Supplementary Information

Structure and Electrical Properties of Tetragonal Tungsten Bronze \( \text{Ba}_2\text{CeFeNb}_4\text{O}_{15} \)

Hongqiang Ma\(^a\), Kun Lin\(^a\), Laijun Liu\(^c\), Baoling Yang\(^a\), Yangchun Rong\(^a\), Jun Chen\(^a\), Jinxia Deng\(^{ab}\), Shogo Kawaguchi\(^d\), Kenichi Kato\(^e\), Xianran Xing*\(^a\)

\(^a\)Department of Physical Chemistry, \(^b\)Department of Chemistry, University of Science and Technology Beijing, Beijing 100083, China

\(^c\)State Key Laboratory Breeding Base of Nonferrous Metals and Specific Materials Processing, Guilin University of Technology, Guilin 541004, China

\(^d\)Japan Synchrotron Radiation Research Institute (JASRI)1-1-1, Kouto, Sayo-cho, Sayo-gun, Hyogo 679-5198, Japan

\(^e\)RIKEN SPring-8 Center Sayo, Hyogo 679-5148, Japan

*Corresponding author

Department of Physical Chemistry, University of Science and Technology Beijing,

Beijing 100083, China

Tel: + 86-10-62334200

Fax: + 86-10-62332525

*e-mail address: xing@ustb.edu.cn
**Fig. S1.** SEM image of selected pellets surface for the as-synthesized BCFN.

The microstructure of BCFN ceramics was observed by scanning electron microscopy (SEM, Supra 55; Zeiss, Oberkochen, Germany). No impurity was observed.
**Fig. S2** XRD patterns of BCFN powder at different temperatures (25 – 600 °C). It shows that no phase transition occurs in the measured temperature.

The high-temperature powder X-ray diffraction patterns were collected on a laboratory diffractometer, (PANalytical X’ Pert\textsuperscript{III}, Holland, Cu Kα, λ=1.5406 Å) and an Anton Par HTK 1200 high-temperature attachment was used. Data were collected in 0.0131° steps. The heating rate was 10 °C/min, and the sample was held for 15 min at a specified temperature to reach heating equilibrium.
**Fig. S3** UV-vis absorbance spectroscopy of as-sintered BCFN powders. Band gap estimated from the intercept of tangents to the plots was ~0.91 eV indicative of the existence of shallow energy levels due to oxygen vacancies.

UV-vis absorbance spectroscopy of the nanostructures was performed using a UV-vis spectrometer (VARIAN, Cary 5000) in a quartz cuvette.
Fig. S4 X-ray photoelectron spectra of Fe2p for surface of as-sintered BCFN pellet. It suggests that the Fe$^{3+}$ reduction to Fe$^{2+}$ and oxygen loss in BCFN are significant in surface.

The surface properties of samples were characterized by X-ray photoelectron spectroscopy (XPS) on a ESCALAB 250 Xi (VG, UK) with Carbon (284.8 eV) as a marker.
Table S1  BVS Values Based on the Data Obtained from SPD Data

<table>
<thead>
<tr>
<th>Atom</th>
<th>BVS</th>
<th>Atom</th>
<th>BVS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce</td>
<td>2.87(2)</td>
<td>O1</td>
<td>1.89(1)</td>
</tr>
<tr>
<td>Ba</td>
<td>2.02(1)</td>
<td>O2</td>
<td>2.06(2)</td>
</tr>
<tr>
<td>Fe1</td>
<td>3.31(3)</td>
<td>O3</td>
<td>1.95(1)</td>
</tr>
<tr>
<td>Nb1</td>
<td>5.10(4)</td>
<td>O4</td>
<td>2.22(3)</td>
</tr>
<tr>
<td>Fe2</td>
<td>3.31(3)</td>
<td>O5</td>
<td>1.98(3)</td>
</tr>
<tr>
<td>Nb2</td>
<td>5.10(4)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Bond valence sums (BVS)\(^1\) calculated from the refinements in Table S1 supports the validity of the structure and indicates the dominated existence of Fe\(^{3+}\) and Ce\(^{3+}\) instead of Fe\(^{2+}\) and Ce\(^{4+}\). Based on the XPS data in Fig. S4, defect concentration in surface are larger than that inside the grains.

---