Electronic Supplementary Material (ESI) for RSC Advances.

Controlled synthesis and enhanced luminescence of BiOCl: Eu^{3+} ultrathin nanosheets

Yangyang Guo[1], Zhijun Zhang[1], Gangqiang Zhu[2], Weibin Zhang[1], Woochul Yang[1,]*

[1]Department of Physics, Dongguk University, Seoul, 04620, Korea

[2]Department of Physics, Shaanxi Normal University, Xi'an, 710062, China

E-mail: wyang@dongguk.edu

Figure S1 shows the XRD patterns and the standard data (JCPDS card No. 06–0249) for ultrathin nanosheet and nanoplate of $Bi_{0.9}Eu_{0.1}OCl$.

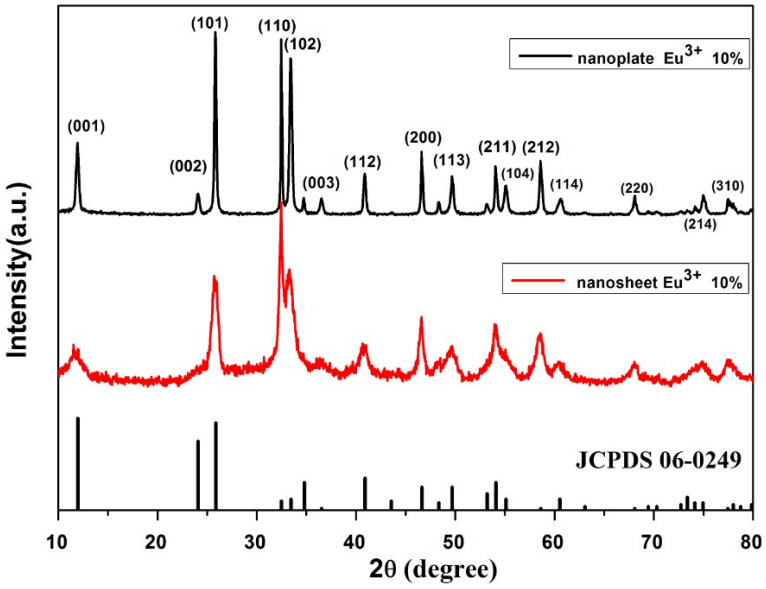

Figure S1. *XRD patterns for ultrathin nanosheet and nanoplate of $Bi_{0.9}Eu_{0.1}OCl$.*

First-principles calculations based on the density functional theory (DFT) with a plane-wave pseudo-potential basis were performed using the VASP (Vienna Ab initio Simulation Package) code.[1] Since the local density approximation (LDA) typically overestimates the adsorption energy while underestimating equilibrium atomic distances of the model system,[2,3]

the uniform generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) method was applied for structural optimization.[4] The plane wave expansion was truncated at the cut-off energy of 300 eV, and the first Brillouin-zone was sampled with a 3×3×1 *k*-point grid. We also tried higher *k*-point and cut-off energy, but there was no extraordinary improvement. The convergence tolerance of the energy was set to 10^{-5} eV/atom, and the maximum allowed force, maximum stress, and displacement were 0.05 eV/Å, 0.05 GPa, and 10^{-3} Å, respectively. These parameters were applied to optimize the unit cell until the deviation was no more than 5%, compared with the unit cell obtained from crystallographic refinement experiments.[5] The electronic structures and optical properties were calculated on the optimized configurations using the hybrid density functional HSE06 (Heyd-Scuseria-Ernzerhof) hybrid functional, [6] which replaces the slowly decaying long-ranged part of the Fock exchange, by the corresponding density functional counterpart.

Figure S2. shows that in this work we used 3x3x2 supercells to establish the BiOCl ultrathin nanosheet models. To set the substitutional doping models ($Bi_{0.9}Eu_{0.1}OCl$ ultrathin nanosheet), the model is that four Eu atoms replace four Bi atoms in the supercell. In the supercell, the total number of atoms reaches to 108, as shown in Figure S3. BiOCl has a tetragonal PbFCl-type structure (P4/nmm space group, NO. 129), and local symmetry D^7_{4h}. BiOCl is characterized by a layered structure with $[Bi_2O_2]$ slabs, and double halogen atom slabs. The Bi atom is coordinated to a square antiprism with four O atoms; the O atom is tetrahedrally coordinated to four Bi atoms; and the Cl atom is localized at the vertex of the pyramid that is formed with four Bi atoms in a planar square. Figures S4 and S5 show the band structures of pure BiOCl and $Bi_{0.9}Eu_{0.1}OCl$ ultrathin nanosheet. For pure BiOCl ultrathin nanosheet, the calculated band gap (the distance between VBM and CBM) is 3.33 eV. For $Bi_{0.9}Eu_{0.1}OCl$ ultrathin nanosheet, the band gap is 3.25eV, and this phenomenon is known as band gap narrowing (BGN), which is consistent with the experiment data, and also

the impurity energy band formed in the middle of the band gap with different Eu^{3+} doping [7, 8,9].

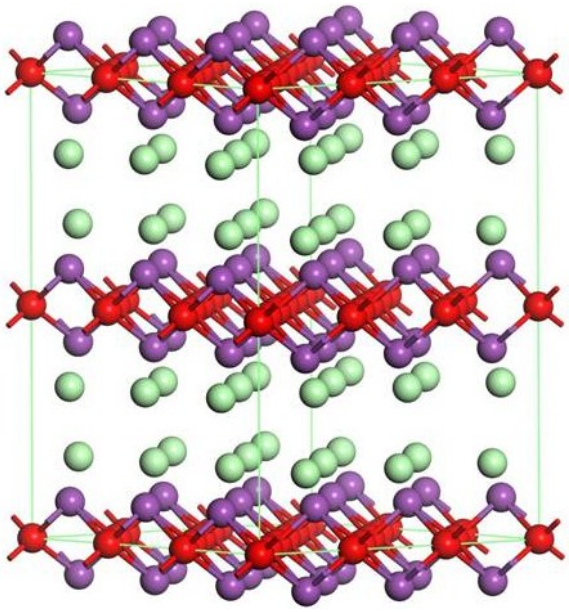

Figure S2. *The crystal structure of pure BiOCl ultrathin nanosheet (a) purple: Bi; red: O; green: Cl.*

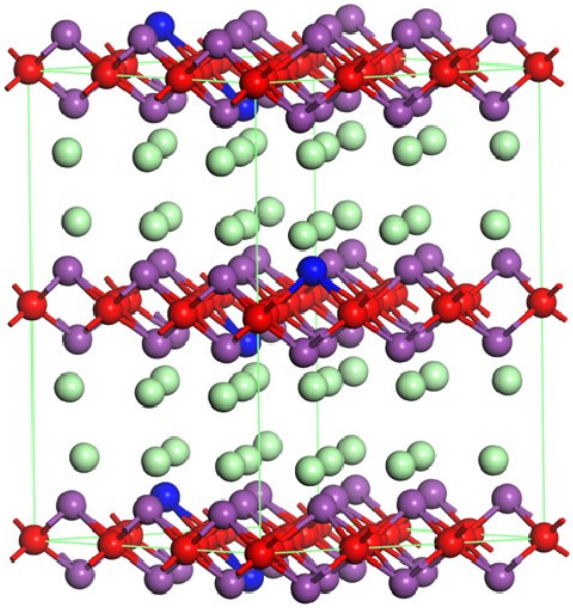

Figure S3. *The crystal structure of $Bi_{0.9}Eu_{0.1}OCl$ ultrathin nanosheet purple: Bi; red: O; green: Cl; blue: Eu.*

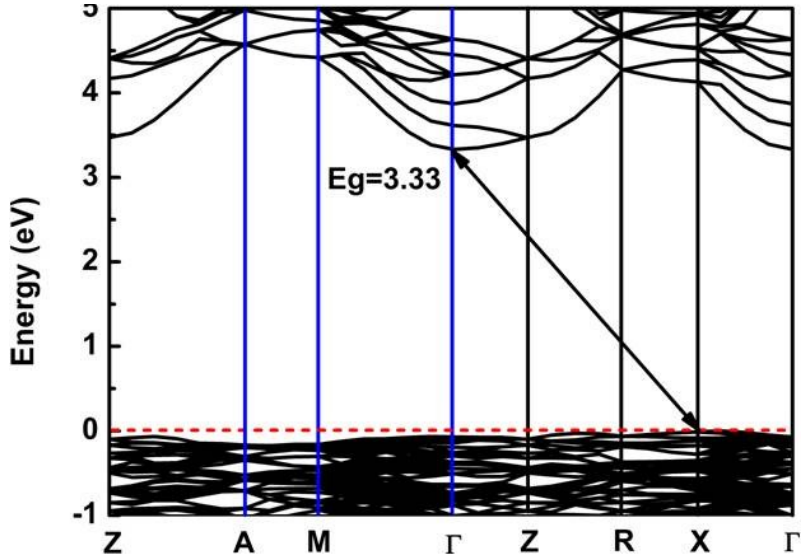

Figure S4. *Band structure of pure BiOCl ultrathin nanosheet mapped out by density functional theory (DFT) calculations.*

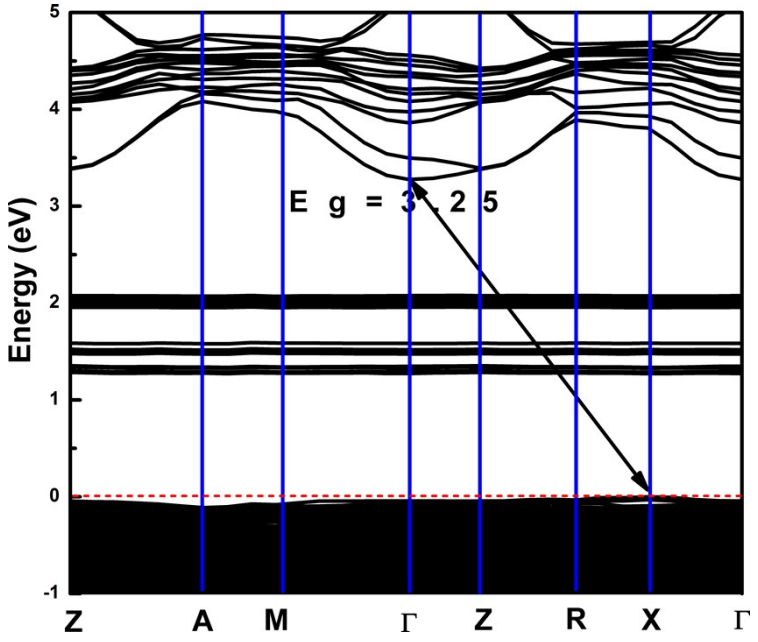

Figure S5. *Band structure of pure $Bi_{0.9}Eu_{0.1}OCl$ ultrathin nanosheet mapped out by density functional theory (DFT) calculations.*

Figures S6 and S7 show the UV–Vis absorption spectra of BiOCl with different Eu^{3+} concentrations of both nanosheets and nanoplates. The insets of Figs. S6 and S7 show the band gap values that were calculated based on the Kubelka-Munk theory. The band gap for the nanosheets was found to be 3.2~3.35 eV, and the red shift for nanoplates 3.36~3.4 eV.

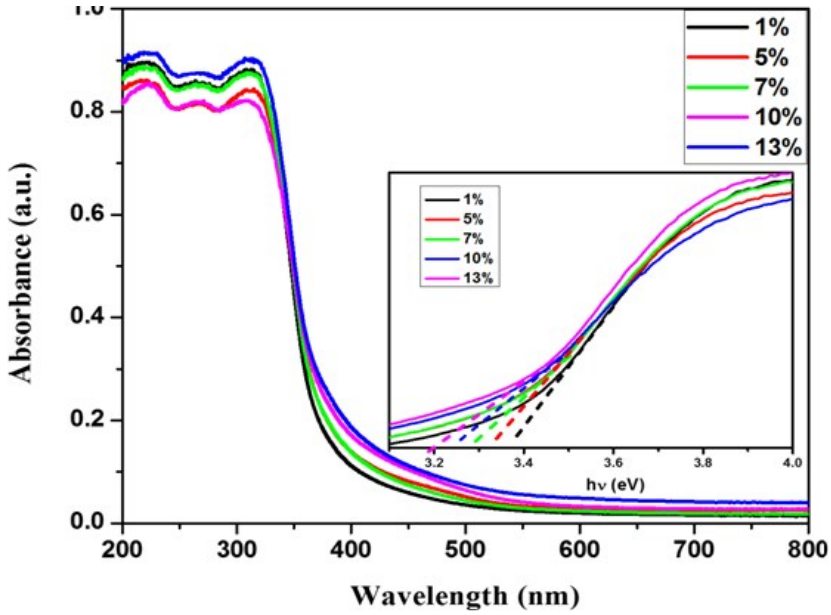

Figure S6. *The UV–Vis absorption spectra of BiOCl ultrathin nanosheet with different Eu^{3+} concentrations.*

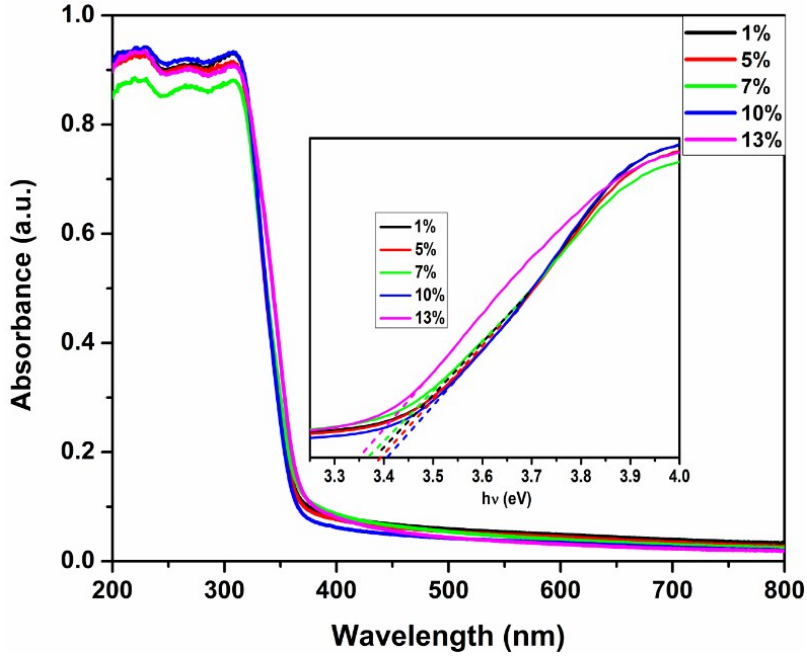

Figure S7. *The UV–Vis absorption spectra of BiOCl nanoplate with different Eu^{3+} concentrations.*

References

(1) Kresse. G, Furthmuller J. Phys Rev B. **1996,** *54*, 11169-11186.

(2) Jeloaica. L, Sidis V. DFT Chem Phys Lett. **1999,** *300*, 157-62.

(3) Lugo-Solis A, Vasiliev I. Phys Rev B. **2007,** *76*, 235431:1-8.

(4) Hammer. B, Hansen. L.B, Norskov. J.K.. Phys Rev B. **1999,** *59*,7413-7421.

(5) Teter. D.M, Hemley. R.J. Science. **1996**, *271*, 53-55.

(6) Grimme. S. J. Comput. Chem. **2006,** *27*, 1787-1799.

(7) Zhao. L.J, Zhang .X.C, Fan. C.M, Liang .Z.H, Han. P.D. Physica B. **2012,** *407*, 3364-3370.

(8) Zhao. Z. Y, Dai. W.W. Inorg. Chem. **2014,** *53*, 13001-13011.

(9) Yi. J, Zhao. Z. Y. J. Lumin. **2014,** *156*, 205-211.