

Oxygen storage capability of $\text{BaYMn}_2\text{O}_{5+\delta}$ studied by high-temperature X-ray diffraction under precisely controlled oxygen pressures

The so-called “oxygen storage materials (OSMs)” have attracted increased attention in the materials research community. OSMs are categorized as oxides with fast and reversible oxygen intake/release capability. Such materials may be applicable to various oxygen-related technologies owing to their potential ability for a precise control of redox reaction, and hence contribute to solutions of energy and environmental issues. Developments of novel OSMs are highly desirable to open up the possibility of various future applications.

We recently reported the remarkable oxygen storage capability of $\text{BaYMn}_2\text{O}_{5+\delta}$ [1]. This oxide crystallizes in a double-perovskite type structure, which contains a layered arrangement of smaller yttrium and larger barium ions at the perovskite A-site. The oxygen site within the yttrium plane is readily filled/unfilled in response to variations in temperature and the surrounding atmosphere, resulting in large oxygen nonstoichiometry ranging $0 \leq \delta \leq 1$, see a schematic illustration in Fig. 1. The oxygen intake/release behaviors of $\text{BaYMn}_2\text{O}_{5+\delta}$ are clearly beyond those of conventional perovskite oxides in terms of the magnitude and sharpness of the processes. This emphasizes the importance of the characteristic crystal structure involving the layered cationic order of Ba^{2+} and Y^{3+} . Understanding of key structural factors of the remarkable oxygen intake/release is particularly important to develop novel/better OSMs. Motivated by such a research background, we examined *in situ* high-temperature X-ray diffraction (XRD) experiments on $\text{BaYMn}_2\text{O}_{5+\delta}$ [2].

Our preliminary investigations revealed that $\text{BaYMn}_2\text{O}_{5+\delta}$ crystallizes in either the oxygenated “ O_6 ” (Fig. 1(a)) or the intermediate “ $\text{O}_{5.5}$ ” form (Fig. 1(b)) at 750°C depending on oxygen pressures $P(\text{O}_2)$, enabling us to study these distinct forms selectively upon varying $P(\text{O}_2)$ at a constant temperature. *In situ* powder XRD measurements were performed at BL02B2 beamline. A large Debye-Scherrer camera equipped with a gas/vapor pressure control system [3] was used for the data acquisition at 750°C under precisely controlled oxygen pressures of $P(\text{O}_2) = 10^3$ and 10 Pa.

Figures 2(a) and 2(b) present XRD patterns for $\text{BaYMn}_2\text{O}_{5+\delta}$ taken at 750°C under $P(\text{O}_2) = 10^3$ and 10 Pa, respectively. The data clearly indicate that this oxide indeed undergoes a distinct structural change upon lowering oxygen pressure, from a slightly oxygen-deficient “ O_6 ” phase ($\text{BaYMn}_2\text{O}_{5.89}$; $P(\text{O}_2) = 10^3$ Pa) to an oxygen-vacancy ordered “ $\text{O}_{5.5}$ ” phase ($\text{BaYMn}_2\text{O}_{5.51}$; $P(\text{O}_2) = 10$ Pa). The $\text{BaYMn}_2\text{O}_{5.89}$ structure was reasonably refined assuming an orthorhombic *Cmmm* unit cell with lattice constants a , b , $c \approx 2a_p$, where a_p denotes the lattice constant of the cubic perovskite structure. The refined $\text{BaYMn}_2\text{O}_{5.89}$ structure is depicted in the inset of Fig. 2(a). Our careful refinement suggests that yttrium resides in a split site at a less symmetrical position with 50% occupancy, see the [001] projection shown in Fig. 2(c). The site splitting for yttrium leads to its random displacements within the yttrium plane. Since the oxygen sites within the yttrium plane are slightly unfilled, nonequivalent distances of shorter Y-O and longer Y- V_O (V_O denotes an oxygen vacancy) may be more favorable. We thus interpret the large yttrium displacement as a consequence of oxygen vacancy formation at the surrounding oxygen sites.

Meanwhile, the pattern for $\text{BaYMn}_2\text{O}_{5.51}$ was fitted well with the orthorhombic *Icma* model (Fig. 2(b); a , $b \approx 2a_p$, $c \approx 4a_p$) that is proposed for a room-temperature “ $\text{O}_{5.5}$ ” structure [4]. The $\text{BaYMn}_2\text{O}_{5.51}$ structure contains alternate ordering of oxygen and vacancy arrays within the yttrium plane (Fig. 2(d)), giving rise to two distinct manganese sites: one with square pyramidal coordination and the other with octahedral coordination. It is thus evident that the “ O_6 ”-to-“ $\text{O}_{5.5}$ ” transformation involves drastic modifications in the Mn polyhedra. Moreover, a closer look at the coordination geometry around manganese has revealed important structural features underlying the

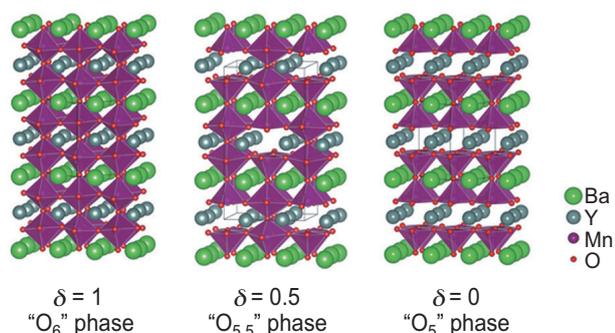


Fig. 1. Schematic illustration of the crystal structures of $\text{BaYMn}_2\text{O}_{5+\delta}$ with oxygen contents $\delta = 1, 0.5$, and 0 (“ O_6 ”, “ $\text{O}_{5.5}$ ”, and “ O_5 ” phases, respectively). The illustration was drawn with VESTA software [5] on the basis of the room-temperature structural models reported in the literature.

remarkable oxygen intake/release. As demonstrated in Fig. 3, both the $\text{MnO}_5/\text{MnO}_6$ polyhedra in the $\text{BaYMn}_2\text{O}_{5.51}$ structure are significantly distorted: the Mn-O bond parallel to the c -axis is much longer than those within the ab plane, while octahedral MnO_6 is largely elongated along the a -axis. This feature is in contrast to the $\text{BaYMn}_2\text{O}_{5.89}$ structure, in which the Mn octahedra are much more isotropic having similar Mn-O bond lengths for all directions.

The peculiar atomic arrangement in $\text{BaYMn}_2\text{O}_{5.51}$ can be understood as a consequence of alternate orbital ordering for the Jahn-Teller active Mn^{3+} ions consisting of d_{z^2} -type orbital along the c -axis at the pyramidal site and that along the a -axis at the octahedral site. It should be noted that this high-temperature structure is essentially identical to the room-temperature structure, indicating the robustness of the orbital-ordered “ $\text{O}_{5.5}$ ” structure in a wide temperature range. As demonstrated by the comparison of Figs. 2(c) and 2(d), the abrupt “ O_6 ”-to-“ $\text{O}_{5.5}$ ” transformation can also be viewed as discontinuous structural reconstruction within the yttrium plane, involving oxygen/vacancy redistribution and yttrium displacement organization,

being triggered by the relative stabilization of the two phases. That is to say, the abrupt jump in the oxygen content and thereby the remarkable oxygen intake/release behaviors are attributed to the exceptional stability of the “ $\text{O}_{5.5}$ ” structure consisting of particular Mn^{3+} orbital ordering, and the instability of the “ O_6 ” structure disrupted by the increased number of oxygen vacancies and associated random displacements of yttrium.

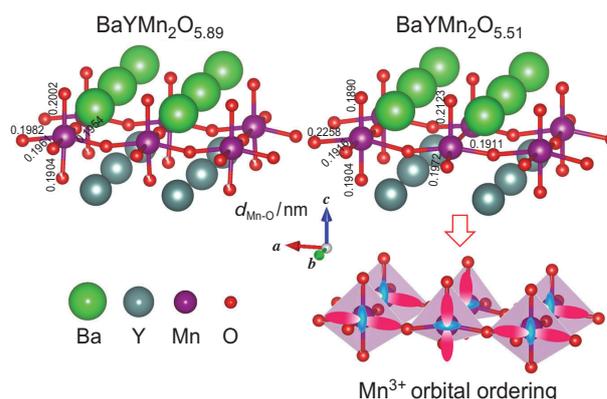


Fig. 3. Atomic arrangements of $\text{BaYMn}_2\text{O}_{5.89}$ (upper left) and $\text{BaYMn}_2\text{O}_{5.51}$ (upper right) at 750°C . The schematic illustration of the Mn^{3+} orbital ordering is also given (bottom right).

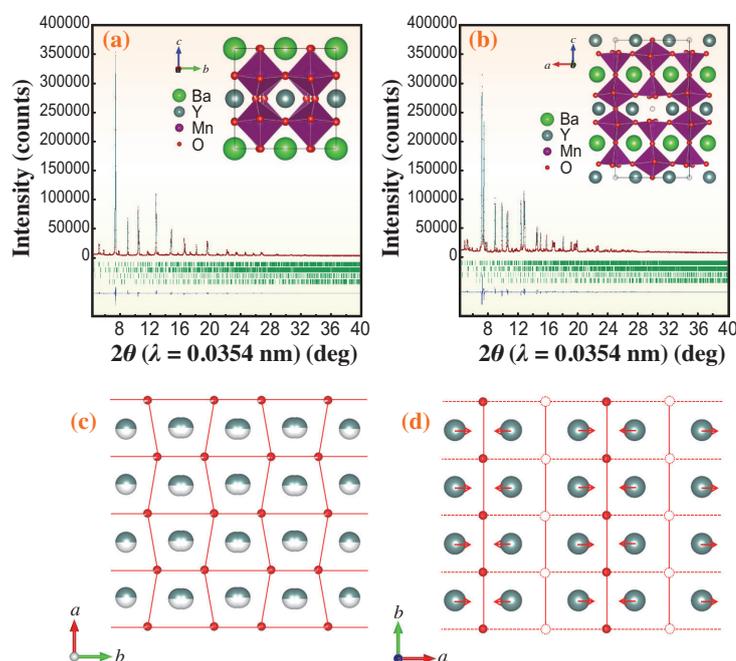


Fig. 2. High-temperature X-ray diffraction patterns for (a) $\text{BaYMn}_2\text{O}_{5.89}$ and (b) $\text{BaYMn}_2\text{O}_{5.51}$ measured at 750°C under $P(\text{O}_2) = 10^3$ and 10 Pa, respectively. The crystal structures were refined by the Rietveld method using the RIETAN-FP program [6]. The resultant crystal structure is visualized in the inset of each figure. The [001] projections of the two structures, showing local atomic arrangements within the yttrium plane are presented in (c) and (d).

Teruki Motohashi^{a,*}, Yoshiki Kubota^b
and Hiroshi Kageyama^c

^a Department of Materials and Life Chemistry,
Kanagawa University

^b Department of Physical Science,
Osaka Prefecture University

^c Department of Hydrocarbon Chemistry,
Kyoto University

*E-mail: t-mot@kanagawa-u.ac.jp

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