Supplementary information

A New Strategy of Interlayer Doping of Li Ion for Photoluminescence Enhancement of Eu³⁺ Doped B ismuth Oxychloride Layered Semiconductor

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1.Experimental Section

1.1. Materials and Synthesis

The Li⁺-Eu³⁺ codoped BiOCl powers were synthesized by the traditional solid-state reaction. The starting materials were NH₄Cl (A.R., Tianjin, China), Bi₂O₃ (99.99%, Sichuan, China), Eu₂O₃ (99.99%, Sichuan, China), Li₂CO₃ (99.99%). The mixture ratio of the reactants was BiOCl: 1%Eu³⁺, xLi⁺ (x = 0, 5, 10, 30 mol %) (molar fraction, the same below). 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 3h in air. It should be noticed that NH₄Cl were added in excess of 20% to supply the chlorine rich atmosphere during the sintering process in order to compensate for volatilization losses.

1.2. Structure and Property Characterization

The crystallinity structures of the samples were confirmed by powder X-ray diffraction (XRD) (Bruker D8-Advance diffractometer using Cu K α (λ =1.5406 Å) radiation). The morphology and particle sizes were determined by a field emission scanning electron microscopy (FE-SEM, Merlin). The presence of Li in the sample was analyzed by atomic absorption spectroscopy (AAS, Agilent Technologies 240FS AA). Fourier transform infrared absorption (FT-IR) was recorded by Bruker TENSOR2 using KBr as a reference. The UV-Vis-NIR absorption spectra of the samples were measured on a Hitachi UV-4100 spectrophotometer. Electron paramagnetic resonance (EPR) spectra were conducted on a Bruker EMX EPR Spectrometer (Billerica, MA). Fluorescence spectral properties and fluorescence decay curves were measured on an Edinburgh Instruments FLS980 spectrometer equipped with both continuous and pulsed xenon

lamps. All measurements were carried out at room temperature.

1.3. Electrical Measurements

(a)The SPV spectroscopic measurement was carried out based on the lock-in amplifier. It is composed of a monochromatic light source which provided by the 500 W xenon lamp (CHFXM-500 W, Global Xenon Lamp Power) and a monochromator (Omni-5007, Zolix), a lock-in amplifier (SR830-DSP) with a light chopper (SR540), a photovoltage cell and a computer. (b) The photocurrents of the prepared samples under light irritation were measured by an electrochemical analyzer in a standard three-electrode system, with the samples as the working electrodes, a Pt foil as the counter electrode, and a saturated calomel electrode as the reference electrode. The photoelectrodes of Li⁺-Eu³⁺ co-doping BiOCl were prepared according to a previously reported method. Under excitation by 365 nm (6W) and pulsed xenon lamps (Filter 420nm), respectively, were utilized as light sources. All the measurements were performed at room temperature.

1.4. Computational Methods

All the calculation results were calculated using the Vienna Abinitio Simulation package (VASP)[1] within the projector augmented-wave approach using the Perdew-Burke-Ernzerhof generalized-gradient approximation (GGA)[2] functional. In order to get a good convergence of the geometry optimization, the cutoff energy is set as 450eV after a series of tests. To ensure adequate accuracy, the Monkhorst-Pack k-points mesh is chosen as 4x4x2. All calculations were spin-polarized starting from a high-spin ferromagnetic configuration. In the present work, 2x2x2 supercells were used for

constructing the Li⁺-doped BiOCl models. To set the interstitial and intercalation doping models, Li⁺ ions in supercells in the form of intercalations or gaps.

2. Results Section

2.1. Photoferroelectric effect

The wavelength-dependent regulation behavior is derived from the IEF. The above unusual PL phenomenon can be mostly ascribed to the occurrence and enhancement of the photoferroelectric effect triggered by the IEF. In addition to the excitation enhancement effect, the intrinsic IEF in the layered BiOCl semiconductor can greatly improve the photoproduction charge separation when the band gap transition happens under irradiation. The separation of the carriers along the [001] direction of the BiOCl sheet by the IEF causes an electric charge accumulation near the surface. Because the divergence of the polarization is equivalent to a distribution of bound charges, it will form an extra photoinduced electric field that degrades the spontaneous IEF and subsequently strengthen the polarization effect on the Eu3+ ions. In addition, the internal electric field changes, which enhances the photoluminescence.

2.2. Electrochemical measurements (SPV)

In the spectral range of 300-368 nm, where SPV is generated by the separation of photogenerated electrons and holes in the band gap, $Bi_{0.99} Eu_{0.01}OCl$ sample generate a SPV response due to the separation role of IEF on the photocarriers. With increase in the Li⁺ doping concentration, the magnitude of SPV was enhanced greatly, especially for the sample with 30% Li. Because the absorption intensity of BiOCl band gap change slightly with doping Li⁺ ion, this indicate that more photogenerated charge carriers are separated and transferred in the material. In the case of 368-700 nm, $Bi_{0.99} Eu_{0.01}OCl$

cannot generate SPV response due to the limitation of band gap. However, with increase in Li⁺ concentration, the SPV responses of Li doped BiOCl are red-shifted to the visible band accompanying with enhanced magnitude. It is consisting with the result of absorption spectra that Li dopant create the oxygen vacancy formation energy in the band gap of BiOCl and improve the absorption intensity of samples at visible band.

2.3 PL Enhancement mechanism

When Li⁺ enters the lattice layer and is doped with the Eu³⁺ activator, due to the charge compensation effect, charge imbalance can be avoided, resulting in charge accumulation and an increase in internal electric field. At the same time, the addition of Li⁺ ion leads to the generation of oxygen vacancies, which changes the chemical properties of local defects, resulting in a decrease in crystallinity. However, the lifetime is substantially unchanged and the luminescence is enhanced. Therefore, we can reasonably draw conclusions that the PL enhancement of doped Li⁺ ion is caused by the suppression of non-radiative relaxation due to an increase in the internal electric field.

 Li⁺ on dopant concentration (mol%)
 Crystallinity (%)

 0
 97.87

 30
 81.01

 Table S2. The content evaluates of Li⁺ ion doped BiOCl crystal by AAS

 Li⁺ on dopant concentration (mol%)
 Content (wt%)

Table S1. The calculate crystallinity of BiOCl crystal.

0

0

Table S3. The intensity ratio of 593 nm to 620 nm in the Li^+ doping BiOCl: Eu^{3+} samples prepared at different Li^+ doping under excitation at 344 and 466 nm.

| Li ⁺ concentration / mol% | 344nm | 466nm |
|--------------------------------------|-------|-------|
| 0 | 2.0 | 2.3 |
| 5 | 2.0 | 2.3 |
| 10 | 2.0 | 2.4 |
| 30 | 2.0 | 2.4 |

Table S4. The intensity ratio of ${}^{5}D_{0} \rightarrow {}^{7}F_{4}$ to ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ (R_{4→2}) in the Li⁺ doping BiOCl: Eu³⁺ samples prepared at different Li⁺ doping under excitation at 344 and 466 nm.

| Li ⁺ concentration / mol% | λ_{ex} =344nm | $\lambda_{ex} = 466 nm$ |
|--------------------------------------|-----------------------|-------------------------|
| 0 | 1.50 | 1.55 |
| 5 | 1.55 | 1.70 |
| 10 | 1.52 | 1.68 |
| 30 | 1.47 | 1.51 |



Fig S1. FE-SEM image of the prepared without Li^+ (a) and with 30% Li^+ (b) doped BiOCI: Eu³⁺ powders



Fig. S2. The FT-IR spectra of the samples.



Fig S3. The EPR of BiOCl: Eu³⁺ with 30% Li⁺-doped.



Fig S4. (a-c) The decay curves for ${}^{5}D_{0}$ - ${}^{7}F_{4}$ radiation level under 466 nm, 344 nm and 314nm excitation.

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