

# Reaction of Silver Sulfide Cluster Anions with Bromine Atoms

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## Abstract

Using a laser double ablation reactor built on the basis of a tandem TOFMS, we studied the reaction of clusters produced by laser ablation of silver (potassium) bromide and silver sulfur powder mixture. The results showed that reactions took place and that Ag/S/Br ternary cluster anions were produced. The formation of Ag/S/Br clusters is considered as the addition of bromine atom to the silver sulfide cluster anions. The results provide ground for the argument we proposed that silver sulfide cluster anions can act as positive hole traps during the exposure process of photo-sensitive silver bromide microcrystals.

## Introduction

In photographic process, two photo-generated charge carriers: a photo-electron and a positive hole (a bromine atom) are generated when photo-sensitive silver halide emulsions are exposed to light. The fate of the two carriers is the most fundamental problem of photographic theory. On the electron, it's popularly considered that  $\text{Ag}_2\text{S}$  specks, which are formed during the sulfur sensitization process of photographic emulsion, are its traps where latent images are formed later on by repeat interaction with interstitial silver ions<sup>[1]</sup>. On the positive hole (Br), Mitchell<sup>[2]</sup> pointed out that it could be trapped by  $\text{Ag}_2\text{S}$  specks. Subsequently, Sonoike<sup>[3]</sup> thought  $\text{S}^{2-}$ -interstitial silver ion complexes were traps of positive hole by observing infrared quenching of luminescence peaks in S-doped silver bromide crystals. Sahyun<sup>[4]</sup> analyzed the recombination behavior of photogenerated charge carriers in microcrystalline powders of II-VI semiconductors. He thought it's possible that  $(\text{Ag}_2\text{S})_n$  centers could act as hole trapping centers. Using a photostimulated desorption (PSD) technique, Kaneda<sup>[5]</sup> studied the properties of chemical sensitization centers in AgBr emulsion grains. He found that sulfur sensitization centers were hole traps. Tani<sup>[6]</sup> pointed out that  $\text{Ag}_2\text{S}$

monomers were traps of holes. Gradually, people begin to take note to the phenomena that sulfur sensitization centers trap positive holes. But there are different viewpoints on the nature and composition of the hole traps. At present, still very little is known about the charge of silver sulfide clusters which is of prime importance for the element process of latent image formation. The reason for this gap in our knowledge is the lack of experimental methods to investigate particularly the charge property.

Today the advancement of experimental methodology of cluster physics and chemistry offers an obvious hope for gaining insight into the positively or negatively charged clusters of silver sulfide. We have studied the formation of silver sulfide cluster ions by laser ablation tandem time-of-flight mass spectrometry<sup>[7]</sup>. We obtained  $\text{Ag}(\text{Ag}_2\text{S})_n^+$ ,  $\text{Ag}_3(\text{Ag}_2\text{S})_n^+$ , etc cationic clusters series and a large number of anionic clusters such as  $\text{AgS}(\text{Ag}_2\text{S})_n^-$ ,  $\text{AgS}_2(\text{Ag}_2\text{S})_n^-$ , etc by laser ablation of pressed discs of silver and sulfur powder mixture. By correlating these clusters with sulfur sensitization centers of photographic emulsions, we considered the cationic clusters as electron traps, Correspondingly, the anionic clusters hole traps. But whether the silver sulfide cluster anions have the reactivity to bromine atom? If yes, what products will be generated after reaction? In this work, we report the reaction results of silver sulfide cluster anions with bromine atom using a laser double ablation reactor.

## Experimental

**Equipment** To study the reactivity of clusters, very complicated apparatus must be applied. Only a few laboratories carried out the clusters reactivity researches<sup>[8-11]</sup>. On the basis of a tandem time-of-flight mass spectrometer of our lab, by reequipping the sample fixture, we designed a easily-operated and credible laser double ablation reactor to study the reactivity of clusters<sup>[12]</sup>. The following is a brief description of the equipment:

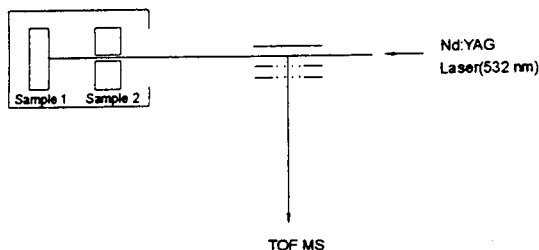


Figure 1. Schematic diagram of a laser double ablation reactor.

Figure 1 schematically shows the equipment which mainly comprises of two samples 1 and 2. In the center of sample 2, a little hole ( $\Phi = 1.0-1.5\text{mm}$ ) is drilled. When sample 2 is ablated by laser (532 nm, 5-20 mJ/pulse, 10 pulses/second), sample 1 is also ablated at almost the same time after the laser beam passes through the hole in sample 2. Keeping the distance of the two samples in 5 - 10mm can make sure that the two samples evaporate and form clusters respectively. The clusters formed from sample 1 fly away from it. Part of the clusters encounter, colloid and react with the clusters formed from sample 2. Finally, all the clusters fly away from the samples and are detected with a time-of-flight mass spectrometer.

**Sample** The reagents included silver powder, silver bromide powder, sulfur powder and sodium bromide. According to requirement, the reagents were mixed in different molar ratio and pressed to disks.

### Results and discussion

Figure 2 shows the TOF mass spectra of anionic clusters obtained from a molar Ag/S=1:1 sample. It can be seen that

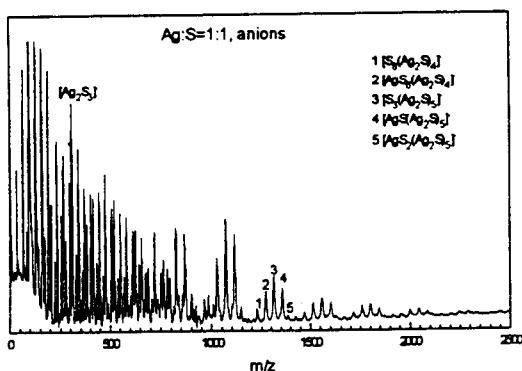


Figure 2. TOF mass spectrum of anions  $[\text{Ag}_n \text{S}_m]$  produced by laser ablation of a sample of molar Ag/S=1:1.

the distribution of peaks are distinctively different in the lower and higher mass regions. In higher mass region the peak groups appear in equal distance which is 248amu, just a  $\text{Ag}_2\text{S}$  unit. It can be concluded that these groups

progresses by addition of  $\text{Ag}_2\text{S}$ . In lower mass region the peak distribution is in disorder. After analyzing it was found that there were  $\text{S}_n^-$  ( $n=2-8$ ) and  $\text{Ag}_p \text{S}_m^-$  cluster anions. All the cluster anions and their intensities in figure 2 are indicated in figure 3.

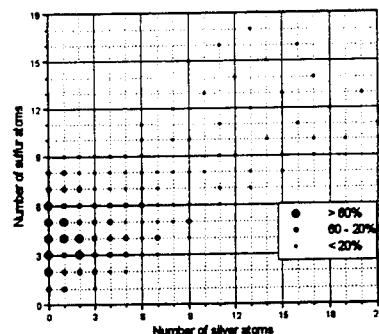


Figure 3. Map of the compositions of  $[\text{Ag}_n \text{S}_m]$  anions in Figure 1. The sizes of the circles indicate relative intensity.

Using the equipment of laser double ablation reactor shown in figure 1, taking Ag/S (1:1) sample as sample 2, AgBr sample as sample 1, maintaining the distance of the two samples in 6mm, we can obtain reaction results shown in figure 4. In higher mass region, there is no difference

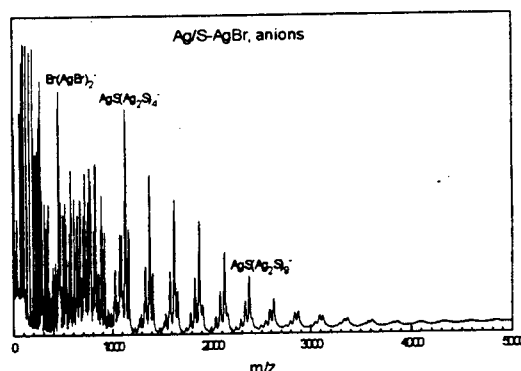
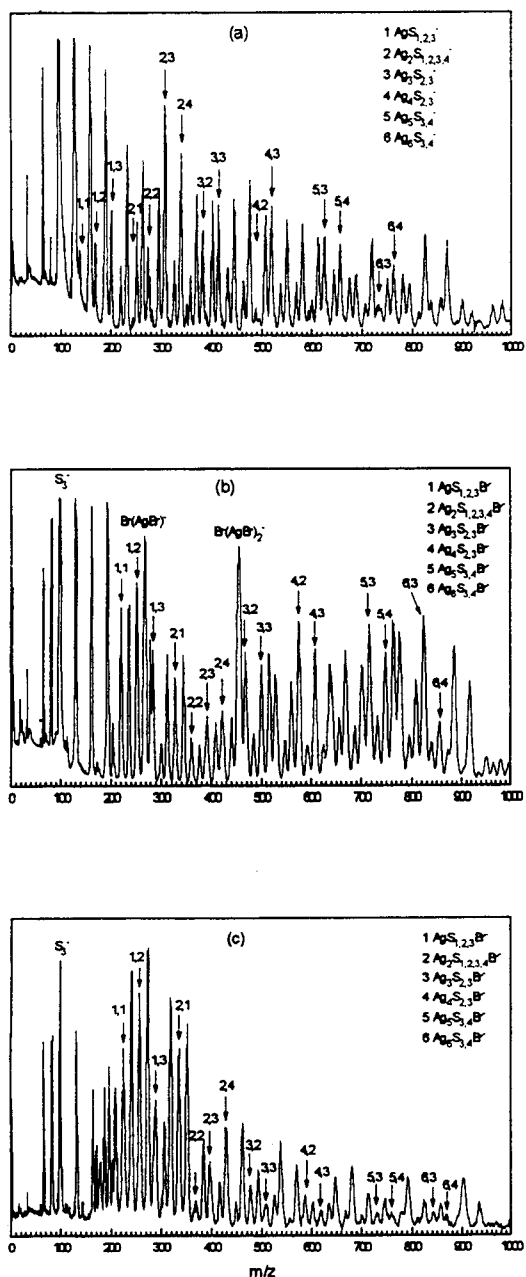


Figure 4. TOF Mass spectrum of cluster anions produced by laser double ablation of samples Ag/S (1:1) and AgBr fixed in the reactor.

between figure 2 and 4. But in lower mass region, two kinds of new clusters comparing with figure 2 emerge (figure 5a and b): one is  $[\text{Br}(\text{AgBr})_n]$  series, the other is  $[\text{Ag}_x \text{S}_y \text{Br}]$  ternary clusters. The ternary clusters, characterized by containing only one bromine atom in each of them, include (1) $[\text{AgSBr}]$ ,  $[\text{Ag}_2\text{SBr}]$ ,  $[\text{Ag}_3\text{SBr}]$ ; (2) $[\text{Ag}_2\text{S}_2\text{Br}]$ ,  $[\text{Ag}_2\text{S}_3\text{Br}]$ ,  $[\text{Ag}_2\text{S}_4\text{Br}]$ ; (3) $[\text{Ag}_3\text{S}_2\text{Br}]$ ,  $[\text{Ag}_3\text{S}_3\text{Br}]$ ; (4) $[\text{Ag}_4\text{S}_2\text{Br}]$ ,  $[\text{Ag}_4\text{S}_3\text{Br}]$ ; (5) $[\text{Ag}_5\text{S}_3\text{Br}]$ ,  $[\text{Ag}_5\text{S}_4\text{Br}]$ ; (6) $[\text{Ag}_6\text{S}_3\text{Br}]$ ,  $[\text{Ag}_6\text{S}_4\text{Br}]$ . Taken away Br atom, the above ternary clusters will become binary

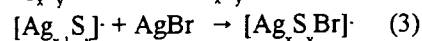
clusters all of which are generated in figure 2. Furthermore, we have found only  $[AgSBr]^-$ ,  $[Ag_2S_2Br]^-$  and  $[Ag_3S_3Br]^-$  clusters using AgBr/S samples (the results obtained from AgBr/S samples will be devoted elsewhere). From



**Figure 5.** TOF Mass spectra (mass number < 1000 amu) of cluster anions produced by laser ablation of samples fixed in the reactor. Samples: (a) Ag/S (1:1); (b) Ag/S (1:1) and AgBr, (c) Ag/S (1:1) and NaBr. Number pairs mean the composition of cluster anions indicated in the figure, i.e. 5,4 means  $Ag_5S_4^-$  or  $Ag_5S_4Br^-$ .

figure 4 it can be concluded that, Ag/S and AgBr samples form clusters respectively as they are laser-ablated.

After the samples were laser-ablated, charged and neutral species were generated simultaneously. The possible pathways involving the formation of Ag/S/Br ternary clusters are as follows:



To the best of our knowledge, judging from the view-point of electronegativity, we have the unquestionable ground to consider that the bromine atom ( $Br^0$ ) has incomparable high reactivity than bromide negative ion ( $Br^-$ ) and to conclude that neither the electron transfer from  $Br^-$  to  $S^{2-}$  nor the replacement of  $S^{2-}$  by  $Br^-$  may occur. For pathway (3), we substitute AgBr for NaBr, still use the equipment shown in figure 1, and obtained figure 5c. Comparing Figure 5b and c, it can be found that the reaction products in figure 5b all emerge in figure 5c. As indicates that pathway (3) is impossible. Therefore, The above ternary clusters were formed through pathway (1). The results implies that silver sulfide cluster anions have the reactivity to bromine atom, the products still bear negative charge, which implies the possibility that silver sulfide cluster anions can act as positive hole traps during the exposure process of photo-sensitive silver bromide microcrystals.

## References

- (a) R. Matejec and E. Moisar, *Photogr. Sci. Eng.* **12**, 133(1968).  
(b) L. M. Kellogg, N. B. Libert and T. H. James, *Photogr. Sci. Eng.* **16**, 115(1972).
- (a) J. W. Mitchell, *J. Photogr. Sci.* **5**, 49(1957).  
(b) J. W. Mitchell, *J. Photogr. Sci.* **6**, 57(1958).
- M. R. V. Sahyun, *J. Imaging Sci.* **33**, 94(1989).
- S. Sonoike, *J. Imaging Sci. Technol.* **36**, 282 (1992).
- T. Kaneda, *J. Imaging Sci. Technol.* **38**, 135 (1994).
- T. Tani, *J. Imaging Sci. Technol.* **39**, 386(1995).
- Bixian Peng, Weidong Cui, Zhongde Yu, Zhen Gao, Qihe Zhu and Fanao Kong, *Science in China: B* **40**, 309(1997).
- J. L. Elkind, F. D. Weiss, J. M. Alford, R. T. Laaksonen and R. E. Smalley, *J. Chem. Phys.* **88**, 5215(1988).
- P. Schnabel, M. P. Irion and K. G. Weil, *J. Phys. Chem.* **95**, 9688(1991).
- K. Fisher, I. Dance, G. Willett and MaNu Yi, *J. Chem. Soc. Dalton Trans.* **6**, 709(1996).
- D. J. Trevor, D. M. Cox and A. Kaldor, *J. Am. Chem. Soc.* **112**, 3742(1990).
- P. Liu, *Master Dissertation thesis*, Institute of Chemistry, Chinese Academy of Sciences, 1997.