PHOTOLUMINESCENT PROPERTIES OF PHOSPHOR BASED ON PEROVSKITE CsPbBr₃ NANOCRYSTALS COMBINED WITH VIOLET LEDS

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The characteristics of an LED lighting system consisting of a commercial violet LED and a green phosphor based on CsPbBr₃ nanocrystals are studied in the context of development of LED illumination sources with antibacterial effects but without harmful effects on human health. The internal efficiency of the nanocrystalline phosphor in a silicone compound was found to exceed 40%, dropping noticeably because of heating for an electric current of ~0.1 A (phosphor excitation intensity ~0.1 W/mm²). This undesirable feature can be diminished by using a remote phosphor design for the illuminators and by using chemical techniques to improve the thermal stability of the nanocrystals.

Keywords: phosphor, LED, antibacterial effect, perovskites, nanocrystals.

Introduction. Ultraviolet (UV) radiation is well known to have bactericidal action. Mercury lamps in the UV-C range (200–280 nm) are widely used to disinfect rooms and aerial and aqueous media. Significant progress in the development of solid-state LED sources of UV radiation has enabled the replacement of mercury lamps in several instances. However, the use of UV-C radiation requires observance of strict safety measures, which limits its use in the presence of living organisms (plants, animals, humans). However, notable bactericidal effects of LED sources of short-wavelength visible radiation with emission maxima at 400 ± 5 nm have been reported. This includes destruction of the SARS-CoV-2 virus (COVID-19), with the effect being enhanced if a commercial white-light LED is used in combination [1–4]. A combination of commercial violet (407 nm) and white-light LEDs was used to develop LED illuminators for disinfection of rooms [5]. It is noteworthy that the electroluminescent emission of semiconducting crystals in white-light LEDs is supplemented in the blue region (maxima at 450–460 nm) by broadband photoluminescence of phosphors to produce white light with given colorimetric characteristics [6]. This development resulted from optimization of the technological process for manufacturing LEDs considering their final cost, energy efficiency, and required colorimetric parameters. The radiation near 400 nm in commercial white-light LEDs is too weak for application as an antibacterial device. However, it is well known that white light can also be obtained by using a violet LED supplemented by two or three phosphors emitting in the blue or greenish-blue and orangish-red regions as the electroluminescent source. Successful development of colloidal optoelectronics principles [7] allowed fully inorganic nanocrystals of the perovskite CsPbBr₃ to be considered a blue-green phosphor and nanocrystals of the perovskite CsPbI₃ [8] or nanocrystals of CdSe that are used in liquid-crystal displays [9], an orange-red phosphor. The photoluminescence spectral range of perovskites is set mainly by their composition (variation of the Cl, Br, I ratio) and partially by their size; of CdSe nanocrystals, by their size owing to the intentional use of a quantum size effect and the core–shell concept.

The present work investigated the luminescent characteristics of phosphors based on perovskite CsPbBr₃ nanocrystals combined with medium-power commercial violet LEDs.

Experimental. Nanocrystals of CsPbBr₃, which are under intense scrutiny as LED sources [11], were chosen as the LED source for testing as a green phosphor for the work because nanocrystalline organic (containing C and H atoms) and hybrid perovskite compounds have poor thermal stability and are being considered mainly for applications in solar cells [10].

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Nanocrystals of CsPbBr$_3$ were synthesized by hot injection in an inert atmosphere as before [12] with slight changes. First, a solution of cesium oleate was prepared. For this, CsCO$_3$ (80 mg) was added to 1-octadecene (3 mL) and oleic acid (0.35 mL). The mixture was evacuated and heated at 120°C for 30 min. Then, the temperature was raised to 150°C. The mixture was heated in an Ar atmosphere until a transparent solution was obtained. The perovskite nanocrystals were synthesized by loading PbBr$_2$ (69 mg), 1-octadecene (5 mL), oleic acid (0.5 mL), and oleylamine (0.5 mL) into a 25-mL three-necked flask. The mixture was heated under vacuum at 120°C for 30 min until the PbBr$_2$ was completely dissolved and then heated to 170°C under an Ar atmosphere. A mixture of 1-octadecene (0.6 mL) and cesium oleate (0.4 mL) heated beforehand to 100°C was quickly injected. The mixture was stirred for 5 s. The flask was placed into an ice bath to cool the solution to room temperature. The obtained solution was centrifuged at 10,000 rpm for 10 min to remove aggregates and redispersed in toluene. The solution was centrifuged in the presence of MeCN (1:1, v/v) at 10,000 rpm for 10 min to remove the excess of ligands and again redispersed in toluene.

A composition for use in the LED source was prepared by mixing the solution of the nanocrystals in toluene with ÉTM-1 silicone resin in a 1:1 ratio on a Vortex-1 laboratory shaker. The solvent was removed using a vacuum device for 30–40 min before adding a hardener to the composition. The silicone composition was placed dropwise (2–5 mg per drop) onto the surface of LEDs. The LED sources were based on UV-1W400 InGaN (LEDGUHON) with an emission band in the range 390–405 nm and SZN05A01S LEDs (Seoul Semiconductor) with a 405–415-nm band.

The spectral and kinetic properties of the perovskites in the composition were investigated by diluting the solution of nanocrystals with silicone resin in a 1:40 ratio, adding hardener, and placing the mixture (200 μL) on a glass substrate (1 × 2 cm). The photoluminescent characteristics of the nanocrystals were measured in the solutions and compound using a Fluorolog-3 spectrophotometer (Horiba Scientific, USA); the electroluminescent characteristics of the LED source, a SPECTRO320 spectroradiometer and an ISP500 integrating sphere (Instrument Systems GmbH). The LED temperature $T_c$ was maintained at 25 ± 0.2°C at the soldering point using a thermostatted stage. The working current of the LEDs was ≤30% of the nominal value. The temperature of the silicone composition placed on the LEDs was not measured. It is noteworthy that the composition could possibly be heated mainly by heat released by the nanocrystals.

**Results and Discussion.** Photoluminescence of the initial solution of perovskite nanocrystals in toluene consisted of a narrow emission spectrum (20 nm) with a maximum at $\lambda = 507$ nm (Fig. 1a). The luminescence decay kinetics were characterized by nonmonoexponential decay with an average lifetime $\tau_{av} = 6.0$ ns (Fig. 1b). The average lifetime was determined by approximating the kinetics as a multi-exponential using the formula $\tau_{av} = \sum \alpha_i \tau_i (\sum \alpha_i \tau_i)^{-1} \cdot 100\%$, where $\tau_i$ and $\alpha_i$ are the time and mass factors of the $i$th component. The relative amplitude $f_i$ of each component was calculated using the formula $f_i = \alpha_i \tau_i (\sum \alpha_i \tau_i)^{-1} \cdot 100\%$. A transfer of nanocrystals from the solution into the silicone compound insignificantly (by 1%) shifted the emission spectrum to longer wavelength with a slight (by 5%) increase of its half-width. The photoluminescence decay kinetics with a transfer into the compound changed very noticeably. More pronounced fast and relatively slow components appeared (Fig. 1b). An approximation gave an average lifetime $\tau_{av} = 25.1$ ns. However, the complicated nature of the decay could be evaluated more adequately by comparing the plots in Fig. 1b and the data in Table 1. Such a change of the kinetics was indicative of a change in the relaxation and recombination processes of charge carriers in the nanocrystals because of the generation of new states at the nanocrystal–compound interface.

The characteristics of the LED system were measured according to the following algorithm considering that the photoluminescent properties of the nanocrystalline phosphors might have depended on the intensity and dose of absorbed exciting radiation. The current was varied at working time intervals of 5 min by jumps in the sequence 1–10–105–10–1 mA, which enabled a simultaneous evaluation of the possible dependence of the phosphor efficiency on the power of the exciting and absorbed radiation and on the operation during a certain period with highly intense excitation (~0.1 W/mm$^2$). The parameters of the starting LEDs without the phosphors were measured in the same cycle. A series of samples with different excitation sources and different masses (2–5 mg) of composition deposited on them were prepared. In general, all samples gave similar results. The data in Figs. 2 and 3 and Table 2 are given for a single sample of nanocrystalline CsPbBr$_3$ phosphor operating together with a UV-1W400 violet LED for clarity. Figure 2a shows its own spectrum. The internal efficiency of the composition was defined as the ratio of the emitted optical power to the absorbed optical power.

The measurements showed that the perovskite nanocrystals had significant internal efficiency (>40%) after they were transferred from the solvent to the silicone composition and deposition of it onto the LED surface. However, the efficiency dropped smoothly as the current was increased from 1 to 105 mA, being restored after decreasing the current with slight changes in the luminescence spectrum (a long-wavelength shift of the spectrum by 1% along the wavelength scale).
Fig. 1. Photoluminescence emission spectra ($\lambda_{ex} = 400$ nm) of CsPbBr$_3$ nanocrystals in toluene solution and silicone compound (a) and photoluminescence decay kinetics ($\lambda_{ex} = 405$ nm) (b).

Fig. 2. Normalized electroluminescence spectra of UV-1W400 violet LED (a) and photoluminescence of silicone composition containing CsPbBr$_3$ nanocrystals (b) measured at currents 1, 10, and 105 mA and at current 10 mA after 105 mA [denoted 10 mA (105)] and 1 mA after 105 mA [1 mA (105)].

The most probable reason for the drop in phosphor efficiency with increasing current was heating of the CsPbBr$_3$ nanocrystals by radiation from the violet LED. The long-wavelength shift of the emission spectrum by $\sim 1\%$ was somewhat indicative of this. It could be related to photo-induced degradation of the nanocrystals, which contributed to the short-wavelength part of the emission spectrum and had the minimal size. The negative effect of heating on the luminescent properties of perovskite nanocrystals is well known and has been documented [13].
TABLE 1. Characteristics of Photoluminescence Decay of CsPbBr₃ Nanocrystals in Toluene and Silicone Compound

| Solution | Compound |
|----------|----------|
| τᵢ, ns  | αᵢ  | fi, % | τᵢ, ns  | αᵢ  | fi, % |
| 1.2     | 0.678 | 30    | 1.1     | 0.616 | 25    |
| 4.9     | 0.310 | 58    | 3.7     | 0.367 | 50    |
| 24.7    | 0.012 | 12    | 20.1    | 0.014 | 10    |
|         |       |       | 140.1   | 0.003 | 15    |
| τᵥᵥ = 6.0 ns |       |       | τᵥᵥ = 25.1 ns |

Fig. 3. Spectra of illuminator system consisting of UV-1W400 violet LED and silicone compound with CsPbBr₃ nanocrystals at currents 1, 10, and 105 mA; dotted lines, initial UV-1W400 LED spectra; solid lines, spectra measured successively at currents 1, 10, and 105 mA; dashed lines, spectra measured at currents 1 and 10 mA after application of 105-mA current for 5 min.

TABLE 2. Characteristics of LED System at Various Currents

| Optical power of UV-1W400 chip without phosphor, mW | Optical power absorbed by phosphor, mW | Current, mA | External efficiency, % | Internal efficiency, % |
|-----------------------------------------------------|----------------------------------------|-------------|------------------------|------------------------|
| 0.43                                                | 0.07                                   | 1.0         | 6.9                    | 42.5                   |
| 10.6                                                | 2.5                                    | 10.0        | 4.3                    | 18.1                   |
| 145                                                 | 31                                     | 105.0       | 1.8                    | 8.5                    |
| After load (action of 105 mA current)               |                                        |             |                        |                        |
| 10.6                                                | 2.1                                    | 10.0        | 3.8                    | 19.4                   |
| 0.43                                                | 0.06                                   | 1.0         | 6.1                    | 40.3                   |
Conclusions. The investigation of the photo- and electroluminescent characteristics of an LED system consisting of a commercial violet LED (395–405 nm) and a silicone composition with perovskite CsPbBr$_3$ nanocrystals found that the composition had an internal efficiency of $\sim 50\%$ at a current of $\sim 1$ mA, which decreased to $\sim 10\%$ at $\sim 0.1$ A and was restored to the initial value after the action of that current stopped. The phosphor based on CsPbBr$_3$ nanocrystals had a photoluminescence spectrum in the initial solution in toluene with a maximum at 507 nm and half-width of 20 nm. These parameters changed slightly upon transferring the nanocrystals into a silicone composition. However, the half-width of the spectrum increased by 10% and the emission spectrum maximum wavelength increased by 1% with a 100-fold increase of the current for operation in the LED system. The results indicated that the perovskite nanocrystals were promising for use in LED illumination sources with bactericidal effects. However, conditions avoiding noticeable heating of the phosphors during operation had to be created to produce the maximum intensity. A solution could be an LED-source design with a distant phosphor that would lessen the heating of the nanocrystals and improve their cooling during operation. Chemical methods for improving the thermal stability of perovskite nanocrystals, e.g., doping with other metal cations [14], use of core–shell structures [15], surface modification of the perovskites [16], addition of a protective layer [17], optimization of the compound composition, etc. should be developed.

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