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# Halide-containing zinc borosilicate glass as a matrix for $CsPbBr_3$ crystal

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**Abstract.** The paper presents the results of studying the region of glass formation in the $B_2O_3$-$SiO_2$-ZnO-NaBr system. The used mode of glass synthesis made it possible to avoid the complete volatilization of bromine from the glass melt. For a series of samples containing 8 mol.% sodium bromide, 12 mol.% $SiO_2$ and variable ratio of $B_2O_3$ and ZnO the dependences of density and refractive index were determined. For the glass composition $60B_2O_3$ – $12SiO_2$ – 20ZnO – 8NaBr additionally containing PbBr and $CsNO_3$, in-situ crystallization of halide perovskite crystals was performed. Based on X-ray phase analysis, the formation of the $CsPbBr_3$ phase was established. Upon excitation at a wavelength of 405 nm, the glass-ceramic sample had a luminescence band with a maximum near a wavelength of 518 nm.

**Keywords:** zinc borosilicate glass, glassy matrix, halide perovskite crystals, $CsPbBr_3$, microhardness

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## Introduction

In recent years, a lot of research has been carried out on the study of luminescent materials. Such materials are used in many optical devices: in solid-state lasers, light-emitting diodes, radiation converters, plasma displays, solar cells, detectors, and low-dimensional quantum devices [1]. One of the matrices for such materials is glass containing functional additives. They can be luminescent nanocrystals, light-absorbing pigments and rare earth elements.

It is well-known that oxide systems are the most chemically stable among glassy materials. Borosilicate glass possesses high resistance to crystallization, high optical uniformity and manufacturability, a wide operating temperature range and high mechanical strength. Borosilicate glasses are used in various fields of science and technology: in optical and optoelectronic devices, sensors, inorganic and organic chemistry, chemical synthesis and vacuum devices [2]. In addition, this material has a low thermal expansion coefficient, which makes it more applicable [3,4]. For glasses containing silicon oxide, ZnO is a common additive. In general, ZnO is a glass modifier, which in boron glasses breaks up B-O-B bonds. In case of modifier, it reduces the inhomogeneities that occur during macroscopic phase separation and increase the chemical resistance of the glass [5]. However, at high concentrations, ZnO can act as a glass former being linked to four oxygen ions in a covalent bond configuration [2]. Typical

additives for oxide glasses, improving their performance are Na and K ions. Noted elements are modifier ions, which modify the structural network of glass, reducing the strength of the bond between the structural groups, which leads to a decrease in the glass transition temperature and an increase of the coefficient of thermal expansion [1,3,4].

In the context of the creation of new glass-based devices, in the past few years, active research has been carried out on glassy matrices for the in situ formation of low-dimensional structures such as nanowires, nanocrystals and quantum dots [6,7]. One of the most studied low-dimensional structures for optoelectronic devices in the last few years is halide perovskites (HP). HP are currently considered the most promising luminescent material for the production of displays, visible light-emitting diodes, lasers, solar cells, and photodetectors. HP crystals have such unique properties as a widely tunable spectral range of radiation, a high luminescence quantum yield (up to 90 %), a narrow emission linewidth, and a relatively simple synthesis technology.

Halide perovskites have demonstrated record high progress in increasing the quantum yield of solar panels based on them. Unfortunately, HP have an extremely short lifetime of no more than 3 years, which is caused by the degradation of their structure under the influence of external factors [8,9]. One of the promising solutions aimed at increasing their service life without reducing their luminescent properties is the production of low-sized crystals directly in a solid-state matrix [10,11].

In this paper, we present the results of studying the glassy system $B_2O_3$-$SiO_2$-ZnO-(NaBr) in the context of a new solid-state matrix for in situ formation of $CsPbBr_3$ crystals. In this work, for the first time, the concentration dependences of the microhardness, density, refractive index, and spectral characteristics of noted system are present.

## Materials and methods

Glass formation was studied in the system (33-60) $B_2O_3$ – 12 $SiO_2$ – (47-20) ZnO – 8 NaBr. The glass components were prepared under laboratory conditions on a balance (ViBRA HT-224RCE) based on the molar composition. In order to achieve homogeneity, the final mixture was ground in an agate mortar for at least 15 minutes. The glass synthesis was carried out in an electric resistance furnace in air at a temperature of 1200 ˚C for 15 minutes. The melt casting was carried out on a brass mold heated to 400 ˚C and then annealed in a muffle furnace at a temperature 30–50 °C lower than glass transition temperature.

For optical measurements, the samples were ground and polished to a thickness of 2-3 mm. X-ray diffraction analysis was carried out on a D8-Advance diffractometer (Bruker). The density of the samples was measured by the hydrostatic method in distilled water under normal conditions. The error did not exceed 0.003 g/cm$^3$. The refractive index $n_D$ was measured with an IRF-23 (LOMO) optical refractometer at a wavelength of 589 nm; alfa-bromonaphthalene was used as the immersion liquid.

The microhardness values of the samples were obtained on a Buehler MICROMET 5103. To measure the transmission spectrum in the range of 200–1100 nm, a spectrophotometer (Analytic Jena, Specord 40) was used. IR spectroscopy was carried out on an FSM 1201 spectrophotometer. The luminescence spectrum was measured on an Avantes-2048 fiber spectrometer under excitation by a semiconductor laser with a wavelength of 405 nm.

## Results and discussion

In this work, compositions were synthesized for the first time to determine the area of glass formation in pseudo ternary ($B_2O_3$ + $SiO_2$) – ZnO – NaBr system. Figure 1 shows the obtained region of glass formation. It can be seen from the figure that the region of glass formation with respect to NaBr is limited to 25 mol. %, while the change in the ZnO content lies in the range

of (10-70) mol.%. The latter is in accordance with the fact that at high concentrations ZnO can act as a glass former [2].

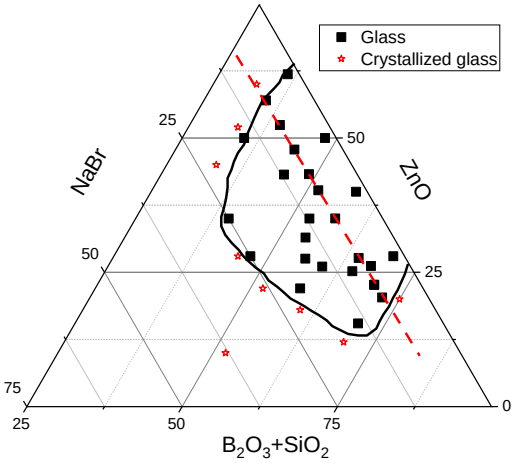



**Fig. 1.** Area of glass formation in ($B_2O_3$ + $SiO_2$) – ZnO – NaBr system

The introduction of NaBr into the matrix served as an additional source of bromine for the subsequent formation of the $CsPbBr_3$ crystalline phase. In the context of a solid matrix for HP nucleation, a series of glass samples containing 8 mol.% of NaBr was chosen. At a higher content of NaBr in glass, a high discrepancy was observed in the content of bromine according to the results of EDX analysis and synthesis (more than 10 %), which indicated its volatilization during high-temperature synthesis from glass melt. For the series with 8 % NaBr, the discrepancy between the experimental and synthesized bromine concentrations did not exceed 5 mol.%. In addition, for samples with a high content of bromine, a tendency to haze on the surface was found, which, apparently, is associated with the low hydrolytic resistance of glasses at a high content of bromine. With a decrease in the content of NaBr, the resistance to moisture increased and at 8 mol.%, the manifestation of the effect of moisture was absent both in the optical transmission spectra and in the measurements of mass loss when the glasses were kept in water for 20 days at T=25 °C.

The compositions of the synthesized glass samples with 8 mol.% of NaBr and their labels are given in Table 1.

**Table 1.** Chemical compositions of synthesized glass samples, mol. % (By batch)

| $B_2O_3$ | $SiO_2$ | ZnO | NaBr | Sample code |
|---|---|---|---|---|
| 60.0 | 12.0 | 20.3 | 7.7 | BSZ-20 |
| 58.0 | 12.0 | 22.0 | 8.0 | BSZ-22 |
| 52.0 | 12.0 | 27.0 | 8.0 | BSZ-27 |
| 45.2 | 12.0 | 35.0 | 7.8 | BSZ-35 |
| 40.0 | 12.0 | 40.0 | 8.0 | BSZ-40 |
| 36.8 | 12.0 | 43.3 | 7.9 | BSZ-43 |
| 32.2 | 12.0 | 47.8 | 8.0 | BSZ-47 |

*Physical properties*. For a series of samples with 8 mol. % of NaBr, the density dependence on the ZnO content is shown in Fig. 2.

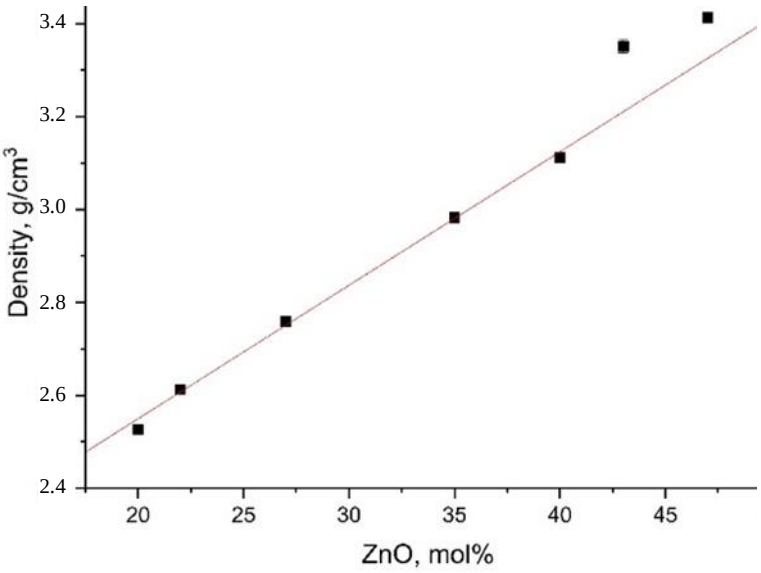



**Fig. 2**. Glass density versus ZnO content (The line is drawn to guide the viewer)

It can be seen from the figure that with an increase in the ZnO concentration, the density of the samples increased from 2.5 to 3.9 g/cm$^3$. This effect can be explained on the basis of two reasons. The first is that ZnO (81.38 g/mol) has a larger molar mass than $B_2O_3$ (69.62 g/mol). The corresponding increase in the content of the heavier element with a decrease in the light element leads to an increase in the density of the glass. A similar character of the influence of additives of components with a higher molar mass on the glass density was obtained earlier for fluoride, phosphate, and borosilicate systems [12-14].

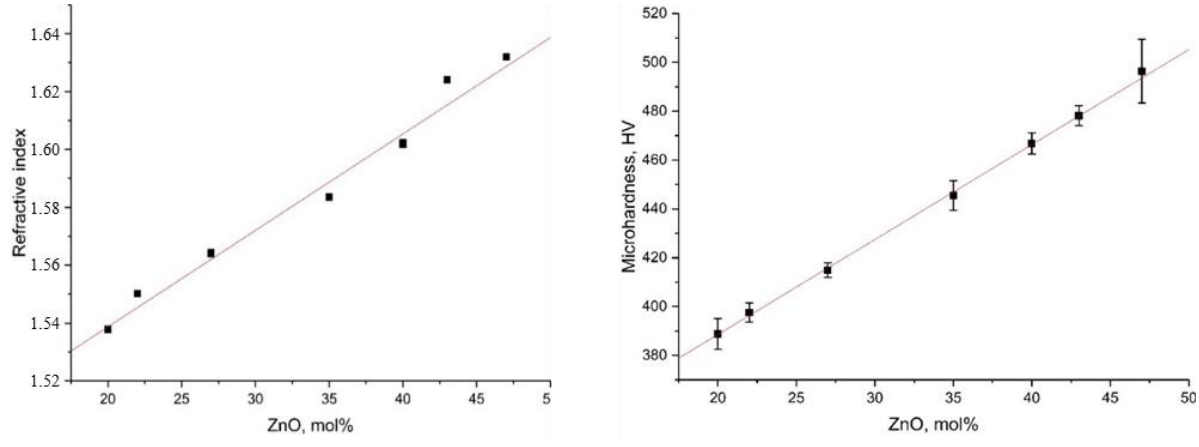
The second possible reason for the dependence is the structural modification of the glass matrix with an increase in the content of zinc oxide. From the point of view of glass formation, it is known that at low concentrations, ZnO will act as a modifier of the structural network of glass. However, the boundary of the transition of the role in glass from a modifier to a glass former depends on the type of matrix [15]. In the case of a glass former, it joins the glass network in the form of [$ZnO_4$] structural units, where zinc is bonded to four oxygen ions in a covalent bond configuration [16].

In the studied compositions, the content of ZnO is relatively high (>20 mol. %), which allows us to assume its glass-forming role. Therefore, with an increase in the ZnO/$B_2O_3$ ratio, the number of unbound oxygen atoms in the glass decreases, which leads to the formation of a more “loose” structure. With an increase in the ZnO content in glass, $Zn^{2+}$ ions occupy intermediate spaces between the structural groups of the glass framework, thereby increasing the density.

It is known that in glassy materials, there is a correlation between density and refractive index [17]. To identify the marked connection, the values of the refractive index for a series of glasses were measured. Fig. 3(a) shows the dependence of the refractive index on the content of ZnO. It can be seen that an increase in the ZnO content leads to an almost linear increase in refractive index, so the value of it increased from 1.53 to 1.63.

Based on a joint analysis of the dependences of density and refractive index, it can be concluded that an increase in the ZnO content leads to a decrease in the average distance between glass structural groups, an increase in the cohesion of the glass framework, and a decrease in the speed of light propagation. A similar, single-phase nature of the dependence reflects the relationship between the structural and optical characteristics of glass and

corresponds to the previously obtained results for phosphate, fluoride, and borosilicate glasses [18,19].




(a) (b)

**Fig. 3**. Dependence of the refractive index (a) and (b) microhardness versus ZnO content in a series of studied glasses

Figure 3(b) shows the dependence of microhardness on the content of ZnO. The microhardness values for the resulting samples ranged from 390 to 500 HV, respectively. A similar character of the dependence was obtained in borosilicate, phosphate, and tellurite glasses [20-22]. An increase in microhardness can be associated with the formation of a denser packing of glass, which correlates with the previously obtained dependence of density on the ZnO content [1].

*Spectral properties*. The spectral transparency region of glass determines the possibility of using it as a matrix for various luminescent particles, for example, halide perovskite crystals. The obtained transmission spectra in the spectral region 200-500 nm for a series of glasses under study are shown in Fig. 4. It can be seen from the presented spectra that the position of the short-wavelength transmission boundary changes depending on the composition of the glasses. An increase in the content of ZnO leads to a shift of the boundary to the visible region from 290 to 335 nm (at the 50 % transmission level). Since the short-wavelength boundary reflects the magnitude of the chemical bonds of the glass structural groups, its shift indicates the effect of the zinc oxide content on the glass matrix. The latter is consistent with the results described above and the conclusion about the glass-forming role of ZnO in the system under study.

The application of glass as a matrix for halide perovskite crystal, a high level of transmission is required in the luminescence excitation wavelength region of $CsPbBr_3$ phase. For the marked phase, the excitation region starting from 300 to 420 nm, thus, it can be stated that the proposed system is applicable in terms of spectral characteristics as a matrix for the $CsPbBr_3$ crystal.

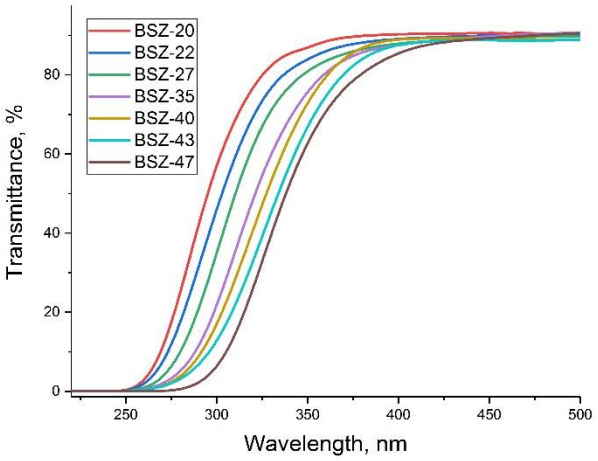



**Fig. 4.** Transmittance spectra of a series of studied glasses

*In-situ nucleation and luminescent properties*. The formation of a crystalline phase in a glassy matrix was carried out by thermal annealing of glasses containing the following components in the initial mixture: $Cs(NO_3)_2$ and $PbBr_2$. The original glass sample with composition $60B_2O_3 – 12SiO_2 – 20ZnO – 8NaBr$ was completely transparent in the visible region of the spectrum after being worked out; the fundamental absorption edge was located around 300 nm. After the annealing procedure in a furnace for 1 hour at a temperature of 460 °C, the appearance of a yellow tint was noted, indicating the formation of an absorption band in the glass. The optical transmission spectra of the original and annealed samples are shown in Fig. 5. As can be seen from the Fig. 5, the value of absorption edge for heat treated glass was shifted to 510 nm.

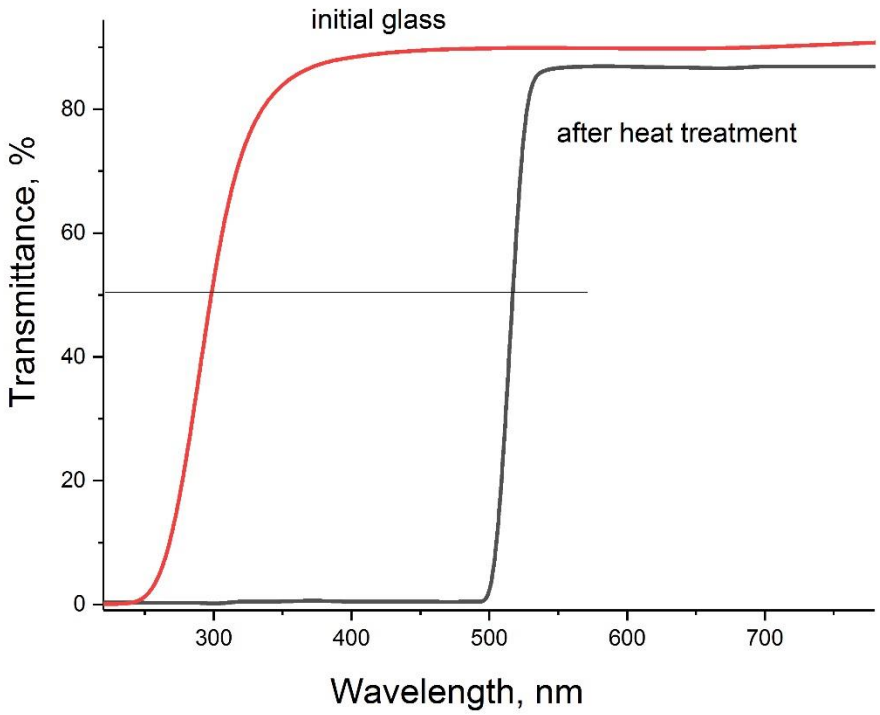



**Fig. 5**. Transmittance spectra of glass samples doped with $CsNO_3$ and $PbBr_2$ before and after annealing for 1 hour at 460 °C

To establish the nature of the change in the spectral characteristic, X-ray phase analysis was carried out, which indicated the formation of a $CsPbBr_3$ phase in the glassy matrix.

The luminescence spectrum was also measured upon excitation by a semiconductor laser with a wavelength of 405 nm, shown in Fig. 6. The position of the maximum of the luminescence band was 518 nm, which corresponds to that described in the literature for the $CsPbBr_3$ phase formed in various glassy systems [3,4,10,11].

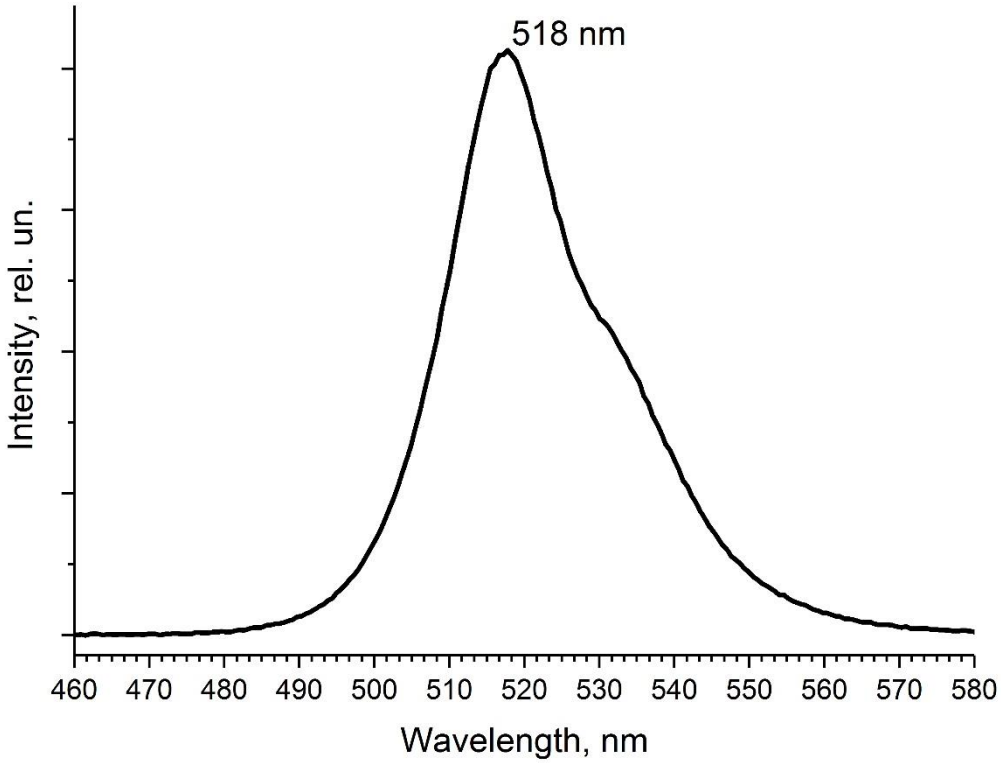



**Fig. 6.** Luminescence peak of a sample with $CsPbBr_3$ crystals nucleated after heat treatment

Visually, the samples had a high uniformity and intensity of green luminescence. The concentration dependences of the luminescence intensity as a function of the zinc oxide content are the subject of further research.

**Conclusion**

In this work, the region of glass formation of $B_2O_3$-$SiO_2$-ZnO-NaBr was determined. The concentration dependences of microhardness, refractive index, and density depending on ZnO content were established. With an increase in the content of zinc oxide, a close to linear increase in the density, refractive index, and glass microhardness was observed. In addition, an increase in the fraction of ZnO in glass leads to a shift in the fundamental absorption limit from 290 to 335 nm. Apparently, the reason for this is the manifestation of the glass-forming ability of ZnO, which causes a decrease in the distance between the structural groups in the glass and increases the strength of the bond between the elements of the glass network. To confirm this assumption and to determine in detail the structural role of ZnO in the studied matrix, additional studies using structure-sensitive methods are required.

In glass sample with composition 60 $B_2O_3$ – 12 $SiO_2$ – 20 ZnO – 8 NaBr, the possibility of nucleation of halide perovskites $CsPbBr_3$ in the studied matrix was demonstrated, and the temperature and time regime of annealing for the formation of the noted crystalline phase was determined. The luminescence spectrum consisted of a single peak, peaking at about 520 nm at an excitation wavelength of 405 nm.

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