Morphological Regularities in the Formation of Silver Halides During In Situ Halidization of Silver Stearate

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The results of an investigation of the sites of silver halide formation on the surface of silver carboxylate crystals, modeled by silver stearate and prepared by the standard in situ process used for thermally developed photographic materials, are reported. For the first time the structure of a silver halide/silver carboxylate interface has been clearly observed. Silver bromide is found to form on the edges of the silver stearate crystal during the initial stages of the reaction. The influence of the nature of the halide source on the silver halide shape and location on the silver carboxylate crystal and the presence of defects in the silver halide crystals are discussed.

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Introduction

The photosensitive composition of silver halide/silver long-chain carboxylates is the basic element in the manufacture of photothermographic materials.[1,2] Various silver halides (AgX), such as silver chloride (AgCl), silver bromide (AgBr), silver bromochloride [AgBr(Cl)], and silver bromiodide [AgBr(I)], are used as the photosensitive components. Silver stearate [$AgC_{18}H_{35}O_2]_2$,[3] (AgSt) and silver behenate [$AgC_{22}H_{43}O_2]_2$ (AgBeh) are the most common silver long-chain carboxylates. Upon exposure latent image centers form in the photothermographic materials, and silver particles forming the visible photographic image are deposited at these centers during the thermal development process. Despite the fact that there is significant patent literature on the methods of preparation of the photosensitive silver halide/silver carboxylate compositions,[4–8] essentially no data are available on the AgX/silver carboxylate interface in relation to the presence of defects and the size and shape of the halide crystals. However, the nature of the interface may determine the photosensitivity of the photothermographic material.

The silver halide portion of the photosensitive thermally developed silver halide/silver carboxylate composition may be formed in different ways, including the common in situ preparation.[9] In situ preparation of silver halide involves a direct exchange reaction between silver carboxylate crystals and solutions of brominating agents. Both inorganic and organic compounds that can form silver halide by reaction with the silver long-chain carboxylate are used as brominating agents.

In this work, we report the structure of a silver halide/silver carboxylate interface, the sites of formation of the halide on the surface of silver carboxylate crystals, the presence of defects, and the shape of AgX crystals in the in situ photothermographic constructions.

Silver stearate (AgSt) was used as the silver long-chain carboxylate. The studies were conducted both on specially grown AgSt crystals and on powders. The major part of the work was performed on the silver bromide/silver stearate system, although some results are included for the AgI/AgSt systems.

Experimental

The AgSt crystals used were grown by slow cooling of a saturated ethanol–pyridine solution (10:1).[10] Plates were obtained with an aspect ratio of ~1:50–1:100 (Fig. 1). Powders were obtained by standard procedures used in the preparation of photothermographic materials.[4–7] All powders were washed with acetone or ether to remove excess stearic acid.
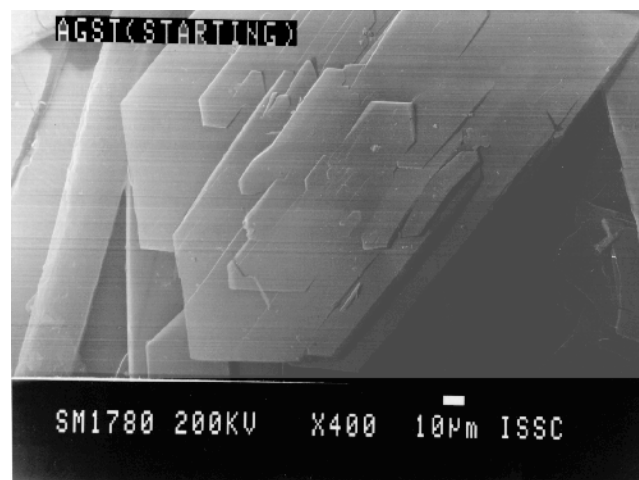

Figure 1. Morphology of AgSt crystals grown from ethanol–pyridine solution. The monocrystals are thin platelets with well-developed (001) base edges.

The in situ bromination reaction was carried out as follows. A freshly prepared solution of pyridinium hydrobromide perbromide (PHP, Aldrich Chemical Co.) or N-bromosuccinimide (NBS, Aldrich Chemical Co.) in ethanol was added to a weighed sample of AgSt. The concentration of the brominating agent varied from 0.01–0.1 mol/mol AgSt. The reaction was carried out at room temperature for 10–30 min; then the samples were washed by alcohol and air dried in the dark. In a similar manner, the AgBr/AgSt system was obtained by halidizing with solutions of $CaBr_2$, $BaBr_2$, or KBr in aqueous ethanol.

Treatment of AgSt crystals with Br_2 solution was carried out as follows. Bromine was dissolved in carbon tetrachloride and then added to a weighed sample of AgSt in an amount such that the AgBr/AgSt ratio in the final preparation was 0.01–0.2 mol AgBr/mol AgSt. The treatment time varied from 1–20 min.

In the preparation of the AgI/AgSt system, CaI_2 and KI solutions were used as halidizing agents. The halide to AgSt ratio was 0.01:1 mol/mol.

SEM and TEM studies of AgSt and AgBr crystals were conducted, using a JEM-2000FXII microscope equipped with a scanning ASID-20 device at an accelerating voltage of 200 kV. For preparation of suitable TEM samples, the AgBr/AgSt crystals were dispersed in water, from each such dispersion a drop was then placed on a Cu TEM grid previously covered with carbon film. After evaporation the grids were introduced onto the TEM cooling holder. All preparations were performed under red light, including transport and insertion into the microscope. These TEM studies used a liquid nitrogen single-tilt holder operating at minimum temperature (–160°C) to avoid, as much as possible, radiation damage by 200-kV electrons. Most crystals of AgBr/AgSt could be observed for over an hour under these conditions. For SEM observation, a thin gold film was thermally deposited on the samples in vacuum.

Results

SEM Investigation of AgBr Crystal Formation During In Situ Halidization of AgSt

1. ***Formation of AgBr Crystals from the Treatment of AgSt Single Crystals with $CaBr_2$.*** These studies have shown that AgBr crystals, confirmed by x-ray diffraction data, form on the lateral faces of AgSt crystals. The crystal size of AgSt remains virtually unchanged with increasing time of the chemical reaction between AgSt and $CaBr_2$, 500–1000 Å (Fig. 2). Silver bromide crystals are generally not observed to
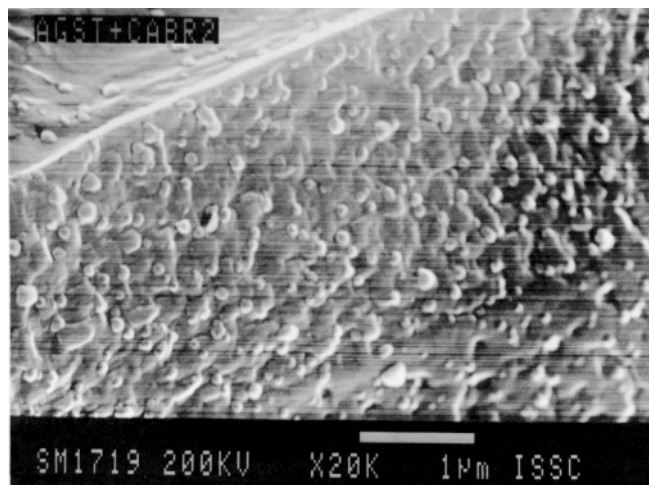

Figure 2. SEM micrograph of the lateral faces of AgSt crystals after treatment with $CaBr_2$ solution. The AgBr crystals are ~1000 Å.
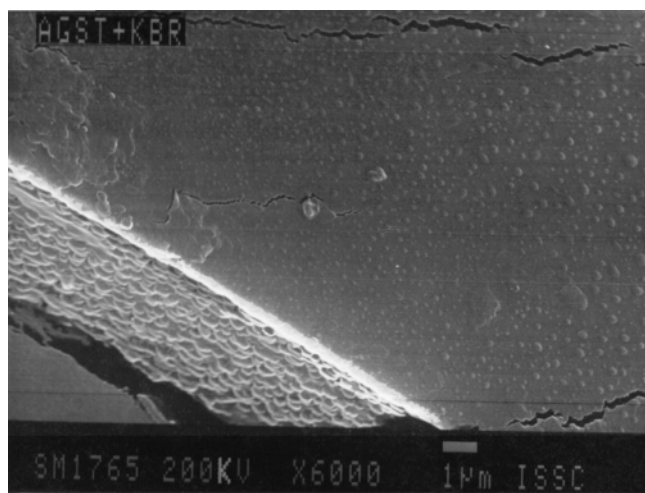

Figure 3. SEM micrograph of the lateral and base faces of AgSt crystals after treatment with KBr solution. AgBr crystals form on both lateral and base (001) planes.

form on the base $(001)_{AgSt}$ plane. Similarly, increasing the $CaBr_2$ solution concentration or treatment time produces no substantial changes in the morphology of the base $(001)_{AgSt}$ plane and does not lead to significant formation of AgBr crystals on its surface. AgBr crystals that do form on the $(001)_{AgSt}$ plane probably do so at defect sites (see below).

When a $BaBr_2$ solution was used as brominating agent, the same morphological uniformity was observed with regard to the formation of AgBr crystals on the AgSt crystal surface. Silver halide crystals formed only on the lateral faces of AgSt crystals.

2. ***Formation of AgBr Crystals by Treatment of AgSt Single Crystals with KBr.*** The morphological patterns of the formation of AgBr crystals on the AgSt crystal surfaces during an exchange reaction with a KBr solution and during the halidization of AgSt crystals with a $CaBr_2$ solution have both similarities and differences. What these processes have in common is that at short treatment times, or at low concentrations, AgBr crystals formed with KBr are predominantly on the lateral faces of the AgSt crystal (Fig. 3). The edge lengths of the AgBr crystals are of the order of several thousand angstroms.

The main difference with this process is the formation of 500- to 700-Å AgBr crystals on the base plane of AgSt. In this case, the number of AgBr crystals formed on the base planes of AgSt crystals increases with the progress of the reaction. The mechanism by which halidization occurs in this case is unclear at this time. The AgBr crystals on the (001) plane have no predominant orientation with respect to the starting silver stearate crystal.

3. ***Formation of AgBr Crystals by Treatment of AgSt Single Crystals with Br_2.*** Despite the potential differences between the reaction of KBr or Br_2 with AgSt [ion exchange versus possible radical mechanism (Hunsdiecker reaction)], the initial formation pattern of silver halide crystals is essentially the same in both cases.
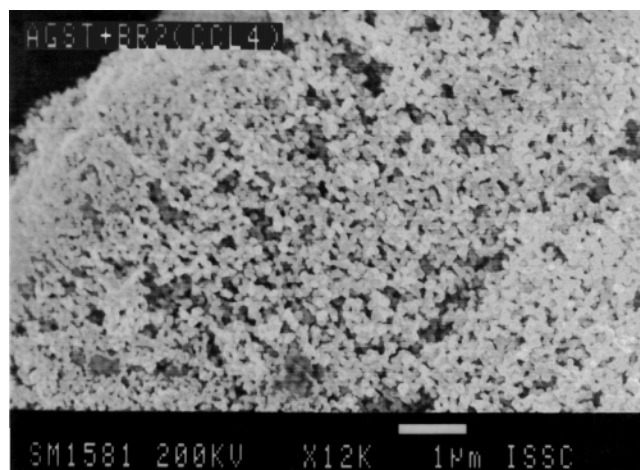
As with the ion exchange reactions above, the formation of AgBr crystals occurs on the lateral faces of AgSt crystals early in the reaction. Later formation of AgBr crystals is observed on the base [001] plane of the AgSt crystal. The diameter of the AgBr crystals is 500–700 Å. In this case, the formation of AgBr crystals is accompanied by AgSt crystal cracking, and
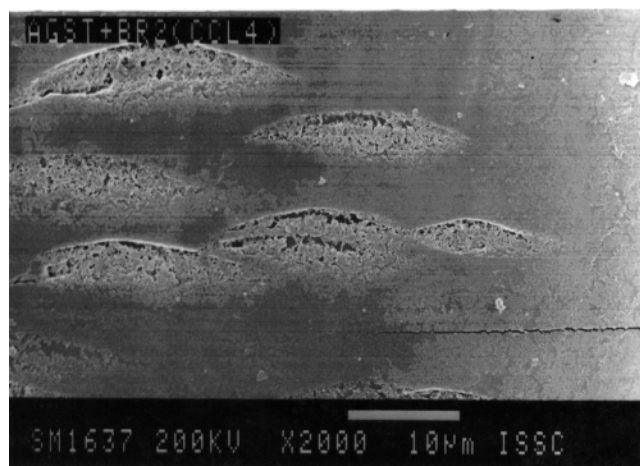
(a)
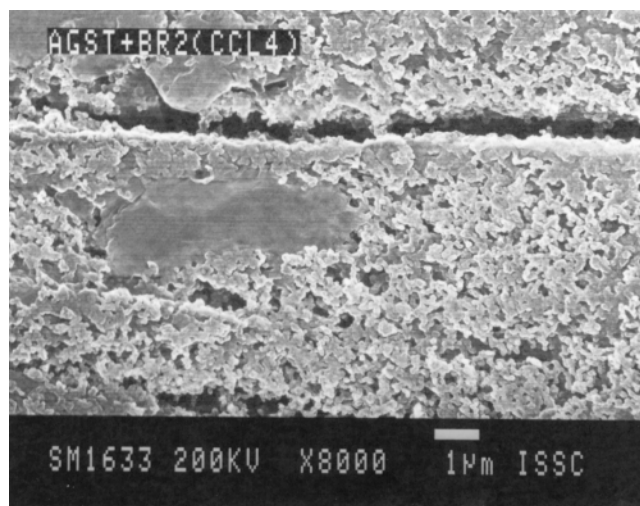
(b)

(c)

Figure 4. SEM micrographs of the cracks on the base planes of AgSt crystals (a) at the initial stage of the reaction with the Br_2 solution; (b) crack at same stage as in (a) at higher magnification; AgBr can now be seen. (c) SEM micrograph of AgBr crystals forming on the base AgSt planes after extended treatment with a Br_2 solution. The AgBr crystals are ~ 500 – 700 Å.

the reaction is localized in the region of the developing crack. Low magnification illustrates the crystal cracking process [Fig. 4(a)], but higher magnification is required to observe the silver halide [Fig. 4(b)]. Pro-
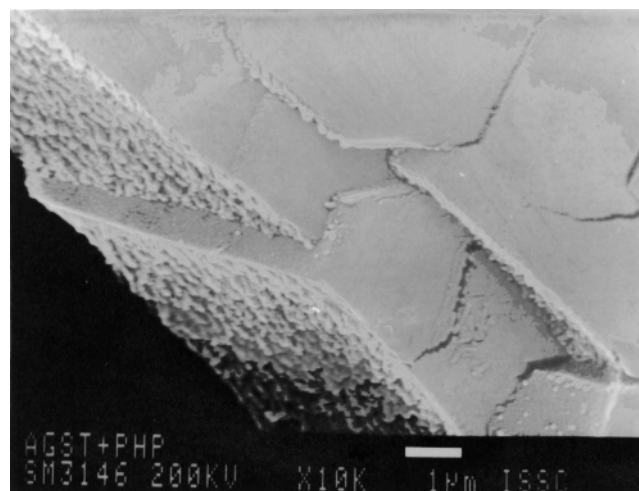

Figure 5. SEM micrograph of AgSt monocrystals after treatment with PHP solution at the initial stage of the reaction. The AgBr crystals form on the lateral faces of AgSt crystals.

longed treatment of AgSt crystals leads to complete coverage of the base plane and the lateral faces of the AgSt crystal with AgBr crystals [Fig. 4(c)]. The AgBr crystals formed on the AgSt surface are not oriented with respect to the starting crystal.

4. *Formation of AgBr Crystals by Treatment of AgSt Crystals with NBS and PHP.* Halidization of silver stearate with either NBS or PHP has been found to produce identical morphological characteristics. As in all of the above halidization cases, AgBr crystals from NBS and PHP initially form on the lateral faces of the AgSt crystal (Fig. 5). As the treatment time increases, AgBr crystals form on the base plane of the AgSt crystal. In this case, the morphology of formation of the silver halide crystals on the base plane of the AgSt crystal differs significantly from that of the processes considered above (1–3).

The silver halide crystals on the base plane of AgSt form chains that are oriented parallel to the (100) direction of AgSt. These AgBr crystals have diameters of 500–700 Å, which are essentially independent of the treatment time of AgSt crystals with NBS or PHP [Figs. 6(a) and 6(b)]. An increase in the treatment time of AgSt crystals with solutions of brominating agents (NBS or PHP) causes only an increase in the number of AgBr crystals and leads eventually to the entire AgSt crystal (lateral and base planes) being completely covered with a layer of silver halide crystals.

Scanning electron microscopy does not allow the shape and structure of the AgBr/AgSt interface and the presence of defects to be observed. To solve these problems, transmission electron spectroscopy was used.

TEM Studies of AgBr Crystal Formation During In Situ Halidization of AgSt Single Crystals.

1. *TEM Studies of AgBr Crystal Formation During In Situ Halidization of AgSt Crystals with CaBr2 and KBr.* Investigation of AgBr crystal formation during in situ bromination with a $CaBr_2$ solution shows that the formation of AgBr crystals occurs on the lateral faces of AgSt crystals. The AgBr crystals formed during this in situ halidization have a cubic shape and diameters of 600 – 800 Å [Figs. 7(a) and 7(b)]. A large number of silver bromide crystals show distinct boundaries in the electron micrographs; the boundaries are most probably associated with the formation of twinning defects in the crystalline structure of AgBr
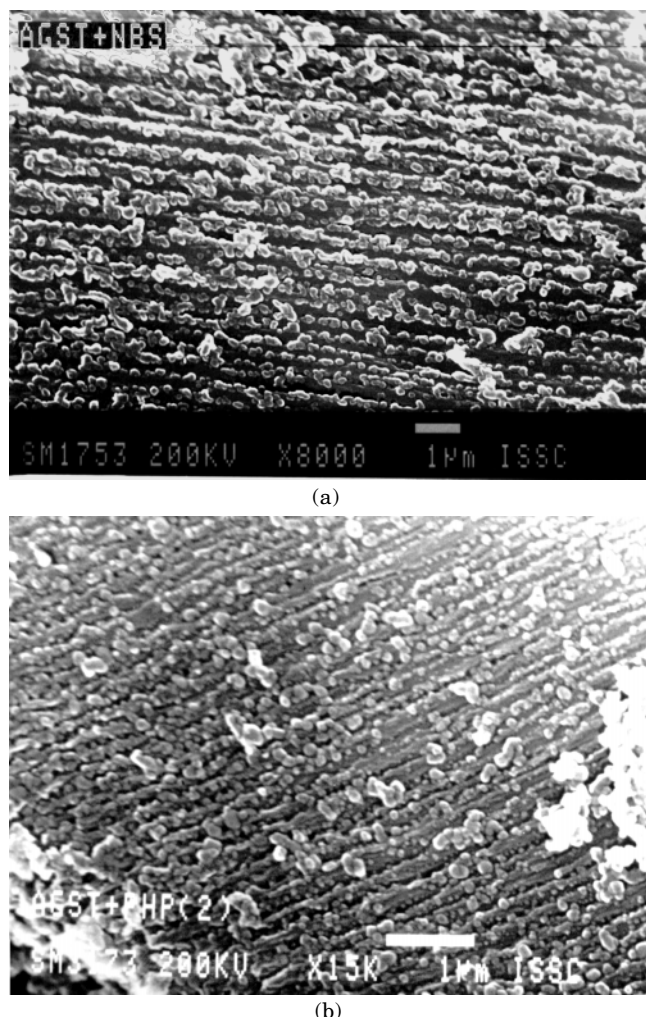
(a)

(b)

Figure 6. SEM micrograph of the base plane of AgSt crystals after extended treatment with solutions of (a) NBS and (b) PHP. The oriented formation of AgBr crystals is observed.

Fig. 7(c)]. The $(111)_{AgBr}$ plane is the most probable twinning plane in the AgBr crystals formed. The TEM studies also show that the precipitation of calcium stearate, $CaSt_2$, apparent from the distinct texture in the micrographs, occurs on the base planes of AgSt crystals. Some precipitation on the lateral planes of the AgSt crystals cannot be conclusively ruled out, but it was not observed in these TEM studies. The $CaBr_2$ halidization process is accompanied by an increase in the surface topography of the base planes of AgSt crystals [Figs. 7(a) and 7(b)].

When the brominating agent is KBr, the base plane of AgSt is smooth after treatment (Fig. 8). This observation can be explained by the fact that the KSt forming during the reaction is quite soluble, by approximately 2 orders of magnitude compared with $CaSt_2$,[11] and does not precipitate on the base plane of AgSt.

Figure 9 shows a high-resolution electron microscope (HREM) image of an interface between the AgSt crystal and the AgBr crystal formed. This is the first time that such a clear image of an interface between in situ formed AgBr and a silver carboxylate has been observed. This image was obtained when the electron beam direction was parallel to the base plane of the AgSt crystal, and hence to the silver layers in the AgSt structure. As can be seen from the image, the black bands of the crystalline AgSt lattice (silver ion layers) are distorted

during the transition to the AgBr crystal contact. This distortion indicates the presence of a transition defect zone, several tens of angstroms in size, at the AgBr/AgSt inter face. The layer spacing in the AgSt crystal can be clearly observed and measured. The 48 Å seen here is in reasonable agreement with the 50.35 Å obtained by x-ray powder diffraction data.[12]

2. ***TEM Studies of Formation of AgBr Crystals During Halidization of AgSt Crystals with PHP.*** Consistent with the SEM studies, the TEM images of the formation of AgBr crystals when using a PHP solution as a brominating agent have shown that the formation of AgBr occurs most readily on the lateral planes of AgSt crystals, but it also occurs on the basal planes. The silver halide crystals have the same dimensions (500–800 Å) and form twins, as in the treatment of AgSt crystals with $CaBr_2$ and KBr solutions [Fig. 10(a)]. Formation of AgBr crystals on the basal plane occurs, in this case, without disruption of the layered AgSt structure [Fig. 10(b)].

3. ***TEM Studies of the Formation of AgI Crystals During Halidization of AgSt Crystals with CaI_2 or KI.*** It is well known that AgI crystals, in contrast to AgBr crystals (which have an NaCl-type structure), can have several crystalline modifications. The stable crystalline AgI structures under standard conditions are the hexagonal or face-centered cubic modification. In this connection, the question arises as to whether an alteration of the silver halide structure (AgI instead of AgBr) has an effect on the process of morphology formation.

The electron microscope studies carried out in this work have shown that during the in situ halidization of AgSt crystals, using CaI_2 and KI as brominating agents, the formation of AgI crystals proceeds in the same manner as in the case of formation of AgBr crystals. The formation of AgI crystals occurs only on the lateral faces of AgSt crystals [Figs. 11(a) and 11(b)]. In this case, the electron micrographs show only the bands of twinning of AgI crystals.

As in the case of halidization with $CaBr_2$ and KBr solutions, when CaI_2 is used, the base plane of the crystal is more irregular (rough) than when KI solutions are used. This roughness is probably associated with the precipitation of poorly soluble $CaSt_2$[11] on the base planes of AgSt crystals.

Analysis of the phase composition of the specimen obtained after treatment of AgSt crystals with a CaI_2 solution, carried out by x-ray diffraction, indicates the formation of a hexagonal AgI phase (Fig. 12).

Discussion

The electron microscope studies of the formation of the silver halide phase during the in situ halidization of AgSt crystals can be summarized as follows:

1. Regardless of the halidizing agents (organic or inorganic) used during the in situ treatment of silver stear-ate crystals, cubic AgBr or hexagonal AgI forms on the lateral faces of AgSt.

2. When solutions of KBr, NBS, or PHP in ethanol, or Br_2 in CCl_4, are used as brominating agents, AgBr crystals also form on the base (001) planes of AgSt crystals. These reactions yield soluble byproducts.

3. When AgSt crystals are treated with $CaBr_2$ or $BaBr_2$ in ethanol, the formation of AgBr crystals occurs only on the lateral faces of AgSt. In these cases, the metal carboxylates byproducts are insoluble in the reaction medium.[11,13]
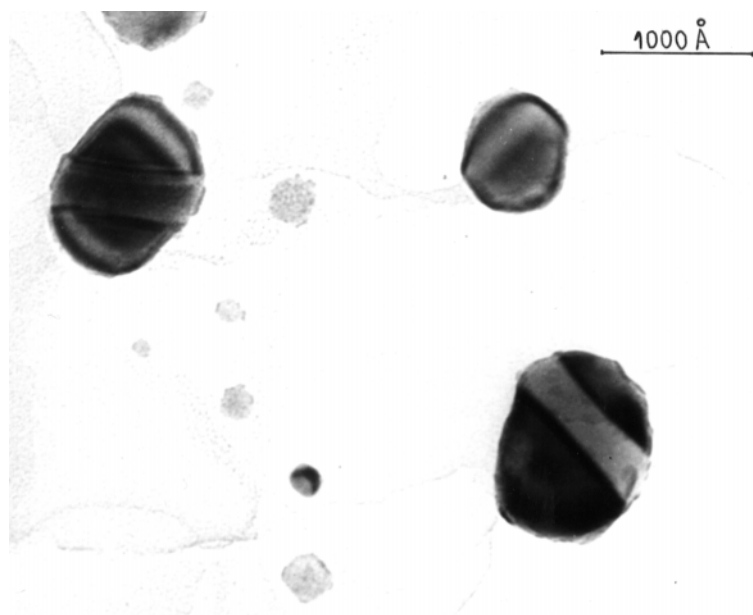
The crystallographic planes of the starting AgSt matrix, on which the AgBr crystals form, must be taken into account to understand the character of the in situ halidization process.
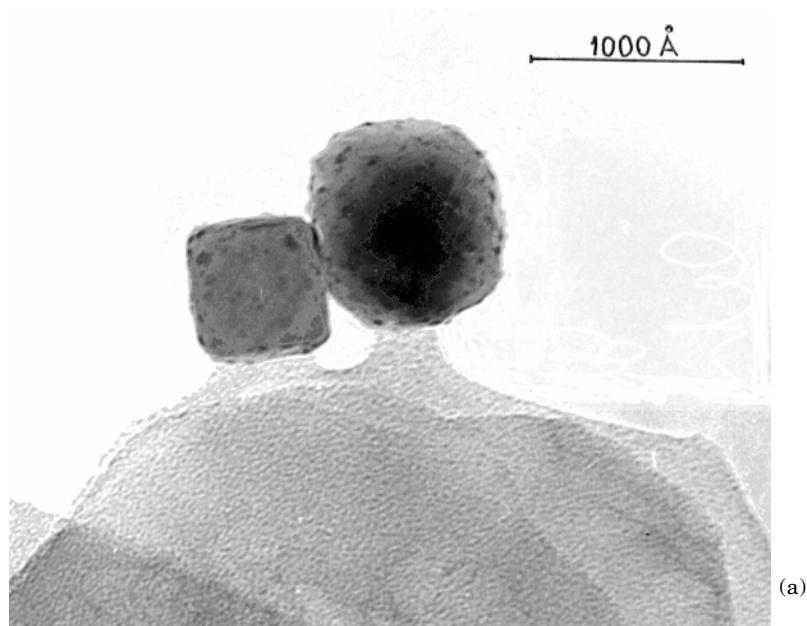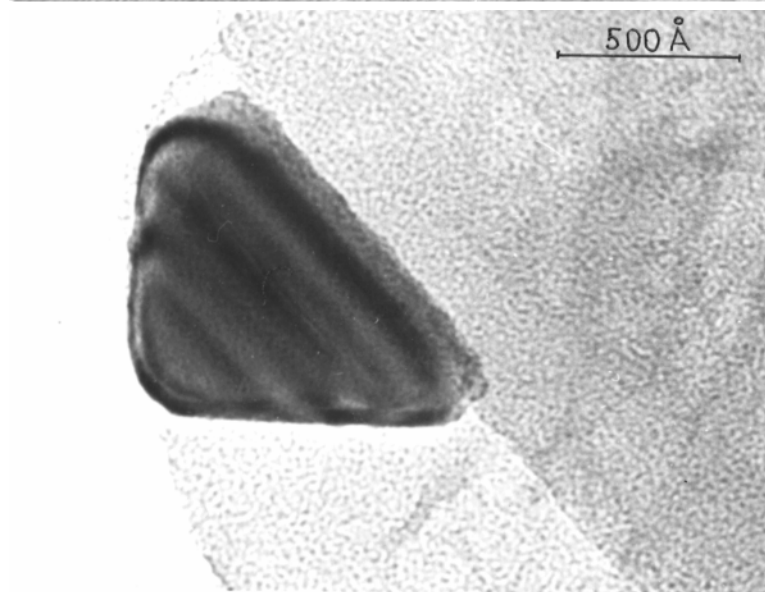
Figure 7. (a,b) TEM micrographs of AgBr crystals with different habits formed on the lateral edges of AgSt crystals after treatment with CaBr$_2$ solution; (c) Twinning defects in the AgBr crystals.
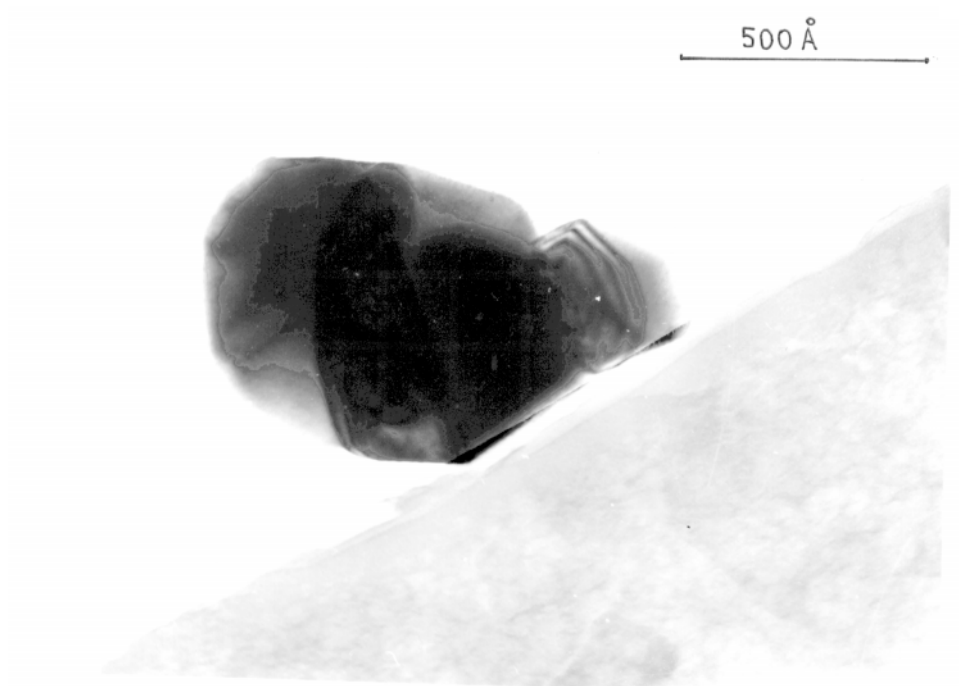
1000 Å

(a)

500 Å

(b)

1000 Å

(c)

Figure 8. TEM micrograph of AgBr crystal formation on the side edge of the AgSt crystal after treatment with KBr solution. In this case, the surface of the AgSt crystal is smoother than that after treatment with $CaBr_2$ (see Fig. 7).
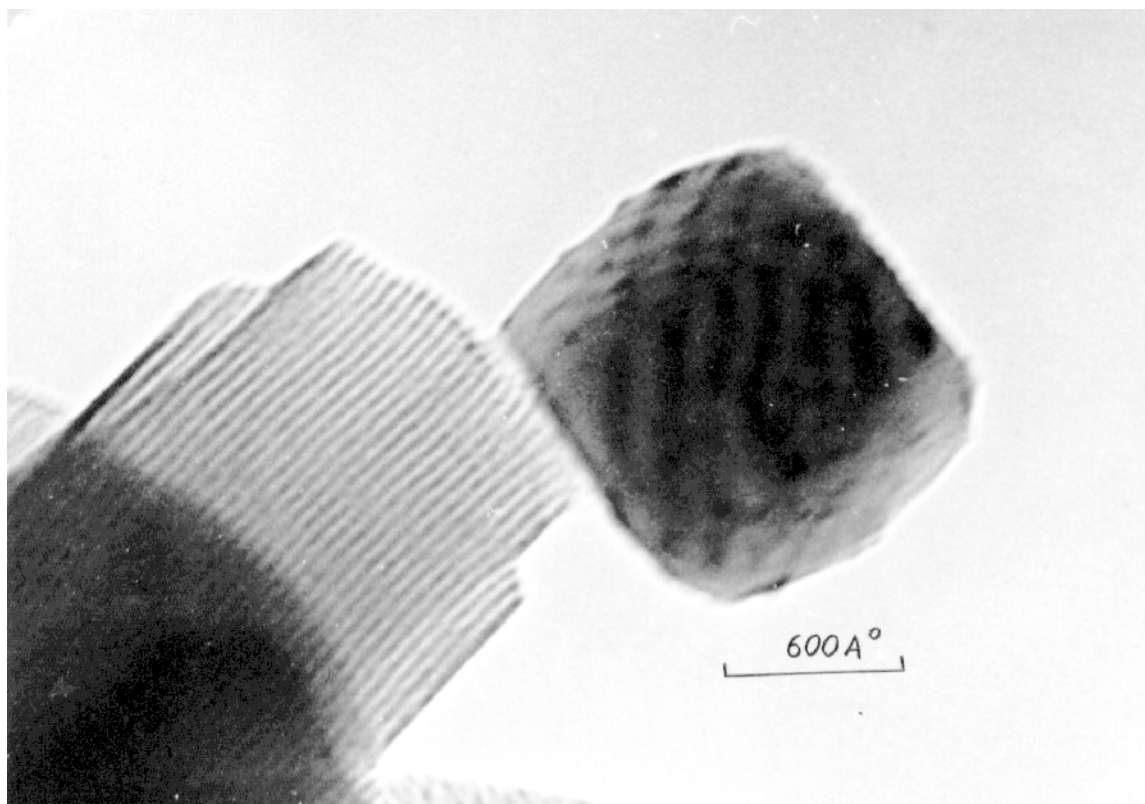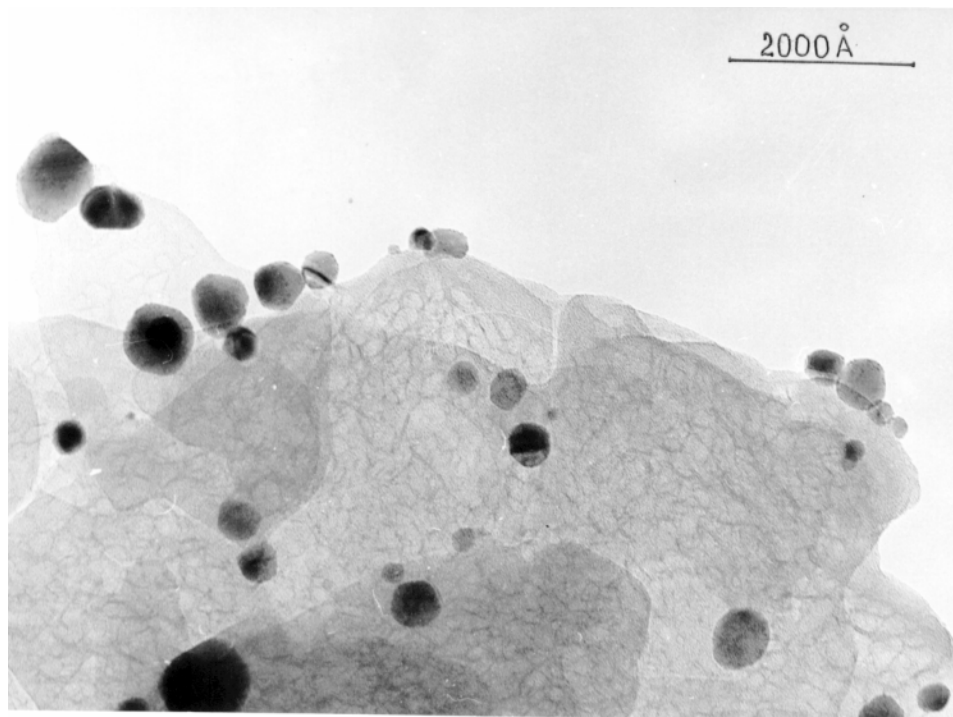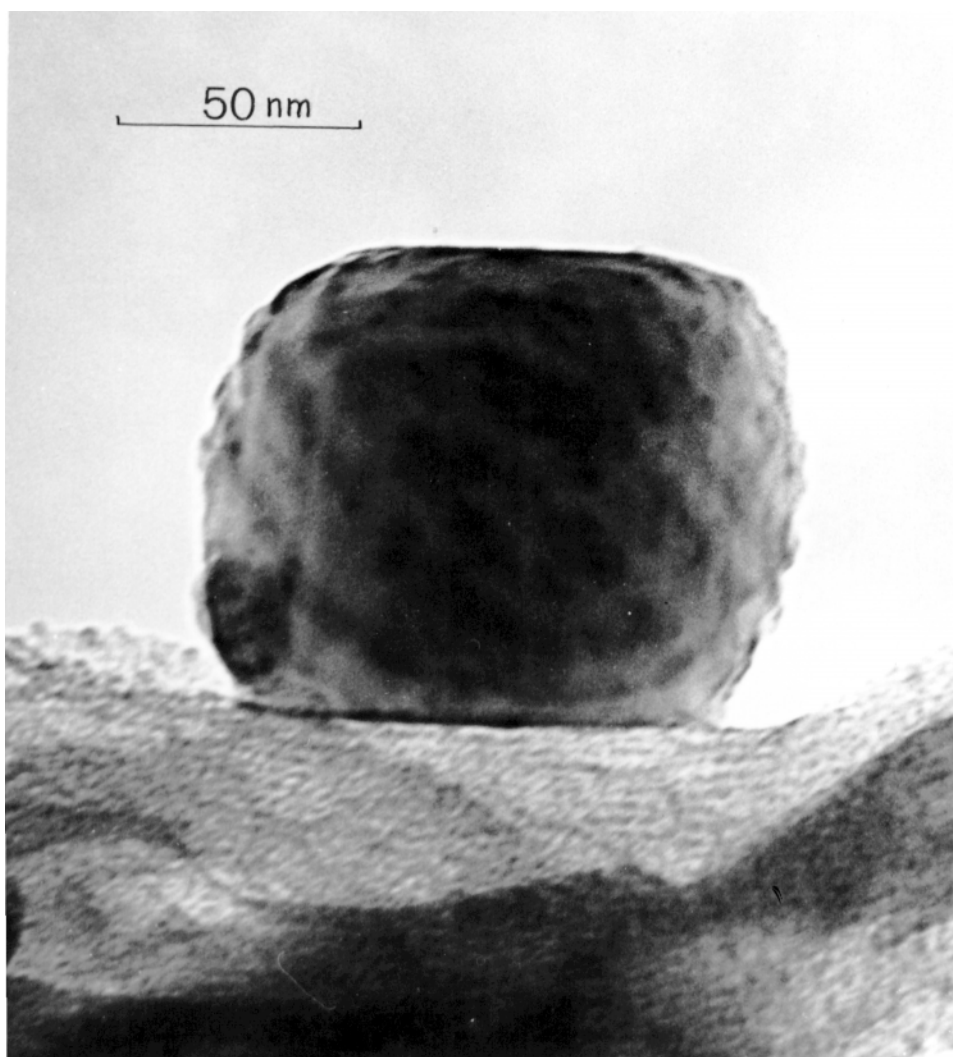

Figure 9. TEM micrograph of AgBr/AgSt interface. At the contact between the crystals, deformation of the AgSt crystalline lattice can be observed.

Figure 10. TEM micrographs of AgBr crystal formation after treatment of AgSt crystals with PHP. The formation of AgBr occurs mainly on the lateral edges of the AgSt crystals (a), but is also evident on the base plane (b).
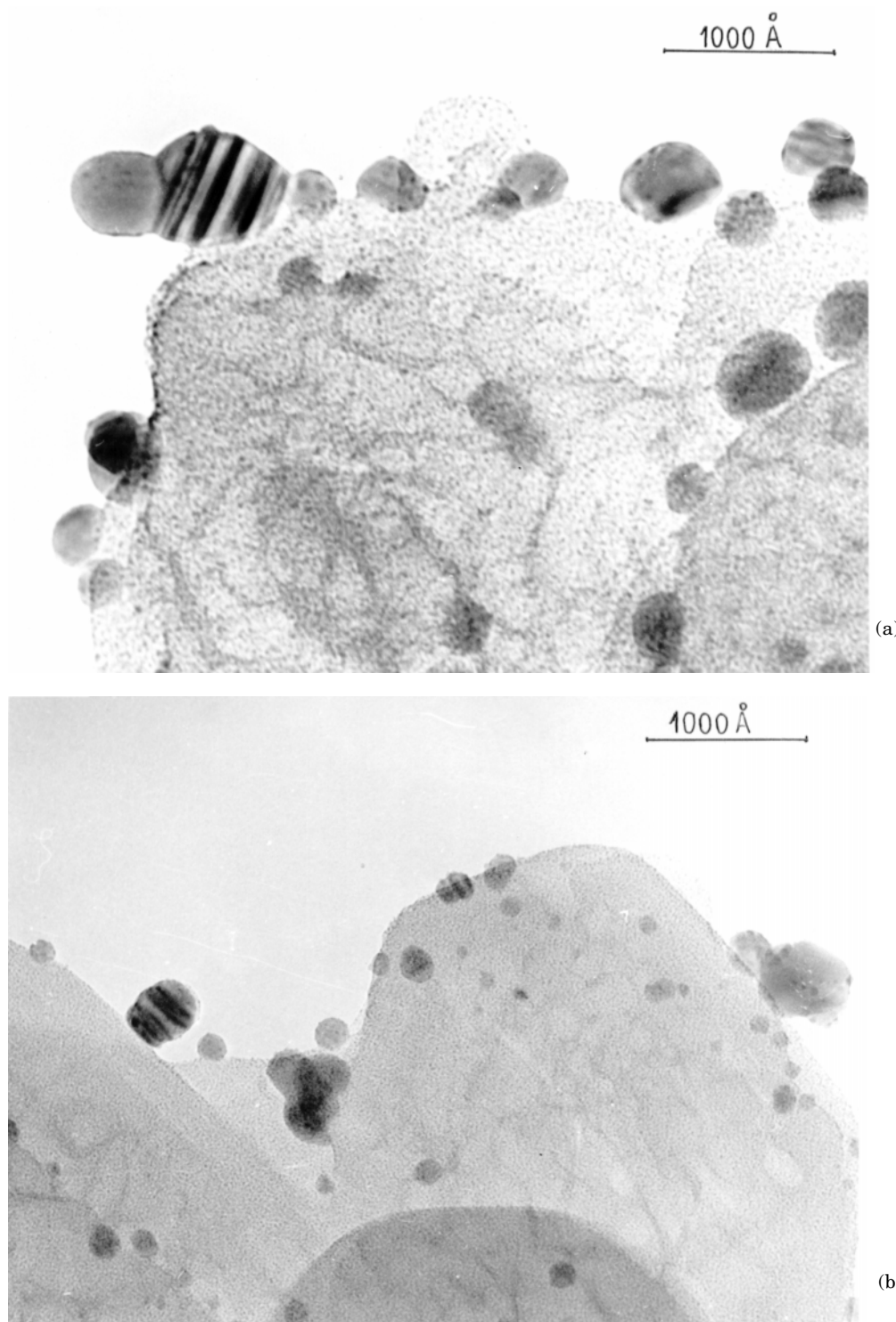
(a)

(b)

Figure 11. TEM micrographs of AgBr crystal formation on the edge of the AgSt crystals after treatment (a) with CaI_2 (a), and (b) with KI.

(a)

(b)

It is known that silver stearate has a triclinic unit cell and forms a layered structure with alternating double silver and carboxylate layers.[3,12] The spacing between the layers of silver ions is 50.35 Å for the crystalline AgSt structure. The AgSt crystals formed during synthesis are plates with the large base (001) plane. With this morphology, the silver layers in the AgSt crystals are parallel to the base plane of the crystals and emerge on the lateral faces of AgSt. This layered structure is responsible for the severe anisotropy of the chemical and physical properties of AgSt crystals. Consequently, the presence of AgSt crystal anisotropy determines the sites where AgX crystals form during the in situ halidization. For the

AgX phase to form during the exchange reaction of halidizing agents with AgSt crystals, a constant supply of silver ions to the reaction site, i.e., to the AgBr/AgSt interface, is required. The diffusion of silver ions in a perfect crystal of the layered AgSt structure is possible only along the silver layers located parallel to the base plane of the AgSt crystal. The movement of silver ions in such a crystal in the direction perpendicular to this plane is impossible because of the long (50.35 Å) hydrocarbon spacing between silver layers. These factors are probably responsible for the formation of AgX crystals beginning on the lateral faces of the AgSt crystals during the in situ halidization.
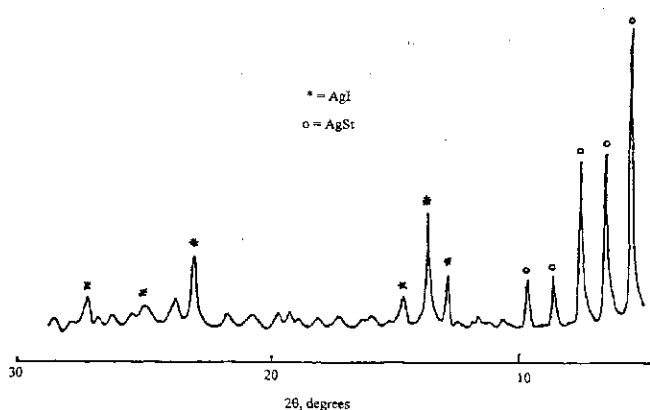
Figure 12. X-ray diffraction pattern of AgSt after treatment with the solution of CaI_2. The formation of hexagonal AgI can be seen.

However, as shown above, AgBr crystals can also form on the base (001) planes of AgSt crystals under certain circumstances. In this case the formation of AgX crystals is probably associated with the presence of various kinds of defects on the surfaces of AgSt crystals, primarily of growth steps and dislocation sites on the surface. The formation of AgX crystals in this case may proceed by a mechanism similar to that of the formation of AgX on the lateral faces of AgSt crystals, because the presence of these defects is associated with the emergence of silver layers on the crystal surface. The formation of AgX on the base plane of AgSt crystals was observed only with large AgSt single crystals and appears to be due to the surfaces of small AgSt crystals being more perfect than the surfaces of specially grown AgSt single crystals.

The difference between the bromination of AgSt crystals with $CaBr_2$ or $BaBr_2$ solutions and that by other brominating agents (i.e., the growth of AgBr crystals only on the lateral faces of AgSt crystals for long treatment times or high concentrations of the brominating agent) may be attributed to the AgBr byproduct, which can be schematically represented as follows:

$$AgSt + M(x)_n \rightarrow AgX + M(St)_n, \text{ where } n = 1\text{–}3$$
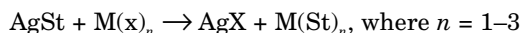
and M is a metal ion (K^+, Ca^{2+}, etc.) or organic compound. The solubility of $CaSt_2$ under these reaction conditions is significantly lower than the solubility of KSt.[11] The organic products of the interaction of AgSt with PHP and NBS

show good solubility. Therefore, in contrast to the treatment of AgSt crystals with solutions of KBr, PHP, NBS, and Br_2, during the treatment of AgSt crystals with solutions of $CaBr_2$ (CaI_2), the precipitation of calcium stearate occurs on the base planes of AgSt crystals along with the formation of AgBr crystals on the lateral faces. The resulting layer of $CaSt_2$ on the (001) AgSt planes prevents the surfaces of the AgSt crystals from interacting with the brominating agent and localizes the exchange reaction on the lateral faces of the silver stearate crystals.

Conclusions

Electron microscope studies of the formation of silver halide crystals during in situ treatment of AgSt crystals with solutions of brominating agents have shown that the formation of AgX crystals occurs on the lateral faces of silver stearate crystals. This localization of the formation of the silver halide phase is associated with the anisotropic structure of the AgSt matrix, i.e., the presence of a layered structure in which the silver layers are separated by long-chain carboxylate groups. We propose that the formation of AgX on the lateral faces of crystals is typical not only of the formation of silver halide on silver stearate, but also of all silver carboxylates of the general formula $[AgC_nH_{2n-1}O_2]_2$, where $n \geq 10$, when the crystals of these silver carboxylates have anisotropic, layered structures.[10,12] ▲

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