The Influence of the Precipitation Method on Defect Formation in Multishell AgBrI (111) Tabular Crystals.

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Abstract

Multishell tabular grains have a higher speed than pure AgBr tabular grains. Usually the shells differ in size and iodide content, but also the precipitation method for the iodide containing shells has an influence on the iodide incorporation. A TEM investigation was performed to determine the defect structure of multishell AgBr (111) tabular crystals containing a shell with a low iodide concentration and one with a high iodide concentration. The twins that induce tabular growth and stacking fault contrast in the region of the iodide shells have been observed, similar to previously studied AgBr/Ag(Br,I) core-shell crystals. Moreover in some of the crystals dislocations have been observed, sometimes even an entire network. The number of dislocations formed varies for the different methods of iodide addition. Also variations in average thickness between the different iodide addition methods have been observed. A higher number of dislocations and thicker crystals point towards a higher local concentration of iodide. These observations allow deciding which iodide incorporation method is most useful for a preferred dislocation pattern.

Introduction

High speed of silver halide (111) tabular crystals is achieved by incorporation of phase boundaries[1]. Nowadays complicated structures like multishell Tab-grains are state of the art. Usually the shells of silver halide tabular crystals differ in size and iodide content, but there is another factor influencing the crystallographic and physical properties of the emulsions. The method chosen for the precipitation of the iodide containing shells has a significant effect on the quality of the iodide incorporation into the crystal.

The defects introduced by the growth of one mixed Ag(Br,I)-shell with low (5 – 20% locally) iodide concentration around a pure AgBr core have been investigated by Goessens et al.[2] They argue that the stress introduced by the iodide shell is reduced by the formation of a series of stacking faults parallel to all {11-2} edges. At the core-shell interface there is a strong distortion field with atom displacements perpendicular to the AgBr-AgBrI interface. Occasionally also an edge dislocation is formed propagating from the iodide shell to the corresponding {11-2} edge of the crystal.

In the crystals used in this study, a second shell with high iodide concentration (40% locally) is introduced giving an even higher sensitivity. The defects formed in these crystals are investigated with Transmission Electron Microscopy (TEM). Four different iodide incorporation methods have been used, giving different results. The influence of the iodide precipitation method was investigated and the thickness of the crystals was measured in relation with the defect structure.

Experimental

A double jet method of an $AgNO_3$ and a KBr solution is used to precipitate the crystals and all parameters are similar to those of the precipitation of real photographic emulsions[3,4]. After the precipitation of a pure AgBr core taking 15% of the total amount of silver, a first mixed AgBrI shell is grown with a local iodide concentration of 11%. This shell will from now on be called the low-iodide shell. The growth process is continued with a pure AgBr shell. After this a pure AgI shell is precipitated, taking 4% of the total amount of silver, this shell will be called the high-iodide shell. In practice this shell will be recrystallised to a mixed AgBrI shell with a local concentration of iodide of approximately 40%. The growth process ends with a third shell of pure AgBr. Four different methods have been used for the iodide incorporation. A first method is on-line Lippman crystal addition, which uses a single jet of on-line produced silver iodide Lippman crystals. The second method is the KI-addition method using a single jet of KI. A third method is the in-situ Lippman crystal addition, using alternating a double jet of I and Ag and a single jet of Ag. The last method consists in off-line Lippman crystal addition using a single jet of AgI.

For the preparation of the samples for TEM investigation, 50 µl of the emulsion is diluted in 50 ml of distilled water. A drop of this mixture is placed on a copper grid, covered with a carbon foil. The microscopes used for this investigation are a Philips CM20 and a Philips CM200 microscope both using an accelerating voltage of 200kV. In order to avoid radiation damage the preparation of the specimens and the mounting in the microscope are performed under red light conditions and during examination the samples were cooled with liquid nitrogen in a Gatan double tilt cooling holder. The working temperature was approximately 100 K.

To measure the thickness of the crystals, a shadow technique was used in which a gold layer was sputtered onto the crystal under a small angle. The length of the shadow behind the crystal is proportional to the thickness of the crystals. For the calibration of the length of the shadow, latex balls of 1 micrometer in diameter are added to the emulsion.

Results

The type of defects formed in the multi-shell crystals is similar for the four methods of Lippman crystal addition, but their frequency of occurrence differs for the four samples. All defects observed in the single-shell crystals by Goessens et al.[2] have also been observed in the multi-shell crystals. All crystals have twins parallel to the tabular face,
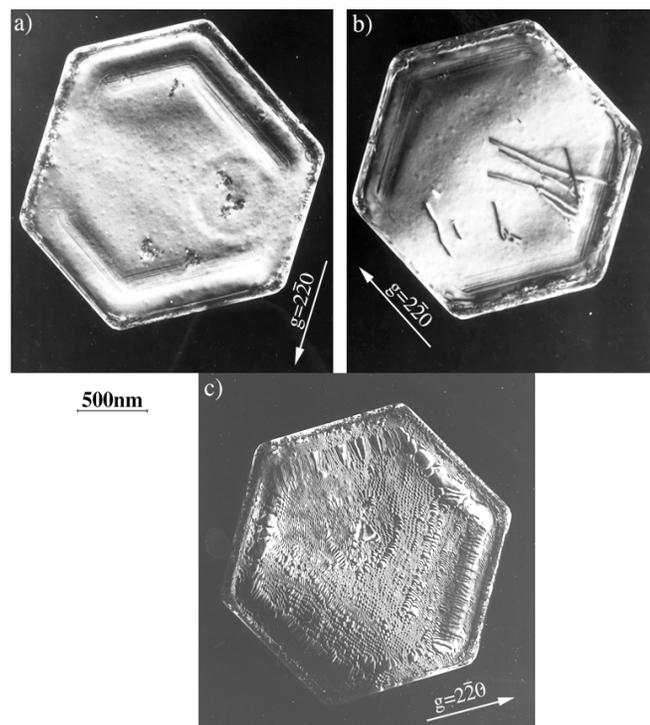
Figure 1. Dark field TEM-images of a) a crystal without dislocations, b) with a limited number of dislocations and c) with a dislocation network.

that have induced the tabular growth and a stacking fault fringe contrast is observed at the location of the low-iodide shell. The contrast induced by the high-iodide shell is more difficult to recognize since it is a very thin shell and it lies at the edge of the crystal where the contrast overlaps with edge fringes observed there.

Three types of defect structures can be distinguished. The first one, like the crystal in figure 1a, contains no dislocations over the center of the crystal, but sometimes a contrast is observed that is due to small inclusions. The second type, like the crystal in figure 1b, contains a limited number of dislocations. The third type, like in the crystal in figure 1c, consists of a whole network of dislocations. Also in many crystals, short dislocations have been observed that propagate from the high-iodide shell to the edge of the crystal. These dislocations were not taken into account for the characterisation of the three types of defect structures.

For each of the four emulsions 33 to 100 crystals have been investigated and the frequency of occurrence of the three types of defect structures was determined. The results are presented in table 1, where the concentrations of each type, are given for the different iodide incorporation methods. The large statistical errors are due to the limited number of crystals that have been examined. 96% of the crystals prepared by on-line Lippman crystal addition contain dislocations. The majority of the crystals contain a limited number of dislocations and 28% of them contain a dislocation network. The method of KI-addition generally produces crystals without dislocations and the least number of dislocation networks. For the in-situ method the three types are almost equally abundant, although the type of crystals with a limited number of dislocations is the smallest. For the fourth method, the offline Lippman crystal addition method, again most crystals contain dislocations, but different from the first method, the crystals with a network or a limited number of dislocations occur equally abundant.

Table 1: relation between iodide incorporation method and dislocation formation

sample	no	limited	network	Total
online	$4 \pm 2\%$	$68 \pm 5\%$	$28 \pm 5\%$	100
KI-addition	$61 \pm 8\%$	$28 \pm 8\%$	$11 \pm 5\%$	36
in situ	$37 \pm 7\%$	$23 \pm 6\%$	$40 \pm 7\%$	52
offline	$9 \pm 5\%$	$45 \pm 9\%$	$45 \pm 9\%$	33

In a second experiment, the relation between the thickness of the crystals, the occurring defects and the method of iodide addition was investigated. The shadow technique reported before was used to measure the thickness. The gold layer introduces extra contrast, which troubles the interpretation of the defect contrast, but in many cases the three types of defect structures can still be distinguished. The crystal in figure 2a contains no extra dislocations, while the crystal in figure 2b contains a dislocation network. For some other crystals it was not clear to which type they belong and they were not taken into account for the measurement of the thickness.
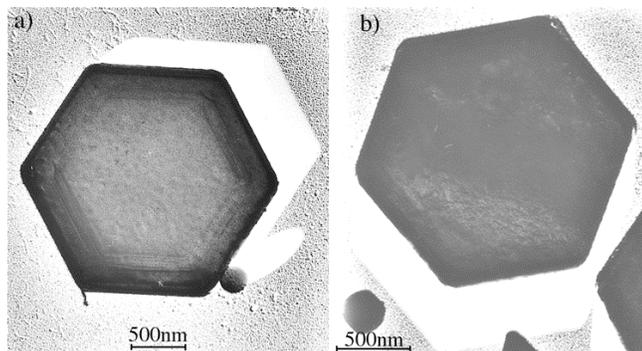
Figure 2. Bright field images of crystals covered with a gold layer to measure the thickness. a) A crystal without dislocations, b) a crystal with a dislocation network.

Table 2: relation between thickness, dislocations and iodide incorporation method.

Sample	Property	No	limited	network
online	Thickness (nm) aspect ratio	184±12 14.5±1.5	206±3 9.4±0.4	216±4 8.73±0.5
KI-add.	Thick(nm) aspect	166±10 13.4±1.3	193±8 13.4±1.6	203±6 11.9±1.1
in situ	Thick(nm) aspect	194±7 10.0±0.9	215±6 9.7±0.6	239±10 9.9±0.7
offline	Thick(nm) aspect	150±7 16.0±1	161±7 13.8±0.8	171±5 14.8±1

The results of the thickness measurements as a function of defect structure and iodide incorporation method are summarised in table 2, in which the average thickness of each type is represented as well as the corresponding aspect ratios. For each value, 10 to 15 crystals have been averaged. For all incorporation methods it was found that the thickness of crystals with a network is larger than or equal to that of crystals with a limited number of dislocations, which are thicker than crystals with no dislocations. This is valid for the absolute thickness as well as for the aspect ratios. Further it was observed that the in-situ method produces the thickest crystals followed by the on-line method, the potassium iodide method and finally the offline Lippman crystal addition method produces the thinnest crystals. This result applies for the three defect structures and is not due to the fact that for some method more dislocation free crystals, which means thinner crystals, are formed than with other methods. The observed differences are in most cases larger than the statistical error. These results are valid for the average thickness, so individual crystals with a dislocation network can be thinner than some individual crystals with no dislocations.
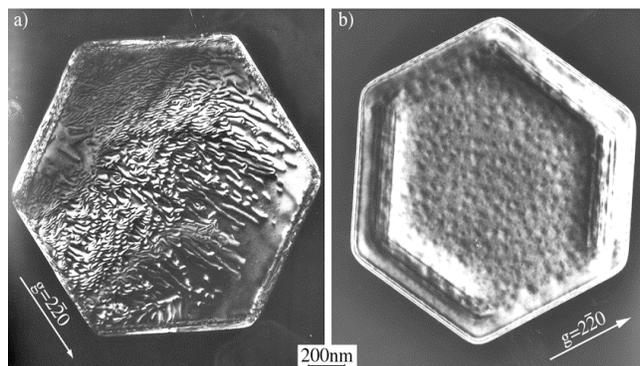
Figure 3a) Dark field TEM-image of a crystal without low-iodide shell, containing a dislocation network and b) dark field TEM-image of a crystal without high-iodide shell.

Furthermore, the relation between the iodide shells and the present defects was investigated. Two emulsions have been precipitated under the same conditions using the same iodide incorporation method as for the sample with the offline Lippman crystal addition, but without the addition of the low-iodide shell or the high-iodide shell respectively. In figure 3a an example of a crystal without the low-iodide shell is shown. The fringe contrast of the low-iodide shell has disappeared, but still crystals without dislocations, with a limited number of dislocations and with a dislocation network are present. The emulsion without the high-iodide shell contains crystals like in figure 3b. The stacking fault contrast due to the low-iodide shell is again visible, but the removal of the high-iodide shell is not so clear in the TEM-images. However, in this emulsion most crystals contain no extra dislocations and hardly any dislocation networks have been observed.

Table 3: relation between iodide shells and dislocation formation

Lippman crystal add.	no dislocations	limited number	network
low & high	9 ± 5%	45 ± 9%	45 ± 9%
high	16 ± 5%	44 ± 7%	40 ± 7%
low	64 ± 6%	32 ± 6%	4 ± 2%

A statistical analysis is given in table 3. The first line belongs to the emulsion with both shells, and is actually the same as the last row in table 1. 91% of the crystals contain dislocations and crystals with a limited number of dislocations and those with the dislocation networks are equally abundant. The results for the crystals containing only the high-iodide shell indicate that the number of networks and limited number of dislocations have slightly decreased, and the number of dislocation free crystals has increased. The difference in number is smaller than the statistical error for all three types, but there is a tendency to form more crystals without dislocations. These measurements indicate that the omission of the low-iodide shell results in a slight decrease of the number of dislocations. On the other hand, the crystals containing only the low-iodide shell show a significant decrease of the

number of dislocations formed. The majority of the crystals contain no dislocations, while hardly any crystals with a dislocation network occur. The number of crystals with a limited number of dislocations has only decreased slightly.

Discussion

The results of table 3 clearly indicate that the addition of the high-iodide shell is the most important factor in the formation of the dislocations and dislocation networks. Also the low-iodide shell has an influence on the defect formation, but its influence is less pronounced. The mixed silver bromo-iodide shell has a larger lattice parameter than pure silver bromide and this difference in lattice parameter results in large stresses at the interface. For low iodide concentrations the introduction of stacking faults reduced the stress, but as of a certain iodide concentration this stress will be too large and misfit dislocations have be formed that compensate for these stresses. The occurrence of the different concentrations of dislocations can be due to fluctuations in the local iodide concentration between the different crystals. A lower local iodide concentration means a smaller difference in lattice parameter and a lower number of dislocations necessary for the compensation of the stress.

The results also indicate a relation between the method of iodide addition and the observed crystal thickness and this can be correlated to the expected effective iodide incorporation of the different methods. It has been observed that the incorporation of a mixed bromo-iodide shell leads to an increase of the thickness of the crystals[5]. The stacking faults formed in the iodide containing shell introduce permanent steps on the top surface, inducing thickness growth. A higher iodide concentration results in a larger number of surface steps and then the thickness growth occurs at a higher speed. The in-situ method is believed to produce the smallest Lippman crystals in a reactive environment. This should lead to the best incorporation of iodide. This investigation has shown that these crystals are the thickest crystals, but with an equal distribution of the three defect structures. In the on-line addition method, the Lippman crystals have grown a bit larger, but are still expected to give a reasonably good incorporation of iodide. It was shown that these crystals are also thick crystals, although a bit thinner than the in-situ method, and that in many crystals dislocations are introduced, but not so many dislocation networks. For the third method, offline Lippman crystal addition, the Lippman crystals were produced in advance and are larger than for the first two methods. It is therefore believed that they can only react at the side faces. This addition method resulted in the thinnest crystals, but still a large number of crystals contain dislocations, a limited number as well as dislocation networks. The fourth method, potassium iodide addition, is believed to give the quickest incorporation of iodide. It was determined that these crystals are also thin crystals, and that only a minority of the crystals contains dislocations. This explanation indicates that a better incorporation of the iodide leads to an increase of the thickness of the crystals.

The relation between the incorporation method and the defect structure does not always agree with the hypothesis presented above. It was found that a higher expected local iodide concentration does not always result in crystals containing a higher number of dislocations and dislocation networks. This hypothesis corresponds very well with the results for the potassium iodide method, which are indeed expected to give rise to crystals that have the smallest number of dislocations. On the other hand the in-situ method is expected to produce crystals with the highest number of dislocations, but this does not correspond with the results of table 1, while the Lippman crystal addition method introduces too many dislocations, according to the expected incorporation of iodide. This indicates that not only the local iodide concentration determines the formation of dislocations, but also other factors, like the homogeneity of the iodide distribution and the iodide incorporation kinetics.

Conclusions

The defect structure of multishell AgBr (111) tabular crystals, with one low-iodide shell and one high iodide shell was investigated. Apart from the usual defects in (111) tabular crystals also dislocations are formed. The formation of the dislocations is mainly due to the incorporation of the high iodide shell, while the low-iodide shell has only a limited influence. Three types were distinguished, one without dislocations, one with a limited number of dislocations and one with a network of dislocations. It was shown that the number of dislocations formed depends on the iodide incorporation method, but no direct mechanism of dislocation formation could be established as yet. Further it was measured that the average thickness of crystals with more dislocations is larger than for crystals without dislocations. These results could be correlated to the incorporation method of the iodide in the crystal.

References

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Biography

Wouter Van Renterghem is a PhD student at the EMAT laboratory of the University of Antwerp. He has studied physics at the same university from which he graduated in 1996. The subject of his research is the characterisation of silver halide microcrystals with transmission electron microscopy. This work is in collaboration with Agfa-Gevaert, Mortsel and is financially supported by the Flemish institute for the encouragement of the scientific and technological research in the industry (IWT).