The Influence of Homogeneous Distributed Iodide on the Bulk and Surface Conductivity of Silver Bromide Crystals

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Introduction

Interstitial silver ions (Ag\textsuperscript{+}) play an important role during the latent image formation process. Their concentration corresponds with the sensitivity of the emulsion.\textsuperscript{[1], [2], [3]} The Ag\textsuperscript{+} concentration of AgX microcrystals can be changed anyway by coadsorption of antifogging agents and sensitizing dyes at the crystal surface. A suitable method for characterization of the Ag\textsuperscript{+} concentration is the measurement of the dielectric loss.\textsuperscript{[4]}

If high sensitizing dye concentrations added, emulsions with octahedral or cubic microcrystals show a dielectric loss spectrum with two peaks, which characterize the ionic conductivity at the subsurface (high frequency (HF) peak) and in the bulk (low frequency (LF) peak). This interpretation is based on the only shifting of the HF peak, which is assigned to the subsurface region, by manipulation at the crystal surface.

The following paper shows, that the insertion of iodide ions in AgBr microcrystals influences both HF and LF peak. Therefore AgBr\textsubscript{1-x}I\textsubscript{x} crystals with homogeneous iodide distribution (x=0.02 to 0.1) have been prepared and a sensitizing dye has been added to the emulsions within a concentration range from 0 to 100 \% theoretical surface coverage.

The Determination of Dielectric Loss

The theory of this method and the apparatus used were treated elsewhere.\textsuperscript{[5], [6], [7], [8], [9]}

For the measurement of the dielectric loss a thin layer (d \leq 0.2 mm) of a photographic emulsion is pressed between two metal plates (figure 1).

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure1.png}
\caption{Figure 1, Measuring principle}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure2.png}
\caption{Figure 2, Example for a plot of measured data}
\end{figure}

During a measurement the dielectric loss (\varepsilon''') is recorded as a function of the frequency. The values of \varepsilon''' are plotted against the logarithm of the frequency (figure 2). A simple relation between the frequency at the maximum of the dielectric loss (maximum frequency, f\textsubscript{max}) and the Ag\textsuperscript{+} concentration is used to evaluate the Ag\textsuperscript{+} concentration [7]:

\[ f_{\text{max}} \sim [\text{Ag}^+] \]

Emulsions with cubic microcrystals show an ideal dielectric loss spectrum with one symmetric peak (figure 3).

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure3.png}
\caption{Figure 3, Ideal Dielectric Loss Spectrum}
\end{figure}

This form of the spectrum can be influenced by variations in crystal structure and by manipulations at the surface. Octahedra show an asymmetric peak. It widens till
the appearance of a double peak by adsorption of spectral sensitizers (figure 4).

![Figure 4, Double Peak (Solid Line) and Two Fitted Peaks (Pointed Line)]

The appearance of the double peak can be explained by the subsurface/bulk model. Different regions of the microcrystals (bulk and subsurface) show different ionic conductivities (figure 5).

![Figure 5, Subsurface and Bulk Regions in Cubes and Octahedra]

Octahedra have (1 1 1)-surfaces, which are much more reactive than the (1 0 0)-surfaces of the cubes. Silver ions at the surface of octahedra can much easier occupy interstitial places. So the dielectric loss spectrum divides into a high frequency peak (HF-peak) and a low frequency peak (LF-peak). According to this the HF-peak corresponds to the subsurface region and the LF-peak corresponds to the bulk region.

For exact evaluation of the double peaks and their maximum frequency special peak fitting software was necessary. We used Microcal's Peak Fitting Module, which is an optional add-on to the program Origin 4.1. Comparing the different models for peak fitting, we obtained best results using the Lorentz-fit (figure 4, $\chi^2 = 3 \times 10^{-5}$)

**The Samples**

Emulsions with homogeneous distributed iodide with a mole fraction from $x_{\text{iodide}}=0$ to $x_{\text{iodide}}=0.1$ have been investigated. Furthermore the influence of an adsorbed sensitizing dye (figure 6) on the Ag⁺ concentration of these iodide containing emulsions has been analyzed. For that the dye concentration has been varied in a range from 0 to 100% theoretical surface coverage.

![Figure 6, Sensitizing Dye]

All emulsions were prepared by conventional pAg-controlled double jet precipitation. To the melted emulsions (40 °C) a solution of sensitizing dye has been added. After that they have been stirred for 20 minutes at 40°C. All emulsions were melted, cast on glass plates and dried over molecular sieves (3 Å) yielding brittle layers with a thickness ~ 100 μm.

Electron microscopy reveals a cubo-octahedral crystal morphology.

**Results**

![Figure 7, Influence of Homogeneous Distributed Iodide on $f_{\text{max}}$]

Figure 7 shows the dependence of $f_{\text{max}}$ on the concentration of homogeneous in the AgBr crystal distributed iodide. With rising iodide both, HF-peak and LF-peak, shift to higher frequencies. But the influence of the iodide on the surface region is much more intensive than on the bulk one. So the difference between HF-peak and LF-peak increases with rising iodide concentration. It should be mentioned, that the apparatus only records spectra till 13 MHz. All $f_{\text{max}}$ above this frequency are estimated by extrapolation using the peak fitting software.

Figure 8 and 9 show the influence of the sensitizer concentration on the HF- and LF-peak at a mole fraction of $x_{\text{iodide}}=0$ and $x_{\text{iodide}}=0.06$. Rising dye concentration rapidly shifts the HF-peak to higher frequencies. In contrast to this the LF-peak is nearly not influenced. This fact does not depend on the iodide concentration.
At a mole fraction of $x_{\text{iodide}}=0.06$ there is a larger difference between the LF-peak and the HF-peak in comparison to $x_{\text{iodide}}=0$ at low dye concentration. $f_{\text{max}}$ of the HF-peak reaches nearly the same value at high dye concentration at both iodide concentrations (figure 9).

The HF-peak is influenced very much by both dye and iodide concentration. With rising concentration of dye and iodide the maximum frequency of the HF-peak increases and seems to reach a limiting value at higher concentrations (figure 11).

**Discussion**

These results support the theory, on which the ionic conductivity of silverhalides divides into bulk and subsurface conductivity. Adsorptiva influence mainly the subsurface conductivity and with this the HF-peak. The bulk conductivity can be influenced by the concentration of homogeneous in the AgBr crystal distributed iodide. This is shown by a LF-peak shifted to higher frequencies by homogeneous distributed iodide. But the iodide also rises the subsurface conductivity, because it is distributed in the whole crystal.

**Acknowledgments**

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**References**