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The Effect of Pressure on Photoluminescence and Photovoltaic Voltage in AgCl Crystals*)

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I Introduction

Pure and doped (e.g. Tl^+, Mn^{++}, Cd^{++}) crystals of AgCl after irradiation by UV light show at low temperatures ($T < 100°C$) characteristic blue-green emission band. The basic luminescence properties of these crystals have been summarized for instance in [1]. The nature of luminiscence centers responsible for the blue-green emission band observed was usually explained by the existence of predominant lattice defects in these crystals — by the cation vacancies. Matyáš in his paper [2] published before proposed the model which attributes the role of luminescence centers to cation vacancies at dislocations and to jogs on dislocations (with an effective charge — e/2).

Further detailed measurements performed in our laboratory brought us to considerable refinement of the model mentioned above [3].

The both models proposed for luminescence centers roughly said cation vacancy or dislocation jog are closely connected to the presence of dislocations in AgCl crystals. The origin of the potential difference observed on AgCl crystals during one-axial deformation was explained by Sonoike [4] as the result of migration of charge carried by moving dislocations. More detailed observations recently finished in our laboratory [5] indicated a certain correlation of Sonoike's results with the physical origin of luminiscence centers described above.

The purpose of this study is to look for the origin of luminiscence centers in silver chloride crystals. We report here the observations of integral blue-green luminescence (IL), measured on normal and deformed AgCl crystals, the measurements of potential difference induced on the opposite crystal surfaces during plastic

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deformation (PPD) and finally the measurements of photovoltaic voltage (PV), because there was found a narrow coherence between IL and PV on these non-deformed crystals [6].

2. Experimental procedure

The details of measuring apparatus of IL, PV and PPD on AgCl samples have already been described [1], [7], [5]. IL was measured at liquid air temperature in a quartz cryostat; the quantum flux density of the radiation falling on the crystal surface was about 1,04 × 10^{14} quanta/sec/cm^2.

PV was measured in the same cryostat and with the same recorder as IL.

The crystal for PPD measurements was cut on two equal parts. Both halves were fixed in the tensile machine and separated by a silver sheet. Both edges of the machine were silvered, shortened and served as one electrode, the middle silver sheet whose surface area was smaller than that of silvered edge served as the second electrode. Evidently electric field appearing in the crystal volume during one-axial plastic deformation had opposite direction to the pressure gradient and so the PPD had positive polarity on the central electrode.

Silver chloride samples (pure and doped) with 0,1 mol% $MnCl_2$ or 0.1 mol% TlCl) used in this work were prepared by a special method [8] in our laboratory.

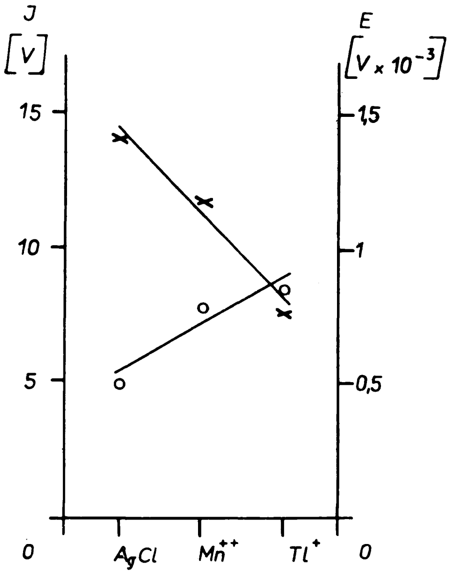


Fig. 1. The course of IL (o) and PV (x) on deformed (500 kp/cm²) pure and doped AgCl samples. IL was measured in volts, PV in millivolts. Measured at liquid air temperature.

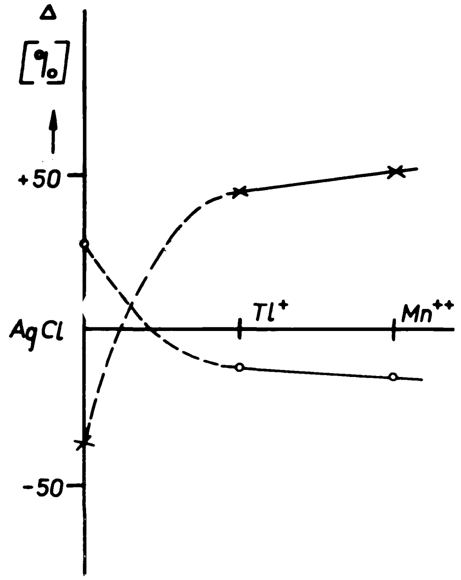


Fig. 2. Relative changes of IL (x) and PV (o) (in %) of pure and doped AgCl samples with deformation (500 kp/cm²). Measured at liquid air temperature.

3. Results

The typical course of IL and PV on deformed pure and doped AgCl crystals is shown in Fig. 1 for one serie of samples. Fig. 2 shows the relative changes of both IL and PV produced by deformation with respect to non deformed samples. Their comparison shows that after crystal deformation we observe generally a decrease of PV with increasing IL in all samples. On the other hand in pure AgCl crystals appears a decrease in IL (already reported in [1]) with deformation while in doped crystals the reverse is true.

Fig. 3. The course of PPD on pure AgCl crystal. Curve 1 – first deformation, curve 2 – second deformation. The stress increases between t_1 and t_2 from 0 to 500 kp/cm^2, since t_2 remain constant.

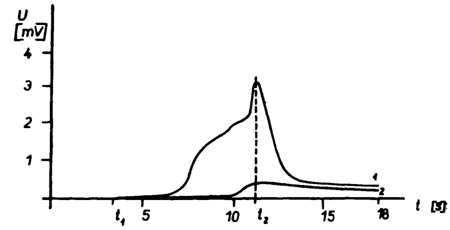


Fig. 4. The course of PPD on Tl doped AgCl crystal. Curve 1 – first deformation, curve 2 – second deformation. The stress increases between t_1 and t_2 from 0 to 500 kp/cm^2, since t_2 remain constant.

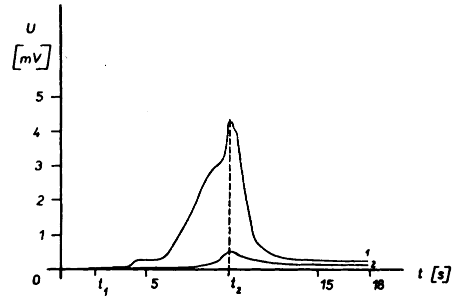
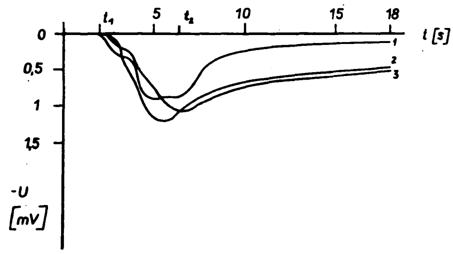


Fig. 5. The course of PPD on Mn – doped AgCl crystal. Curve 1 – first deformation, curve 2 – second deformation, curve 3 – third deformation. The stress increases between t_1 and t_2 from 0 to 500 kp/cm^2, since t_2 remain constant.



The typical behavior of the PPD kinetics in pure and doped AgCl crystals are shown on Fig. 3–5. Tensile stress used for sample deformation increased linearly from 0 to 500 kp/cm^2. Curve No 1 represents on all figures the course of PPD during first deformation, curve No 2 and No 3 represent the courses of PPD during following second and third deformations. All tests have been performed at room temperature.

Comparing all figures one can conclude that the course of PPD on pure and AgCl/Tl$^+$ crystals is similar in the polarity of the potential difference measured (the smaller electrode positive) and in the shape of the curves. On the other hand the course of PPD observed on AgCl/Mn^{++} crystals is quite different from both preceding cases: the polarity is opposite, the recovery is slower and the decrease of the sharp peaks appears till after the third deformation.

4. Discussion

Let us start first with the observations of the course of PPD. We shall limit us only on the initial region of the whole curves when the charge transfer is probably realized by fast — moving dislocations [4]. We assume further that the PPD observed during plastic deformation is closely connected with the motion of charged dislocations jogs. The jogs move simultaneously with the dislocation in the opposite direction to the stress gradient and one pair of these jogs always transports to the electrode on crystal surface a net charge –e. Our assumption is quite reasonable because the surface charge density transfered during one deformation to the electrode is approximately 1.2×10^{-8}C/cm^2. If we accept the charge transport by jogs, than for the given crystal width ($\sim 10^{-2}$ cm) we receive the density of one jog on two hundreds ionic distances what is an acceptable value for this type of ionic crystals.

According to our assumption the negative charge moves in the direction of the stress gradient and so the direction of electric field strength is opposite to the stress gradient. If the charge is transfered by dislocation jogs, than the negative charge should be transported to the electrode with large surface area what was observed.

By repeating the deformation we diminish the number of dislocation jogs and at the same time the measured PPD. In the case of pure crystals and AgCl/Tl crystals the curves obtained have qualitatively the same course for the monovalent foreign cations do not influence the charge of dislocation jogs. The opposite PPD polarity observed on AgCl/Mn^{++} crystals was reported for the case Cd^{++} -ions elsewhere [4].

The other group of IL and PV observations have been carried out at low temperatures where almost only electron eventually hole processes play predominant role. Both processes — IL and PV as well depend mainly on the presence of photoelectrons which can easily move along dislocations "canals". Photoelectron can be captured roughly said either by a trap or by a recombination luminescence centre (e.g. jog with localized hole). In the case of PV they can move up to the metal electrode giving it a negative excess charge. We may except that the photoelectron diffusion along the dislocations will be restricted by both types of defects discussed above — by traps and luminescence centres. Considering the role of luminescence centres only it can be said that the more jogs are present in dislocation "canals", the less number of photoelectrons will reach the metal electrode and the less photovoltaic voltage will be observed. On the other hand that means that the number of radiation recombinations will be higher and so we observe higher value of IL. In our opinion the deformation (see part I) diminish number of dislocation jogs and thus in deformed samples the processes connected with IL and with PV are in partial mutual competition, the luminescence increase should produce the decrease of photovoltaic voltage and vice versa. Our results on all samples are in good agreement with this conclusion. IL measured on pure crystals decreased after deformation and PV simultaneously increased. In doped crystals IL increased after deformation but PV decreased.

The positions of doped ions in the host lattice can be explained in one model so, that manganese ion substitutes a silver ion at a normal lattice position with a charge compensation on two dislocation jogs located at neighbouring lattice positions. The probable position of thallium ion is an interstitial site located between two dislocation kinks without any direct charge in the lattice neighbourhood. In both cases the jogs in doped non — deformed crystals are blocked and the plastic deformation releases dislocation jogs from their impurity atmosphere. So in the case of doped crystals IL increases after deformation and PV decreases in agreement with results obtained.

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