

# Silver Halide/Silver Carboxylate Photothermographic Imaging Systems: Characteristic Properties of Structure and Development

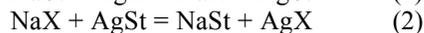
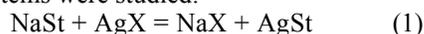
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## Abstract

Photothermographic silver halide/silver carboxylate imaging systems have been investigated by electron microscopy, dielectric and luminescence spectroscopy. The interface properties have been elucidated in these photothermographic type systems. During the preparation of the silver carboxylate, alkali cations from the alkali metal soaps may enter the interface between the silver halide and developing silver carboxylate and form a structure with very specific spectral characteristics. The interface structure depends on the silver carboxylate preparation mode.

## Introduction

It is well known that the photographic characteristics of photothermographic materials strongly depend on the mode of preparation of the photosensitive AgX/Ag carboxylate composition. One possible reason for these differences is the difference in the structure of AgX/Ag carboxylate interface. It is believed that the interface may play an important part in the mechanism of latent image formation and subsequent development.<sup>1</sup> As it is rather difficult to investigate the interfaces in real photothermographic systems the following model systems were studied:



where St is stearate,  $\text{H}_{35}\text{C}_{18}\text{O}_2^-$ . The first reaction is fundamental to the preparation of silver carboxylates in the presence of AgX (prepared by conventional double jet precipitation methods), "preformed AgX", and the second is a model for an "in situ" preparation mode of a photothermographic system (the AgX is prepared by the exchange reaction of a halide for the carboxylate).

## Results and Discussions

### Electron microscopy and X-ray studies of AgX/AgSt compositions

The structure of the AgBr/AgSt interface as a result of "in situ" halidization of silver carboxylates has been reported recently.<sup>2</sup> In the present work we investigated the interface reaction (1) produces in the AgX/AgSt system. Treatment of AgBr crystals by sodium stearate was carried out under conditions commonly used for preparation of real imaging materials. After treatment with sodium stearate, the samples were filtered, dried and studied by electron microscopy (EM) and X-ray techniques.

EM studies of these samples show that a compound having a layered structure forms on the surface of the AgBr crystals, Figure 1.

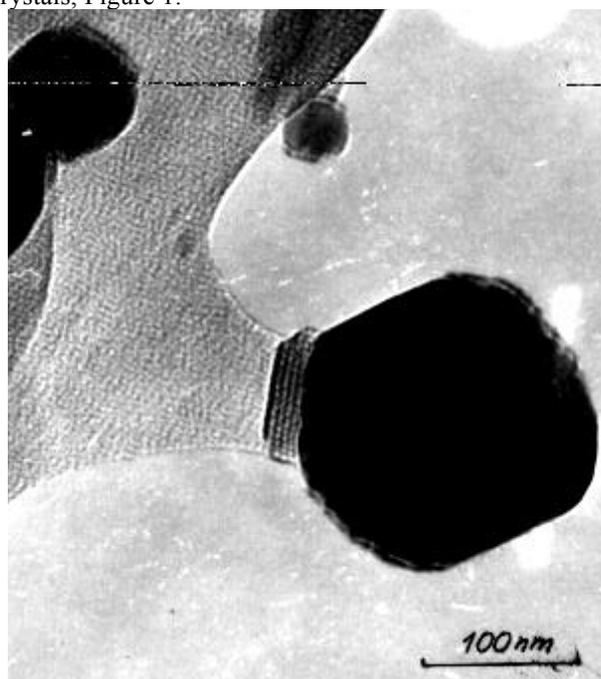


Figure 1. Interface between AgBr and AgSt.

The layers are located parallel to the surface of the AgBr crystal, and, in contrast to the "in situ" AgBr/AgSt composition, are not directly connected to the AgBr crystalline lattice. In studies of the formation of preformed composition we have found that intense diffraction lines appear in X-ray spectra due to the layered structure of the compounds which do not belong to the silver stearate or sodium stearate phase. The observed reflections were assigned to two phases that are clearly observed and separated by the X-ray data. The first phase has an interlayer spacing of  $d_{001} = 48.98\text{\AA}$ , and the second phase  $d_{001} = 45.01\text{\AA}$ . For silver stearate and sodium stearate this parameter is  $48.8\text{\AA}$  and  $45.6\text{\AA}$  respectively.

Broadening of the AgBr X-ray lines is also observed. It is most probable that the X-ray diffraction observed for the layered compound belongs to a solid solution based on silver stearate with partial substitution of the silver ions by sodium ions and on a sodium stearate based solid solution with partial substitution of sodium ions by silver ions.

### Luminescence spectroscopy studies of AgX/AgSt compositions

Additional data on the interface structure were obtained using low temperature luminescence. According to reaction (1), of the four components only AgX, irradiated at 365 nm, results in luminescence. At the beginning of the reaction the luminescence from the interface is masked by the luminescence from the bulk portion of AgX. In view of this factor, reaction (1) is carried out in an excess of NaSt (1:10 mole fraction in an aqueous solution).

Since luminescence of AgCl is more convenient for detection than AgBr the former was chosen as the starting reagent in this model system. After completion of reaction (1) X-ray diffraction analysis showed the AgCl phase was absent. However, both EM and luminescence studies indicate the presence of a AgCl phase. The luminescence spectrum (LS) of the remaining AgCl is shifted and distorted compared to the LS of the bulk phase (see Figure 2).

To understand the nature of this LS, reaction (2) was carried out between the solid components. Since AgCl forms at the interface in this reaction, the greatest difference between the LS of the bulk and interface phases will be observed early in the course of the reaction. Silver chloride can be detected at the early stages of the solid state reaction (Figure 3) of  $\text{NaCl} + \text{AgSt} = \text{AgCl} + \text{NaSt}$ :

As the reaction proceeds, both the amount of AgCl and intensity of the LS increase. Figure 3 shows the LS of AgCl at the interface compared to pure AgCl. Additional fine structure, observed in the LS of AgSt from the interface may be assigned to the admixture levels in the forbidden band of AgCl. The difference between the LS in Figure 1, spectrum 1 and Figure 3, spectrum 1 confirms that the interface formed during the preformed mode of preparation of the AgCl/AgSt system differs from that formed when the "in situ" method is used. At equilibrium, the interface in the preformed system is close to the interface obtained in the system prepared by the "in situ" mode.

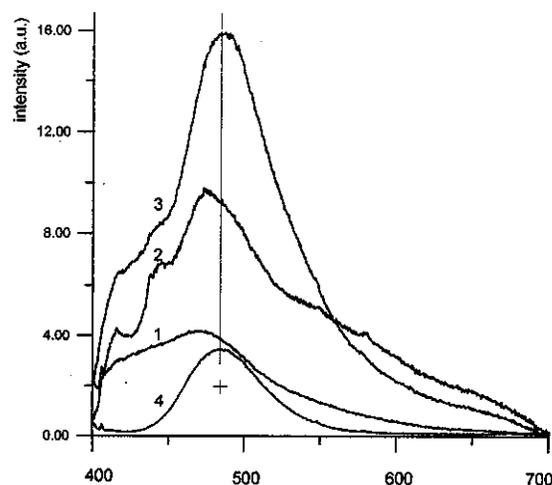


Figure 2. Luminescence spectra of AgCl/AgSt interface: 1 = directly after synthesis, 2 = after 1 day, 3 = after 2 days, 4 = luminescence of AgCl.

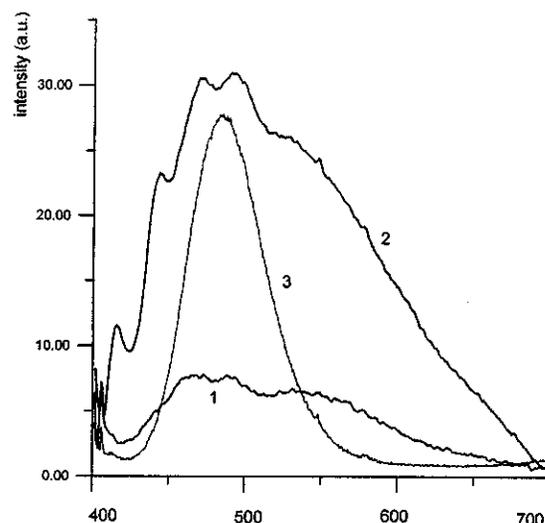


Figure 3. Luminescence spectra (77 K) of AgCl from the solid state reaction of NaCl with AgSt. 1 = after 24 hours, 2 = after 150 hours, 3 = AgCl.

### Incorporation of alkali cations into the interface

The nature of the admixture levels assigned to AgCl in the interface region may be refined further. If this level is due to the presence of alkali cations within the AgCl lattice, the structure of the LS spectra may depend on the cation involved in exchange reaction (2). The LS of AgCl formed by reactions  $\text{LiCl} + \text{AgSt} = \text{AgCl} + \text{LiSt}$  and  $\text{KCl} + \text{AgSt} = \text{AgCl} + \text{KSt}$ , are shown in Figure 4 and Figure 5 respectively.

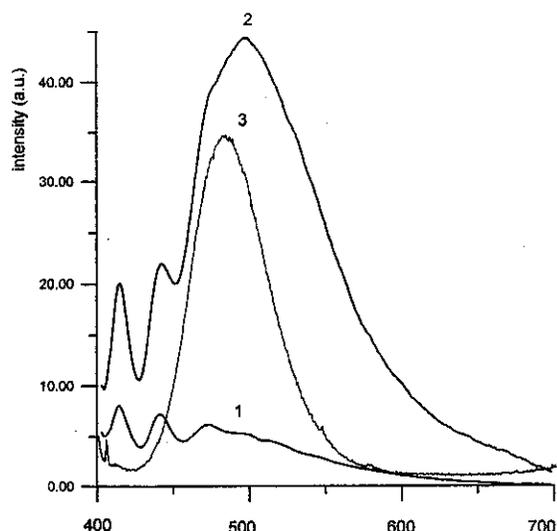


Figure 4. Luminescence spectra (77 K) of AgCl from the solid state of the reaction of LiCl with AgSt. 1 = after 24 hours, 2 = after 150 hours, 3 = AgCl.

One can see that the reaction (in air at room temperature) develops differently for the different chlorides. In the case of KCl, the band above 480 nm remains unchanged, but the band at 480 nm, which is typical of pure AgCl, grows. For the AgCl phase obtained from LiCl, the growth of the band at 480 nm (which is a superposition of two unresolved bands at 480 nm and above 480 nm) is observed. In the LS of AgCl obtained from NaCl by the exchange reaction at room temperature, all the bands grow so that all five bands become resolvable in the final spectrum. Two bands, at 416 nm and 442 nm, which were missing at the initial stage of AgCl formation from NaCl, were pronounced at the initial stage of AgCl formation from LiCl. Also, the splitting of the main band at 480 nm into two bands with  $\lambda_{\max} = 468$  and  $\lambda_{\max} = 493$  nm and a broad band at 530 nm are clearly observable. As expected, the most significant changes in the structure of the AgCl phase are observed on the sample obtained from NaCl which forms a continuous solid solution with AgCl. The least significant differences in the spectra are observed for AgCl obtained from KCl.

For AgCl obtained from LiCl, the change in the interface structure is intermediate between the first two cases. The first two bands at 413 nm and 440 nm are probably associated with the introduction of water components, for example, of a proton to  $\text{Ag}^+$  sites or  $\text{OH}^-$  to  $\text{Cl}^-$  sites in the interface region of AgCl. Of the three salts, LiCl is the most hygroscopic. The hygroscopic nature of LiCl has a pronounced effect on the early stage of formation of the AgCl phase. NaCl is also hygroscopic but to a lesser extent than LiCl. KCl is considered to be the least hygroscopic; consequently, the latter bands are missing in the corresponding LS of AgCl.

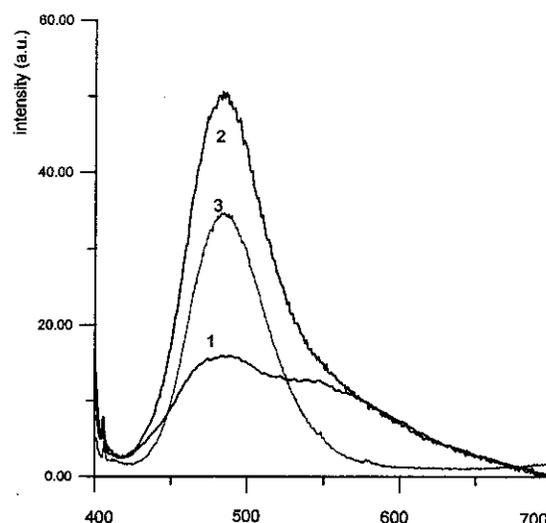


Figure 5. Luminescence spectra (77 K) of AgCl from the solid state reaction of KCl with AgSt. 1 = after 24 hours, 2 = after 150 hours, 3 = AgCl.

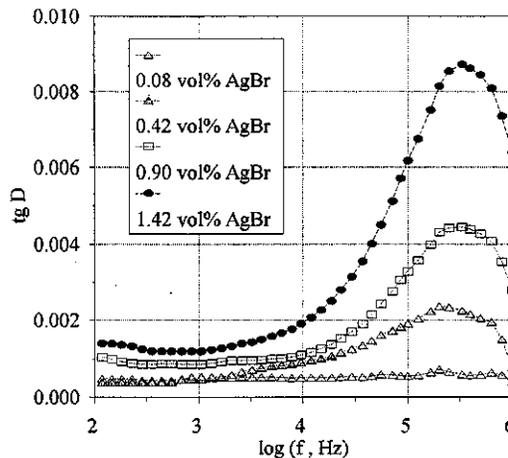


Figure 6. Dielectric spectra of AgSt-AgBr mixtures.

### Dielectric spectroscopy

The silver halide/silver carboxylate system used in the preparation of photothermographic imaging materials has also been investigated by dielectric spectroscopy. This experimental technique enables the dielectric loss peak of powdered samples containing at least 0.5 volume percent AgBr to be observed. The position of the dielectric loss peak is found to depend on the method of silver halide/silver carboxylate preparation. These results can be explained by variation of the morphology, the surface or interface structure of the AgBr in the mixtures and films. In photographic materials the Maxwell-Wagner polarization occurs due to the presence of heterogeneous inclusions of an ion conductive AgBr phase, and as a result a peak in the dielectric spectra is observed. At low volume concentration, with anisotropic AgBr grain shapes, the frequency of the peak,  $f_{\max}$ , is given by simple relation  $f_{\max} = \sigma/2\pi\epsilon$ , where  $\sigma$  and  $\epsilon$  are the conductivity and the dielectric constants of AgBr. As the conductivity of AgBr microcrystals is mainly

caused by the surface or interface conductivity, the value of  $f_{\max}$  can be used to characterize the AgBr interface properties in these model mixtures. Dielectric spectra of AgBr/AgSt mixtures with different volume concentrations of AgBr (grain size about 0.05  $\mu$ ) were measured (Figure 6).

As seen from the spectra, the height of the dielectric maximum monotonically increases with the AgBr concentration. The method is very sensitive and allows the dielectric peak to be determined for AgBr concentrations of less than 0.3 volume percent. Therefore, the interface structure of AgBr and, consequently, the  $f_{\max}$  values are expected to be also different.

## Conclusions

The interfaces in model photothermographic systems have been investigated by electron microscopy, luminescence and dielectric spectroscopy. The structure of the interface depends on the method of AgX/AgCarboxylate preparation and may influence the properties of the resulting photothermographic materials.

## References

1. C. Zou, M. R. V. Sahyun, B. Levy, N. Serpone, *J. Imag. Sci. Tech.*, **40**, 94, 1996.
2. B. B. Bokhonov, L. P. Burleva, W. C. Frank, J. R. Miller, M. B. Mizen, M. R. V. Sahyun, D. R. Whitcomb, J. M. Winslow, C. Zou, *J. Imag. Sci. Tech.*, **40**, 85, 1996.