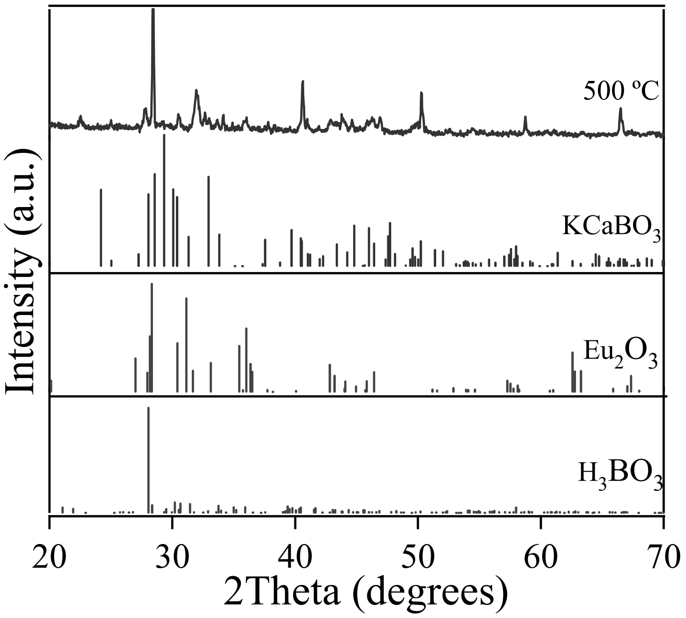
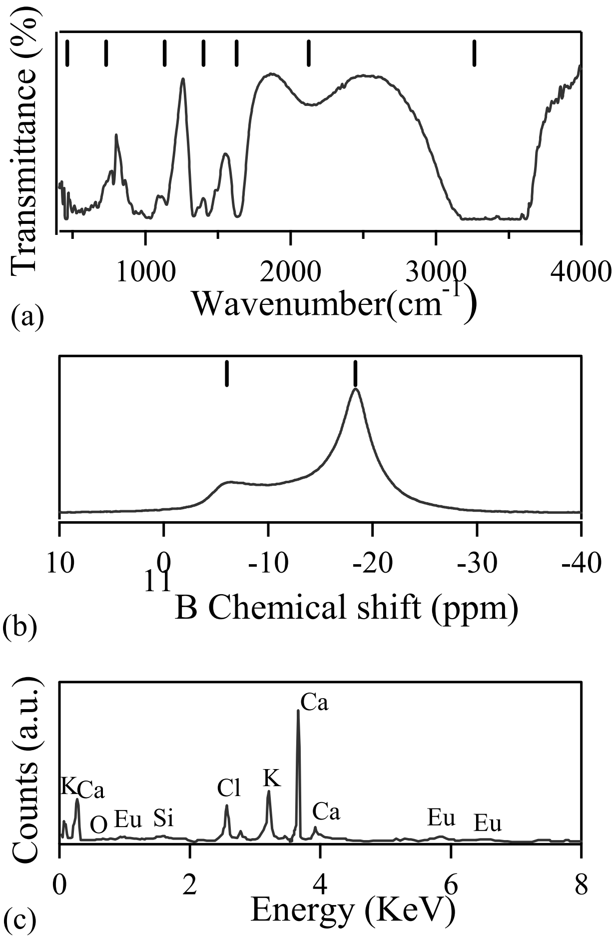
Supplementary data

The following results and discussions are for the low-temperature (500˚C) processed phosphors.



Sup-Figure 1: Room temperature XRD patterns of $KCaBO_3$:Eu^{3+} sample treated at 500 ºC.

Note: The diffraction pattern of the phosphor prepared at 500 ºC shows mixed phase and some of the XRD peaks coincide with the standard monoclinic phase $KCaBO_3$ (an analogous of $LiBaBO_3$; JCPDS card no. 00-023-0472). Presence of Diffraction peaks related to triclinic H_3BO_3 (JCPDS card no. 73-2158) and monoclinic Eu_2O_3 (JCPDS card no. 34-0072) which suggests the incomplete reaction at low temperature annealing.

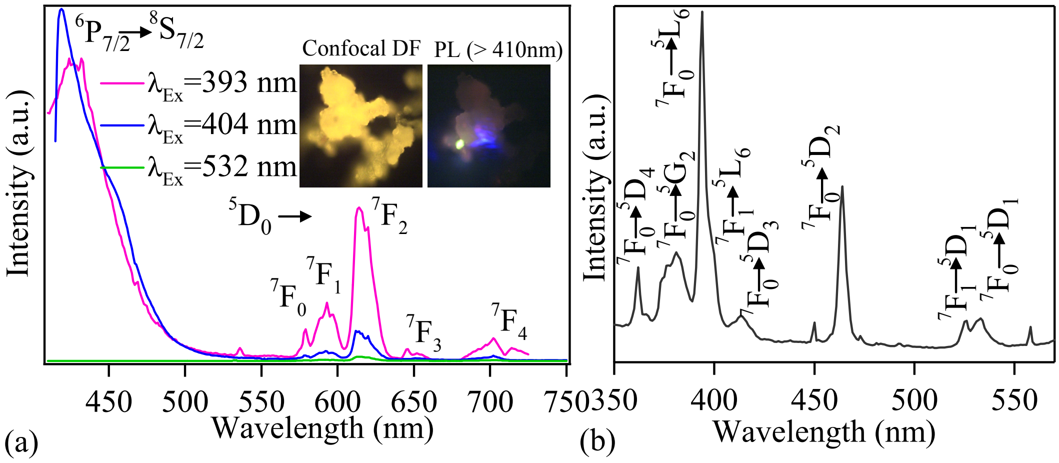


Sup-Figure 2: Room temperature (a) FTIR (b) ^{11}B-MAS NMR chemical shift and (c) EDX spectra of $KCaBO_3:Eu^{3+}$ sample treated at 500 ºC.

Note: The FTIR spectrum (sup-Fig 2a) is rich in transmission dips of different vibrational energies of various B-O bonds and shows strong annealing temperature dependence. The broad transmission dips at 3430 cm^{-1} and 1630 cm^{-1} corresponds to the O–H stretching vibrations, while the broad band at ~2100cm^{-1}, appeared only at 500 ºC temperature, has been attributed to water related symmetric hydrogen bonds.[17-19] However, the broad nature of spectra in the spectral region between 2000 and 3500 cm^{-1} got widened in the sample heated at 500 ºC due to the co-existence of residual KCl and $CaCl_2$ in the crystal lattice and their transmission decreases with the increase of annealing temperature.[20] The asymmetric stretching vibrations of $(BO_3)^{-3}$ units are in the region 1200-1613 cm^{-1} and the symmetric stretching vibrations of $(BO_3)^{-3}$ units is observed around 1149 cm^{-1}. The sharp IR bands at 707 cm^{-1} could be attributed to the bending vibration of triangular BO_3 units and the bands around 480 cm^{-1} is of di-borate group.[17,18] Furthermore, the IR absorptions due to boron in a tetrahedral oxygen coordination were also found in the between 900 and 1100 cm^{-1} in the sample synthesized at 500 ºC, suggesting the existence of the mixed phase.

The basic NMR pattern (sup-Fig 2b) of the sample annealed at 500 ºC is consists of a sharp peak (-18ppm) superimposed over a broad peak (-6ppm), which appears as shoulders symmetrically placed on either side of the sharp peak. The broad peak can be attributed to the trigonally coordinated BO_3 structural units and the sharp peak to the tetrahedrally coordinated BO_4 structural units as in most of the borate containers, boron exists in both BO_3 and BO_4 structural units. As ^{11}B is a quadrupolar nuclei (I = 3/2), due to the lack of cubic symmetry, boron nuclei in BO_3 structural units suffers from significant quadrupolar interaction resulting in a broad resonance peak. However, in this case the spectrum shows negligible quadrupolar interaction and hence gives a sharp peak. Moreover, a distinct difference in peak positions and shapes can be seen in the spectra at higher temperature annealed samples. (sup-Fig 2b)

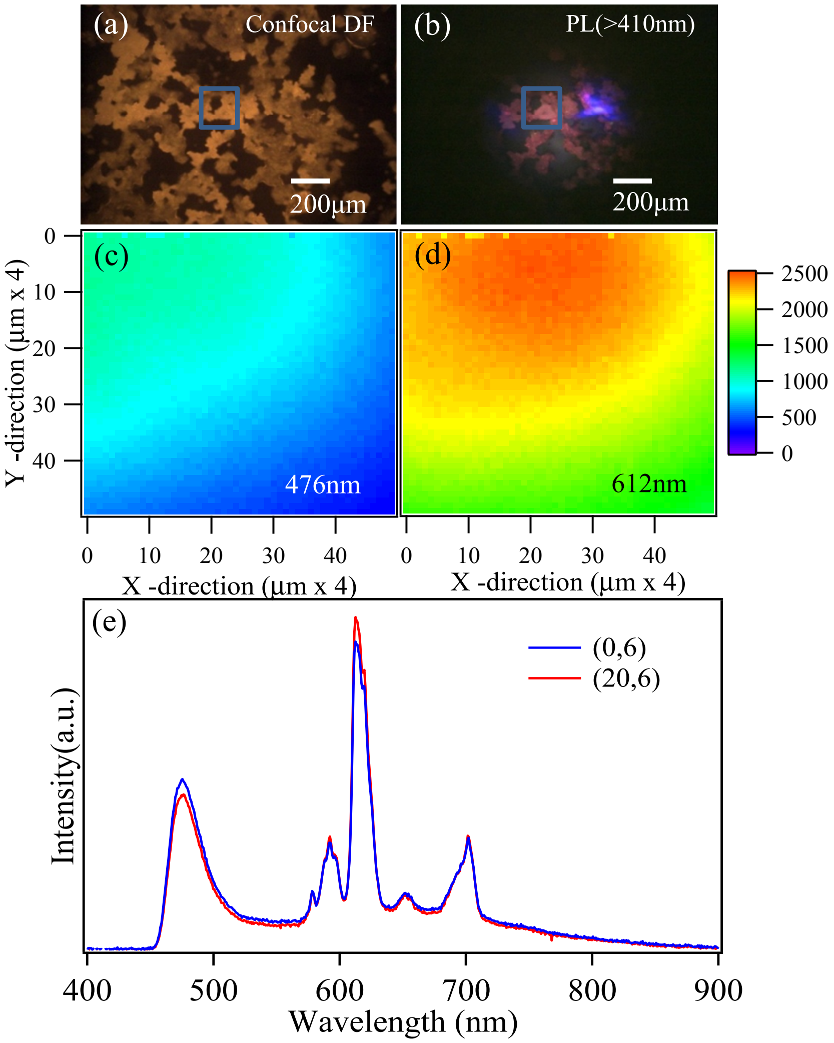
The qualitative EDX microanalysis (sup-Fig 2c) of the chemical composition of $KCaBO_3:Eu^{3+}$ annealed at high temperature is performed indicating that the major components of the resultant phosphor are K, Ca, B, O and Eu elements. Prominent trace of Cl, from initial chemical ingredients is also witnessed.



Sup-Figure 3: Room temperature (a) emission spectra (λ_{ex}= 393, 404 & 532nm) and (b) excitation (λ_{em}=616nm) of the $KCaBO_3:Eu^{3+}$ powders annealed at 500 ºC temperature.

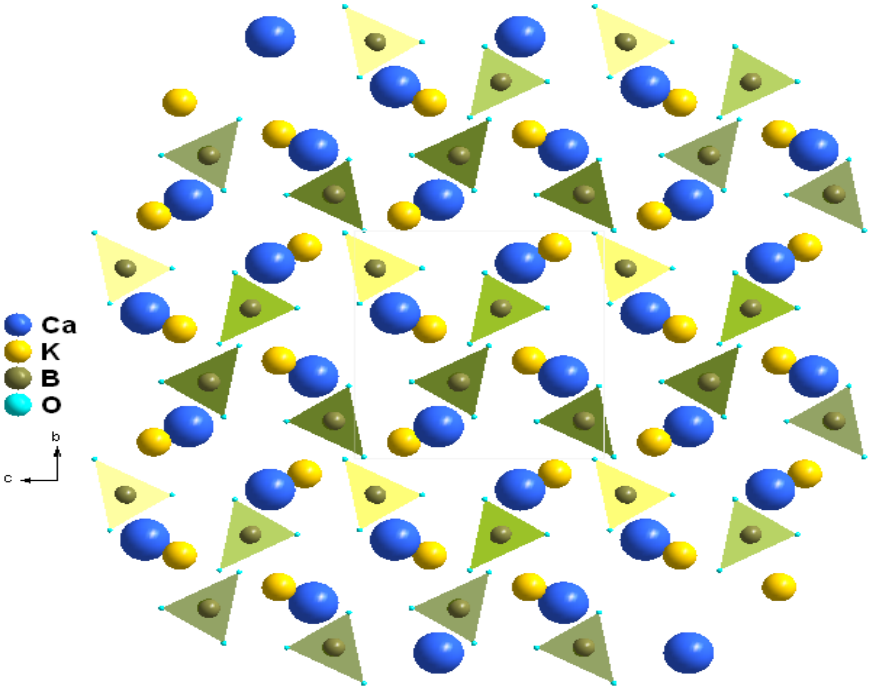
Note: The PL spectra show red-orange emission even to the naked eye (sup-Fig 3a (inset)). The spectrum is dominated by a strong featureless violet-blue emission band (about 80 nm FWHM) at 429 nm, when excited with wavelength 404 nm. Essentially this emission band is not part of typical Eu^{3+} emission transitions. The broad emission at 429 nm can be identified as a result of Eu^{2+}, where the emission is related to the transition from lowest $(4f^6)5d$ excited state $^6P_{7/2}$ to the $^8S_{7/2}$ ground state of Eu^{2+} ion and corresponding discussion can be found in the main text.

The excitation spectra (sup-Fig 3b) show rich spectral lines spanning 350 to 500 nm covering all commercially available UV/blue/violet LEDs to improve the color rendering property for W-LED. These characteristic transitions are from the ground $^7F_0$ and $^7F_1$ (thermally populated) states to various excited states of Eu^{3+}.



Sup-Figure 4: Confocal **(a)** image light (white light illuminated dark field mode) and **(b)** PL (λ_{ex}= 404nm) images recorded using high-resolution images for $KCaBO_3:Eu^{3+}$ phosphors annealed at 500°C. (Colors are not to be scaled).The PL spatial scans (4µm step) monitored at (c) 476nm and (d) 612nm PL peaks respectively (see text).

Note: To know the coexistence of Eu^{3+}/Eu^{2+} photoluminescence and its microscopic distribution within the 500 ºC annealed phosphor, the PL spatial mapping has been performed over 200×200 μm^2 . Unlike 700 ºC annealed phosphor, the red photoluminescence (612nm), related to Eu^{3+} is found to be equally intense to the photoluminescence related to Eu^{2+} (476nm) (sup-Fig. 4e).Moreover, the 500ºC annealed phosphor is having almost uniform distribution of Eu^{2+}/Eu^{3+} emission locations throughout the sample (Fig.4c and Fig. 4d).



Supl-Figure 5: Diamond drawing of the monoclinic $KCaBO_3$ from the LeBail fitting procedure of the powder X-ray diffraction pattern of the sample annealed at 900ºC (see Fig1 from the mail text).

Note : It is found that the structure can be constructed from a stack of [KBO] and [CaO] layers along the [100] direction, distributed alternately. In the [KBO] layers, the isolated $[BO_3]^{3-}$ anionic groups distribute along two directions, some of them run parallel with the [011] direction, while the others run parallel to the [011] direction. Those KO_5 polyhedra share corners with each other via bridging-oxygen atoms, and locate in the intersections of [011] and [0-11] as a bridging role, joining the adjacent BO_3 triangles. In the [CaO] layers, the Ca atoms are coordinated with seven oxygen atoms, forming mono-capped distorted trigonal prisms, sharing edges with each other.