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Peculiarities of photoinduced heating of perovskite nanocrystals with effective anti-Stokes photoluminescence under near-resonant laser excitation

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The optical properties of a photoluminescent material based on $CsPbBr_3$ perovskite nanocrystals were studied in this work. The laser heating of the obtained samples was studied under three different regimes of laser excitation: the photoluminescence band appears in the Stokes region, in the anti-Stokes region, and coincides with the excitation line. It was found that under laser excitation of a certain wavelength, this material is able to demonstrate predominantly anti-Stokes (upconversion) photoluminescence. A method is proposed for estimating the PL quantum yield from data on absorption, photoheating, and the position of the photoluminescence band of a sample at two different wavelengths. The external photoluminescence quantum yield of $CsPbBr_3$ nanocrystals was experimentally determined to be 91±4%. The results of this work can be useful for the development of optical cooling technology and can be used in the development of laser devices based on perovskite materials.

Keywords: perovskite nanocrystals, upconversion photoluminescence, quantum yield, laser heating.

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1. Introduction

At present, halide nanocrystals with perovskite nanocrystals (PNCs) represent a new class of nanomaterials that can be widely used in various laser and optoelectronic devices due to their effective photo- and electroluminescence [1,2]. The exciton photoluminescence (PL) of PNCs at room temperature is usually in the form of a rather narrow band tunable over the entire visible range when the chemical composition of PNCs is changed, so PNCs are promising for applications in light-emitting devices [3–5]. A significant fraction of anti-Stokes (upconversion) photoluminescence (ASPL) can be observed in PNCs as a result of photoexcitation [6,7]. Since the energy of ASPL quanta exceeds the energy of excitation photons, additional energy capture from PNCs occurs and optical cooling of PNCs under the action of laser radiation (LR) [8] is possible.

The position of the PL band depends on the size of the PNCs due to the quantum size effect [9]. Moreover, it was recently found that the ratio between the Stokes and anti-Stokes PL intensities under resonant excitation into PL band can also be dependent [10,11]. One of the reasons for the increase in the ASPL fraction in the PL spectrum of PNCs with sizes ~ 10 nm and less may be the strengthening of the electron-phonon interaction and the weakening of the quasi-momentum selection rules during the upconversion process of simultaneous photon and phonon absorption [11]. The possibilities for using such PNCs in the realization of laser optical cooling are improved.

The aim of this work is to study the peculiarities of laser heating of $CsPbBr_3$ PNCs under highly efficient PL excitation in both the Stokes and anti-Stokes regions of the spectrum. A method for determining the PL quantum yield is proposed based on the influence of PL processes on the equilibrium temperature of PNCs under LR exposure

2. Preparation of samples

Stoichiometry violations [12] and various defects [13,14] in PNCs lead to a sharp increase in the probability of nonradiative recombination processes and, consequently, to the degradation of photoluminescent properties of PNCs. Therefore, the PL efficiency of PNCs is highly dependent on the quality of the synthesized nanocrystals. In our work, $CsPbBr_3$ PNCs were synthesized by the well-known ligand-assisted reprecipitation method at room temperature [15]. A mixture of 0.4 mmol (85.1 mg) of cesium bromide (CsBr), 0.48 mmol (176.2 mg) of lead bromide ($PbBr_2$), 600 μl of octylamine and 10 ml of dimethylformamide obtained under argon atmosphere was stirred for 10 h at 400 rpm. Then, 0.5 ml of the resulting mixture was added to 10 ml of toluene and oleic acid solution taken

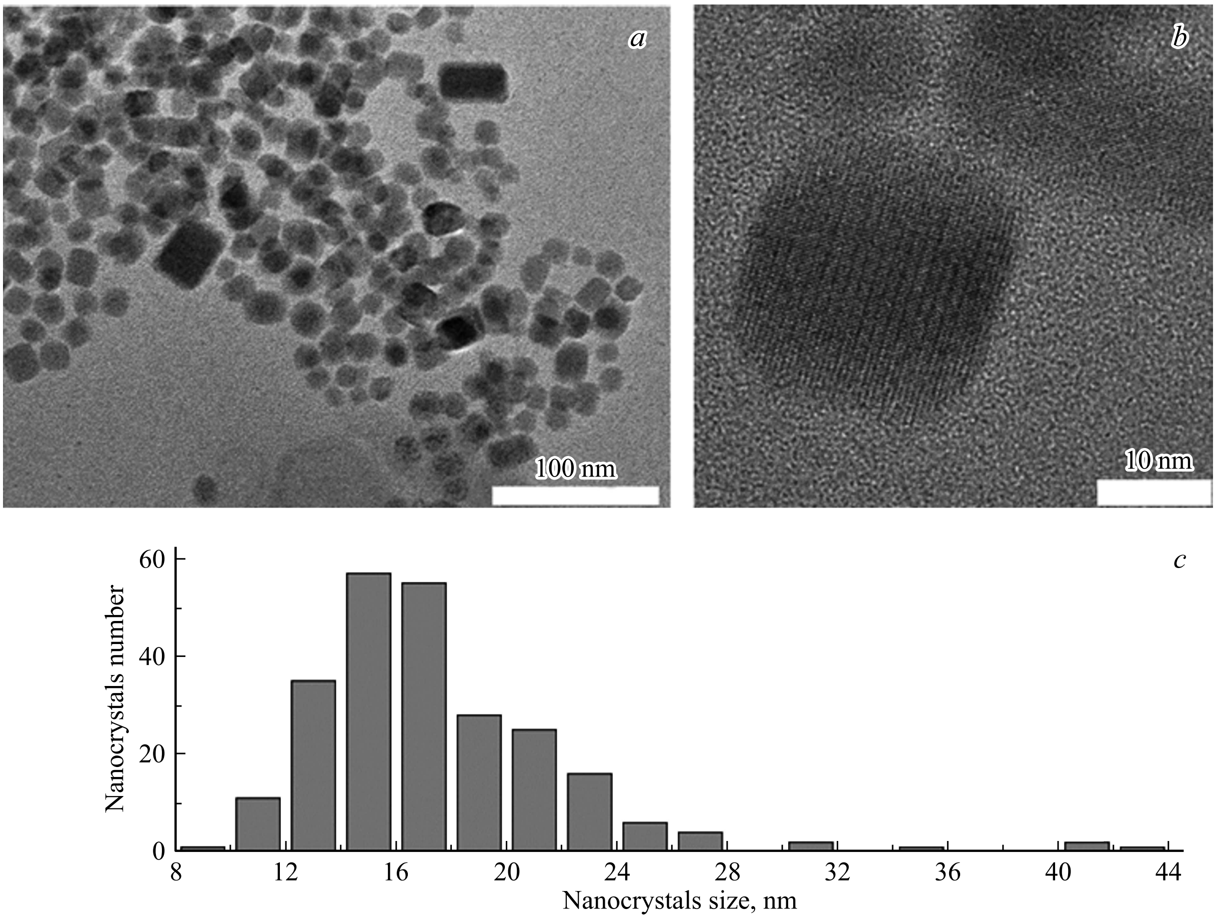

Figure 1. *a, b* — TEM photographs of $CsPbBr_3$ PNCs before being placed in the solid-state UV light-curing resin; *c* — size distribution of PNCs.

in the ratio of (5 : 1). At this stage of synthesis, the solution appeared a characteristic green-yellow color, which should be maintained at all subsequent stages of PNC synthesis. Next, the mixture was centrifuged for 5 min at 9000 rpm. The supernatant (upper part of the solution) was collected and mixed with methyl acetate at a ratio of 1 : 1 followed by centrifugation for 10 min at 9000 rpm, and the resulting precipitate was dispersed in toluene (diluted to a PNC concentration of 10 mg/ml). In the next step of the synthesis, didodecyldimethylammonium bromide (DDAB) was used as a surface ligand [16]. It is known that DDAB can significantly improve the stability and luminescent properties of PNCs [17]. A solution of DDAB in toluene (23.1 mg/ml) was mixed with the obtained PNCs at a ratio of 1 : 10 and stirred for 4 h at 400 rpm. The resulting colloidal solution was washed twice with methyl acetate (the PNC solution was diluted 3 times with methyl acetate and concentrated again by centrifugation for 10 min at 9000 rpm). The final PNC precipitate was dispersed in toluene at a concentration of 10 mg/ml. After such treatment, the colloidal solution of PNCs in toluene remained stable for a long time (up to six months) due to the effective surface passivation.

$CsPbBr_3$PNC suspensions were treated for 15 min in an ultrasonic bath and centrifuged before being applied to the substrates. In the first centrifugation step (10 min at 1000 rpm), the upper part of the solution was collected, i. e. the largest PNCs and their possible agglomerates were removed. In the second centrifugation step (5 min at 12,000 rpm), the concentrated lower part of the solution was taken. Thus, sample concentration and removal of the smallest defective PNCs occurred. The PNCs were then mixed with the UV resin. After curing under UV illumination, the $CsPbBr_3$ PNCs appeared suspended in the resin volume, securely separated from each other and isolated from the atmosphere. To facilitate the escape of ASPL radiation (which can be re-absorbed in the volume), the samples were formed as thin films. In our case, the thickness of the films was 15 μm.

3. Experiment

Transmission electron microscopy (TEM) photographs of the synthesized and selected PNCs by two-step centrifugation were obtained using a JEOL JEM-2100 transmission electron microscope (Japan) and are shown in Figure 1, *a, b*.

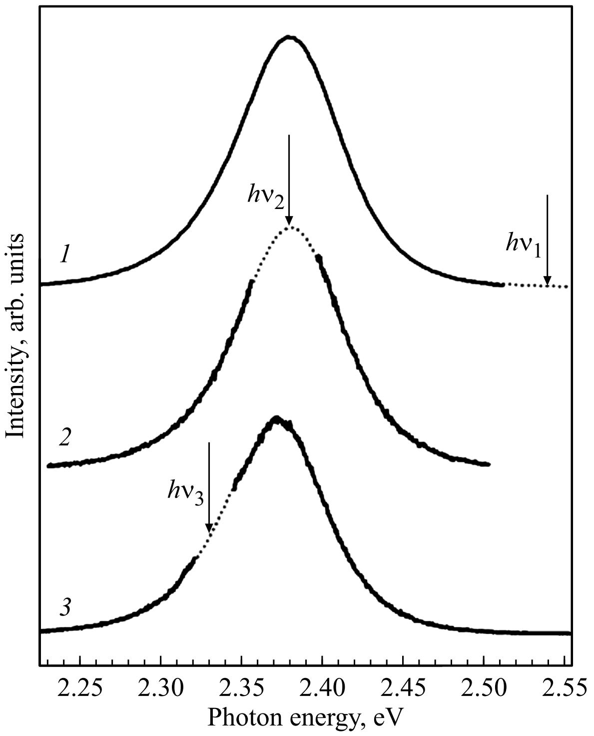

Figure 2. PL spectra of $CsPbBr_3$ PNCs under laser excitation with energies $h\nu_1 = 2.54$ eV (curve *1*), $h\nu_2 = 2.38$ eV (curve *2*), $h\nu_3 = 2.33$ eV (curve *3*). The dotted line shows the approximated parts of the spectra near the excitation lines.

Figure 1,*b* shows a photograph of a single nanocrystal, confirming the high degree of crystallinity of the synthesized samples. Figure 1,*c* shows the size distribution of PNCs, according to which the average size of PNCs is 18 nm.

Figure 2 shows the PL spectra of PNCs suspended in resin under PL excitation in three different modes: a) by photons 2.54 eV (488 nm, argon laser), when almost the whole PL band is in the Stokes region; b) by photons 2.38 eV (520 nm, laser diode), when the excitation is almost in resonance with the PL band and the fraction of ASPL is close to 50%; c) by photons 2.33 eV (532 nm, laser diode), when the overwhelming part of PL is in the anti-Stokes region, i.e., predominantly upconversion PL is observed. The spectra were obtained using a DFS-52 Raman spectrometer with a double monochromator without the use of notch-filters. The integral fraction of ASPL in the case of excitation at 532 nm reaches 85 ± 4%. It can be concluded that in the formed sample under excitation with certain wavelengths a significant dominance of ASPL over the Stokes part of PL is possible, and in general the PL process proceeds in this case with capture of additional energy from PNCs.

Next, the laser heating behavior of the investigated composite sample under PL excitation in the above three cases was investigated. In the first case, the energy of incident photons exceeds the energy of photoluminescent photons, and the energy difference between incident and luminescent photons (~ 140 meV for each act of absorption-re-emission) is converted to heat. In the second case, the energy of incident photons coincides with the average value of the PL photons energy, i.e., the PL process as a whole does not contribute thermal energy, and the heating of the sample under the action of LR is caused only by cases of nonradiative absorption. Finally, in the third case, the incident photon energy is less than the PL photon energy, the PL process requires additional energy input ($\sim$50 meV per an act of absorption-re-emission). Thus, in the third regime, the heating of the sample due to nonradiative absorption is compensated by optical cooling during upconversion. The degree of compensation is determined by the quantum yield of the PL (η_q).

Laser heating of PNC film in UV resin when exposed to radiation of different intensities (LR power was changed, spot area remained constant) was recorded using a thermal imager. The collected data are presented in Figure 3.

In the case of 2.54 eV photons, the laser heating is the largest, smaller at 2.38 eV photon energy and almost absent ($\leq 0.3 \pm 0.1$ K) at photon energy 2.33 eV.

Obviously, the heating efficiency (the slope of the dependences in Figure 3) depends on the absorbed fraction of radiation incident on the sample. Therefore, the absorption spectrum of the investigated sample was further measured. The measurements were carried out using an integrating sphere. The sample on a diffuse-scattering (white) holder was placed in the center of the sphere, where radiation from the monochromator was directed at it through one of

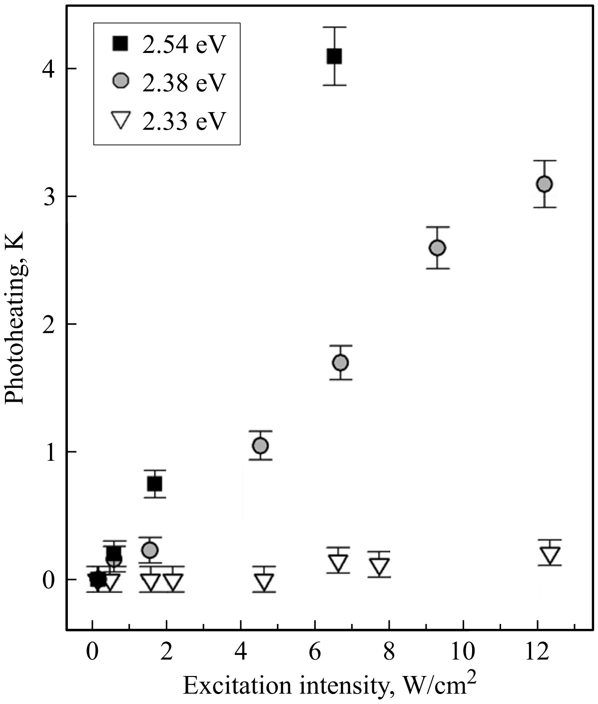

Figure 3. Photoheating of $CsPbBr_3$ PNC film in UV resin as a function of laser excitation intensity. The photoheating was counted from the ambient temperature.

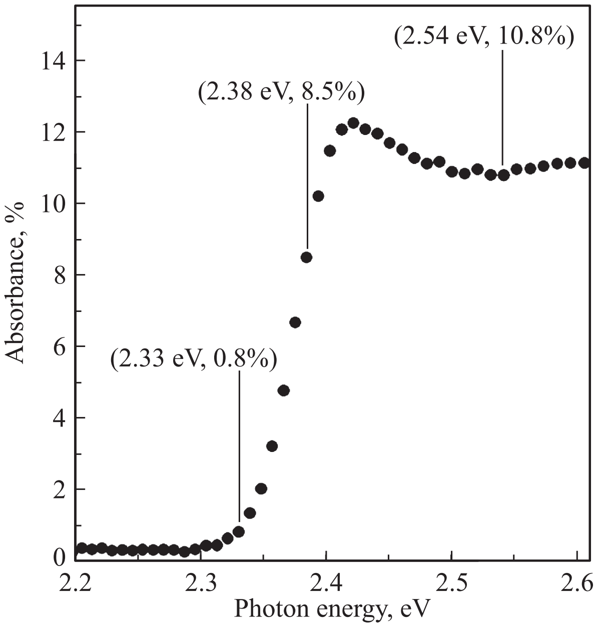

Figure 4. Absorption spectrum of $CsPbBr_3$ PNC film in UV resin.

the ports. The spectrum of an empty slide was recorded as a reference spectrum (zero absorption). The spectrum from the PNC film on a slide was then recorded. The optical absorption data were obtained from the difference of these two measurements (Figure 4).

The spectrum clearly shows the exciton absorption peak of the PNCs $CsPbBr_3$. UV resin is highly transparent in the visible part of the spectrum, and its absorption is negligible (its absorption starts at 3 eV and increases sharply further into the UV band).

The absorption in the sample of photons with energy 2.33 eV is lower than the absorption of photons with energy 2.38 eV by more than 10 times. The heating efficiency observed in Figure 3 (ratio of recorded heating to LR intensity) for these photon energies also differs by a factor of $\sim$ 10 times (0.3 and 3.0 K respectively at 12 W/cm^2). Thus, the weak heating of the sample when exposed to 2.33 eV (532 nm) photons can be explained simply by the small absorption of radiation in the sample.

However, the absorption of photons with energies of 2.38 and 2.54 eV differs by a factor of no more than 1.3 times. The drop in the heating efficiency by a factor of more than 2 times when reducing incident photon energy from 2.54 to 2.38 eV cannot be explained only by the difference in absorption. Consequently, the photoluminescent properties of the material play a significant role on the heating behavior. At a high value of the PL quantum yield η_q tending to unity, the efficiency of laser heating under resonant excitation (2.38 eV) tends to zero, since photons with the same average energy are re-emitted, while the efficiency of laser heating under the action of photons of 2.54 eV does not fall to zero, but tends to some value due to the difference in the energies of PL photons and incident ones. Based on the ratio of laser heating efficiencies at 488 and 520 nm (2.38 and 2.54 eV, respectively), and considering the difference in absorption at these wavelengths, the η_q of the investigated sample can be determined.

4. Analysis of data and discussion of results

The external quantum yield of PL by definition — is the ratio of the number of photoluminescent photons to the number of absorbed photons. Expressing η_q through the incident laser power P_L and PL power P_{PL}, the following expression can be obtained:

$$\eta_q = \frac{P_{PL}\lambda_{PL}}{AP_L\lambda_L}, \tag{1}$$

where A — the fraction of LR absorbed in the sample, λ_L — the wavelength of the incident LR, λ_{PL} — the average wavelength of the PL. Hence

$$P_{PL} = \eta_q AP_L \cdot \frac{\lambda_L}{\lambda_{PL}}. \tag{2}$$

The power going to heat the sample P_H is the difference between the absorbed power and the emitted power due to PL:

$$P_H = AP_L - P_{PL}. \tag{3}$$

Substituting (2) into (3), we obtain the following expression:

$$P_H = AP_L\Big(1 - \frac{\lambda_L}{\lambda_{PL}} \cdot \eta_q\Big). \tag{4}$$

Note that from expression (4) the condition for optical cooling follows, i. e., when P_H becomes less than zero:

$$\Big(1 - \frac{\lambda_L}{\lambda_{PL}} \cdot \eta_q\Big) < 0 \quad \text{or} \quad \eta_q > \frac{\lambda_{PL}}{\lambda_L}. \tag{5}$$

At a constant area of LR exposure (as in our experiment), the equilibrium temperature recorded in the exposure zone is directly related to the heating power of the sample. Neglecting heating nonlinearity:

$$\Delta T = k \cdot P_H, \tag{6}$$

where k is some coefficient of proportionality determined by the geometrical parameters of the laser beam and heat dissipation from the sample. Expressing from here P_H and substituting into (4), we obtain

$$\frac{\Delta T}{P_L} = Ak\Big(1 - \frac{\lambda_L}{\lambda_{PL}} \cdot \eta_q\Big). \tag{7}$$

The expression in the left part (7) — the laser heating efficiency, or the tangent of the slope of the dependences shown in Figure 3, i. e., these are experimentally available values.

For the ratio of heating efficiencies at 488 and 520 nm, according to (7), we finally obtain

$$\left(\frac{\Delta T}{P_L}\right)_{488}\Big/\left(\frac{\Delta T}{P_L}\right)_{520} = \frac{A_{488}}{A_{520}}\left(1-\frac{488\,\text{nm}}{\lambda_{PL}^{488}}\cdot\eta_q\right)\Big/\left(1-\frac{520\,\text{nm}}{\lambda_{PL}^{520}}\cdot\eta_q\right), \quad (8)$$

where the index 488 or 520 indicates at which excitation the value is taken.

Expression (8) allows us to estimate the η_q of the investigated PNCs based on the analysis of its heating under the action of LR of two different wavelengths (when the geometrical parameters of LR at these wavelengths coincide). Note that the assumption used here is that η_q is approximately the same for the two wavelengths analyzed. In the opposite case, assuming that the value of η_q drops significantly upon excitation at 520 nm, it is difficult to explain the observed decrease in photoinduced heating compared to the case of excitation at 488 nm. This assumption is also consistent with the high efficiency of the upconversion single-phonon process in PNCs [7,11].

From the heating efficiency, optical absorption and PL band position data obtained under excitation at 488 and 520 nm in our work, the value of $\eta_q = 91 \pm 4\%$ was obtained. If we take another pair of wavelengths (488 and 532 or 520 and 532 nm) instead of 488 and 520 nm to calculate by the expression (8), then, firstly, in our case the error will be too large due to the inaccurate determination of heating at the wavelength of 532 nm (0.3 ± 0.1 K, the relative error is large). Secondly, under excitation at 532 nm, when the ASPL contribution dominates, the value of η_q may change due to the large difference in energies between photoluminescent and incident photons (~ 0.1 eV). Processes with such an energy difference are less probable and can be interpreted in the framework of the multiphonon absorption model [18].

The threshold value of η_q, required to realize optical cooling when the sample we investigated is excited at 532 nm (with $\lambda_{\text{PL}} \approx 523.5$ nm), according to (5), is 98.4%. Thus, the η_q of the composite obtained in this work is not high enough to observe optical cooling when exposed to LR 532 nm.

5. Conclusion

In the present work, a method was implemented to obtain $CsPbBr_3$ nanocrystal layers with high PL quantum yield and high fraction of ASPL, and laser-induced heating under nonresonant and resonant laser excitation was investigated. It is shown that η_q can be successfully determined experimentally by the effect of PL processes on the equilibrium temperature of PNCs when exposed to LR. The method of calculating the η_q of the PNCs proposed in this work involves only obtaining data on the ratio of the sample photoheating efficiencies and the ratio of absorption at the two wavelengths, as well as data on the PL band position. The results, methods and materials obtained in this work can be useful for the development of optical cooling technologies and the development of laser devices based on perovskite materials.

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Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] I.L. Braly, D.W. DeQuilettes, L.M. Pazos-Outón, S. Burke, M.E. Ziffer, D.S. Ginger, H.W. Hillhouse. Nature Photonics, **12** (6), 355 (2018).

[2] A.F. Gualdrón-Reyes, S. Masi, I. Mora-Seró. Trends Chem., **3** (6), 499 (2021).

[3] L. Protesescu, S. Yakunin, M.I. Bodnarchuk, F. Krieg, R. Caputo, C.H. Hendon, R.X. Yang, A. Walsh, M.V. Kovalenko. Nano lett., **15** (6), 3692 (2015).

[4] Q. Ou, X. Bao, Y. Zhang, H. Shao, G. Xing, X. Li, L. Shao, Q. Bao. Nano Mater. Sci., **1** (4), 268 (2019).

[5] B.R. Sutherland, E.H. Sargent. Nature Photonics, **10** (5), 295 (2016).

[6] A.D. Wright, C. Verdi, R.L. Milot, G.E. Eperon, M.A. Pérez-Osorio, H.J. Snaith, F. Giustino, M.B. Johnston, L.M. Herz. Nature Commun., **7** (1), 11755 (2016).

[7] S. Ye, M. Yu, M. Zhao, J. Song, J. Qu. J. Alloys Compd., **730**, 62 (2018).

[8] S.T. Ha, C. Shen, J. Zhang, Q. Xiong. Nature Photonics, **10** (2), 115 (2016).

[9] S.H. Kim, K.D. Park, H.S. Lee. Energies, **14** (2), 275 (2021).

[10] K.S. Sekerbayev, G.K. Mussabek, N.S. Pokryshkin, V.G. Yakunin, Y.T. Taurbayev, Y. Shabdan, Z.N. Utegulov, V.S. Chirvony, V.Y. Timoshenko. JETP Lett., **114**, 447 (2021).

[11] K.S. Sekerbayev, Y.T. Taurbayev, G.K. Mussabek, S. Baktygerey, N.S. Pokryshkin, V.G. Yakunin, Z.N. Utegulov, V.Y. Timoshenko. Nanomater., **12** (18), 3184 (2022).

[12] A.Y. Grishko, M.A. Komkova, E.I. Marchenko, A.V. Chumakova, A.B. Tarasov, E.A. Goodilin, A.A. Eliseev. Nano Research, 1–8 (2023).

[13] J.S. Yao, J.C. Zhang, L. Wang, K.H. Wang, X.C. Ru, J.N. Yang, J.J. Wang, X. Chen, Y.H. Song, Y.C. Yin, Y.F. Lan, Q. Zhang, H.B. Yao. J. Phys. Chem. Lett., **11** (21), 9371 (2020).

[14] F. Li, Y. Liu, H. Wang, Q. Zhan, Q. Liu, Z. Xia. Chem. Mat., **30** (23), 8546 (2018).
[15] S. Sun, D. Yuan, Y. Xu, A. Wang, Z. Deng. ACS Nano, **10** (3), 3648 (2016).
[16] E. Moyen, H. Jun, H. Kim, J. Jang. ACS Appl. Mater. Interfaces, **10** (49), 42647 (2018).
[17] M.I. Bodnarchuk, S.C. Boehme, S. Brinck, C. Bernasconi, Y. Shynkarenko, F. Krieg, R. Widmer, B. Aeschlimann, D. Günther, M.V. Kovalenko, I. Infante. ACS Energy Lett., **4** (1), 63 (2018).
[18] Granados del Águila, T.T.H. Do, J. Xing, W.J. Jee, J.B. Khurgin, Q. Xiong. Nano Research, **13**, 1962 (2020).

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