### **Electronic Supplementary Information (ESI)**

# Contrasting Effect of the Ta/Nb Ratio in (111)-Layered B-Site Deficient

### Hexagonal Perovskite Ba<sub>5</sub>Nb<sub>4-x</sub>Ta<sub>x</sub>O<sub>15</sub> Crystals on Visible-Light-Induced

## Photocatalytic Water Oxidation Activity of Their Oxynitride Derivatives

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Distances (Å)	x = 0	x = 1	x = 2	x = 3	x = 4
(Ba1)O <sub>12</sub>					
(Ba1)–(O1) x 6	2.8973(1)	2.89788(5)	2.89736(6)	2.89728(3)	2.89460(6)
(Ba1)–(O2) x 6	2.853(12)	2.821(15)	2.82(2)	2.808(20)	2.828(18)
<(Ba1)–O>	2.875(2)	2.860(3)	2.8570(4)	2.853(4)	2.8614(4)
(Ba2)O <sub>12</sub>					
(Ba2)–(O1) x 3	2.974(2)	2.978(4)	2.994(4)	2.997(3)	3.020(3)
(Ba2)–(O2) x 6	2.903(8)	2.905(12)	2.905(19)	2.906(19)	2.905(13)
(Ba2)–(O3) x 3	2.699(12)	2.694(15)	2.672(19)	2.677(17)	2.642(17)
<(Ba2)–O>	2.870(2)	2.870(3)	2.869(4)	2.871(4)	2.868(3)
(Ba3)O <sub>12</sub>					
(Ba3)–(O2) x 3	3.202(12)	3.227(16)	3.24(2)	3.274(20)	3.266(19)
(Ba3)–(O3) x 6	2.938(6)	2.938(10)	2.943(13)	2.948(13)	2.945(11)
(Ba3)–(O3) x 3	2.789(12)	2.805(15)	2.87(2)	2.805(17)	2.774(16)
<(Ba3)–O>	2.967(3)	2.977(4)	2.986(5)	2.994(4)	2.983(4)
(B1)O <sub>6</sub> <sup>[a]</sup>					
(B1)–(O2) x 3	2.261(11)	2.249(16)	2.22(2)	2.22(2)	2.218(17)
(B1)–(O3) x 3	1.817(8)	1.808(12)	1.807(16)	1.810(15)	1.841(14)
<b1)o></b1)o>	2.039(4)	2.029(5)	2.014(7)	2.014(7)	2.030(6)
(B2)O <sub>6</sub> <sup>[a]</sup>					
(B2)–(O1) x 3	2.074(3)	2.071(3)	2.069(3)	2.071(2)	2.067(2)
(B2)–(O2) x 3	1.943(10)	1.972(15)	1.983(17)	1.975(16)	1.965(16)
<(B2)–O>	2.009(3)	2.022(4)	2.026(5)	2.023(5)	2.016(4)
Angle (°)					
(O2)-(B1)-(O2)	82.0(6)	80.3(6)	81.0(12)	81.1(12)	82.3(9)
(O2)-(B1)-(O3)	86.7(7)	87.1(10)	87.2(12)	87.6(12)	87.3(11)
(O3)-(B1)-(O3)	102.5(6)	103.0(9)	102.4(11)	101.6(10)	101.4(9)
(O1)-(B2)-(O1)	88.59(11)	88.79(11)	88.91(11)	88.79(8)	88.90(8)
(O1)-(B2)-(O2)	89.0(6)	88.4(8)	88.3(10)	88.1(9)	88.6(8)
(O2)-(B2)-(O2)	93.3(7)	94.4(10)	94.4(14)	94.8(14)	93.9(10)

**Table S1.** Selected interatomic distances and bonding angles from crystal structure refinement for Ba<sub>5</sub>Nb<sub>4-x</sub>Ta<sub>x</sub>O<sub>15</sub> at 293 K in space group *P*-3*m*1 (No. 164); Z = 1.

Notes: [a] B1 and B2 correspond to octahedral sites containing Nb/Ta atoms.



**Figure S1.** EDS analyses: gray images, Ta mapping images (*green*), Nb mapping images (*blue*), and EDS spectra of (a) BaNbO<sub>2</sub>N, (b) BaNb<sub>0.75</sub>Ta<sub>0.25</sub>O<sub>2</sub>N, (c) BaNb<sub>0.50</sub>Ta<sub>0.50</sub>O<sub>2</sub>N, (d) BaNb<sub>0.25</sub>Ta<sub>0.75</sub>O<sub>2</sub>N, and (e) BaTaO<sub>2</sub>N crystal structures.



**Figure S2.** IR absorption spectra of BaNbO<sub>2</sub>N, BaNb<sub>0.75</sub>Ta<sub>0.25</sub>O<sub>2</sub>N, BaNb<sub>0.50</sub>Ta<sub>0.50</sub>O<sub>2</sub>N, BaNb<sub>0.25</sub>Ta<sub>0.75</sub>O<sub>2</sub>N, and BaTaO<sub>2</sub>N measured from 1000 nm - 10  $\mu$ m. The reference was measured using bare CaF<sub>2</sub> plate.