Chimica Techno Acta

Transparent peer-review report

Manganese- and bismuth-containing phosphors based on $MMeBO_3$ (M = Li, Na, K; Me = Mg, Ca, Sr, Ba, Zn) for white LEDs

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Contents

1st peer-review round

Reviewer #1 | minor revision

This review covers solid state synthesis conditions, investigation of crystallographic and optical properties of borates of the MMeBO 3 (M = Li, Na, K; Me = Mg, Ca, Sr, Ba, Zn) family doped and co-doped with transition metals and rare-earth metals. This is a very nice manuscript summarizing previously obtained results in a field of research of these borates.

This work can be published in Chimica Techno Acta after a minor revision.

1. It follows from the Table 2, that there are at least 3 crystal systems characteristic to the borates of the MMeBO 3 family, but the Figure 1 represents only the orthorhombic NaCaBO 3 structure. Probably, it would be clearer if the authors present all the crystal structures that differ in its crystal system and space group in the Figure 1 to mark diversity and differences of the MMeBO 3 borates.

2. P. 11, s. 6.2: Probably, an additional Table with temperature-dependent luminescent properties (temperature of thermal quenching, PL intensity) of the investigated borates could gain in a better visibility of described results.

3. P. 19, Table 5 is entitled “Quantum efficiency of doped borates MMeBO 3 ”, but there are several additional borates, silicates and phosphates families. The same with the Table 6 caption.

3. It is recommended to check and correct typo errors throughout the manuscript.

4. It is recommended to check and correct English language by using free software and / or tools.

Some grammar errors are common (i.e., “is”, “are” are missed etc.) as well as some incorrect terms are used such as “the carrier matrix”, “syngony”, “rhombic system” etc.

Reviewer #2 | minor revision

The manuscript “Manganese- and bismuth-containing phosphors based on MMeBO3 (M = Li, Na, K; Me = Mg, Ca, Sr, Ba, Zn) for white light-emitting diodes” by Tatyana Khamaganova and Alexandra Logvinova contains extensive review material on the borates with the general formula MMeBO3, their crystal structure and some luminescent properties. I have carefully considered this manuscript and recommend major revision. The submission contains some typos. For instance, when discussing luminescent properties, photoluminescence spectra are not provided.

The choice of figures and their relevance, for example, Fig. 8, raises questions.

The abbreviation NCB: 0.01Ce3+ in the Key findings should be explained. Some pages contents unknown symbols, page 3, selection 2.1., the second paragraph, for instance.
The presentation of some type of the crystal structures of the discussed borates as a figure will be useful for the better understanding of the readers.
Fig. 1 has very bad quality.
The article needs to be prepared more carefully before submission to the editorial office.

Reviewer #3 | minor revision

The work is devoted to the synthesis, structures and luminescent properties of borate materials MMeBO3, M = Li, Na, K; Me = Mg, Ca, Sr, Ba, Zn, Cd, doped with divalent Mn2+ ions, as well as heavy metal ions Bi3+, Pb2+, co-doped with REE (Ce3+, Eu3+, Eu2+).
There are a number of questions and comments on the work, although the article corresponds to the profile of the journal:
The title of the article is not very well chosen, since it does not contain all the chemical elements included in this family, the luminescence of which is the subject of this review.
Page 3, line 3. Plasma panels for television and other basic applications have not been produced since 2014, so this can hardly explain the relevance of these luminescent materials.
Page 2, line 9. It is not clear what the transition from a high-energy state to a low-energy state means for a crystal. This is not usually written like that.
Page 2, paragraph 4. What does it mean made of REE. These metals themselves are not transparent. Perhaps they meant materials containing REE in their composition?
Page 5. It is not clear why 2 of the four directions are repeated. An explanation is needed. I would also like to note that page 5 does not have footnotes everywhere.
Page 9, lines 4-5. This statement is too categorical. Usually only the ratio between transitions in intensity changes

Editor's comments

- Please use our new template to prepare your revision: https://chimicatechnoacta.ru/public/journals/6/miscdocs/CTA_template_2025.docx;
- Abstract must be presented in one paragraph;

- Please chose only one (closely related) number of goals listed at https://sdgs.un.org/goals and indicate this number in the corresponding place (first page) of the template;
- Under your revision, please pay attention to the following recent papers that are close in topic of the manuscript. If you feel that some of these papers are indeed relevant, you are encouraged to include and discuss them in order to enhance the novelty and relevance of your work:
https://doi.org/10.1039/D2QI00168C
https://doi.org/10.1007/s42247-023-00595-9
https://doi.org/10.47852/bonviewJOPR42022256
https://doi.org/10.1111/jace.18671
https://doi.org/10.1016/j.ijleo.2024.171604
https://doi.org/10.1016/j.mlblux.2023.100210
https://doi.org/10.1002/adfm.202213442
https://doi.org/10.1021/acs.jpcc.2c01679
https://doi.org/10.1016/j.ijleo.2022.169024
https://doi.org/10.1039/D2TC01243J
https://doi.org/10.1016/j.optmat.2023.114809
https://doi.org/10.1039/D2NJ04629F
https://doi.org/10.1021/acs.chemmater.9b04739
https://doi.org/10.1016/j.mseb.2021.115306
https://doi.org/10.1111/jace.17755
https://doi.org/10.1039/D2TC02732A

Editor's decision

Major revision.

Responses to the comments of Reviewer #1

The authors are grateful to the reviewer for attention to the work and the comments made. All comments and wishes of the reviewer have been taken into account.

1. Since the spectral-luminescent characteristics of the impurity ion in the crystal depend

on the features of its crystal environment, the authors considered it possible to limit themselves to Table 2. Table 2 presents data on the crystal system, space

group and coordination of ions in the structures of the corresponding borates. In addition, earlier [47] we described the structures of borates LiMeBO3, Me = Mg, Ca, Sr, Ba, Zn, Cd. In Figure 1, we have shown the structure with NaCaBO3 as the most interesting. It contains mixed positions of Na^{+} and Ca^{2+}.

This review provides links to works containing the results of decoding crystal structures, and if desired, you can always refer to the original source.

2. Page 11. 6.2. Thermal stability of phosphors

The modified text is highlighted in red. Table 3 added.

Table 3 Particle size, chromaticity coordinates (λex = 427 nm) at temperatures of 25°C and 150°C and activation energies of the studied borates

Composition	Particle size, microns	CIE (x,y)		E_a, эВ
		25° C	150° C	
$LiMgBO_3$: $0.04Mn^{2+}$	12.35	(0.715, 0.285)	(0.707, 0.293)	0.254
$Li_{0.94}Na_{0.06}MgBO_3$: $0.04Mn^{2+}$	28.53	(0.717, 0.283)	(0.709, 0.291)	0.256
$Li_{0.94}K_{0.06}MgBO_3$: $0.04Mn^{2+}$	43.25	(0.717, 0.283)	(0.709, 0.292)	0.261

3. Page 19. Tables 6 and 7. Table titles have been corrected and changed.
4. The manuscript has been carefully checked for errors and typos.

Responses to the comments of Reviewer #2

The authors thank the reviewer for his careful reading of the manuscript and for the recommendations offered.

1. The list of figures has been expanded in accordance with the reviewer's wishes.

2. Regarding Figure 8 (now 10). In our opinion, the figure on the contrary is very clear and appropriate in our manuscript. It is a confirmation of the possibility of creating a phosphor based on $NaCa_{0.96}BO_3$: $0.01Ce^{3+}$,$0.03Mn^{2+}$ with effective

characteristics, low correlated temperature and color coordinates close to white light.

Often in publications one can see extensive studies of the functional properties of objects of study, performed at the proper level and on high-quality equipment. However, these experiments do not find application. In this case, the authors of the work confirmed their research on new fluorescent materials and created an LED device emitting white light (shown on the tab of Figure 8). The modified text is highlighted in red.

6.4.2. White LEDs based on $MMeBO_3$ borates

Abbreviation NCB:0.01 Ce^{3+}. The abbreviation refers to the names of the described borates and

other classes of compounds (the first letters of the corresponding element in the chemical formula of the compound are indicated).

In the text, an explanation is given for $NaCaBO_3$: Ce^{3+}, Tb^{3+}, Mn^{2+} – NCB: 0.01Ce^{3+}, 0.05Tb^{3+}, 0.03Mn^{2+}), and in Table 6, the borate $NaSr_{0.89}BO_3$: Ce^{3+}, Tb^{3+}, Mn^{2+}– *NSB:0.01Ce^{3+}, 0.07Tb^{3+}, 0.03Mn^{2+} is marked with an asterisk.

2. Page 3, section 2.1. in the second paragraph “sizes of 3–5 μm”, page 9, section 6.1.1. ~ 43.25, ~ 28.53, ~ 12.35 μm corrected to microns.

3. Figure 1. Projection of the $NaCaBO_3$ structure along the [001] according to [52] replaced by the another.

All comments and questions have been addressed and the manuscript has been revised accordingly.

Responses to the comments of Reviewer #3

The authors are grateful to the reviewer for attention to the work and fair comments. All comments have been taken into account and accepted for development.

We believe that the title of the manuscript as a whole reveals the essence of the presented work and does not require changes. Since, if we introduce co-doped

elements (Ce^{3+}, Eu^{3+}, Eu^{2+}) into the title, we will have to considerably expand the information on lanthanide doping.

In this case, the focus of the article will shift to them, which is not the purpose of this work.

1. Of course, solid–state lighting is a broad concept and includes, among other things, a type of lighting based on LEDs. We agree that LED lighting is by no means limited to plasma panels, backlighting of phone and TV screens. Therefore, the text in the introduction has been corrected and the phrase about plasma and electroluminescent panels has been removed.

In this case, the focus of the paper will shift to them, which is not the purpose of this paper.

2. Ibid. An inaccuracy in the phrase explaining the concept of luminescence has been corrected.

As is known, the phenomenon of luminescence occurs as a result of the emission transition of electrons in molecules or crystals from one energy level to another, lower one.

3. The phrase has been clarified and changed. Currently, the most popular phosphors on the market are made from REE. Currently, the most popular phosphors on the market are made of materials containing REE.

4. Page 5. The main elements of the structure are isolated BO_3 - anionic groups distributed parallel to four directions, namely [301], [301], [032] and [032]. When listing the directions, some of the dashes at the top are missing. They were restored [301] [$3\bar{0}1$] [032] [$03\bar{2}$].

5. On page 5, footnotes are not present everywhere. Indeed, there are practically no references in the description of crystal structures. This is explained by the fact that immediately before the description of the structures there is table 2 Coordination numbers of cations in the structures of $MMeBO_3$. It contains references to each structure mentioned in the description. Following the reviewer's comment, a clarifying addition was made to the text (see Table 2), which was placed at the end of the sentence "All known orthoborates of the

composition $MMeBO_3$, despite the same formula, differ in structure: most of them are assigned to the monoclinic syngony, $LiCaBO_3$ and $NaCaBO_3$ belong to the rhombic system."

6. Page 9. Lines 4-5. Changes have been made to the text

In the excitation spectra of both phosphors, lines attributed to 4f transitions of Eu^{3+} ($^7F_0 \rightarrow {}^5D_2$ at 466 nm and $^7F_0 \rightarrow {}^5L_6$ at 395 nm) were observed, as well as a broad charge transfer (CT) band O^{2-} - Eu^{3+} in the UV region. The line intensities of the 4f - transitions of Eu^{3+} were higher in the $LiMg_{0.749}BO_3$ sample: $Eu^{3+}_{0.25}$, $Bi^{3+}_{0.001}$.

Responses to the Editor's comments

We apologize for the delay related to the annual report and participation in the conference. The article has been revised in accordance with the comments and questions of the reviewers.
You have proposed a number of recent paper to increase novelty and relevance.
We report that almost all of them are devoted to the study of borate glasses and are not suitable for inclusion in our review. However, we have taken your wishes into account and updated the list of references, including several recent works.
All comments and questions have been processed, and appropriate edits have been made to the text of the manuscript. The modified text is highlighted in red.

2nd peer-review round

Reviewer #1 | -

The reviewer did not accept (or did not provide a response to) the second invitation for the revised manuscript and its related items in the required deadline.

Reviewer #2 | -

The reviewer did not accept (or did not provide a response to) the second invitation for the revised manuscript and its related items in the required deadline.

Reviewer #3 | -

The reviewer did not accept (or did not provide a response to) the second invitation for the revised manuscript and its related items in the required deadline.

Final Editor's decision

Accept.