

## Calculation of Oxygen Defect Structure in Layered $\text{GdBaCo}_2\text{O}_{5+\delta}$ by First-principles DFT with Monte Carlo Simulations

Hiromasa Shiiba<sup>1</sup>, Masanobu Nakayama<sup>1,2</sup>, Toshihiro Kasuga<sup>1</sup>, Robin W Grimes<sup>3</sup>, John A Kilner<sup>3</sup>

<sup>1</sup>Nagoya Institute of Technology

<sup>2</sup>Japan Science and Technology Agency, PRESTO

<sup>3</sup>Imperial College London

<sup>1</sup>Gokiso, Showa, Nagoya, Aichi, 466-8555, Japan

<sup>2</sup>4-1-8 Honcho Kawaguchi, Saitama 332-0012, Japan

<sup>3</sup>South Kensington Campus, London SW7 2AZ, UK

### Introduction

Mixed ionic-electronic conducting double perovskite  $\text{LnBaCo}_2\text{O}_{5+\delta}$  (Ln = rare earth) oxides have recently attracted considerable attention as cathode materials for solid oxide fuel cells (SOFCs), since such materials are expected to lower the presently required high operating temperatures to a more moderate temperature range (i.e. 500–700 °C). Therefore, various candidate materials have been investigated in terms of their crystal structure, oxygen diffusivity and electrochemical properties [1].  $\text{GdBaCo}_2\text{O}_{5+\delta}$  (GBCO), where  $0 \leq \delta \leq 1$ , is an example of a double perovskite oxide with relatively high mixed conductivity [2, 3]. The difference in size between the large Ba cation and the small Gd cation results in the formation of alternating GdO and BaO layers (... , GdO, CoO<sub>2</sub>, BaO, CoO<sub>2</sub>, GdO, ...) along the c axis (Fig. 1). One of the notable features of GBCO is its ability to accommodate large deviations from  $\text{ABO}_3$  stoichiometry arising from oxygen vacancy formation. Indeed, according to structural studies, the parent stable composition of  $\text{GdBaCo}_2\text{O}_5$  contains 1/6 of an oxygen vacancy per formula unit and forms an oxygen-ordered structure at low temperatures [3]. Specifically, the oxygen stoichiometry of GBCO is close to  $\delta = 0.5$  at room temperature, and its crystal symmetry is orthorhombic (space group: Pmmm), where oxygen ions and vacancies alternate along with b-axis in the GdO layer. The change in symmetry from orthorhombic Pmmm to tetragonal P4/mmm takes place around 450–500 °C [3]. However, Tarancón et al. reported that the phase transition exerts no appreciable effect on the cathode performance [3] and the oxygen transport properties (diffusivity and/or surface exchange) [1]. The reason for this lack of correlation between the phase transition and oxygen transport properties remains unclear.

The aim of this study is to clarify and demonstrate the detailed oxygen/vacancy arrangement in GBCO as a function of composition ( $\delta$ ) and temperature. First-principles calculations based on density functional theory (DFT) have been carried out with the aid of the cluster expansion approach and Monte Carlo (MC) simulations.

### Method

The Vienna ab initio simulation package (VASP) was utilised with the generalised gradient approximation (GGA-PBE) + U and projector-augmented wave (PAW) methods. For the GGA + U calculations, the U values for the f-orbitals of Gd and the d-orbitals of Co were set to 6.9 eV and 6.0 eV following relevant previous reports. Then a subset of the calculated ~150 total energies corresponding to different oxygen/vacancy arrangements within the GBCO framework was converted into effective cluster interactions (ECIs) to quickly obtain a precise estimate of the total energy E of the crystal for an arbitrary oxygen/vacancy arrangement. Finally MC simulations were employed using fitted ECI values. The temperature was varied between 300 and 2000 K, and the

ATAT program package was used for the cluster expansion approach and the MC simulations.

### Results and Discussion

The temperature dependence of the oxygen/vacancy arrangement for the superstructure at  $\delta = 0.5$  has been investigated with the canonical MC approach. At low temperatures (300 K) all oxygen vacancies are located in the GdO layer, and we confirmed the aligned structure of oxygen/vacancy arrangement in the GdO layer (Fig. 2(a)). Starting from 900 K, oxygen occupancy gradually increases and decreases with temperature in the GdO and CoO<sub>2</sub> layers, respectively, and this tendency accelerates at around 1200 K, where a phase transition occurs. On the other hand, all oxygen sites are fully occupied in the BaO layer up to 2000 K, indicating a strong attraction for oxygen to the BaO layer. The one-dimensional oxygen/vacancy arrangement along the b-axis is well preserved at 1000 K, whereas the one-dimensional arrangement is diminished at 1300 K. In contrast, the oxygen/vacancy arrangement in the CoO<sub>2</sub> layer does not indicate superstructure formation. Considering the oxygen/vacancy arrangement, a two-dimensional diffusion path is formed in the a-b plane (i.e. normal to the c-axis), in which oxygen hops between the GdO and CoO<sub>2</sub> layers. The random arrangement of vacancies in the GdO layer in the high-temperature phase at  $\delta = 0.5$  still shows a partial linear alignment directed along the a- and b-axes (Fig. 2(b)). In other words, the oxygen/vacancy ordering appearing in the low-temperature phase still exists within a short range even in the high-temperature phase, even though long-range ordering, that is, crystal structure symmetry, is broken. Unchanged short-range oxygen/vacancy ordering remaining after the phase transition may account for the fact that the phase transition does not affect oxygen diffusivity, as reported in [3].

### References

- [1] A. Tarancón, S. J. Skinner, R. J. Chater, F. Hernández-Ramírez, J. A. Kilner, J. Mater. Chem., **17** (2007) 3175–3181.
- [2] A.A. Taskin, A.N. Lavrov, Y. Ando, Appl. Phys. Lett., **86** (2005) 091910.
- [3] A. Tarancón, D. Marrero-López, J. Peña-Martínez, J. C. Ruiz-Morales, P. Núñez, Solid State Ionics, **179** (2008) 611-618.

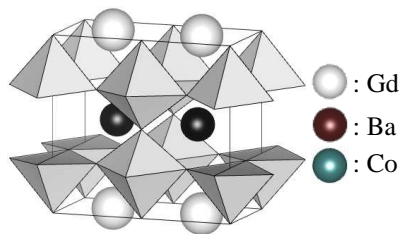


Fig.1. Crystal structure of  $\text{GdBaCo}_2\text{O}_{5.5}$ .

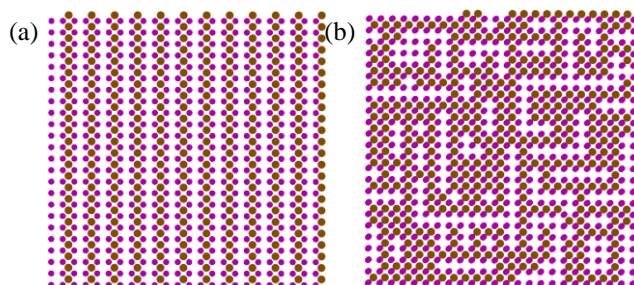


Fig.2. Oxygen/vacancy configuration of oxygen sites in the GdO layer at (a) 300 K and (b) 1500 K for  $\delta = 0.5$ .