New Model of AgHal Microcrystals Formation and Growth during Double Jet Crystallization

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Abstract

On the basis of previously carried out experiments on a re-crystallization of bimodal AgBr dispersions in gelatin gel the new theoretical model of formation and growth of new phase particles during a mass crystallization has been developed. According to this model the process of growth AgHal microcrystals is caused by recrystallization process in the system consisting of larger growth centers and fine fresh-formed particles. Tabular crystal nuclei have the greatest enlargement rate; therefore its growth is accompanied by fast disappearance of fine particles. However if concentration of the growth centers in system is too low then the processes of interaction of fine particles among themselves gives the essential contribution to total crystallization process. As a result the decreasing of morphological uniformity of final microcrystals can take place.

Introduction

In modern photographic materials the photoprocess is controlled by an individual recording element. Silver halide grains with a complex structure are widely used as such elements. However, the creation of the assemblage of similar microparticles is a difficult technological problem, as 1 liter of a synthesized photoemulsion should contain up to 10^{16} structured microcrystals with the size of about 1 μm.

The use of a controllable double-jet crystallization (CDC) technique is considered to allow one to solve most of the problems concerning the preparation of photoemulsions[1]. Nevertheless, this method has its disadvantages. The CDC method is not suitable enough for the synthesis of emulsions with monodisperse heterophase tabular grains, which are widely applied in modern photographic materials. It is accounted for by the lack of theoretical knowledge about the kind of processes proceeding during the formation and growth of microparticles in the course of mass crystallization.

As is known, in most cases, the Berry model[2] modified later by Wey and Strong[3] is used to describe the CDC process. According to this model, a continuous neoformation of fine particles takes place during the emulsification. These fine particles are used as the material for growing larger crystals by the Ostwald ripening mechanism.

Wey and Strong put forward the main problem, which has to be solved while interpreting the resulting experimental data on mass crystallization. If a supersaturation in solution degree could be measured, experimental values of crystal growth rate could be correlated with the theoretical model to find out the mechanism of growth. Unfortunately, the level of supersaturation for mass crystallization cannot be measured more or less accurately. Besides, the growth rate of grains during emulsification is not constant. In this case the mechanism for enlarging the crystals is inevitably relatively uncertain.

In their model[3] Wey and Strong used a traditional approach to the growth of crystals in solution. As is known, this kind of growth includes, at least, two things proceeding simultaneously[4]: the transport of a dissolved substance from a supersaturated solution to a crystal surface at the expense of bulk diffusion and the inclusion of the dissolved substance into a crystal lattice (surface integration). In the opinion of Wey and Strong any of these stages can be limiting for the growth of crystals.

It should be taken into account that the process of dissolving newly formed particles (embryos) can be also a limiting stage if we strictly follow the Berry model. Also, the surface of growing crystals in most papers on this subject matter was considered to be isotropic, though the process of growth, in many respects, can be due to a specific role of corners and edges of silver halide microcrystals.

It should be also noted that the growth of AgHal microcrystals by the physical ripening (PR) technique when a bimodal mix of monodisperse grains with a large difference in the size exists in the system is absolutely analogous to the Berry model. The investigation of similar systems is facilitated by the processes of mass transfer taking place in the closed system and can be controlled better. Therefore, in our opinion, for the development of an adequate model of crystal growth during CDC, it is necessary to take into account the experimental data obtained when studying the processes of mass transfer in the course of PR.

In colloid chemistry, the theory developed in the late 1950s and the early 1960s by Lifshits and Slyozov[5] and also, independently by Wagner[6] (the LSW-theory) is used as the base theory for interpreting the experimental data on Ostwald ripening. However, the main goal of the LSW-theory is to find out the stationary size distribution during PR of a polydisperse system. Therefore, it not applicable to

bimodal systems. Nevertheless, to interpret the experimental data, most authors of papers devoted to the investigation of the process of physical ripening of silver halides, prefer to use the LSW-theory only[7-8].

Having analyzed all these papers, it can be concluded that the dissolution of smaller particles in bimodal AgHal dispersion can be a limiting stage only when small and large crystals do not greatly differ in size[8]. That is why, the mass transfer of a large crystal during its growth is traditionally represented as an interaction with an isotropic medium where the concentration of a dissolved substance is constant. This, in its turn, explains the lack of interest for studying the behavior of fine particles during physical ripening.

On the other hand, the experimental data available at present allow one to find a new approach to creating a modified theoretical model for AgHal mass crystallization. These experimental data include the results of the experiments on the preparation of tabular microcrystals by the physical ripening technique of fine emulsions. Electron microscope studies showed that in this case the growth of tabular grains is accompanied by the concentration decrease, the size of fine crystals themselves remaining practically unchangeable (see. Fig. 1)[9]. This experimental datum, on the whole, contradicts the common ideas about Ostwald ripening according to which the growth of large particles should be accompanied by continuous and simultaneous reduction of the size of all fine crystals without any exception.

Similar problems arise while interpreting the experimental data on the recrystallization of AgBr fine crystals in gelatin gel[10]. It was experimentally found out that effective mass transfer in the system takes place only at a rather high concentration of particles (a small interparticle distance). If an interparticle distance exceeds a certain critical value, the growth rate of particles in the system is sharply reduced, and even lengthy ageing does not result in the disappearance of a part of initial fine crystals.

The development of the model of mass transfer in the bimodal systems, not contradicting the available experimental data is important at the moment. Additional data can be obtained when making experiments on physical ripening in the system in which mass transfer through the solution is carried out between motionless particles. This immobility is provided for by the recrystallization process realization in a gel medium.

Theoretic model of recrystallization process in bimodal system

The theoretical model of recrystallization of a fine emulsion is necessary for correct interpretation of the results obtained. As is known, a fine AgBr emulsion obtained by a double-jet technique, usually contains microcrystals with an average size in the 40 - 80 nm range with a high degree of uniformity (C_v<20 %) and with the shape close to spherical. The physical ripening of this emulsion in the excess of bromide ions results in tabular microcrystals and a complete disappearance of initial fine crystals (see. Fig.1).
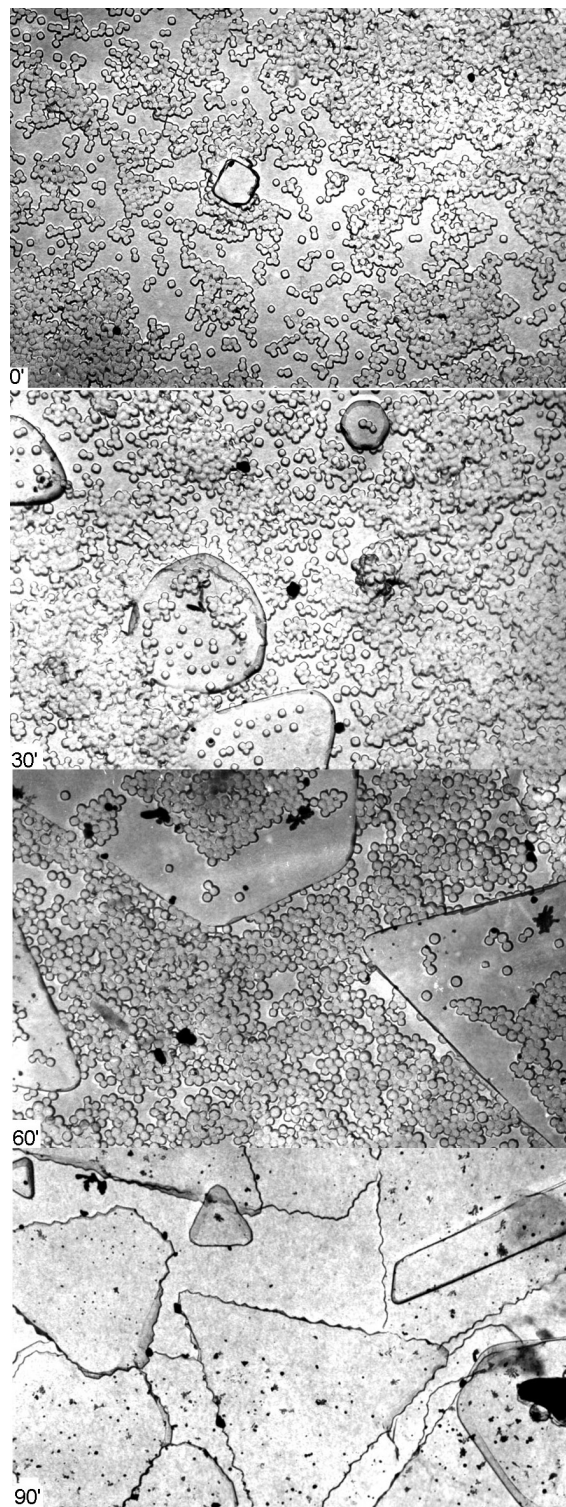
Fig. 1. *Electron microphotographs of carbon replicas of microcrystals formed during physical ripening of fine emulsion. The ripening conditions: t=60°C; pBr=1.0; gelatin concentration 30 g/l; initial fine microcrystal concentration 3.5×10^{15} l^{-1}.*
0' - initial emulsion (×6000); 30' - 30 minute physical ripening (×6000); 60' - 60 minute physical ripening (×6000); 90' - resulting emulsion (×4000).

It was experimentally shown that in the course of the synthesis of a fine emulsion, the so-called twinned crystals containing 2D defects of a crystal lattice are formed in addition to common isometric microcrystals[12]. These crystals are able of fast and effectively anisotropical growing during Ostwald ripening due to the appearance of a crystal structure defect on the surface, and to the presence of nonequilibrium edges on lateral faces of a growing crystal. The relative amount and the type of resulting twinned crystals or embryos are caused by the conditions of fine emulsion crystallization.

The mechanism for the formation of twinned crystals up to now remains a disputable question. The consideration of this question is beyond the scope of the given paper. The fact that certain growth centers i.e. microcrystals which are acceptors of the material during Ostwald ripening are present in the initial fine emulsion is of great importance.

As far as the process of recrystallization is concerned, its driving force is usually the difference in microparticle solubilities. For spherical particles the solubility depends on the particle radius according to the Gibbs-Thomson equation.

$$S_r = S_\infty \exp\left(\frac{2\sigma V_m}{rRT}\right), \qquad (1)$$

where S_r - the solubility of particle with radius r, S_∞ - the solubility of macro particle, σ - specific surface energy, V_m - molar volume.

That is why, the gradient of concentration and mass transfer from smaller particles to larger ones by means of diffusion through a solution according to Fick's first law appears if there are particles of different sizes in the system.

$$j = -D\frac{\Delta C}{\Delta x}, \qquad (2)$$

where j - the diffusion flow of dissolved substance, D - diffusion coefficient, $\Delta C/\Delta x$ - concentration gradient of dissolved substance.

In the absence of twinned crystals in a fine emulsion, recrystallization proceeds according to the classical model, i.e. larger isometric microcrystals grow and smaller ones dissolve. Thus, in a fine emulsion there are, at least, two types of potential growth centers - the embryos of tabular crystals and larger isometric crystals. On the basis of final results of physical ripening of a fine emulsion it can be assumed that due to a high initial growth rate of the embryos of tabular crystals, their solubility becomes essentially lower than that for large isometric crystals. Therefore, isometric crystals fail to get the material for their growth and are not observed after the ripening process.

Recrystallization in a gel medium gives somewhat different results. As all microcrystals are motionless, mass transfer occurs only between the neighboring particles. In this case each pair of interacting particles there can be characterized by the following interactions:

Microcrystals have different sizes. According to the Gibbs-Thomson equation the concentration of a dissolved substance near the surface of smaller particles is higher. As a result there appears the gradient of the concentration of a dissolved substance and diffusion from a smaller crystal to a larger one in terms of Fick's first law. However, it should be stressed that the gradient value is inversely proportional to the distance between interacting crystals.

The tabular crystal and a common isometric crystal are the neighbors. Lower solubility of the embryos is caused by their larger size. Besides, the appearance of a two-dimensional defect on the surface is due to a local increase in surface energy. This results in a higher rate of mass transfer for a particular local area. All other regularities of mass transfer are similar to the previous case.

Microcrystals have almost the same sizes. In this case surface concentrations of the dissolved substance are the same, therefore, there is no gradient of concentration (and mass transfer).

Under ordinary conditions, the relative concentration of both tabular crystal and large isometric crystal embryos is insignificant. Therefore, the probability of the neighborhood of these particles is extremely low. On the whole, as a rough model for the given system is a three-dimensional set whose sites are occupied by fine particles and where tabular crystal embryos or larger isometric crystals are incorporated. During recrystallization the dissolution of smaller crystals should proceed in a layer-wise manner, i.e. first, the particles nearest to the growth center, and only after their disappearance the microcrystals of the next layer.
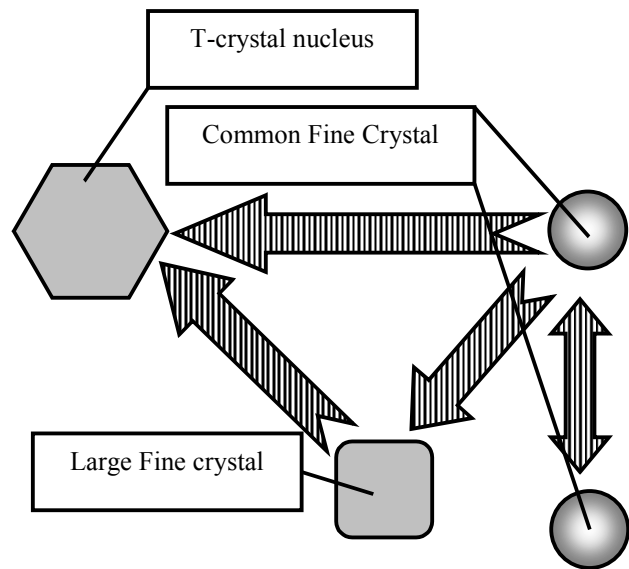
Fig.2. Mass transfer during recrystallization in the gel medium. The length of arrows characterizes the intensity of the process.

However, the neighborhood of crystals with different sizes does not always automatically result in a mass transfer start. In our opinion, a necessary condition for the dissolution of a smaller crystal to begin is the existence of a suffi-

ciently high (above the critical value) gradient of the con-centration of the dissolved substance in its neighborhood. If the gradient value is below critical, the dissolution proceeds at the rate close to zero, which cannot be registered. In its turn, both the difference in solubility and the distance be-tween the neighboring particles determine the gradient value:

$$\frac{\Delta C}{l} \geq K_{grad} ,\qquad (3)$$

where ΔC - the difference in solubility of larger and smaller particles; l - the distance between larger and smaller particles; K_{grad} - the gradient critical value of the concentration of the dissolved substance.

For this reason the mass transfer between the remote particles becomes impossible. Hence, for each growth cen-ter there is a limiting size of the area where it can create the concentration gradient value above critical (see Fig.3). It is a zone of an effective mass transfer for the given type of the growth center. During the crystal growth as a geometrical dimension increases, its solubility continues to decrease in according to the Gibbs-Thomson equation with a further expansion of the zone of effective mass transfer. However, this expansion appears to be limited because of the loga-rithmic character of solubility vs. the particle size.

Thus, results of recrystallization in a gel medium are mostly affected by an average interparticle distance. At a high concentration of microcrystals (a low interparticle dis-tance value) there is a growth of only most fast-growing particles as their zones of effective mass transfer are inter-sected. The final result of this recrystallization is the system including tabular crystals only, the size of these crystals practically coinciding with that of tabular crystals, obtained by the physical ripening technique.

On the other hand, at a low concentration of microcrys-tals slow-growing and fast-growing particles succeed to get the material (i.e. tabular crystal embryos and fine crystals with the size above the average). Also, a part of fine crystals does not participate in the recrystallization process at all. Hence, the morphologies of crystals resulting from recrys-tallization in gel at high and at low concentrations of parti-cles essentially differ.

Discussion

Our experimental data, on the whole, confirm the sug-gested theoretical model. It makes possible to specify the peculiarities of mass transfer during AgHal photoemulsion synthesis by the controllable double-jet crystallization tech-nique. It should be noted once again that according to the Berry model, the mass transfer in this case is similar to the one during physical ripening in a bimodal system. The only difference consists in a continuous generation of fine parti-cles during the CDC in the system.

T-crystal nucleus

Large crystal of fine emulsion

Common fine crystal
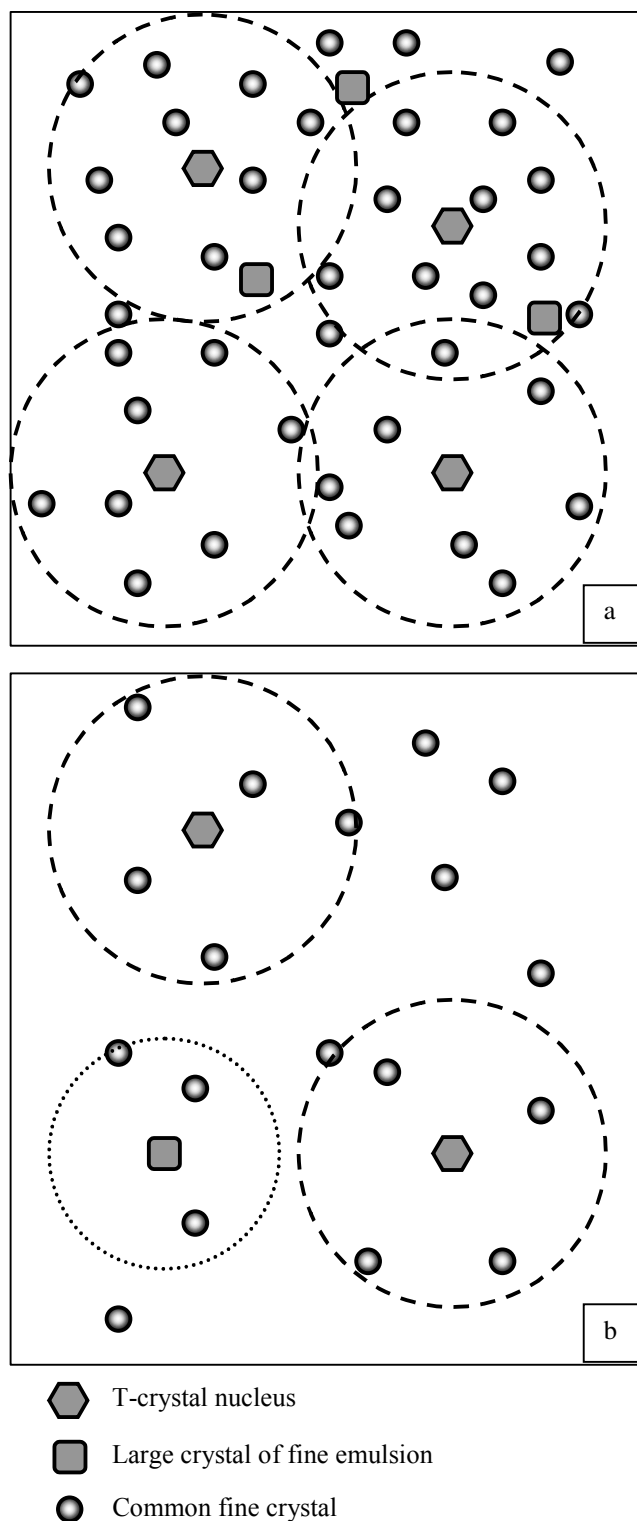
Fig.3. The interaction of silver bromide microparticles in gel me-dium under conditions of high (a) and low (b) particle concentra-tion. The dashed line corresponds to border of the zone of the ef-fective mass transfer.

It can be assumed that the size (and, consequently, solubility) of newly formed fine particles does not depend much on the conditions of crystallization. This is caused by a very high level of supersaturation of the reaction mix in the point of injecting the reagent solutions. Thus, the resulting system appears to be bimodal because it contains growth centers (large crystals) and fine particles with an approximately unchangeable size which serve as the material for the growth of larger particles (see Fig.4). Under these stationary conditions the dynamic balance between the number of newly formed and dissolved fine particles is achieved. As a result, the concentration of fine particles in the system does not change any longer.

A greater part of the system space is to be expected to occupy the neighboring environment of fine particles at a rather low concentration of the growth centers, the volumetric concentration of the dissolved substance coinciding with a surface equilibrium concentration for fine particles. It is in the neighborhood space of the growth centers that the gradient of the concentration responsible for mass transfer of the dissolved substance towards these centers appears. The dissolution of smaller crystals occurs in the area with the concentration gradient value above critical, i.e. in the close proximity from the growth centers. The dimension of the zone of intensive mass transfer is determined by an average interparticle distance for fine particles. When necessary, it is possible to change this distance by varying the rate of the addition of reagent solutions (i.e. the concentration of fine particles).

Within the framework of this model, the data on the critical rate of adding the reagents[12] can be easily interpreted. As is known, Wey and Strong[3] considered the critical rate to be the rate of introduction of the reagent solutions whose excess resulted in the neo-formation of crystals in the system. At first sight it is not absolutely simple to account for the reduction in critical growth rate values due to the increase of an average size of growing crystals. However, the neo-formation of particles for larger crystals is likely to be always observed at a higher rate of the introduction of reagent solutions, i.e. at higher concentrations of fine particles. Under these conditions the total dimension of diffusion zones in the system remains practically unchangeable. Therefore, only an insignificant part of fine particles appears to be involved into the interaction with large growing crystals. The neo-formation of crystals, in our opinion, is caused by the processes of fine particles interacting with each other by means of the Ostwald ripening mechanism due to statistical size distribution of these particles.

The above mentioned is true for growing the crystals by the physical ripening technique for fine emulsions. The rate of the enlargement of the growth centers, in this case, depends on the difference in their solubility from smaller crystals and on an average interparticle distance in the system. The amount of fine crystals in the area of the effect of the concentration gradient around the growth centers remains rather large due to mobility. However, if the concentration of fine crystals in the system is kept at a high level for rather a long time (e.g. if the concentration of tabular crystal embryos is low and their enlargement proceeds for a

very long time), the growth centers - isometric crystals - can be large enough for their solubility to be comparable with that of tabular crystals. These crystals do not dissolve any more and can be found in a final emulsion after a recrystallization process[10].
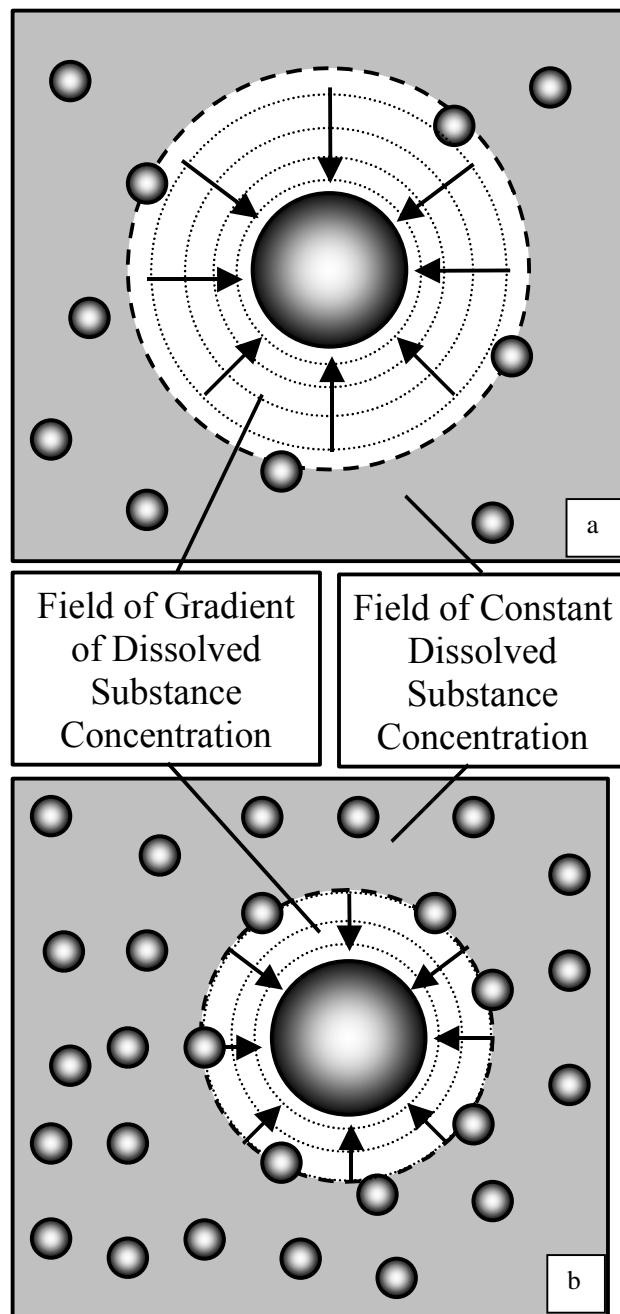
Fig. 4. *Interaction of growing microcrystals with the fresh formed particles during double jet crystallization under conditions of low (a) and high (b) rate of reagents introduction. The dimension of the zone of intensive mass transfer is determined by an average interparticle distance for fine particles*

Summing it all up, it can be concluded that though a theoretical development of the Berry model suggested in the present paper is of a qualitative character so far, nevertheless, it allows us to describe numerous phenomena in uniform manner concerning controllable double-jet crystallization. In our opinion, a strict adherence to the Berry model could account for a great number of the facts concerning mass crystallization of silver halides.

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Biography

Timothy A. Larichev was born in Tomsk (Russia) on May 9, 1964. In 1986 graduated from the State University of Kemerovo, Chemical Department. Since 1988 he works on Kemerovo State University's Inorganic Chemistry Chair. Doctor of Chemistry since 2002. Field of research is the mass crystallization processes of silver halides. He is the author of more than 50 scientific publications.