# Photoluminescence features of AgBr nanoparticles formed in porous glass matrices

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The photoluminescence of AgBr nanoparticles formed by a two stage liquid-gas microsynthesis technology in two types of porous glass with different sizes of pores was investigated. Polyvinyl alcohol (Polinol) was used as a binder. It has been found that AgBr nanoparticles in the glasses with smaller pores luminesce more intensively, and we attribute this phenomenon to the differences in pore size distributions. The luminescence spectra were shown to have two maxima corresponding to AgBr nanoparticles formed within the nanopores of two different sizes characteristic of each of the matrices. In both cases, the spectra excited by xenon lamp irradiation are more intensive than those stimulated by a 337-nm nitrogen laser. Comparing the maxima shifts in the phosphorescence excitation spectra with ones in phosphorescence spectra we can conclude that the luminescence and phosphorescence centers in AgBr nanoparticles are of identical nature in the matrices of both types. The investigation results fit neatly into the inherently consistent quantum confinement model and are well correlated with the poroscopic spectra of both types of glass.

Keywords: porous glasses, silver bromide, nanoparticles, luminescence properties, quantum confinement.

## 1. Introduction

It is well known [1] that AgBr crystallizes into a face-centered cubic crystal lattice with NaCl structure (space group $O_h^5$) or into a simple cubic crystal lattice with CsCl structure (space group $O_h^1$) depending on the acidity of the medium. The most probable shape of nanocrystallites are cubes characteristic for these space groups. AgBr is one of the basic photographic materials and its photographic properties are the result of

deviations from an ideal crystal structure. Since there is no immediate correlation between concentration of the ingredients of the reaction and the concentration of the nanoparticles obtained the latter can be evaluated only qualitatively. The metal silver phase in this case was not formed as its appearance would be accompanied by sample blackening, which was not observed. The majority of defects in AgBr are the Frenkel defects concentrated near the surface of its particles [2].

To provide the high-resolution photographic material with good radiation sensitivity the task of vital concern is to create AgBr particles within the medium preventing formation of large conglomerations. The presence of nanodimensional pores makes porous silicate glasses a good medium for the purpose [3–6]. They are of interest not only as a model medium for investigating various quantum confinement effects, *etc*., but they are also promising as a matrix for creating radiation sensitive, photoresponsive and photochromic materials with extended range of sensitivity, resolution and, possibly, optical density. These perspectives come about through the possibility of introducing into the matrix a considerable amount of sensitive material avoiding at the same time the danger of large conglomerations developing, which reduce the material resolution and deteriorate its radiation sensitivity. The pore size distribution restricts nanoparticle size growth within the pores, whereas special features of the formation technique ensure nanoparticle fineness. The size of the nanoparticles being formed is determined by the microsynthesis technique. Small AgBr particles will tend to form the energetically advantageous crystallites of space group $O_h^5$. Energetically unfavorable coral-like "sprouting" of AgBr into the adjacent pores could occur at the excess concentration of the reaction components within pores, but we deliberately created a deficient concentration. If, along with the nanoparticles, large microcrystallites of irregular shape were formed inside the pores, the position of the photoluminescence spectra peak would correspond to single-crystal AgBr in polyvinyl alcohol ($\sim 800$ nm). Therefore, the nanoparticle contribution would become apparent through additional spikes shifted into the short-wave region. However, we have observed the system shift of all maxima towards higher energies. Such a shift is characteristic of the system of nanoparticles without any single-crystal formations.

In the present paper, a technique of silver-halide nanoparticle formation is suggested, which does not result in the development of such conglomerations. The photoluminescence centers in AgBr particles are known to be concentrated near their surface interacting directly with binder molecules, thus the selection of a binder is crucial. It has been shown earlier [7–9] that gelatin is not a suitable binder because its molecules are too big to transport AgBr nanoparticles into the nanopores. For this purpose, we employed polyvinyl alcohol (Polinol), a substance not commonly used for creation of photosensitive media. Since Polinol molecules are essentially smaller than gelatin ones, the Polinol being a binder serves also as a delivery vehicle transporting silver particles into the finest pores. For AgBr particles formed with Polinol assistance within porous matrices of two types [10] we succeeded in observing the quantum confinement effect. The results of investigating the phosphorescence excitation spectra and phosphorescence and luminescence ones can be consistently

explained in terms of the quantum confinement model. The effects induced by formation of AgBr nanoparticles within the pores of two predominant sizes, characteristic of each of the two matrices, fit neatly within the frame of the model. At the same time, all observations demonstrate a good correlation with the poroscopic spectra for both types of glasses [11].

## 2. Experiment

The special features of the liquid-gas microsynthesis procedure are such that, in spite of the wide range of pore sizes in the matrix (from several to hundreds of nanometers), only small particles (of the order of several nanometers) can develop within the pores. This should be expected from the minimum total energy principle, and this is confirmed by the photoluminescence spectra where the position of spectrum peaks, being substantially different from that typical of a single crystal, shifts into the higher energy region, which is a manifestation of the quantum confinement effect characteristic of nanoparticles. Thus, in our investigation, we can consider only small pores since our technique [12] ensures no contribution of large ones to photoluminescence. Thus an *A*-type porous silicate glass was selected as a matrix with pores of minimal sizes prevailing in the range of pore size distribution under consideration. To trace a possible system shift we used for comparison a *C*-type glass as a reference material with somewhat larger prevalent pore sizes. Both types of glass were produced without silica gel leaching out [13].

The pore size distributions in both types of glass were obtained earlier [11]; as can be seen in Fig. 1 they are relatively narrow. We were trying to create the nanoparticles of AgBr, so our interest is only with the fine pores which should limit the growth of AgBr particles within a nanometric range of sizes where quantum confinement effects can be observed. Defining role in our studies was played by two smallest fractions in pore size distributions, since it is just in such pores that the silver halide nanoparticles can form. These two fractions in *A*- and *C*-type glasses are distinguishable, as can be seen in Fig. 1, and due to this difference the matrix type influences the nanoparticle forming conditions and, therefore, their luminescent
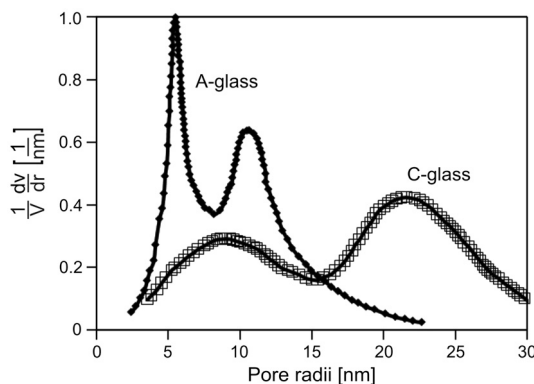


Fig. 1. Pore-size distribution spectra for *A*- and *C*-type porous silicate glass.

spectra. We did not take into account a possible presence of large pores in the matrices of both types since we extended to AgBr the microsynthesis technique developed for CdS [12, 14]. Owing to such a technique, on the inner surfaces of large pores only the islets of binder monolayer can appear containing the same AgBr nanoparticles, which do not lead to development of additional maxima in photoluminescence spectra.

To create AgBr nanoformations within the matrix we saturated the appropriate porous glass with one-molar $AgNO_3$ aqueous solution with a 3% Polinol addition. After an hour's holding in the solution necessary for silver ions to penetrate into the finest pores, the specimen was exsiccated for 30 minutes at approximately 40 °C, and after that for twenty-four hours it was held in bromine vapors.

In the case of silver haloids, the photoluminescence centers at low temperatures are the same centers that provide photosensitivity at room temperature. These two properties of silver haloids are complementary, which means that if there is a photo-luminescence at liquid-nitrogen temperature, at room temperature the photosensitivity should be expected. However, an increase in the intensity of photoluminescence is not connected directly with photosensitivity growth, but is only indicative of an increase in the quantity of silver halide nanoparticles with the suitable relationship between their volume and their surface area.

Being actually one and the same recombination process the fluorescence and phosphorescence are distinguished only by the excited-state lifetimes of the lumines-cence centers. However, as fluorescence correlates with the size of particles containing these centers, and phosphorescence characterizes the centers themselves and makes it possible with sufficiently good resolution to distinguish the traps indistinguishable within the lifetime range of up to $10^{-5}$ s, both phenomena are conveniently studied separately in the different sample excitation modes. The luminescence and phospho-rescence spectra excited by a 337-nm nitrogen laser or 1 kW xenon lamp were recorded at 77 K with standard equipment [15]. The laser and xenon lamp sample excitation regimes do not require any special calibration for comparison of results. Both sources of excitation are parts of one and the same installation, use the same register system and the excitation mode is changed by a simple switch in the exciting unit. We did not investigate the efficiency of quantum luminescence in this case, since this exceeds the scope of the problem formulated.

To record the phosphorescence spectra excited by the xenon lamp two monochromators are used. The first performs a spectral decomposition of the lamp light, and through the second one a luminescence beam goes from the sample before hitting a photodetector. A possible internal photoelectric effect as a result of xenon lamp irradiation could have a significant influence on single-crystal AgBr, but for the carriers inside nanoparticles the forbidden band is considerably wider and the photoelectric threshold shifts towards higher energies.
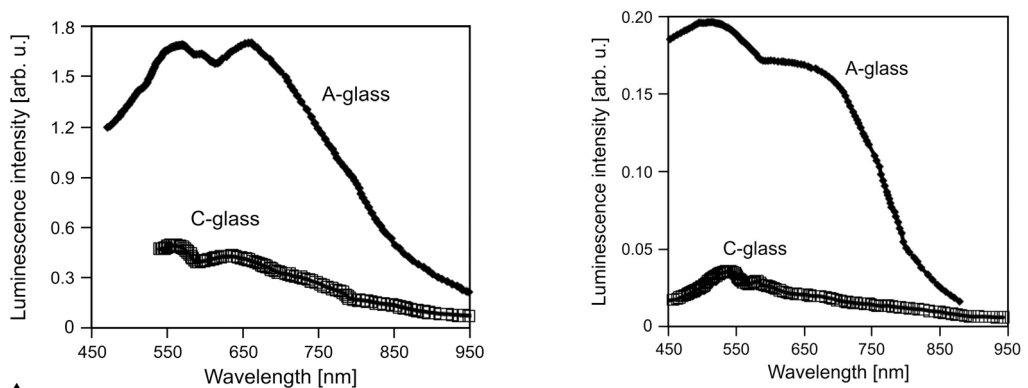
At the beginning, knowing from the photoluminescence spectrum in what spectral range it is necessary to look for the phosphorescence peak, the sample is excited by a sufficiently broadband within this range. Having the peak located, the second monochromator in front of the photodetector is adjusted to the corresponding

wavelength. After that the first monochromator scans the broad spectral band of the excitation source providing as a result the excitation spectrum of this particular maximum of the phosphorescence spectrum. Such a procedure makes it possible to segregate maxima of the phosphorescence spectrum, which can overlap in photoluminescence investigation. Each separate maximum corresponds to a specific type of traps, and therefore the spectrum of phosphorescence excitation shows the excitation energy of this particular trap.

Optical polarization inside such essentially isotropic system as porous glass is possible only for sufficiently long molecules, for example, organic dyes or liquid crystals sensitive to the conditions on the surface inside the pores. But in our case, for sufficiently symmetrical nanoparticles the optical polarization is hardly probable and was not investigated.

## 3. Results

For *A*- and *C*-glasses with AgBr nanoparticles created with Polinol assistance the luminescence spectra excited by a 337-nm nitrogen laser are presented in Fig. 2; and in Fig. 3 are the ones excited by 430-nm xenon lamp. Comparing the spectra in Figs. 2 and 3 shows that for both types of glass the intensity of luminescence excited by xenon lamp is almost 10 times higher. The spectra of AgBr nanoparticles in *A*-type matrix for both methods of excitation have two characteristic maxima with approximately 130-nm system shift. The laser-excited spectrum shows a more intensive short-wave maximum against the background of relatively insignificant overall luminous intensity. With a xenon lamp excitation the intensity redistribution between the maxima occurs, they become comparably-intensive and the luminosity of both sharply increases. The same effect is observed for *C*-type matrix, but here



Fig. 2. Photoluminescence spectra of AgBr nanoparticles excited by 337-nm nitrogen laser in two types of porous glass.

Fig. 3. Photoluminescence spectra of AgBr nanoparticles excited by 430-nm xenon lamp in two types of porous glass.

the system shift between maxima is less almost by half (about 70 nm), the lumines-
cence intensity is substantially lower and there is no intensity redistribution. With both
excitation methods in the luminescence spectra of AgBr nanoparticles in *C*-type
matrix only the short-wave maximum is strongly pronounced, while the second one
at 430 nm excitation is diffuse and spread-out, and at 337-nm excitation it is barely
perceptible.

In the photoluminescence spectra we observe the shift of the peak into the short-
-wave region in comparison with the spectra of AgBr microcrystallites, known from
the literature, obtained with the same binding agent. It is precisely a manifestation of
the quantum confinement effect. The phosphorescence spectra and the phosphores-
cence excitation spectra do not refer to the quantum confinement effect, and their
comparison just helps to separate the contributions into the luminosity from
energetically close long- and short-lived centers.

The system shift of the spectra can also be traced through comparison of maxima
position in phosphorescence excitation spectra and those in the phosphorescence
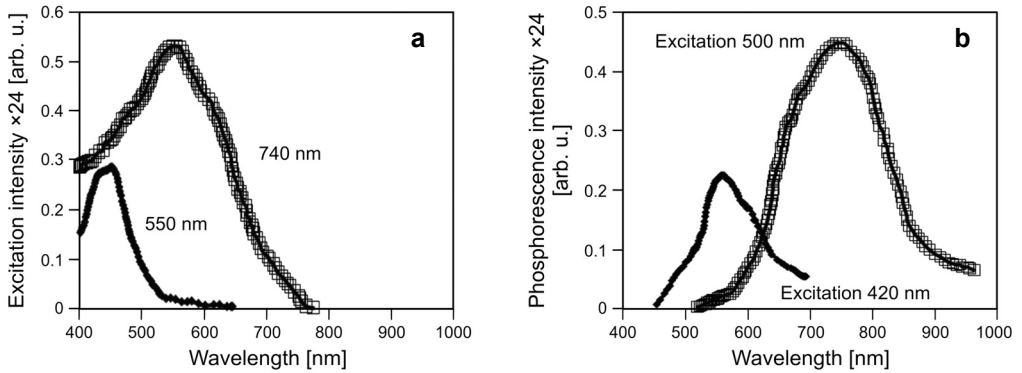


Fig. 4. Phosphorescence excitation spectra (**a**) and phosphorescence ones (**b**) of AgBr nanoparticles in *A*-glass.
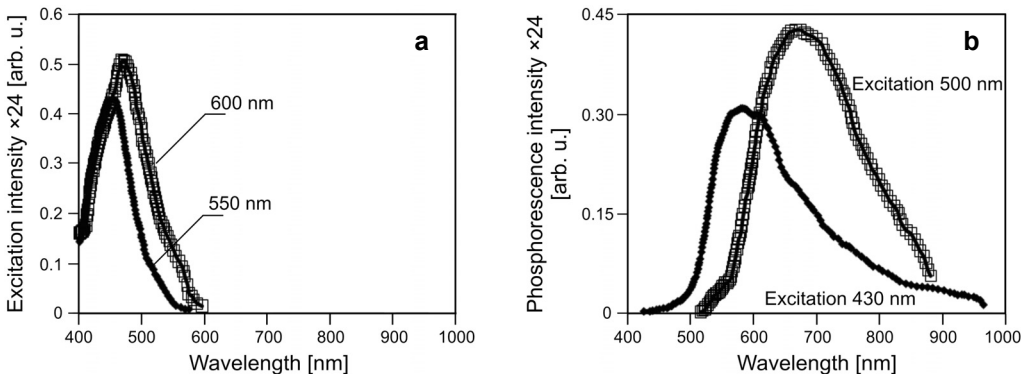


Fig. 5. Phosphorescence excitation spectra (**a**) and phosphorescence ones (**b**) of AgBr nanoparticles in *C*-glass.

spectra of AgBr nanoparticles Polinol-implanted into both types of matrices. For *A*-type matrix these spectra are shown in Fig. 4, and for *C*-type glass in Fig. 5. A single-humpedness of all maxima indicates that the corresponding traps are elementary ones without any fine structure. In the phosphorescence spectra of AgBr nanoparticles in *A*-glass two maxima can be seen at a wavelength $\lambda_{max}$ of approximately 580 and 720 nanometers, for which there are also two corresponding peaks in the spectra of their phosphorescence excitation with $\lambda_{max} \approx 420$ nm and 550 nm, respectively. In the phosphorescence spectra of *C*-glass with AgBr nanoparticles also two maxima of luminosity are observed (approximately at 570 nm and 660 nm) for which there are also two corresponding peaks in the spectra of their phosphorescence excitation with $\lambda_{max} \approx 440$ nm and 465 nm, respectively. Thus, the maxima in the spectra of phosphorescence excitation, just as the maxima of phosphorescence spectra for both matrices, are shifted into the long-wave region with an increase in the exciting wavelength.
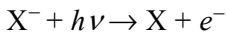
## 4. Discussion

It is known [16] that at 77 K the photoluminescence spectrum of AgBr microcrystals in a Polinol binder solution demonstrates one strongly pronounced maximum at 680 nm. Both maxima that we observed in the luminescent spectra were shifted from 680-nm into the short-wave region, which is explained by the quantum confinement effect and confirms that we succeeded in creating AgBr nanoparticles. The presence of two peaks in the photoluminescence spectra corresponds to the nanoparticles formed in pores of two basic fractions (see Fig. 1). The absence of any traces of a 680-nm peak in the spectra confirms that our two stage liquid-gas technique of microsynthesis prevents the reagents from filling the large pores where the microcrystals could form.

As can be seen in Fig. 1, the luminosity of nanoparticles created in *C*-type matrix is considerably weaker, for there are fewer pores of appropriate sizes than in *A*-type matrix. The long-wave excitation power of xenon lamp is higher than that of a pulsed laser, so the intensity of laser-stimulated luminosity for both glasses is 10 times lower. Because the xenon lamp is more powerful and can activate some radiative recombination centers in bigger particles, the lamp-excited *A*-glass photoluminescence demonstrates the intensity redistribution from the maxima of the AgBr nanoparticles in favor of those radiative recombination centers. At the same time, since the pulsed laser UV radiation fades being scattered strongly by the fine pores, the majority of the carriers in bigger particles recombine nonradiatively. For *C*-glass nanoparticles the effect is practically nonexistent because of the weak luminous intensity.
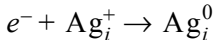
As the wavelength of the exciting radiation shortens the maxima of phosphorescence the excitation spectra are shifted into the short-wave region simultaneously with the respective peaks in phosphorescent spectra, for two sizes of AgBr nanoparticles in the matrices of both types. This is the evidence that quantum confinement effect takes place for AgBr nanoparticles in pores of appropriate sizes.

Presented in Figs. 4 and 5 the phosphorescence spectra and the corresponding phosphorescence excitation spectra, as well as their system shift with the change in the excitation wavelength, confirm that luminescence and phosphorescence centers in AgBr nanoparticles are of identical nature for matrices of both types.
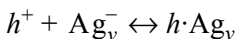
The investigation of light emission by AgBr crystallites [17, 18] has shown that lattice defects can play the role of luminescence centers. As is known [2], the luminescence centers in AgBr without binder are the atom-molecule dispersion centers formed by the elementary combinations of interstitial atoms with silver ions. They can be distinguished by the presence of cation vacancies in these centers [17]. The only one peak in the phosphorescence spectra (Figs. 4, 5) suggests that there is only one type of luminescence centers, namely, the inherent in AgBr Frenkel defects [1], that is, the complexes of interstitial silver ions $Ag_i^+$ and silver vacancies $Ag_v^-$ [2]. In this case, the Polinol binder molecules stabilize the surface interstitial luminescence centers in AgBr through their agglomeration. When light falls on the surface of AgBr nanoparticle a photoelectron is generated in the conduction band at the expense of the halogen electron [18]:

$$X^- + h\nu \rightarrow X + e^-$$

After being generated, the electron tends to be bonded with an interstitial silver ion $Ag_i^+$ to form a neutral atom $Ag_i^0$:

$$e^- + Ag_i^+ \rightarrow Ag_i^0$$

Simultaneously with a nonequilibrium electron a nonequilibrium hole $h^+$ is formed, which also tends to be neutralized. The lifetime of a nonequilibrium hole, however, does not correlate with the electron lifetime. This is a consequence of different trapping mechanisms: it was shown [18] that traps for the holes are the mobile, negatively charged lattice defects, namely, the silver vacancies $Ag_v^-$, with which they form the hole complexes:

$$h^+ + Ag_v^- \leftrightarrow h{\cdot}Ag_v$$

Formation of the hole complexes $h{\cdot}Ag_v$ reduces energy of the components sufficiently for their stabilization and reduction in the probability of the hole ejection back into the valence band. As a result of the concentration gradient creation the holes diffuse to a nanoparticle surface where their lifetime is much longer than within the bulk of crystallite, and where they are in equilibrium with the adsorbed bromine. The final result of this equilibrium is the stimulation of an increase in the number of holes at the surface, which makes up for the phosphorescence.

The fundamental absorption edge in AgBr can reach 500 nm [3, 19], hence the subsequent recombination of nonequilibrium carriers is a band-to-band one. Thus

the shift of phosphorescence excitation maximum into short-wave region with a decrease in the sizes of AgBr nanoparticles makes it possible to speak about such a manifestation of the quantum confinement effect as the band-gap broadening.

## 5. Conclusions

For porous glasses a liquid-gas microsynthesis technique is developed for the Polinol assisted formation of AgBr nanoparticles within the pores.

The technique ensures the uniformity of bulk distribution of AgBr nanoparticles within the matrix and makes it possible to increase silver halide concentration in gelatin- or Polinol-type binding solutions. In that way, it opens up prospects both for creating more responsive radiation sensors and for further development of photochromic media.

Two maxima in the luminescence spectra of AgBr nanoparticles correspond to the two fractions of predominant pore sizes. This is confirmed by the system shift of maxima in the photoluminescence spectra, in phosphorescence excitation spectra, and in the phosphorescence ones, depending on the prevalent pore sizes in each glass.

Upon transition from AgBr nanoparticles in *A*-type glass to the ones created in *C*-glass a tendency towards weakening the quantum confinement effect takes place, which manifests itself in the reduced system shift of the luminescence spectra peaks into the long-wave region with a simultaneous sharp decrease in their intensity.

A single-humpedness of all maxima in phosphorescence spectra and in the corresponding phosphorescence excitation spectra indicates that the related traps are elementary ones without any fine structure. And the maxima simultaneous system shift with the change in the exciting wavelength confirms that luminescence and phosphorescence centers in AgBr nanoparticles are of identical nature for matrices of both types.

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