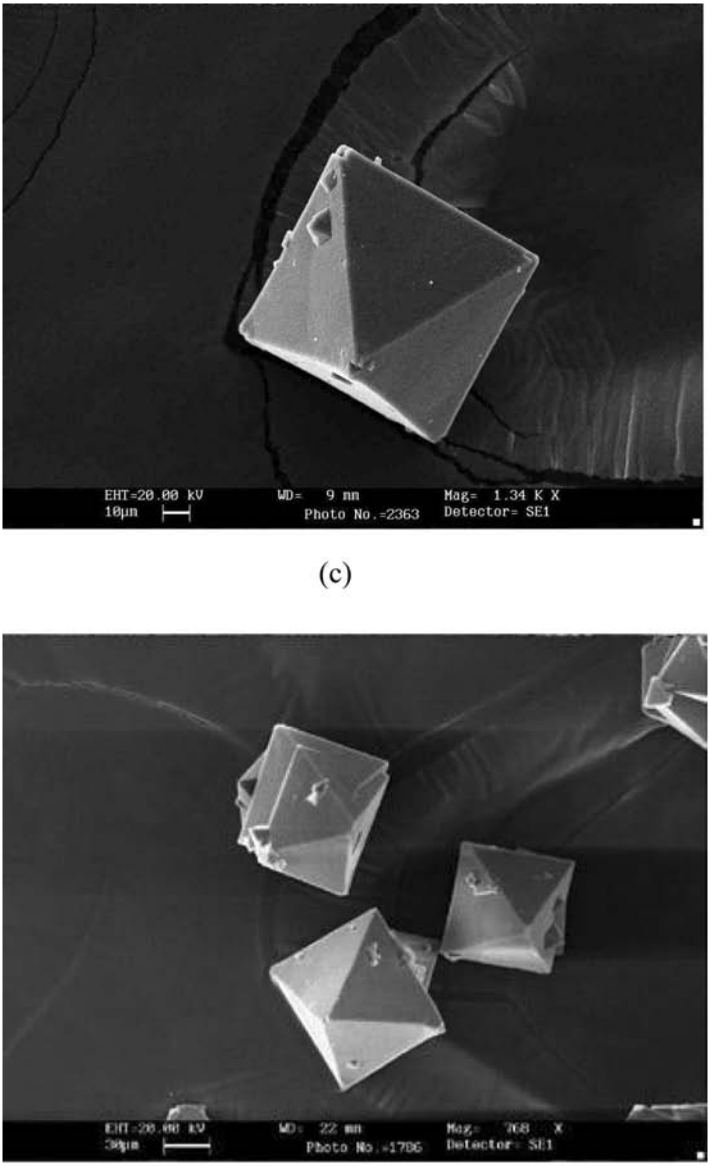

(c)

(d)

FIGURE 2 (Continued)

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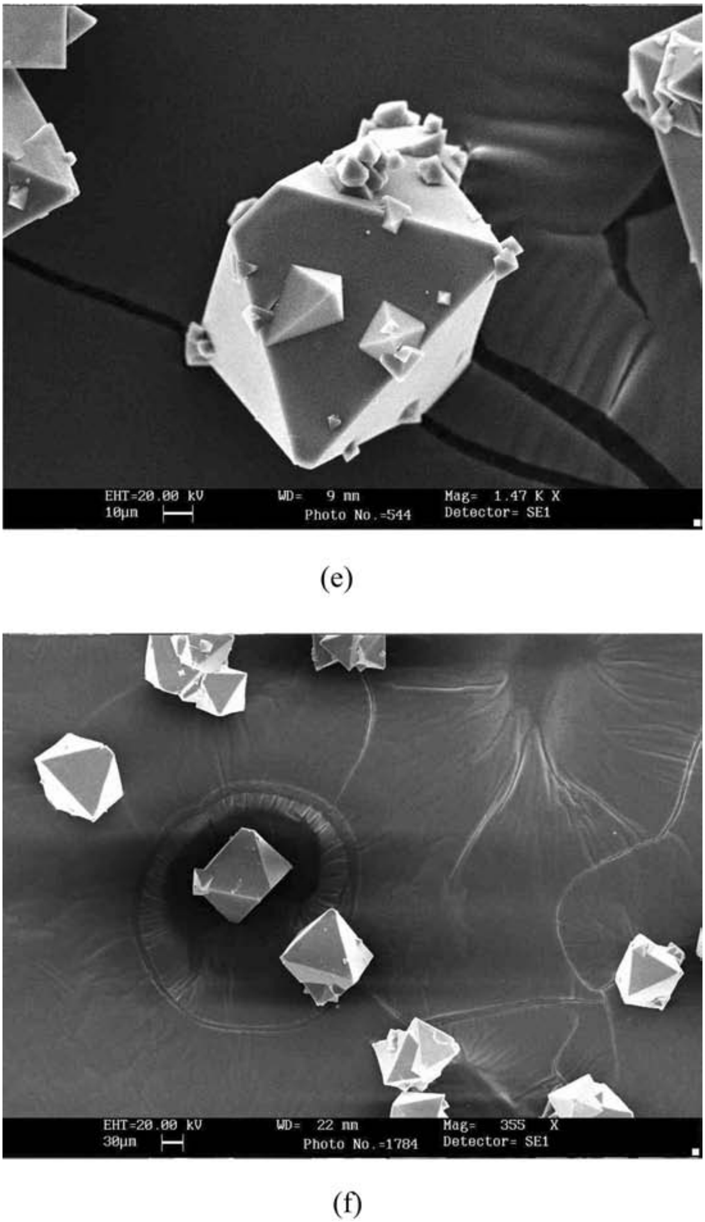

FIGURE 2 (Continued)

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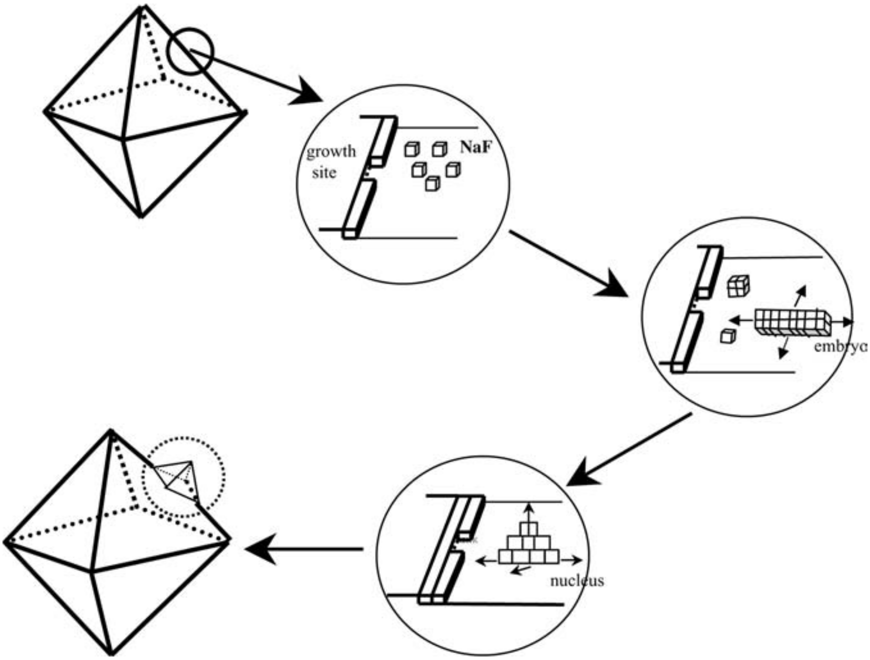

FIGURE 3 Conceptual diagram for mechanism of surface crystal formation on mother crystal of NaF.

crystal significantly increased because the surface crystal formation was promoted by the high interfacial supersaturation.

It was of interest to note that the higher population of the surface crystals was found in NaOH excess species than in NH_4F excess species because of the more inhibition effect of NaOH than NH_4F. In the aqueous solution, additives of NH_4F and NaOH were dissociated as ions, respectively, as follows, (Bailar *et al.*, 1990)

$$2NH_4F = NH_4^+ + HF_2^- + NH_3 \tag{1}$$

$$NaOH = Na^+ + OH^- \tag{2}$$

Actually, these ions additives gave an inhibition effect on the surface integration in the crystal growth process via blocking the growth site by adsorption on the crystal surface [11–13]. The effectiveness of blocking the growth site by the absorbed ions depended on the ionic sizes, as depicted in Figure 5. By virtue of the compatible radii of Na^+ and OH^- with the crystal ions (Na^+ and F^-), the excess ions would be effectively

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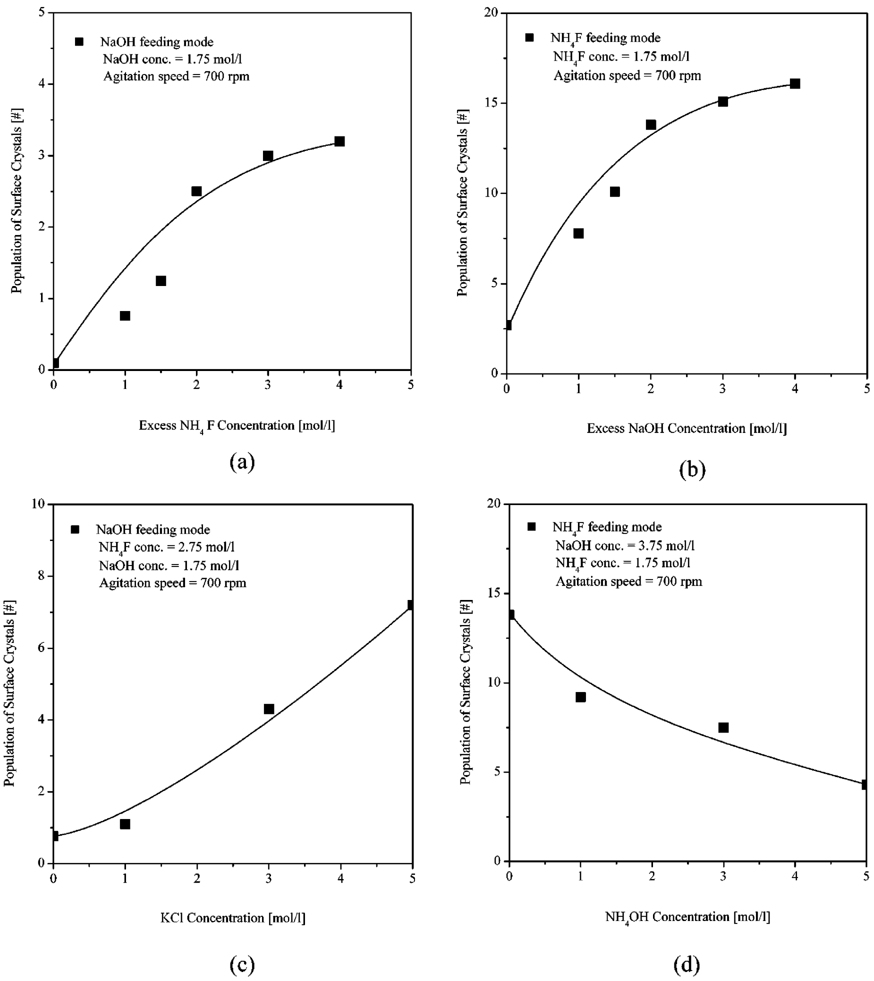

FIGURE 4 Effect of excess species and ionic additives on surface crystal formation. (a) excess NH_4F at NaOH feeding mode, (b) excess NaOH at NH_4F feeding mode, (c) KCl additive in excess NH_4F at NaOH feeding mode, and (d) NH_4OH additive in excess NaOH at NH_4F feeding mode.

adsorbed on the crystal surface, leading to the strong inhibition of the surface integration [8]. However, NH_4^+ and HF_2^- ions dissociated from the NH_4F additive were large in comparison with the crystal ions and thereby were hardly so effective to inhibit the surface integration as Na^+ and OH^- ions. Accordingly, the surface crystal formation was more promoted by the additive of NaOH than by NH_4F (Figures 4(a) and (b)). The size of each

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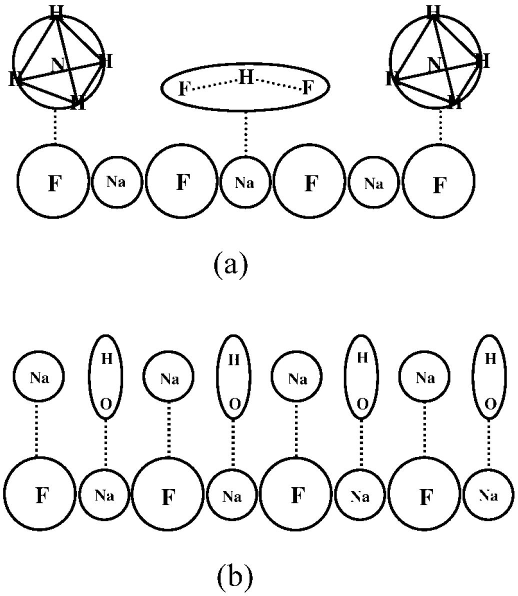

FIGURE 5 Conceptual diagram for adsorption of ionic additives on NaF crystals: (a) adsorption of ionic species of excess NH_4F; (b) adsorption of ionic species of excess NaOH.

ion dissociated from the excess species in the solution was summarized in Table 1 [14].

The effect of excess species of NaOH and NH_4F on the surface crystal formation was confirmed by ionic additives of KCl and NH_4OH applied to the crystallization, as shown in Figures 4(c) and (d). It appeared that when KCl was added to the crystallization under the excess NH_4F of 1.0 mol/l, an effective inhibition of the surface integration was achieved by the compact adsorption of additive ions on the crystal surface due to small size of ionic radii. Therefore, the population of the surface crystal was significantly promoted as increasing the KCl concentration (Fig. 4(c)). In contrast, when NH_4OH was added to the crystallization under the excess NaOH of 2.0 mol/l additive, the effective inhibition of the surface integration appeared relaxed by the additive of NH_4OH, which is larger in size than

TABLE 1 Radii of ionic Species (Unit: Å)

Na^+	F^-	NH_4^+	H_2F^-	OH^-	K^+	Cl^-
0.98	1.33	1.43	2.55	1.18	1.33	1.81

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excess species. As a result, it was found that the population of the surface crystals on the mother crystal was reduced as increasing the NH_4OH concentration (Fig. 4(d)). From above results of additive effect it could be inferred that the additive molecules were involved in the solute molecular transport and lattice integration of the crystal growth process, modifying the surface crystal formation on the mother crystal, as proposed in the mechanism.

4. CONCLUSION

In NaF crystallization the surface crystal formation on the mother crystal was predominantly dictated by the interfacial supersaturation on the mother crystal determined by bulk diffusion and surface integration of the crystal growth process, which depended on reactant concentration, agitation speed, ionic size of additives and their concentration. As the interfacial supersaturation increased, the surface crystal formation was promoted and the higher population of the surface crystals was found. As the interfacial supersaturation increased by the promotion of the bulk diffusion, the increase of reactant concentration and agitation speed facilitated the surface crystal formation. Also, as the inhibition of the surface integration resulted in the increasing the interfacial supersaturation, the additives of NaOH, NH_4F and KCl enhanced the surface crystal formation. Meanwhile, the inhibition effect of NaOH additive was reduced by addition of NH_4OH because of relaxation effect of NH_4OH on compact adsorption of NaOH on the crystals. Those experimental results of additives and excess species effects would support the mechanism of the surface crystal formation.

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