

## ***In situ* Observation of Oxygen Vacancy Order-Disorder Transition in NdBaCo<sub>2</sub>O<sub>5.5</sub> Layered Perovskite Oxide**

Ohhun Kwon<sup>1</sup>, Yong In Kim<sup>2</sup>, Jong Chan Kim<sup>3</sup>, Hanbeom Jeong<sup>4</sup>, Guntae Kim<sup>1</sup>, Young-Min Kim<sup>2</sup> and Hu Young Jeong<sup>5\*</sup>

<sup>1</sup> Department of Energy Engineering, Ulsan National Institute of Science and Technology (UNIST), Ulsan, Republic of Korea.

<sup>2</sup> Department of Energy Science, Sungkyunkwan University (SKKU), Suwon, Republic of Korea.

<sup>3</sup> School of Materials Science and Engineering, UNIST, Ulsan, Republic of Korea.

<sup>4</sup> Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology (KAIST), Daejeon, Republic of Korea.

<sup>5</sup> UNIST Central Research Facilities (UCRF) and School of Materials Science and Engineering, UNIST, Ulsan, Republic of Korea.

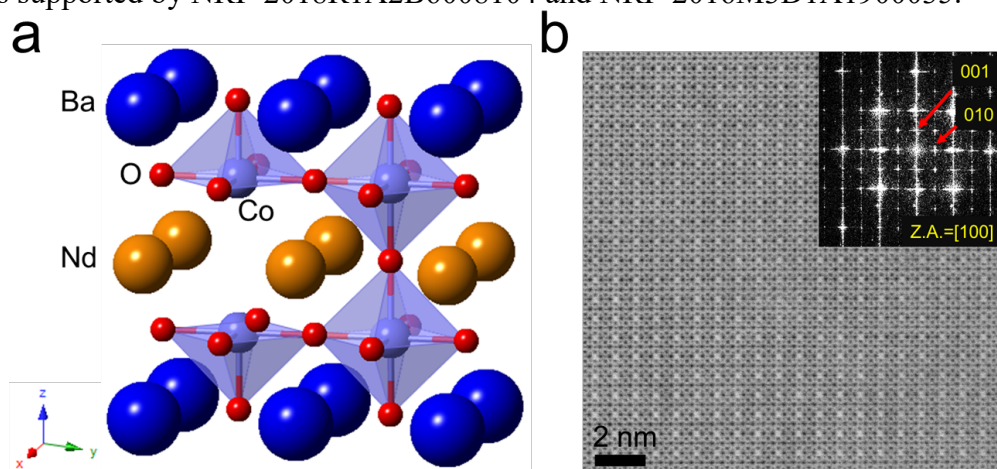
\* Corresponding author: hulex@unist.ac.kr

Perovskite oxides (ABO<sub>3</sub>) have been researched because of their structural flexibility and excellent catalytic properties in the solid oxide fuel cells (SOFCs), solar cells, metal air batteries, and other applications [1, 2]. Generally, the catalytic properties of the perovskite oxides are determined by the dynamics and concentration of oxygen vacancies. In terms of the oxygen kinetics, a layered perovskite oxide has attracted much attention due to its specific structural characteristic. The layered perovskite has a constitutional formula of AA'B<sub>2</sub>O<sub>5+δ</sub> with a stacking sequence of [A'O]-[BO<sub>2</sub>]-[AO<sub>δ</sub>]-[BO<sub>2</sub>] such as LnBaCo<sub>2</sub>O<sub>5+δ</sub> (Ln = Pr, Nd, Sm, and Gd) [3]. It is known that most oxygen vacancies are located on the LnO layer, enhancing the mobility of oxygen ion. However, the location of the oxygen vacancies in the layered perovskite is still not clearly demonstrated. Here, we report on the A-site cation ordering and the location of the oxygen vacancies in the NdBaCo<sub>2</sub>O<sub>5.5</sub> (NBCO) layered perovskite using scanning transmission electron microscope (STEM). Furthermore, we observe oxygen vacancy ordering-disordering transition in the NBCO as temperature increases via *in situ* heating TEM.

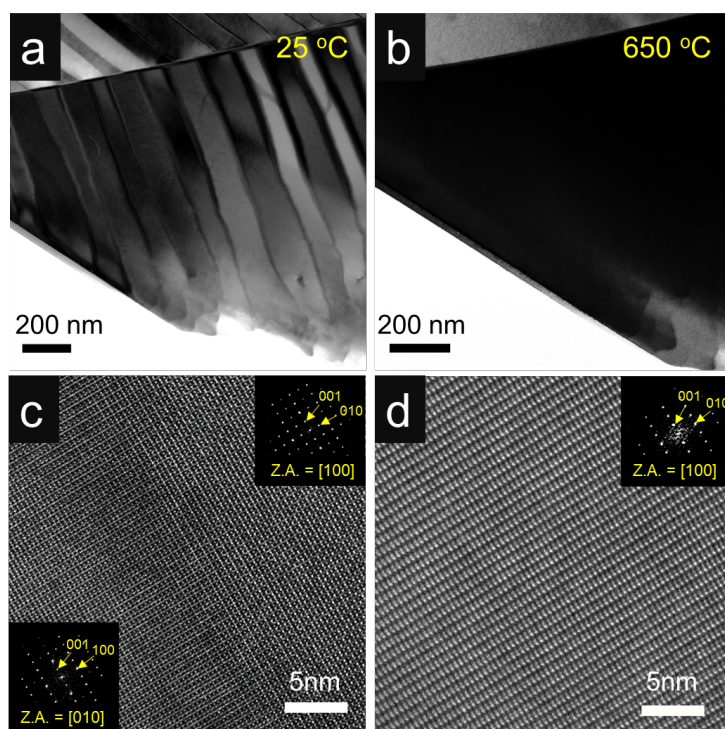
The NBCO sample was prepared by the Pechini method, and then sintered at 1200 °C for 4 h in air. The cross-section sample of the NBCO for TEM analysis was fabricated by focused ion beam (FIB) technique. Figure 1a presents schematic illustration of the ordered stacking sequence [BaO]-[CoO<sub>2</sub>]-[NdO<sub>0.5</sub>]-[CoO<sub>2</sub>] and oxygen vacancy ordering along the Nd layer [4]. It was confirmed by the annular bright-field (ABF) scanning TEM image in Figure 1b, showing regular contrast changes in both directions ([001] and [010]) owing to both A-site ordering of BaO and NdO layers and oxygen vacancy ordering in NdO layer. The A-site ordering and oxygen vacancy ordering were also observed by weak additional spots between main spots in the fast-Fourier transformed (FFT) pattern, which is indexed with (001) and (010) planes of orthorhombic structure (*Pmmm*). To understand the dynamic change of oxygen vacancy ordering in NBCO, we utilized *in situ* TEM under various temperature conditions. As shown in BF-TEM image (Figure 2a), dark and bright domains were alternately observed at 25 °C. The zone axes of dark and bright domains are [010] and [100] directions (Figure 2c), respectively, indicating that the different orientation leads to the contrast difference of domains. When the temperature increased to 650 °C, the contrast difference disappears (Figure 2b) because all domains change from oxygen vacancy ordering (*Pmmm*) to disordering (*P4/mmm*) (Figure 2d). From cross-sectional TEM images and *in situ* experiment, we can demonstrate that oxygen vacancy ordering is placed in NdO layer and vanishes at high temperatures [5].

## References:

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 [3] S Choi et al., Scientific Reports **3** (2013), p. 2426.  
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 [5] This work is supported by NRF-2018R1A2B6008104 and NRF-2016M3D1A1900035.



**Figure 1.** (a) Schematic illustration of NBCO. (b) Annular bright-field (ABF) image and fast Fourier transform (FFT) of the NBCO.



**Figure 2.** Bright-field (BF) TEM image of NBCO at (a) 25 °C and (b) 650 °C. High resolution (HR) TEM image of NBCO at (c) 25 °C and (d) 650 °C.