Diffusion Path of Oxide Ions in Apatite-type La9.25Si6.0O25.88

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Solid oxides exhibiting high ionic conductivity have been the subject of considerable research interest. In particular, the oxide-ion conductors are useful materials for fuel cells, catalysts, gas sensors and batteries. The development of improved electrolyte materials for these applications requires a thorough understanding of the crystal structure and diffusion path of mobile oxide ions, which determine the mechanism of ionic conduction. Lanthanum silicates La10-xSi6O26+delta having apatite-type structure are one of the promising groups exhibiting significant oxide ion conductivity but the understanding of the conduction mechanism in this structure remains subject to uncertainties. Here, we have investigated the crystal structure and diffusion pathway of oxide ions in apatite-type compound La9.25Si6.0O25.88 at 1558 degrees Celsius.

The neutron powder diffraction data were collected at 1558 degrees Celsius on HERMES installed at the JRR-3M reactor. Incident neutron beams with a fixed wavelength of 0.18265 nm were obtained by a vertically focusing (331) Ge monochromator. A furnace [1] with an MoSi2 heater was used to heat the sample and the sample temperature was maintained within +- 1.5 degrees Celsius. during the measurement. The resulting diffraction data were analyzed by the Rietveld method with RIETAN-FP [2] and whole-pattern fitting approach based on the maximum-entropy method (MPF) [3]. The MEM calculation was done with the unit cell divided into 100 X 100 X 80 pixels and whole-pattern fitting using RIETAN-FP.

The Rietveld refinement was performed with hexagonal space group P63/m through the neutron powder diffraction data measured at 1558 degrees Celsius. Attempts to refine the structure considering an interstitial oxygen atom site were not successful, so the refinement were performed without interstitial site. The calculated pattern agreed well with that of observed pattern. The reliability values obtained from the refinement were Rwp = 2.15 %, Rp = 1.67 %, RI = 1.20 % RF = 0.72 % and S = 2.05. The refinement was carried out with anisotropic thermal displacement parameters for all the cations and anions. The thermal displacement parameters of oxygen O3 atoms showed strong anisotropic along the a-axis with large U11 value (0.00123(3) nmˆ2) while that of O4 showed stronger anisotropic along the c-axis with larger U33 value (0.0025(1) nmˆ2). The structure consists of six isolated [SiO4] tetrahedra containing three kinds of oxygen atoms (O1, O2, O3). The oxygen atoms O3 and O4 displayed large displacement parameters, suggesting directionality in the movements of oxide ions around their stable positions. The probability densities of O4 atoms were connected with that of nearest-neighbor O4 atoms, indicating diffusion along a pathway parallel to the c axis. The O4 atoms migrated linearly to the nearest-neighbor O4 and followed one-dimensional tunnel extending along the c axis of the hexagonal P63/m framework. On the other hand, the probability densities of O3 atoms were largely distributed perpendicular to the c axis. The main diffusion pathway

involved one-dimensional migration along the hexagonal channels of the apatite-type structure. The directionality in the movements of oxide ion O3 also suggests another migration pathway perpendicular to the c-axis.

References

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