Luminescent properties of blue phosphor 
$\text{Ba}_2\text{CaB}_6\text{O}_{12}:\text{Eu}^{2+}$ under vacuum-ultraviolet 
and ultraviolet excitation

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The luminescence of Eu$^{2+}$ in Ba$_2$CaB$_6$O$_{12}$ has been 
investigated under vacuum ultraviolet and ultraviolet excitation. 
Two different crystallographic sites are available for Eu$^{2+}$ in 
Ba$_2$CaB$_6$O$_{12}$. In this structure, there are linear rows of three 
cations in the order of Ba$^{2+}$, Ca$^{2+}$ and Ba$^{2+}$, Ca$^{2+}$ being in the 
central position. The emission spectra of Eu$^{2+}$ under vacuum 
ultraviolet and ultraviolet consist of two broad bands peaking at 
445 and 465 nm, which are associated with the f$\rightarrow$d transitions of 
Eu$^{2+}$ in the sites of Ba$^{2+}$ and Ca$^{2+}$, respectively. Two weak peaks in 
vacuum ultraviolet range are observed at 160 nm and 200 nm.

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The vacuum ultraviolet (VUV) excited luminescence has been extensively studied on the basis of its 
applications in the plasma display panels (PDPs) and 
the mercury-free lamps$^{1-3}$. The PDPs have been 
widely applied in the flat display and lighting 
devices. The plasma of xenon and helium provides 
excitation in a PDP or mercury-free lamp. The main 
emission of this plasma consists of 147 and 172 nm 
bands compared with the 254 nm line of the mercury 
discharge used in fluorescent lamps. The phosphors 
coated inside the cell are excited by VUV. The 
phosphors then convert the VUV into the visible light, 
which in general includes blue, green and red 
emissions. Since the phosphors are exposed directly 
under the high energy VUV light, the stability of 
these phosphors is critical for the lifespan of the devices$^{1-3}$. In current commercial PDPs$^{4,5}$, the red 
phosphor is Y$(\text{Gd})\text{BO}_3$:Eu$^{3+}$, the green phosphor is 
Zn$_2$SiO$_4$:Mn$^{2+}$ and the blue one is BaMgAl$_{10}$O$_{17}$:Eu$^{2+}$ 
(BAM). The former two phosphors are quite stable 
while the BAM degrade under VUV excitation, which 
leads to a sharp decrease in the luminous efficiency$^{5}$.

This instability is caused by the degradation of the 
host structure and the oxidation of the dopant Eu$^{2+}$ 
during the annealing process in the panel manufacture 
and the operation of the panels under VUV bombardment$^{5}$. This is a critical problem that affects 
the luminance of the PDPs. Many efforts have been 
made to overcome the degradation of BAM, such as 
the compositional variations and the introduction of 
trivalent ions into BAM$^6$. However, no breakthrough 
has been achieved up to now. In addition to that, new 
phosphors for replacing the BAM are extensively 
being searched$^{2,9}$. The requirement is that the phosphor host lattice must absorb efficiently in the 
waveband range between about 140 and 180 nm, 
which can then transfer the energy to the dopant ions 
having a strong emission in the visible region$^{9-11}$. It is 
reported that the borates, phosphates and silicates 
have special potential for VUV excitation since the 
host absorption band is located in the VUV region. For 
example, the blue phosphor CaMgSi$_2$O$_6$:Eu$^{2+}$ 
(CMS), is reported to be a good candidate$^7$ for the 
replacement of BAM applied in PDPs. Unfortunately, CMS shows strong thermal quenching behaviour 
during the operation of the panels, which is not 
applicable$^8$ for PDPs.

We report here the synthesis and the luminescent properties of a new blue phosphor Ba$_2$CaB$_6$O$_{12}$:Eu$^{2+}$ 
under VUV and ultraviolet UV excitation. The results 
show that it might be a candidate for the applications 
in PDPs.

Experimental

The phosphor was obtained using the stoichiometrical mixtures: BaCO$_3$, CaCO$_3$, H$_3$BO$_3$ (10% excess for the evaporation) and Eu$_2$O$_3$ (5 mol% of the Ba$^{2+}$) and heating them at 1073 K for 5 h in H$_2$/N$_2$ 
(5% H$_2$). The structure was checked by a Rigaku 
D/MAX-IIB X-ray powder diffractometer using CuK$_\alpha$ 
($\lambda=0.1542$ nm) radiation. The samples appeared as a 
single phase.

The UV excitation and its emission spectra were 
recorded at room temperature with a SPEX dm3000f 
spectrofluorometer equipped with 0.22 SPEX1680 
double mono-chromators and a 450 W xenon lamp as 
the excitation source. The excitation in the VUV 
region and its emission spectra were measured by a
self-assembled VUV spectrometer with a 150 W deuterium lamp as an excitation light. The excitation spectra in VUV region were corrected by sodium salicylate. Due to the variation of the xenon and deuterium lamps emission spectra with the wavelength, the lamp powder output was corrected. The photomultiplier tube sensors for all the spectra were also corrected due to their different sensitivity at different wavelength. All measurements were performed at room temperature.

Results and discussion

The excitation and emission spectra of the Eu$^{2+}$ doped Ba$_2$CaB$_6$O$_{12}$:Eu$^{2+}$ are shown in Fig. 1. The emission spectrum was obtained under 254 nm excitation. The spectrum is unsymmetrical with a peak at around 445 nm with a shoulder at 465 nm. The excitation spectrum was obtained by monitoring the emission at 445 nm. The emission and absorption spectra of Eu$^{2+}$ usually consist of broad bands due to transitions between the $^8S_{7/2}(4f^{-7})$ ground state and the crystal field components of the $4f^{6}5d$ excited state configuration which is the $4f^{6}5d \rightarrow 4f^{-7}$ transition. In this case, the emission of Eu$^{2+}$ can vary from ultraviolet to red depending on the host lattice since the 5d electron is located on the outermost orbital, which is easily affected by the ionic surroundings. In addition to the covalency, the size of the cation and the strength of the crystal field, the emission of Eu$^{2+}$ also shows variations in its spectroscopic features. However, Eu$^{2+}$ can also show $f \rightarrow f$ transition. This transition can only occur when the $^6P_{7/2}$ level is situated below the lowest $4f^{6}5d$ level. The relative intensity of the line and band emissions depend on the transition probabilities corresponding to the emissions, the energy difference between the two emission levels and the temperature.

It was reported that the structure of Ba$_2$Ca(B$_2$O$_6$)$_2$ is built from nearly planar B$_2$O$_6$ rings, and is related to the high temperature form of BaB$_2$O$_4$ (refs 13,14). The barium sites are coordinated by 9 oxygen ions and the coordination of calcium is octahedral. The common feature in these crystal structures is that three (large) cations are arranged in a line arrow. This implies that there are two different sites available for Eu$^{2+}$: one site at the end, the other in the center, which is also confirmed by the emission spectra with two peaks as shown in Fig. 2. A divalent europium ion in these chains experiences, in addition to the negative charges of the nearest anion neighbours, a positively charged ion on only one side, whereas the central ion experiences positive charges on both sides. The positive charges can orient one $d$ orbital preferentially. This will lower its energy and therefore result in the Eu$^{2+}$ emission at longer wavelengths. These lattices have thee linear rows of Ba$^{2+}$, Ca$^{2+}$ and again Ba$^{2+}$. A divalent europium ion is expected to prefer the barium site because of the ionic radii$^{14}$. Eu$^{2+}$ on the terminal barium sites is expected to have its emission at shorter wavelengths than Eu$^{2+}$ on the central calcium sites. Because of the site preference of Eu$^{2+}$ based on ionic radii$^{15}$, the emission at shorter wavelengths is expected to have higher intensity. This is confirmed by the emission intensities of these two peaks: the one at 445 nm has higher intensity than the one at 465 nm, as shown in Fig. 2. The Eu$^{2+}$ ions occupy preferentially the terminal sites in the row

![Fig. 1](image1.png)  
**Fig. 1**—The excitation (a) and emission (b) spectra of Eu$^{2+}$ in Ba$_2$CaB$_6$O$_{12}$ and emission spectra of Eu$^{2+}$ in BAM (c).

![Fig. 2](image2.png)  
**Fig. 2**—The emission spectra of Eu$^{2+}$ in Ba$_2$CaB$_6$O$_{12}$ for the excitation in the VUV-UV region: (a) $\lambda_{em,}=437$ nm; (b) $\lambda_{ex,}=160$ nm.
where they exhibit as predicted, the shorter wavelength emission. However, part of the Eu\(^{2+}\) ions occupies the central site in the row where they have the longer wavelength emission\(^{14}\).

As a comparison, the emission spectrum of Eu\(^{2+}\) in BAM is also shown in Fig. 2. Both emission spectra were obtained under 254 nm excitation. It can be observed that these two emission features are almost identical. The chromaticity for BAM is \(x=0.142, y=0.08\) while that for Ba\(_2\)CaB\(_6\)O\(_{12}\) is \(x=0.155, y=0.091\). However, the later compound was synthesized at lower temperature (1130 K) while the BAM must be synthesized at around 1870 K. Thus, Ba\(_2\)CaB\(_6\)O\(_{12}\) can be preferred in terms of the energy saving during the synthesis.

The VUV-UV spectra and its emission spectra of Eu\(^{2+}\) doped Ba\(_2\)CaB\(_6\)O\(_{12}\) are shown in Fig. 3. The emission peak is at around 445 nm, which is identical to that excited under 254 nm excitation. It can be observed that the emission intensity is much lower than that excited under 254 nm. The excitation peak is at around 160 nm, which is assigned to the band gap of the host, reflecting the energy difference of conduction band and valence band of the host Ba\(_2\)CaB\(_6\)O\(_{12}\) and is mainly determined by the energy of antibonding and bonding orbital of the anions. It is reported\(^{16}\) that five processes are involved in the VUV excited luminescence of rare earth ions: (i) The \(f\rightarrow f\) transition of the rare earth ions: a direct photon absorption promotes one \(f\)-electron from the ground state to the 4\(f\) excited levels within the 4\(f\)\(^{n}\) ground state configuration; (ii) The \(f\rightarrow d\) transitions of the rare earth ions; (iii) Charge transfer band (CTB) from coordination anions to the rare earth ions; (iv) The absorption of the host lattice; and, (v) The 4\(f\rightarrow 6s\) transition of rare earth ions. Another band with peak at around 200 nm is also observed. The band is similar to the band of Eu\(^{2+}\) in CaO, which is ascribed to the sensitizer band of Ca-O (rather than the band of B-O), i.e. the excitation energy is absorbed by the host and then transferred to the activator in the relaxation process\(^{16}\). However, since no detailed structure data were reported for Ba\(_2\)CaB\(_6\)O\(_{12}\), it is uncertain if this O atom is so called “free oxygen atom”, namely, this oxygen atom is only bonded to the Ca rather than B or Ba.

Fig. 3—Schematic diagram of the proposed model for the excitation and emission processes of Eu\(^{2+}\) in Ba\(_2\)CaB\(_6\)O\(_{12}\) under VUV and UV excitation.

It is unfortunate that the emission intensity under VUV excitation is much lower than that excited under 254 nm. This may be explained by the fact that the UV irradiations directly excite the Eu\(^{2+}\) ions via 4\(f\)\(^5\)5\(d\)\(^1\) level (direct excitation), where efficiency is only governed by the amount of Eu\(^{2+}\) ions. However, the emission mechanism under VUV excitation is different from under UV excitation. It was reported that during VUV excitation, the excitation initially induces the creation of electron/hole pairs causing the excited electrons from the valence band into conduction band\(^{17}\). These pairs migrate toward the dopant Eu\(^{2+}\) ions and are trapped leading a radiative recombination via the excited state of the activators or they create an exciton like state, which then can transfer its energy to the dopants. A schematic diagram of proposed model for the excitation and emission process under VUV and UV excitation is depicted in Fig. 3. Such a host-activator process is an indirect excitation and the luminescence efficiency of Eu\(^{2+}\) in this host under VUV excitation is governed by the transfer efficiency from the host to activator rather than by the amount of Eu\(^{2+}\) ions. It is expected that such process will reduce the efficiency of the energy transfer to the Eu\(^{2+}\) ions and results in a weaker intensity in its emission.

In Ba\(_2\)CaB\(_6\)O\(_{12}:\)Eu\(^{2+}\), the emission of Eu\(^{2+}\) is exhibited by two different sites in the lattice under both the vacuum ultraviolet (VUV) and ultraviolet (UV) excitation. In these structures, there are linear rows of three cations, which can be occupied by Eu\(^{2+}\) ion. It is observed that the emission spectra of Eu\(^{2+}\) under VUV and UV consist of two broad bands with peaks at 437 and 467 nm, which are associated with the \(f\rightarrow d\) transitions of Eu\(^{2+}\) in the sites of Ba\(^{3+}\) and Ca\(^{2+}\), respectively. The longer wavelength emission is due to Eu\(^{2+}\) on the central position in the row while the shorter wavelength emission is due to the terminal
Two weak peaks in VUV range are observed at 160 and 200 nm. The former is derived from the absorption of BO$_3^{3-}$, and the later is associated with the absorption of Ca-O. The energy transfer from the host to activator is observed.

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