Diffusion path of oxide ions in the yttria-doped ceria

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Abstract

Scattering amplitude distribution of an yttria-doped ceria material (Ce0.93Y0.07O1.96, space group: Fm-3m) has been investigated between 23 oC and 1434 oC by the maximum-entropy method (MEM) combined with the Rietveld analysis using neutron powder diffraction data. The refined unit-cell and atomic displacement parameters increased with an increase of temperature. The results of the MEM analysis reveal that the oxide ions have a positional disorder spreading over a wide area. One possible diffusion path of the oxide ions lies on the tie line along the <100> directions. The other pathway of the oxide ions can be seen along the <110> directions. The curved feature in the diffusion path would be common in various ionic conductors.

(1) Introduction

Atomic transport in solids is one of the central themes in contemporary solid state science and technology. Crystalline ionic conductors have extensively been studied by numerous researchers because of their many applications in solid oxide fuel cells (SOFCs), sensors, catalysts, and batteries. The development of better electrolyte materials requires a better understanding of the mechanism of ionic conduction, and crucial to this is a comprehensive knowledge of the crystal structure. Therefore, many researchers have studied the crystal structure and diffusion path of the ionic conductors. It is well known that the ionic conductor has a positional disordering for the mobile ions. To describe the spatial distribution and disorder of the mobile ions, various techniques such as the split-atom model, the anharmonic thermal motions, the probability density function, the Fourier synthesis have been applied. Recently the maximum-entropy method has been developed for the determination of accurate structural features through the electron and nuclear density distribution in the crystalline materials. In the present work we focus on an oxide-ion conductor, yttria-doped ceria solid solution, Ce0.93Y0.07O1.96 [1].

(2) Experiments

A ceria-yttria solid solution Ce0.93Y0.07O1.96 sample was prepared from a precursor carbonate including Ce and Y atoms. The precursor carbonate was calcined at 1200 oC and then crushed and ground by a ball-milling technique. The Ce0.93Y0.07O1.96 powders thus obtained were pressed into pellets, and then sintered at 1500 oC for 3 h in air. The sintered product was cylindrical with the size of 19 mm in diameter and 30 mm in height. These pellets were used for the high-temperature neutron diffraction measurements. Neutron powder diffraction experiments were carried out in air in the temperature range from 23 oC to 1434 oC. Neutron powder diffraction measurements were conducted in air with a 150-detector system, HERMES, installed at the JRR-3M reactor in Japan Atomic Energy Agency, Tokai, Japan. Neutrons with wavelength 1.82035 were used. The neutron diffraction data were analyzed by a combination technique of the Rietveld analysis and the maximum-entropy method (MEM).

(3) Results and discussion

All the reflections in the neutron powder

diffraction patterns of Ce0.93Y0.07O1.96 in the whole temperature range of 23 oC to 1434 oC were indexed by a single phase with the cubic fluorite-type structure. Rietveld analysis was carried out assuming the fluorite-type structure with the symmetry where the cation (Ce4+ and Y3+) and anions (O2- and its vacancy) were put at 4a 0,0,0 and at 8c 1/4,1/4,1/4, respectively. The isotropic atomic displacement parameters were used for all the atoms. The calculated profile agreed well with the observed data. The refined crystallographic parameters and the reliability factors in the Rietveld analyses are shown in Table 1. The unit-cell parameter increased with an increase of temperature. Both the isotropic atomic displacement parameters for the cations B(CY) and for the anions B(O) also increased with temperature. The B(O) was larger than the B(CY), suggesting a larger diffusion coefficient of oxide ions. These features are consistent with the previous results in Rietveld analyses for the non-doped and doped ceria materials.

Maximum-entropy method (MEM) analyses were carried out using the structure factors obtained in the Rietveld analysis. Number of structure factors derived in the analysis was 11. In the MEM calculations we used the 111 peak intensity at the lowest 2theta position that is the most important information for the MEM analysis. The MEM map provided much information on the positional disorder of oxide ions, comparing with the structural model obtained in the Rietveld analysis. The conventional simple models consisted of atom spheres are no longer appropriate to describe the positional disorder of oxide ions at high temperatures. The present results reveal that the oxide ions in the Ce0.93Y0.07O1.96 have a complicated disorder and spread over a wide area, comparing with cations. The spatial distribution of oxide ions at 1434 C was larger than that at 23 C, corresponding to the larger atomic displacement parameters. There were two types of bulges in the MEM distribution map. The other exists along the <110> directions. These directions of oxide ions are opposite side of the Ce and Y cations. The bulges are attributable to the repulsion between the cations and oxide ions. Such anisotropic feature in the neutron scattering amplitude have been observed in the ceria materials.

Reference

[1] Masatomo Yashima, Syuuhei Kobayashi and Tadashi Yasui, " Positional disorder and diffusion path of oxide ions in the yttria-doped ceria Ce0.93Y0.07O1.96" , Faraday Discussions, 134, 369-376 (2007).