

Optical properties of silver halide fibres: ageing effects

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Abstract. The relation between the structure of fibres extruded from mixed silver halides $\text{AgBr}_{1-x}\text{Cl}_x$ and their IR optical losses and luminescence properties is studied. The recently established ageing effect of the considerable growth of mean grain size of the fibre's polycrystalline structure (typically from 20 to 1000 nm in two years) is correlated with IR and luminescence measurements. IR spectra measured in the interval 3.0–13 μm show growth of the concentrations of molecular impurities. The luminescence measurements are used for the characterization of the fibre's structure ordering. The luminescence decay kinetics is analysed theoretically in terms of the diffusion-controlled recombination of spatially well-correlated Frenkel defects. The considerable difference between the diffusion properties of monocrystals and fibres is established. This is caused by partial disorder (the grain structure effect) of the initially polycrystalline structure arising due to the fibre extrusion.

1. Introduction

Fibres extruded from mixed silver halides and thallium halides are widely used for the transmission of laser radiation in the far- and middle-infrared (IR) spectral region [1]. For ecological and toxicological reasons the former fibres are to be preferred. Prolonged studies [1] have demonstrated that the best characteristics are achieved for the particular compositions $\text{AgBr}_{0.75}\text{Cl}_{0.25}$ and $\text{AgBr}_{0.5}\text{Cl}_{0.5}$. This is why the present study concerns fibres of these two kinds. The crystalline preforms for fibre fabrication must satisfy demanding criteria, including high purity of the initial material and absence of voids, internal stress and inclusions of different phases. At present the growth technology of such monocrystals is well developed as that for further extrusion from them of optical fibres. The typical IR losses at the CO_2 laser wavelength are as small as 0.2–0.4 dB m^{-1} . However, optical losses usually tend to grow with time due to the fibre's ageing and exploitation. The mechanism and dynamics of ageing are studied in the present paper.

It is well known that optical losses consist of two parts: scattering losses and radiation absorption. Real fibres contain several types of scattering centres: voids, grain and phase boundaries and metal colloids. A number of absorption bands due to impurities have been observed in fibres [1]. A long-wavelength absorption band always arises due to a multi-phonon process. Another absorption mechanism is caused by free carriers [2].

Extruded fibres are known to have a polycrystalline structure. Since their losses caused by light scattering are determined, in particular, by mean grain size, the development with time of grain size characterizes well the *effect of ageing* on the fibre optical properties. Studies [3, 4] have demonstrated that the mean grain size depends on the extrusion technique and, for just-prepared low-loss fibres, is about 15–20 nm. The grain size grows monotonically with time, reaching to 1 μm after 20 months' ageing [3, 4]. Besides, appearance of the new phase of AgBr has also been observed [4], the size of AgBr inclusions being up to 0.5 μm . Both of these effects contribute considerably to the scattering losses and thus to the increase in optical losses in fibres during their ageing.

It is well known that luminescence spectroscopy is very sensitive to the local structure and composition of crystals. Besides, the luminescence of bulk silver halides has been studied very well [5]. This is why we performed here the first luminescence study in order to characterize the fibre ageing effect. In parallel, we used IR spectroscopy to investigate the correlation between the ageing and luminescence properties.

2. The experiment and samples

The fibres were manufactured in the Institute of General Physics of the Russian Academy of Sciences (Moscow) by hot extrusion from two kinds of crystals: $\text{AgBr}_{0.5}\text{Cl}_{0.5}$

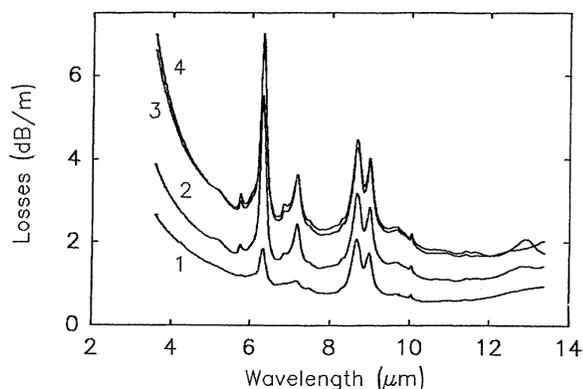


Figure 1. Spectra of total IR losses in the $\text{AgBr}_{0.75}\text{Cl}_{0.25}$ fibre (F2 type) measured immediately after extrusion (1) and 5 months (2), 9 months (3), 12 months (4) thereafter.

and $\text{AgBr}_{0.75}\text{Cl}_{0.25}$. Fibre samples were kept in a non-hermetic loose polymer tube under the typical laboratory environmental conditions.

Three kinds of fibres were studied here. F1 are $\text{AgBr}_{0.5}\text{Cl}_{0.5}$ fibres whose minimum losses (at $10.0 \mu\text{m}$) just after extrusion were 0.5 dB m^{-1} ; at the wavelength of $6.25 \mu\text{m}$ (H_2O absorption), losses are 1.2 dB m^{-1} . F2 are $\text{AgBr}_{0.75}\text{Cl}_{0.25}$ fibres with losses of 0.7 dB m^{-1} at $10.0 \mu\text{m}$ and 5.0 dB m^{-1} at $6.25 \mu\text{m}$. F3 are $\text{AgBr}_{0.75}\text{Cl}_{0.25}$ fibres which reveal minimum losses 0.5 dB m^{-1} at $10.0 \mu\text{m}$ and 1.1 dB m^{-1} at $6.25 \mu\text{m}$. These three kinds of fibres differ in the extrusion technology used and therefore in ageing and other secondary processes.

Spectra of total loss measurements were measured with a Bruker-IFR 113V spectrophotometer in the spectral region $3\text{--}13 \mu\text{m}$. Quenched samples, both fibres and monocrystals, were also studied; these samples were kept for 4 h at 450 K and then cooled rapidly in liquid nitrogen.

Samples containing the colloidal silver centres were prepared by exposing them for 5 h to the integral Hg lamp light and the resulting sample colouration was well observed.

The luminescence decay kinetics was measured over a wide temporal range (10 ns to 1 ms) after excitation by a pulsed nitrogen laser ($h\nu = 3.67 \text{ eV}$, pulse duration 8 ns). The luminescence decay was measured using a time-correlated single-photon-counting system whose time resolution could be set to 10, 40 and 160 ns and which allowed photon counting in a gate (with gate widths 1 and 10 μs). The system consisted of 127 channels. We had a well-defined zero time (the detection system is synchronized with respect to the laser light pulse) which allowed us to combine the luminescence decay kinetics measured in the different time ranges. The luminescence intensity is plotted in arbitrary units in the double logarithmic coordinates $\ln I$ versus $\ln t$. All luminescence measurements were performed at 100 K.

3. Results

3.1. IR optical loss changes

Figure 1 shows typical fibre (F2) IR loss spectra measured during storage. Fibres of this kind are known to reveal a large ageing effect (optical losses rapidly grow with time). In the ageing process the scattering losses increase during one year from 1.7 to 6.0 dB m^{-1} at $4.0 \mu\text{m}$. The absorption peaks due to intra-molecular impurity vibrations increase considerably. The algebraic dependence of the losses as a function of the wavelength λ in the region $3\text{--}5 \mu\text{m}$ is due to the scattering losses on the grain boundaries, voids, grains of AgBr phase and other scattering centres whose concentration and mean size change with the fibre ageing. Detailed analysis of the mechanisms of scattering losses and their dependence on the wavelength λ has been presented for F2 fibres in [3]. It should be noted here that, for some fibres extruded by a modified method from pure and structurally perfect monocrystals, the ageing effect was very weak. In some cases the Rayleigh scattering even decreased during fibre storage [3]. In the present study this was the case for F1 and F3 fibres.

The IR spectra measured just after extrusion show the absorption bands characteristic of the intra-molecular impurity vibrations; similar bands are well known in alkali halide crystals. In particular, the band at $6.25 \mu\text{m}$ results from the deformational H_2O vibration, whereas that at $7.14 \mu\text{m}$ is very probably the deformational OH^- vibration. (However, it is not excluded that it could be the degenerate valence asymmetric vibration (ν_{as}) of the NO_3^- ($7.3 \mu\text{m}$) ion.) Peaks at $8.5\text{--}8.9 \mu\text{m}$ could be due to the three-fold degenerate ν_{as} vibration of the SO_4^{2-} ion. In this case the number of peaks depends on the local distortion of the atomic configuration around the impurity molecule [6]. All studied fibres exhibited molecular impurities whose concentration increased with ageing.

3.2. Luminescent properties

The luminescence of $\text{AgBr}_{1-x}\text{Cl}_x$ solid solutions is very well known [5, 7]. At liquid nitrogen temperature (LNT) and $x \neq 0$ a wide band is predominant; it could be excited both via the exciton absorption band and via the interband transitions. Traditionally, this band is ascribed to radiative exciton recombination. In our solid solution compositions it peaks at 2.45 eV. Figure 2 shows the decay kinetics of the excitonic luminescence both for monocrystals (M) and for three fibres (F1, F2 and F3). For the same composition the decay kinetics is *slower* in the fibres than in monocrystals. The decay kinetics in the fibre with pronounced ageing behaviour (F2) is faster than that in fibre F3 with the small ageing effect. Our experiments with quenched crystals and fibres have shown that their decay kinetics became slower after quenching. This effect is more remarkable in fibres (see curve F1_q in figure 2(a)).

It is well known that silver halides reveal an efficient colloid formation under irradiation by light. Colloids are known to accumulate mainly on the surface and grain boundaries; the effect of 'decoration' is well observed in the light-irradiated fibres. We found no appreciable

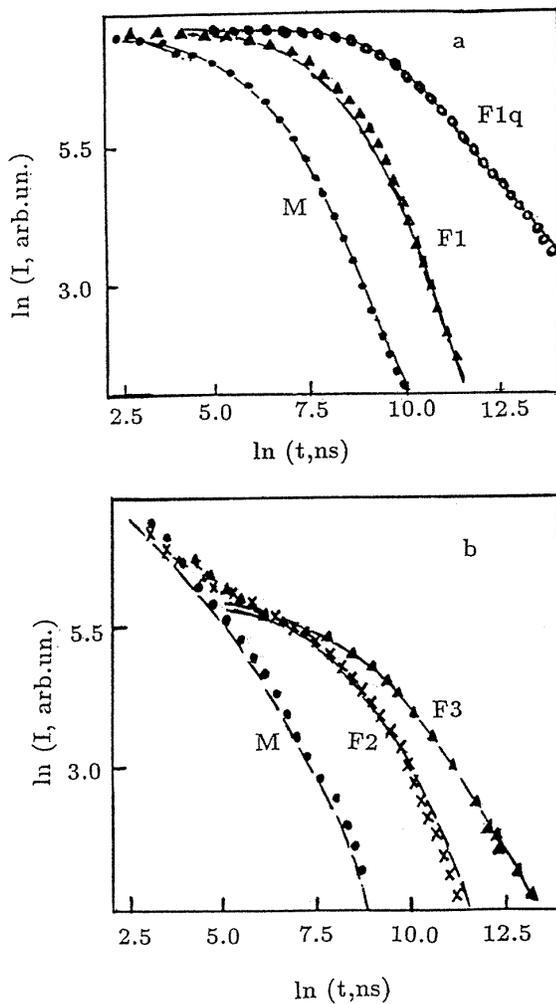


Figure 2. The experimental luminescence decay kinetics (points) measured at 100 K and their theoretical approximation (broken lines) for the two solid solutions $\text{AgBr}_{0.5}\text{Cl}_{0.5}$ (a) and $\text{AgBr}_{0.75}\text{Cl}_{0.25}$ (b), including both monocrystals (M) and the fibres of three kinds (F1, F2 and F3) described in the text. F1_q is the kinetics for F1 fibre after its quenching. The theoretical fitting parameters are $\alpha = 0.05 \text{ eV } \text{\AA}^3$, $R_0 = 1 \text{ \AA}$, $l_1 = 2.45 \text{ \AA}$ (50%) and $l_2 = 4.78 \text{ \AA}$ (50%). In (a) the activation energy $E_a = 0.0975 \text{ eV}$ and the pre-exponential factors of diffusion are $D_0 = 3.5 \times 10^{11} \text{ \AA}^2 \text{ s}^{-1}$ (M), $1.2 \times 10^{10} \text{ \AA}^2 \text{ s}^{-1}$ (F1) and $3.5 \times 10^9 \text{ \AA}^2 \text{ s}^{-1}$ (F1_q). In (b) $E_a = 0.065 \text{ eV}$, $D_0 = 3.5 \times 10^{11} \text{ \AA}^2 \text{ s}^{-1}$ (M), $3.5 \times 10^8 \text{ \AA}^2 \text{ s}^{-1}$ (F2) and $8 \times 10^7 \text{ \AA}^2 \text{ s}^{-1}$ (F3), respectively. Luminescence measurements were performed 3–5 months after fibre extrusion.

change in the luminescent *decay* law as a result of such colloid formation. However, the luminescence intensity dropped considerably, whereas IR optical losses grew due to increasing scattering [2].

Summing up, our main experimental findings are:

(i) the decay kinetics of the excitonic luminescence for monocrystals and polycrystalline fibres strongly differ, namely the luminescence could serve as a sensitive probe of the fibre local structure;

(ii) this kinetics differs also for the fibres with different structural ordering (F2 and F3); fibres with smaller ageing effect exhibit slower decay;

(iii) sample quenching results in additional reduction in the luminescence rate; and

(iv) colloid existence does not affect the luminescence decay kinetics.

For better understanding of these effects, theoretical simulations of the excitonic luminescence were performed.

4. A theory of luminescence decay for monocrystals and fibres

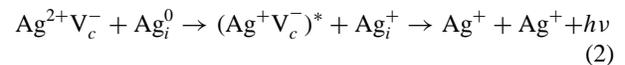
The decay kinetics of the 2.45 eV excitonic luminescence band studied for the two solid solutions, $\text{AgBr}_{1-x}\text{Cl}_x$, and shown in figures 2(a) and (b) are quite complicated and cannot be described in terms of a first- or second-order law. In other words, the luminescence intensity I neither obeys the usual relation between I and defect concentration n ,

$$I \propto dn/dt = -Kn^\gamma \quad (1)$$

($\gamma = 1$ or 2 is called the *reaction order* and K the reaction rate), nor results from a combination of several exponentials, which would be typical for intrinsic excitonic decay. First- and second-order simple decay kinetics are widely observed in diffusion-controlled recombination processes when defects are randomly distributed.

That led us to the idea [5, 8] that this complicated kinetics observed in the present study arises due to the diffusion-controlled recombination of primary Frenkel defects which are *spatially strongly correlated*, analogously to the recently studied case of alkali halides [9].

Thus, we ascribed [5, 8] the intrinsic luminescence peak at 2.45 eV to the following recombination process of primary radiation-induced Frenkel defects:



Here $\text{Ag}^{2+}\text{V}_c^-$ is a hole trapped by a cation vacancy (this centre was identified by short-lived absorption measurements [10]); $(\text{Ag}^+\text{V}_c^-)^*$ is an exciton whose radiative decay is monitored; Ag_i^0 and Ag_i^+ are an interstitial silver atom and ion, respectively, and Ag^+ is a cation in a regular lattice site.

To analyse *quantitatively* this recombination kinetics, the following model is used. A pair of complementary Frenkel defects is created under irradiation at relative distance l (or, in general, with a certain probability at several distances l_i). In particular, in pure AgCl crystals the shortest possible relative distances between Ag^{2+} and its complementary Ag_i^0 at the cube centre are 2.45, 4.78, 6.28 and 7.49 \AA , hereafter called first to fourth nearest neighbours (NN), respectively. Interstitial silver atoms start to migrate with the diffusion coefficient

$$D = D_0 \exp[-E_a/(kT)] \quad (3)$$

and recombine with the $\text{Ag}^{2+}\text{V}_c^-$ centre according to the reaction (2) when approaching it to within the annihilation

radius R_0 . Their annihilation is stimulated by the *elastic interaction* of defects. The latter arises due to overlap of the deformation fields of a perfect lattice around both point defects and its energy is known to decrease as $\varphi(r) = -\alpha/r^3$, where r is the distance between defects [9]. A mathematical formalism describing this process has been presented in more detail in [8, 9]. It is based on the kinetic equation for the *joint probability density* Y of finding at time t a pair of dissimilar defects A and B which reads

$$\frac{\partial Y}{\partial t} = D \left(\Delta Y + \frac{1}{kT} \nabla(Y \nabla \varphi) \right) \quad (4)$$

subject to the boundary and initial conditions: an *annihilation* of close defects at their contact

$$Y(r < R_0, t) = 0 \quad (5)$$

and the initial distribution

$$Y(r, 0) = \delta(r - l)/(4\pi l^2) \quad (6)$$

or a sum of several δ -functions if several kinds of primary pairs are present.

Therefore, the following set of *five* parameters should be defined in our phenomenological model of the correlated diffusion-controlled recombination: the annihilation radius R_0 , relative initial distance between defects l (or several distances l_i and the statistical weights of the corresponding pairs), an activation energy of the diffusion E_a and its frequency factor D_0 , both entering equation (4), and, finally, the elastic interaction constant α . Most of these parameters could be estimated from the independent experiments or taken analogously to those in alkali halides. We used such an initial guess and then varied the parameters to obtain the best fit to the experimental curves shown in figure 2. However, since several parameters are involved, the reasonable question arises of whether the decay kinetics under study could be described by a unique set of parameters or different sets might give the same kinetics. In order to answer this reasonable question, the role of the different parameters was studied in detail and the results obtained are plotted in figures 3–5.

Firstly, it is clear that an increase in the diffusion coefficient D via a decrease in E_a accelerates the defect motion and thus the intensity decay rate, figure 3(a). This effect cannot be simulated by any variation in the initial defect distribution. In principle, the rate of decay of the luminescence could also be simulated by varying the pre-exponential diffusion factor D_0 by several orders of magnitude, figure 3(b). However, its change is limited by a physically realistic variation of the frequency factor ν_0 of defect hopping ($D_0 = \nu_0 \lambda^2/6$, where λ is the hopping length) which is typically of the order of the frequency of LO phonons (10^{13} s^{-1}). The choice among several E_a and D_0 values giving the same diffusion coefficient D could be easily distinguished as the sample temperature T is changed.

The first term in equation (4) corresponds to continuous diffusion whereas the second one corresponds to the defect

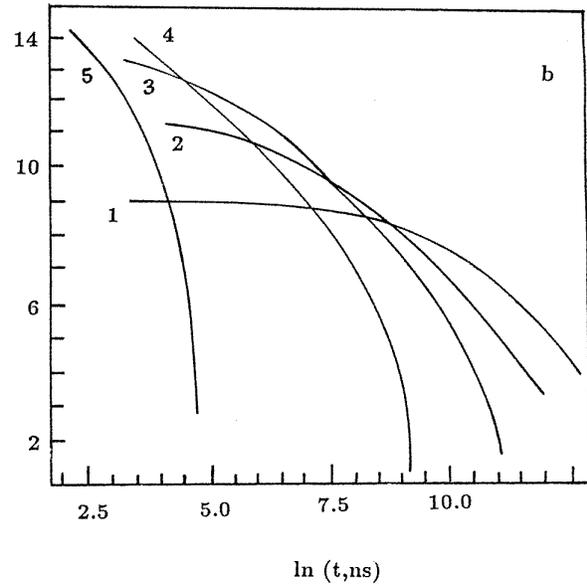
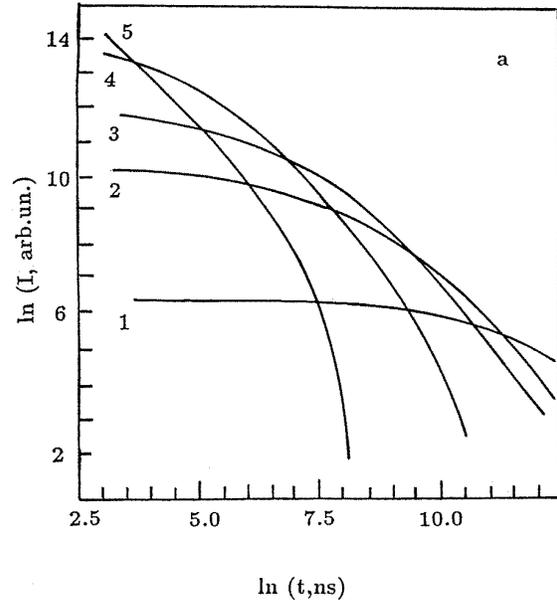


Figure 3. (a) Calculated kinetics of the correlated annealing for the different activation energies of diffusion, E_a (eV): (1), 0.15; (2) 0.12; (3), 0.105; (4), 0.082; and (5), 0.06. Parameters are $\alpha = 0$, $R_1 = 1.0 \text{ \AA}$, $T = 100 \text{ K}$, $D_0 = 3.5 \times 10^{11} \text{ \AA}^2 \text{ s}^{-1}$, $l_1 = 2.5 \text{ \AA}$ (50%) and $l_2 = 4.78 \text{ \AA}$ (50%). (b). The effect of the diffusion pre-exponential factor D_0 ($\text{\AA}^2 \text{ s}^{-1}$): (1), 3.5×10^8 ; (2), 3.5×10^9 ; (3), 3.5×10^{10} ; (4), 3.5×10^{11} ; and (5), 3.5×10^{13} . Other parameters are as in (a) with $E_a = 0.07 \text{ eV}$.

drift in the elastic field $\varphi(r)$. The portion of defects recombined at the time t is given by the flux of interstitial atoms through the annihilation sphere of radius R_0 .

Variation of the annihilation radius R_0 is illustrated in figure 4(a). As R_0 increases, so does the luminescence rate decay. The more important fact is that only the *initial* reaction stage is affected by R_0 varying. More drastic

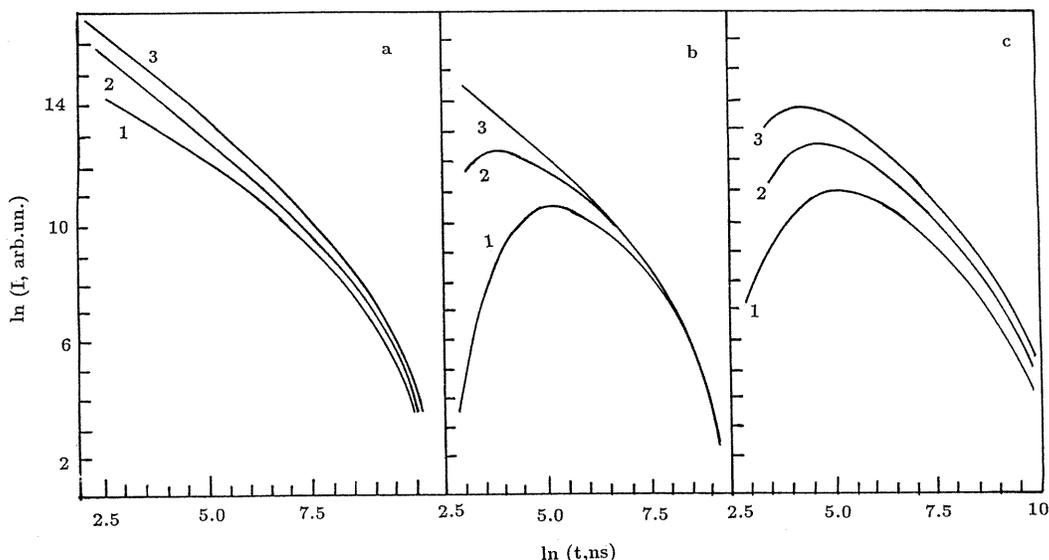


Figure 4. (a) The effect of the annihilation radius R_0 (Å): (1), 1.0; (2), 2.0; and (3), 3.0. (b) The effect of different initial distributions between defects (l_n denotes n th nearest neighbours taken always in equal concentrations): (1), $l_5 = 11.08$ Å and $l_6 = 12.49$ Å; (2), $l_3 = 6.28$ Å and $l_4 = 7.49$ Å; and (3), $l_1 = 2.50$ Å and $l_2 = 4.78$ Å. (c) The effect of the annihilation radius R_0 (Å) for well-separated defects (third and fourth nearest neighbours): (1), 1.0; (2), 2.0; and (3), 3.0.

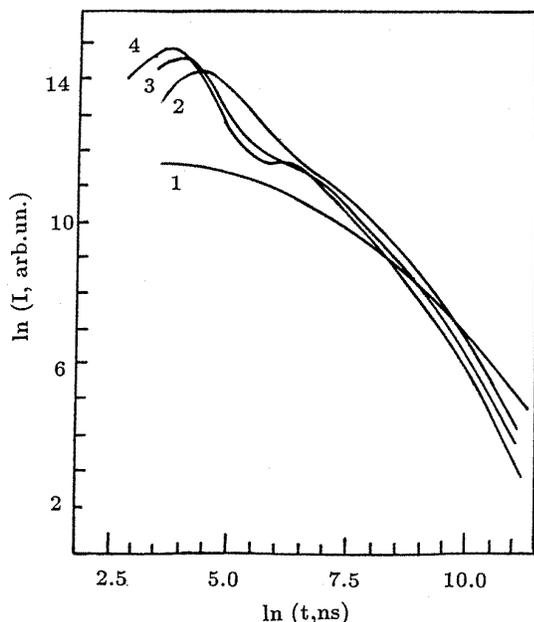


Figure 5. The correlated annealing kinetics calculated for different values of the elastic interaction constant α ($\text{eV } \text{Å}^3$): (1), 0; (2), 0.2; (3), 0.4; and (4), 0.57. $l_1 = 2.50$ Å, $l_2 = 4.78$ Å.

consequences are found when varying the initial defect distribution, figure 4(b). If nearest neighbour defects at the shortest distances are absent, the kinetics could turn out to reveal a *peak* at some characteristic time (which is necessary for the distance defects to come into the recombination region), figure 4(b) and (c).

All previous studies neglected the elastic defect interaction. Its effect is shown in figure 5. An increase

in the defect interaction enhances the recombination rate and the luminescence intensity. Even more important is the fact that it resolves better the different stages due to the contribution of defects separated by different distances. As a result, the plot of $\ln I$ versus $\ln t$ could reveal the distinctive step structure.

After this preliminary study of the role of the different phenomenological parameters in the decay kinetics, we applied our model to the interpretation of the kinetics under study. The fitted parameters obtained for the two compositions of interest are given in the caption for figure 2. The activation energy for the Ag_i^0 diffusion is known to increase with the Cl concentration; it is nearly a linear function of composition x [5].

The initial distribution consists predominantly of first and second nearest neighbours in equal concentrations. That is, primary Frenkel defects are very well spatially correlated, as was earlier concluded for alkali halide crystals [9]. The general conclusion could be drawn that the elastic interaction is not important in silver halides; we found an interaction constant $\alpha \leq 0.05 \text{ eV } \text{Å}^3$ which is two orders of magnitude less than that for the primary Frenkel defects (F- and H-centres) in alkali halides [9]. This is probably due to the very small deformation of the surrounding lattice by the interstitial Ag_i^0 occupying a cube centre, unlike its analogue, the H-centre in alkali halides, which forms a quasi-molecule, X_2^- with a regular anion and occupies a *single* anion site and thus strongly distorts the lattice around the defect [11]. In other words, Ag_i^0 fits much better to the cube centre position than does the H-centre in alkali halides.

5. Discussion

The theoretical approximation of experimental results obtained for the different kinds of fibres (figure 2) shows

that the pre-exponential diffusion coefficient D_0 decreases in fibres compared with that in monocrystals for both investigated fibre compositions. Extrusion of fibres is definitely accompanied by the production of numerous grain boundaries in their polycrystalline structure. Usually surface diffusion of point defects occurs considerably faster than that in the bulk. That is, if the defect recombination in fibres were to have occurred on the grain surface, then the recombination process would have been characterized by the large D_0 value. Since our study has shown the opposite effect, namely that the parameter D_0 is reduced, then recombination on the grain surface is not predominant in fibres. On the other hand, an extrusion procedure produces also numerous dislocations and local imperfections which could effectively reduce the silver atom diffusion (for example through temporary trapping of Ag_i^0 [8]). It seems that such effects dominate in the fibres under study. Possibly, the recombination mechanism is quite complicated and may be limited by some effect of grain size. At the moment this is an open question.

As was stated in section 2, fibres F2 and F3 differ only by their extrusion technology and thus they differ in terms of their structural changes during the ageing process. Thus, our study of IR optical loss spectra has shown that the grain size in F3 fibres did not change appreciably (at least, during a period of about 9 months), but in F2 fibres this size considerably increased. That is, the luminescence study has demonstrated once more the correlation between the mean grain size and the radiation-induced defect diffusion characterized by the magnitude of D_0 .

Our second important conclusion is that quenching both of monocrystals and of fibres results in *slower* decay kinetics; that is, the pre-exponential diffusion factor D_0 again decreases. Probably, this arises due to an additional reduction in the mean grain size after samples quenching, which is accompanied by the greater contribution of temporary Ag_i^0 trapping by imperfections, similarly to the case of the mono-polycrystalline transitions happening under extrusion. This idea could be checked by comparative IR-losses measurements for the quenched and annealed fibres.

Lastly, we have shown that the preliminary creation of silver atom colloids at high concentrations does not affect at all the luminescence decay kinetics observed for fibres. This indicates that colloids are very probably accumulated *locally*, on the fibre's external and internal surfaces (grain boundaries). In this case they do not change mean grain sizes and do not affect appreciably the silver

atom migration. It should be noted that IR losses grow in fibres in parallel with the colloid concentration due to the scattering losses.

It is clear that further careful studies of the fibre microscopic structure are necessary in order to establish a clearer correlation of the structure with the relevant luminescence kinetics which serve as the structure sensitive probe. One of the primary problems to be solved is that of obtaining a better understanding of the relation between the pre-exponential diffusion factor D_0 and the mean size of the grains. Since the latter is typically of the order of 100 Å, as the fibre is extruded, Ag_i^0 diffusion could potentially be dependent on the grain size due to nanoscopic effects.

Acknowledgments

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