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New $Na_2BaY_4F_{16}$ matrix for up-conversion phosphors

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In the process of investigation of NaF-BaF_2-YF_3 system, a new phase $Na_2BaY_4F_{16}$ (monoclinic crystal system, $C2/m$, $Z = 2$, lattice parameters $a = 12.1948(3)$ Å, $b = 8.2486(2)$ Å, $c = 7.0894(2)$Å, $\beta = 119.893(3)^\circ$ was prepared by solid-state synthesis. The first up-conversion luminescence studies have been carried out for $Na_2BaY_4F_{16} : Yb^{3+}$, Er^{3+} under excitation at 980 nm. The highest luminescence energy yield for $Na_2Ba(Y_{0.87}Yb_{0.12}Er_{0.01})_4F_{16}$ was 5.5% at a pump power density of 1 W/cm^2.

Keywords: up-conversion phosphors, fluorides of rare-earth elements, barium fluoride, sodium fluoride.

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Introduction

Up-conversion luminescence is the process of conversion of low-energy radiation into high-energy radiation by mechanisms of incremental energy summation through metastable energy levels [1]. Rare-earth ions exhibit high up-conversion efficiency over a wide spectral range, especially when pumped in the near-infrared into the absorption band of Yb^{3+}($^7F_{7/2} \rightarrow {}^5F_{5/2}$) ions [2,3]. Up-conversion phosphors are applied as optical thermometers [4–6], gas sensors [7,8], for bioimaging in soft tissues [9,10], and for protective labeling [11,12].

Host is one of the main factors affecting the efficiency of up-conversion. The spectrum and efficiency of radiation conversion will change depending on the selected host, which can be quantified by the energy yield of luminescence [13]. Alkali and alkaline-earth metal fluorides having low phonon energies are one of the most efficient host. The characteristic frequencies of phonon vibrations for metal fluorides, widely used as host for phosphors, are: β-$NaYF_4$ — 360 cm^{-1} [14], CaF_2 — 322 cm^{-1} [15], SrF_2 — 285 cm^{-1} [15,16], BaF_2 — 241 cm^{-1} [17]. The energy yield of up-conversion luminescence increases with the decrease of frequency of phonon vibrations of the lattice.

The decrease of the symmetry of the crystal structure increases the efficiency of up-conversion [18]. Hexagonal $NaYF_4$ is a well-studied host with high efficiency of conversion of excitation infrared radiation into the visible range. At a dopant ratio of 21.4% Yb and 2.2% Er, the quantum yield of up-conversion luminescence reaches 10.5% under excitation at a wavelength of 980 nm with a pump power density of 30 W/cm^2 [19]. The quantum yield on SrF_2:Yb^{3+}, Er^{3+} single crystals was 6.5% under excitation at 976 nm (230 W/cm^2) [20]. The maximum quantum yield was observed in BaF_2 single crystals doped with 2% Er^{3+} and 3% Yb^{3+} under excitation by radiation with a wavelength of 976 nm (at 490 W/cm^2) and amounted to 10.0% [17].

BaF_2 (CaF_2, SrF_2) crystals with fluorite structure, are unfavorable matrices for efficient up-conversion process due to high symmetry [21], but introduction of Yb ions^{3+} and Er^{3+} leads to the formation of crystal structures with trigonal or tetragonal symmetry, which increases the probability of radiative transitions [22]. The reverse process is also possible, since multiple defects quench luminescence due to radiation-free relaxation.

Crystalline matrices containing heavy metal ions combined with rare earth elements are good candidates for high luminescence. Matrices based on barium and yttrium fluorides doped with rare-earth ions are promising candidates for creating high-efficiency up-converters [23,24]. Up-conversion is a nonlinear optical process, the efficiency of which depends on many factors such as the matrix material, the point symmetry group of the luminescence center, the type and concentration of doping impurities, and the presence of luminescence quenching impurities on the surface. These factors make it difficult to predict the behavior of a system with multiple activator ions. Therefore, the acquisition of experimental data is the main method for selecting matrices and dopant ion concentrations [25].

Preliminary studies have revealed a very complex pattern of phase formation in the system of $NaF-BaF_2-YF_3$ [26,27], which differs from that known in the literature for the system of $NaF-BaF_2-GdF_3$ [28]. The primary studied phase was obtained by synthesis by spontaneous crystallization in sodium nitrate melt [27,29,30]. A mixture of barium, yttrium, sodium nitrate salts and sodium fluoride was placed in a porcelain crucible, incubated for

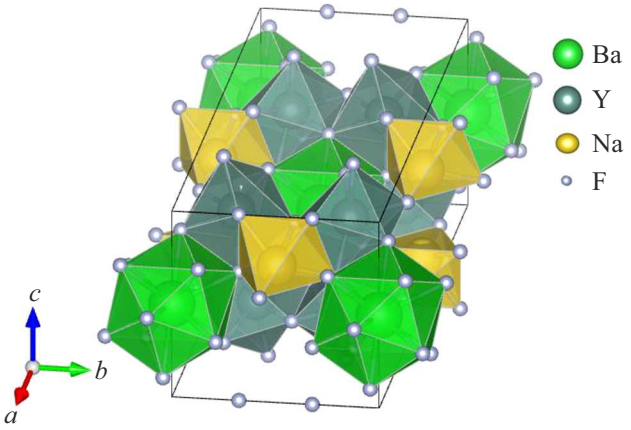

Figure 1. Projection of the lattice cell of $Na_2BaY_4F_{16}$.

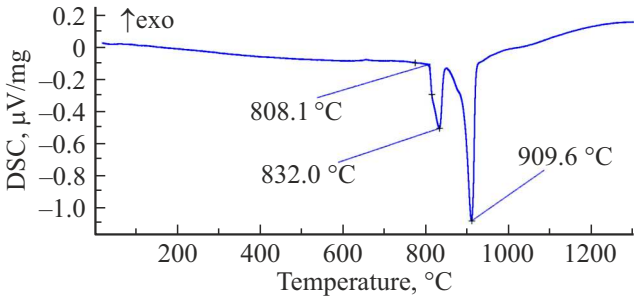

Figure 2. Thermogram of sample $Na_2BaY_4F_{16}$.

1 h at 500°C. The resulting speck was washed with distilled water.

The aim of this study was to synthesize an up-conversion phosphor based on one of the phases formed in the ternary system of $NaF-BaF_2-YF_3$.

Experiment procedure

Crystals in the system of $NaF-BaF_2-YF_3$ were obtained by solid-phase synthesis method. The mixtures of pure fluoride powders were annealed at 760°C in nickel capillaries sealed in copper containers, holding time was 295 h. In order to create up-conversion phosphors, additionally, syntheses with doping with erbium and ytterbium fluorides were carried out according to calculations using the chemical formula $Na_2Ba(Y{:}Yb,Er)_4F_{16}$. The nominal compositions were calculated on the assumption of yttrium ion substitution. The annealing was carried out at 780°C, and the holding time was 180 h. Barium hydrofluoride was used as the fluorinating atmosphere in all syntheses. Hardening was performed in liquid nitrogen.

X-ray phase analysis was performed using Bruker D8 Advance diffractometer (radiation CuK_α) with processing of experimental data in TOPAS software.

A transparent single crystal of suitable quality (size $(85 \times 36 \times 39\,\mu m)$) was selected using an optical polarizing microscope and glued onto a glass filament using epoxy glue. The single-crystal X-ray diffraction experiment was performed using Rigaku XtaLAB Synergy-S diffractometer (MoK_α). The crystal structure was solved by the charge sign reversal method [31] and processed in the JANA2020 software package [32].

Differential thermal analysis was performed using Netzsch STA 449 F3 Jupiter in a Pt-Rh crucible with lid in an argon atmosphere at a heating rate of 20°C/min to 1300°C.

Spectroscopic studies included recording spectra of up-conversion luminescence and diffusion-scattered excitation laser radiation in the range of 300–1000 nm, and calculating the energy yield (EQ) of up-conversion luminescence. Measurements of the up-conversion luminescence spectra in the visible range were performed using the method described in Ref. [33]. A setup consisting of a fiber optic spectrometer LESA-01-BIOSPEC (BIOSPEC, Russia) and a modified integrating sphere (Avantes, Netherlands) connected by fiber optic light guides was used for measurements.

The initial samples were grinded in an agate mortar before measurement. A powder containing no activator ions was used as a reference non-absorbing sample. The sample (powder sandwiched between two cover glasses) was placed inside the integrating sphere for measurements. Excitation radiation from a semiconductor laser with a wavelength of 974 nm was focused onto the sample so that the power density at the sample surface was 1 W/cm^2. The integrating sphere was pre-calibrated using LEDs with different wavelengths and known power measured with a LabMax®-TO meter (Coherent, USA). Scattered laser radiation and up-conversion luminescence were collected by fiber optic light guides and transmitted to the spectrometer. The luminescence efficiency was calculated using the following formula:

$$EQ = \frac{P_e^S}{P_{974\_ab}^S} = \frac{P_e^S}{P_{974\_sc}^R - P_{974\_sc}^S},$$

where P_e^S is the emission power of the sample in the visible range, $P_{974\_ab}^S$ is the laser power absorbed by the sample. The latter is equal to the difference between $P_{974\_sc}^R$ — the scattered radiation power from the non-absorbing comparison sample — and $P_{974\_sc}^S$ — the scattered radiation power from the studied sample.

Results and discussions

When the synthesis was carried out at 760°C and with 295 h exposure time, the powders in the system of $NaF-BaF_2-YF_3$ with nominal molar composition of 25–20–55 mol.% were found to be melted. A single crystal of suitable micron-sized quality was selected from the resulting polycrystalline melt. X-ray diffraction analysis allowed determining the phase composition as $Na_2BaY_4F_{16}$. The crystal lattice corresponds to monoclinic

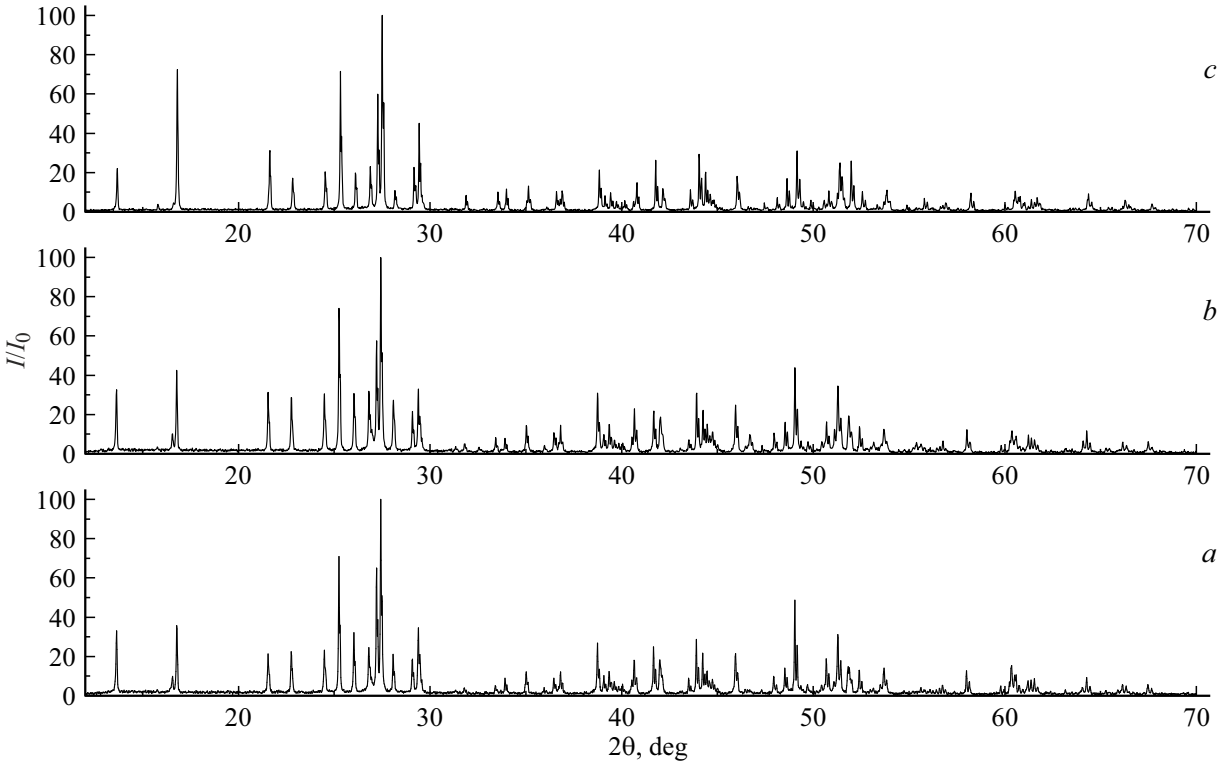

Figure 3. Difractograms of samples: (*a*) $Na_2BaY_4F_{16}$, (*b*) $Na_2Ba(Y_{0.97}Yb_{0.02}Er_{0.01})_4F_{16}$, (*c*) $Na_2Ba(Y_{0.80}Yb_{0.18}Er_{0.02})_4F_{16}$.

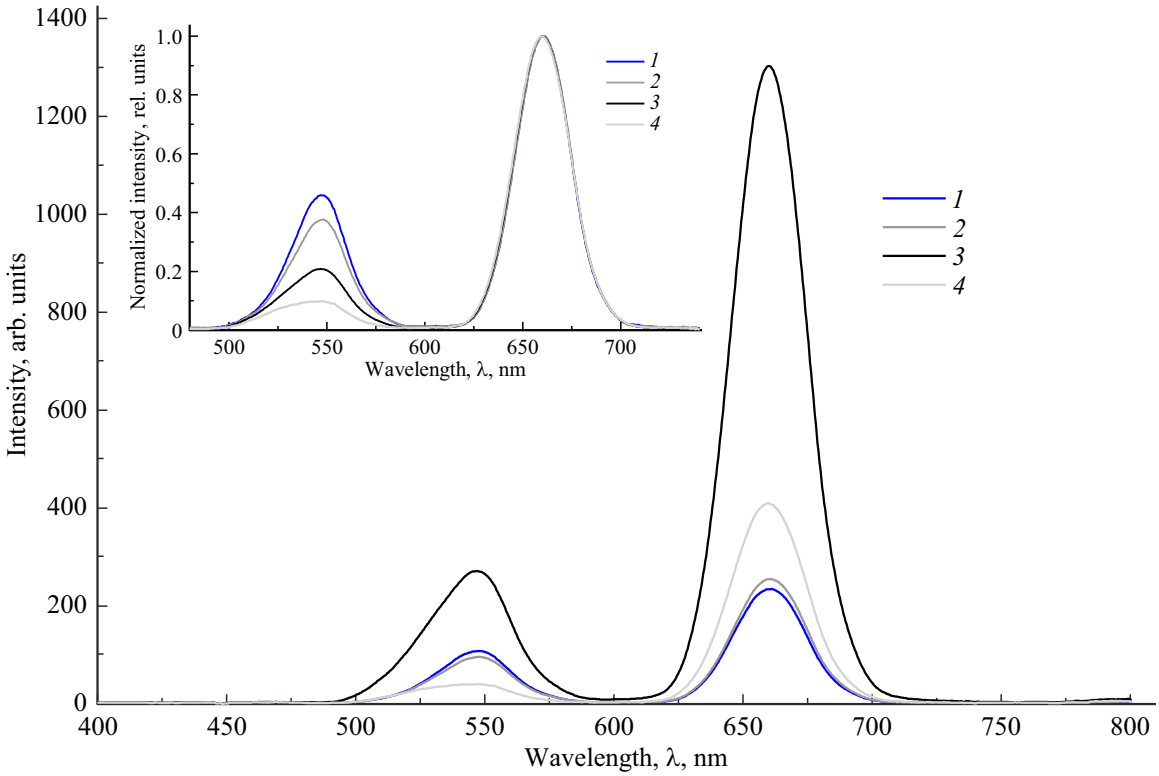

Figure 4. Up-conversion luminescence spectra under excitation at 974 nm with a pump power density of 1 W/cm^2: *1* — $Na_2Ba(Y_{0.97}Yb_{0.02}Er_{0.01})_4F_{16}$, *2* — $Na_2Ba(Y_{0.96}Yb_{0.02}Er_{0.02})_4F_{16}$, *3* — $Na_2Ba(Y_{0.87}Yb_{0.12}Er_{0.01})_4F_{16}$, *4* — $Na_2Ba(Y_{0.80}Yb_{0.18}Er_{0.02})_4F_{16}$. On the inset: spectra normalized to the maximum intensity of the red luminescence band.

Energy yield (EQ) of up-conversion luminescence for $Na_2Ba(Y_{1-x-y}Yb_xEr_y)_4F_{16}$ compounds with different molar ratio of rare earth ions

Sample composition	Ratio Er^{3+}:Yb^{3+} (mol. %)	EQ,%
$Na_2Ba(Y_{0.97}Yb_{0.02}Er_{0.01})_4F_{16}$	1 : 2	2.5
$Na_2Ba(Y_{0.96}Yb_{0.02}Er_{0.02})_4F_{16}$	2 : 2	2.6
$Na_2Ba(Y_{0.87}Yb_{0.12}Er_{0.01})_4F_{16}$	1 : 12	5.5
$Na_2Ba(Y_{0.80}Yb_{0.18}Er_{0.02})_4F_{16}$	2 : 18	3.2

crystal system, space group $C2/m$, $Z = 2$, lattice parameters $a = 12.1948(3)$ Å, $b = 8.2486(2)$ Å, $c = 7.0894(2)$ Å, $\beta = 119.893(3)°$, $V = 618.25(3)$ (Å^3), $R_{obs} = 0.013$. The coordination numbers for yttrium is 8 and 12 for barium (Fig. 1).

According to differential thermal analysis, the compound melts with decomposition at 808°C (Fig. 2).

Solid-phase syntheses were carried out after establishing the chemical formula of the new phase. The suspensions of pure fluorides were taken in molar ratio of components according to the chemical formula $Na_2BaY_4F_{16}$. The powder mixtures were annealed according to the methodology presented above. The synthesized substance $Na_2BaY_4F_{16}$ conformed to the determined structure and was single phase (Fig. 3, *a*). We also carried out syntheses with doping by a pair of Er^{3+}, Yb^{3+} by solid phase sintering with calculation by yttrium ion substitution of matrix $Na_2BaY_4F_{16}$. Single-phase samples with composition of $Na_2Ba(Y_{0.97}Yb_{0.02}Er_{0.01})_4F_{16}$, $Na_2Ba(Y_{0.96}Yb_{0.02}Er_{0.02})_4F_{16}$, $Na_2Ba(Y_{0.87}Yb_{0.12}Er_{0.01})_4F_{16}$, $Na_2Ba(Y_{0.80}Yb_{0.18}Er_{0.02})_4F_{16}$, which have a crystal structure with monoclinic crystal system to that of the matrix (Fig. 3, *b, c*).

Analysis of the up-conversion luminescence spectrum of samples with composition of $Na_2Ba(Y_{0.97}Yb_{0.02}Er_{0.01})_4F_{16}$, $Na_2Ba(Y_{0.96}Yb_{0.02}Er_{0.02})_4F_{16}$, $Na_2Ba(Y_{0.87}Yb_{0.12}Er_{0.01})_4F_{16}$, $Na_2Ba(Y_{0.80}Yb_{0.18}Er_{0.02})_4F_{16}$ revealed luminescence bands characteristic of Er^{3+} ion in the green and red parts of the spectrum (Fig. 4), which correspond to the energy transitions $^2H_{11/2}$, $^4S_{3/2} \rightarrow {}^4I_{15/2}$ (maximum at wavelength 548 nm with a short-wavelength shoulder around 520 nm) and $^4F_{9/2} \rightarrow {}^4I_{15/2}$(maximum at wavelength 660 nm).

The analysis of the spectral composition with respect to the ratio of the intensities of the up-conversion luminescence bands in the red and green parts of the spectrum (inset in Fig. 4) showed that the relative intensity of the green luminescence band decreases with the increase of the ytterbium concentration at a fixed erbium concentration compared to the red band and an the ratio of the intensity of the red luminescence band to the green increases [34,35]. The ratio of red luminescence to green luminescence is of the order of 2 for sample of $Na_2Ba(Y_{0.97}Yb_{0.02}Er_{0.01})_4F_{16}$ and it is close to 4 for $Na_2Ba(Y_{0.87}Yb_{0.12}Er_{0.01})_4F_{16}$.

The energy yield of up-conversion luminescence for this series of samples belonging to the solid solution of $Na_2Ba(Y_{1-x-y}Yb_xEr_y)_4F_{16}$, under excitation at a wavelength of 974 nm and a pump power density of 1 W/cm^2 is presented in the table. The maximum energy yield of up-conversion luminescence was obtained for the sample of $Na_2Ba(Y_{0.87}Yb_{0.12}Er_{0.01})_4F_{16}$ and was 5.5%. It should be taken into account that this energy yield may not be the maximum, because the optimal ratio of doping components has not been found yet.

Conclusions

A new crystalline phase of $Na_2BaY_4F_{16}$ of monoclinic syngony, spatial group $C2/m$ was obtained by phase synthesis of samples in the system of $NaF-BaF_2-YF_3$. It was found using the differential thermal analysis data that $Na_2BaY_4F_{16}$ compound melts with decomposition at 808°C. When this matrix is doped with Er^{3+} and Yb^{3+} ions, the luminescence spectra exhibit luminescence bands characteristic of the erbium ion under excitation at 974 nm. The maximum energy yield of up-conversion luminescence was obtained for the sample $Na_2Ba(Y_{0.87}Yb_{0.12}Er_{0.01})_4F_{16}$ and was 5.5% with a pump power density of 1 W/cm^2.

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Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] F. Auzel. Chem. Rev., **104** (1), 139 (2004). DOI:10.1021/cr020357g
[2] Y. Wei, S. Yang, C. Zhang, G. Chen, A.H. Li. Ceramics Int., **49**(19), 31618 (2023). DOI: 10.1016/j.ceramint.2023.07.115
[3] D. Pominova, V. Proydakova, I. Romanishkin, S. Kuznetsov, K. Linkov, N. Tabachkova, A. Ryabova. Photonics, **11** (1), 38 (2023). DOI: 10.3390/photonics11010038
[4] J.A. Sanz-García, G. Lifante-Pedrola, J.E.M. Santiuste, E. Cantelar. J. All. Comp., **1010**, 177529 (2025). DOI: 10.1016/j.jallcom.2024.177529
[5] S. Bedamati, M. Behera, R.A. Kumar, K. Shwetabh, K. Kumar. J. Mol. Liq., **411**, 125685 (2024). DOI: 10.1016/j.molliq.2024.125685
[6] M. Runowski, A. Bartkowiak, M. Majewska, I.R. Martın, S. Lis. J.Luminesc., **201**, 104 (2018). DOI: 10.1016/j.jlumin.2018.04.040
[7] H. Wu, X. Zhang, Y. Zhao, X. Leng, H. Xinyue, B. Li. Opt. Mater., **128**, 112441 (2022). DOI: 10.1016/j.optmat.2022.112441

[8] B. Zheng, J. Fan, B. Chen, X. Qin, J. Wang, F. Wang, R. Deng, X. Liu. Chem. Rev., **122**(6), 5519 (2022). DOI: 10.1021/acs.chemrev.1c00644
[9] S.L. Lin, Z.R. Chen, C.A. Chang. Nanotheranostics, **2**(3), 243(2018). DOI: 10.7150/ntno.25901
[10] G.M. Han, H. Li, X.X. Huang, D.M. Kong. Talanta, **147**, 207(2016). DOI: 10.1016/j.talanta.2015.09.059
[11] S. Wang, J. Zhu, Y. He, Z. Li, J. Lin, S. Liao, F. Huang, P. Huang, Y. Zheng, X. Li, D. Chen. Las. Photon. Rev., **16**(8), 2200039 (2022). DOI: 10.1002/lpor.202200039
[12] C. Zhang, Q.S. YinGe, J. Qi, Q. Han, W. Gao, Y. Wang, M. Zhand, J. Dong. Mater. Res. Bull., **112801** (2024). DOI: 10.1016/j.materresbull.2024.112801
[13] S. Fischer, B. Fröhlich, K.W. Krä mer, J.C. Goldschmidt. J. Phys. Chem. C, **118**(51), 30106 (2014). DOI: 10.1021/jp510209x
[14] J.F. Suyver, J. Grimm, M.K. Van Veen, D. Biner, K.W. Krämer, H.U. Güdel. J. Luminesc., **117**(1), 1 (2006). DOI: 10.1016/j.jlumin.2005.03.011
[15] D.G. Mead, G.R. Wilkinson. J. Phys. C, **10**(7), 1063 (1977). DOI: 10.1088/0022-3719/10/7/016
[16] H.R. Soni, S.K. Gupta, M. Talati, P.K. Jha. J. Phys. Chem. Sol., **72**(8), 934 (2011). DOI: 10.1016/j.jpcs.2011.04.018
[17] E.I. Madirov, V.A. Konyushkin, A.N. Nakladov, P.P. Fedorov, T. Bergfeldt, D. Busko, I.A. Howard, B.S. Richards, S.V. Kuznetsov, A. Turshatov. J.Mater. Chem. C, **9**(10), 3493 (2021). DOI: 10.1039/d1tc00104c
[18] A. Aebischer, M. Hostettler, J. Hauser, K. Krämer, T. Weber, H.U. Güdel, H.B. Bürgi. Angewandte Chem. Int. Ed., **45**(17), 2802 (2006). DOI: 10.1002/anie.200503966
[19] M. Kaiser, C. Würth, M. Kraft, I. Hyppänen, T. Soukka, U. Resch-Genger. Nanoscale, **9**(28), 10051 (2017). DOI: 10.1039/C7NR02449E
[20] D. Saleta Reig, B. Grauel, V.A. Konyushkin, A.N. Nakladov, P.P. Fedorov, D. Busko, I.A. Howard, B.S. Richards, U. Resch-Genger, S.V. Kuznetsov, A. Turshatov, C. Würth. J. Mater. Chem. C, **8**(12), 4093 (2020). DOI: 10.1039/C9TC06591A
[21] S. Balabhadra, M.F. Reid, V. Golovko, J.-P. R. Wells. J. All. Comp., **834**, 155165 (2020). DOI:10.1016/j.jallcom.2020.155165
[22] R. Reisfeld, C. K. Jørgensen. In: *Lasers and Excited States of Rare Earths*, ed.by R. Reisfeld, C. K. Jørgensen (Springer, Berlin, Heidelberg, 1977). DOI: 10.1007/978-3-642-66696-4_1
[23] A.C.S. de Mello, A.B. Andrade, G.H.G. Nakamura, S.L. Baldochi, M.E.G. Valerio. J. Luminesc., **138**, 19(2013). DOI: 10.1016/j.jlumin.2012.12.001
[24] N. Jurga, D. Przybylska, D. Żychlińska, T. Grzyb. J. All. Comp., 178146 (2024). DOI: 10.1016/j.jallcom.2024.178146
[25] E.M. Chan. Chem. Soc. Rev., 44(6), 1653(2015). DOI:10.1039/c4cs00205a
[26] P.P. Fedorov, A.A. Volchek, V.V. Voronov, A.A. Alexandrov, S.V. Kuznetsov. Cond. Matt. Interphas., 26(2), 314 (2024). DOI:10.17308/kcmf.2024.26/11942
[27] A.A. Volchek, S.N. Volkov, V.V. Voronov, A.A. Alexandrov, P.P. Fedorov. V sb. XIII Vserossijskaya konferentsiya s mezhdunarodnym uchastiem „Khimiya tverdogo tela i funkcional'nye materialy 2024". Saint-Petersburg, September 16-20, 2024. Theses of reports. P. 126 (in Russian).
[28] L.N. Pavlova, P.P. Fedorov, L.A. Ol'khovaya, D.D. Ikrami, B.P. Sobolev. Cristallogr. Rep., **38**(2), 221 (1993).
[29] P. Fedorov, M. Mayakova, A. Alexandrov, V. Voronov, S. Kuznetsov, A. Baranchikov, V. Ivanov. Inorganics, **6**(2), 38 (2018). DOI:10.3390/inorganics6020038
[30] P.P. Fedorov, A.A. Alexandrov. J. Fluorine Chem., **227**, 109374 (2019). DOI:10.1016/j.jfluchem.2019.109374
[31] L. Palatinus, G. Chapuis. J. Appl. Crystall., **40** (4), 786-(2007). DOI:10.1107/S0021889807029238
[32] V. Petříček, L. Palatinus, J. Plášil, M. Dušek. Z. Kristallogr.-Crystall. Mater., **238**(7−8), 271(2023). DOI: 10.1515/zkri-2023-0005
[33] D.S. Yasyrkina, S.V. Kuznetsov, A.V. Ryabova, D.V. Pominova, V.V. Voronov, R.P. Ermakov, P.P. Fedorov. Nanosystems: physics, chemistry, mathematics, **4**(5), 648 (2013).
[34] J. Liu, H. Deng, Z. Huang, Y. Zhang, D. Chen, Y. Shao. Phys. Chem. Chem. Phys., **17**(23), 15412 (2015). DOI: 10.1039/C5CP01632K
[35] A. Punjabi, X. Wu, A. Tokatli-Apollon, M. El-Rifai, H. Lee, Y. Zhang, C. Wang, Z. Liu, E.M. Chan, C. Duan. ACS nano, **8**(10), 10621 (2014). DOI: 10.1021/nn505051d

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