

ELECTROLUMINESCENCE OF SILVER HALIDES AT LOW TEMPERATURES

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Electroluminescence of silver halides crystals and thin foils was investigated. The microscopic observations of electroluminescence and silver inclusions were carried out for the crystals studied. The measurements of brightness *vs* voltage for the segment of fixed emitting line and for a complete cell were carried out. The oscillograms of the light peaks on voltage of silver halides crystals and thin foils were studied by excitation with sinusoidal voltages and rectangular pulses. The results obtained lead to the conclusion that the electroluminescence of silver halides is due to the silver inclusions. The shape of the brightness waves can be explained on ground of Fischer's and Maeda model with the assumption of a special kind of the emitting sharp pointed lines.

Introduction

In recent years much studies of the luminescence and photoconductivity of silver halides polycrystalline and monocrystalline have been carried out [26, 29, 32, 35, 36]. Several papers were concerned with the effect of the electric field on the luminescence of silver halides.

Recently Smith [35] during the measurements of thermally stimulated currents in AgCl and AgBr observed that under certain conditions these currents were accompanied by the momentary light emission.

Electroluminescence of the mixed system silver bromo-iodide powder phosphors was first observed by Kiciak [37], Łożykowski *et al.* [38] published the results of the first studies the low temperature electroluminescence of polycrystalline powder phosphors (pure and doped) and the thin halides foils as well.

In the next paper of Łożykowski *et al.* [39] concerning to the electroluminescence of silver halides an attempt was made towards interpretation the experimental facts on the ground of Fischer [13] and Maeda [5] model.

The main object of present paper is to provide the direct evidence of the reality Fischer's and Maeda model in the case of electroluminescent silver halides phosphors.

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General remarks

It is well known that the silver halides crystals contain a great number of the metallic silver precipitated in imperfections lines and in boundaries between adjacent crystallites. The process of the silver precipitation is mainly occurred under illumination with U. V. or visible light (photolytic silver) and by the electric field action as well (electrolytic silver) [16, 18].

It has been demonstrated by Hedges and Mitchell [21] that the pattern of the silver precipitated is identical with the mosaic structure of crystal.

As follows from our investigations, the pattern of electroluminescence emission of silver halides is similar to picture of the silver precipitated (Fig. 1).

The above fact allowed to suppose [38, 39], that the occurrence of electroluminescence in



Fig. 1. Microphotograph of electroluminescence emission freshly prepared cell (AgCl + 1 mol % AgI) excited with sinusoidal voltage of 200 V, 1 kHz. The long photograph side corresponds to 1 mm of the sample

silver halides is closely connected with the printed out silver and consequently with the crystal imperfections lines.

There are several reports that in ZnS phosphors the electroluminescence emission is connected with the decorated imperfection lines, however these inclusions were very difficult to direct observation [6, 7, 11].

We have a quite different situation in the case of silver halides crystals in which the silver inclusions lines are easily visible under the microscope.

At present exist two alternative models which might be used for explanation of the new found electroluminescent lines. It is the impact ionization model given by Maeda [5], and the bipolar field emission proposed by Fischer [13]. Maeda [5] assumes the existence of the high local field near the conducting phase. The main feature of the Fischer's model is the simultaneous field emission of electrons and holes from the opposite ends of the conducting inclusion with trapping of injected holes in activator centres and recombina-

tion with mobile electrons at field reversal. Theoretical considerations of both Maeda and Fischer and the experimental results obtained by Fischer strongly support Lehmann's observations [3], who established that the brightness voltage relation of the individual emitting elements is described by the equation:

$$I = A \exp \left(- \frac{B}{V} \right) \quad (1)$$

and the brightness of whole electroluminescent cell fits better the equation:

$$I = A' \exp \left(- \frac{B'}{\sqrt{V}} \right) \quad (2)$$

Experimental

For the measurements of the brightness *vs* voltage of the emitted lines the silver halides crystals were used. The dependence of over all emission on the applied voltage was carried out on thin silver chloride foils.

a. Crystals

The crystals studied were obtained from the commercial pure material by Bridgeman's method in glass and silica tubes evacuated to 10^{-2} mm Hg.

Samples of about 1 cm in diameter and 1–3 mm thick were cut from large crystals. They were polished with sodium tiosulphate solution [29, 30, 31, 33]. The measurements were made with the electroluminescent cells in which one electrode was a semiconducting quartz plate isolated by a mica plate the other was an Aquadac contact. As a dielectric the silicone oil DC 703 was used. With the electroluminescent cell described above we have measured the spectral distribution of electroluminescence for the crystals investigated. The shape of electroluminescence emission spectra for the silver halides crystals and for the thin layers appears to be quite similar [39].

We also studied electroluminescence in electroluminescent cells without mica foil. In this case the cells were quickly deteriorated especially as high voltage is applied. The microscopic observations of electroluminescence of silver halides were carried out at the liquid air temperature with a setup shown in Fig. 2.

Because of the setup the microscopic examinations could be performed with magnification not higher as 200.

Dependence of electroluminescence on voltage and frequency of excitation was studied by means of a photomultiplier connected with the usual arrangement.

b. Thin foils

The thin silver chloride foils were prepared as follows. A semiconducting quartz plate covered by mica sheet was placed into the molten silver chloride powder [33]. The thin layer was formed between quartz and mica plate due to the capillary forces.

After one hour the molten layer was withdrawn and slowly cooled. Next, the samples obtained were annealed at 300°C in air atmosphere during 24 hours.

The electroluminescence of the foils obtained was investigated with electroluminescent cell of usual construction containing a mica plate. As a dielectric the silicone oil was used. The electroluminescent cell was placed directly into liquid air. Electroluminescence was excited with sinusoidal voltages in frequency range from 10 Hz to 10 kHz.

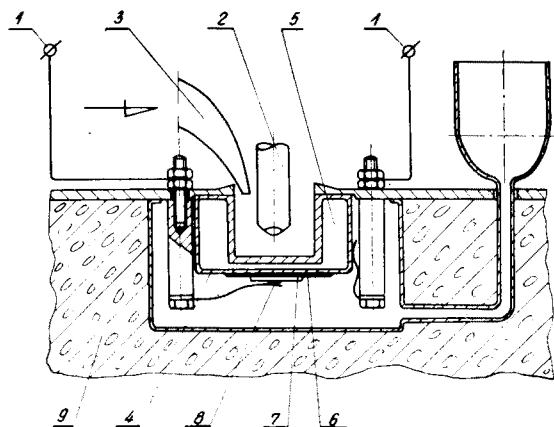


Fig. 2. Experimental arrangement for observation of electroluminescence in liquid air temperature. 1 — contacts, 2 — objective of microscope, 3 — hot nitrogen, 4 — quartz vessel with one semiconducting window, 5 — vacuum, 6 — mica, 7 — sample, 8 — aquadac, 9 — thermal isolation

Results

We have investigated electroluminescence of pure AgCl and AgBr crystals obtained in our laboratory and crystals kindly provided by Moser of the Kodak Research Laboratories. The electroluminescence of mixed crystals AgCl+1% mol AgJ, AgBr+1 mol AgJ and thin foils was investigated as well. The results presented in this paper are essentially based on observation of electroluminescence in AgCl and AgCl+1% mol AgJ because of the high intensity of the light emitted by these crystals.

The measurements of brightness *vs* voltage and frequency were carried out in the liquid air temperature only (the sample was directly inserted into the liquid air).

a. Crystals

The electroluminescence emission in silver halides crystals was found to be inhomogeneous in the bulk of crystal. The visual microscopic observations reveal a number of the long emitting lines which form an irregular mosaic structure. Under the microscope large single emitting lines are visible. Figure 1 shows typical electroluminescent lines. Visual observation shows that brightness of the whole cell is nearly constant when the applied voltage is kept constant. However study with a microscope gives a quite different pattern of the emission. Some of the emitting lines disappeared from time to time and new glow lines appear in the same region.

When the applied voltage is sufficiently high but still below the breakdown point the clusters of new mobile lines are observed originating at fixed space lines. It was possible to detect electroluminescence lines visually already at 5 V.

The intensity of the light emission of a certain segment of a line increases with the voltage applied. With increasing intensity of the light emitted by this segment two different effects can be observed. The length of the electroluminescent line increases and branches of line appear. It was observed that the brightness of a complete cell increases more rapidly with the applied voltage than that of the brightness of a segment of a line. The measurements of brightness *vs* voltage for the segment of fixed emitting line were carried out with the setup described previously. On the ocular of the microscope a 1P21 photomultiplier was mounted.

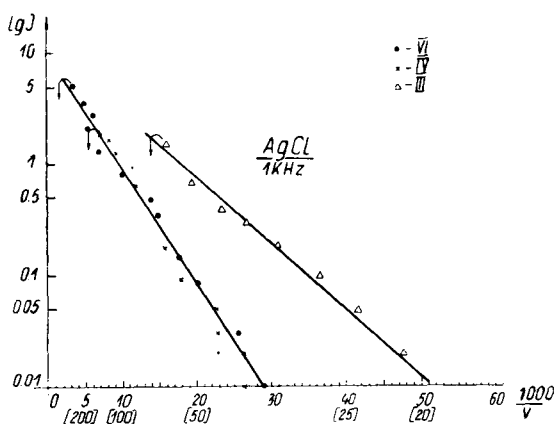


Fig. 3. Log brightness *vs* (voltage)⁻¹ for segment of electroluminescent line of AgCl crystal. Electroluminescent cell with mica plate

Figure 3 shows the results obtained. These results were confirmed on measurements for a great number of crystals. It can be seen that the brightness of small segment of electroluminescent line *vs* voltage is described by the equation (1).

It is in good accordance with the theoretical predictions given by Maeda and Fischer.

It must be noted that the above dependence is fulfilled in whole range of the measured intensity, the last point gives the value of applied voltage above which electroluminescent line does not any more glow. The same experimental points do not yield a good straight line for the $\log J$ *vs* $V^{-1/2}$ especially at the higher voltages applied.

By means of a microscope we have made an experimental which allowed to observe simultaneously the printed out silver under illumination with red light and green electroluminescent lines (Figs 4a and 4b).

The above pictures show the region of mixed crystal AgCl+1% mol AgJ which was repeatedly used in electroluminescence investigations and thus containing a great number of silver precipitations. The close connection of electroluminescence with printed out metallic silver is obvious.

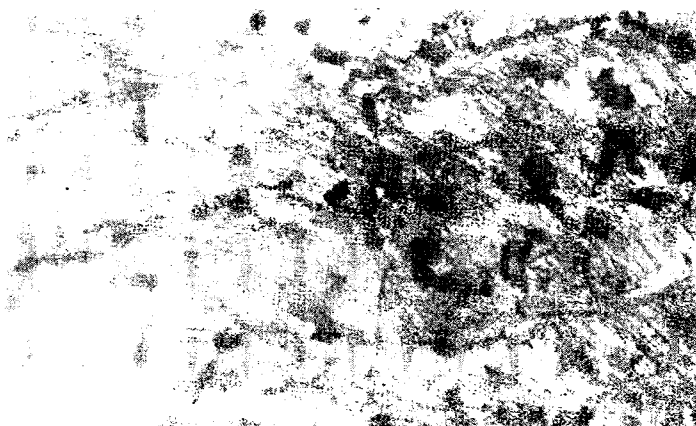
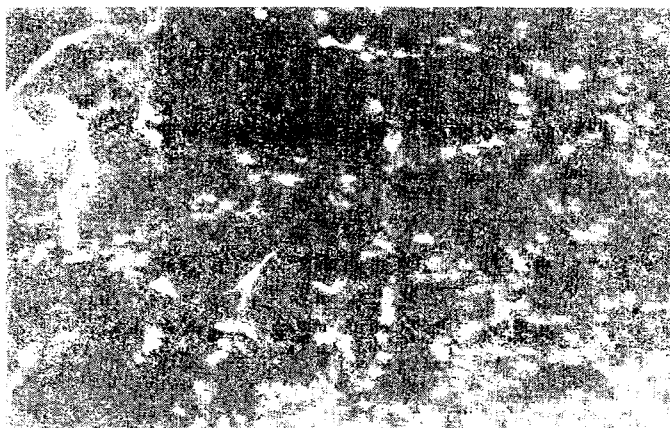
*a**b*

Fig. 4. *a* — microphotograph of silver precipitations in $\text{AgCl} + 1 \text{ mol } 1 \% \text{ AgI}$. The long photograph side corresponds to 1 mm of sample. *b* — microphotograph of electroluminescence emission in above shown region (100 V, 3 kHz)

b. Thin silver halides foils

The visual observation indicates that electroluminescence emission of thin silver halides layers appear to be more homogeneous in comparison with the emission of crystals investigated.

Figure 5 shows the intensity of the emitted light as a function of applied voltage.

Such dependence of brightness on applied voltage was observed for all samples investigated.

The voltage dependence of over-all intensity can be described by equation (2).

In the region of high voltages a deviation from this equation is observed, which we are for the time being unable to explain. The dependence of brightness *vs* log frequency at constant voltage is given in Figure 6.

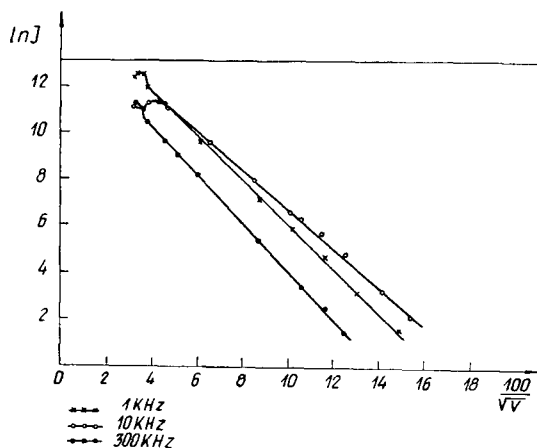


Fig. 5. Log brightness vs (voltage) $^{-1/2}$ for silver chloride foil. Electroluminescent cell with mica plate

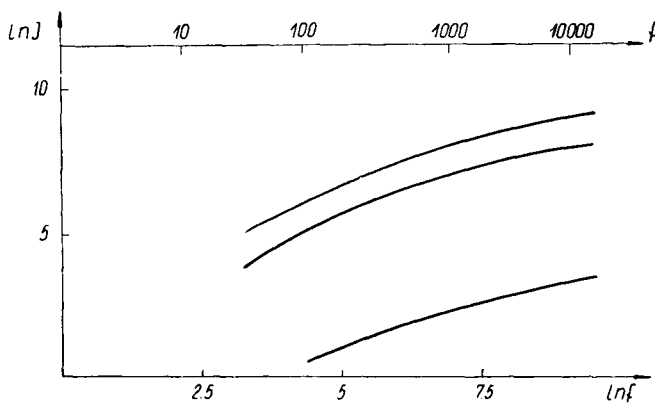


Fig. 6. Log brightness vs log frequency at constant voltage for AgCl foil. Electroluminescent cell with mica plate

Forming process

For the occurrence of the electroluminescence of freshly prepared samples of silver halides some kind of preliminary forming process is often required, *viz.* illumination with U. V. and simultaneous application of a high voltage. The value of applied voltage must exceed many times the threshold for visual observation of electroluminescence (*e. g.* 1 kV, 1 kHz).

When the high voltage is applied the silver precipitation occurs due to large current flowing through the crystal. In some cases a high voltage is required only without U. V. irradiation. In this case the emitting lines near the electrode can be observed, which after a short time extend over the already stabilized emission region.

Crystals which did not show the electroluminescence emission without forming process are silver chloride crystals obtained from Kodak.

However only for a few crystals prepared in our laboratory the preliminary forming process was required.

We believe that the above difference is due to the preparation method used (our crystals were prepared without chloride atmosphere). The observations described lead to the conclusion that the main feature of the preliminary forming process is to form sharp pointed conducting silver inclusion where the field-emission takes place. The process of the silver precipitation in silver halides due to electric field was reported in literature [20, 21].

It must be noted that preliminary forming process is required only once for a particular specimen.

Brightness waves

The oscillograms of the light peaks and voltage of silver halides crystals and thin layers were studied by excitation with sinusoidal voltages and rectangular pulses. The measurements were carried out with electroluminescent cell containing a mica sheet.

Figs 7a and 7b show electroluminescence brightness wave for AgCl and AgBr + 1% mol AgJ mixed crystal respectively. At "moderate" voltage amplitudes one high intensity peak which constitutes the major component of the light emission is observed for every cycle and the secondary one of low intensity. In some cases a trace of second maximum can be observed. At voltages at which the clusters of mobile lines appear the shape of brightness waves is changed (Fig. 7b). The brightness waves obtained for crystals are in general quite similar to those for thin layers.

The observed shape of the brightness waves can be explained on the ground of Fischer's model with the assumption of a special kind of the emitting sharp-pointed line. We assume the conducting silver inclusion in the shape of a "rough filament" which starts from the metallic electrode and has a tip (or tips) in the bulk of crystal.

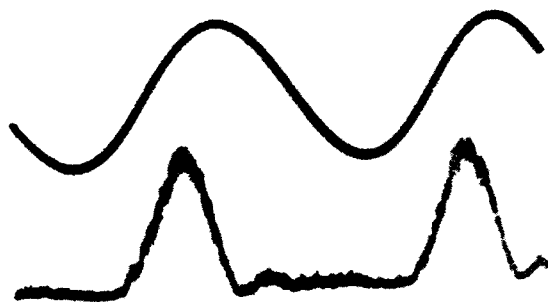
A more detailed illustration of the events occurring at successive cycles of the voltage applied is given in Figs 8a-f.

When the external field is applied in such way that the metallic electrode is positive, holes are injected from the tip of conducting line. This process comes to stop as the polarization field reduces the field strength at the tip. Since the holes are less mobile than the electrons the process of holes trapping occurs near the tip. If the external field drops to zero the emission of electrons occurs due to decreasing polarization field.

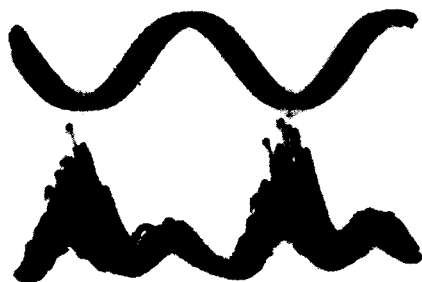
At voltage reversal the field strength at the emitting tip increases and reaches a maximum (the residual polarization field adds to the external field).

Some of the field emitted electrons recombine with trapped holes giving rise to a light pulse, the other are trapped far of the emitting tip and then build up a new polarization field.

At repeated voltage reversal the field emission of holes becomes more easy, because of the total field at the tip is the sum of the polarization field and the applied field. The above considerations lead to conclusion that the light is emitted when the metallic electrode is becoming less positive and reaches the maximum when this electrode is negative. It is in good accordance with the results obtained for the brightness waves excited with low



a



b

Fig. 7. *a* — oscillogram of light and voltage of AgCl crystal. Sinusoidal voltage of 300 V, 300 Hz. *b* — oscillogram of light output with instability maximum of AgBr+1 mol % AgJ excited with "high amplitude" voltage

frequency rectangular pulses. When square waves pulses of negative polarity (metallic electrode negative) is applied to electroluminescent cell a pulse of light emission is observed at the beginning of the pulse of the external field.

With the pulses of opposite polarity the higher pulse of light is observed upon the decreasing branch of the voltage. With the sinusoidal excitation the second light peak of low intensity can be explained by assumption that in the bulk of crystal the conducting silver inclusions are also present not having direct contact with metallic electrode and thus working according to Fischer's model. It must be mentioned, that recombination of field emitted holes, either with trapped electrons or electrons released by field action, can be possible.

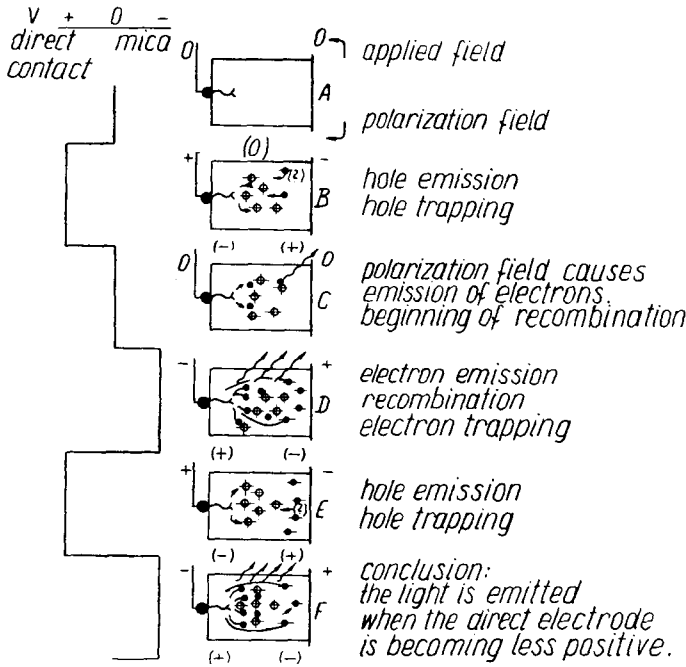


Fig. 8. Illustration of the events occurring at successive cycles of the voltage applied

The probability the releasing of the electrons from shallow traps directly by field is low because electrons due to their high mobility are trapped far from the emitting tip [22] *et al.* A justification of our assumption that only one end of emitting line is active can be obtained from the microscopic observation of the silver precipitated.

It must be noted that all results can be also explained on ground of the inverted Maeda model [13].

Additional observations

We also studied the electroluminescence of silver halides crystals in electroluminescent cells without mica plate.

These experiments lead to the conclusion that the electroluminescence emission occurs only when the internal field is changing.

It is in good agreement with the Maeda and Fischer's models which assume that the conducting inclusions are active only in a. c. field.

As mentioned above silver halides show a great facility in producing of printed out silver. This property is responsible for the occurrence of electroluminescence (preliminary forming process) and for the deterioration of electroluminescent cells as well. For the long time operating cells the decrease of brightness occurs and silver precipitations in great number can be observed with naked eye.

Microscopic observations allow to suppose that some of the emitting silver lines make contact between each other and give the long lines joining the opposite crystals edges.

The deteriorated sample can be regenerated by annealing at 300°C. The annealed samples were again strongly electroluminescent but the deterioration process occurred more quickly. Deterioration process strongly depends on the operating conditions and increases with frequency and temperature.

It must be noted that the deterioration process did not prevent the investigations because the brightness of electroluminescent cell is nearly constant during a long time when a "moderate" voltages are applied (e. g. a sample 2 mm thick was working during the 2 hours with voltage applied of 300 V, 1 kHz).

As already mentioned the mixed crystals show high intensity of electroluminescence emission and do not require the preliminary forming process. It is very difficult to give an explanation of this fact. The thermoluminescence measurements (with X-ray excitation) show that mixed crystals have a shallower traps than those of the pure AgCl.

We suppose that this fact may be responsible for the case with which the forming process proceeds in these crystals. It is well known that the U. V. excitation the mixed crystals AgCl+AgJ yields much higher intensity of the photoluminescence emission in comparison to the pure silver chloride crystals.

Conclusion

It can be considered as established that electroluminescence of silver halides is due to the conducting silver inclusions. In these inclusions either bipolar field-emission takes place or impact ionization process occurs in local high intensity field.

The above mechanism were proposed by Maeda and Fischer in order to explain electroluminescent lines in isolating powder particles of ZnS.

The great facility in producing of printed out silver makes the silver halides phosphors very convenient substance for studies of electroluminescent lines.

It must be noted that all our results are in good qualitative agreement with the theoretical predictions given by Maeda and Fischer.

The observed shape of the brightness waves can be explained on ground of Fischer's model with the assumption of a special kind of the emitting sharp-pointed lines.

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