Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.


**ELECTRONIC SUPPLEMENTARY INFORMATION**

# Rare-earth-free zinc aluminium borate white phosphors for LED lighting

P. Gaffuri,[a,b] M. Salaün,[a] I. Gautier-Luneau,[a] G. Chadeyron,[c] A. Potdevin,[c]
L. Rapenne,[b] E. Appert,[b] V. Consonni,[b] A. Ibanez,[a]

[a] *Univ. Grenoble Alpes, CNRS, Grenoble INP, Institut Néel, 38000 Grenoble, France*

[b] *Univ. Grenoble Alpes, CNRS, Grenoble INP, LMGP, 38000 Grenoble, France*

[c] *Université Clermont Auvergne, CNRS, SIGMA Clermont, Institut de Chimie de Clermont-Ferrand, F-63000, Clermont-Ferrand, France*

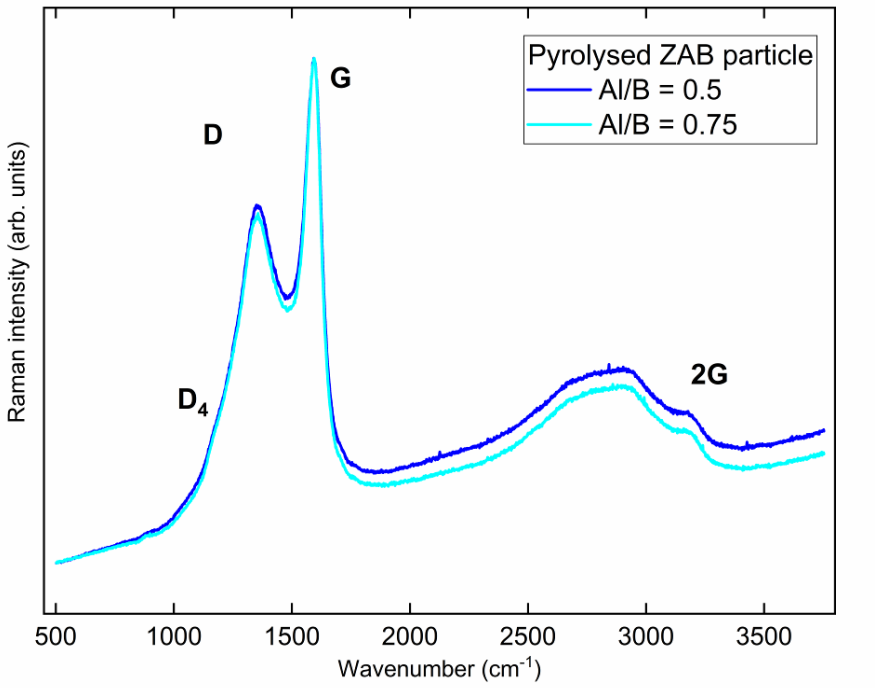


***Fig. S1*** *Raman spectra of pyrolysed ZAB powders, prior to their calcination, using the 488 nm excitation of an $Ar^+$ laser.*

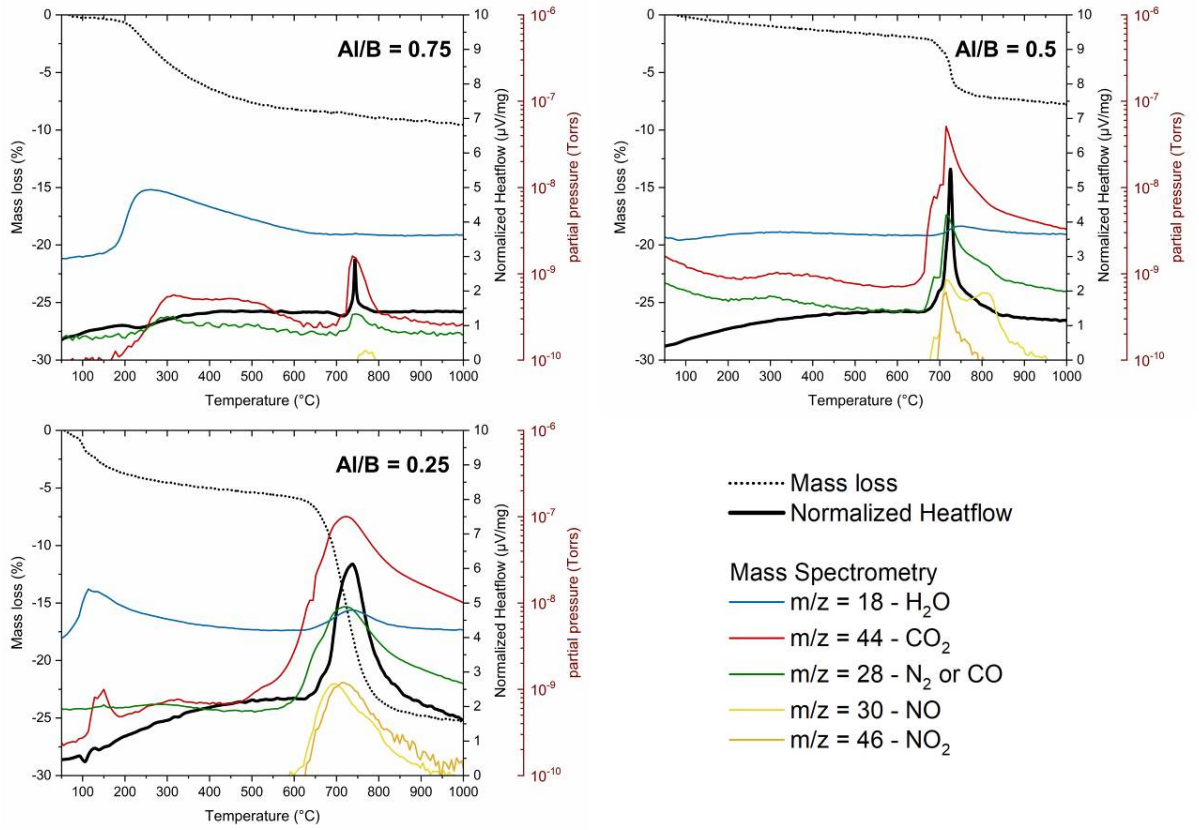


***Fig. S2*** *Thermogravimetric analyses (TGA) (dark dotted curve) coupled with differential thermal analyses (DTA) (dark curve) and mass spectrometry (MS) of 15 mg of ZAB powder with Al / B ratio of 0.25, 0.5, and 0.75, calcined at 600°C. The calcinated powder were heated under $O_2$ atmosphere at the rate of 10°C $min^{-1}$, from room temperature to 1000°C. The loss of $CO_2$ from 600°C to 800°C is attributed to oxidation of organic species trapped in the matrix.*

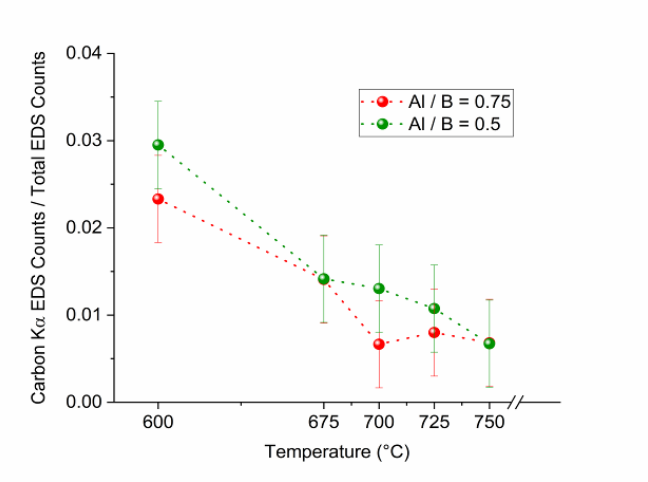


***Fig. S3*** *Counts of the carbon Kα X-ray, divided by the total counts of Zn, Al, B, O and C Kα X rays, in several ZAB single particles with Al / B ratio of 0.5 and 0.75, and calcination temperature ranging from 600 to 750°C, by SEM-EDS operating at 5 KV.*

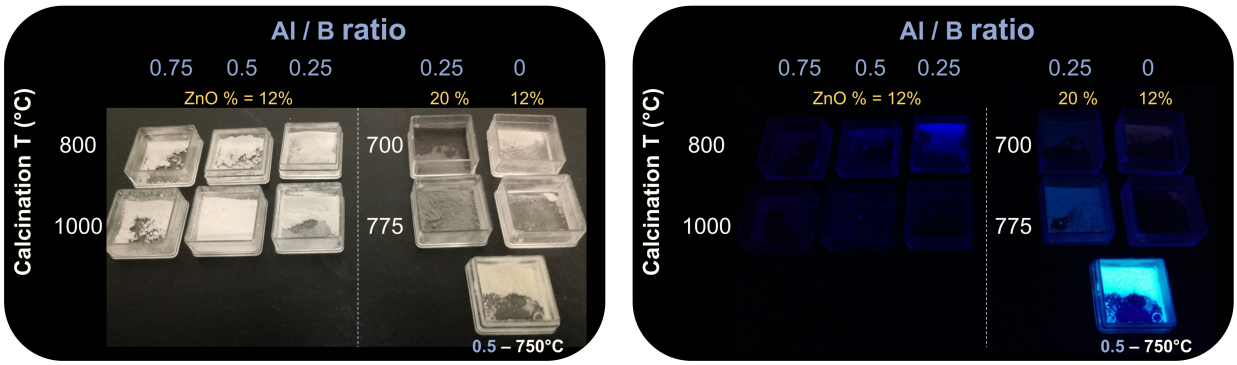


***Fig. S4*** *Photographs under daylight (left panel) and under NUV illumination at 365 nm (right panel) of non-luminescent ZAB powders of optimized compositions, but with a $T_{Ca}$ over 800°C, or for compositions leading to an early strong crystallisation (i.e. zinc-rich and aluminium-free). For comparison, the optimized luminescent ZAB powder with Al/B = 0.5 and $T_{Ca}$ = 750°C under the same illuminations is shown on the bottom right of each panel.*

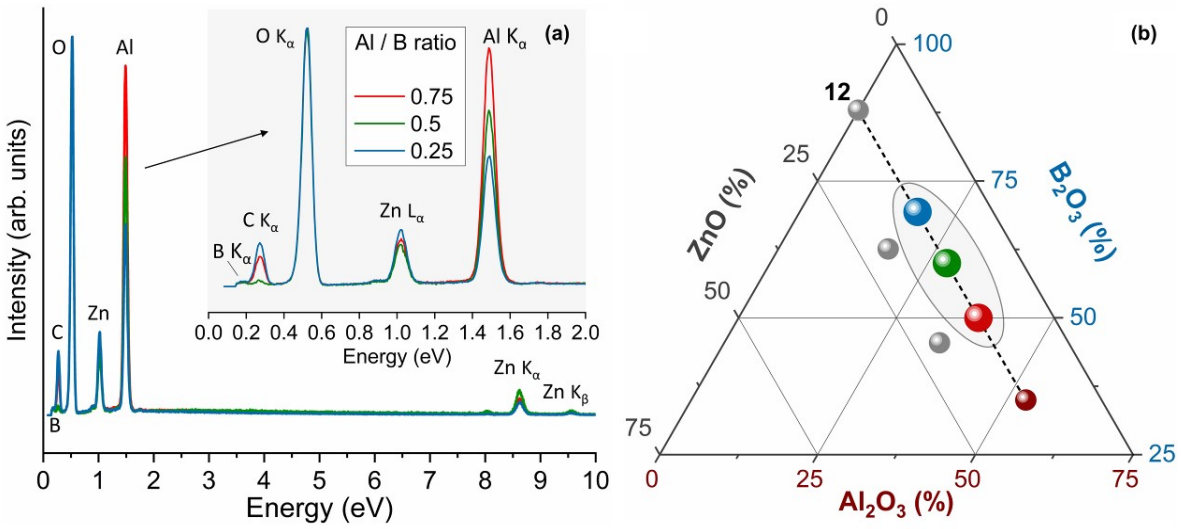


***Fig. S5 (a)*** *Typical SEM-EDS spectra of single particle of the three optimized luminescent ZAB compositions highlighted in (b). Spectra are normalized by the oxygen peak to show the varying aluminium content. The boron peak is not reliably quantifiable, nor are the variations in the carbon peak, primarily due to the carbon tape where the particles were dispersed.* ***(b)*** *ZnO-$Al_2O_3$-$B_2O_3$ ternary diagram showing the initial chemical composition ratios of the synthesized ZAB phosphors. Optimized luminescent ZAB phosphors are represented by the circled blue, green and red dots, with a constant ZnO molar ratio of 12%, and Al / B precursor molar ratios of 0.25, 0.5 and 0.75, respectively. For higher Al / B ratio (dark red dot), a weak luminescence was observed. Compositions leading to non-luminescent powders due to matrix crystallization are represented by grey dots.*

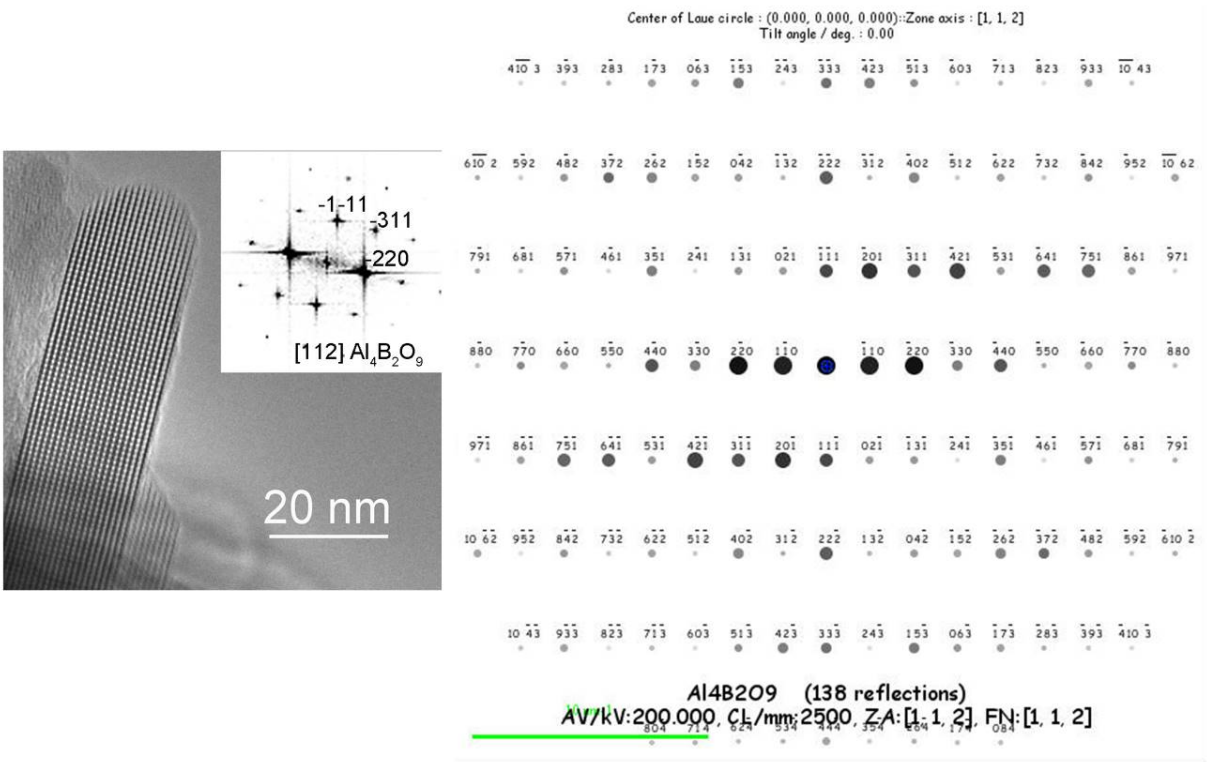


***Fig. S6*** *TEM micrograph of the surface of ZAB particles with Al / B = 0.25 calcinated at 700°C shown in Fig.2. The inset shows the corresponding FFT pattern, indexed as* $Al_4B_2O_9$ *along the [112] zone axis, as shown by the JEMS file on the right, with (220) plane along the growth direction, and (111) plane perpendicular to the growth direction.*

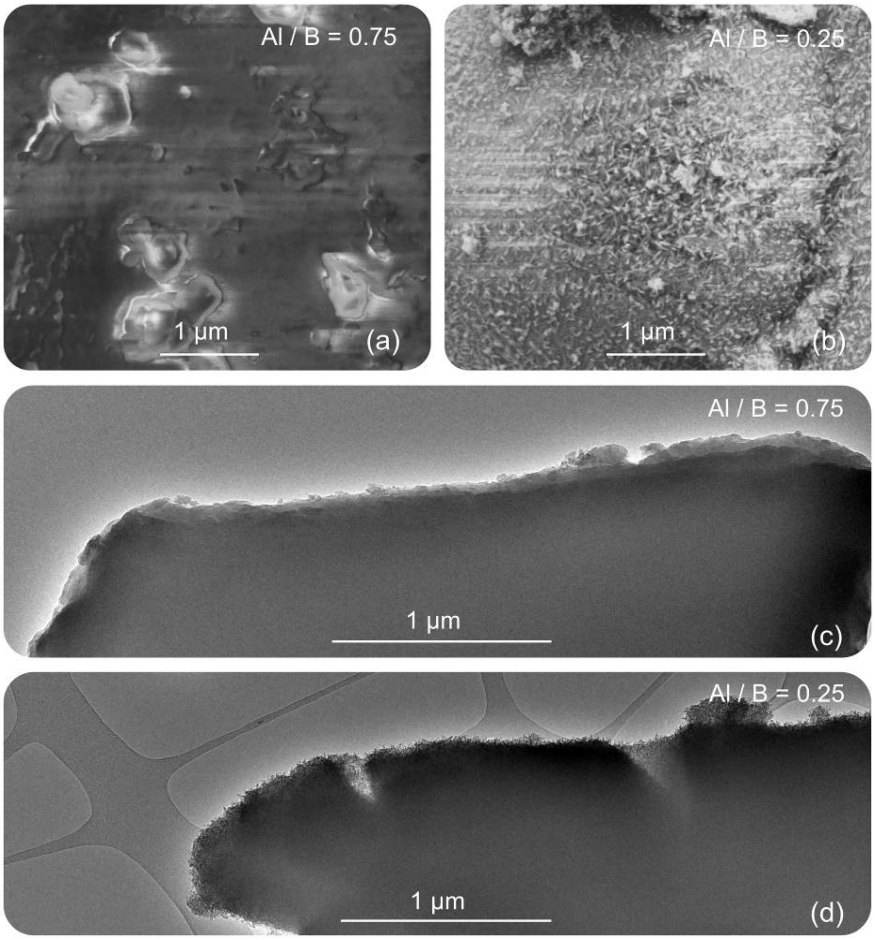


***Fig. S7 (a)-(b)*** *FESEM micrographs showing the surface of ZAB particles with Al / B = 0.75 and 0.25, respectively, calcinated at 700°C.* ***(c)-(d)*** *Bright-field TEM micrographs showing the surface of ZAB particles with Al / B = 0.75 and 0.25, respectively, calcinated at 700°C.*

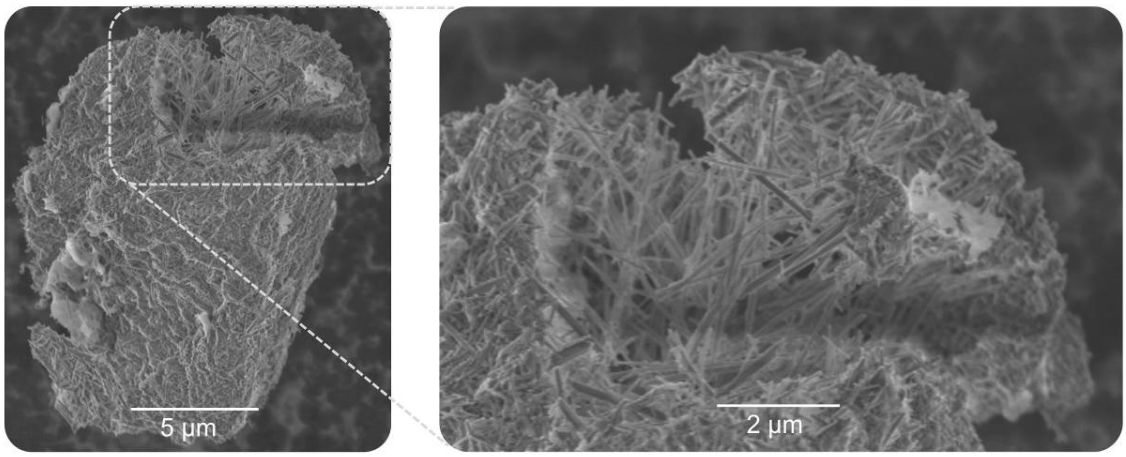


***Fig. S8*** *FESEM micrograph of ZAB particle calcinated at 1000°C. Large whiskers are visible, even in the core of the particles, showing the absence of an amorphous core.*

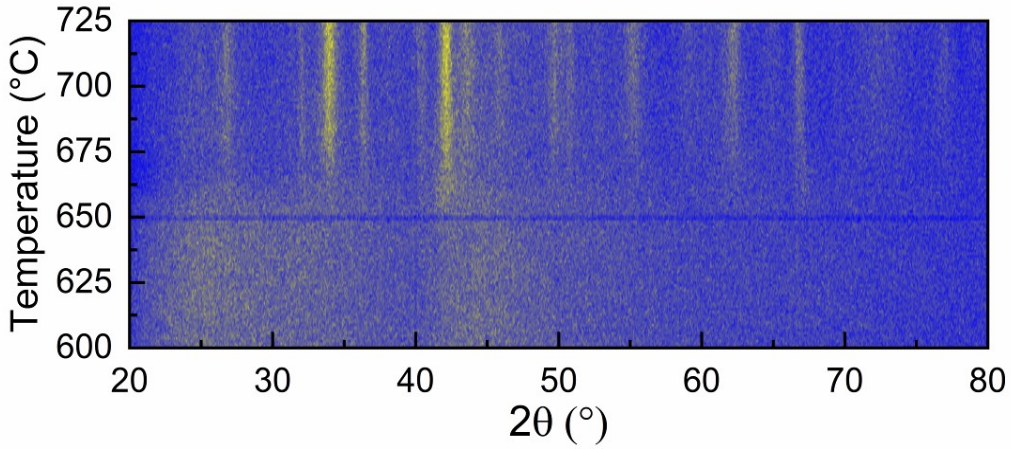


***Fig. S9*** *In-situ temperature XRD diffractogram of pyrolysed ZAB particles with Al / B = 0.5 calcinated under air. The temperature of crystallization is shown to be similar as for sample with Al / B = 0.25.*

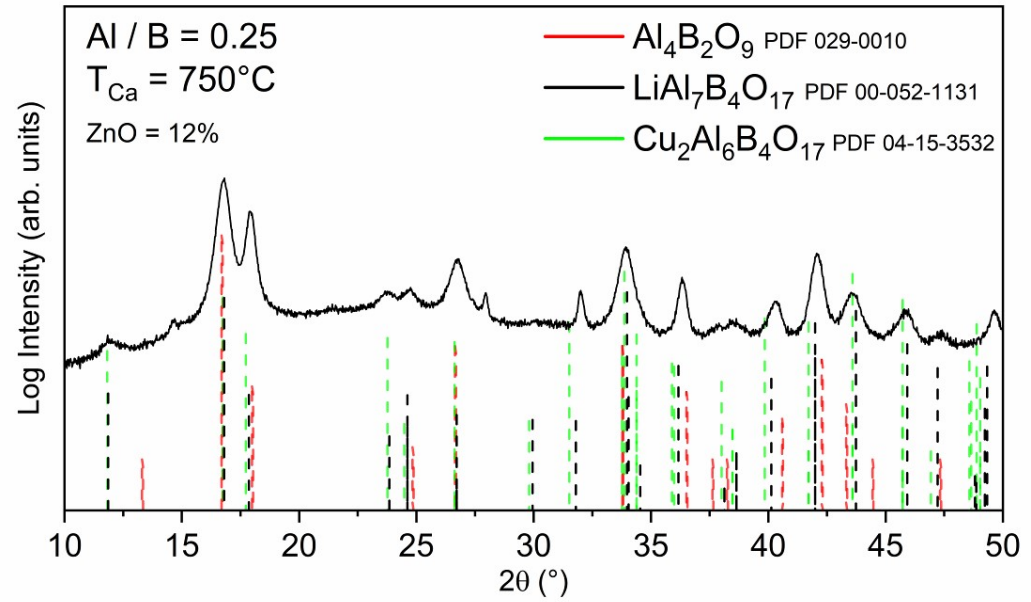


***Fig. S10*** *Typical powder X-ray diffraction pattern of a luminescent ZAB powder compared with corresponding pdf files of most similar crystallographic phases.*

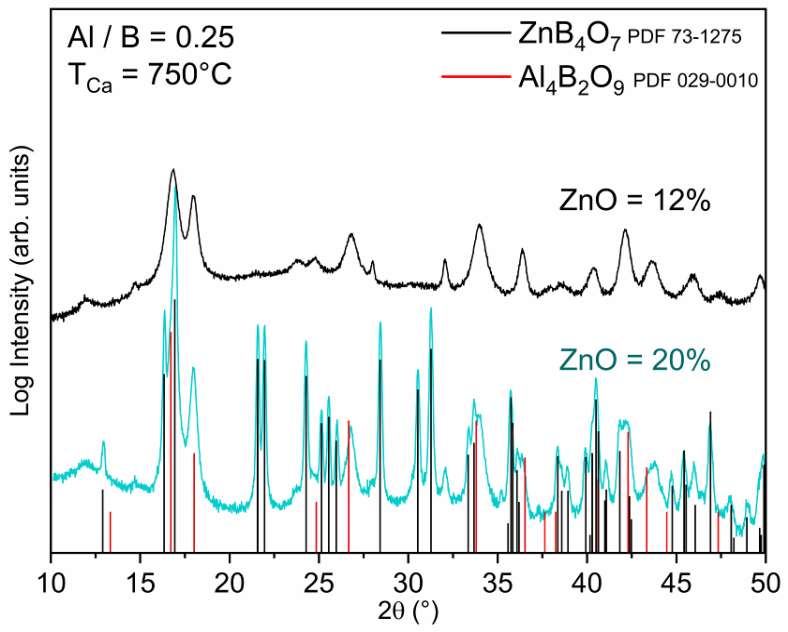


***Fig. S11*** *Powder X-ray diffraction pattern of zinc-rich ZAB powder, and the same with higher zinc content, showing clearly the strong crystallization of $ZnB_4O_7$ majority phase, and $Al_4B_2O_9$ secondary phase.*

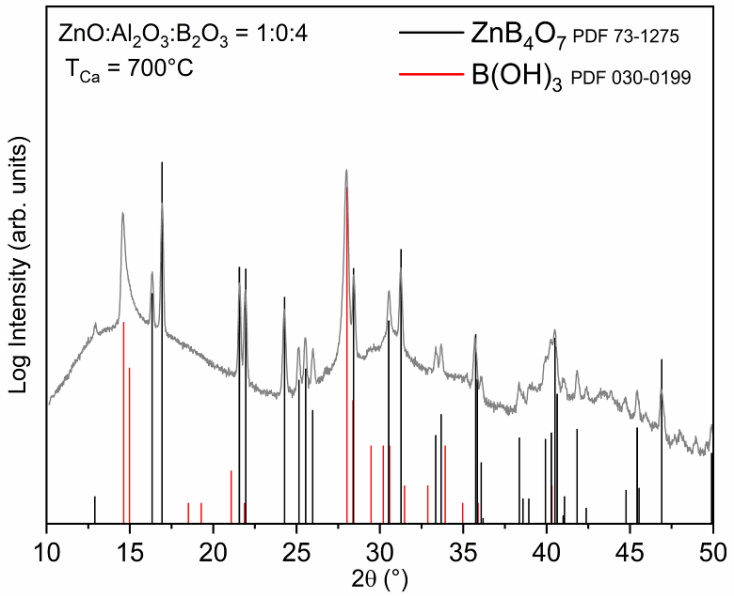


***Fig. S12*** *Powder X-ray diffraction pattern of aluminium-free ZAB powder showing clearly a strong crystallization of the matrix into $ZnB_4O_7$ and $B(OH)_3$ phases.*

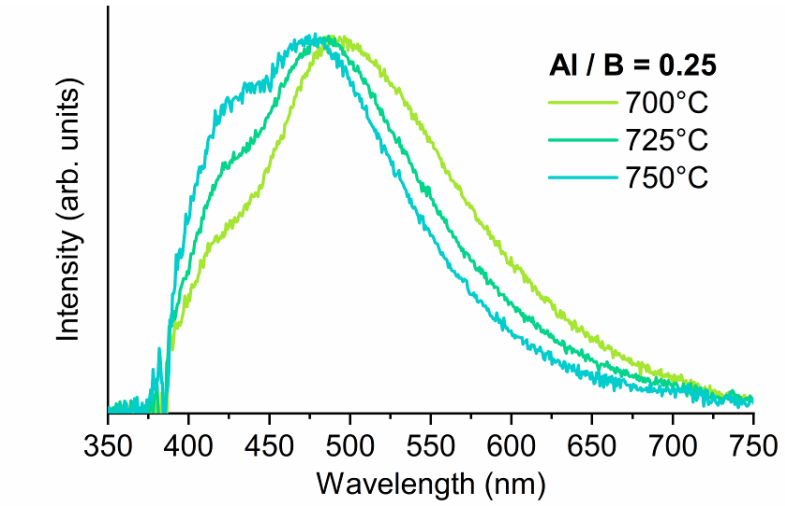


***Fig. S13*** *Normalized room-temperature photoluminescence spectra of ZAB particles excited at 385 nm, with Al / B ratio of 0.25 and calcination temperature in the range of 700 to 750°C. The excitation peak at 385 nm was systematically measured without the sample as a reference, and later removed from the PL spectra. The similarity with samples having Al / B ratio of 0.5 is shown once again.*

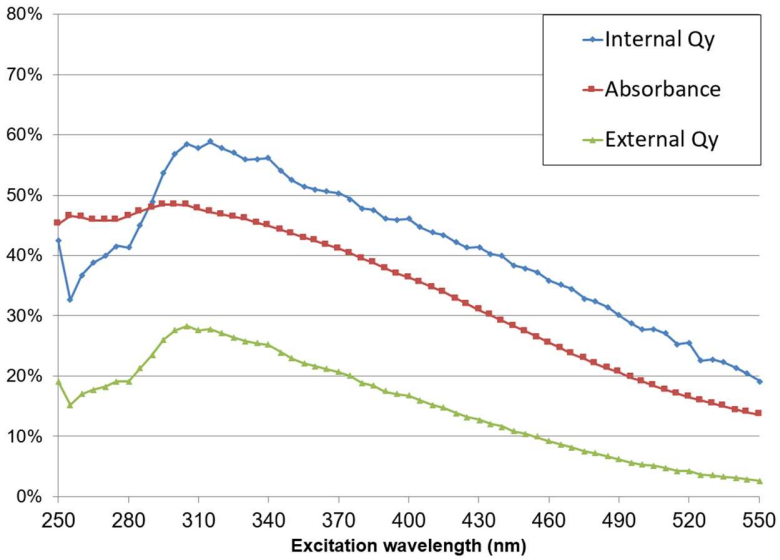


***Fig. S14*** *Evolution of the quantum yields (Qy) and absorbance of ZAB phosphor with Al / B ratio of 0.5, calcinated at 725°C. All other ZAB phosphor showed a maximum of iQY and eQY near 305nm*

***Table S1*** *iQY, eQY, and colour point coordinate according to CIE 1931 chromaticity diagram of three ZAB phosphors, with* $\lambda_{exc}$ *= 385 and 305 nm.*

| | $\lambda_{exc}$ | iQY | eQY | *x* | *y* |
|---|---|---|---|---|---|
| **Al/B = 0.5 $T_{ca}$ = 700°C** | 385 | 22.5 ± 1.1 | 15.0 ± 4.4 | 0.27 | 0.38 |
| | 305 | 34.6 ± 1.7 | 24.0 ± 5.2 | 0.25 | 0.31 |
| **Al/B = 0.5 $T_{ca}$ = 725°C** | 385 | 45.8 ± 2.3 | 19.1 ± 4.4 | 0.25 | 0.32 |
| | 305 | 53.2 ± 2.7 | 25.7 ± 5.1 | 0.21 | 0.21 |
| **Al/B = 0.75 $T_{ca}$ = 675°C** | 385 | 27.9 ± 1.4 | 16.3 ± 4.3 | 0.26 | 0.28 |
| | 305 | 41.5 ± 2.1 | 25.5 ± 5.1 | 0.25 | 0.27 |

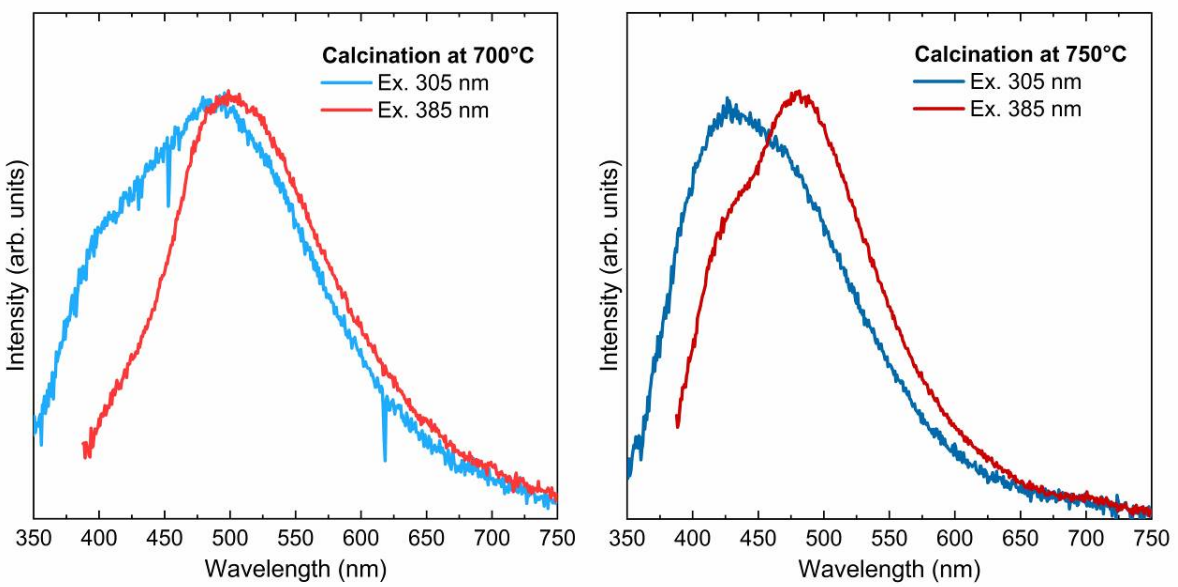


***Fig. S16*** *Normalized room-temperature photoluminescence spectra of ZAB particles with Al / B ratio of 0.5 and calcination temperature of 700 and 750°C. Changing the excitation wavelength from 305 to 385 nm led to a redshift of the PL.*

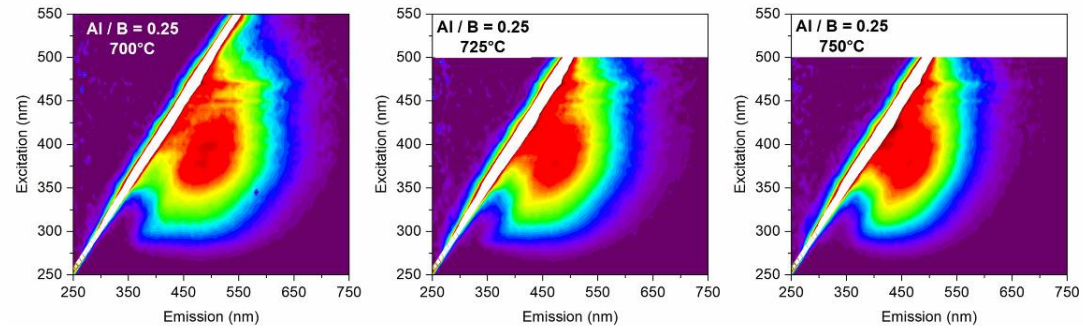


***Fig. S17*** *Maps of the luminescence emission as a function of the excitation of Zinc Aluminium Borate particles with Al / B ratio of 0.25 and calcination temperature in the range of 700 to 750°C. Emission spectra have been recorded using a step of 5 nm for excitation wavelength, from 250 to 550. A rainbow color intensity map was used, red being the most intense, and purple the least intense. The higher intensities for excitation at 450 and 470 nm are measurement artefacts.*

***Table S2*** *Position and normalized area of each of the three Gaussian function used to fit PLE spectra, shown in Fig. 7, of ZAB phosphors with Al / B ratio of 0.5 and 0.75, and calcinated at the temperature of 700 and 750 °C, and 600 and 700 °C, respectively.*

| | | Peak 1 | Peak 2 | Peak 3 |
|---|---|---|---|---|
| **Al/B = 0.5**<br>**$T_{Ca}$ = 700°C**<br>$R^2$ = 99.1% | Position ($cm^{-1}$) | 25126 | 28331 | 31501 |
| | Norm. peak area | 0.28 | 0.24 | 0.48 |
| **Al/B = 0.5**<br>**$T_{Ca}$ = 750°C**<br>$R^2$ = 99.3% | Position ($cm^{-1}$) | 25144 | 28550 | 32644 |
| | Norm. peak area | 0.06 | 0.32 | 0.62 |
| **Al/B = 0.75**<br>**$T_{Ca}$ = 600°C**<br>$R^2$ = 99.5% | Position ($cm^{-1}$) | 25040 | 28547 | 31615 |
| | Norm. peak area | 0.32 | 0.24 | 0.45 |
| **Al/B = 0.75**<br>**$T_{Ca}$ = 700°C**<br>$R^2$ = 99.5% | Position ($cm^{-1}$) | 25169 | 28494 | 31797 |
| | Norm. peak area | 0.27 | 0.24 | 0.49 |