

Electronic Supplementary Information for

Coordination environment evolution of Eu^{3+} during the
dehydration and re-crystallization processes of
 $\text{Sm}_{1-x}\text{Eu}_x[\text{B}_9\text{O}_{13}(\text{OH})_4]\cdot\text{H}_2\text{O}$ by photoluminescent
characteristics

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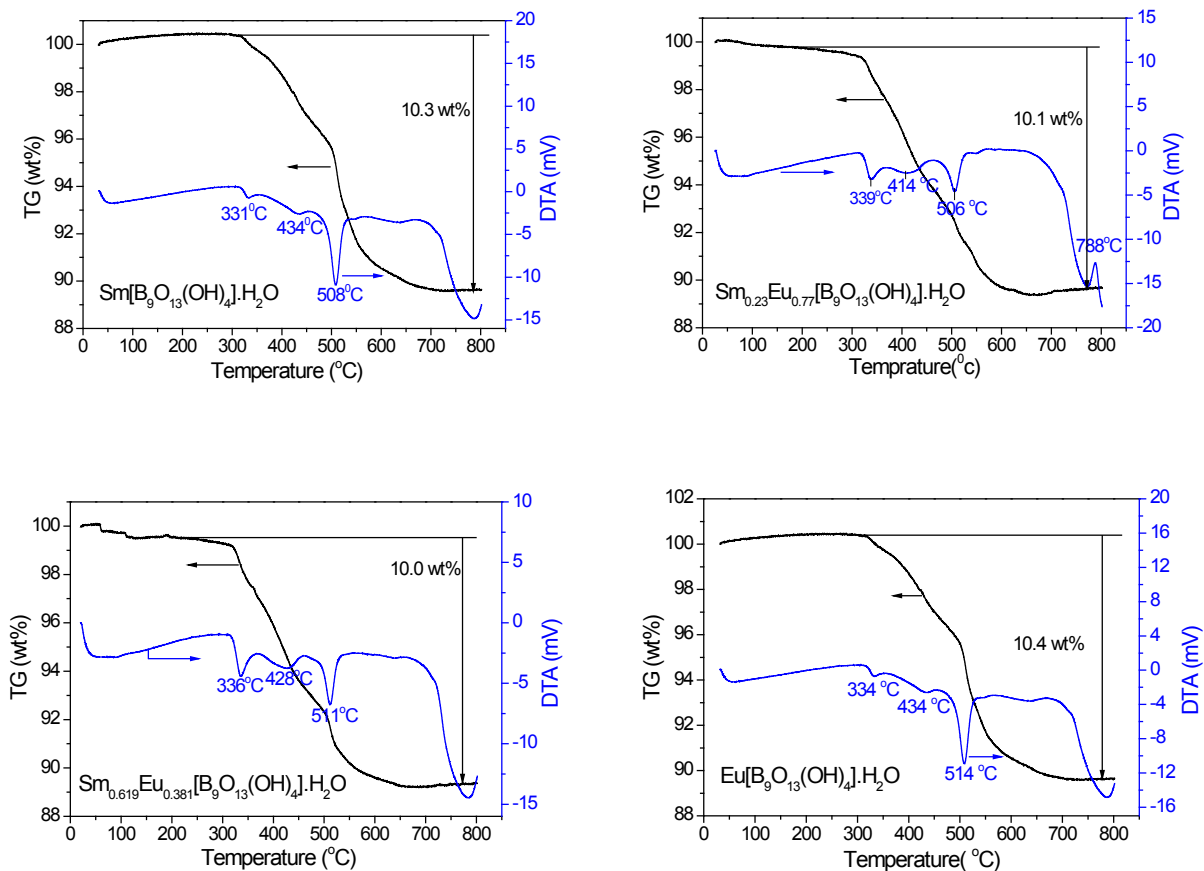


Figure S1 Thermogravimetric analysis (TG) and differential thermal analysis (DTA) curves of as-synthesized $\text{Sm}[\text{B}_9\text{O}_{13}(\text{OH})_4]\cdot\text{H}_2\text{O}$, $\text{Sm}_{0.23}\text{Eu}_{0.77}[\text{B}_9\text{O}_{13}(\text{OH})_4]\cdot\text{H}_2\text{O}$, $\text{Sm}_{0.62}\text{Eu}_{0.38}[\text{B}_9\text{O}_{13}(\text{OH})_4]\cdot\text{H}_2\text{O}$, $\text{Eu}[\text{B}_9\text{O}_{13}(\text{OH})_4]\cdot\text{H}_2\text{O}$ using Shimadzu DTG-60H thermo-gravimetric analyzer in N_2 , with a heating rate of 10 °C/min from 50 °C to 800 °C.

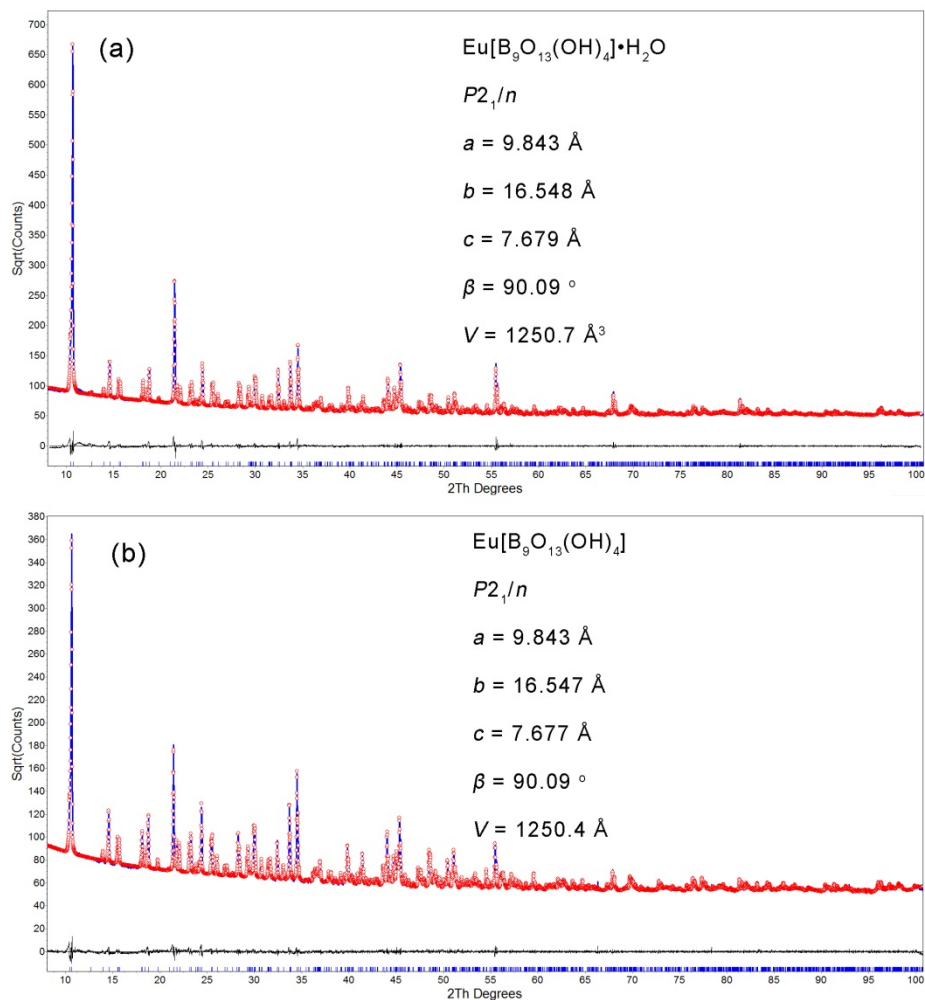


Figure S2. Le Bail fitting of the powder XRD patterns for $\text{Eu}[\text{B}_9\text{O}_{13}(\text{OH})_4]\cdot\text{H}_2\text{O}$ and $\text{Eu}[\text{B}_9\text{O}_{13}(\text{OH})_4]$ (collected by PANalytical Empyrean with Cu $K\alpha$ radiation). The circles \circ represents the observed data and the blue solid line is the calculated pattern; the marks below the diffraction patterns are the expected reflection positions and, the difference curve (in black) is also shown below the diffraction curves. Cell parameters are shown in Figure, which were obtained by Le Bail fitting in TOPAS. Note that the intensity is in square root.

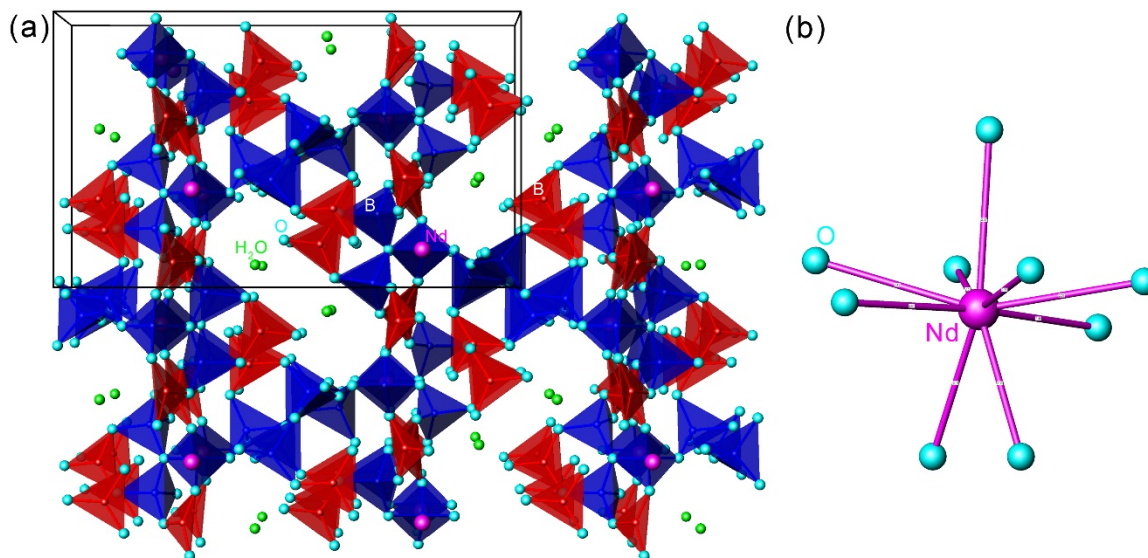


Figure S3. (a) The covalent framework of $\text{Eu}[\text{B}_9\text{O}_{13}(\text{OH})_4]\cdot\text{H}_2\text{O}$; (b) local coordination of Eu^{3+} .

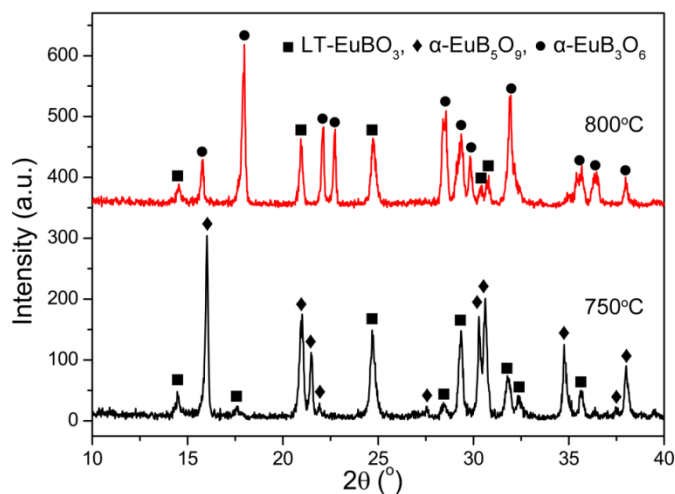


Figure S4. X-ray diffraction patterns of $\alpha\text{-EuB}_5\text{O}_9$ synthesized by conventional solid state reaction.

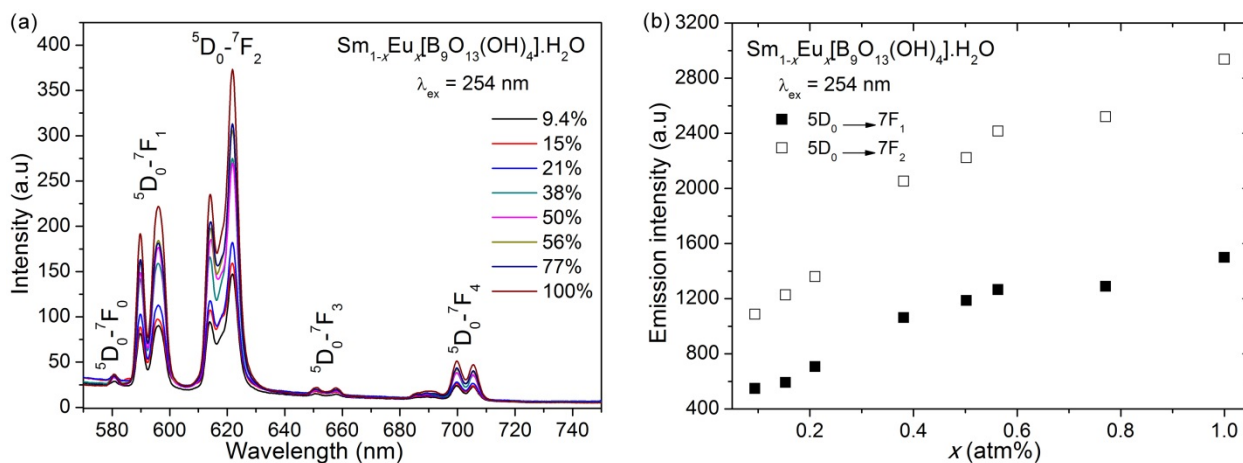


Figure S5. (a) Emission spectra of the $\text{Sm}_{1-x}\text{Eu}_x[\text{B}_9\text{O}_{13}(\text{OH})_4]\cdot\text{H}_2\text{O}$ ($x=0.09-1.00$) samples. (b) Dependence of the emission intensity at 254nm with the doping amount x .

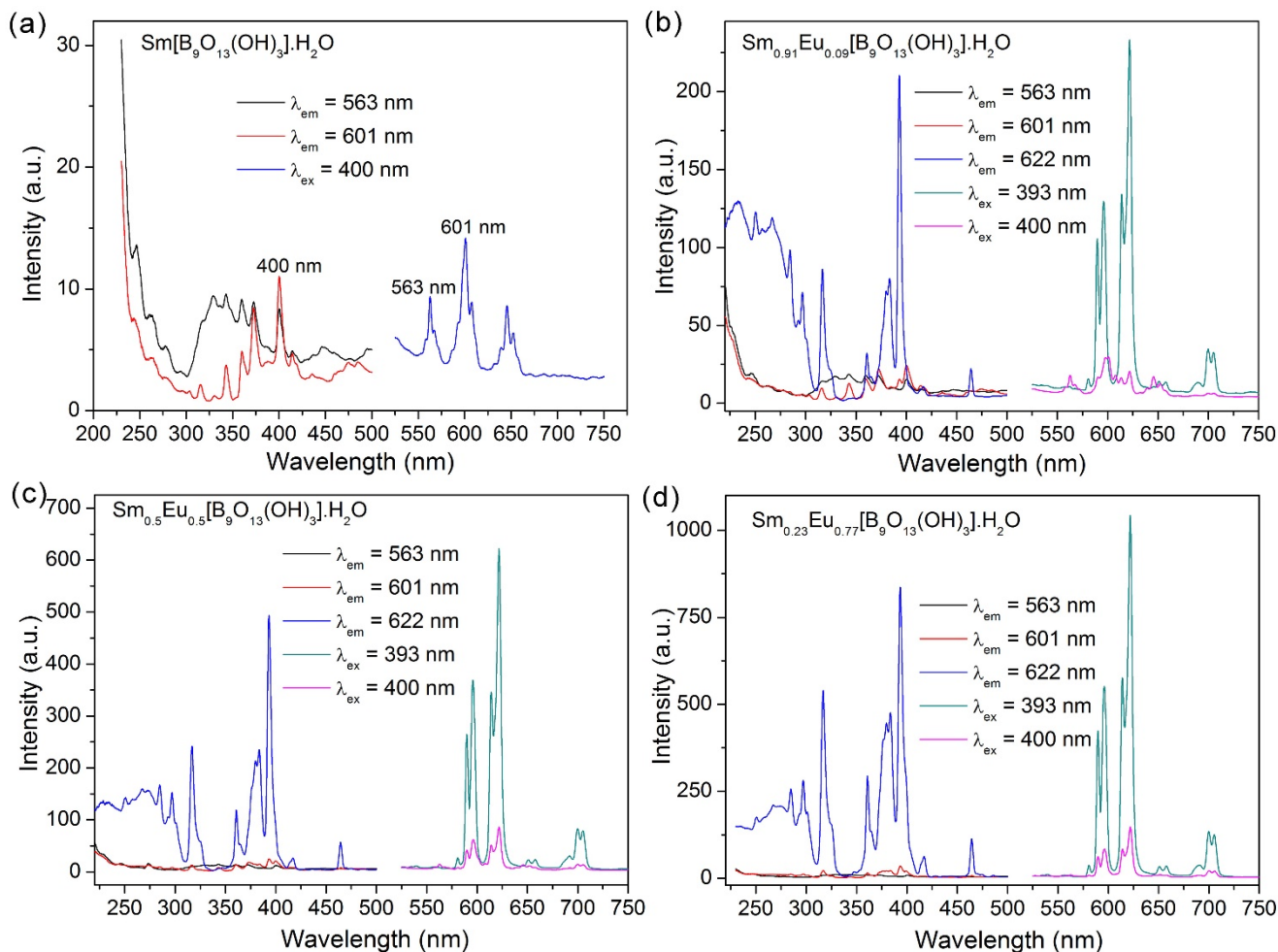


Figure S6. The Sm^{3+} luminescent intensities in the pure Sm-compound are pretty low, as shown in (a), and the strongest absorption occurs at ~ 400 nm. It shows strong emission peaks at 563 and 601 nm.

The latter one show a bit overlapping with the Eu^{3+} $f-f$ transition, while the peaks around 563 nm belong to Sm^{3+} only. In (b-d), there are spectra for $\text{Sm}_{1-x}\text{Eu}_x[\text{B}_9\text{O}_{13}(\text{OH})_3]\cdot\text{H}_2\text{O}$ with three representative concentrations. First, by monitoring 622 nm, which is the strongest emission peak for Eu^{3+} , we can barely see any absorption peaks of Sm^{3+} ; second, by monitoring the Sm^{3+} emission at 563 nm, it shows very limited absorptions for Sm^{3+} ; third, when excited by 393 nm irradiation, the main characteristic of emission belongs to Eu^{3+} , while the Sm^{3+} emissions are not recognizable; when excited by 400 nm irradiation, there show mixed emissions of both Eu^{3+} and Sm^{3+} , although the contribution from Sm^{3+} is small. According to the above observations, we could conclude that the emission of Sm^{3+} can be almost ignored and basically show no influence to the Eu^{3+} luminescence. In other words, Eu^{3+} and Sm^{3+} are very likely separated activators.

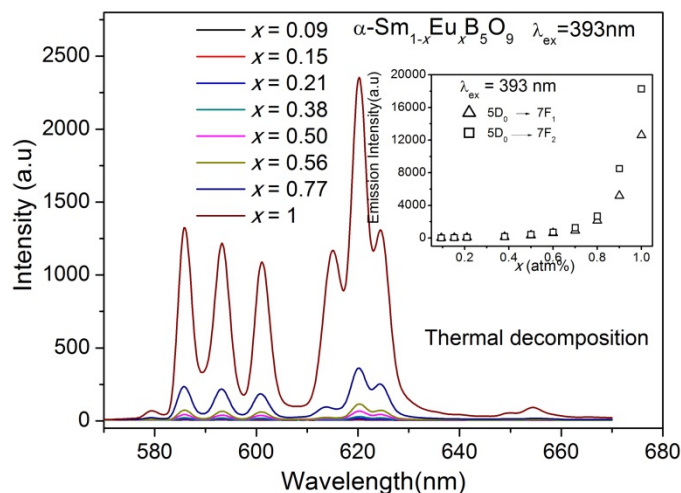


Figure S7. Emission spectra of $\alpha\text{-Sm}_{1-x}\text{Eu}_x\text{B}_5\text{O}_9$ ($x = 0.09\text{-}1.00$) synthesized by thermal decomposed method and variation of the emission intensity with the doping concentration (insert).

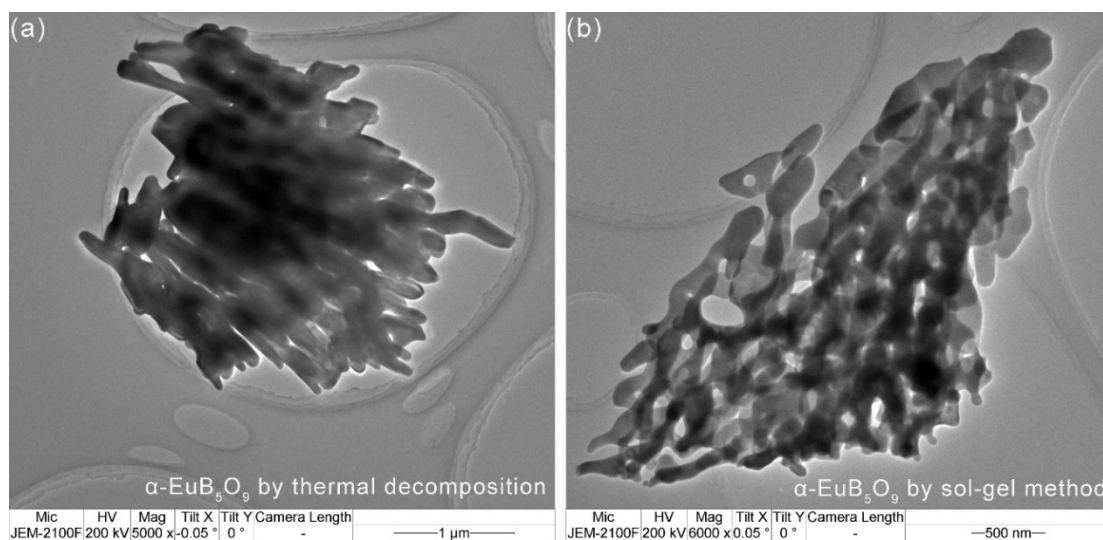


Figure S8. TEM images of $\alpha\text{-EuB}_5\text{O}_9$ synthesized by thermal decomposition and sol-gel method.

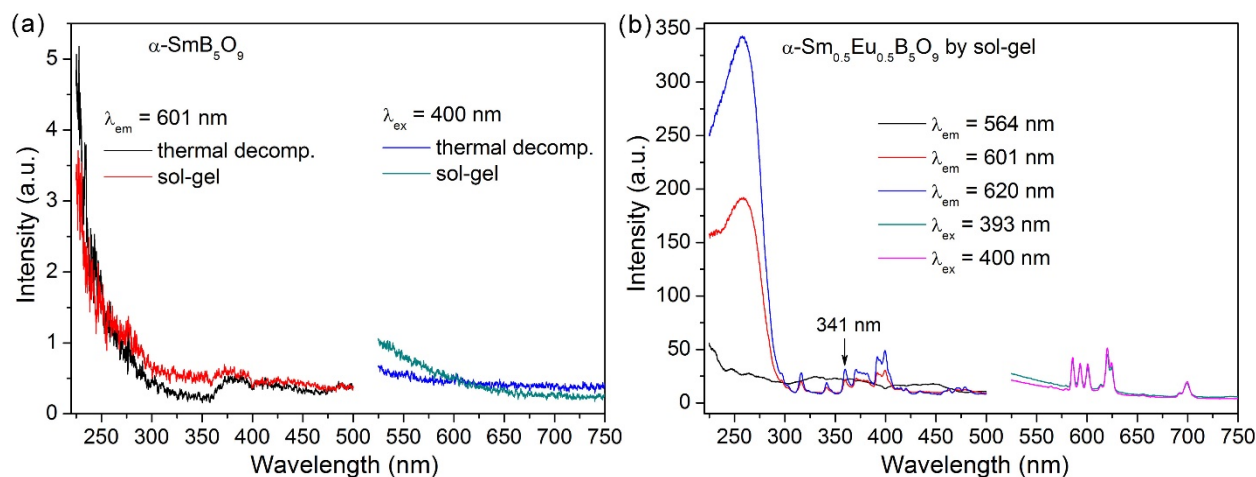


Figure S9. (a) the supposed Sm^{3+} absorption and emission peaks are located at 400 and 601 nm, respectively. However, we did not observe any intensities for $\alpha\text{-SmB}_5\text{O}_9$. (b) when excited by $f\text{-}f$

transitions at 393 and 400 nm, the emission patterns are predominant by $\text{Eu}^{3+} {}^5\text{D}_0 \rightarrow {}^7\text{F}_J$ transitions. By monitoring the Eu^{3+} emissions at 601 and 620 nm, the CT absorption of Eu^{3+} is very strong, while there is also a small peak at 341 nm, which might belong to the $\text{Sm}^{3+} f-f$ transition, so, it is probably an indication of Sm^{3+} to Eu^{3+} energy transfer. Since we are interested with the 254 nm-excited spectra, this plausible energy transfer will not alter our speculations on the Eu^{3+} luminescence for α -pentaborates in the main text.

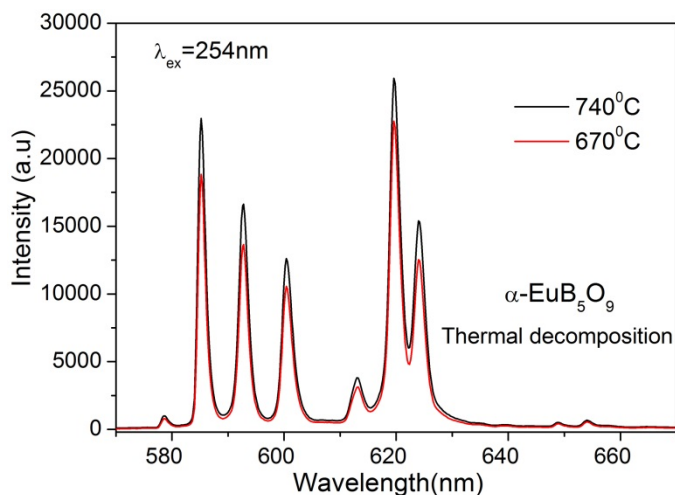


Figure S10. Emission spectra of $\alpha\text{-EuB}_5\text{O}_9$ obtained by thermal decomposition (calcined at 670 °C and 740 °C).