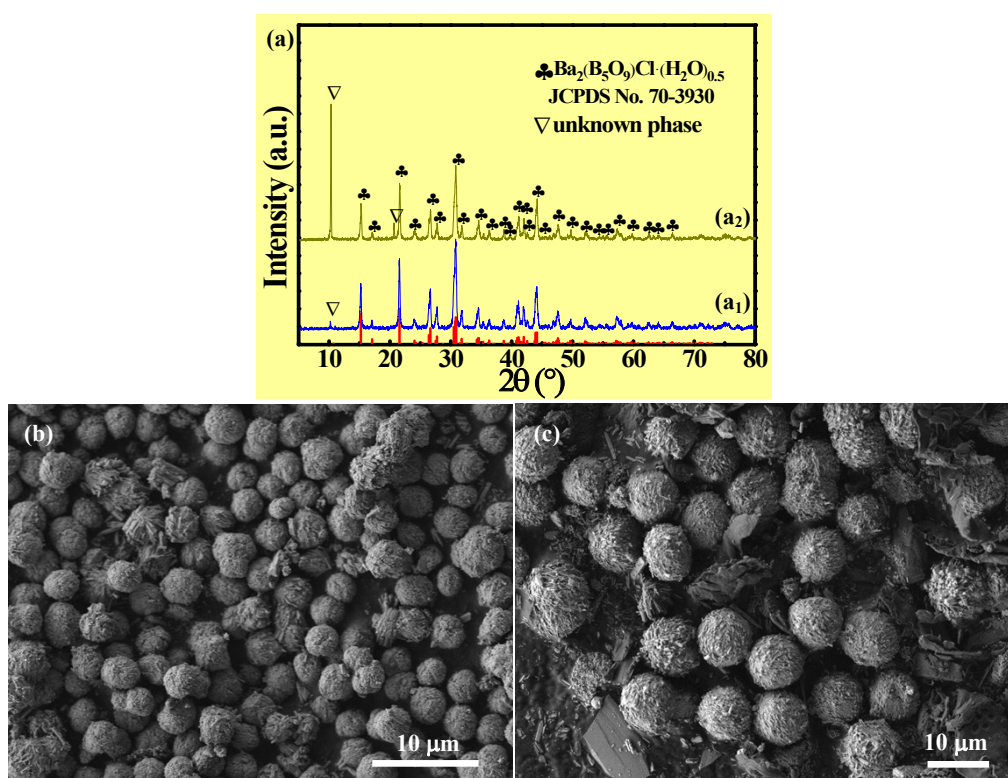


*Electronic Supplementary Information for:*

**Hierarchical  $\text{Ba}_2(\text{B}_5\text{O}_9)\text{Cl}\cdot(\text{H}_2\text{O})_{0.5}$  microspheres: surfactant-assisted facile hydrothermal synthesis,  $\text{Tb}^{3+}$  doping and photoluminescent properties**

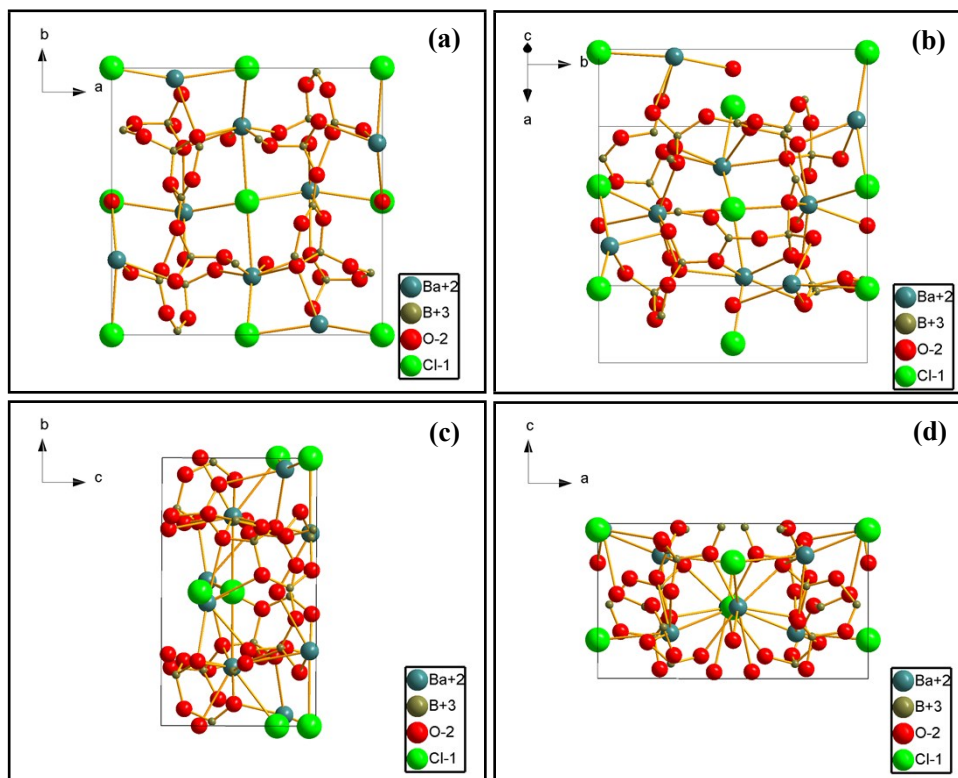
*Xiuping Chen, Linlin Zhang, Zhaoqiang Zhang, Lin Zhu, Wancheng Zhu<sup>1</sup>,*

Department of Chemical Engineering, Qufu Normal University, Shandong 273165, China.

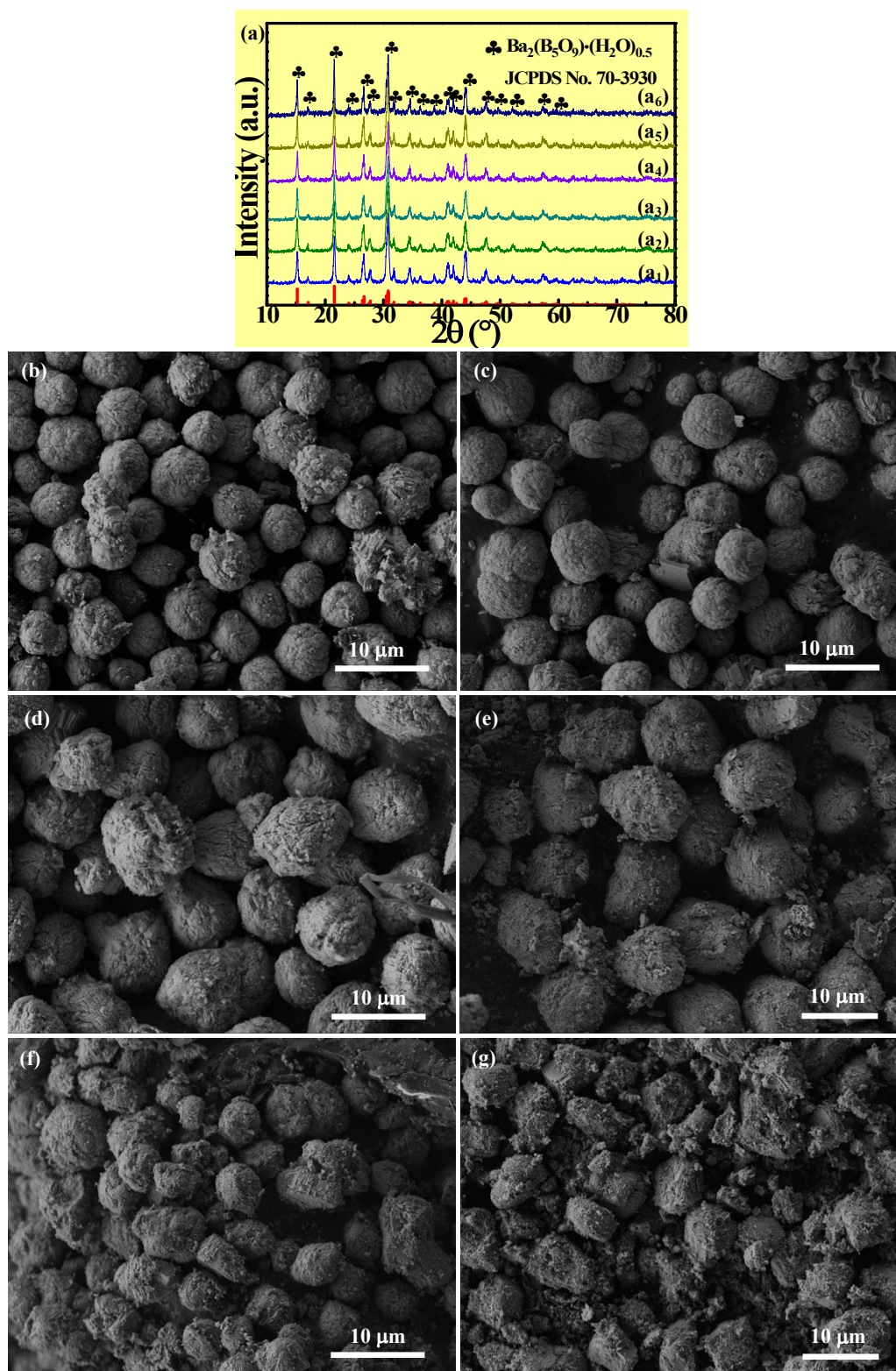


**Fig. S1.** XRD patterns (a) and SEM images (b-c) of the  $\text{Ba}_2(\text{B}_5\text{O}_9)\text{Cl}\cdot(\text{H}_2\text{O})_{0.5}$  microspheres obtained at 160  $^\circ\text{C}$  for different time with the molar ratio of Ba:B:OH as 1:2:1 and initial reactant concentration of  $\text{BaCl}_2$  as 0.313 mol  $\text{L}^{-1}$ . Time (h): (a<sub>1</sub>, b)-12.0, (a<sub>2</sub>, c)-18.0.

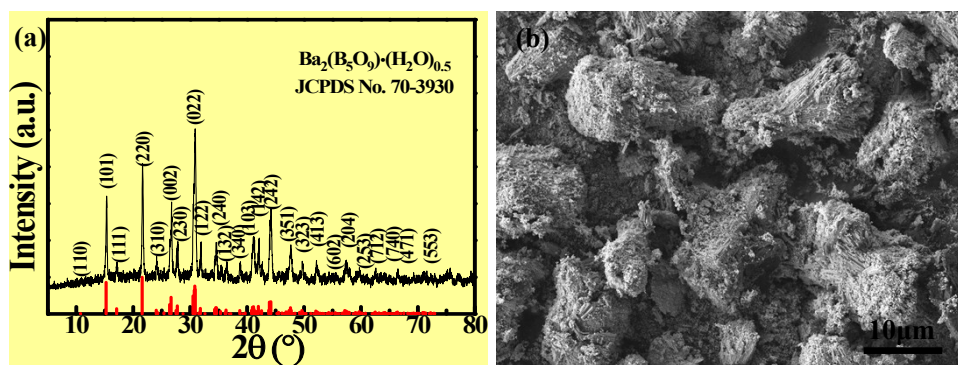
<sup>1</sup> Corresponding author. Tel.: +86-537-4453130; E-mail: [zhuwancheng@tsinghua.org.cn](mailto:zhuwancheng@tsinghua.org.cn) (W. Zhu).



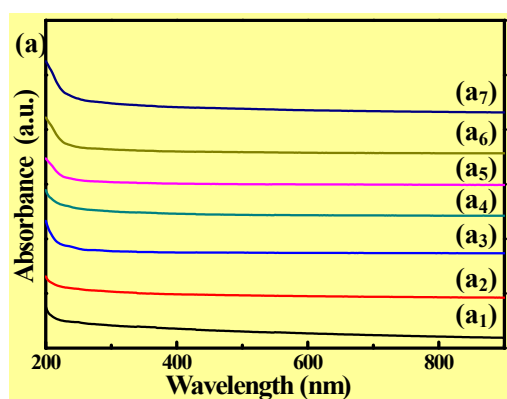
**Fig. S2.** Orthorhombic structure model of  $\text{Ba}_2(\text{B}_5\text{O}_9)\text{Cl}\cdot(\text{H}_2\text{O})_{0.5}$  (JCPDS No. 70-3930,  $a = 11.716 \text{ \AA}$ ,  $b = 11.574 \text{ \AA}$ ,  $c = 6.7 \text{ \AA}$ ,  $\alpha = 90^\circ$ ,  $\beta = 90^\circ$ ,  $\gamma = 90^\circ$  and space group of  $\text{Pnn}2(34)$ ) viewed from different directions. Directions: (a)- $[001]$ , (b)- $[-101]$ , (c)- $[-100]$ , (d)- $[-010]$ .



**Fig. S3.** XRD patterns (a) and SEM images (b-g) of the hydrothermal products obtained at 160  $^\circ\text{C}$  for 6.0 h in the presence of EDTA-2Na as 8.395 mmol  $\text{L}^{-1}$ , with the molar ratio of Ba:B:OH as 1:2:1 and reactant concentration of  $\text{BaCl}_2$  as 0.313 mol  $\text{L}^{-1}$ , whereas with different doping molar percentage of  $\text{Tb}^{3+}$  in  $\text{Ba}^{2+}$  ions. Doping molar percentage (%): (a<sub>1</sub>, b)-1, (a<sub>2</sub>, c)-2 (a<sub>3</sub>, d)-4, (a<sub>4</sub>, e)-6, (a<sub>5</sub>, f)-8, (a<sub>6</sub>, g)-10.



**Fig. S4.** XRD pattern (a) and SEM image (b) of the hydrothermal product obtained at 160  $^\circ\text{C}$  for 6.0 h in the absence of EDTA-2Na, with the molar ratio of Ba:B:OH as 1:2:1, reactant concentration of  $\text{BaCl}_2$  as  $0.313 \text{ mol L}^{-1}$ , and doping molar percentage of  $\text{Tb}^{3+}$  in  $\text{Ba}^{2+}$  ions as 6%.



**Fig. S5.** UV-vis spectra of the  $\text{Tb}^{3+}$  doped  $\text{Ba}_2(\text{B}_5\text{O}_9)\text{Cl}\cdot(\text{H}_2\text{O})_{0.5}$  microspheres with different doping percentage of  $\text{Tb}^{3+}$  in  $\text{Ba}^{2+}$  ions. Doping molar percentage (%): (a<sub>1</sub>, b)-0, (a<sub>2</sub>, c)-1, (a<sub>3</sub>, d)-2, (a<sub>4</sub>, e)-4, (a<sub>5</sub>, f)-6, (a<sub>6</sub>, g)-8, (a<sub>7</sub>, h)-10.