Effects of Iridium Doping in Cubic and Octahedral AgBr Grains on the Latent Image Formation Process

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Effects of iridium doping on the differences in photographic behavior between cubic and octahedral AgBr grains have been investigated. The experimental AgBr grains were prepared without spectral or chemical sensitization. The iridium ions were incorporated into the major shell region of each grain (shell/core = 36/1) with different concentrations of iridium (0 ~ 10^{-5} mol Ir/mol Ag). Regardless of the iridium doping amount, it was observed that latent images of cubic grains are almost all located at the surface, while in octahedral grains some latent images are also located inside the grains. These features are explained by relating the latent image position to the potential difference across the space charge layer in octahedral and cubic grains. Undoped octahedral grains exhibited reduced effectiveness in latent image formation than undoped cubic grains. Introduction of iridium doping (with a concentration of 10^{-6} mol Ir/mol Ag) remarkably eliminates this reduced effectiveness observed for octahedral grains. In addition, iridium doping gives the octahedral grains a higher sensitivity increase during delayed latent image formation, compared to cubic grains. Such behavior is discussed in terms of a greater number of electrons being temporarily trapped by iridium centers.

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Introduction

Metal dopants have often been incorporated into silver halide grains in order to manipulate their photographic behavior. For example, complexes of iridium, rhodium or iron have been used for various purposes. Among these complexes, iridium salts have particularly been investigated in detail in relation to their photographic and physical effects.[1] As typical examples of the photographic effects of iridium, it is well known that iridium doping affects high-intensity reciprocity failure[2] or delays latent image formation.[3] Depending upon the iridium level, the latent image formation process can even continue for several days.[4]

In order to explain these photographic features, it has been proposed that iridium can act as an electron trap[3] or as a hole trap.[2,3] By combining ESR measurements with studies on the rate of delayed latent image formation, the role of doped iridium was elucidated more precisely.[4–6] Discussion of the role of doped iridium was consequently more focused on how iridium can trap and release electrons, and how it is involved in the process of delayed latent image formation.[4–6]

It was reported that iridium doping in AgBr or in AgCl grains results in different kinetic properties (decay time, activation energy, etc.).[4,6] These facts suggest that the environment surrounding the doped iridium is important for controlling the process of latent image formation. It was also reported that different shapes of AgBr grain exhibit different physical properties, for example ionic conductivity[7,8] and concentration of R-centers.[9] Therefore it appeared interesting to investigate how iridium doping effects the latent image formation of AgBr grains of different shapes because interaction of doped iridium ions with electrons may be different between octahedral and cubic grains.

In this article, the some significant differences in photographic behavior between cubic and octahedral AgBr grains will be presented. Next it will be shown how iridium doping affects these differences in photographic behavior. Some remarkable differences in the effectiveness of latent image formation and in delayed latent image formation will be discussed.

Experimental

Sample Preparation

Two different types of silver bromide grains were prepared: cubic AgBr and octahedral AgBr. Cubic AgBr grains were precipitated at a pH of 4 and a pAg of 6.1, using a controlled, double jet technique. The edge length was 0.3 µm. Octahedral AgBr grains were of same size but were precipitated at a pAg of 7.8 (pH also 4).

Iridium doping was carried out by addition of potassium hexachloroiridate into the bromide solution, added during crystal formation. The iridium was incorporated into the major shell region of the crystals (shell/core =

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36/1) in both cubic and octahedral grains. The grains were not spectrally or chemically sensitized.

In order to investigate the effect of R-centers on delayed latent image formation, reduction sensitization was applied to octahedral grains containing iridium (10^{-6} mol Ir/mol Ag) using DMAB (dimethylamine borane). The DMAB concentration was varied from 0 to 10^{-4} mol/mol Ag. These grains were ripened for 1 hr at 60°C with DMAB. AgBr emulsions were coated on cellulose triacetate base at a coating weight of 4.3 g Ag m^{-2}.

Sensitometric Evaluation

The coated samples were exposed to a tungsten lamp (color temperature 2856K) for 5 sec through a continuous wedge. After exposure, samples were aged at room temperature (15 sec until 48 h), then developed totally by use of a mixture of MAA-1[10] and thiosulfate for 10 min at 23°C. Densities of developed samples were measured using a TCD-MK2 densitometer (Wakasa Optical Institute). To illustrate the behavior of delayed latent image formation, value of Log E giving the density of 1/2 D_{max} in the characteristic curve is plotted versus the delay time from exposure to development.

Surface development was carried out with MAA-1[10] only. For some selected samples, an internal development was done with a bleaching procedure before development with MAA-1 and thiosulfate. The bleach solution consisted of K_3FeCN_6 (3 g/L) and phenosafranine (0.0125 g/L); bleaching time was 10 min at 23°C.

Latensification

A gold latensification method and a double exposure method were both applied in order to demonstrate the existence of sub-latent image centers. In the case of gold latensification, the coated samples were treated with a 1×10^{-4} M gold solution for 30 sec, just before development. The gold solution comprised of $HAuCl_4 \bullet 3H_2O$ (0.14 g/L), 1N KSCN (5.2 cc/L) and NaCl (1.8 g/L).

For the double exposure method, coated samples were first exposed using the same procedure described above. After this first exposure, a second blanket exposure was given 15 sec prior to development. The second exposure time was 5 sec, as well. The second exposure intensity was determined as yielding a density of 0.02 above base plus fog in the absence of a first exposure.

Photoconductivity Measurement

Electron lifetime measurements were carried out using a microwave photoconductivity technique, employing a Q-band reflection instrument. The third harmonic of a Nd:YAG pulsed laser (355 nm) was used for exposure of the coated sample. Duration of the laser pulse was 3 nsec.

Results

Photographic Behavior of Cubic AgBr with Different Concentrations of Iridium

The sensitometric results obtained for cubic grains after 60 min aging from exposure to development are shown in Fig. 1. As can be seen in this figure, the incorporation of $IrCl_6^{2-}$ up to a level of 10^{-7} mol Ir/mol Ag results in a sensitivity increase. Further increase of the iridium amount yields a severe loss of sensitivity. Such desensitization begins with an iridium concentration of 10^{-6} mol Ir/mol Ag.

Delayed Latent Image Formation. For investigating delayed latent image formation, the delay time between exposure and development was varied from 15 sec to 48 h. Some typical results are shown in Figs. 2a ~ 2c. Figure 3 shows values of Log E giving densities of 1/2 D_{max} at different delay times. In the case of a low level of doped iridium (0 ~ 10^{-7} mol Ir/mol Ag), the delayed formation of latent image scarcely occurs, as can be seen in Fig. 2a and Fig. 3. In the case of a medium level of iridium (10^{-6} mol Ir/mol Ag), a slight enhancement of latent image formation is observed during the first 10 min after exposure (see Fig. 2b and Fig. 3). After reaching its maximum value, the sensitivity slowly decreases, that is, latent image fading occurs.

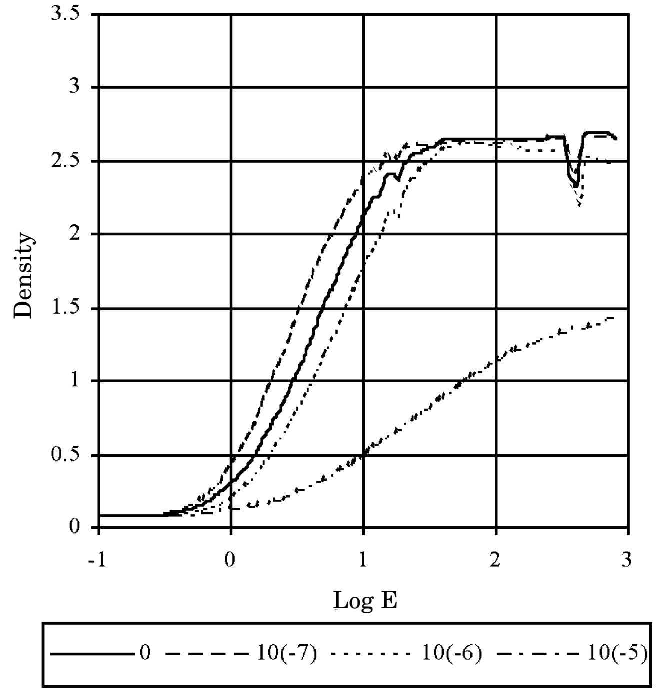

Figure 1. Sensitometric consequences of incorporation of $[IrCl_6]^{2-}$ into cubic AgBr. $[IrCl_6]^{2-}$ concentration in mol/mol Ag.

As shown in Fig. 2c, in case of a high level of doped iridium (~10^{-5} mol Ir/mol Ag), a tremendous loss of sensitivity is observed. However a slow but distinct increase in sensitivity is still detected on aging.

Location of Latent Image. In order to determine the location of latent images, the density after total development was compared to the density after surface development. The density difference between total and surface development corresponds to the density produced by the internal images. Such differential results for cubic grains are presented in Fig. 4. The difference in the density between total and surface development is found to be small and independent of iridium concentration. This indicates that only a very small fraction of latent image is located inside cubic grains. In addition, more direct evidence concerning the latent image location will be shown later.

Behavior of Octahedral AgBr with Different Concentrations of Iridium

The sensitometric results obtained for octahedral grains after 60 min aging from exposure to development are shown in Fig. 5. With no iridium doping, the sensitivity of octahedral AgBr grains is rather low compared to that of cubic AgBr grains. On the other hand, the increase of sensitivity with increasing amounts of doped iridium (0 – 10^{-6} mol Ir/mol Ag) is more dramatic, compared to the results with cubic grains.

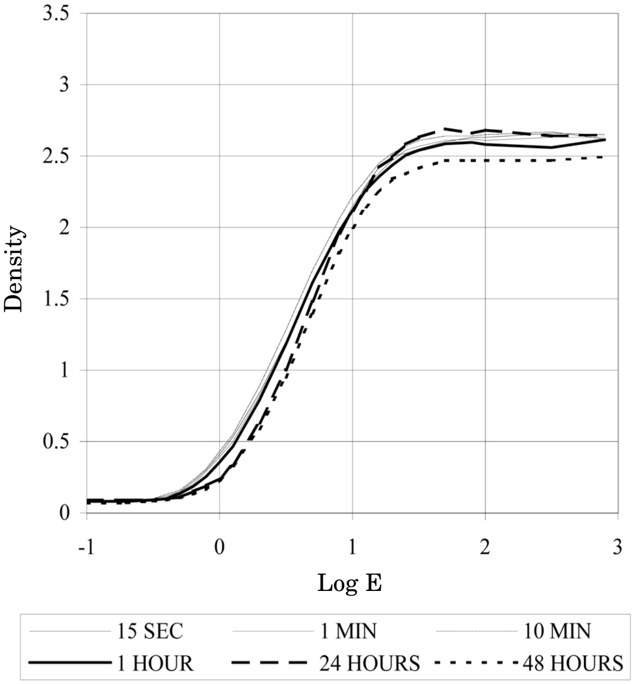

Figure 2a. Sensitometric behavior of cubic AgBr without iridium doping at different delay times between exposure and development.

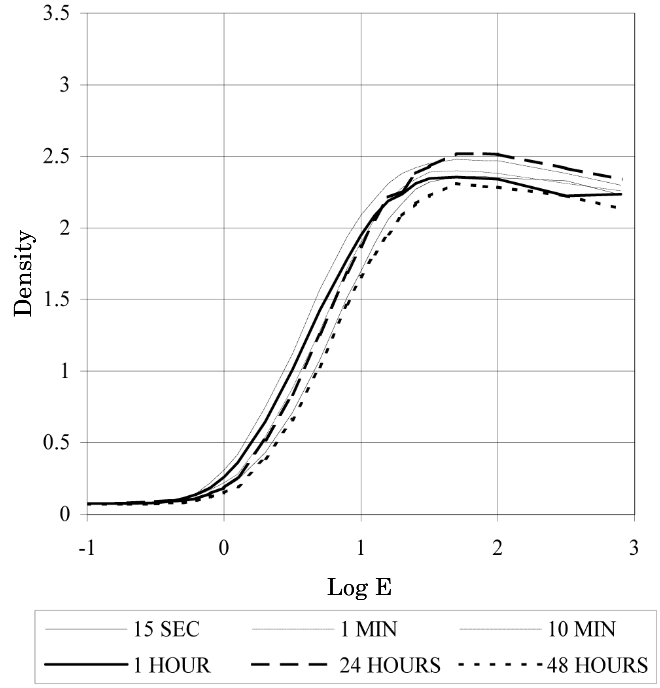

Figure 2b. Sensitometric behavior of cubic AgBr with 10^{-6} mol $[IrCl_6]^{2-}$/mol Ag at different delay times between exposure and development.

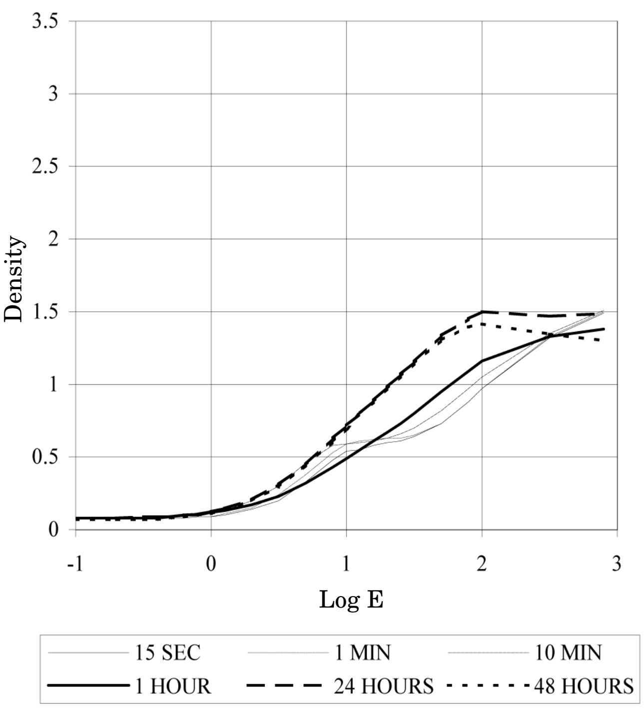

Figure 2c. Sensitometric behavior of cubic AgBr with 10^{-5} mol $IrCl_6^{2-}$/mol Ag at different delay times between exposure and development.

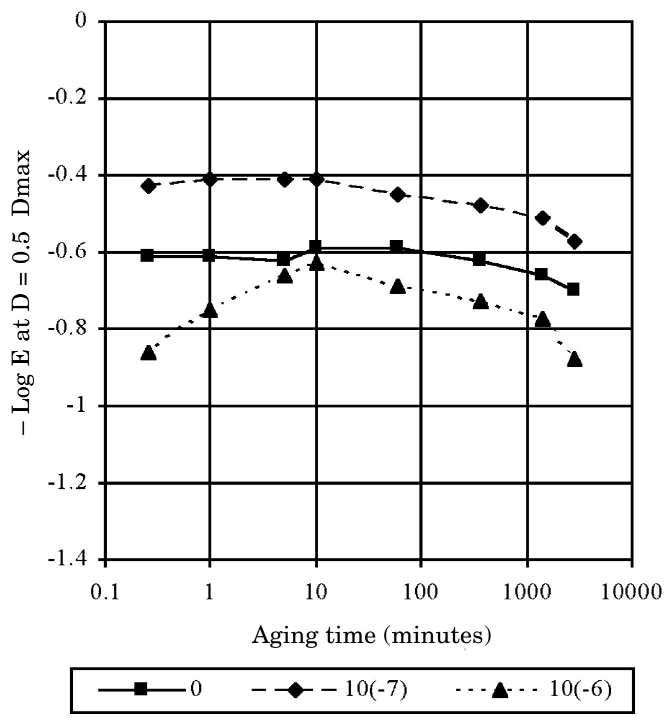

Figure 3. Sensitivity of cubic AgBr with different levels of $IrCl_6^{2-}$ at different delay times between exposure and development. $IrCl_6^{2-}$ concentration in mol/mol Ag.

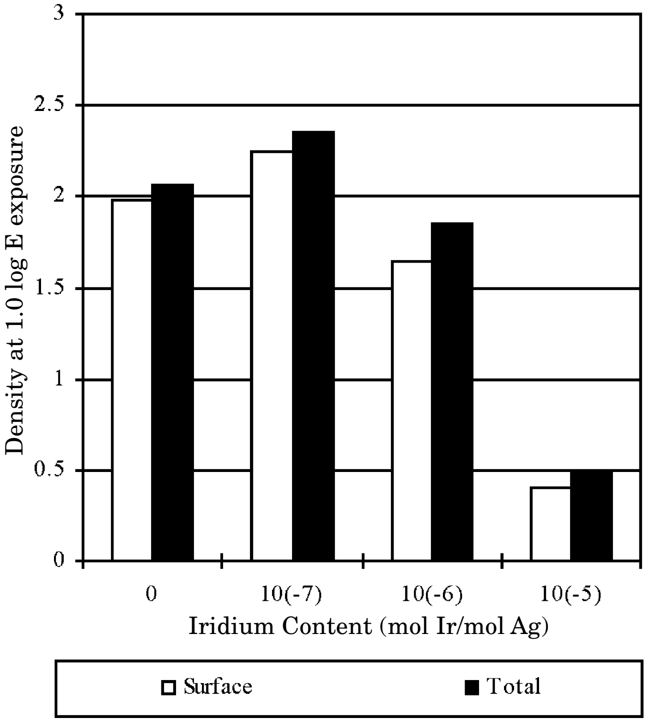

Figure 4. Surface and total development of cubic AgBr with different levels of $IrCl_6^{2-}$. $IrCl_6^{2-}$ concentration in mol/mol Ag.

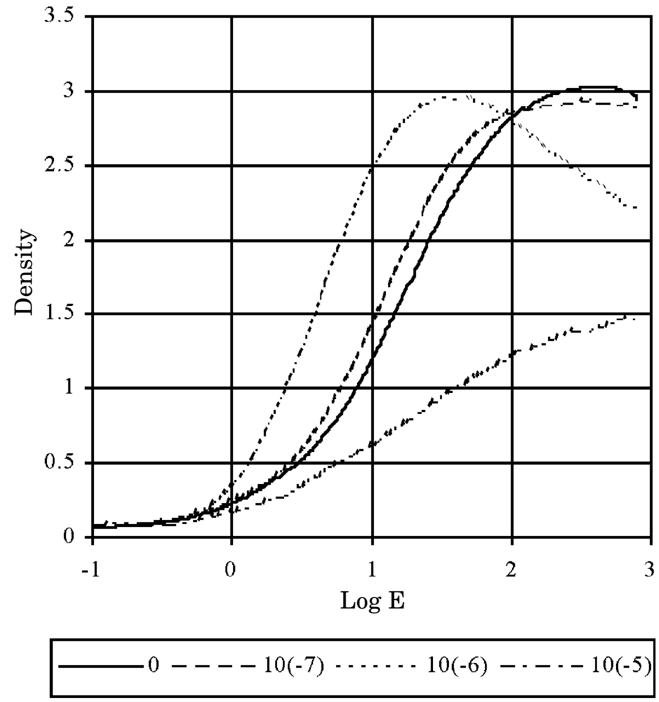

Figure 5. Sensitometric consequences of incorporation of $IrCl_6^{2-}$ into octahedral AgBr. $IrCl_6^{2-}$ concentration in mol/mol Ag.

Delayed Latent Image Formation. Figures 6a through 6c present some typical results of delayed latent image formation. Figure 7 shows the values of Log *E* obtained by the same method as for cubic grains at different aging time (15 sec to 48 h) between exposure and development (corresponding to Fig. 3). With no iridium, the sensitivity increase after aging is not visible. However, with iridium doping, especially at the concentration of 10^{-6} mol Ir/mol Ag, a striking delayed latent image formation can be observed, as shown in Fig. 6b and Fig. 7. After reaching maximum sensitivity at 1 h after exposure, rapid fading of latent image occurs. In case of higher iridium concentration (10^{-5} mol Ir/mol Ag), a slow but definite enhancement of latent image is observed with increasing aging time between exposure and development.

Location of Latent Image. Comparison between total and surface development is presented in Fig 8. As observed for cubic grains, the density difference between total and surface developments looks independent of the iridium concentration. However this density difference for octahedral grains is much larger than for cubic grains. It indicates that the number of latent images located internal to octahedral grains is much greater than for cubic grains. In order to confirm this feature more directly, the sensitometric results obtained by internal development are shown in Fig. 9, including results with cubic grains. These results definitely indicate that more latent images are present in the interior of octahedral grains than in the interior of cubic grains.

Analysis of Differences in Photographic Behavior Between Octahedral and Cubic AgBr Grains

Determining the Presence of Sub Latent Images

It is known that the interstitial silver ion concentration in octahedral AgBr grains is higher than in cubic AgBr grains by one order of magnitude.[7] The higher interstitial silver ion concentration may cause increased dispersion of latent image, i.e., formation of sub-latent images. In order to determine if the lower sensitivity of undoped octahedral grains compared to undoped cubic grains is caused by latent image dispersion, a gold latensification method was applied to the octahedral grains. As can be seen in Fig. 10, gold treatment of undoped octahedral grains does not lead to any significant increase of sensitivity. The gold latensification was also used to ascertain the cause of the striking delayed latent image formation over the first 10 min after exposure of iridium doped octahedral grains (10^{-6} mol Ir/mol Ag). Figure 10 reveals that during the first 10 min after exposure the gold treatment does not give any additional increase in sensitivity. Only in the region where latent image fading occurs (at aging times longer than 1 h), does the gold treatment show its latensification effect, resulting in a higher sensitivity for iridium-doped octahedral grains.

To confirm furthermore whether or not sub-latent images are involved in the process of the delayed latent image formation, a double exposure method was applied to the same iridium doped octahedral grains. As can be seen in Fig. 11, the double exposure does not give any additional increase in sensitivity under conditions of delayed latent image formation. On the other hand, it shows a latensification effect after 1 h aging. The results obtained by the double exposure method and those obtained by the gold treatment are thus the same.

Analysis of Latent Image Fading. To investigate the cause of latent image fading after long aging (longer than 1 h between exposure and development), exposed samples were aged *in vacuo*. The results obtained for octahedral grains with 10^{-6} mol Ir/mol Ag are shown in Fig. 12. The samples kept under vacuum do not exhibit the fading of the latent image that was observed under ambient conditions.

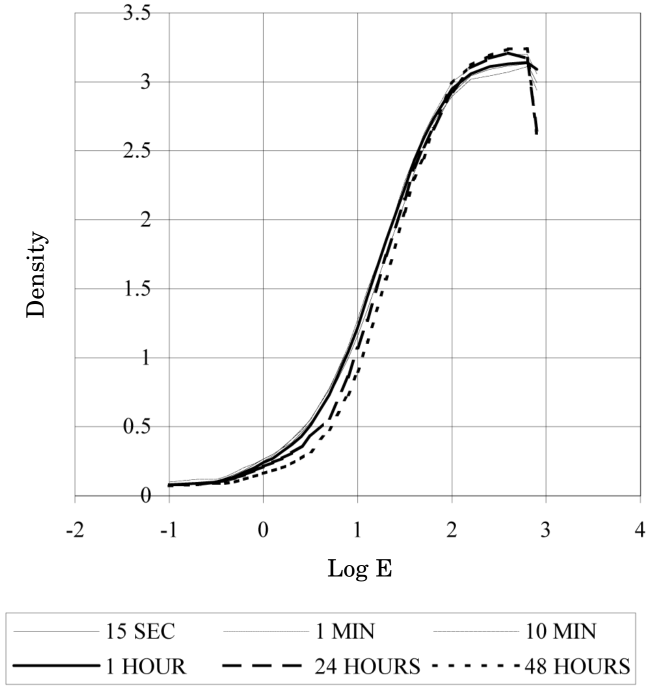

Figure 6a. Sensitometric behavior of octahedral AgBr without iridium doping at different delay times between exposure and development.

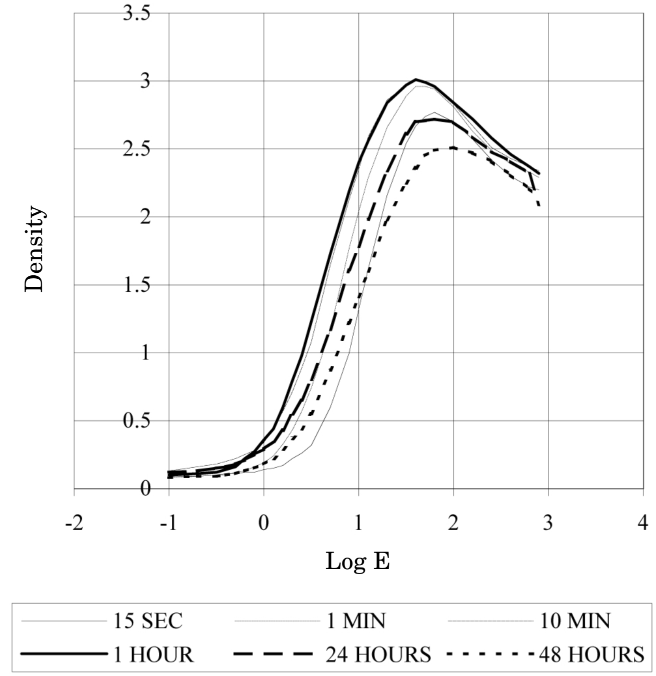

Figure 6b. Sensitometric behavior of octahedral AgBr with 10^{-6} mol $IrCl_6^{2-}$/mol Ag at different delay times between exposure and development.

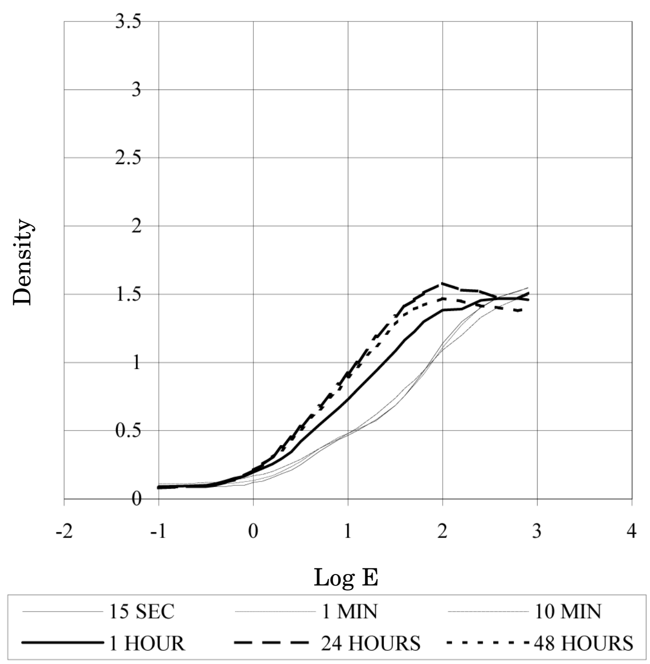

Figure 6c. Sensitometric behavior of octahedral AgBr with 10^{-5} mol $IrCl_6^{2-}$/mol Ag at different delay times between exposure and development.

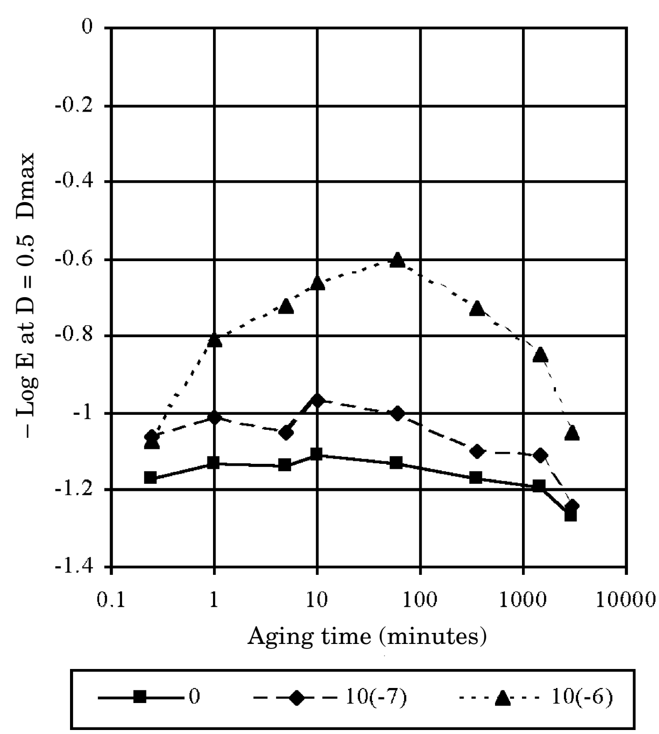

Figure 7. Sensitivity of octahedral AgBr with different amounts of $IrCl_6^{2-}$ at different delay times between exposure and development. $IrCl_6^{2-}$ concentration in mol/mol Ag.

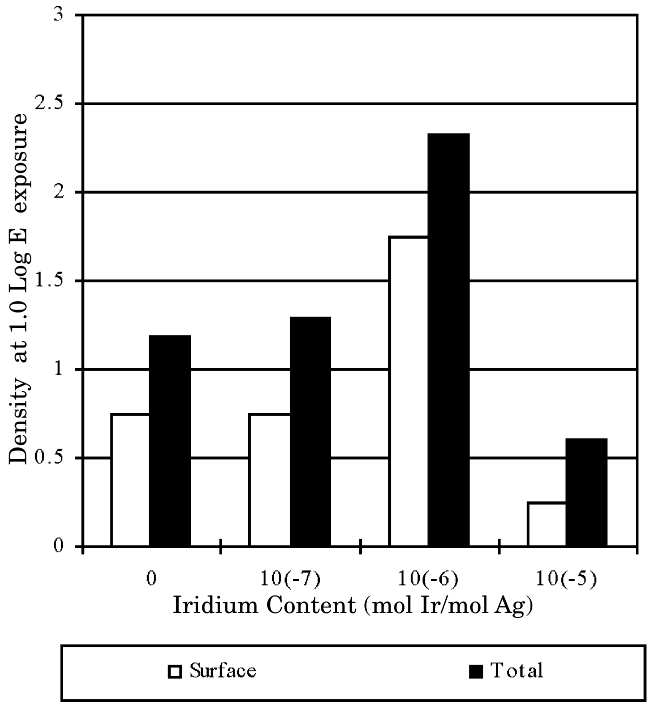

Figure 8. Surface and total development of octahedral AgBr with different amounts of $IrCl_6^{2-}$. $IrCl_6^{2-}$ concentration in mol/mol Ag.

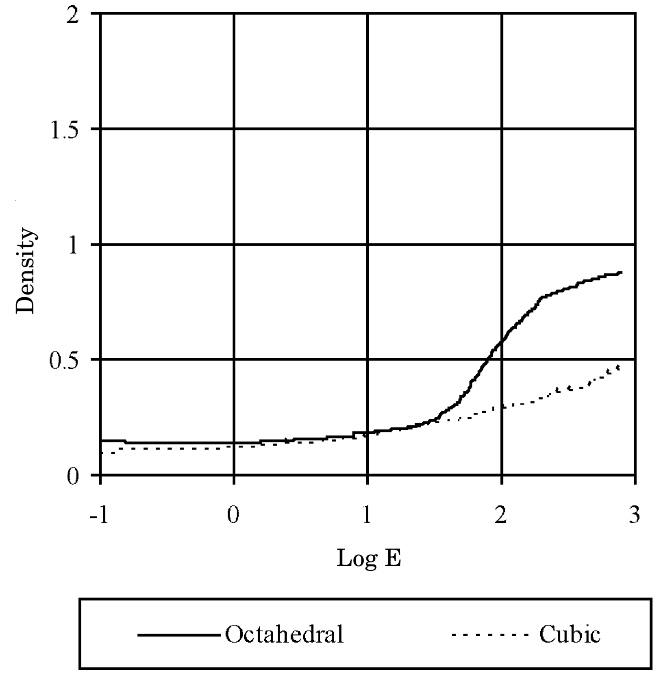

Figure 9. Internal development of cubic and octahedral AgBr doped with 10^{-6} mol $IrCl_6^{2-}$/mol Ag

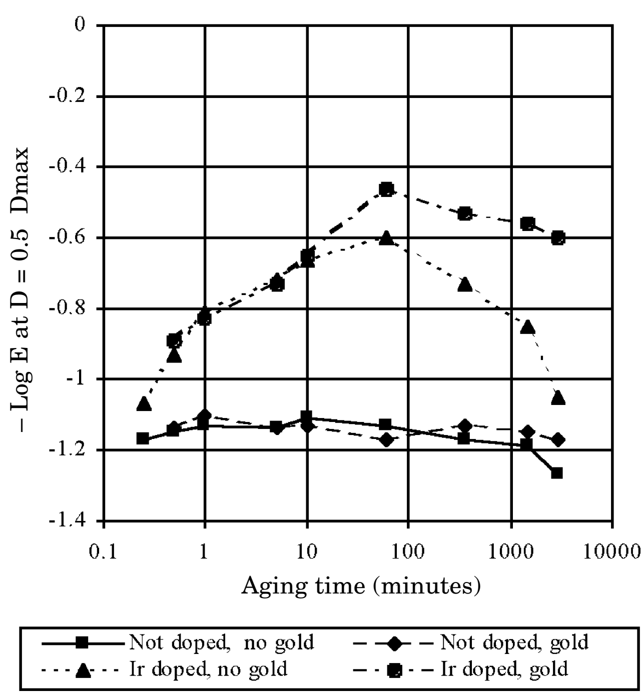

Figure 10. Gold latensification of octahedral AgBr with 10^{-6} mol $IrCl_6^{2-}$ per mol Ag and without doping.

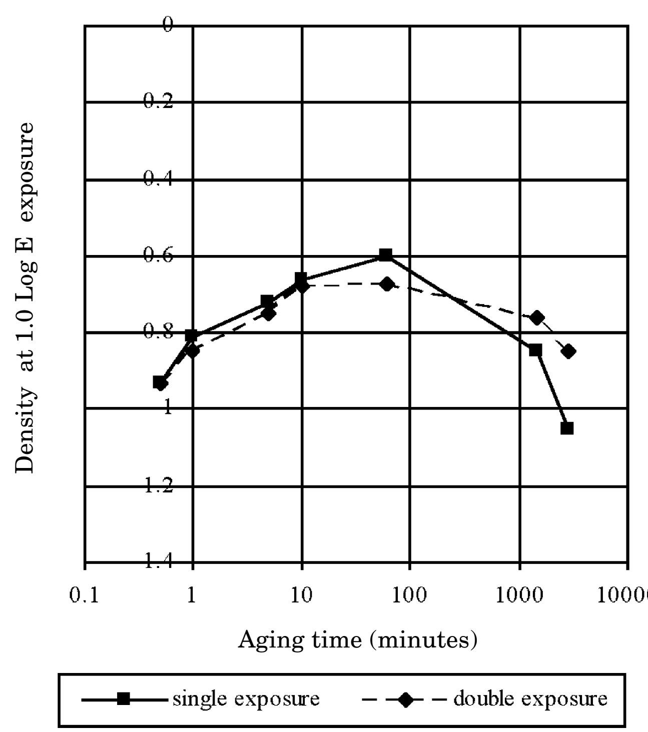

Figure 11. Latensification of octahedral AgBr with 10^{-6} mol $IrCl_6^{2-}$ per mol Ag with and without double exposure.

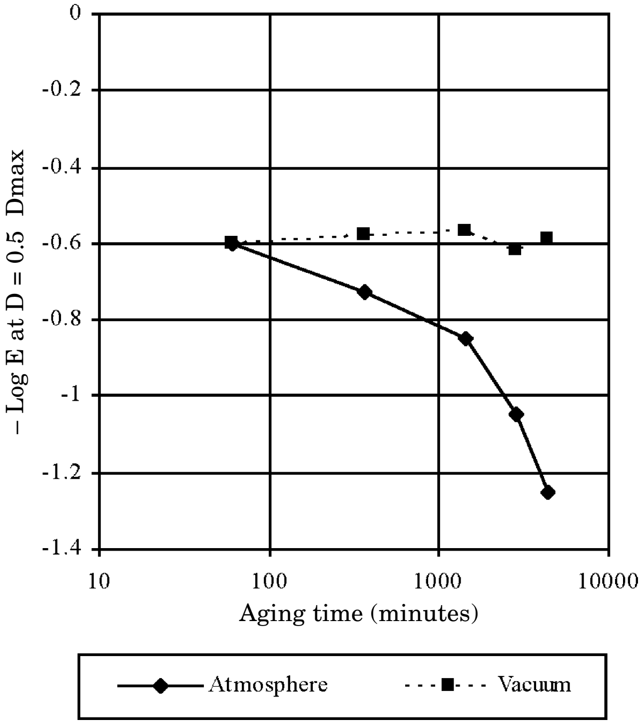

Figure 12. Sensitometric behavior of octahedral AgBr with 10^{-6} mol $IrCl_6^{2-}$ per mol Ag and under vacuum.

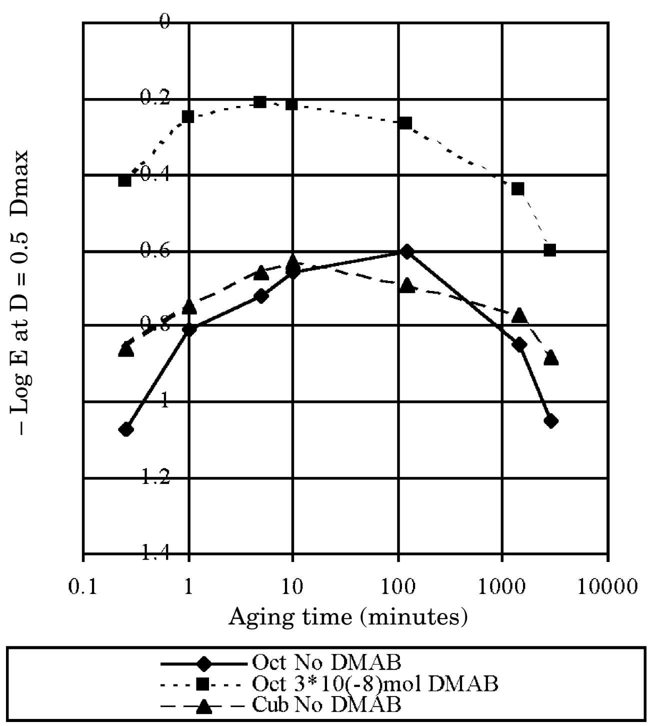

Figure 14. Effect of reduction sensitization in octahedral AgBr on retarded latent image formation. All grains contain 10^{-6} mol $IrCl_6^{2-}$ per mol Ag.

Introduction of R-centers using DMAB. For octahedral grains with 10^{-6} mol Ir/mol Ag, R-centers were introduced using the reduction agent DMAB. Photoconductivity measurements were executed on the coated samples of the octahedral grains treated with different

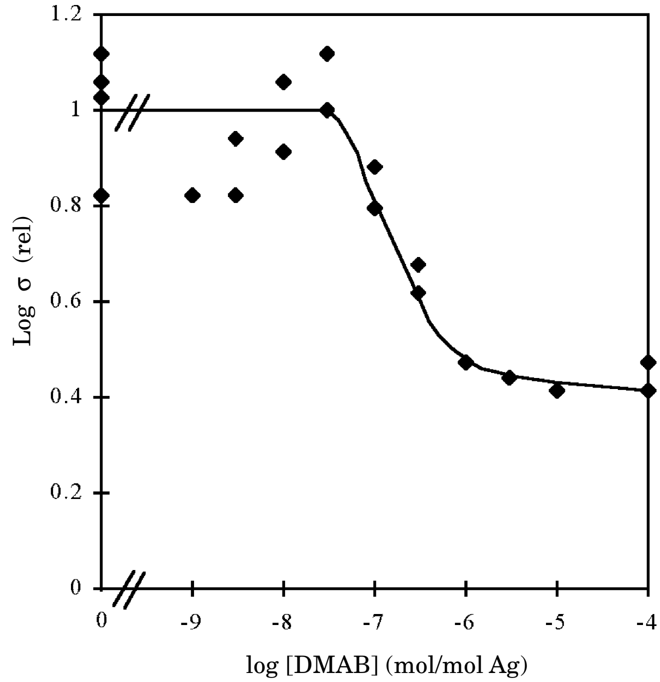

Figure 13. Photoconductivity of reduction sensitized octahedral AgBr grains containing 10^{-6} mol $IrCl_6^{2-}$ per mol Ag.

concentrations of DMAB. Based on the photoconductivity results shown in Fig. 13, the concentration of 3×10^{-8} mol DMAB/mol Ag was determined as the maximum giving R-centers without additional introduction of P-centers, using the same procedure reported by Tani.[11]

In Fig. 14, the delayed latent image formation results are presented for three different grains: octahedral grains with DMAB (3×10^{-8} mol/mol Ag), octahedral grains without DMAB and cubic grains without DMAB. All three grains contain the same amount of iridium (10^{-6} mol Ir/mol Ag). This figure indicates that by applying DMAB to octahedral grains, the maximum density is reached after only 10 min, as observed in cubic grains, although the absolute density becomes much higher than that of cubic grains. Also the relative increase of the density during the delayed latent image formation is close to that of cubic grains without DMAB and not so large as in octahedral grains without DMAB.

Discussion

Reactions Concerned with Latent Image Formation.

It is known that an iridium center doped into silver halide grains can play a role as a temporary trap for photoelectrons.[3] For discussing the latent image formation process involving doped iridium, it is important to consider the following basic reactions. These reactions will occur successively and/or competitively.

Reaction 1: the reversible trapping of electrons by iridium centers.

$$e^- + Ir^{3+} \longrightarrow Ir^{2+}$$

$$Ir^{2+} \longrightarrow e^- + Ir^{3+}$$

Reaction 2: the reversible reaction of electrons with interstitial silver ions.

$$e^- + Ag_i^+ \longrightarrow Ag^0 \ (\longrightarrow Ag_n)$$

$$Ag^0 \longrightarrow e^- + Ag_i^+$$

Reaction 3: the irreversible recombination of electrons with positive holes.

$$e^- + h^+ \longrightarrow \text{recombination}$$

Reaction 4: the irreversible destruction of latent images.

$$Ag_n \longrightarrow n\, Ag_i^+ + n\, e^-$$

In Reaction 2, electrons are both photogenerated on exposure and also by detrapping from iridium centers. These electrons contribute to the formation of Ag^0, (and finally latent image center; Ag_n with $n \geq 4$). Recently it has been reported that electrons contributing to latent image formation are not directly supplied from iridium centers, but by decomposition of Ag^0 formed near the iridium center.[4] However, in this article, a simplified model is adopted for the sake of its convenience.

Difference in Photographic Behavior Between Cubic and Octahedral Grains Without Iridium Doping

In the case where no iridium is incorporated, photoelectrons can only be trapped via Reaction 2 to form latent images, or recombine with positive holes via Reaction 3. The comparison of Figs. 1 and 5 show that the sensitivity of the octahedral grains is much lower than that of cubic grains when iridium is not incorporated. This difference in sensitivity indicates that the latent image formation process in octahedral grains is less effective than in cubic grains.

Several possible causes can be considered for this reduced effectiveness. One is formation of sub-latent images instead of latent images, i.e., latent image dispersion. However this possibility can be neglected, because the latensification results (see Fig. 10 and 11) did not reveal the existence of such sub-latent images, in line with the theory that in unsensitized grains the growth rate of sub-latent images into latent image growth is greater than the formation rate of sub-latent images (nucleation).[12] As a result, sub-latent images should grow immediately into latent images.

The second possible cause can be that in the case of octahedral grains photoelectrons are captured more competitively by electron trapping centers. The greater difference between total and surface development in octahedral grains (see Fig. 8) indicates that latent image formation occurs not only at the surface but also more frequently at the interior of these crystals, compared to the cubic grains (see Fig. 4). This result seems to support the second explanation for the lower effectiveness of latent image formation in octahedral grains, i.e., more competitive electron trapping reactions may result in decreasing the efficiency of further growth of Ag^0 according to Reaction 2.

It was further reported by Takada[8] that the potential difference between the surface and the interior of AgBr octahedral crystals is greater than that of cubic crystals. In addition, it was suggested that a larger band bending in the space charge layer should drive electrons to the interior of the crystals.[8] It was confirmed by Tani that a greater potential difference leads to the formation of more internal latent image.[13] Taking the results of those investigations into account, the different distribution of latent images related to the different efficiency of latent image formation can be explained in terms of the different structure of the space charge layer between octahedral and cubic grains.

More frequent recombination (Reaction 3) can be also considered as the third possible cause for the reduced effectiveness of latent image formation in octahedral grains. Although direct evidence has not yet been obtained, we suggest that the concentration of intrinsic R-centers in octahedral grains is lower than that in cubic grains, due to pAg differences during the crystal growth process.[13] These R-centers can react with positive holes, reducing recombination and also producing additional electrons (Lowe's hypothesis).[14]

$$Ag_2 + h^+ \longrightarrow 2\, Ag_i^+ + e^-$$

In order to investigate the effect of R-centers on the sensitivity, R-centers were introduced in the octahedral grains by using DMAB. Although these grains contain iridium with 10^{-6} mol Ir/mol Ag, their sensitivity is still lower than that of cubic grains. As can be seen in Fig. 14, by introducing additional R-centers to octahedral grains, their sensitivity was increased tremendously even above the sensitivity of the cubic grains. This fact implies that the recombination reaction must also be taken into account as a possible cause for reduced effectiveness of latent image formation in octahedral grains. These data also show that the process of delayed latent image formation was almost completed 10 min after exposure of these grains, also as observed for cubic grains. This feature will be discussed later.

Here it is worth noting that without iridium doping, delayed latent image formation cannot be observed in either cubic or octahedral grains. This means that photoelectrons are simply used up just after exposure due to the reaction with Ag_i^+ or by recombination with h^+. Therefore it is clear that the delayed latent image formation observed experimentally is definitely related to the doped iridium, as previously suggested.[4]

Difference in Photographic Behavior Between Cubic and Octahedral Grains with Iridium Doping

In both cubic and octahedral AgBr grains, the introduction of iridium doping in low concentrations results in an increase of sensitivity. However the further increase of doped iridium amount brings about a severe loss of sensitivity. The increasing sensitivity as shown in Figs. 1 and 5 can be explained by Reaction 1. As a small amount of iridium enables electrons to be trapped temporarily (Reaction 1), fewer electrons will recombine with positive holes. When the iridium amount is further increased, electron trapping via Reaction 1 becomes dominant over Reaction 2 (the reaction of electron with Ag_i^+). That is, most electrons are trapped by the many iridium centers present in the grains. After being released from iridium centers, these electrons will immediately be re-trapped by other iridium centers close to them. Electron trapping by iridium centers occurs successively and more frequently than the reaction of electrons with Ag_i^+ ions. It is considered that the lack of available electrons for Reaction 2 causes the low sensitivity due to the existence of many iridium centers.

The iridium concentration at which the maximum sensitivity is reached is approximately one order of magnitude higher in octahedral grains than in cubic grains. This fact suggests that in octahedral grains a higher level of doped iridium is necessary to sufficiently utilize photoelectrons for the latent image formation, because in undoped octahedral grains the latent image formation process is less effective, as discussed earlier.

The introduction of iridium does not seem to affect the distribution of latent image centers, as can be seen in Fig. 4 and in Fig. 8. In case of cubic grains, most of latent images are still present at the surface of grains, even though many iridium ions are doped into the grains. This implies that doped iridium centers do not direct the flow of electrons from the sensitivity centers where latent images are formed, consistent with our earlier results.[4]

As described already, delayed latent image formation is not noticeable in undoped cubic and octahedral grains. However when iridium is incorporated, the delayed latent image formation is recognizable in a different way for cubic and octahedral grains at medium iridium concentration (10^{-6} mol Ir/mol Ag) (compare Fig. 2b to Fig. 6b). In case of octahedral grains, a more remarkable enhancement of sensitivity with delay time was observed. Here it should be made clear that sub-latent images are not involved in this process, insofar as the latensification results did not reveal their presence (see Figs. 10 and 11). The difference in the delayed latent image formation between cubic and octahedral grains can be explained by the hypothesis that in octahedral grains a larger number of electrons may be temporarily trapped by iridium centers. For this hypothesis, the following two possible reasons can be proposed.

The first reason is that the number of electrons, which have not been involved in the latent image formation just after exposure, is possibly larger in octahedral grains than in cubic grains, given that the undoped octahedral grains show a reduced effectiveness of latent image formation immediately after exposure. This means that the remaining electrons, which have not been involved in the latent image formation, can be trapped in greater number by iridium centers in the case of octahedral grains. The greater number of such electrons subsequently being released from iridium ions (via Reaction 1) can contribute over time to latent image formation in octahedral grains, resulting in a more noticeable delayed latent image formation.

The second possible reason is that in the case of octahedral grains, electrons migrate more frequently to the interior of the grains, compared to the case of cubic grains. Experimental results concerning the location of latent images, especially the results shown in Fig. 9, strongly suggest this possibility. As discussed already, owing to the larger potential difference in the space charge layer electrons can migrate more readily into the interior of octahedral grains where most of the doped iridium ions are present. This means that electrons, which are migrating to the interior of octahedral grains, can be trapped by iridium ions with a higher probability.

Due to one or both of the above reasons, electrons produced photolytically just after exposure are trapped more frequently by iridium ions doped into octahedral grains. In the case of intermediate concentration of iridium, the electrons trapped and released successively by iridium ions will eventually combine with interstitial silver ions on the time scale of the present experiments. Consequently, the delayed latent image formation occurs more dramatically in octahedral grains than in cubic grains. It is interesting to note that the maximum sensitivity reached after aging (~100 min) in octahedral grains is rather close to that achieved in cubic grains. The proper concentration of iridium ions can compensate for the lower effectiveness of latent image formation observed in octahedral grains.

It is also worth noting the effect of the introduction of R-centers into octahedral grains on delayed latent image formation. Its introduction appears to diminish the effect of iridium doping, as can be seen in Fig. 14.

After reaching the maximum sensitivity around 1 h after exposure, strong latent image fading occurs. This suggests that the latent image centers produced in the process of delayed latent image formation in the presence of doped iridium may be less stable than those produced without doped iridium. These less stable image centers are easily degraded to relatively stable sub-latent images (see Figs. 10 and 11), which are considered to be equivalent to stable P-centers.[11] The decomposition of these less stable image centers is driven by the presence of moisture and/or oxygen, insofar as the latent image fading can be completely prevented *in vacuo* condition, as can be seen in Fig. 12.

Conclusion

In the case of no iridium doping, the effectiveness of the latent image formation in octahedral AgBr grains is lower than in cubic AgBr grains. This reduced effectiveness observed for octahedral grains can be explained in terms of more competitive relationship among latent image centers that capture photoelectrons. Larger band bending across the space charge layer of octahedral grains drives electrons more readily to the interior of these grains. Another possible reason for the lower effectiveness of octahedral grains is more frequent recombination of electrons and positive holes.

The introduction of iridium doping at an appropriate concentration (10^{-6} mol Ir/mol Ag) increases the sensitivity more dramatically for octahedral grains than for cubic grains. In the case of octahedral grains, as a temporary electron trap, the doped iridium seems to compensate the more competitive relationship among latent image centers or the more frequent recombination of electrons with positive holes. The iridium doping does not affect the distribution of latent image centers in either octahedral or cubic grains.

The introduction of iridium doping gives octahedral grains a more dramatic enhancement of sensitivity due to delayed latent image formation as well, compared to cubic grains. This difference can be explained by the hypothesis that in octahedral grains a greater fraction of electrons may be temporarily trapped at iridium centers.

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References

1. B. H. Carroll, *Photogr. Sci. Eng.* **24**, 265 (1980).
2. H. Sakai and S. Baba, *J. Soc. Photogr. Sci. Tech. Jpn.* **31,** 34 (1968), *ibid.* **31,** 81 (1968).
3. H. Zwicky, *J. Photogr. Sci.* **33**, 201 (1985).
4. T. Owaki and A. Hirano, *J. Soc Photogr Tech. Jpn.* **62**, 209 (1999).
5. G. Vekeman, V. B. Peng, W. Maenhout-Van der Vorst, and F. Cardon, *J. Imaging Sci.* **32**, 187 (1988).
6. R. S. Eachus and R. E. Graves, *J. Chem. Phys.* **65**, 1530 (1976).
7. K. Ozeki, S. Urabe and T. Tani, *J. Imaging Sci.* **34**, 136 (1990).
8. S. Takada, *J. Photogr. Sci. Tech. Japan* **44**, 81 (1981).
9. T. Tani, *J. Imaging Sci. Technol.* **41**, 577 (1997).
10. T. H. James, W. Vanselow and R. F. Quirk, *Photogr. Sci. Eng.* **19B**, 170 (1953).
11. T. Tani, *Photographic Sensitivity*, Oxford University Press, New York, 1995, pp. 97–99.
12. R. Hailstone, *Introduction to image recording in silver halides*, tutorial during IS&T 49th Annual Conference; unpublished.
13. T. Tani and M. Saito, *Photographic Sci. Eng.* **23**, 323 (1979).
14. T. Tani, *Photographic Sensitivity*, Oxford University Press, New York, 1995, p. 104.