**Stabilization $Eu^{2+}$ in $Li_2B_4O_7$ with $BO_3$ Network through $U^{6+}$ Co-doping and Defect Engineering**

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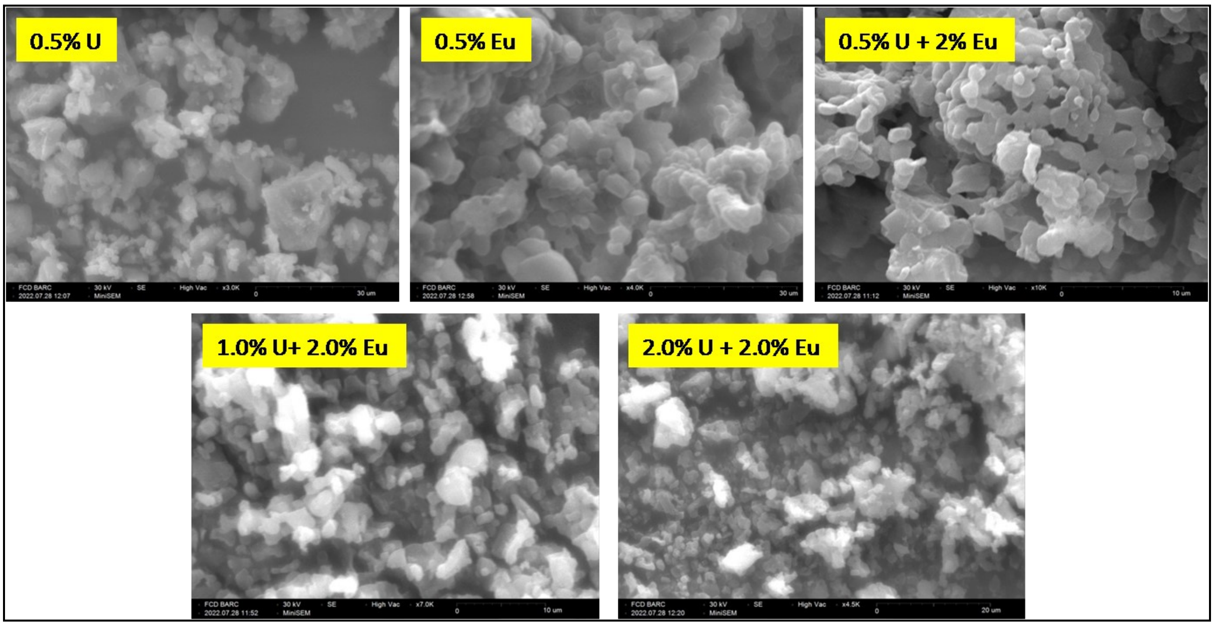


**Figure S1:** SEM images of doped (0.5% $Eu^{3+}$ and 0.5% $U^{6+}$) and co-doped (2.0% $Eu^{3+}$ and 0.5 to 2.0% $U^{6+}$) samples of LTB.

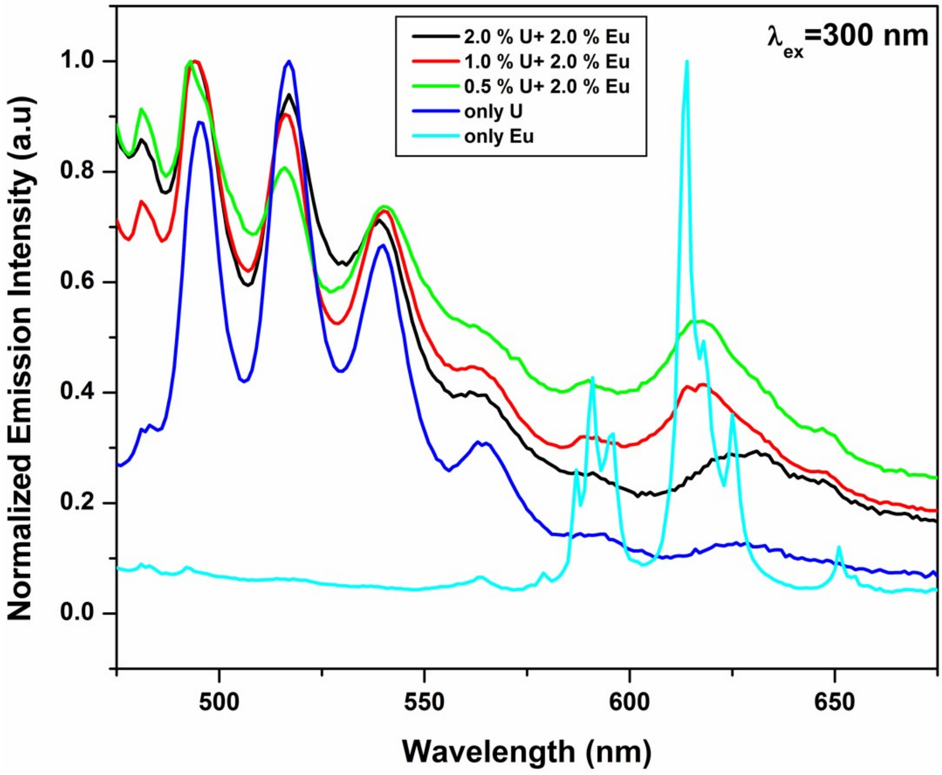


**Figure S2:** Photoluminescence emission spectra of doped (0.5% $Eu^{3+}$ and 0.5% $U^{6+}$) and co-doped (2.0% $Eu^{3+}$ and 0.5 to 2.0% $U^{6+}$) LTB samples.

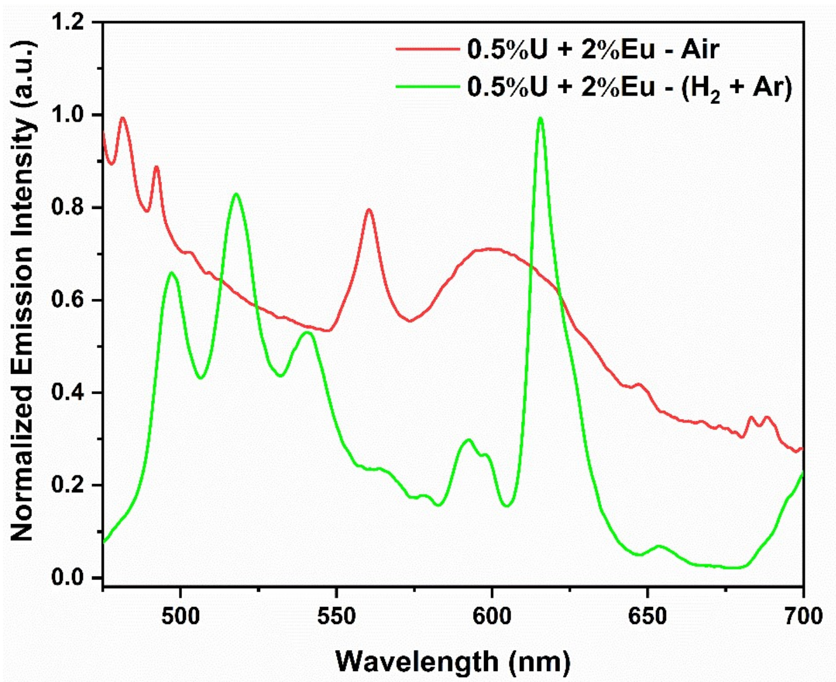


**Figure S3:** Photoluminescence emission spectra of 2% $Eu^{3+}$ and 0.5% $U^{6+}$ co-doped LTB samples annealed in air and a reducing atmosphere (92% Ar + 8% $H_2$).

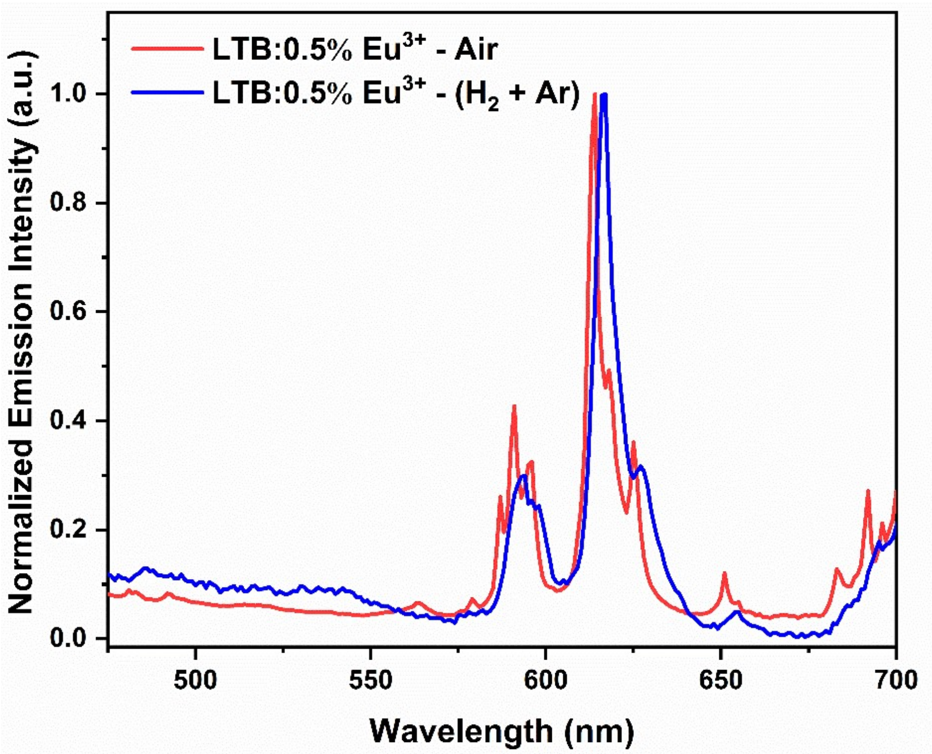


**Figure S4:** Photoluminescence emission spectra of LTB:0.5% $Eu^{3+}$ annealed in air and a reducing atmosphere (92% Ar + 8% $H_2$).

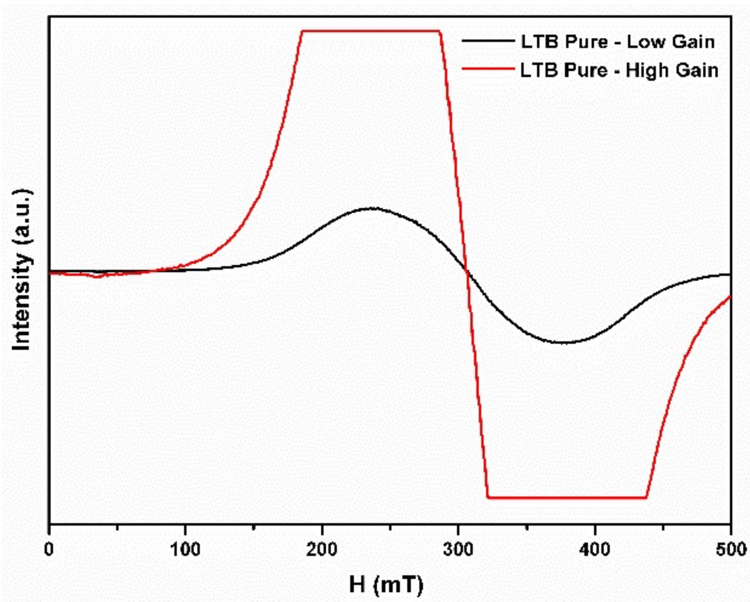


**Figure S5:** ESR spectra of LTB pure sample at 100 K recorded at low gain and high gain.

The resonance signal in the pure LTB sample gets saturated at a higher gain of $4\times10^4$. Therefore, the ESR spectra for pure LTB was obtained at a lower gain value of $2\times10^3$.

**Table S1: Recent Borate based luminescent materials having divelent europium ion (2020-22)**

| System | Flux | Temperature | Remarks | Ref. |
|---|---|---|---|---|
| $Eu^{2+}$ single-doped$K_2SrCa(PO_4)_{2x}(BO_3)_x$ white phosphors | 97%$N_2$/3%$H_2$ | 1400 °C for 4 h | Very high temperature is needed | **[1]** |
| $LiSrB_9O_{15}$:$Eu^{3+}$/$Eu^{2+}$ | Self-reduction | 800°C | Self reduction is triggered by $BO_4$ network | **[2]** |
| $SrAl_2O_4$:$Eu^{2+}$,$Dy^{3+}$ borate glass | under carbon reduction atmosphere | 1500 °C for 1 h | Very high temperature is needed | **[3]** |
| $Eu^{2+}$: $NaBa_4(BO_3)_3$ co-doped with different cations $Dy^{3+}$, $Ho^{3+}$and $Nd^{3+}$ | 95%$N_2$ +5%$H_2$ | 900 °C for 8 h | - | **[4]** |
| $Eu^{2+}$-doped$Ba_3Lu(BO_3)_3$phosphor | 10% $H_2$ + 90% $N_2$ | 1250 °C for 6 h | Very high temperature as well as higher hydrogen flux | **[5]** |
| $Eu^{2+}$, $Dy^{3+}$: $NaSr_4(BO_3)_3$ | under a reductive atmosphere | 880 °C for 8 h | - | **[6]** |
| $KSr_4B_3O_9$: $Eu^{2+}$ | $N_2$/$H_2$ | 900 °C for 10 h | High temperature is needed | **[7]** |
| $LiSr_4(BO_3)_3$:$Eu^{2+}$, $Dy^{3+}$ | 5% $H_2$ and 95% $N_2$ | 950 °C for 8 h | High temperature is needed | **[8]** |
| $NaBaB_9O_{15}$:$Eu^{2+}$ | under the reducing atmosphere | 725 °C for 30 h | High thermal duration of more than a day is required | **[9]** |
| $Sr_{3-x-y}B_2O_6$:x$Eu^{2+}$,y$RE^{3+}$ (RE = Nd, Gd, Dy) | 5%$H_2$-95%$N_2$ | 1280–1310 °C for 5–20 h | High temperature and time is needed | **[10]** |
| $Sr_6(BO_3)_3BN_2$:$Eu^{2+}$ | Covered corundum crucible | 1300 °C, for 12 h | High temperature is needed | **[11]** |
| $Eu^{2+}$/$Eu^{3+}$ doped strontium borates: $SrB_4O_7$, $SrB_2O_4$ and $Sr_3(BO_3)_2$ | Covering the crucibles with a lid | Pre-calcined at 700 °C for 5 h and further heat-treated at 850 °C for 5 h | - | **[12]** |
| $Ba_3ScB_3O_9$:$Eu^{2+}$ phosphor | $H_2$ (20%) and $N_2$ (80%) | 1150 °C for 6 h | Very high hydrogen flux | **[13]** |
| $Ca[B_8O_{11}(OH)_4]$: Eu | | 350 °C for 12 h | Hydroxyl ion may affect the PL | **[14]** |
| $Sr[B_8O_{11}(OH)_4]$:$Eu^{2+}$ | No reducing atm. used | 350 °C for 12 h | Self reduction | **[15]** |
| $Eu^{2+}$ in $SrB_4O_7$ | Covered | 850 °C for | - | **[16]** |

| | | | | |
|---|---|---|---|---|
| | crucibles | another 5 h | | |
| $Ce^{3+}$-$Eu^{2+}$ in $LiSr_4(BO_3)_3$ phosphors | 5% $H_2$/95% $N_2$ | 1000 °C for 3 h | High temperature is needed | **[17]** |
| LTB:Eu2+ | 8% H2+92% Ar | 750 oC | Low flux<br>Lower temperature<br>$U^{6+}$ assisted Co-doping ass | **This work** |

**Table S2:**The calculated g values for pure LTB, doped (0.5% $Eu^{3+}$ and 0.5% $U^{6+}$) and co-doped (2.0% $Eu^{3+}$ and 0.5 to 2.0% $U^{6+}$) LTB samples at both room temperature (rt) and 100 K.

| | Frequency (GHz) | $H_1$ (mT) | $g_1$ | $H_2$ (mT) | $g_2$ |
|---|---|---|---|---|---|
| **LTB pure - RT** | 9.437 | 304.42 | 2.2158 | - | - |
| **LTB-0.5%Eu- RT** | 9.437 | 326.67 | 2.0649 | - | - |
| **LTB-0.5%U- RT** | 9.437 | 304.43 | 2.2157 | - | - |
| **LTB-0.5%U-2%Eu- RT** | 9.437 | 344.83 | 1.9561 | 156.36 | 4.3140 |
| **LTB-1%U-2%Eu- RT** | 9.437 | 334.15 | 2.0187 | 156.4 | 4.3129 |
| **LTB-2%U-2%Eu- RT** | 9.437 | 342.57 | 1.9690 | 160.62 | 4.1996 |
| **LTB pure - 100 K** | 9.435 | 306.94 | 2.1972 | - | - |
| **LTB-0.5%Eu- 100 K** | 9.435 | 311.64 | 2.1640 | - | - |
| **LTB-0.5%U- 100 K** | 9.435 | 308.89 | 2.1833 | - | - |
| **LTB-0.5%U-2%Eu-100 K** | 9.435 | 303.82 | 2.2197 | 148.48 | 4.5420 |
| **LTB-1%U-2%Eu-100 K** | 9.435 | 306.18 | 2.2026 | 148.58 | 4.5389 |
| **LTB-2%U-2%Eu-100 K** | 9.435 | 308.46 | 2.1863 | 156.47 | 4.3101 |

The 'g' value of free-electron is ~2.0023, but the shift in the 'g' value occurs depending on the environment and the spin-orbit coupling. The 'g' value or the resonance position is specific for a given radical present in a particular environment. The energy required for the spin transition is related to the applied magnetic field (B), g-factor, and the constant $\beta_e$, called the Bohr Magneton:

$h\nu = g\beta_e B$…..(1)

Where '*v'* is the frequency of microwave radiation and '*h'* is the Planck's constant. The 'g' values are calculated using the above equation 1.

The ESR spectra were recorded in X-band of the microwave region with a frequency of ~9.43 GHz for both at room temperature and 100 K. The attenuation was kept as 15 dB.

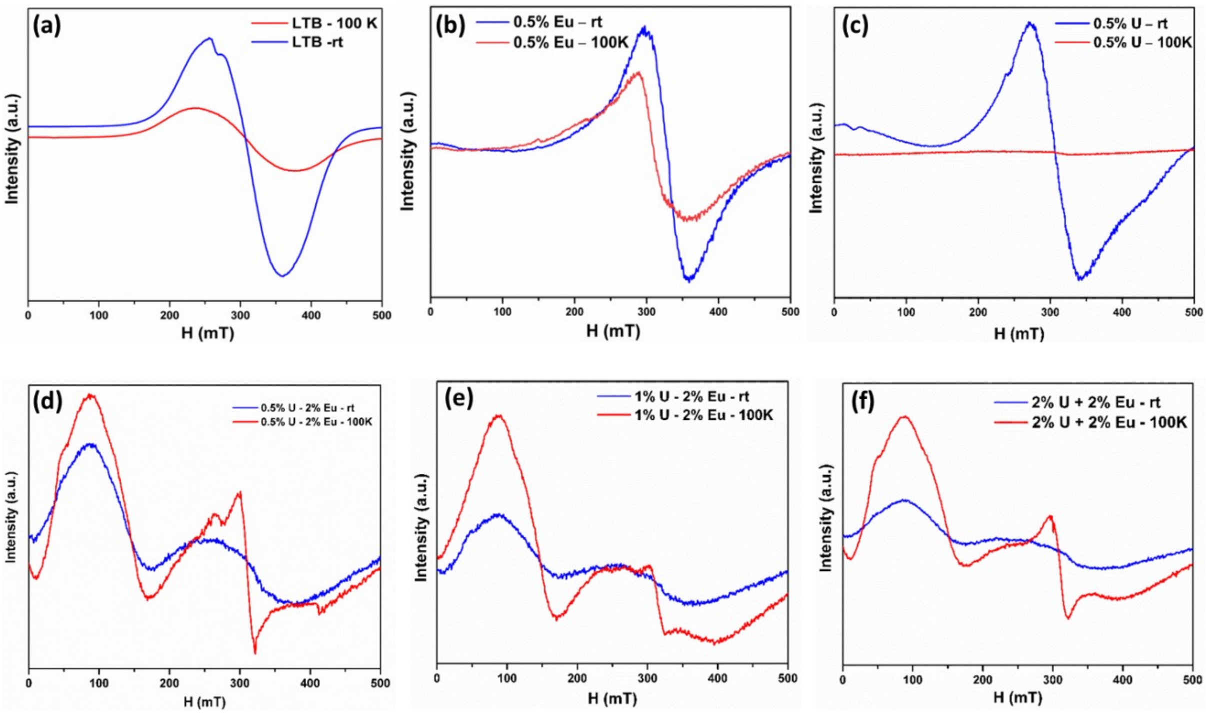


**Figure S6:**ESR spectra of (a) LTB (b) 0.5% $Eu^{3+}$ doped LTB (c) 0.5% $U^{6+}$ doped LTB (d) 2% $Eu^{3+}$ and 0.5% $U^{6+}$ doped LTB (e) 2% $Eu^{3+}$ and 1% $U^{6+}$ doped LTB and (f) 2% $Eu^{3+}$ and 2% $U^{6+}$ doped LTB, at room temperature and 100 K.

[1] J. Zhao, X. Wu, Y. Zhang, K. Li, J. Yu, H. Wang, B. Li, Design of $K_2SrCa(PO4)_{2-x}(BO_3)_x$:$Eu^{2+}$ phosphors with full-visible spectrum by crystal structure modification, Journal of Luminescence 251 (2022) 119273.
[2] P. Fan, Z. He, Y. Chen, X. He, C. Huang, Q. Miao, Q. Zhang, X. Liu, L. Li, Co-existence and unique co-emission properties of $Eu^{3+}/Eu^{2+}$ and $Sm^{3+}/Sm^{2+}$ in $LiSrB_9O_{15}$ host lattice, Journal of Luminescence 251 (2022) 119169.
[3] S. Gültekin, S. Yıldırım, O. Yılmaz, İ.Ç. Keskin, M.İ. Katı, E. Çelik, Structural and optical properties of $SrAl_2O_4$: $Eu^{2+}/Dy^{3+}$ phosphors synthesized by flame spray pyrolysis technique, Journal of Luminescence 206 (2019) 59-69.
[4] R. Li, H. Li, C. Chang, Z. Sun, Enhanced afterglow behavior of a new $Eu^{2+}$: $NaBa_4(BO_3)_3$ yellow phosphor co-doped with different cations $Dy^{3+}$, $Ho^{3+}$ and $Nd^{3+}$, Ceramics international 48 (2022) 8914-8920.
[5] Z. Tang, F. Du, H. Liu, Z. Leng, X. Sun, H. Xie, M. Que, Y. Wang, $Eu^{2+}$-Doped Layered Double Borate Phosphor with Ultrawide Near-Infrared Spectral Distribution in Response to Ultraviolet–Blue Light Excitation, Advanced Optical Materials 10 (2022) 2102204.
[6] R. Li, H. Li, C. Chang, Photoluminescence and afterglow behavior of a new orange long-lasting borate phosphor $Eu^{2+}$, $Dy^{3+}$: $NaSr_4(BO_3)_3$, Journal of Luminescence 243 (2022) 118659.
[7] Q. Lv, X. Ma, Y. Dong, Y. Li, B. Shao, C. Wang, S. Yang, C. Wang, Ratiometric optical thermometer with high-sensitive temperature sensing based on tunable luminescence of $Ce^{3+}$-$Eu^{2+}$ in $KSr4B_3O_9$ phosphors, Advanced Powder Technology 33 (2022) 103769.
[8] R. Li, H. Cao, H. Li, D. Zhang, C. Chang, Polychromatic luminescence of $LiSr_4(BO_3)_3$:$Eu^{2+}$, $Dy^{3+}$ persistent phosphors, Ceramics international 48 (2022) 20546-20554.
[9] Y. Zhuo, S. Hariyani, J. Zhong, J. Brgoch, Creating a Green-Emitting Phosphor through Selective Rare-Earth Site Preference in $NaBaB_9O_{15}$:$Eu^{2+}$, Chemistry of Materials 33 (2021) 3304-3311.
[10] K.-W. Chae, T.-R. Park, C. Cheon, II, J.S. Kim, Persistent luminescence of $RE^{3+}$ co-doped $Sr_3B_2O_6$:$Eu^{2+}$ yellow phosphors (RE = Nd, Gd, Dy), Journal of Luminescence 194 (2018) 649-655.
[11] S.G. Jantz, R. Erdmann, S. Hariyani, J. Brgoch, H.A. Höppe, $Sr_6(BO_3)_3BN_2$: An Oxido–Nitrido–Borate Phosphor Featuring $BN_2$ Dumbbells, Chemistry of Materials 32 (2020) 8587-8594.
[12] T. Zheng, M. Runowski, P. Woźny, S. Lis, Influence of matrix on the luminescence properties of $Eu^{2+}/Eu^{3+}$ doped strontium borates: $SrB_4O_7$, $SrB_2O_4$ and $Sr_3(BO_3)_2$, exhibiting multicolor tunable emission, Journal of Alloys and Compounds 822 (2020) 153511.
[13] S. Lai, T. Hu, M.S. Molokeev, Z. Xia, Photoluminescence tuning in $Ba_3ScB_3O_9$:$Eu^{2+}$ phosphor by crystal-site engineering, Physics Open 8 (2021) 100077.
[14] P. Liang, W.-L. Lian, Z.-H. Liu, $Ca[B_8O_{11}(OH)_4]$ : $Eu^{2+}$ – A Highly Efficient Deep Blue-Emitting Phosphor Prepared by Low-Temperature Self-reduction, Chemistry – A European Journal 27 (2021) 13819-13827.
[15] P. Liang, W.-L. Lian, Z.-H. Liu, Highly efficient blue-emitting phosphor of $Sr[B_8O_{11}(OH)_4]$:$Eu^{2+}$ prepared by a self-reduction method, Chemical Communications 57 (2021) 3371-3374.
[16] T. Zheng, M. Runowski, P. Rodríguez-Hernández, A. Muñoz, F.J. Manjón, M. Sójka, M. Suta, E. Zych, S. Lis, V. Lavín, Pressure-driven configurational crossover between $4f^7$ and $4f_65d^1$ States – Giant enhancement of narrow $Eu^{2+}$ UV-Emission lines in $SrB_4O_7$ for luminescence manometry, Acta Materialia 231 (2022) 117886.
[17] C. Li, B. Chen, D. Deng, M. Wu, H. Yu, H. Li, C. Shen, L. Wang, S. Xu, Ratiometric optical thermometer with high-sensitive temperature sensing based on synergetic luminescence of $Ce^{3+}$-$Eu^{2+}$ in $LiSr_4(BO_3)_3$ phosphors, Journal of Alloys and Compounds 838 (2020) 155675.