

Characterization of the Phase and Structure of Interfaces Formed During the Synthesis of Silver Halide-Silver Carboxylate Compositions

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In the preparation of the $\text{AgX}[\text{AgO}_2\text{CR}]_2$ components that are used in photothermographic imaging films, where $\text{X} = \text{Br}$ or Cl and $\text{R} =$ linear alkyl chain, the reaction of silver ions with sodium fatty acid salts produces various silver soap structures containing different interface properties, depending on the starting silver ion source. Use of pre-prepared silver bromide microcrystals and silver nitrate, for example, has been shown to produce a $\text{AgBr}/[\text{AgO}_2\text{CR}]_2$ epitaxial interface. Conversely, we now find that silver chloride can be reacted directly with NaO_2CR to prepare a $[\text{Ag}(\text{O}_2\text{C}_n\text{H}_{2n-1})]_2$ product without needing to add silver nitrate. In this article we report the results of our continuing investigation, by TEM and X-ray diffraction, of the nature of the interface formed between prepared silver halides and $[\text{AgO}_2\text{CR}]_2$.

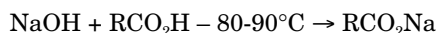
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Introduction

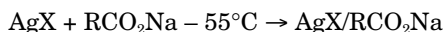
Mixtures of photosensitive silver halide and silver soap (silver complexes of fatty acids, $[\text{AgO}_2\text{CR}]_2$) have been used in the production of photographic materials for many years.^{1,2} These materials, after light exposure, are thermally developed to generate metallic silver, for a black and white image. The silver halide can be spectrally^{1,3} and/or chemically sensitized⁴ for relatively high light sensitivity, approaching 1 erg/cm.^{2,5} The latent image is thermally developed by reduction of silver ion from silver carboxylates, either comprised of a single chain or having a mixture of chain lengths (normally in the range of C_{18} – C_{22}).⁶ It is the optimization of the AgX and silver carboxylate components of these materials that can contribute to the production of high quality imaging materials,³ such as the Kodak DryView™ laser imaging system.

Obtaining a AgX /silver carboxylate ($\text{X} = \text{Br}$ or Cl) composition can be accomplished by different routes.^{1,2} One such route is in situ halidization of the silver fatty acid carboxylate complexes by using various halidizing agents in which the halide is exchanged for the carboxylate. Another route is to add separately prepared silver halide microcrystals into the silver soap preparation or formulation processes (“preformed” or ex situ processes).^{1,2,7,8}

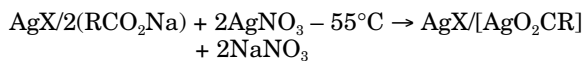
The “preformed” process comprises a series of chemical reactions in which the silver carboxylates are precipitated onto the surface of the silver halide microcrystals. In this case, the sodium salts of the fatty acids are prepared first, under aqueous^{1,2} or aqueous/organic⁹ solvent conditions:



and a dispersion of the AgX microcrystals, in gelatin, is added to the sodium soap solution:



Addition of silver nitrate to this mixture produces the $\text{AgX}/[\text{AgO}_2\text{CR}]_2$ silver soap dispersion by the exchange of carboxylate for nitrate:



The investigation of the processes occurring in the synthesis of the AgBr via the in situ component of preparation of a photothermographic composition has been reported^{10–12} where it was shown that the light sensitive silver halide is formed on the lateral edges of silver stearate (AgSt) crystals. This observation is consistent with the solid-state structure of $[\text{AgO}_2\text{CR}]_2$ in which the available silver ions are located on the lateral edges of the crystal while the basal plane is exclusively comprised of the terminal methyl groups of the hydrocarbon chain.¹³

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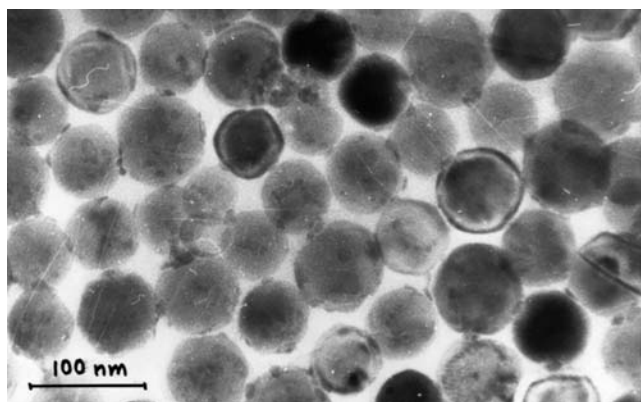


Figure 1. TEM of the starting AgBr crystals.

The investigation of the structure of the epitaxial interface and the morphology of the silver particles formed during the photothermographic process in AgBr/AgSt, prepared via the in situ process, has also been reported.¹⁴ While the structure of the interface formed in the in situ preparation was described, there have been no experimental data reported regarding the structure of the interface boundary for the “preformed” material. In fact, there is some disagreement regarding the existence of an epitaxial interface between the silver bromide and silver carboxylate of certain photothermographic imaging constructions as well as its possible role in the imaging chemistry.^{15–17} It is uncertain whether the process by which an epitaxial interface might be produced was carried out in those investigations, however.

We report here the results of the continuing investigation¹⁸ of the phase composition and the morphology characteristics of the photothermographic composition formed as the result of preparing the “preformed” photothermographic material, that is, the reactions in which the silver bromide is present during the reaction of silver nitrate with the sodium fatty acid salts. We show that not only is the epitaxial phase present and that it is easily formed, but that it can be characterized by conventional analytical techniques.

Experimental

Crystals of AgBr (68–70 nm), AgCl (200 nm), and AgCl/AgBr core/shell crystals in gelatin were prepared by standard procedures.¹⁹ The AgCl/AgBr core/shell crystals were 10% AgBr in the core and 90% AgCl in the shell. The micrographs of the initial silver halide crystals are shown in Fig. 1 and Fig. 2.

The reaction of silver halide crystals with a solution of the sodium fatty acid salts was carried out under different conditions: either standard times and temperatures for the synthesis of the photothermographic compositions¹⁹ or for longer times and at higher temperatures. After reaction, the products were washed, dried, and investigated with an electron microscope and by X-ray diffraction.

SEM and TEM studies were conducted using a JEM-200FXII microscope equipped with a scanning ASID-20 device at an accelerating voltage of 200 kV, as described previously.¹²

X-ray analysis of the reaction products between pure silver halides and sodium stearate and wide-angle data for the core/shell silver halide reaction with NaSt were collected by use of a Philips vertical diffractometer, Cu K α radiation, graphite diffracted beam monochromator, and proportional counter registry of the scattered radiation.

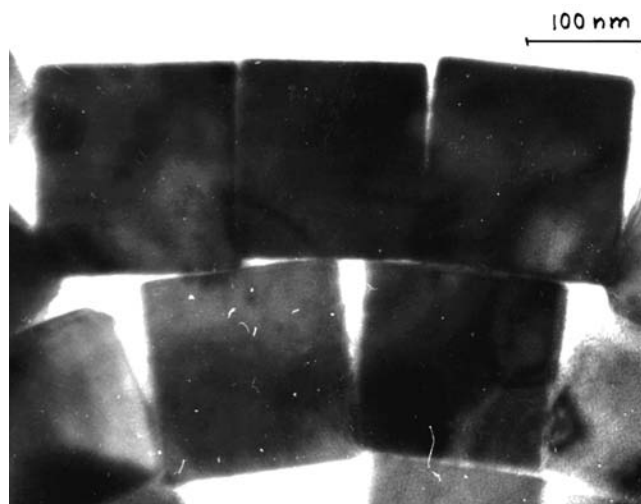


Figure 2. TEM of the starting AgCl crystals.

Results and Discussion

Reaction of the AgBr crystals with a solution of sodium stearate reveal intense reflections in the X-ray diffraction that do not correlate at all with the diffraction patterns of silver stearate or sodium stearate, Fig. 3, either one of which may be expected to be present after the reaction.

The X-ray diffraction pattern is found to be composed of two portions that can be correlated with the formation of two compounds having a lamellar structure similar to the structure of silver stearate. One of these phases formed in the reaction has an interlayer spacing of $d_{001} = 50.0$ Å, and the second phase has $d_{001} = 45.1$ Å. For comparison, we found the d_{001} value for silver stearate to be 48.7 Å, comparable to the literature.^{20,21} By comparison, the d_{001} values for the α -, β -, and γ -phases of sodium stearate are 52.1, 46.8 and 44.1 Å, respectively.²² Most importantly, the interlayer spacing parameter of $d_{001} = 50.0$ Å corresponds neither to a silver stearate phase nor to a sodium stearate phase but, rather, to a layered structure intermediate phase in which the even order layer line reflections are diminished in intensity. The even order layer line reflections are also diminished in the second phase, as shown in Fig. 3b. Consequently, we propose that the reaction of silver bromide with sodium stearate leads to the formation of a solid solution with a structure close to that of silver stearate and sodium stearate in which a portion of the silver ions have been exchanged with sodium ions (in the AgSt), and sodium ions have been exchanged for some of the silver ions (in the NaSt). This type of analysis of intermediate phase composition by X-ray diffraction is a known technique and has been applied successfully on various systems.^{23–25}

The AgBr peaks are very intense after the reaction is complete, Fig. 3a. It is also significant that the electron microscope investigation showed that, after the reaction of the AgBr crystals with the silver stearate solution, there does not appear to be a significant change in the size of the AgBr dimensions, Fig. 4.

A layered structure compound is formed, which is based on the silver stearate structure, and the AgBr crystals are arranged on the surfaces of this material from the reaction of silver stearate crystals such that the ionic layers in the stearate structure in some cases appear to be parallel to the surface of the silver halide, Fig. 5.

From these data, we conclude that the reaction of silver bromide crystals proceeds via the following reaction:

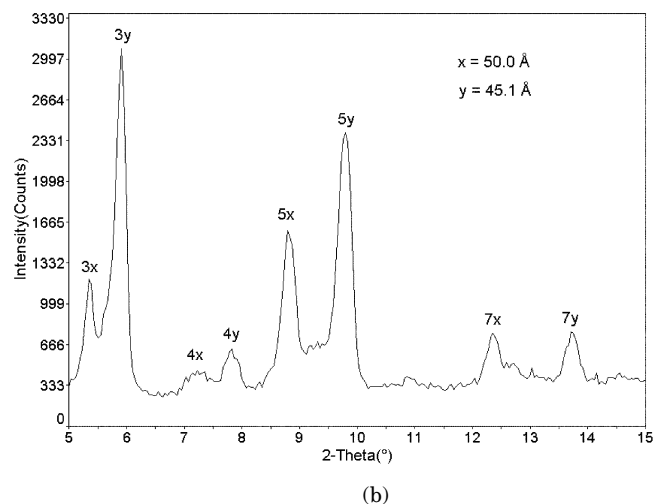
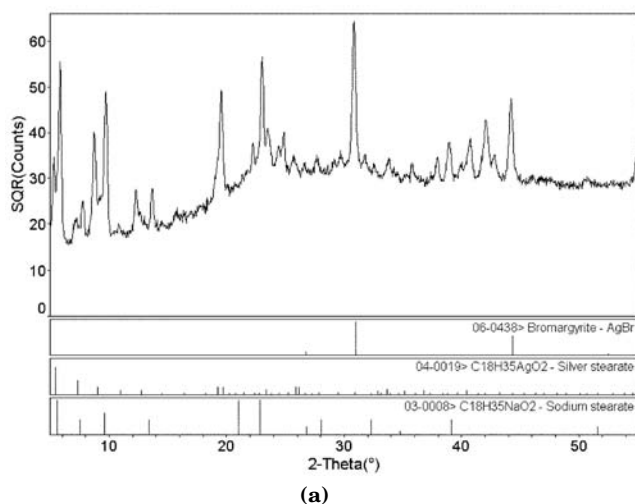


Figure 3. X-ray diffraction of the products resulting from the reaction between AgBr and NaSt (a) with reference diffraction patterns, (b) the 5 – 15 2-theta region expanded.

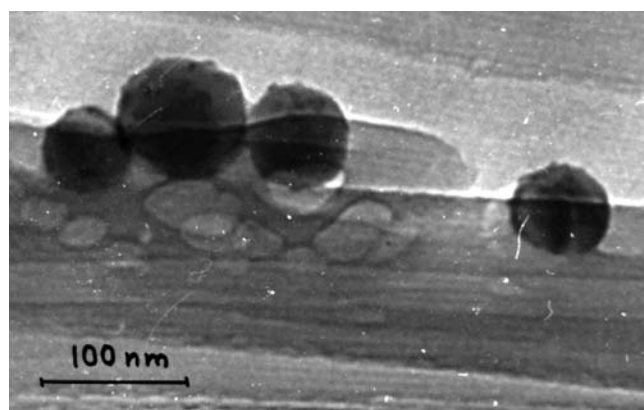


Figure 4. TEM of the products resulting from the reaction between AgBr and NaSt.



It is most likely that the appearance of the layered compound in the X-ray diffraction pattern corresponds to the formation of mixed crystals of sodium and silver stearate ($\text{Ag}_{1-n}\text{Na}_n\text{St}$, $\text{Na}_{1-n}\text{Ag}_n\text{St}$). The X-ray diffraction pattern shows that this new phase has a layered structure in which the d_{001} is intermediate between pure silver stearate and pure sodium stearate.

In addition to silver bromide, silver chloride can also be used as the light sensitive component in the $\text{AgX}/[\text{AgO}_2\text{CR}]_2$ composition.^{1,2} For these systems, after the reaction of AgCl crystals with a dispersion of sodium stearate, the X-ray diffraction showed that three new phases appeared, two of which are layered compounds, Fig. 6.

However, in contrast to the silver bromide case, using silver chloride crystals results in significant differences. First, after the reaction, the peaks due to AgCl have nearly disappeared from the X-ray diffraction pattern. Second, unlike the reaction with silver bromide crystals, phases are formed with interplanar spacings very close to those of silver stearate. The X-ray diffraction pattern shows three phases with $d_{001} = 49.5$, 48.5 , and 44.8 Å. The phase with interlayer spacing of $d_{001} = 48.5$ Å is very close to that of pure silver stearate and produces well defined odd and

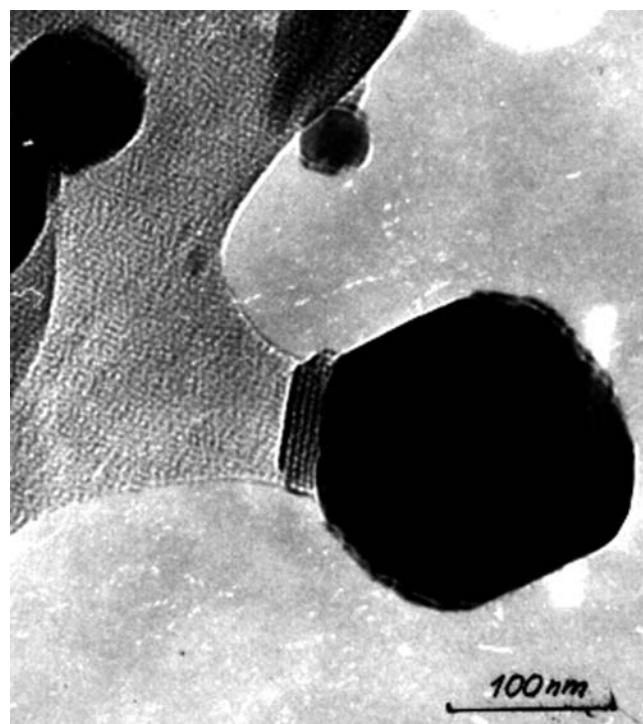


Figure 5. TEM of the interface of the products resulting from the reaction between AgBr and NaSt (Reference 18, reprinted with permission of IS&T).

even order layer line reflections. The second phase shows reflections in the X-ray diffraction pattern that are identical to those that appeared upon reaction of silver bromide, have the interlayer spacing of $d_{001} = 44.8$ Å (compared to 44.1 Å from the AgBr reaction), have diminished intensity for even orders of layer lines, ($4z$ in Fig. 6b and $4y$ in Fig. 3b) and correspond to a phase that can be best designated as $\text{Na}_{1-n}\text{Ag}_n\text{St}$. The third phase corresponds to the structure described above as $\text{Ag}_{1-n}\text{Na}_n\text{St}$ with $d_{001} = 49.5$ Å, while d_{001} was found to be 50.0 Å in the case of AgBr. As in the AgBr case, the X-ray pattern for this phase demonstrates diminished odd order layer lines, however, for AgCl the odd

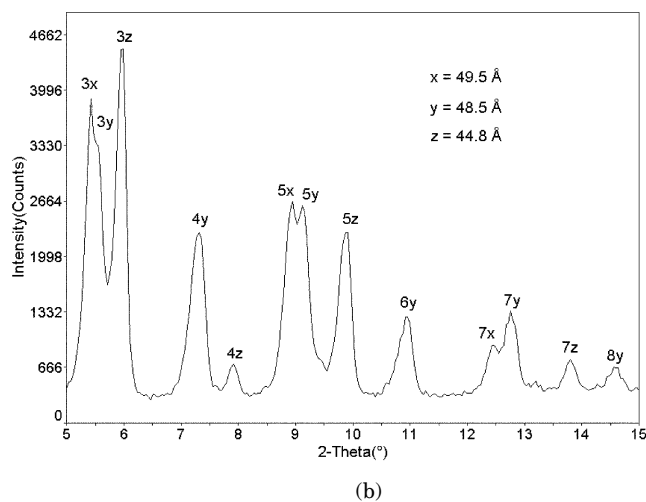
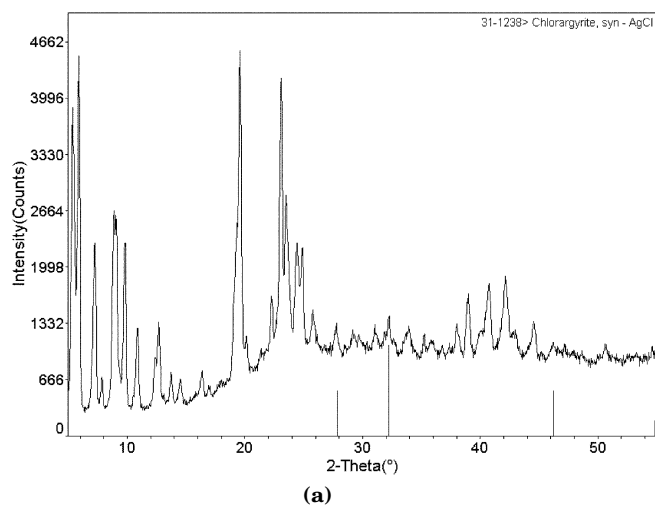


Figure 6. X-ray diffraction of the products resulting from the reaction between AgCl and NaSt, (a) with AgCl reference diffraction pattern, and (b) the 5 – 15 2-theta region expanded.

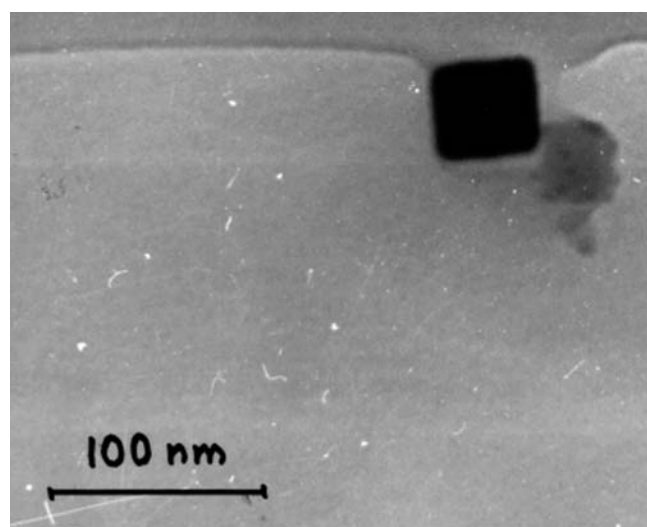
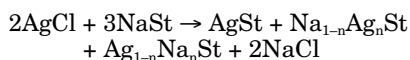


Figure 7. TEM of the products resulting from the reaction between AgCl and NaSt.

order layer lines have completely disappeared (no 4x, 6x, or 8x reflections in Fig 6b). The small difference between the d_{001} for AgCl and AgBr may be explained by a small difference in the “n” content in both products. Therefore, the reaction occurring with the AgCl crystals can be written schematically as follows:



The NaCl byproduct was removed in the aqueous phase and is not seen in the X-ray diffraction pattern.

The electron microscope investigation of this system showed that, consistent with the X-ray diffraction data, a significant change occurred in the dimensions and concentration of the silver halide crystals after the reaction of the silver chloride crystals with the sodium stearate. That is, reaction of a sodium stearate solution with cubic AgCl crystals (2000 Å diameter) results in a significant decrease in both the number of crystals and their sizes. The AgCl crystals after the reaction are no larger than 500 Å, Fig. 7.

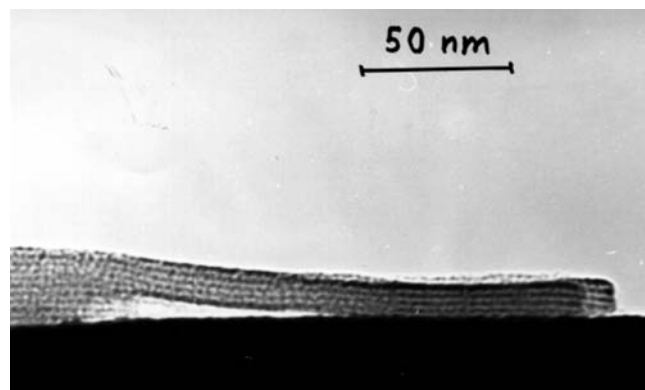


Figure 8. TEM of 0.15 μ AgCl crystals after treatment with NaSt solution.

At the same time, the TEM showed that the reaction of large AgCl cubic crystals led to the formation of silver stearate phases on the AgCl crystal surfaces. In this case, the silver ions in the layered silver stearate phase are arranged parallel to the AgCl crystal surface. The interface is seen clearly in the TEM picture, Fig. 8, and is significantly different than the structure of the interface appearing in the in situ photothermographic material where the layer of silver ions in the silver stearate structure are arranged perpendicular to the surface of the silver halide crystal.¹²

The formation of the silver fatty acid complexes in the reaction of the silver halide crystals may be the result of the similarity of the solubility products of the halides and the silver carboxylates formed in the reaction. It is known that the aqueous solubility of AgX decreases in the order $\text{Cl} > \text{Br} > \text{I}$.²⁶ The silver halide crystal solubility depends on the size of the crystal and the nature of the halide. The smaller the crystal size, the higher its surface energy, and solubility is increased. Taking these factors into account, it is reasonable that the formation of the pure silver stearate phase from reaction of silver chloride, and the formation of mixed $\text{Na}_{1-n}\text{Ag}_n\text{St}$ crystals from reaction of silver bromide, is the result of the higher solubility of the AgCl relative to AgBr.

One of the most interesting conclusions resulting from this work is the fact that the formation of the silver stearate phases directly from the reaction of the silver halide with

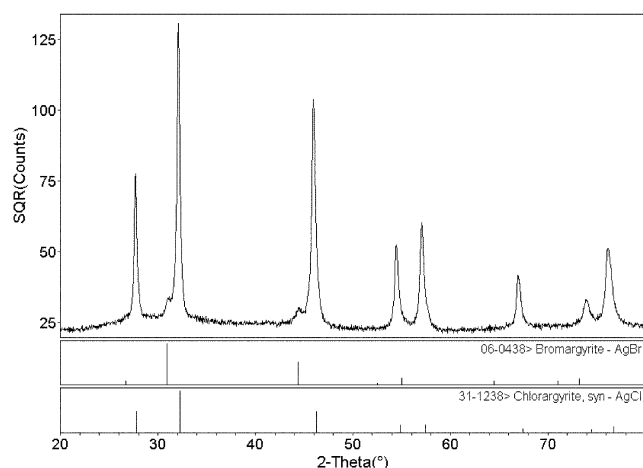


Figure 9. X-ray diffraction pattern of the starting AgBr/AgCl core/shell crystals.

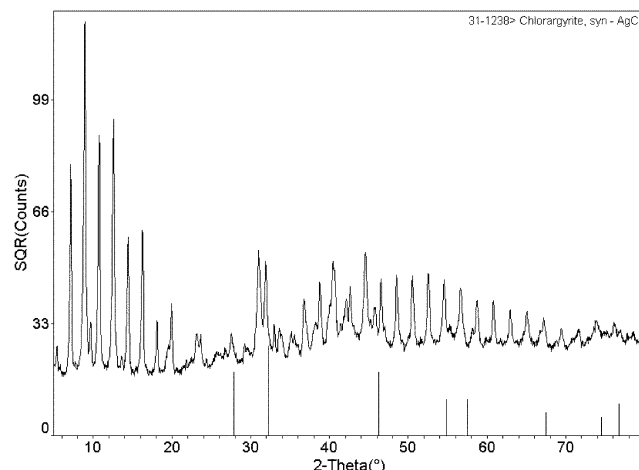


Figure 10. X-ray diffraction pattern of the products resulting from the reaction of AgBr/AgCl with a solution of sodium stearate (2 hrs, 50°C).

the sodium fatty acids can be observed. In this case, the preparation of a $\text{AgX}/[\text{AgO}_2\text{CR}]_2$ photothermographic composition may be carried out without using the intermediate reaction of sodium fatty acid salts with the silver salt solutions (such as silver nitrate).

In order to demonstrate this effect, a core-shell silver halide crystal was used as the starting silver halide crystals. The core was silver bromide and the shell silver chloride in order to allow the reaction of the sodium fatty acid soap to proceed with the AgCl shell resulting in the $[\text{AgO}_2\text{CR}]_2$ encapsulated AgBr as the final product. The X-ray diffraction of the initial crystals is shown in Fig. 9. The sample is composed of a major silver chloride phase, which appears to possess a slightly larger lattice than pure AgCl. A separate AgBr phase is also observed at a level consistent with the core-shell structure.

The reaction of this AgBr/AgCl crystal composition with a solution of sodium stearate does lead to the formation of a silver stearate phase, as confirmed by the X-ray diffraction analysis. The layered structure of silver stearate is clearly observed. In contrast to the use of pure AgCl, however, the X-ray diffraction also showed the reflections from residual silver halide, Fig. 10. In addition, a very small amount of a phase having a layered structure (45.3 Å) was observed, although its low intensity prevents a definitive assignment of its composition.

Conclusions

From the TEM and X-ray diffraction of materials prepared by the addition of silver ion to a mixture of silver halide grains and sodium carboxylates, it is clear that an epitaxial interface is formed between the AgX and $[\text{AgO}_2\text{CR}]_2$ components. This epitax is not only detectable, but it can be characterized and has been found to be comprised of mixed phases of varying Ag^+/Na^+ composition. Furthermore, this phase is easily formed under normal reaction conditions, the extent of the reaction being related to the nature of the halide. This mixed phase is a feature of the preparation process, that is, the addition of silver nitrate to a dispersion of AgX and sodium soaps, and would not be expected to form simply by mixing separately prepared dispersions of AgX and $[\text{Ag}(\text{O}_2\text{C}_n\text{H}_{2n-1})_2]$. This mixed phase may contribute to the photographic properties of films prepared from these materials. ▲

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