Electronic Supplementary Information:

Unusual red luminescence and super thermal stability of a new narrow band emission phosphor for backlight display application

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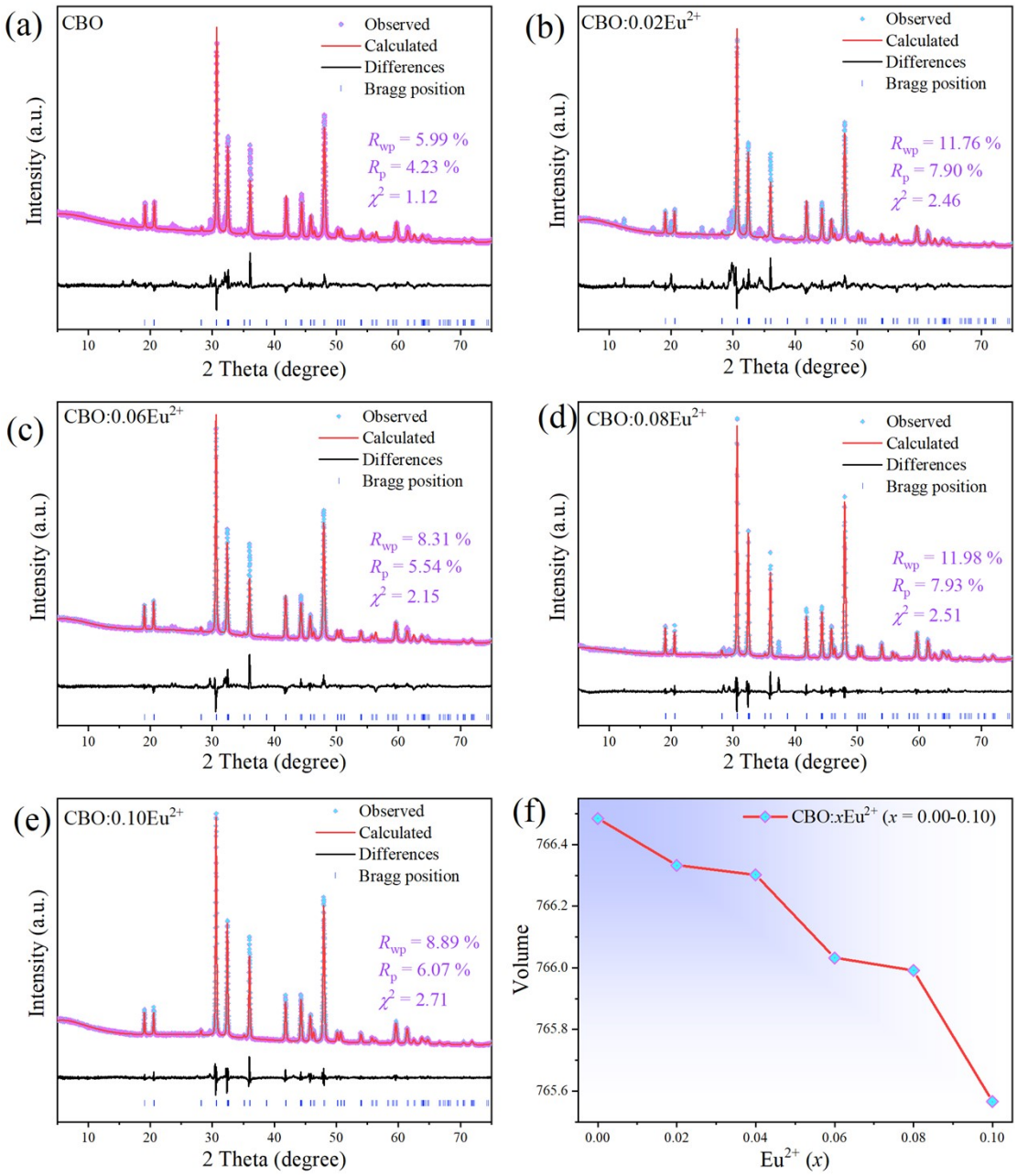

Figure S1. The rietveld refinement of the powder XRD profiles of (a) CBO, (b) CBO:0.02Eu^{2+}, (c) CBO:0.06Eu^{2+}, (d) CBO:0.08Eu^{2+}, and (e) CBO:0.10Eu^{2+}, respectively; (f) The Volume of CBO:$x$$Eu^{2+}$ (x = 0.00-0.10).

Table S1. Refined Crystallographic Parameters of the CBO:xEu^{2+} (x = 0-0.10) Samples.

x	0.00	0.02	0.04	0.06	0.08	0.10
Crystal System	Trigonal system					
Space Group	R-3c					
a (Å)	8.6331 (139)	8.6316 (151)	8.6289 (204)	8.6313 (123)	8.6330 (141)	8.6326 (89)
c (Å)	11.8681 (280)	11.8794 (299)	11.8725 (405)	11.8777 (245)	11.8679 (284)	11.8736 (175)
β (Å)	90	90	90	90	90	90
γ (Å)	120	120	120	120	120	120
V (Å^3)	766.485 (27)	766.333 (29)	766.302 (39)	766.032 (24)	765.991 (27)	765.566 (18)
U_{iso}	0.03959	0.03879	0.03390	0.02217	0.00946	0.00399
2θ-Interval (°)	5-75					
Z	6					
R_{wp} (%)	5.99	11.76	11.60	8.31	11.98	8.89
R_p (%)	4.23	7.90	7.87	5.54	7.93	6.07
χ^2	1.12	2.46	1.51	2.15	2.51	2.71

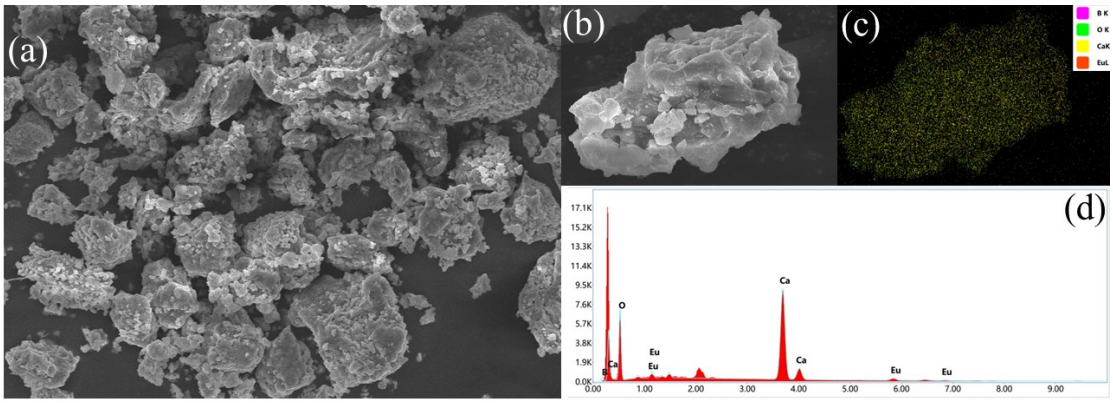

Figure S2. (a) and (b) SEM diagrams of CBO:Eu^{2+} phosphor at different magnification; (c) element mappings of Ca, B, O and Eu; (d) element content analysis of Ca, B, O and Eu.

Table S2. Optical properties of CBO:Eu^{2+} and commercial phosphors.

phosphor	The strongest PLE peak	PLE range	The strongest PL peak	PL range	FWHM
$Sr_2SiN_8:Eu^{2+}$	~395 nm ~450 nm	250-570 nm	610 nm	500-750 nm	85 nm
$Y_2O_3:Eu^{3+}$	260 nm	230-600 nm	624 nm	500-730 nm	Sharp emission
$CaAlSiN_3:Eu^{2+}$	466 nm	200-600 nm	650 nm	500-800 nm	100 nm
$K_2SiF_6:Mn^{4+}$	~420 nm ~455 nm	300-500 nm	631 nm	610-650 nm	Sharp emission
CBO:Eu^{2+}	465 nm	400-625 nm	640 nm	570-725 nm	50 nm

Thanks to highly condensed network structure, CBO:0.04Eu^{2+} shows a surprising narrow-band red emission at 640 nm with FWHM of only 50 nm under 465 nm excitation. Therefore, such PLE band of CBO:0.04Eu^{2+} matches well with the blue LED chip. As shown in the inset (Fig. 3b), the as-prepared powder gives a red light under 365 nm lamp irradiation, and CBO:0.04Eu^{2+} displays a pale red body color under natural light which is since the phosphor absorbs part of the short-wavelength visible light. Moreover, the peak wavelengths and FWHM values of CBO:$x$$Eu^{2+}$ are basically unchanged for different Eu^{2+} doping concentrations (Fig. 3a). The corresponding PLE spectrum of CBO:0.04Eu^{2+} monitored at 640 nm exhibits a broad band from 560 to 750 nm, indicating that it can be excited by blue to red light.

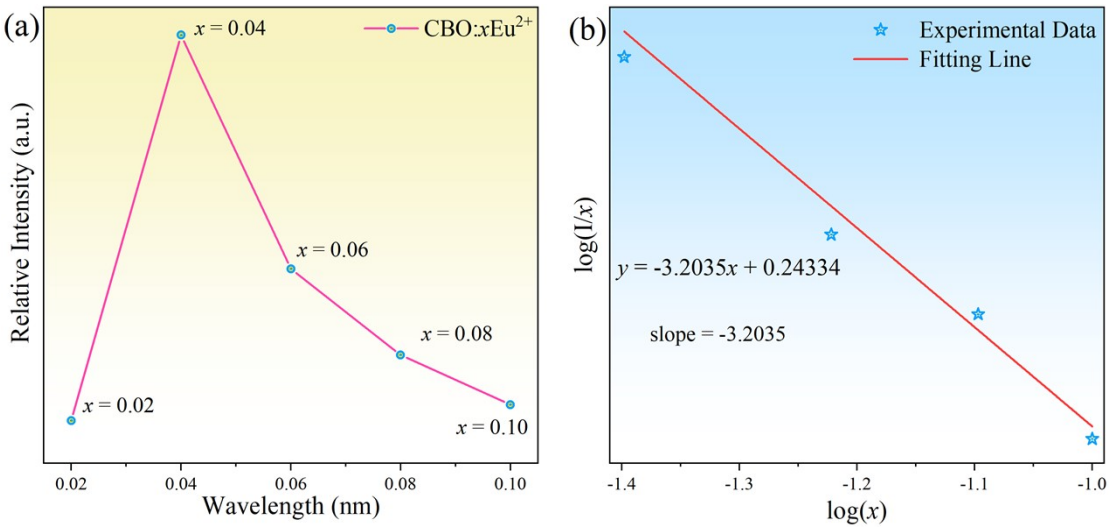

Figure S3. (a) The relative intensity of CBO:xEu^{2+} dependent on the Eu^{2+} content. (d) Fitting line of log(I/x) versus log(x) in CBO:xEu (x = 0.04−0.10) phosphors.

The nonradiative energy migration mainly contains three possible pathways: electric−multipolar interaction, radiation reabsorption, and exchange interaction (R_c) between activators. To clarify the energy-transfer mechanism of CBO:xEu^{2+}, the critical distance was calculated by eq 1:[1]

$$R_c = 2\left(\frac{3V}{4\pi x_c N}\right)^{1/3} \quad (1)$$

where x_c represents the optimized concentration of Eu^{2+} in the CBO host, V stands for the unit cell volume, and N denotes the number of ion sites for Eu^{2+} per unit cell. For the CBO host, x_c = 0.04, N = 6, and V = 765.61 Å^3 calculates that the R_c value is about 12.66 Å. It is well-known that exchange interaction is the dominant role only if R_c is shorter than 5 Å, and thus the concentration quenching in CBO:xEu is more likely through the electric−multipolar interaction. Moreover, the multipolar interaction type can be determined by the following equation 2:

$$\frac{I}{x} = k\left[1 + \beta(x)^{\frac{\theta}{3}}\right]^{-1} \quad (2)$$

where I is the emission intensity at the current concentration, x means the Eu^{2+} concentration, and the values of k and β are constant. The constant θ determines the type of electric-multipolar interaction, for which θ = 6, 8, and 10 refers to dipole-dipole (d-d), dipole-quadrupole (d-q), and quadrupole-quadrupole (q-q) interactions,[2-4] respectively, whereas θ = 3 represents the energy migration between nearest or next nearest Eu^{2+} cations. Equation 2 can be reduced to eq 3 because $\beta(x)^{\theta/3} \gg 1$, as follows:

$$\log\left(\frac{I}{x}\right) = K - \frac{\theta}{3}\log x \quad (K = \log k - \log b) \quad (3)$$

Fig. S3b shows the dependence of log(I/x) on log(x), which can be fitted linearly, and the slope equals −3.2035. Thus, the θ value is calculated as 9.6105, close to 10, implying that the quenching mechanism originates from the quadrupole-quadrupole interactions.

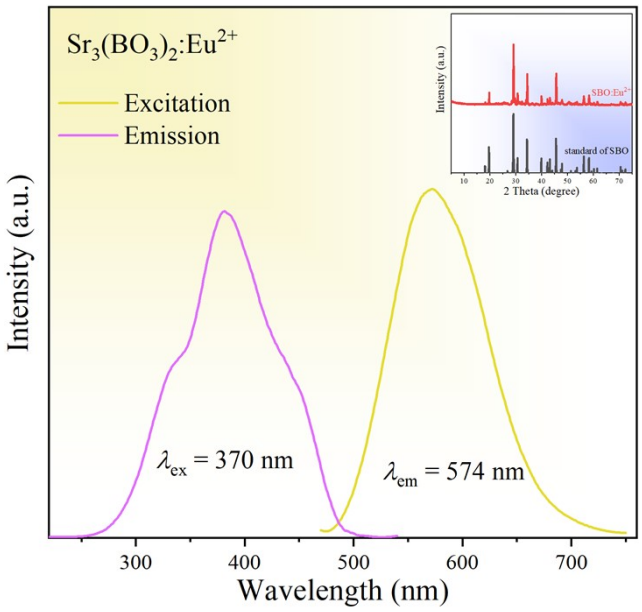

Figure S4. PL and PLE spectra of SBO: Eu^{2+} phosphor, the inset shows XRD for Eu^{2+}-doped SBO.

The external quantum efficiency (EQE) and internal quantum efficiency (IQE) of phosphor CBO:0.04Eu were measured using an integrated sphere on a FLS1000 instrument with a $BaSO_4$ blank tablet as reference (Fig. S5). The EQE and IQE, as well as absorption efficiency (α_{abs}), could be obtained by equations (4), (5), and (6):[5]

$$EQE = \frac{\varepsilon}{\delta} = \frac{\int L_S}{\int E_R} \quad (4)$$

$$IQE = \frac{\varepsilon}{\alpha} = \frac{\int L_S}{\int E_R - \int E_S} \quad (5)$$

$$\alpha_{abs} = \frac{\alpha}{\delta} = \frac{\int E_R - \int E_S}{\int E_R} \quad (6)$$

where α means the absorbed photon numbers, ε means the emitting photon numbers, δ represents the number of excited photons by the light source, L_S means the emission spectrum, E_R stands for the total reflection spectrum of $BaSO_4$ reference, and E_S represents the reflection spectrum of CBO:0.04Eu^{2+}. Accordingly, the α_{abs}, *IQE*, and *EQE* for phosphor CBO:0.04Eu^{2+} were calculated to be 24 %, 15 %, and 42 %.

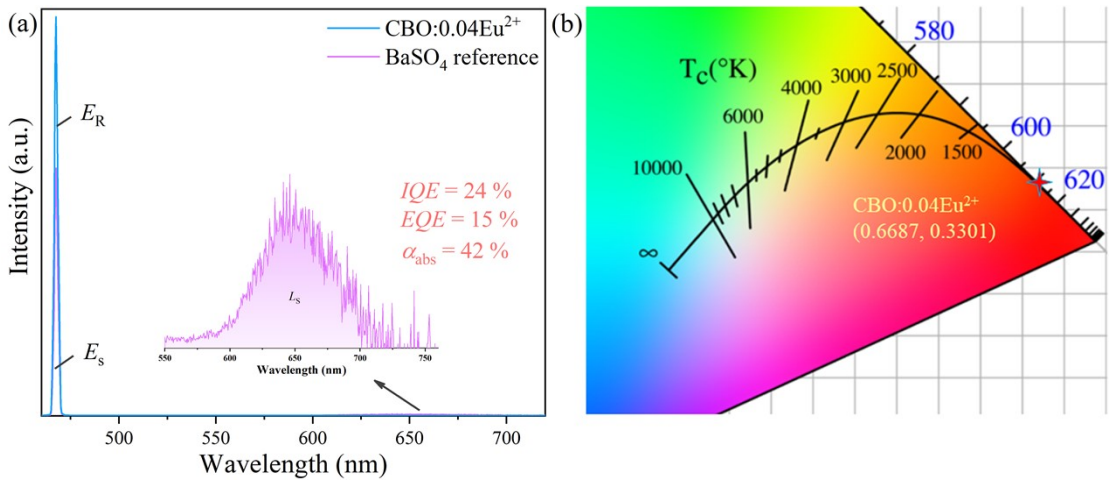

Figure S5. (a) excitation line of $BaSO_4$ and emission spectrum of CBO:0.04Eu^{2+} phosphor collected by using an integrating sphere; (b) CIE chromaticity diagram of CBO:0.04Eu^{2+}.

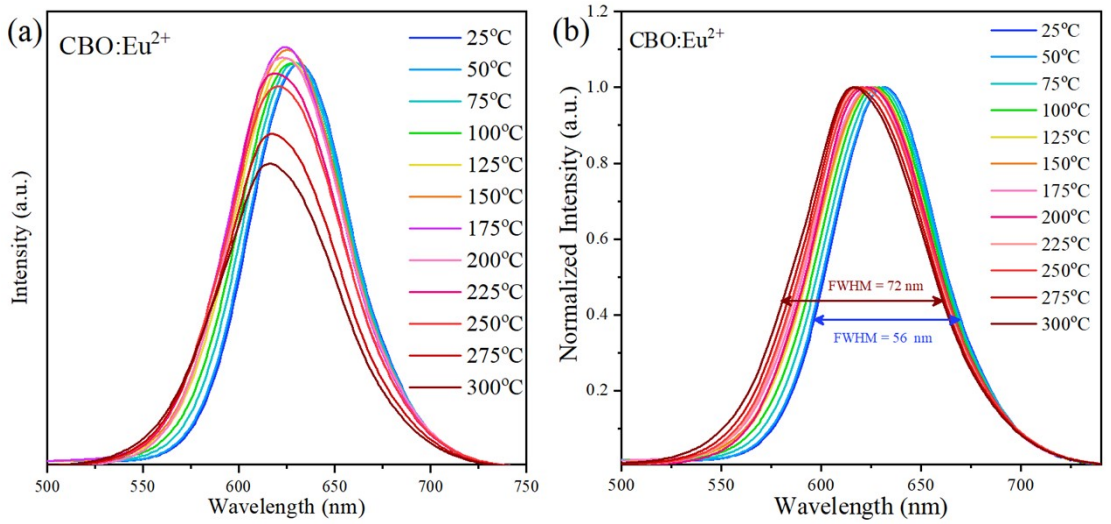

Figure S6. (a) The temperature-dependent PL spectra of CBO:0.04Eu^{2+} at different temperatures from 25 to 300 °C; (b) FWHM of CBO:0.04Eu^{2+} in different temperatures.

Notes and references

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