XAFS Study of the Local Structures in Perovskite-type Solid Oxide Crystal Electrolytes

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Defective perovskite type oxides are excellent candidates for electrolytes of solid oxide fuel cells operating at intermediate temperature. Recently some researchers reported that $Ba_2In_2O_5$ has a characteristic order-disorder transition temperature at 930°C and this compound shows higher oxide ion conductivity than that of stabilized zirconia at above the temperature. The results of XRD patterns obtained for $Ba_2In_2O_5$ were indexed to orthorhombic lattice at room temperature, on the other hand, at high temperature of 1100°C, the pattern was indexed to cubic lattice. The refined crystal parameters using Rietveld method for $Ba_2In_2O_5$ before and after the phase transition revealed that $Ba_2In_2O_5$ belonging to *Ibm2* space group transformed to a cubic structure with *Pm3m* space group. These results indicate that disordering of oxygen vacancy is important to construct a novel defective perovskite type ion conductor having high oxide ion conductivity.

We attempted to stabilize the disorder phase by doping of trivalent cations, such as Gd^{3+} and Ga^{3+}. The refined crystal parameters using Rietveld method for $Ba_2In_{2-x}Gd_xO_5$ (x = 0, 0.2, 0.3) revealed that the oxides belonging to cubic structure with *Pm3m* space group. In the defect perovskite oxides, there are two kinds of B site cation sites, that is 6 and 4 coordinate, respectively and the average coordination number is 5. The electrical conductivities of Gd-doped $Ba_2In_2O_5$ did not show a sharp discontinuity. These results indicated that the disorder phase of defective perovskite type structure was stabilized by doping Gd cations. It is very important to clarify the local structures of B-site cations of In and Gd in order to design the oxide ion diffusion path. In this work, the local structures of B-site cations were analyzed by EXAFS measurement.

Pure and doped $Ba_2In_2O_5$ powder was prepared by usual solid state reaction starting with $BaCO_3$, In_2O_3 and dopant metal oxides. The resulted fine powders of the undoped and doped oxides were sandwiched between thin Scotch® tapes films.

Figure 1 shows Foulier transform data of In K-edge EXAFS spectrum of $Ba_2In_2O_5$ oxide. Foulier transform data of $Ba_2In_{2-x}Gd_xO_5$ (X = 0, 0.2, 0.3) show a peak between 1.2 and 2.0 Å. The peaks are attributed to the nearest oxygen atoms around In cation. In order to analyze the coordination number of In cation, The prominent shell in the resulting radial distribution were back-Fourier transformed. Results of the parameter fitting of the EXAFS function for $Ba_2In_{2-x}Gd_xO_5$ (X = 0, 0.2, 0.3) indicate that the coordination number of In cation decrease with increasing Gd content. This result indicates that coordination number of Gd cation is not 4 but 6 preferably.

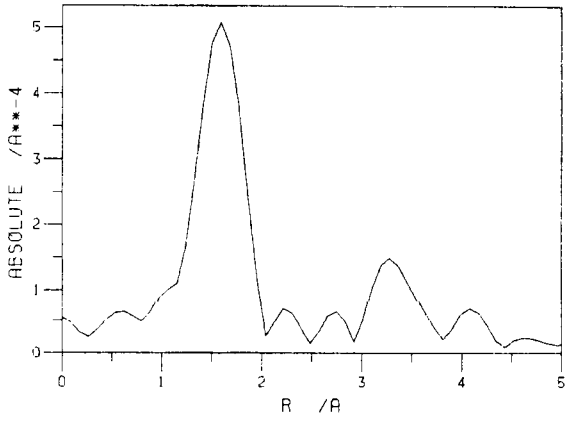

Figure 1. Foulier translation data of In K-edge EXAFS spectrum of $Ba_2In_2O_5$ oxide.