Localization of Latent Image in Heterophase AgBr(I) Tabular Microcrystals

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Abstract

Processes of the formation of heterophase microcrystals with a AgBr/AgBr(I) structure and the correlation of their structure with photographic properties of emulsion layers prepared on their basis have been investigated. In the course of the experiment, pBr of the synthesis of initial emulsions, the temperature of physical ripening of emulsion microcrystals and the algorithm of incorporation of iodide varied. The research has allowed us to determine the parameters of the crystallization resulting in the formation of microcrystals with improved photographic characteristics. When creating the local zones saturated with iodide, the sensitivity centers and the latent image are in the subsurface area. The analysis of our experimental data enables us to compare the efficiency of these methods as to their photographic characteristics and to evaluate the prospect of combining these methods.

Introduction

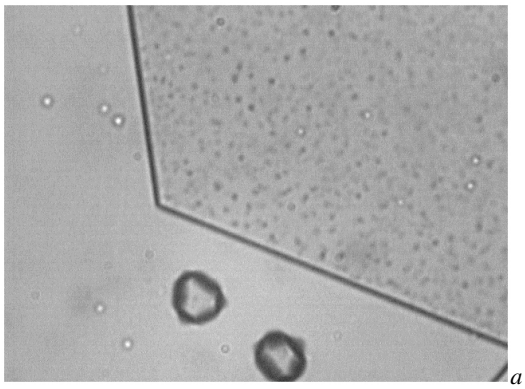
One of the important problems in modern photographic practice is to increase photographic speed of silver halide microcrystals. The increase in the efficiency of a photoprocess is known to be probable when preparing photographic layers on the basis of AgBr/AgBr(I) heterophase tabular microcrystals with a lateral shell which allow one to concentrate photolytic silver in the microcrystal core. However, the preparation of these crystals is rather difficult due to the change of optimum values of crystallization parameters depending on the halide structure of the lateral shell.

According to the patent literature, a perspective opportunity of increase in photographic speed is to create extended defects of a crystalline lattice in a subsurface area of AgBr microcrystals by incorporating the solution of potassium iodide during the growth of a microcrystal before the total quantity of silver bromide is added. The formation of dislocations is caused by the formation of structural defects on the boundary when cocrystallizing silver bromide and silver iodide. Crystals with similar defects demonstrate the increase in the efficiency of a photoprocess. However, the mechanism and the kinetics of the process of the growth of similar microcrystals and techniques for achieving high sensitivity of emulsions remain unknown.

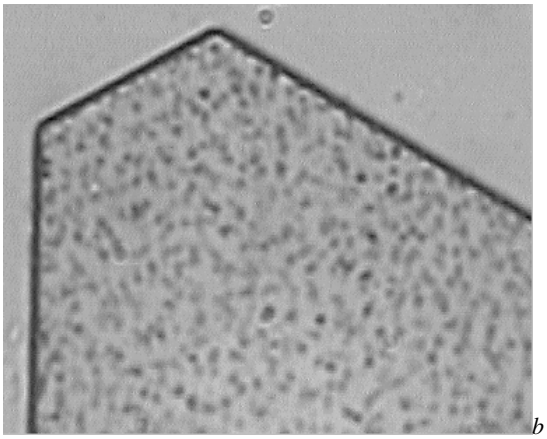
Experiment

The study of the processes occurring when introducing iodide in tabular grains is complicated by very small sizes of these grains. In order to model these processes in more convenient conditions we carried out an experiment on the influence of silver iodide on large crystals of silver bromide, mainly of a hexagonal habit (50 microns).

Optical microphotos of initial crystals (a) and the crystals attacked by the potassium iodide solution with various concentration (b, c, d, e) are presented in Fig. 1.



a



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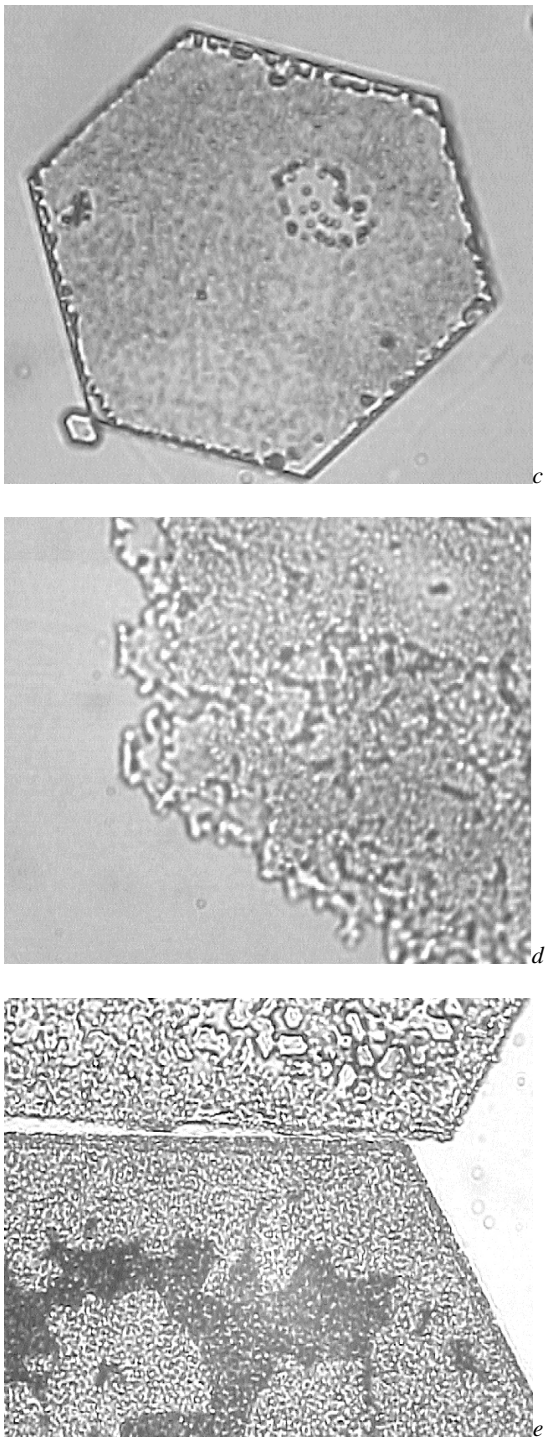


*Figure 1. A microphoto of modeled tabular grains: a - C (KI) = 0 mol/l, b - (KI) = 5*10^{-5} mol/l, c - (KI) = 5*10^{-4} mol/l, d - (KI) = 5*10^{-3} mol/l, e - (KI) = 2*10^{-3} mol/l.*

As seen from Fig. 1 (e), the increase in the concentration of silver iodide in the system results in the dissolution of silver bromide tabular grains, while a 2 hour contact (or more) of silver iodide with large tabular grains results in the destruction of these crystals (Fig. 1 (d)). Experimentally we determined the optimum concentration of iodide ions, responsible for concentrating silver iodide on silver bromide without substrate tabular grains being dissolved (Fig. 1 (b)). An important factor to be taken into account is the duration of the interaction of silver iodide and silver bromide. This interaction should last 2–10 min. to ensure the concentrating of silver iodide without a microcrystal being destructed.

Thus, the state of a grain surface depends on the concentration of the added potassium iodide solution and the duration of its effect on a substrate crystal.

Model experiments allowed us to develop the technique of the synthesis of emulsions with heterophase tabular grains with zones of the increased content of iodide.

Different ways of adding silver iodide into the structure of tabular grains were tested. To be able to compare various techniques of the introduction of iodide, we carried out the initial stage of the synthesis in all the cases in the same way. The weight ratio of silver bromide and silver iodide for all the types of emulsions was the same.

At the first stage a fine AgBr emulsion was prepared by the method of double-jet crystallization. To obtain core tabular grains, physical ripening of a fine emulsion at high temperature and in the presence of a solvent was carried out before initial microcrystals disappeared. An average equivalent diameter of the resulting tabular microcrystals is 0,78 microns, the variation factor - 28 %.

Emulsion A

To create the zone with the increased content of silver iodide, 1 M potassium iodide was added into the emulsion containing AgBr core tabular grains with a pulse method. Then the microcrystals were built up.

The microphoto of coal replicas of the resulting tabular grains are presented in Fig. 2 (a). As seen, tabular grains are, mainly, of a hexagonal habitus.

Emulsion B

To synthesize emulsion B, the technique of creating the zone enriched in iodide, consisting in alternating pulse introduction of potassium iodide and potassium thiocyanate was used. Then the microcrystals were built up.

The microphoto of the resulting tabular microcrystals is presented in Fig. 2 (b). As seen, the introduction of KSCN during the growth of AgBr tabular microcrystals results in a partial dissolution of crystals.

Emulsion C

To synthesize emulsion C, the technique of creating the zone enriched in iodide, by stepwise formation of the AgBr(I) 20% lateral shell and a pulse introduction of iodide was used. Then the microcrystals were built up. The microphoto of the resulting tabular microcrystals is presented in Fig. 2 (c).

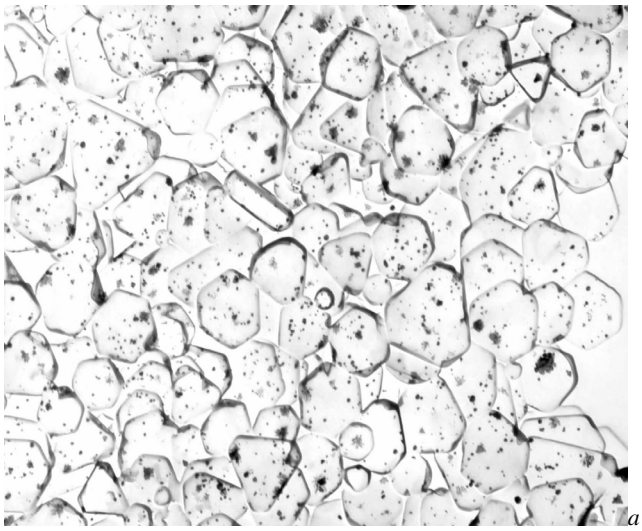
The comparison of Fig. 2 (a) and 2 (c) enables us to see that simultaneous built-up of the AgBr(I) lateral shell and a pulse introduction of iodide results in the average grain size decrease and the coefficient of variation of projected grain sizes increase. Therefore, it was necessary to investigate the

influence of the way of introducing KI on crystallographic and granulometric characteristics of AgBr/AgBr(I) grains.

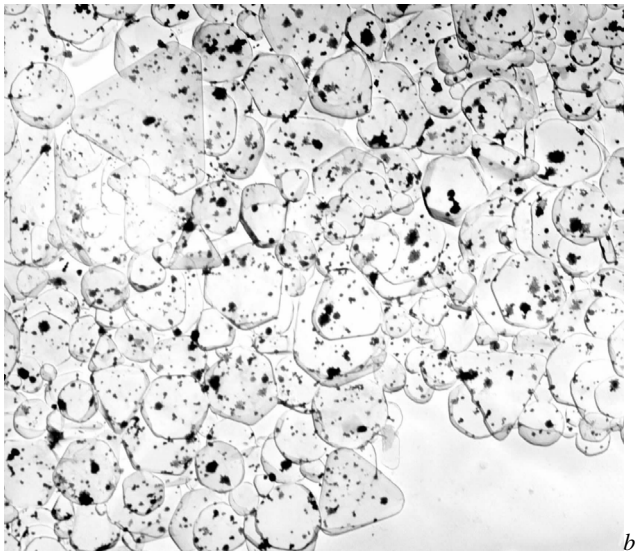
Emulsion D

To synthesize emulsion D, the technique of creating the zone enriched in iodide by the formation of lateral shell AgBr(I) 20% was used. Then the microcrystals were built up.

The microphoto of the resulting tabular microcrystals is presented in Fig. 2 (d). As seen, tabular grains of the emulsion D have a hexagonal and a triangular habit.



a



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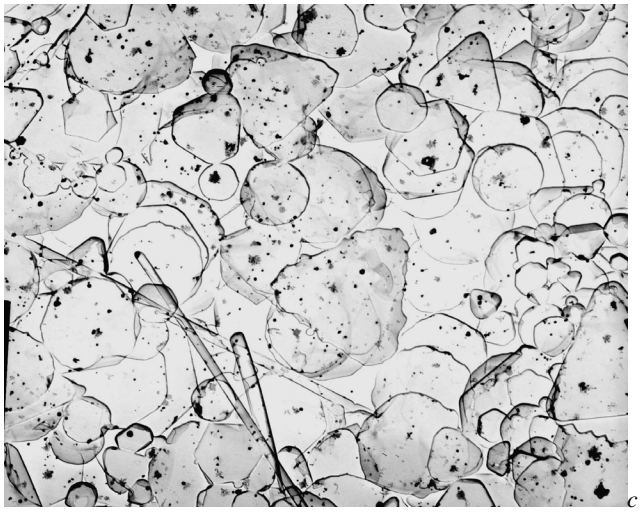
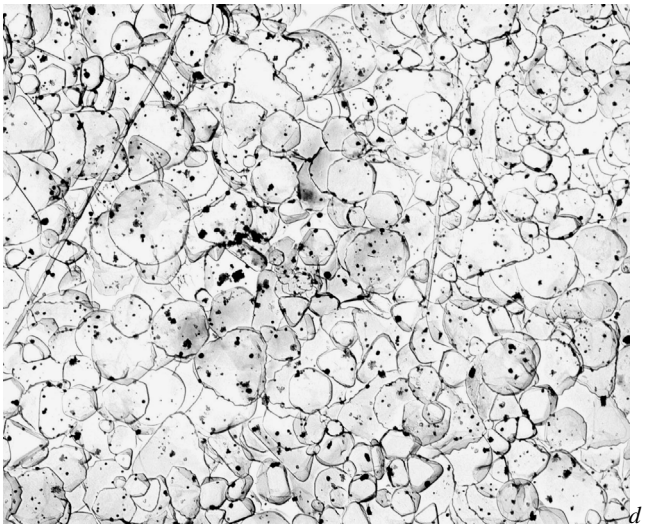


c

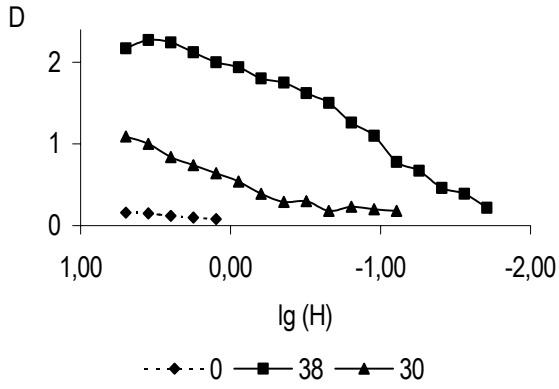


d

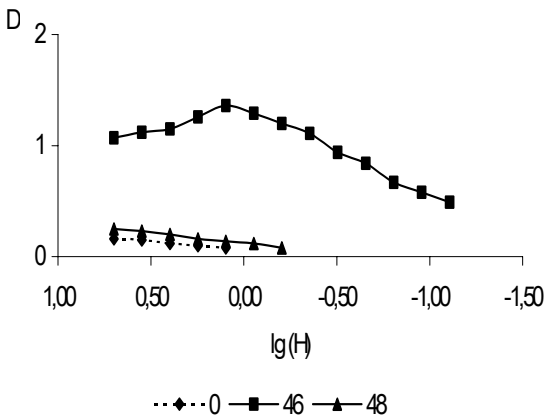
Figure 2. Microphotos of AgBr/AgBr(I) tabular grains of emulsions with zones of the increased content of iodide: a - emulsion A, b - emulsion B, c - emulsion C, d - emulsion D.

Thus, the techniques of the synthesis of photographic emulsions with different ways of introducing iodide developed by the present authors allowed us to obtain heterophase tabular grains with similar crystallographic characteristics which make it possible to estimate photographic characteristics of emulsion layers prepared on their basis at the next stage.

For this purpose photographic emulsions of all types undergo sulfur-plus-gold sensitization and the sulfur-plus-gold sensitization in the presence of potassium thiocyanate. The introduction of potassium thiocyanate was found out to differently influence photographic characteristics of these emulsions. For A and B emulsions, chemical sensitization in the presence of potassium thiocyanate results in the change of the shape of a characteristic curve (Fig. 3 ( ) and 3 (b)).

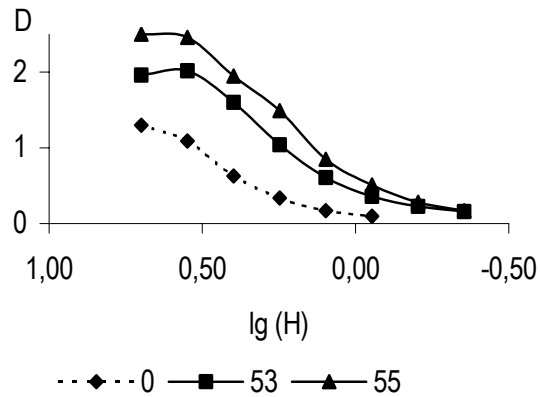


a

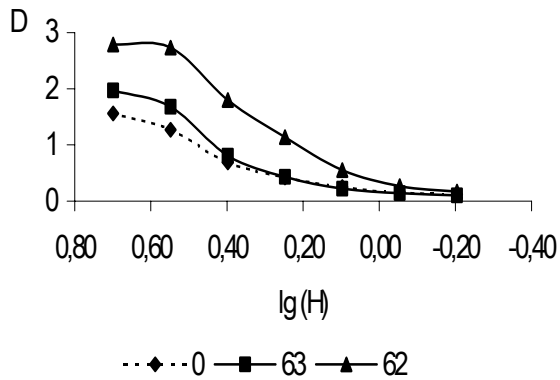


b

Figure 3. Characteristic curves of emulsion layers on the basis of emulsion A (a), emulsions B (b): 0 - an unsensitized emulsion; 38, 46 - chemical sensitization in the presence of potassium thiocyanate; 30, 38 - chemical sensitization without potassium thiocyanate.



a



b

Figure 4. Characteristic curves of emulsion layers on the basis of emulsion C (a), emulsions D (b): 0 - an unsensitized emulsion; 53, 63 - chemical sensitization in the presence of potassium thiocyanate; 55, 62 - chemical sensitization without potassium thiocyanate.

When creating the local zones saturated with iodide, in the structure of grains, the sensitivity and the latent image centers are supposed to be located under the surface. The introduction of potassium thiocyanate before the incorporation of chemical sensitizers allows these centers to appear on the surface, thus increasing the efficiency of a photoprocess.

For C and D emulsions inverse dependence (Fig. 4 (a) and 4 (b)) is observed.

Chemical sensitization in the presence of potassium thiocyanate results in the decrease of the value of optical density of darkening.

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The concentration of sodium thiosulfate was varied for the optimization of the chemical sensitization process in the course of further experiments.

The increase in the concentration of a sensitizer for A and B emulsions can be said to result in an essential increase in photographic speed (criterion 0,85). Further increase of thiosulfate concentration results in the growth of fog optical density.

C and D emulsions underwent sulfur-plus-gold chemical sensitization in the presence of potassium thiocyanate. A significant growth of the fog was observed with increase in the concentration of sodium thiosulfate. Sulfur-plus-gold chemical sensitization without potassium thiocyanate with increase in the concentration of sodium thiosulfate results in an insignificant change of photographic speed, and the fog optical density increases considerably. The best sensitometric characteristics for photolayers on the basis of emulsion A obtained by the present authors are given in Fig.5.

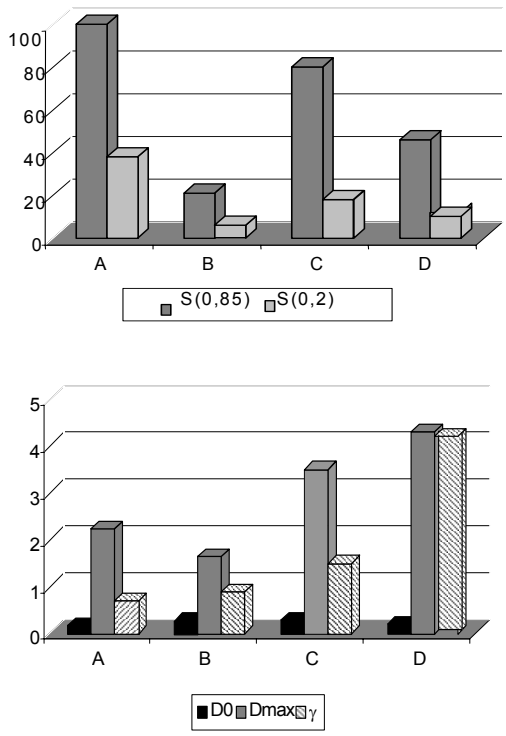
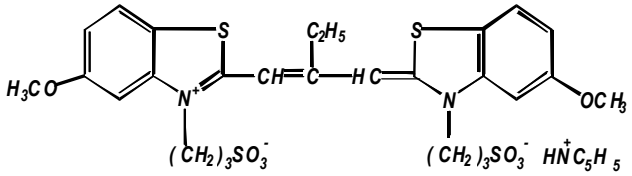


Figure 5. Optimum photographic characteristics of the emulsions under investigation.

Spectral sensitization with Dye which has a maximum absorption at λ=570 nanometer was carried out for three types of photographic emulsions (A, C, D). The structural formula of the dye –



The fog optical density was found out to decrease from 0,3 up to 0,2 and photographic speed to increase from 50 up to 120 due to the adsorption of the dye on the emulsion A grains (Fig. 6.).

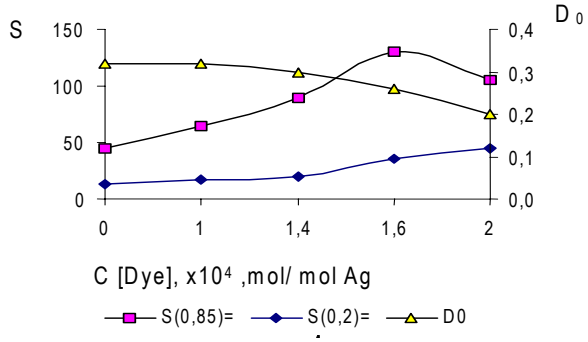


Figure 6. Photographic speed and fog optical density vs. the concentration of Dye (for the emulsion).

When increasing the concentration of Dye, the photographic speed of emulsion C considerably grows (criteria 0,2 and 0,85). The fog optical density decreases from 0,63 up to 0,15. The further increase in the concentration of the dye is accompanied by photographic speed decrease and fog optical density increase (Fig. 7.).

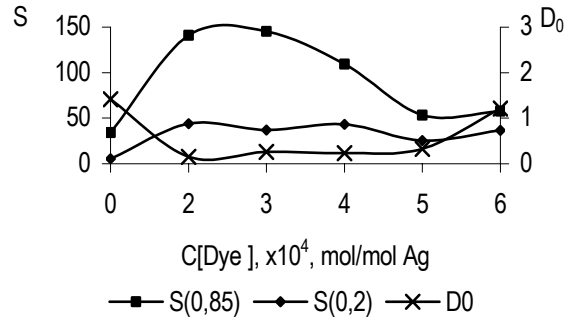


Figure 7. Photographic speed and fog optical density vs. the concentration of Dye (for the emulsion).

The photographic speed for emulsion D after the dye is added increases almost 4 times as much. The fog optical density increases too. When increasing the concentration of the dye, the fog level is reduced up to a certain value (Fig.8).

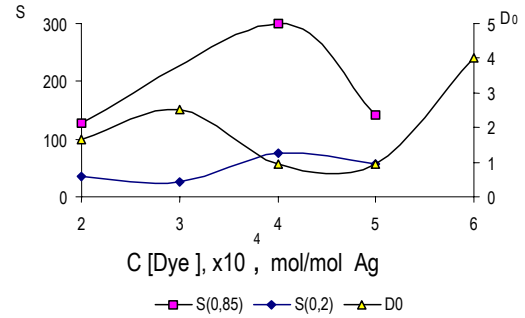


Figure 8. Photographic speed and fog optical density vs. the concentration of Dye (for the emulsion D).

Thus, grains with the zones of the increased contents of silver iodide possess a number of similar properties: they easily fog a) when attacked by potassium thiocyanate, b) at higher concentrations of sodium thiosulfate, they possessing higher photographic speed.

The analysis of our experimental data allows us to compare the efficiency of these techniques from the point of view of photographic characteristics, and in addition to it, to estimate the prospect of combining these techniques.

Biography

Aigul B. Abisheva was born in Pavlodar (Kasakhstan) on July 19, 1980. In 2002 he graduated from Kemerovo State University, the Chemistry faculty. Now he is a post-graduate of Kemerovo State University, the Physics faculty. His field of research is mass crystallization processes of silver halides, the author of 11 scientific publications..