Crystallography

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Crystal Structure and Electron Density Distribution of $La_{0.4}Ba_{0.6}CoO_{3-\delta}$

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Introduction

Mixed oxide-ionic and electronic conducting ceramics (MIECs) have attracted considerable attention owing to their applications such as oxygen separation membranes, oxygen sensors and cathodes of solid oxide fuel cells (SOFCs) for the needs of green socieities. For the cell performance, novel MIECs with high ionic and electrical conductivities are required. The lanthanum barium cobaltite, $La_{0.4}Ba_{0.6}CoO_{3-\delta}$, has been reported with the smallest overpotential in $La_{1-x}Ba_xCoO_{3-\delta}$ ($0 \le x \le 1$) and high electrical conductivity at high temperatures [1]. The purpose of this work is to investigate the crystal structure and electron density distribution of $La_{0.4}Ba_{0.6}CoO_{3-\delta}$.

Experiments

$La_{0.4}Ba_{0.6}CoO_{3-\delta}$ samples were prepared by a conventional solid state reaction. Synchrotron x-ray powder diffraction experiments of $La_{0.4}Ba_{0.6}CoO_{3-\delta}$ were performed from 25.6 to 1000°C by the multiple-detector system installed at the BL-4B2 beam line of the Photon Factory, KEK, Japan. A monochromatized 1.19724 Å x-ray was utilized. The crystal structure $La_{0.4}Ba_{0.6}CoO_{3-\delta}$ was refined by the Rietveld method with a computer program RIETAN-FP [2]. The electron-density distribution of $La_{0.4}Ba_{0.6}CoO_{3-\delta}$ was investigated by a maximum-entropy method (MEM, PRIMA). To confirm the validity of the MEM analysis, MEM-based pattern fitting (MPF) was applied.

Results and discussion

Synchrotron powder diffraction patterns indicated that the $La_{0.4}Ba_{0.6}CoO_{3-\delta}$ material has a cubic perovskite-type structure with $Pm\bar{3}m$ space group in the whole temperature range. The refined unit-cell parameters and atomic displacement parameters of $La_{0.4}Ba_{0.6}CoO_{3-\delta}$ increased with increasing temperature. The reliability factors and goodness of fit at 25.6°C (Fig. 1) in the Rietveld analysis were R_{wp} = 8.41 %, R_I = 2.51%, R_F = 1.04% and S = 1.82. The refined unit-cell parameters were $a = b = c$ = 3.91537(3) Å at this temperature. The oxygen atoms showed larger atomic displacement parameters perpendicular to the Co-O bond with larger $U_{22}(O) = U_{33}(O)$ = 0.0026(1) nm^2 > $U_{11}(O)$ = 0.0014(1) nm^2. This suggests that the oxygen diffusion path of $La_{0.4}Ba_{0.6}CoO_{3-\delta}$ is similar with that for $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ [3]. The crystal structure of $La_{0.4}Ba_{0.6}CoO_{3-\delta}$ consists of CoO_6 octahedron and La,Ba cations. Fig. 2 shows the covalent bonds between Co and O atoms. The minimum electron density at Co-O bond increased with temperature increasing from 25.6 to 400°C and then decreased from 400 to 1000°C.

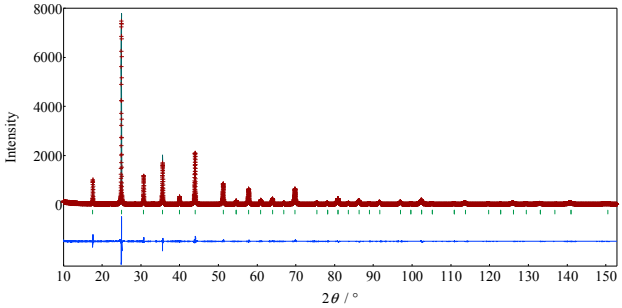

Fig.1. Rietveld synchrotron x-ray diffraction profile fitting result of $La_{0.4}Ba_{0.6}CoO_{3-\delta}$ at 25.6°C.

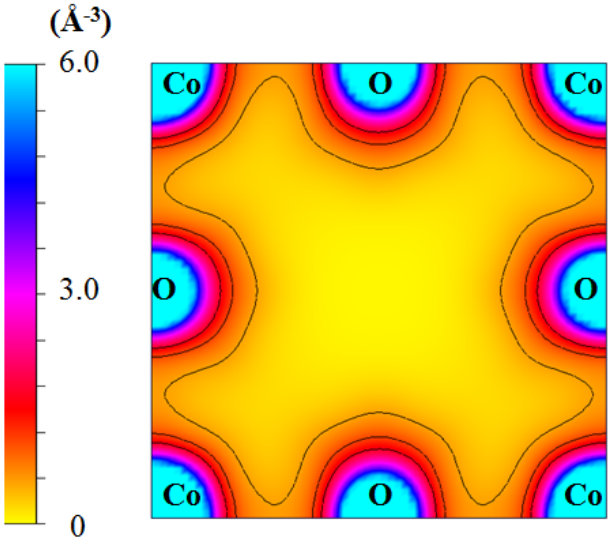

Fig.2. MEM experimental electron density distributions of $La_{0.4}Ba_{0.6}CoO_{3-\delta}$ at 25.6 °C.

References

[1] T. Ishihara, S. Fukui, H. Nishiguchi, Y. Takita, Solid State Ionics, 152, 609 (2002).
[2] F. Izumi, K. Momma, Solid State Phenom, 130, 15 (2007).
[3] M. Yashima, T. Tsuji, J. App. Cryst., 40, 1166 (2007)

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