

## Diffusion Path of Oxide Ions in a Fast-ion Conductor $\text{La}_{0.64}(\text{Ti}_{0.92}\text{Nb}_{0.08})\text{O}_3$ with a Double Perovskite-type Structure

Roushown Ali(A,B), Masatomo Yashima(B), Fujio Izumi(A)

(A) Quantum Beam Center, National Institute for Materials Science, 1-1 Namiki, Tsukuba, Ibaraki 305-0044; (B) Department of Materials Science and Engineering, Interdisciplinary Graduate School of Science and Engineering, Tokyo Institute of Technology, Nagatsuta-cho 4259-J2-61, Midori-ku, Yokohama-shi, 226-8502, Japan.

Materials with high oxide-ion conductivities have received special attention in recent years owing to the potential applications of such materials in batteries and solid-oxide fuel cells. Information on the diffusion path and positional disorder of mobile oxide ions at high temperatures, where the materials work most efficiently, is indispensable for developing better oxide-ion conductors.

The lanthanum titanate solid solution  $\text{La}_{2+x}/3(\text{Ti}_{1-x}\text{M}_x)\text{O}_3$  ( $\text{M} = \text{Al}$  or  $\text{Nb}$ ,  $0.05 < x < 0.20$ ) has an A-site deficient double perovskite-type structure and exhibits high oxide-ion conductivity at high temperature. Yoshioka [1] studied the electrical properties of  $\text{La}_{2+x}/3(\text{Ti}_{1-x}\text{Nb}_x)\text{O}_3$  ( $x = 0.05-0.15$ ) and reported that a sample with  $x = 0.10$  displayed the highest ionic conductivity ( $10^{-2} \text{ S cm}^{-1}$  at  $700 \text{ C deg.}$ ) of the samples examined. In this study, we have examined the crystal structure and pathway of oxide-ion diffusion in A-site deficient layered double perovskite-type oxide,  $\text{La}_{0.64}(\text{Ti}_{0.92}\text{Nb}_{0.08})\text{O}_3$ , at high temperature.

Neutron powder diffraction data for  $\text{La}_{0.64}(\text{Ti}_{0.92}\text{Nb}_{0.08})\text{O}_3$  were collected at  $496 \text{ C deg.}$ ,  $1008 \text{ C deg.}$  and  $1358 \text{ C deg.}$  using powder diffractometer HERMES with a furnace [2] to heat the sample. The sample temperature was maintained within  $\pm 1.5 \text{ C deg.}$  during each measurement. Incident neutron wavelength was  $0.18143 \text{ nm}$ . The diffraction data were analyzed by the Rietveld method followed by application of MPF [3] using the computer programs RIETAN-2000 [4]. The MEM calculations were performed with the unit cell divided into  $64 \times 64 \times 128$  pixels. To reduce the

bias imposed on the nuclear density by the simple structural model adopted in the Rietveld analyses, an iterative procedure called the REMEDY cycle was employed following MEM analyses.

All reflections in the neutron powder diffraction patterns for  $\text{La}_{0.64}(\text{Ti}_{0.92}\text{Nb}_{0.08})\text{O}_3$  at  $496 \text{ C deg.}$ ,  $1008 \text{ C deg.}$ , and  $1358 \text{ C deg.}$  were indexed on the basis of a tetragonal  $P4/mmm$  cell. Refinements of anisotropic atomic displacement parameters ( $U_{ij}$ ) for cations resulted in no significant improvement in the reliability (R) factors. Therefore,  $U_{ij}$  were refined only for oxygen sites in subsequent Rietveld refinements. The oxygen atoms located at  $4i$  site displayed large anisotropy in the atomic displacement parameters, suggesting a directionality in the movements of oxide ions around the stable positions.

At  $496 \text{ C deg.}$ , the  $\text{O}_3$  atoms are localized near the stable  $4i$  site ( $1/2, 0.0, 0.234$ ). The  $\text{O}_3$  atoms display small bulges in the  $[101]$  direction which become larger at  $1008 \text{ C deg.}$  and  $1358 \text{ C deg.}$  The probability density of an  $\text{O}_3$  atom is connected with that of nearest-neighbor  $\text{O}_3$  atoms, indicating diffusion along a pathway following the  $[100]$  and  $[010]$  directions. The  $\text{O}_3$  atoms migrate to the nearest-neighbor  $4i$  site through a triangle formed by adjacent  $\text{La}_1$ ,  $\text{La}_2$ , and  $(\text{Ti}, \text{Nb})$  atoms. At the intermediate points, the densities of the coherent-scattering lengths of oxide ions ( $4i$  site) are  $0.13 \text{ fm}^{-3}$  at  $1358 \text{ C deg.}$ ,  $0.10 \text{ fm}^{-3}$  at  $1008 \text{ C deg.}$ , and  $0.03 \text{ fm}^{-3}$  at  $496 \text{ C deg.}$  Such an increase in the density of oxide ions with increasing temperature is consistent with the higher conduc-

tivity at higher temperatures.

The O3 atom migrates following a curved route so as to maintain a relatively constant distance from (Ti,Nb) atoms rather than a direct linear path. Yashima et al. [5] in their study of the nuclear density distribution of an ideal cubic perovskite-type compound  $(\text{La}_{0.8}\text{Sr}_{0.2})(\text{Ga}_{0.8}\text{Mg}_{0.15}\text{Co}_{0.05})\text{O}_{2.8}$  found similar curved migration pathways.

The oxide-ion conductor with an ideal perovskite-type structure exhibits diffusion paths along the [100], [010] and [001] directions to form a three-dimensional network of equivalent diffusion pathways, as shown by Yashima et al. [5]. On the contrary, in the present double perovskite-type  $\text{La}_{0.64}(\text{Ti}_{0.92}\text{Nb}_{0.08})\text{O}_3$ , a two-dimensional diffusion pathway is present, by which O3 atoms migrate along the [100] and [010] directions. This two-dimensional feature is attributable to the layered structure of the  $\text{La}_{0.64}(\text{Ti}_{0.92}\text{Nb}_{0.08})\text{O}_3$ , which consists of La-occupied La1-O1, (Ti,Nb)-O, and La-deficient La2-O2 layers.

#### References

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