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Creating nanoscale luminescence centres in silver halides suitable for infrared application

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Abstract. This study shows the possibility of creating luminescence centres in silver halide media using substances based on rare-earth elements such as neodymium, ytterbium and dysprosium. These luminescent substances in the form of fine particles of both nanoscale and microscale dimensions can be introduced into the AgCl₀.₂₅Br₀.₇₅ ceramic matrix highly transparent in the spectral range of 0.5–35 μm. Our theoretical and experimental studies showed that the introduction of luminescent nanoparticles or microparticles at the amount of 0.5 wt.% into AgCl₀.₂₅Br₀.₇₅ ceramics neither reduces the level of its transmission in the MIR region nor shortens the range of transmission. What is more, we proved that the luminescent properties of nanoparticles remain well preserved after doping silver halide ceramic media with them. Therefore, silver halides doped with rare-earth elements in question can be used for developing the sources of coherent middle infrared radiation, with appropriate energy levels being excited by optical radiation or pulsed electric field.

1. Introduction

The task of creating simple, compact, and high-power sources of coherent radiation in the range of 5–1000 μm has become more and more urgent with the active development of fibre lasers for the wide range of wavelengths [1]. The lasers’ active media are transparent at the radiating wavelength and have inclusions in the form of ions luminescent upon pumping. In general, the active media are transparent merely in the visible and near-IR spectral regions. As typical examples of such items, one can mention lasers based on yttrium oxide, yttrium-aluminum garnet (YAG), or glasses doped with rare earth elements.

The long-wavelength transmission edge for phosphate glasses is 2.5 μm, YAG – 6 μm, and yttrium oxide – 10 μm. That is why they are not suitable as matrices for use in the middle- and far-infrared ranges. The core issue is the lack of natural substances luminescent within the entire optical region from 5 to 1000 μm. However, this issue can be solved by creating new materials introducing active luminescence centers (in the form of particles) into existing optically transparent materials. These materials include silica, germanium, silver halides, to name but a few. Unlike silica and germanium, silver halides are suitable for producing optical fibers. Moreover, they are transparent at the wavelengths of 0.46–30 μm (up to 40 μm depending on composition) and at the wavelengths of 260–5500 μm [2]. Thus, the optical systems based on silver halides, being transparent in the visible range,
can be tuned easier when compared to conventional ones because they allow using visible light for the beam alignment. The refractive index \( n \) of silver halides, measured at room temperature, spans from 2.0 to 2.4 in the visible and infrared ranges, whereas it is of 2.6–2.7 in the terahertz range. The typical absorption coefficient of silver halides is \( 10^{-4} – 10^{-5} \) cm\(^{-1}\). They are non-hygroscopic and possess good plasticity. Therefore, they are suitable for extruding optical fibers (which have the attenuation coefficient of 0.1–0.4 dB/m at \( \lambda = 10.6 \) µm) [3–5].

The questions to be addressed here: to what extent the incorporated nanoparticles deteriorate the transparency of silver halides, and what is the nature of luminescence in the chosen optical materials?

It is well-known that nanoscale particles with dimensions of 2–60 nm are prone to agglomeration, i.e., to the formation of larger structures up to 100 nm and more [6, 7]. In some cases, the agglomerates can be about a micron in size. In this connection, one more question inevitably arises how much randomly distributed microsize particles affect the transparency of chosen matrix in the middle- and far-infrared regions, where the radiation wavelengths are tens of microns.

This study aimed to investigate the optical properties of silver halide ceramics with luminescent particles incorporated in them. Following this aim, first, we checked the possibility of creating luminescent centers using neodymium, ytterbium, and dysprosium ions in the form of nanoscale and microscale particles of ytterbium oxide, neodymium oxide, and dysprosium oxide, respectively. Then, we studied the dependence between particle size and the transparency of the ceramics in the infrared region. Moreover, we investigated the luminescent characteristics of the particles. For this purpose, we performed theoretical calculations of Rayleigh scattering and Mie scattering, and we also measured the transmission spectra of the samples.

2. Theoretical calculations

As the first step of that part, we performed theoretical calculations of attenuation due to Rayleigh scattering.

Attenuation due to scattering is given by the following equations:

\[
\delta = 1 - \exp(-\alpha_d d),
\]

(1)

\[
\alpha_d = N \sigma,
\]

(2)

where: \( \alpha_d \) is the attenuation due to scattering, \( d \) is the sample thickness, \( N \) is the nanoparticle number per volume unit, \( \sigma \) is the Rayleigh-scattering cross-section per particle.

Rayleigh-scattering cross-section per particle was calculated using the equation below [8]:

\[
\sigma = \frac{24 \pi^3}{\lambda^2} V^2 \left( \frac{n_1/n_2 - 1}{n_1/n_2 + 2} \right)^2,
\]

(3)

where: \( V \) is the nanoparticle volume, \( \lambda \) is the wavelength, \( n_1 \) and \( n_2 \) are refractive indices of nanoparticles and AgCl\(_{1-x}\)Br\(_x\) medium, respectively.

The values of refractive indices \( n_1 \) and \( n_2 \) at various wavelengths were taken from [9, 10]. The average particle volume \( V \) was evaluated using the nanoparticle size distribution function (see section 3.2, figure 3).

The reflection coefficient was acquired using the following formula:

\[
R = \frac{(n_2 - 1)^2 + (\alpha \lambda / 4\pi)^2}{(n_2 + 1)^2 + (\alpha \lambda / 4\pi)^2},
\]

(4)

where: \( \alpha \) – attenuation coefficient gained from our experimental data.

The calculation results show that the radiation attenuation measured during our experiments can be attributed to absorption on defect structures. To make a comparison, we determined the electromagnetic field scattering induced by micron-size particles. The Rayleigh approximation is not
appropriate in this case, and the application of Mie's theory would lead to cumbersome calculations. Therefore, we numerically solved the Helmholtz equation for an alternating electromagnetic field in an AgCl_{1-x}Br_x medium doped with Y_2O_3 particles of 1 \mu m in radius. A similar calculation was performed earlier by the given authors in [11], where the calculation model is described in detail. Comparing the energies of the incident and scattered electromagnetic waves obtained in the numerical solution, we determined the attenuation of electromagnetic radiation in the sample. The calculation results are shown in figure 1. In the figure, one can see that micron-sized particles (figure 1 (b)) scatter radiation much stronger than nano-sized particles (figure 1 (a)). However, the theoretical losses are still much less than those obtained in the experiment, which confirms the significant role of absorption.

![Figure 1](image-url)

**Figure 1.** The dependence of transmittance (solid line) and scattering losses (dashed line) on the wavelength: (a) Rayleigh scattering on nanoparticles, (b) Rayleigh scattering on microparticles.

3. **Experimental measurements**

3.1. **Sample preparation technique and conditions of recording transmission spectra**

For the synthesis of AgCl_{1-x}Br_x solid solutions, we used a hydrochemical method called thermal-zone crystallization-synthesis (TZCS) [12], which is based on the different solubility of chemical substances in acid solutions depending on temperature. This method makes it possible to carry out both the synthesis of single-phase homogeneous raw materials of given compositions and their purification simultaneously. According to this method, poorly soluble substances with a purity of 99.9 wt.% are loaded into a reactor pre-filled with a solution of 5 M hydrochloric acid. The reactor should have two temperature zones with the following parameters: the lower zone of the reactor is heated to a temperature of about 95°C, while the mother liquor of the upper zone is cooled to 70°C. This creates a temperature gradient, which, in turn, leads to the emergence of convective flows. The flows move the mother liquor from the hot zone to the cold one. With this, the solid solution of a given composition precipitates in the cold zone on account of the lower solubility of silver halides at a colder temperature. At the same time, highly soluble impurities remain dissolved in the acid solution. It should be noted that the recrystallization of substances can be carried out multiple times to achieve the desirable purity. During a single recrystallization cycle, the amount of impurities may be reduced to 10^{-4}–10^{-3} wt.%, with a yield of the end-product up to 98% [3, 12].

In this study, the TZCS method was used to obtain the raw material of AgCl_{0.25}Br_{0.75} composition with the purity of at least 99,999935 wt.% (regarding inorganic impurities). Further, the raw material was used to grow single crystals which serve as a matrix for obtaining the samples under investigation. In this way, we obtained the samples of the following compositions:
Sample No. 1 nano-powder 10 wt.% (Yb\textsubscript{0.1}Y\textsubscript{1.9}O\textsubscript{3}): AgCl\textsubscript{0.25}Br\textsubscript{0.75}
Sample No. 2 nano-powder 10 wt.% (Nd\textsubscript{0.02}Y\textsubscript{1.98}O\textsubscript{3}): AgCl\textsubscript{0.25}Br\textsubscript{0.75}
Sample No. 3 nano-powder 0.56 wt.% Yb\textsubscript{2}O\textsubscript{3}: AgCl\textsubscript{0.25}Br\textsubscript{0.75}
Sample No. 4 micro-powder 0.5 wt.% Nd\textsubscript{2}O\textsubscript{3}: AgCl\textsubscript{0.25}Br\textsubscript{0.75}
Sample No. 5 micro-powder 0.5 wt.% Dy\textsubscript{2}O\textsubscript{3}: AgCl\textsubscript{0.25}Br\textsubscript{0.75}

The sample preparation technique included the following steps:
1. To break up agglomerates of rare earth oxide nano-powders, we applied an ultrasonic treatment to a suspension of these powders in isopropyl alcohol for 40 minutes;
2. The obtained suspension was mixed with an AgCl\textsubscript{0.25}Br\textsubscript{0.75} raw material, and after that the mixture was evaporated and dried;
3. The obtained samples were heated at 850°C for compositions containing yttrium oxide and at 600°C for compositions not containing yttrium oxide for 2 hours and cooled to room temperature;
4. Then, plane-parallel plates were obtained from the abovementioned materials by the hot pressing technique using a Specac 15 Ton manual hydraulic press (the applied load on the sample area of ~150 mm\textsuperscript{2} was 10 tons, the temperature was 150°C). [13]. The plate thickness spans from 130 to 220 μm with an accuracy of ± 5 μm.

In the visible and near infrared ranges, the investigation of samples’ transmission features was carried out using a Shimadzu UV-1800 spectrophotometer (in the range from 190.0 to 1100.0 nm with a step of 0.1 nm) [14]. In the range from near to far IR, an IR-Fourier spectrometer IR-Prestige-21, Shimadzu was used (in the range from 1.28–28.6 μm). The recording conditions were as follows: the beam splitter – KBr, the detector – DLaTGS, the frequency range – 7800–350 cm\textsuperscript{-1}, the resolution – 4 cm\textsuperscript{-1} [15].

3.2. Investigation of particle distribution via SEM
To clarify the nature of nanoparticle distribution in the AgCl\textsubscript{0.25}Br\textsubscript{0.75} matrix, we acquired the images of sample surfaces using a scanning electron microscope AURIGA CrossBeam (Carl Zeiss NTS, Germany) with the following parameters: maximum magnification – 125 000x, accelerating voltage – 30 kV. The preliminary sample preparation included the deposition of a conducting carbon layer on the samples. For this purpose, a Gatan 681 ion-beam coater was used. A carbon layer of about 5 nm in thickness was deposited for 2 minutes. The vacuum during spraying was 5×10\textsuperscript{-3} torr.

Figure 2 represents a photograph of 10 wt.% (Nd\textsubscript{0.02}Y\textsubscript{1.98}O\textsubscript{3}): AgCl\textsubscript{0.25}Br\textsubscript{0.75} ceramic surface at 5500x magnification. The photograph shows that some of the nanoparticles are agglomerated up to 200 nm and more in the longest dimension.

![Figure 2. SEM photo of nanoparticles in 10 wt.% (Nd\textsubscript{0.02}Y\textsubscript{1.98}O\textsubscript{3}): AgCl\textsubscript{0.25}Br\textsubscript{0.75} ceramics (sample No. 2). The scale bar is 100 nm.](image)

![Figure 3. The particle size distribution for 10 wt.% (Nd\textsubscript{0.02}Y\textsubscript{1.98}O\textsubscript{3}): AgCl\textsubscript{0.25}Br\textsubscript{0.75} ceramics (sample No. 2).](image)
The particle size distribution is shown in figure 3. The number of nanoparticles selected for size measurements was 100. As seen in the graph depicts, the maximum of the nanoparticle distribution curve is about 40 nm.

We also carried out experiments to reveal the impact of micro-sized particles of neodymium oxide on the transparency of AgCl$_{0.25}$Br$_{0.75}$ ceramics. Using an Olympus optical microscope, we found out that Nd$_2$O$_3$ micro-powder is a combination of individual particles with a size of about 1–2 µm and their agglomerates (see figure 4), which are easily broken when mixed with silver halides.

![Figure 4. SEM photo of Nd$_2$O$_3$ microparticles.](image)

3.3. IR spectroscopy data

Absorption spectra. First, we prepared the samples of AgCl$_{0.25}$Br$_{0.75}$ ceramics without adding nano- or microparticles. Figure 5 shows the transmission spectrum of a AgCl$_{0.25}$Br$_{0.75}$ sample. The transmittance of this sample is around 75% in the wavelength range from 1.8 to 26 µm, and there are no absorption windows on the spectrum.

![Figure 5. The transmission spectrum for AgCl$_{0.25}$Br$_{0.75}$ transparent ceramics.](image)

Figure 6 below shows the transmission spectra of samples No. 1 (nano-powder 10 wt.% (Yb$_{0.1}$Y$_{1.9}$O$_3$): AgCl$_{0.25}$Br$_{0.75}$) and No. 2 (nano-powder 10 wt.% (Nd$_{0.02}$Y$_{1.98}$O$_3$): AgCl$_{0.25}$Br$_{0.75}$). As seen in this figure, the transparency of ceramics with incorporated nanoparticles noticeably decreased, but the decrease is associated with the strong absorption of Y$_2$O$_3$ rather than the absorption of neodymium.
ions. To verify this statement, we prepared nano-powder ceramics from pure ytterbium oxide and micro-powder ceramics from neodymium and dysprosium oxide in $\text{AgCl}_{0.25}\text{Br}_{0.75}$.

Figure 7 represents the transmission spectrum of the ceramics made from ytterbium oxide nano-powder and $\text{AgCl}_{0.25}\text{Br}_{0.75}$ solid solution. It can be seen from the graph that the transmittance of this sample in the wavelength range of 4–16 $\mu$m is more than 60% for unpolished surfaces.

![Figure 7](image)

**Figure 7.** The transmission spectrum of ceramics sample No.3 (0.56 wt.% $\text{Yb}_2\text{O}_3$: $\text{AgCl}_{0.25}\text{Br}_{0.75}$). Ytterbium oxide is introduced into the matrix in the form of nano-powder.

Similar measurements were conducted for transparent samples made from the micro-powder of neodymium and dysprosium oxides (see figure 8).

![Figure 8](image)

**Figure 8.** The transmission spectrum of ceramics: (a) sample No. 4 (0.5 wt.% $\text{Nd}_2\text{O}_3$: $\text{AgCl}_{0.25}\text{Br}_{0.75}$), (b) sample No. 5 (0.5 wt.% $\text{Dy}_2\text{O}_3$: $\text{AgCl}_{0.25}\text{Br}_{0.75}$).

Thus, having assessed the obtained spectra, we have drawn the following conclusion: when rare-earth elements (Nd, Yb, Dy) are introduced into the $\text{AgCl}_{0.25}\text{Br}_{0.75}$ matrix in the form of nano- and micro-powders of their oxides, the transmittance of silver halide samples decreases insignificantly.

3.3.1. Luminescence spectra. To estimate the emissive capacity of $\text{Nd}^{3+}$: $\text{Y}_2\text{O}_3$ nanoparticles incorporated in silver halides, we investigated samples’ optical properties upon the excitation of luminescence spectra by an LDD-10 diode laser beam at the wavelength of 806 nm (Semiconductor
Devices, St. Petersburg). The spectra were recorded using a spectrometer based on an MDR-23 monochromator supplied with an electronic control unit (OKB Spectr, St. Petersburg).

Figure 9 shows that ceramic samples prepared from 10 wt.% (Nd$_{0.02}$Y$_{1.98}$O$_3$):AgCl$_{0.25}$Br$_{0.75}$, when heated during sintering to 600°C, exhibit weak luminescence properties. On the contrary, the samples obtained at a heating temperature of 850°C are similar in their luminescence spectrum to optical ceramics made of 1 wt.% Nd$^{3+}$:Y$_2$O$_3$, i.e., we observe distinct luminescence peaks (see figure 10).

4. Conclusion

Our theoretical and experimental studies have shown that the introduction of nanoparticles, as well as microparticles, into the AgCl$_{0.25}$Br$_{0.75}$ transparent medium, virtually does not reduce its transmission in the mid-IR region. In this case, the refractive index of the particles should not differ greatly from the refractive index of the silver halide $\Delta n < 10\%$. An insignificant decrease in the transmittance of ceramic samples is caused not by scattering of radiation by particles but by absorption on inhomogeneities. It was also revealed that the luminescent properties of nanoparticles do not change when these particles are introduced into media consisting of AgCl$_{0.25}$Br$_{0.75}$ solid solutions. It allows us to create silver halide sources of coherent radiation in the mid-IR region. The corresponding energy levels can be excited by an optical radiation or a pulsed electric field [16].

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