Effect of bismuth substitution for lead in CsPbBr₃ perovskite

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Abstract. The effect of bismuth substitution for lead at concentrations of 0.5 – 5 % on absorption and luminescence of dispersed CsPbBr₃ perovskites has been studied by means of diffuse reflectance spectroscopy and luminescence techniques, respectively. The considerable red shift of the absorption edge of CsPbBr₃ has been observed, as well as a decrease in exciton luminescence with increasing dopant concentration.

1. Introduction

Organic-inorganic hybrid lead halide perovskites attracted the attention of researchers during the 1970s and again in the 1990s [1], particularly for their unique semiconducting and conducting properties [2]. Perovskite-based materials of the general formula ABX₃₋₃, where A = CH₃NH₃⁺ or another monovalent organic cation, B = Pb (or Sn), and X / Y = Cl, Br, I anions, have promising optical and electrophysical properties. In particular, they are characterized by low Urbach energy of ~ 15 meV; a Stokes shift of less than 20 meV; a high mobility of charge carriers of more than 10 cm²/V·s; a significant diffusion length of up to 1 μm [3]; and high absorption in the visible range of wavelength (with an absorption coefficient of more than 10⁴ cm⁻¹) [4]. These unique properties of the perovskite family come to naught due to their instability under the action of moisture, oxygen, UV radiation, heat (especially in the case of Sn-containing perovskites) [5] and lead toxicity [6].

Therefore, an intensive search for new perovskite (perovskite-like) lead-free materials with the useful properties displayed by lead trihalides is ongoing. Two possible search directions were offered in 2015 - 16: 1) chalcogenide perovskites [7], 2) halide double perovskites of the general formula A₂BB’X₆ where A = Cs, organic cation (e.g., CH₃NH₃⁺), other monovalent cations, B = Sb, Bi; B’ = Cu, Ag, Au, K; and X = Cl, Br, I [8,9].

The first direction is represented by just a few publications. There are serious difficulties in the synthesis due to the formation of several phases even at an insignificantly elevated temperature. The second search direction gave encouraging results due to Density functional theory (DFT) ab initio calculations [10] and the possibility of varying the perovskite composition [11]. For example, when examining Cs₂AgBiBr₆, the authors of [12] found a long-lived photoluminescence (about 660 ns) at room temperature and offered this material as promising for photoelectrochemical applications. In addition, the authors showed that, in contrast to the halogenide perovskites (ABX₃₋₃,), the halide double perovskites (A₂BB’X₆) provide an opportunity for variation of the perovskite composition. In the present work, we investigated the influence of Bi-concentration on optical properties of CsPbBr₃ perovskite.
2. Experiment
The incorporation of dopants was achieved in situ by adding a mixture of trivalent-ion (Bi$^{3+}$) bromide salt and CsBr into a crystallization solution containing a mixture of PbBr$_2$ (99%, Sigma) in hydrobromic acid, and then heating to the required temperature for solvent removal and annealing at 150°C in N$_2$-atmosphere. Then, the obtained powders were dissolved in Dimethylformamide (DMF) (0.2 g/5 ml) and applied on glass substrates with subsequent heating at 120°C. We observed a color change from orange to deep red in Bi-doped powders.

The phase formation was analyzed by the X-ray diffraction method using a Rigaku Miniflex II diffractometer with Cu K$\alpha$ radiation (with an anode current of 15 mA and an accelerating voltage of 30 kV) in the angle range of 10° $\leq$ 2$\theta$ $\leq$ 60° with a scanning speed of 5.0°/min. Structural data for the perovskite phase was taken from the ICSD database. The phase analysis by the Rietveld method was carried out using the TOPAS (Bruker AXS) software.

The diffuse reflectance spectra $R(\lambda)$ and absorbance spectra ($A(\lambda) = 1 - R(\lambda)$) were recorded in the 380 - 800 nm spectral range at ambient conditions using a Cary 5000 spectrophotometer equipped with a DRA 2500 external diffuse reflectance accessory. The optical-grade Spectralon was used as a reference standard.

Photoluminescence spectra of perovskites studied have been obtained in the invisible range using a Fluorolog-3 spectrofluorimeter (Horiba Jobin Yvon).

The surface morphology was explored by scanning electron microscopy (using a Zeiss Supra 40 VP system) for all synthesized thin films.

3. Results and discussion
Before carrying out any experiments, we evaluated the perovskite tolerance factor, which should be calculated to estimate the possibility of a heterovalent incorporation (isoelectronic with Pb$^{2+}$) and must be within the range 0.80 – 1.00 to allow the formation of a perovskite structure. The tolerance factors for the samples of CsPb$_{(1-x)}$Bi$_x$Br$_3$ ($x$ = 0.0, 0.5, 0.1, 0.2, 0.5 wt) were calculated to be 0.861, 0.862, 0.862, 0.863 and 0.864, respectively.

The phase composition and structure of the films were identified as the orthorhombic perovskite phase of CsPbBr$_3$ at room temperature. The X-ray diffraction (XRD) pattern of CsPbBr$_3$ shows strong diffraction peaks, which can be assigned to the orthorhombic crystal structure (space group Pbnm) (figure 1(a)).

Note that the growth of Bi concentration results in a decrease in the crystal lattice parameter (figure 1(b)). This is probably due to the size factor: the ionic radius of Bi$^{3+}$ at the VI-coordination position (by Shannon) is 1.03 Å, and the ionic radius of Pb$^{2+}$ at the same position is 1.19 Å. Therefore, the bismuth doping with substitution of Pb positions decreases the crystal lattice parameters.

Figure 1. X-ray diffraction patterns of CsPb$_{(1-x)}$Bi$_x$Br$_3$ ($x$ = 0.0, 0.5, 0.1, 0.2, 0.5 wt%) (a); the crystal lattice parameters (cell volume) vs Bi-concentration (b).
To demonstrate the incorporation of Bi into the perovskite lattice, the XPS spectra of pure and doped CsPbBr3 samples were also studied. The survey spectra are presented in figure 2.

The peaks related to the binding energies (BE) of ~737.5 eV and ~723.6 eV correspond to Cs 3d3/2 and Cs 3d5/2, respectively. As depicted in figure 4, binding energies of 142.2 eV and 137.6 eV in the spectra of samples correspond to the peaks of Pb4f 5/2 and Pb4f 7/2, respectively. The representative high-resolution XPS spectra for the Bi 4f-doublet is resolved at 158.2 eV (Bi 4f 7/2) and 164.2 eV (Bi 4f5/2) binding energies. The Bi4f 7/2 peak overlaps with the Cs4p 3/2 peak at BE ~ 158.2 eV. The presence of Bi signals and an increase in their intensity with dopant concentration indicated a uniform distribution of Bi and also confirmed the effectiveness of the doping process.

Figure 2. (a) XPS spectra of pure and Bi-doped (0.5, 0.1, 2 and 5 wt%) CsPbBr3 samples (b) XPS spectra of Cs 2d states, (c) Pb 4f states, (d) Bi 4f states, (e) Br 3d states in a perovskite.

Figure 3 (a) shows that incorporation of bismuth leads to a significant red shift of the fundamental absorption edge. The biggest shift takes place at the lowest concentration of bismuth (0.5%) in good...
agreement with previous studies [13]. A green band around 2.4 eV (515 - 520 nm) has been detected in the emission spectra at room temperature (figure 3(b)). This band assigned to exciton luminescence of CsPbBr₃ is well known (for example, see [14]).

![Absorbance spectra of Bi-CsPbBr₃ and the emission spectrum of the pure CsPbBr₃ sample (right scale).](image)

**Figure 3.** (a) Absorbance spectra of Bi-CsPbBr₃ and the emission spectrum of the pure CsPbBr₃ sample (right scale). (b) Luminescent emission spectra of the same samples under excitation by monochromatic light (λₑₓ = 405 nm), recorded at room temperature. Bi concentration: 0, 0.5, 1.0, 2.0 and 5.0 %.

It should be noted that a monotonic reduction of the photoluminescence intensity with increasing dopant concentration is in agreement with the results of [13]. At the same time, the authors of [13] observed a monotonic blue shift of the adsorption fundamental absorption edge with increasing bismuth concentration in the 0.25 – 10% range, as well as a corresponding shift of luminescent band maximums. The authors of [13] attributed these shifts to the Burstein–Moss effect. The present studies do not confirm the results of [13], since we observed a red shift of the fundamental absorption edge (figure 3 (a)) and an irregular shift of luminescent peaks in the 0 - 5% bismuth concentration range for CsPbBr₃. The divergence of our results from those presented in [13] can be tentatively related to the size effect, since we have dealt with CsPbBr₃ powders (micron size particles) while the authors of [13] studied nanocrystalline thin films. In this regard, it should be noted that a red shift has been observed for millimeter-size MAPbBr₃ single crystals [15], as well as for MAPbCl₃ millimeter-size single crystals and thin films with 10 μm domains [16]. The red absorption shift for thin films was found to be less than that for MAPbCl₃ single crystals.

4. Conclusions
Dispersed CsPbBr₃ perovskites doped with Bi (0.5 - 5 wt.% ) have been synthesized and characterized by means of X-ray diffraction and X-ray photoelectron spectroscopy. It has been shown that Bi³⁺ cations occupy the positions of lead ions, and the reduction of the lattice cell volume correlates with an increase in dopant concentration. Introduction of Bi into the CsPbBr₃ lattice leads to a considerable red shift of the absorption edge of perovskites studied, as well as to a red shift of the exciton luminescent emission. The results concerning the reduction of exciton luminescence with bismuth incorporation are in agreement with those presented in [13]. However, the authors of [13] found a blue shift of the absorption edge in Bi-doped CsPbBr₃. A possible explanation for the inconsistency of our results with those presented earlier in [13] may be that nano crystals and microcrystals of CsPbBr₃ respond differently to Bi incorporation.

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