Dependence of Crystal Structure and Protonic Conduction on Compositions in Gallate-Based High Temperature Protonic Conductors with Layered Structures

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Solid oxide fuel cell, which is so-called SOFC, can be regard as a new and clean energy source, and has been widely investigated in recent decades. As an electrolyte of the SOFC, LaBaGaO4-based high-temperature protonic conductors with a layered structure have drawn much attention, because of the high conductivity, high ionic transport number and high chemical stability against ambient acid gases, like CO2. In the proton conductors, a partial substitution of an aliovalent cation for the host cation introduces some defects, such as an oxygen vacancy and an interstitial proton. Diffusions of these defects through the crystals dominate the proton-uptake and conduction processes at elevated temperature. Thus, in order to understand the protonic conduction mechanism, it is important to investigate the crystal structures, especially the sites and the occupancies of the oxygen and proton. At this moment, however, there is not sufficient knowledge on the crystal structures of the LaBaGaO4 system.

In this study, neutron diffraction patterns of La1-xBa1+xGa1-yMgyO4-d with a layered structure were measured with HERMES installed at JRR-3, and then the crystal structures were analyzed based on the Rietveld method by using the Rietan-FP program.

La1-xBa1+xGa1-yMgyO4-d(x=0~0.1, y=0~0.05) were synthesized by a conventional solid-state reaction using each metal oxide or carbonate as a starting material. Phase identifications of the samples were carried out with powder X-ray diffraction measurements. We also investigated the electrical conductivities at the temperature range from 573 to 1173 K under various PO2 and PH2O, and then discussed the protonic-conduction properties at the elevated temperature. Neutron diffraction measurements of the samples were performed in order to investigate the crystal structure in detail.

From X-ray diffraction patterns, it was indicated that La1-xBa1+xGa1-yMgyO4-d synthesized in this work had a single phase of a layered structure regardless of the composition, and a change of the lattice constants reflected a difference of the ionic radii of the constituent cations. Conductivity measurements revealed that LaBaGaO4 began to exhibit protonic conduction under moisturized conditions at high temperature by substituting Ba and Mg for La and Ga, respectively.

Rietveld analyses using neutron diffractions indicated that all the La1-xBa1+xGa1-yMgyO4-d had an orthorhombic layered structure (S. G.; P212121) in air. From the refined structure parameters, it was found that atomic displacement parameters of the oxygens were larger than those of the other constituent elements. This suggests that oxygen vibrations play an important role for the protonic conduction, because the proton can be considered to diffuse via a hydrogen bond in the case of the high-temperature protonic conductors. It was also clarified that the oxygen amounts of La1-xBa1+xGa1-yMgyO4-d which were estimated from the refined occupancies, were larger than those predicted from the electroneutrality condition; that is, 4-d=4-x/2-y/2. This may be due to a progress of a hydration reaction, which can be described as below with the Kr ger-Vink notation;

(1/2)Vo..+(1/2)H2O(g) + (1/2)Oox -> <- OHo.

where $V_O^{\cdot\cdot}$, O_{ox} and $OH_O^{\cdot}$ represent oxygen vacancies, O^{2-} at the O^{2-} sites and an interstitial proton coordinating an oxide ion, respectively.