Electronic supplementary information (ESI†)

Ultra-sensitive photoluminescence modification of Eu^{3+} ion based on light tuning surface potential of Bi_3O_4Cl layered semiconductor and application for facile UV light detector

Rui Hu, Yongjin Li*, Zhaoyi Yin, Tianhui Wang, Jianbei Qiu*, Zhengwen Yang, and Zhiguo Song*

School of Materials Science and Engineering, Kunming University of Science and Technology, Kunming, 650093, PR China

**Corresponding Author:*

E-mail: liyongjin@kust.edu.cn (Y. Li).

qiu@kust.edu.cn (J. Qiu).

songzg@kust.edu.cn (Z. Song).

Table S1. Rietveld Refinement and Lattice Parameters of Bi_3O_4Cl and $Bi_3O_4Cl:5\%Eu^{3+}$

	Bi_3O_4Cl	$Bi_3O_4Cl:5\%Eu^{3+}$
space group	$I1_2/a^1(15)$	$I1_2/a^1$ (15)
a (Å)	5.695	5.683
b (Å)	5.648	5.636
c (Å)	18.573	18.541
β (deg)	91.52	91.35
Z	4	4
V (Å^3)	597.20	593.75

According to the Rietveld refined results, the as-prepared $Bi_3O_4Cl:Eu^{3+}$ phosphor is assigned to the monoclinic system and belongs to the $I1_2/a^1(15)$ space group. The lattice parameters are confirmed as a = 5.683 Å, b = 5.636 Å, c = 18.541 Å, β = 91.52°, Z = 4, and V = 593.75 Å^3.[1,2] Compared with the standard cell parameters and cell volume that derive from PDF#86-2221, all values of $Bi_3O_4Cl:Eu^{3+}$ sample show a significant shrinkage, proving the vast substitution of Eu^{3+} ions (1.066 Å, CN = 8) for the bigger Bi^{3+} sites (1.17 Å, CN = 8).

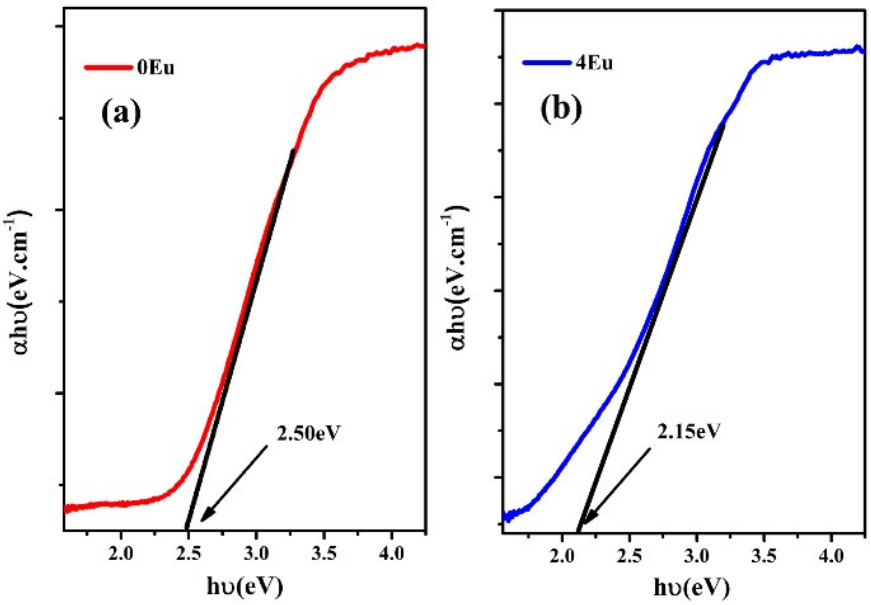

Fig. S1. Plots of $(\alpha hv)^{1/2}$ *vs*. the photon energy (hv) for the as-synthesized undoped Bi_3O_4Cl sample (a) and the Bi_3O_4Cl:4%Eu^{3+} sample (b).

As showed in **Fig. S1a-b**, the absorption edge of Eu^{3+} doped Bi_3O_4Cl sample slightly redshifts compared with that of undoped one (for simplifying, just represented the representative curves of sample with 0 and 4 mol% Eu^{3+}). It indicates that Eu^{3+} ion dopant forming impurity energy levels decreases the forbidden gap of Bi_3O_4Cl, and the calculation of energy band structure is being done by our group.[2]

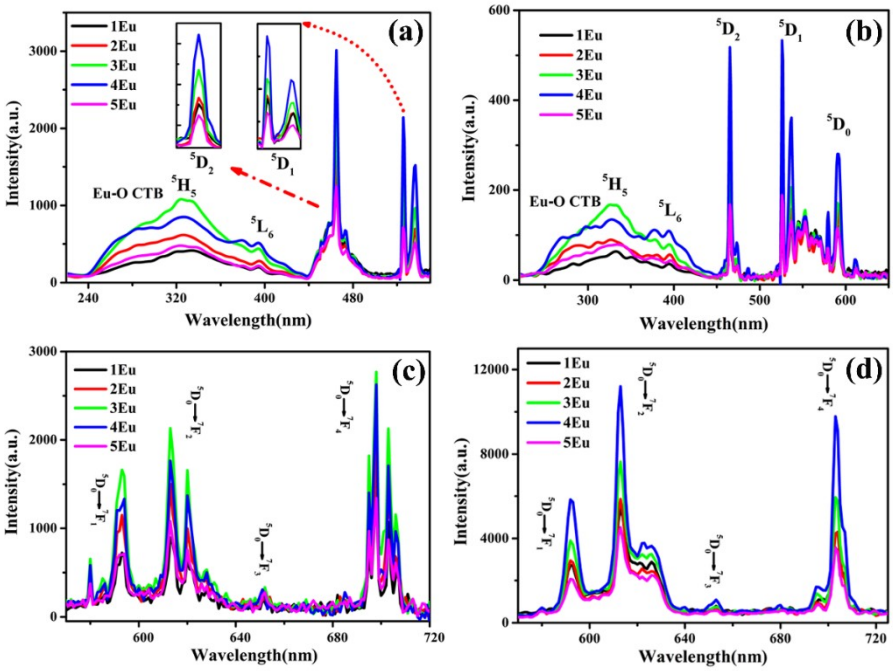

Fig. S2. (a)-(b) Excitation spectra of Bi_3O_4Cl: xEu^{3+} (x = 1, 2, 3, 4, and 5 mol%) micorcrystals recorded at λ_{Em} = 613 nm and 704 nm; (c)-(d) Emission spectra of the same samples upon 320 nm and 465 nm excitation. The insets are the enlarged excitation spectra in $^7F_0 \rightarrow {}^5D_2$ and $^7F_0 \rightarrow {}^5D_1$ transition region, and other excitation bands followed the similar tendency but without presentation for simplifying.

Fig. S2 presents the excitation spectra (a-b) and emission spectra (c-d) of prepared Eu^{3+} doped Bi_3O_4Cl samples with different concentration of Eu^{3+} ions. It shows that whether under absorption-edge (394 and 465 nm) or intraband (526 nm) excitation, the concentration dependence of the emission intensity of Eu^{3+} ion are totally same, except that under deep-UV excitation (320 nm) (Figure S3c-d). This indicates that the photoexcited electrons from broadband excitation may be excited via intermediate electron-hole pair states of semiconductor.

As for the decay times of Eu^{3+}-related emission for Bi_3O_4Cl:4%Eu^{3+} sample, all decay profiles keep following the single exponential decay equation: $I = A\exp(-t/\tau)$,[3,4] where parameters A, I, and t are represent the constant, luminescent intensity, and the decay time,

respectively. Therefore, under 465 nm excitation, the lifetimes of sample were calculated to 1.00 ms (λ_{Em} = 613 nm), 0.92 ms (λ_{Em} = 620 nm), 0.91 ms (λ_{Em} = 698 nm), and 0.99 ms (λ_{Em} = 704 nm), respectively. Meanwhile, under 320 nm irradiation, the obtained results are 1.24 ms (λ_{Em} = 613 nm), 1.17 ms (λ_{Em} = 620 nm), 1.15 ms (λ_{Em} = 698 nm), and 1.17 ms (λ_{Em} = 704 nm), respectively.

Reference

[1] R. D. Shannon, *Acta Crystallographica.* **1976**, *A32*, 751.

[2] X. P. Lin, T. Huang, F. Q. Huang, W. D. Wang, J. L. Shi, *J. Phys. Chem. B* **2006**, 110, 24629.

[3] P. Du, J. S. Yu, *Chem. Eng. J.* **2017**, *327*, 109.

[4] J. Zhou, Z. G. Xia, *J. Mater. Chem. C* **2014**, *2*, 6978.