

# Journal of Alloys and Compo<mark>unds</mark>

Volume 883, 25 November 2021, 160846

# Luminescence in the system Al<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub>

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# Highlights

- Combustion synthesis of phosphors in Al<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub> system reported.
- Al<sub>4</sub>B<sub>2</sub>O<sub>9</sub>, Al<sub>5</sub>BO<sub>9</sub> and Al<sub>18</sub>B<sub>4</sub>O<sub>33</sub> were successfully prepared.
- Luminescence of Ce<sup>3+</sup> and Cr<sup>3+</sup> observed in as-combusted powders.
- Characteristic luminescence in form of narrow R lines of Cr<sup>3+</sup> was observed in Al<sub>5</sub>BO<sub>9</sub> and Al<sub>18</sub>B<sub>4</sub>O<sub>33</sub>.

#### Abstract

Three compounds in the system Al<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub>, viz. Al<sub>4</sub>B<sub>2</sub>O<sub>9</sub>, Al<sub>5</sub>BO<sub>9</sub> and Al<sub>18</sub>B<sub>4</sub>O<sub>33</sub> were successfully prepared by facile <u>combustion synthesis</u>. Activation by 3d transition element Cr<sup>3+</sup> and 4f <u>lanthanide</u> Ce<sup>3+</sup> was attempted. Characteristic luminescence in form of narrow R lines of Cr<sup>3+</sup> was observed in Al<sub>5</sub>BO<sub>9</sub> and Al<sub>18</sub>B<sub>4</sub>O<sub>33</sub>. Interaction of Cr<sup>3+</sup> with the surrounding was represented by the Racah parameters. Broad band emission of Ce<sup>3+</sup> arising from allowed d-f transitions in near ultraviolet (nUV) region in all 3 compounds is reported for the first time.

#### **Graphical Abstract**



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#### Introduction

The investigations on the system Al<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub> have a long history. A compound was identified as back as 1887 [1]. The correct composition, however, was established much later as Al<sub>18</sub>B<sub>4</sub>O<sub>33</sub> [2]. Another compound, Al<sub>4</sub>B<sub>2</sub>O<sub>9</sub>, was also discovered around the same time [3]. None of these compounds have the composition of the natural mineral jeremejevite which is AlBO<sub>3</sub>. This compound could not be prepared at normal pressure. Following these early studies, a first systematic phase diagram was given by Gielisse and Foster [4]. ICDD data mention several other phases like Al<sub>3</sub>BO<sub>6</sub> [5] most of which are metastable; Al<sub>5</sub>BO<sub>9</sub> being notable as a stable phase at normal temperature and pressure [6]. Decterov et. al. have given a detailed history of the phase diagram of Al<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub> system [7].

Subsequently, these compounds were found to be useful for several applications [8]. Owing to low-cost, "suitability for large scale production, high strength, and low thermal expansion and conductivity, these compounds are used as reinforcer in metal matrix composites". It has high resistance against boron-rich glass melts and thus finds use in refractory linings [9]. Applications in catalytic converter, for thermal sealing and insulating materials in hypersonic vehicles, have also been mentioned [10]. Boron being a good neutron absorber, the aluminoborates find application in construction of reactor components.

Notwithstanding the abovementioned applications, those related to luminescence are few. Some scattered references mention luminescence in one of the phases, but systematic study is still lacking. Luminescence of Tb<sup>3+</sup> [11] was investigated by Guangyan

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et al. Eu<sup>2+</sup> in Al<sub>4</sub>B<sub>2</sub>O<sub>9</sub>, has been mentioned by Zheng and Chen, but emission is very weak and the excitation spectra are poorly resolved [12]. Yerpude et al., on the other hand, found Eu<sup>3+</sup> [13] in this host. Luminescence of Nd<sup>3+</sup>-Yb<sup>3+</sup> [14] and associated upconversion [15] has been also described. Luminescence of some lanthanides in Al<sub>18</sub>B<sub>4</sub>O<sub>33</sub> has been mentioned, though there is huge difference in sizes of Al<sup>3+</sup> and trivalent lanthanide ions Ce<sup>3+</sup>[11], Eu<sup>3+</sup> [16], [17], [18], Tb<sup>3+</sup> [19], Er<sup>3+</sup> [20]. In recent years only, some luminescence studies have also been reported for Al<sub>5</sub>BO<sub>9</sub>, particularly, trivalent Eu<sup>3+</sup> [21] and Sm<sup>3+</sup> [22]have been investigated.

Considering this lack of information on luminescence, we have undertaken the work on luminescence in system  $Al_2O_3$ - $B_2O_3$ . Luminescence of  $Ce^{3+}$  and  $Cr^{3+}$  is reported here.  $Ce^{3+}$  usually gives strong photoluminescence due to allowed nature of the f-d transitions.  $Cr^{3+}$  can suitably occupy  $Al^{3+}$  substitutional site and give line emission in oxidic hosts. Hence, these two activators were chosen. Three phases,  $Al_{18}B_4O_{33}$ ,  $Al_4B_2O_9$  and  $Al_5BO_9$ , could be prepared using combustion method by just changing the Al:B ratio in the starting mixture.

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#### Experimental

Known stable phases, Al<sub>18</sub>B<sub>4</sub>O<sub>33</sub>, Al<sub>4</sub>B<sub>2</sub>O<sub>9</sub> and Al<sub>5</sub>BO<sub>9</sub>, were prepared by combustion synthesis. A detailed description is presented in our earlier work [23]. Salient points are as follows. "Aluminium nitrate has exothermic reaction with urea. Reagent grade (Indian Rare Earths, Ltd.) Cerium oxalate/Chromium oxides were converted to the corresponding nitrates by dissolving in minimum amount of nitric acid. The nitrates were dried by prolonged, gentle warming. Stoichiometric amounts of hydrated...

# $Al_4B_2O_9$

The formation of  $Al_4B_2O_9$  was ascertained with the help of XRD. In Fig. 1 comparison of the measured pattern with the ICDD data file 79–1477 is made. The measured pattern is noisy due to small particle size typical of combustion synthesis. Notwithstanding the noisy pattern, sharp lines are observed superposed at the positions matching with the

ICDD file. Thus, simple combustion synthesis has produced Al<sub>4</sub>B<sub>2</sub>O<sub>9</sub>. Methods described in literature are much more cumbersome. Four different methods for...

# Conclusions

Three phases in the system Al<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub> viz. Al<sub>4</sub>B<sub>2</sub>O<sub>9</sub>, Al<sub>5</sub>BO<sub>9</sub> and Al<sub>18</sub>B<sub>4</sub>O<sub>33</sub> could be prepared by the one step combustion synthesis just by changing Al:B ratio in the starting mixture. These could be activated by Ce<sup>3+</sup> and Cr<sup>3+</sup>. Owing to large difference in ionic sizes of the host Al<sup>3+</sup> and Ce<sup>3+</sup>, only 0.2% Ce<sup>3+</sup> could be incorporated. New results on luminescence of Cr<sup>3+</sup> in these compounds are presented. Line emission originating from  $^{2}E \rightarrow {}^{4}A_{2g}$  transition around 700 nm is observed for Al<sub>5</sub>BO<sub>9</sub> and Al<sub>18</sub>B<sub>4</sub>...

### CRediT authorship contribution statement

S.G.Revankar – Synthesis, Manuscript writing, K.A.Gedekar- Synthesis and Editing, S.P.Puppulwar-Editing of manuscript, S.P.Wankhede- Synthesis and Editing, P.D. Belsare – Characterization, S. V. Moharil – Basic concept and Editing....

### **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper....

#### Acknowledgements

We are thankful to Department of Physics, RTM Nagpur University for the help provided in recording XRD. Crystal structure diagrams are prepared using Vesta software [41]. We are grateful to the copyright owners for permitting free use....

#### **Recommended articles**

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High thermal stability near-infrared aluminoborate phosphor with spectral tunability and its rice lighting application

2024, Materials Today Chemistry

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Energy transfer controlled color-tunable luminescence of Tm<sup>3+ </sup>/Dy<sup>3+</sup> co-doped aluminoborosilicate glass-ceramics 2023, Journal of Non-Crystalline Solids

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#### First observation of luminescence in synthetic boralsilite

2022, Optik

Citation Excerpt :

...Luhr et al. prepared and analysed some phases at ambient pressure. Considering that aluminoborates could be successfully synthesized by combustion synthesis [15], we attempted the preparation of Boralsilite by the same technique. Details of the experimental methods can be found in our earlier work [16]....

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# Luminescence in synthetic boromullite prepared by combustion synthesis 🤊

2024, Radiation Effects and Defects in Solids

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