

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_i^+) play an important role during the latent image formation process. Their concentration corresponds with the sensitivity of the emulsion. [1], [2], [3] The Ag_i^+ 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_i^+ concentration is the measurement of the dielectric loss. [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 micro crystals influences both HF and LF peak. Therefore $\text{AgBr}_{1-x}\text{I}_x$ 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. [5], [6], [7], [8], [9]

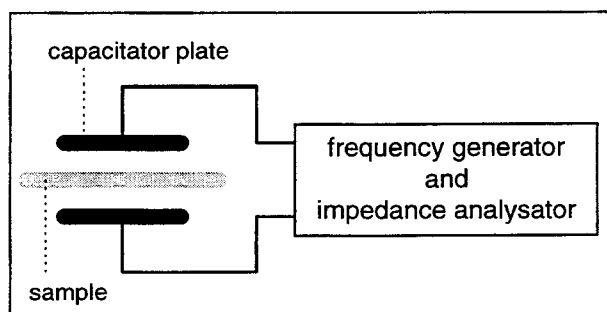


Figure 1, Measuring principle

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).

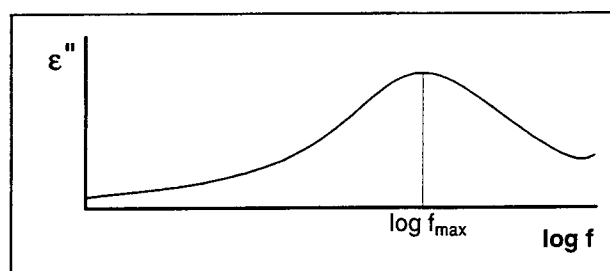


Figure 2, Example for a plot of measured data

During a measurement the dielectric loss (ϵ'') is recorded as a function of the frequency. The values of ϵ'' 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_{\max}) and the Ag_i^+ concentration is used to evaluate the Ag_i^+ concentration [7]:

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

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

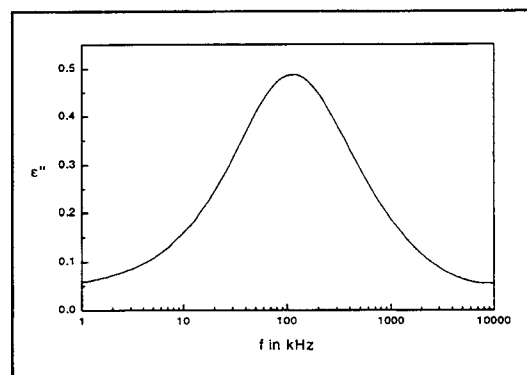


Figure 3, Ideal Dielectric Loss Spectrum

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).

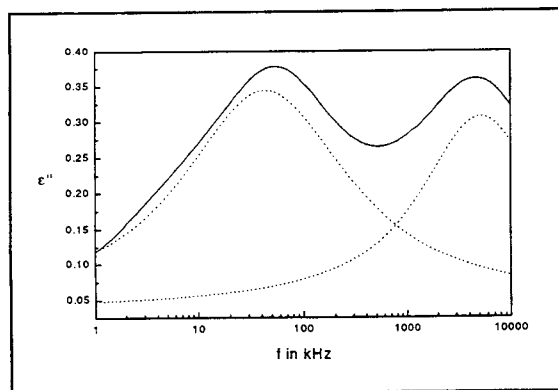


Figure 4, Double Peak (Solid Line) and Two Fitted Peaks (Pointed Line)

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)

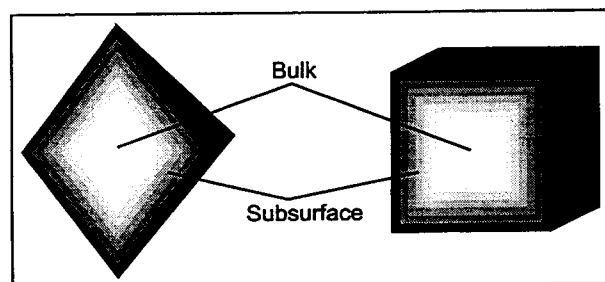


Figure 5, Subsurface and Bulk Regions in Cubes and Octahedra

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, $\chi^2 = 3 \cdot 10^{-6}$)

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_i^+ 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.

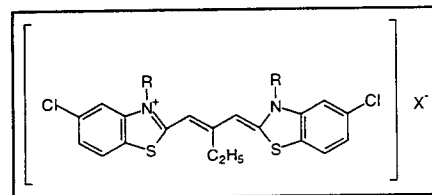


Figure 6, Sensitizing Dye

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-octahedric crystal morphology.

Results

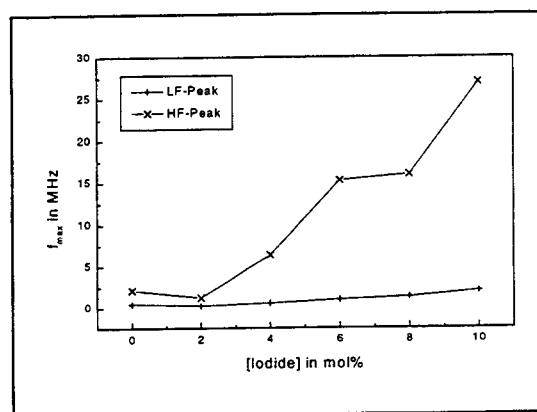


Figure 7, Influence of Homogeneous Distributed Iodide on f_{max}

Figure 7 shows the dependence of f_{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_{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.

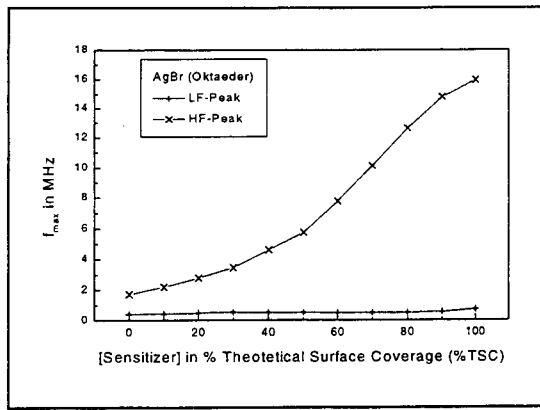


Figure 8, Dependence of f_{max} on the Sensitizer Concentration (AgBr, Octahedra)

At a mole fraction of $x_{Iodide}=0.06$ there is a larger difference between the LF-peak and the HF-peak in comparison to $x_{Iodide}=0$ at low dye concentration. f_{max} of the HF-peak reaches nearly the same value at high dye concentration at both iodide concentrations (figure 9).

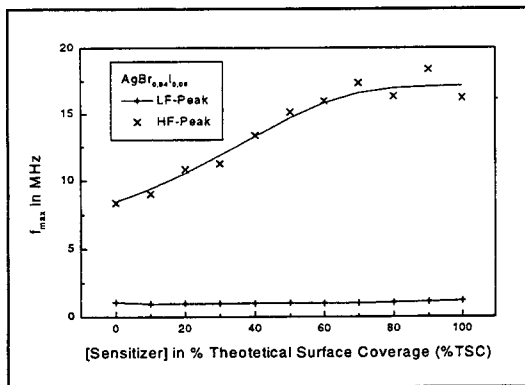


Figure 9, Dependence of f_{max} on the Sensitizer Concentration (AgBr_{0.94}I_{0.06})

Figure 10 and 11 give a survey of the position of the LF-peak and HF-peak of all samples. There is nearly no influence of the dye concentration on the LF-peak. In contrast to this result the iodide concentration influences f_{max} of the LF-peak much more (figure 10).

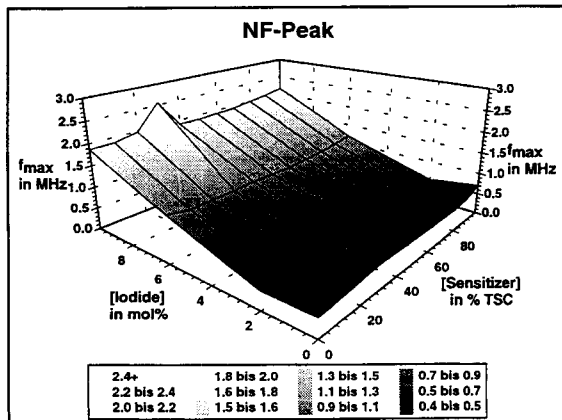


Figure 10, Influence of Iodide and Sensitizer on the NF peak

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).

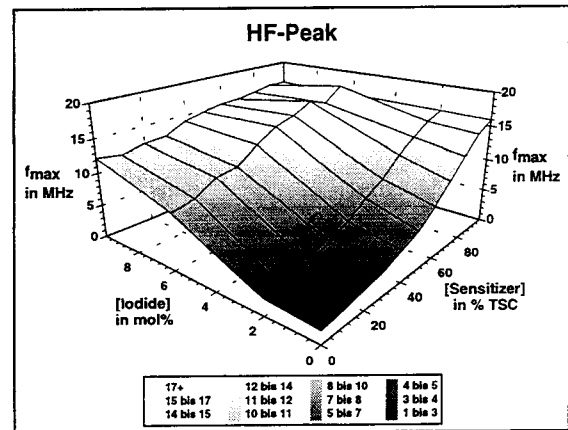


Figure 11, Influence of Iodide and Sensitizer on the HF peak

Discussion

These results support the theory, on which the ionic conductivity of silverhalides divides into bulk and subsurface conductivity. Adsorptive 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

- Walther, W.: *Photographische Verfahren mit Silberhalogeniden*, Fotokinoverlag, Leipzig (1983)
- Siegel, J.; Grossmann, J. von; Beberdich, H.; Rittmeier, K.; Israel, G.; Strösser, R.; Sydow, M.: *J. Inf. Rec. Mats.* **19**, 347-363 (1991)
- Harenburg, J.: *PhD-thesis*, Merseburg (1996)
- Biesen, J van: *J. Appl. Phys.* **41**, 1910 (1970)
- Heieck, J.: *PhD-thesis*, Verlag Shaker, Aachen (1993)
- Heieck, J.; Granzer, F.: *J. Imag. Sci. Tec.* **38**, 464-474 (1994)
- Beberdich, H.; Ullmann, H.: *J. Inf. Rec. Mats.* **21**, 383-407 (1994)
- Wilken, D.: *Diplomarbeit*, Merseburg (1995)
- Wilken, D.; Detering, A.; Israel, G.; Siegel, J.: *Proc. IS&T 49th Ann. Conf.*, Minneapolis, 84-86 (1996)