Variation in Silver Chloride Morphology as a Function of Silver Iodide Impurity Level

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Abstract

Recent advances in the preparation of silver chloride emulsions show that silver chloride can exhibit a wide range of crystal morphologies similar to the variety known for silver bromide when the appropriate growth modifying ligands and precipitation conditions are employed. This behavior is clearly evident when iodide is used as the growth modifier creating a morphology-iodide level relationship that is similar to the morphology-excess bromide relationship known for silver bromide emulsions. This activity of iodide on silver chloride, along with recent experiments with sodium thiosulfate suggests that even more general relationships may exist between {111} facestabilizing modifiers and the initiation of tabular grains with {100} major faces.

Introduction

The preparation of silver chloride emulsions with enhanced photographic sensitivity continues to be of interest due to the ability of silver chloride based materials to be more rapidly and efficiently developed and stabilized than silver bromide based materials.¹ High surface-to-volume ratio crystal morphologies are an important aspect of achieving higher sensitivity from silver chloride emulsions.² A wide range of preparation methods for both the {111}³⁻²⁴ and {100}²⁵⁻³⁹ tabular crystal morphologies have been reported in the past two decades. Unfortunately, there has been little recent discussion that would tie together common factors among these various processes.^{40,41}

In the case of silver bromide, it is well known that the morphology can be varied widely by predominantly changing the excess bromide level.⁴²⁻⁴⁵ Figure 1 is a diagram of this relationship described by H. R. Wilgus⁴⁵ showing that as the concentration of excess bromide increases (pAg increases), the {111} crystal face becomes dominant. At higher excess bromide levels, twinning occurs to produce morphologies such as the doubly twinned tabular crystal.

This behavior is primarily attributed to the growth modifying properties of the multiple halide silver complexes that increase in concentration with increased excess bromide.⁴³⁻⁴⁵



Figure 1. Diagram of silver bromide as a function of the excess bromide level as described by H.S. Wilgus

Further efforts to create thinner grains or optimize the morphological purity have shown that controlling other factors such as gelatin level and type, supersaturation, and the use of ligands like iodide and ammonia⁴⁶⁻⁴⁸ can shift the relationship shown in Fig. 1.

To prepare high aspect ratio silver chloride morphologies, it has been shown that excess halide alone is insufficient and the use of growth modifiers is essential.^{40,41} The formation of {111}-surface silver chloride tabular crystals has centered on the use of strongly adsorbed organic ligands,⁴⁻²⁴ while the formation of {100}-surface tabular crystals has included both organic growth modifiers and low levels of inorganic ligands like halide, which can create a lattice disruption without destabilizing the {100} face.²⁵⁻⁴⁰ There appears to be little commonality in these growth-modifying processes.

A broader look at the behavior of iodide as a chloride growth modifier suggests that a more general relationship may exist that includes the full spectrum of silver chloride morphologies. Experiments with other ligands known primarily for their ability to stabilize the {111} crystal face suggest that this behavior may be generalized beyond iodide.

Morphology as a Function of Iodide Level

The {111}-face of high chloride emulsions can be stabilized by iodide levels of about 1 mol % or greater allowing the formation of octahedral morphologies.⁴¹ At even higher levels, iodide can also induce twinning to produce doubly twinned {111} face tabular crystals near its solubility limit of 7-mol %.⁴ Considering all the types of silver chloride morphologies produced over the range of iodide levels up to its solubility limit at about 7%, a diagram can be constructed that is similar to that in Fig. 1 for silver bromide. Figure 2 shows the progression of silver chloride morphologies that appear over the roughly 4 decades of iodide impurity levels used to form them.



Figure 2. Silver chloride grain morphologies as a function of the iodide impurity level.

Other Factors

As with silver bromide, secondary factors caused by the influence of the peptizer and the system solubility can strongly influence the activity of the modifying ligand causing the resulting morphologies to shift to different ligand levels or disappear completely.



Figure 3. Silver chloride {111}-faced tabular emulsions made with 7% iodide and oxidized gelatin.

For example, Figs. 3 and 4 show scanning electron micrographs of silver chloride crystals made with 7% iodide as a modifier. In Fig. 3, {111}-faced tabular crystals are formed when oxidized gelatin is used. Figure 4 shows the resulting cubo-octahedra and octagedra when regular (non-oxidized) gelatin is the peptizer.



Figure 4. Silver chloride emulsion made identically to Fig. 3 except regular gelatin was used.

At low levels of iodide, changing from oxidized gelatin in Fig. 5 to regular gelatin in Fig. 6 shows that again the more strongly adsorbed non-oxidized gelatin reduces the influence of the iodide and in this case results in an emulsion with fewer unwanted twinned grains.



Figure 5. {100}-face silver chloride tabular emulsion made with too high an iodide level causing excessive formation of unwanted twinned grains.



Figure 6. {100}-face tabular silver chloride emulsion made identically to the emulsion shown in Fig. 5 except that regular gelatin was used to reduce the twinning effect of the iodide.

The overall solubility of silver in the system also appears to be an important factor. This solubility results from the temperature, excess halide level, and the complexation of silver by the modifying ligands.¹ Table I shows that for the $\{100\}$ -face tabular crystals formed with low levels of iodide, a higher percentage of thinner grains are formed at low excess halide levels (high silver ion potential) where the system solubility is lower.

Table I. Iodide initiated {100}-tabular silver chloride emulsion characteristics as a function of excess halide level and system solubility

Silver ion Potential (mV)	System solubility (moles/liter)	Number percent tabular grains	Grain Thickness (um)
130	2.8x10 ⁻⁵	60	0.36
145 160	2.0x10 ⁻⁵ 1.5x10 ⁻⁵	<u>85</u> 92	0.32
188	1.2x10 ⁻⁵	92	0.19
260	2.5x10 ⁻⁵	77	0.11

The ripening rate of fine crystals or high surface -to-volume crystals is also strongly influenced by the system solubility. If the system solubility is too low, supersaturation will tend to be too high during crystal growth causing the fine crystals to stabilize rather than ripen. Conversely, if the system solubility is too high, excessive ripening may cause the high aspect ratio crystals to ripen into thicker crystals with lower surface-to volume ratio.

Other {111}-Face Stabilizers

The fact the iodide can produce both $\{100\}$ -faced^{2,27} and $\{111\}$ -faced⁴ grain morphologies in silver chloride suggests that a relationship may exist between the factors that stabilize $\{111\}$ crystal surfaces and the formation of the defect responsible for $\{100\}$ -faced tabular crystal growth. Support for this supposition is shown in Figs. 7 and 8 where sodium thiosulfate was used to modify silver chloride precipitations. In this case, higher levels of sodium thiosulfate produced the $\{111\}$ -faced low aspect ratio twinned tabular crystals shown in Figure 7, while at lower levels, the $\{100\}$ -faced tabular crystals shown in Figure 8 were produced



Figure 7. {111}-surface tabular silver chloride crystals made with sodium thiosulfate as a growth modifier



Figure 8. {100}-surface tabular silver chloride emulsion made with sodium thiosulfate as the growth modifier.

Discussion

The variety of morphologies produced by a wide range of iodide levels suggests that a more general relationship exist between crystal morphologies and modifier level, similar to that for excess bromide levels with silver bromide. Iodide ion has a lower electronegativity than chloride or bromide leading to reduce polarity of the silver iodide molecule. This reduced polarity has been implicated as a strong factor in the stabilization of {111} crystal faces and the formation of twinning defects. These properties may also be important in the formation of the defect that causes anisotropic growth in {100}-faced tabular silver chloride. This behavior also appears to occur for other ligands besides iodide suggesting an even more general relationship may exist. Factors, such as the competition for surface adsorption caused by the peptizer or excess chloride ion, and increases in the system solubility caused by the modifier influence these ligand level-morphology relationships.

While many ligands capable of producing both {111}and {100}-faced silver chloride tabular crystals may exist, the fact that iodide is very active at low levels, does not increase system solubility, and enhances spectral and chemical sensitization^{49,50} suggest it is probably the ligand of choice for producing high-aspect-ratio silver chloride emulsions for practical high-speed applications.

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Biography

Thomas Brust received his Bachelor of Science degree in Chemical Engineering from the University of Michigan at Ann Arbor in 1984. He worked as a semiconductor device fabrication engineer at Texas Instruments before joining Eastman Kodak Company in 1985. He has been working as a silver halide materials scientist since 1987 with his primary interest in emulsion crystal architecture and performance.