Introduction  Oxide-ion conductors have attracted much attention due to their wide applications such as oxygen gas sensors and solid oxide fuel cells (SOFCs). However, high oxide-ion conductivities are attained for the materials with limited crystal structures such as the fluorite-type and perovskite-type structures. Therefore, the exploration of a new structure family of oxide-ion conductors is challengeable and necessary for the development of the applications mentioned above. Many oxide-ion conductors containing cation species with $d^{10}$ electronic configuration such as Ba:In:O$_3$ and $\delta$-Bi:O$_3$ exhibit high oxide-ion conductivities. Herein, we focus on the compositions containing antimony (Sb) as an essential element. In this work, we report a new structure-type oxide-ion conductor Bi$_2$GaSb$_3$O$_{11}$. The chemical composition Bi$_2$GaSb$_3$O$_{11}$ was chosen by screening 402 Sb-containing materials through the bond-valence-based energy calculations.

Experiment  We selected 402 Sb-containing oxides registered in the Inorganic Crystal Structure Database (ICSD) before the screening by the BV method. A program softBV was used to estimate the energy barrier for oxide-ion migration $E_b$ based on the bond-valence-based energy. Bi$_2$GaSb$_3$O$_{11}$ was synthesized by the solid-state-reaction method. Synchrotron X-ray powder diffraction data of Bi$_2$GaSb$_3$O$_{11}$ were measured in air at 27-800 °C on beamline BL02B2 at SPring-8. Neutron-diffraction (ND) data of Bi$_2$GaSb$_3$O$_{11}$ were measured at 26-600 °C by Time-Of-Flight (TOF) neutron diffractometer IMATERIA. The ND data were analyzed by the Rietveld method. Direct current (DC) electrical conductivity $\sigma_{DC}$ of Bi$_2$GaSb$_3$O$_{11}$ was measured by a four-probe method in flowing dry and wet air. The oxygen partial pressure $P(O_2)$ dependence of $\sigma_{DC}$ was measured at constant temperature 916 °C in the $P(O_2)$ range from $8.1 \times 10^{-1}$ to $5.5 \times 10^{-2}$ atm controlled using nitrogen, oxygen and argon gas mixtures. Alternating current (AC) impedance spectra with Pt electrodes were recorded in the temperature range of 582 to 893 °C. Bond-valence-based energy landscapes (BVELs) for a test oxide ion were examined to investigate oxide-ion diffusion pathways in Bi$_2$GaSb$_3$O$_{11}$.

Result & discussion  Bi$_2$GaSb$_3$O$_{11}$ composition was selected by screening 402 Sb-containing materials by the bond-valence-based-energy calculations. Bi$_2$GaSb$_3$O$_{11}$ was synthesized by solid-state reactions and its electrical conductivity and crystal structure were investigated at high temperatures. No phase transitions were observed between 26 and 800 °C. The crystal structure of data from 26 to 600 °C. In the refined structure, two (Ga$_{1/2}$Sb$_{3/2}$)O$_{10}$ octahedra share their edges to form a (Ga$_{2/3}$Sb$_{4/3}$)O$_{10}$ unit (Fig. 1). Bi$_2$GaSb$_3$O$_{11}$ exhibited a high bulk ionic conductivity of $6.2 \times 10^{-3}$ S cm$^{-1}$ at 893 °C with a low activation energy of 0.68(2) eV (Fig. 2). Oxide-ion conduction was strongly suggested by the oxygen partial pressure dependence of electrical conductivity, polarization measurements, wide band gap, and electrical conductivities in wet and dry atmospheres. The bond-valence-based-energy calculations for the refined crystal structure at 600 °C indicated that oxide ions three-dimensionally migrate through the curved paths along the edges and on the O–O–O faces of (Ga$_{2/3}$Sb$_{4/3}$)O$_{10}$ unit in Bi$_2$GaSb$_3$O$_{11}$ (Fig. 3).

Keywords: oxide ion conductor, crystal structure, bond-valence-based energy calculation