



**Supplement 1:** X-ray photoelectron spectroscopy (XPS) of the NLBN-W-0.02 and NLBN-W-0.05 ceramics. (a) W 4f<sub>7/2</sub> spectra of the as-sintered and 1 min sputtered NLBN-W-0.02 and NLBN-W-0.05. (b) W 4f<sub>7/2</sub> spectra of the NLBN-W-0.02 at different depths (100-500 nm).

The 7/2 spin-orbit component of W 4f core level photoemission of the NLBN-W-0.02 and NLBN-W-0.05 are both located at 35.38 eV, which is consistent with that of WO<sub>3</sub> (reference 62 in the revised manuscript). This suggests that W in the +6 oxidation state was incorporated into the layered perovskite structure in Na<sub>0.5</sub>La<sub>0.5</sub>Bi<sub>2</sub>Nb<sub>2-x</sub>W<sub>x</sub>O<sub>9</sub> (NLBN-W). Furthermore, no shifting for W 4f<sub>7/2</sub> spectra indicates that W ion both in the surface and in the bulk was the same oxidation state, +6.