

## Electronic supplementary information

### Intense one-band near-infrared upconversion luminescence induced by using spontaneous polarization BiOCl sheet crystals as hosts for Yb<sup>3+</sup> and Tm<sup>3+</sup> ions

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### Experimental

#### The preparation of Yb<sup>3+</sup>-Tm<sup>3+</sup> co-doped BiOCl layered micrometer crystals

The Yb<sup>3+</sup>-Tm<sup>3+</sup> co-doped BiOCl layered micrometer crystals were synthesized by the traditional solid state reaction. NH<sub>4</sub>Cl (A.R.), Bi<sub>2</sub>O<sub>3</sub> (99.99%), Yb<sub>2</sub>O<sub>3</sub> (99.99%) and Tm<sub>2</sub>O<sub>3</sub> (99.99%) were used as the starting materials. The mixture ratio of the reactants was: BiOCl:x% Yb<sup>3+</sup>,1% Tm<sup>3+</sup> ( $x = 1, 2.5, 5, 7.5, \text{ and } 10$  mol%). The weighed raw materials were thoroughly mixed in an agate mortar and then placed in a corundum crucible. Then, the powders were sintered at 500 °C for 3 h in air. Some

excessive  $\text{NH}_4\text{Cl}$  (20 mol%) is necessary for loss of Cl source at high temperature to obtain the pure phase formation.

### **The preparation of $\text{Yb}^{3+}$ - $\text{Tm}^{3+}$ co-doped $\text{BiOCl}$ nanocrystals**

The  $\text{Yb}^{3+}$ - $\text{Tm}^{3+}$  co-doped  $\text{BiOCl}$  nanocrystals were prepared by the hydrothermal. The hydrothermal method is described as follows: appropriate amounts of high purity  $\text{Bi}_2\text{O}_3$  (4N),  $\text{Tm}_2\text{O}_3$  (4N) and  $\text{Yb}_2\text{O}_3$  (4N) powders were dissolved in hot concentrated  $\text{HNO}_3$  to prepare  $\text{Bi}(\text{NO}_3)_3$ ,  $\text{Tm}(\text{NO}_3)_3$  and  $\text{Yb}(\text{NO}_3)_3$  solutions, respectively. Then,  $\text{Bi}(\text{NO}_3)_3$ ,  $\text{Tm}(\text{NO}_3)_3$  and  $\text{Yb}(\text{NO}_3)_3$  were added slowly into deionized water solution containing stoichiometric amounts of  $\text{KCl}$  (GR). The pH value of the mixed solution was adjusted to 6.0 by adding drop-wise dilute  $\text{NH}_3\cdot\text{H}_2\text{O}$  solution. After being continuously stirred for 0.5 h, the mixture was transferred into a 100.0 mL Teflon-lined stainless steel autoclave until 80% of the autoclave volume was filled, and subsequently heated at 160 °C for 12 h. Naturally cooled to room temperature, the precipitates were washed with absolute alcohol and deionized water for several times and dried at 80 °C in air. To improve the crystallinity of the nanocrystals, the final products were annealed at 450 °C for 2 h in air.

### **The preparation of $\text{Yb}^{3+}$ - $\text{Tm}^{3+}$ co-doped $\text{LaOCl}$ layered micrometer crystals**

The  $\text{Yb}^{3+}$ - $\text{Tm}^{3+}$  co-doped  $\text{LaOCl}$  layered micrometer crystals were synthesized by the traditional solid state reaction.  $\text{NH}_4\text{Cl}$  (A.R.),  $\text{La}_2\text{O}_3$  (99.99%),  $\text{Yb}_2\text{O}_3$  (99.99%) and  $\text{Tm}_2\text{O}_3$  (99.99%) were used as the starting materials. The mixture ratio of the reactants was: of  $\text{LaOCl}$ :1%  $\text{Yb}^{3+}$ ,1%  $\text{Tm}^{3+}$ . The weighed raw materials were thoroughly mixed in an agate mortar and then placed in a corundum crucible. Then,

the powders were sintered at 500 °C for 3 h in air. Some excessive  $\text{NH}_4\text{Cl}$  (20 mol%) is necessary for loss of Cl source at high temperature to obtain the pure phase formation.

### **The preparation of $\text{Yb}^{3+}$ - $\text{Tm}^{3+}$ co-doped $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ layered micrometer crystals**

The  $\text{Yb}^{3+}$ - $\text{Tm}^{3+}$  co-doped  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  layered micrometer crystals were synthesized by the traditional solid state reaction.  $\text{TiO}_2$  (A.R.),  $\text{Bi}_2\text{O}_3$  (99.99%),  $\text{Yb}_2\text{O}_3$  (99.99%) and  $\text{Tm}_2\text{O}_3$  (99.99%) were used as the starting materials. The mixture ratio of the reactants was:  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ : 1% $\text{Yb}^{3+}$ , 1% $\text{Tm}^{3+}$ . The mixture ratio of the reactants was:  $\text{Bi}_{3.92}\text{Yb}_{0.04}\text{Tm}_{0.04}\text{Ti}_3\text{O}_{12}$ . The weighed raw materials were thoroughly mixed in an agate mortar and then placed in a corundum crucible. Then, the powders were sintered at 850 °C for 2 h in air. Some excessive  $\text{Bi}_2\text{O}_3$  (3 mol%) is necessary for loss of Bi source at high temperature to obtain the pure phase formation.

### **The detail of Photocurrent test**

The indium doped tin oxide (ITO, China Southern Glass Co., Ltd., Shenzhen, China) substrates were cleaned by ultrasonication in distilled water, absolute ethanol, and isopropanol for 15 min sequentially. Both edges of the conducting glass substrates were covered with adhesive tape. Typically, the aqueous slurries of the  $\text{BiOCl}$  were spread on an ITO glass substrate with a glass rod, using adhesive tapes as spaces. The suspension was prepared by grinding 40 mg of  $\text{BiOCl}$  powder, 80  $\mu\text{L}$  of Nafion perfluorinated resin solution (5wt% in lower aliphatic alcohols and water, contains 15-20%), 300  $\mu\text{L}$  of isopropanol and 400  $\mu\text{L}$  water, and the film was dried in air and annealed at 90 °C for 10 min. A 0.5 M  $\text{Na}_2\text{SO}_4$  aqueous solution was used as

the electrolyte. All measurements were carried out at room temperature.

### **Computational methods**

CASTEP is a state-of-the-art quantum mechanics-based program designed specifically for solid-state materials science. In our calculated process, the DFT+U approach was introduced into an on-site correction so as to describe systems with localized d or f electrons and produce the calculations of refined electronic structures. Here, the U values of Yb 4f electrons is adopted using 6 eV. The exchange-correlation effects of valence electrons (Bi: 6s26p3, O: 2s2 2p4, Cl: 3s23p5, Eu: 4f75s25p66s2) were described by the revised Perdew–Burke–Ernzerhof for solid of generalized gradient approximation (GGA). The Monkhorst-Pack scheme K-points grid sampling was set as 4×4×2 for the irreducible Brillouin zone. A 60×60×80 mesh was used for fast Fourier transformation. An energy cutoff of 430 eV was used for expanding the Kohn-Sham wave functions. The minimization algorithm was chosen the Broyden-Fletcher-Goldfarb-Shanno (BFGS) scheme.

In the present work, 3×2×2 supercells were used for constructing the Yb-doped BiOCl models. To set the substitutional doping models, one Bi atom in the supercell was replaced by a Yb atom. In the supercell, the total number of atoms is reached to 108, and the corresponding of Yb concentration is about 1.389% (atomic fraction), which was comparable to that used in the experiments.

## Results Section

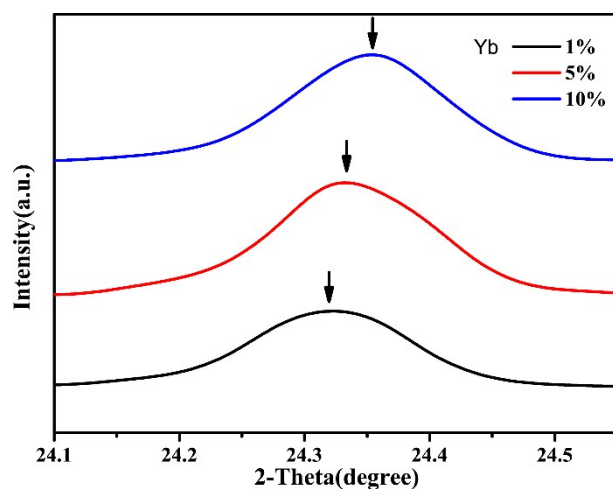


Fig. S1. Enlarged XRD patterns of  $\text{Tm}^{3+}$ - $\text{Yb}^{3+}$  co-doped  $\text{BiOCl}$  microcrystals with different  $\text{Yb}^{3+}$  concentration.

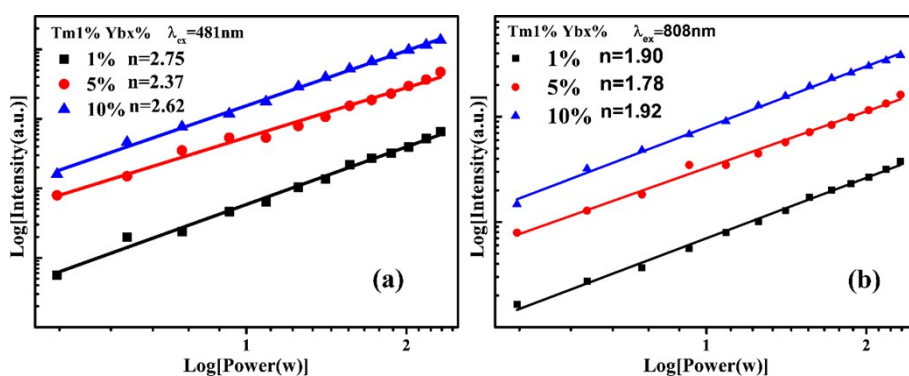


Fig. S2. Power dependence of the UC emission intensities of  $\text{Tm}^{3+}$ - $\text{Yb}^{3+}$  co-doped  $\text{BiOCl}$  microcrystals with different  $\text{Yb}^{3+}$  concentration at 481 nm (a) and 808 nm (b).

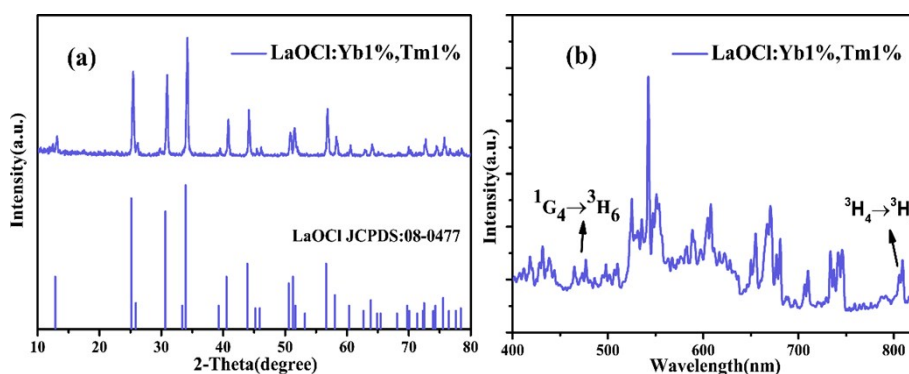


Fig. S3. (a) XRD patterns of the  $\text{LaOCl}:1\% \text{Yb}^{3+},1\% \text{Tm}^{3+}$  microcrystals; (b) UC emission spectra of the  $\text{LaOCl}:1\% \text{Yb}^{3+},1\% \text{Tm}^{3+}$  microcrystals under 980 nm excitation.

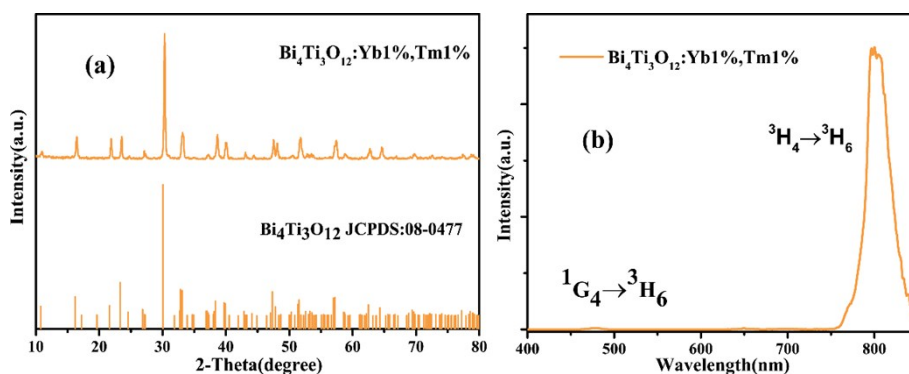


Fig. S4. (a) XRD patterns of the  $\text{Bi}_4\text{Ti}_3\text{O}_{12}:1\% \text{Yb}^{3+},1\% \text{Tm}^{3+}$  microcrystals; (b) UC emission spectra of the  $\text{Bi}_4\text{Ti}_3\text{O}_{12}:1\% \text{Yb}^{3+},1\% \text{Tm}^{3+}$  microcrystals under 980 nm excitation.

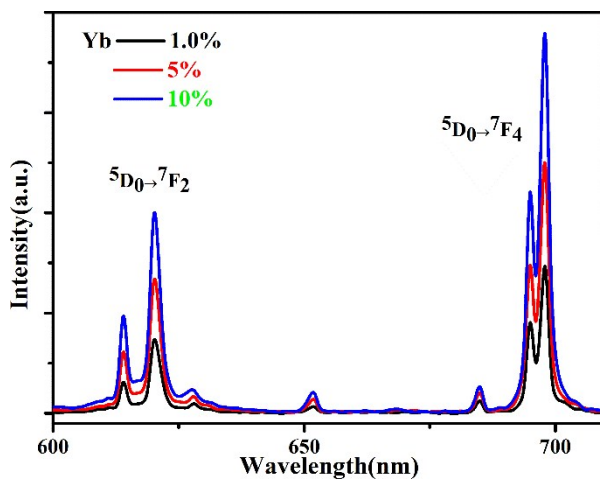


Fig. S5. Emission spectra of the  $\text{Eu}^{3+}\text{-Yb}^{3+}$  co-doped  $\text{BiOCl}$  microcrystals with different  $\text{Yb}^{3+}$  concentration under excitation at 466 nm

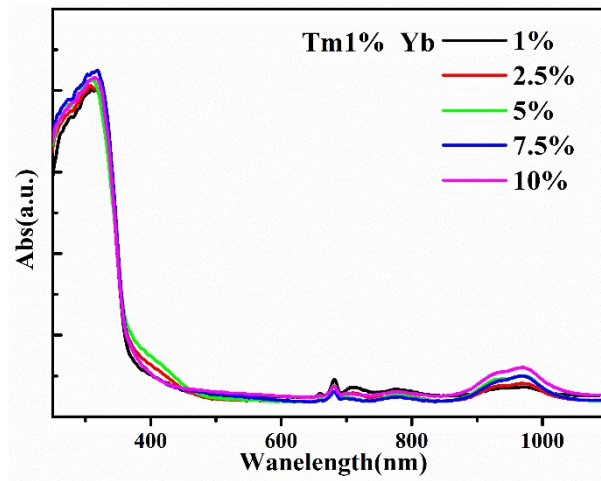
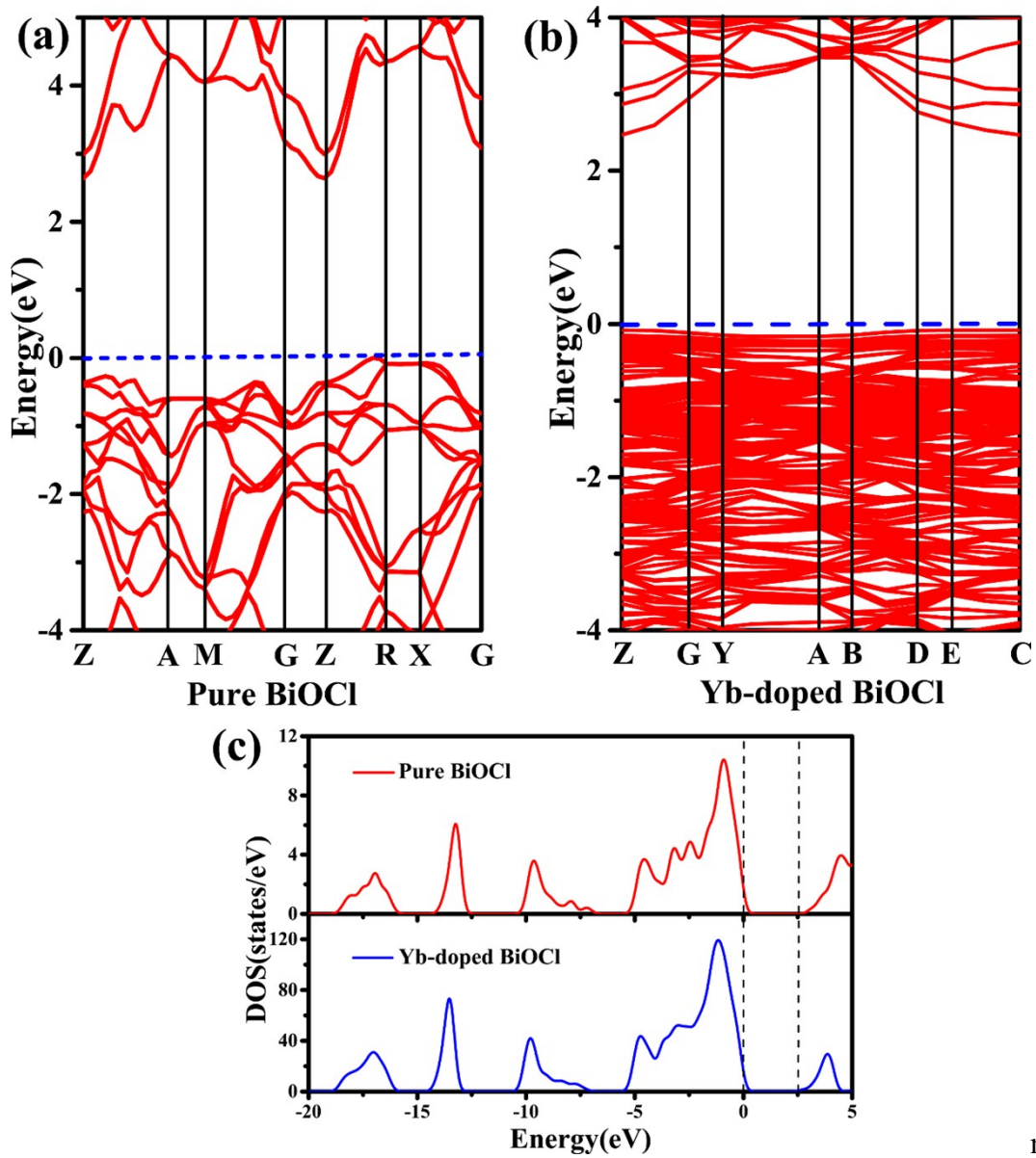


Fig. S6. UV-Vis-NIR absorption spectra of Tm<sup>3+</sup>-Yb<sup>3+</sup> co-doped BiOCl microcrystals with different Yb<sup>3+</sup> concentration



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Fig. S7. Calculated electronic energy band structures of (a) pure BiOCl and (b)  $\text{Yb}^{3+}$ -BiOCl crystals; (c) DOS of pure BiOCl and  $\text{Yb}^{3+}$ -BiOCl crystals.



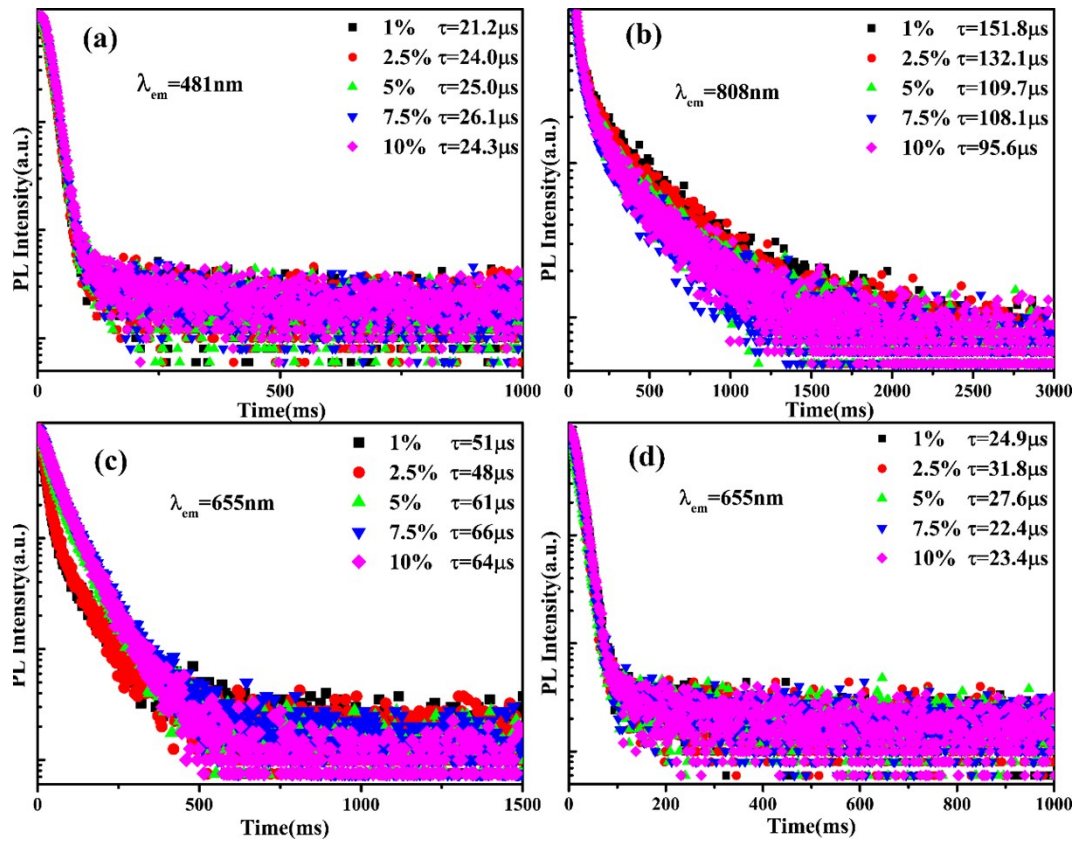


Fig. S8. UC luminescence decay curves at (a) 481 nm (b) 808 nm and (c) 655 nm from the Tm<sup>3+</sup>-Yb<sup>3+</sup> co-doped BiOCl nanosheets with different Yb<sup>3+</sup> concentration; (d) UC luminescence decay curves at 655 nm from the the Tm<sup>3+</sup>-Yb<sup>3+</sup> co-doped BiOCl nanosheets with different Yb<sup>3+</sup> concentration.