Supercrystallization of NaCl from Solution Irradiated by Soft X-Rays

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It was found that irradiation of a water solution of NaCl with the diffractometer DRON3-M (Russian device) had a large influence on two-step processes of crystallization. The irradiation in the first stage of crystallization of the solution produces metastable radicals of water and excited seeds, which stimulate a very fast crystallization after switching off irradiation. After the crystals reach a sufficient size, the crystal growth can be explained by creation of vacancy-interstitial pairs in the growing crystal due to irradiation. The increase of linear dimensions of the growing irradiated crystals is proportional to the square root $\sqrt{t}$ of crystallization time because most important place in crystallization takes the ions diffusion by irradiated vacancies.

1. Introduction

Crystallization from solution can be considered to be a two-step process [1]. The first step is a phase separation and is called nucleation. The second step is the growth of nuclei to crystals. The requirement for crystallization is supersaturation of solutions, which are not at equilibrium. Every system tends to equilibrium and the transition of a supersaturated solution to the equilibrium state proceeds by stochastic processes of nucleation and crystallization. The relation between the nucleation and crystal growth defines the crystal size distribution. The purity of crystals is strongly dependent on the growth rate. Fast growth may lead to liquid inclusions. For these reasons, the control of crystallization rate is necessary. The industrial crystallization processes require constant rate of crystallization, which can be achieved by measuring supersaturation and by temperature control. This method does not make it possible to achieve an exactly constant rate of crystal growth, because supersaturation level depends on crystal growth, cooling profiles and cooling rate [1]. Stochastic processes depend not only on temperature and diffusion processes but also on generation of charged radicals and superdiffusion of impurities by irradiation [2–5]. In this paper, we will consider influence of irradiated vacancies in NaCl crystals on its crystallization from water solution. Multiple ionization of Cl^- and Na^+ ions by X-rays is the reason of vacancy formation [6] by a Varley-type mechanism based on the Auger effect. At a time of about 10^{-13} s, which is longer than the period of lattice oscillations, the generated perturbed electrostatic potential can transport Cl^- ion into an interstitial state, whence it can diffuse through the

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crystal. The anion vacancy trapping an electron forms an F center [6, 7] (an F center is a vacancy in the halide sublattice with a trapped electron) taking part in crystal coloration [6] and crystallization. Irradiation can also create H centers [7] (an H center is an interstitial halide ion with a trapped hole). It is known that heavy irradiation by fast electrons causes formation of large vacancy voids, chlorine bubbles and sodium colloids. F centers facilitate diffusion of Na^+ and Ca^+ ions by vacancies, and increase crystallization rate.

Crystallization rate can also be increased in a water solution previously saturated with free radicals [8] by X-ray irradiation.

2. Production of free radicals in NaCl water solution by X-rays

Action of ionizing radiation upon water produces free radicals and electrons [8]. X-rays can change ion charge in solution by the Auger effect [8] and cause various reactions. We consider only the ones that are most important for crystallization. The photoelectric effect can initiate dissociation reactions of water molecules

$$H_2O \rightarrow H + OH, \quad H_2O \rightarrow H^+ + OH^-, \tag{1}$$
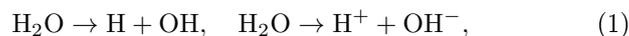
production of hydrated electrons e_a and unstable radicals H_2O^+:

$$H_2O + h\nu \rightarrow H_2O^+ + e_a + h\nu_f, \quad \nu_f < \nu. \tag{2}$$
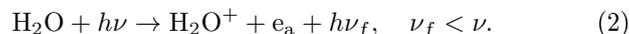
H_2O^+ decomposes within 10^{-13} s and produces weakly bound complex H_3O^+ or metastable radicals [8]:

$$H_2O^+ + H_2O \rightarrow H_3O^+ + OH. \tag{3}$$

The metastable radicals H_3O^+ consist of a neutral molecule H_2O and a proton H^+ interacting by covalent bonds, electrostatic forces and the Van der Waals bonds [8], which have a longer range proportional to $1/r^7$. Those metastable radicals $\cdot H_3O^+$ collect Na^+ and Cl^- to metastable nucleus by the Van der Waals and electrical forces. These processes correspond to the following chemical reaction [8]:

$$H_3O^+ + OH^- \rightarrow 2H_2O, \qquad\qquad (4)$$

photoeffects

$$Cl^- \rightarrow Cl + e_a, \qquad\qquad (5)$$

$$Na^+ \rightarrow Na^{2+} + e_a \qquad\qquad (6)$$

and the Auger effects [9]:

$$Cl^- \rightarrow Cl^+ + 2e_a, \qquad\qquad (7)$$

$$Na^+ \rightarrow Na^{+3} + 2e_a. \qquad\qquad (8)$$
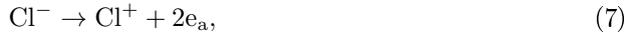
X-rays produce not only Na^+, Cl^- but also ions Na^{2+}, Na^{3+} and Cl^+, charged radicals $H_2O_2^{2-}$, H_3O^+, F centers, vacancies in Na^+ and Cl^- sublattices, which affect ions diffusion and surface tension of the crystals taking part in radiation-enhanced crystallization. A very important role can be played by negative F centers, which enhance diffusion of positive ions Na^+, Na^{2+}, Na^{3+} (6), (8) and Cl^+ (7) in the growing crystal. The metastable radicals can produce metastable nucleus, which increase crystallization rate in an irradiated solution after switching of X-rays. Crystallization is limited by conservation of charge and by the fact that protons and chlorine ions cannot interact directly. In irradiated solutions, there are excited seeds with complicated chemical and structural configurations, which participate in the fast crystallization. The irradiated solution, like the one in the simple case discussed in [10], must eventually reach the state with the lowest accessible energy. Crystals of especially small sizes are unstable [11] and this instability is increased by irradiation with X-rays. After fast reverse reactions (5), producing negative chlorine ions Cl^- and reaching critical size [11], when negative volume energy excites the positive surface energy, the crystals begin to grow with a very large rate. Metastable radicals, irradiated vacancies and ions with large charges and strongest attractive forces can significantly increase the rate of crystallization processes [1].

3. Crystallization experiments with irradiated solutions

Crystallization of small (10–1000 μm) NaCl crystals from a supersaturated non-irradiated and previously irradiated (W anode voltage 30 kV, current 20 mA) solution in a drying drop placed on a glass was investigated.

Sizes of small crystals were measured by a Russian optical microscope Lumam-IZ and an internet camera for photographing the crystals and measuring distances with a highest resolution of 0.01 mm. An original C++ program, which processes measurement data, can present graphically the kinetics of crystal growth. For crystals with size 1 mm or greater, we used the in-camera lens Helios-44-2 with a simple exact line and the same C++ program.

We applied soft X-rays emitted by a Russian diffractometer DRON-3M with a W anode ($U_a = 30$ kV, $I_a = 20$ mA, irradiation time 1 h) for irradiation of a supersaturated NaCl solution in water at 22 °C. The incident X-ray photons cause the Auger effect in Na^+

and Cl^+, as well as dissociation of water (1) and production of metastable radicals of water molecules. In addition to solvent electrons, the charged metastable radicals $H_2O_2^{2-}$, H_3O^+ are produced by chemical reactions. They can produce excited nucleation centers for ions taking part in fast crystal growth. Those metastable radicals participate in slow decomposition and in fast crystallization. The radial crystal growth rate is proportional to diffusion flow of the dissolved material towards the crystal surface. The diffusion in an excited medium irradiated by X-rays can be significantly enhanced. This phenomenon has been named superdiffusion [5].
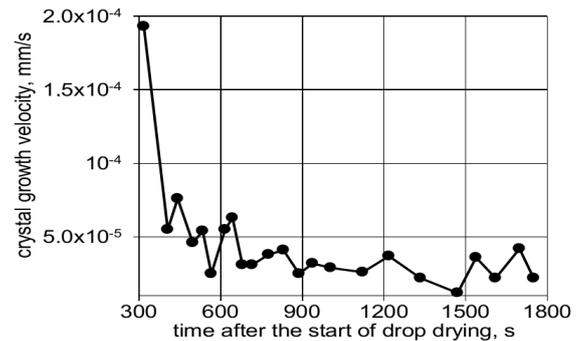
Fig. 1. NaCl growth rate from water solution dependence on time after the start of drop drying at 22 °C. Growing of crystal in drop was measured from initial size 61 μm to 109 μm.
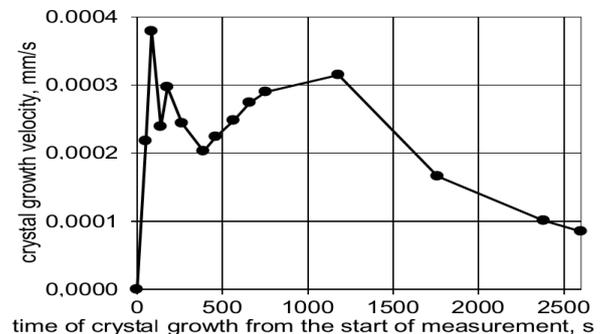
Fig. 2. Time dependence of NaCl crystal growth rate from water solution at 22 °C irradiated with X-rays (W anode, voltage 30 kV, tube current 20 mA). Growing of crystal in drop was measured from 137 μm till 279 μm.

Now we can compare the crystallization processes in the evaporating drops from a simple solution and an irradiated solution. The measured crystallization rates for crystal of initial size 61 μm in drop from a supersaturated NaCl water solution at 22 °C are presented in Fig. 1. The rates of crystal growth with the initial sizes about 137 μm are presented in Fig. 2 for drop from irradiated solution, where crystallization is at first fast growing and then slows down until 500 s. The crystallization rate

in irradiated solution in Fig. 2 is at first time very fast growing, because the metastable charged radicals H_2O^+, H_3O^+ and $H_2O_2^{2-}$ initially increase the critical nucleus formation and later crystals growing rate and destination of the close packing of ions in the lattice are coursed by reverse chemical reactions for (2), (3), and (4). From 500 s to 1500 s, the linear crystallization rate in the drop of irradiated solution of NaCl presented in Fig. 2 is about 10 times greater than in Fig. 1 for non-irradiated solution. This phenomenon, which is caused by superdiffusion and assisted by metastable charged radicals, vacancies and metastable seeds, will be named "supercrystallization".
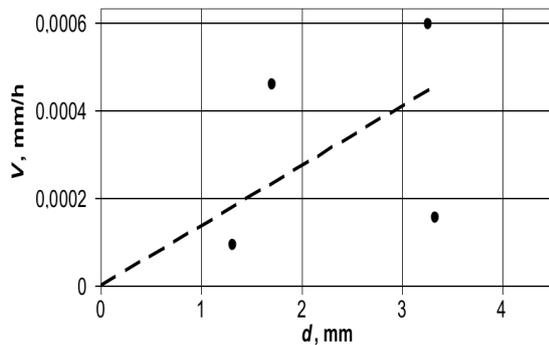
Fig. 3. Dependence of the rate of NaCl crystal growth from water solution at 22 °C on initial crystal size.
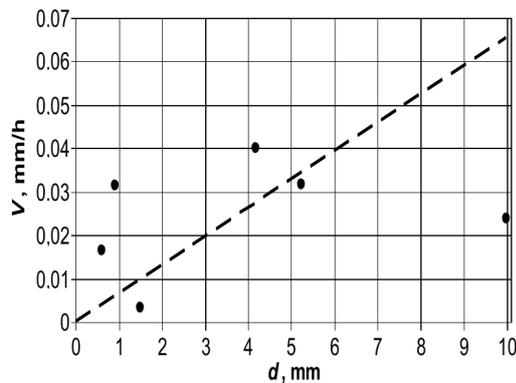
Fig. 4. Dependence of the rate of NaCl crystal growth from water solution at 22 °C on initial crystal size under 3 h time irradiation with X-rays (W anode, 30 kV, 20 mA).

We provided the measurements of dependence of the crystallization rates on the initial sizes of crystals hanging on the hairs in the cylindrical test-tube with 2 cm diameter and 4 cm depth. The results without irradiation and with irradiation are presented in Fig. 3 and Fig. 4. The reason why the linear approximation has been chosen in Fig. 3 is that we cannot achieve a higher accuracy of repeated measurements of growing crystals sizes without changing of crystallization conditions.

The significant increase of crystallization rate was achieved using X-ray irradiation. It was achieved in a

certain range of initial size of the crystals. X-ray irradiation prolonged crystallization of those crystals in a supersaturated solution at 20 °C. The comparison of growth rates presented in Fig. 3 and Fig. 4 for crystallization of non-irradiated and irradiated crystals indicates that irradiation causes an increase of linear crystallization rate by a factor 100 and depends on initial sizes on complicated way. The phenomenon of fast growing presented in Fig. 4 is related to superdiffusion of ions from the surface [5] into the irradiated bulk of crystal.

In this case, vacancies, point defects, and induced chemical reactions created by the radiative Auger effect changes Coulomb interactions of electric dipoles or ions with neighboring atoms or ions [10]. The crystal growth rate depends not only on the presence of metastable radicals but also on supersaturation of solution due to an increase of H^+ concentration [1].

Generation of vacancies in sodium chloride crystals has been achieved by double ionization of sodium cations due to the Auger effect. The resulting positive ions Na^{3+} displace one of nearest-neighbor chlorine ions by the Coulomb interaction, producing negative, neutral and positive Cl vacancies [12] in sufficiently large quantities for enhancing ion diffusion in the crystal. Vacancy charge can change spontaneously during energy transitions [11], depending on the charge magnitude. The energy released during transitions between Cl vacancies [12] of different charge states varies from 3 eV to 5 eV and can generate lattice distortions and relaxations important for diffusion processes. In addition, crystallization depends on concentration of irradiated vacancies, which produce voids in a crystal [7] (concentration $10^{13}-10^{14}$ cm^{-3}) with a radius of about 20–30 nm. They are caused by reactions of divacancy agglomerates filled with chlorine and sodium colloids.
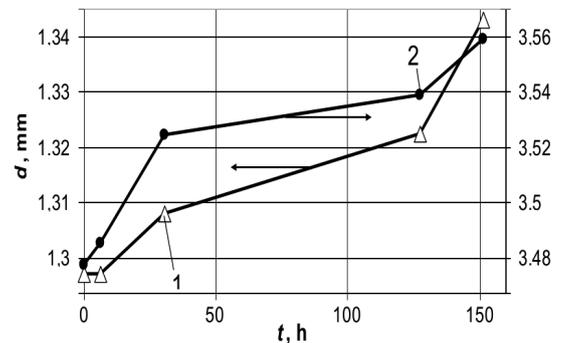
Fig. 5. Time dependence of NaCl crystal growth starting from different initial sizes (1.297 mm (curve 1) and 3.477 mm (curve 2)) in absence of X-ray irradiation.

The dependence of sizes of not irradiated and irradiated crystals was presented in Fig. 5 and Fig. 6 on the initial size and on time t and square root of crystallization time $\sqrt{t}$. It indicates the different character of not irradiated and irradiated crystals growth. Crystallizations rates are characterized by different diffusions flows.
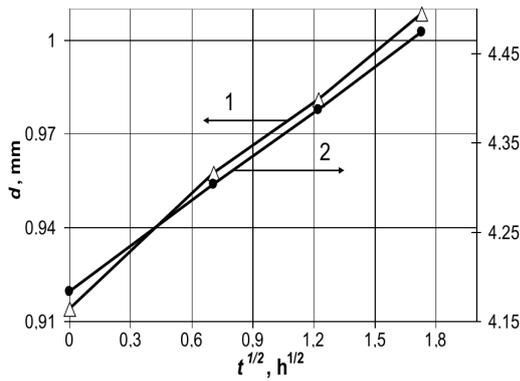
Fig. 6. Dependence of NaCl crystal growth on $\sqrt{t}$ in the case of two initial sizes (0.914 mm (line 1) and 4.183 mm (line 2)). X-ray irradiation regime is 30 kV and 20 mA.

Crystals growing on the hairs in the cylindrical test-tube with 2 cm diameter and 4 cm depth was coursed by evaporation. The not irradiated crystals growing depends on relative supersaturation of solution, size of crystal and solid–liquid interfacial energy in complicated way.

The sizes of not irradiated crystals in Fig. 5 can be approximately presented like some lines depending on crystallization time interval. The growth of crystal in this case depends on diffusion rate and flow of Na^+ and Cl^- ions into the surface of crystal and their incorporation in the lattice. If relative supersaturation and evaporation stay constant, the crystallization rate is constant also. In this case, flow of ions into the crystal and its size must be approximately proportional to the time of crystallization. We have the essentially different situation for crystallization enhanced by irradiation of X-rays when we have ions diffusion not only in interface region but also in the bulk of growing crystal.

The size of fast growing crystals presented in Fig. 6 in this case is proportional to square root of crystallization time [7, 4] and weakly depends on other factors. The number of introduced ions [7, 4] in the bulk of growing crystal

$$N(t) = 0.5492 N_s x_0, \quad x_0 = 1.616\sqrt{Dt} \qquad (9)$$

is proportional to ions concentration N_s on the surface of crystal and to the square root of the crystallization time and the ions diffusion coefficient D. Here, x_0 is the maximum penetration depth of ions into the crystal, which is proportional to the square root $\sqrt{t}$ of the crystallization time t. The diffusion coefficients and crystallization rates can be increased many times [5] by generation of metastable vacancies in growing crystals using X-ray radiation.

The theoretical expression of crystallization rate [13] can be obtained using the spherical nucleus approximation of the Gibbs free energy

$$\Delta G = \frac{4}{3}\pi R^2 \rho_s \Delta\mu + 4\pi R^2 \gamma, \qquad (10)$$

where $\Delta\mu$ is the difference of chemical potential between the liquid and the solid ($\Delta\mu < 0$) and γ is the liquid--solid free energy density. R is the nucleus radius. These constants can be obtained from the critical size of nuclei (seeds), corresponding to the beginning of crystallization of the liquid ($\Delta G < 0$), and probabilities to form crystals of different sizes.

The results presented in Fig. 6 are particularly interesting. Crystallization rates are governed by ions diffusion from the solution into the bulk of excited crystals [4]. In this case, an increase of the crystal size in some direction due to crystallization must be proportional to the amount of ions introduced across the orthogonal crystallization surface. This amount is proportional [4] to $\sqrt{Dt}$, where the t is the crystallization time and D is the diffusion coefficient. That is why the crystals sizes dependence on $\sqrt{t}$ has been plotted in Fig. 6. Linearity of that dependence confirms that crystal growth is caused by vacancy diffusion into the crystal. During crystallization of NaCl, the diffusion coefficients are significantly increased by irradiated chlorine vacancies. The metastable radicals H_3O^+ are also important for nucleation like active molecular aggregates whose interaction with negative ions Cl^- can increase ions diffusion flows and crystallization rate. From the data presented in Fig. 4, Fig. 6 for the case of irradiated crystallization and Fig. 3, Fig. 5 for the case of non-irradiated crystallization, we conclude that irradiation can cause an increase of crystallization rates.

4. Conclusions

X-ray irradiation causes an increase of the small crystals growth rate of NaCl crystals in a drop of solution from 2 till 10 times (Fig. 1, Fig. 2). Comparing crystallization in not irradiated (Fig. 5) and in irradiated (Fig. 6) solutions we obtained increasing linear rates of crystallization for lesser crystals (1.297 mm and 0.914 mm consequently, curve 1 and line 1) 200 times and for bigger (3.477 mm and 4.183 consequently, curve 2 and line 2) about 700 times. For non-irradiated case (Fig. 5) crystallizations rates for lesser and bigger crystals practically coincide and approximately equal 0.00015 mm/h. For crystallization with irradiation (Fig. 6) we obtained linear crystallization rate 0.034 mm/h for lesser crystal and for bigger 0.097 mm/h. From obtained results, we can confirm that dividing crystallization rates and increasing of sizes by crystallization we obtain the same 2.9 relation. The increase of crystallization rate in bigger crystal is based on irradiation of more vacancies taking part in crystal growing. The linear dependence of crystals size (Fig. 6) on $\sqrt{t}$ [4, 14] indicates that in the rate of crystallization processes most important place take the ions diffusion by irradiated vacancies in the crystal bulk.

Due to ions diffusion by vacancies created by X-ray radiation, the ions deposited from the solution onto the crystal surface can diffuse into the bulk much faster. The rate of growth of the new crystals in drop a non-irradiated

solution (Fig. 2) decreases with increasing size of the crystals, whereas in an irradiated solution (Fig. 1) this decrease has been observed until the crystal size reaches ≈ 0.23 mm. Further on, their growth rate increases by irradiated vacancies density increasing in the growing crystal.

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