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Structural changes of the high temperature proton conductor $SrZr_{1-x}Yb_xO_{3-\delta}$

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Introduction

Perovskite-type strontium zirconate $SrZrO_3$ exhibits appreciable proton conduction in hydrogen-containing atmosphere at high temperature when a few mol% of trivalent cations such as Yb^{3+}, Y^{3+}, Ga^{3+} and In^{3+} are substituted for Zr^{4+} ions. The chemical stability of $SrZrO_3$-based oxide is much better, and Yb-doped $SrZrO_3$ oxide shows the highest proton conductivity. The proton conductivity depends on the amount of dopant Yb ions and shows the maximum value when substituted for Yb ions by 10 mol% [1, 2].

In order to understand the electrical properties of these materials, it is necessary to study the precise crystal structure of $SrZrO_3$ and doped $SrZrO_3$. In our previous study, it was found that $SrZrO_3$ undergoes a sequence of phase transitions as follows, *Pnma* → *Imma* → *I*4/*mcm* → *Pm*-3*m*, at 790, 875 and 1120°C, respectively. Here we have used synchrotron X-ray diffraction technique, having higher angular resolution, to investigate the structural change and the phase transition temperature of $SrZr_{1-x}Yb_xO_{3-\delta}$ (x = 0.05 and 0.1).

Experiments

The powder samples of 5 and 10 mol% Yb-doped $SrZrO_3$ were synthesized by solid-state reaction. To obtain higher angular resolution as possible with good counting statistics, we performed synchrotron X-ray powder diffraction experiments from 25°C to 1084°C for Yb-doped $SrZrO_3$ at the beam line BL-3A at the Photon Factory, High Energy Accelerator Research Organization (KEK), Japan. A monochromatized 0.99930Å X-ray was used for high-temperature diffraction measurements. To improve the angular resolution a Si (111) analyzer crystal was installed between the sample and the scintillation counter. The temperature was kept constant within ± 0.5°C during each data collection.

Results and discussion

Figure 1 shows the synchrotron X-ray diffraction patterns of 10 mol% Yb-doped $SrZrO_3$ in in the 2θ range from 27.8° to 28.0°. At 666, 688 and 710°C, we observed Bragg reflections from two phases, *Imma* and *I*4/*mcm*, indicating that the phase transition is discontinuous and of first order. The result of this study made clear that the $SrZr_{1-x}Yb_xO_{3-\delta}$ (x = 0.05, 0.1) undergoes a sequence of same phase transitions as $SrZrO_3$ does.

Figure 2 shows the transition temperatures against x in $SrZr_{1-x}Yb_xO_{3-\delta}$. The transition temperatures of the Yb-doped $SrZrO_3$ decrease with increasing amount of dopant Yb ions in spite of substitution of Zr^{4+} ions by Yb^{3+} ions with a large ionic radius. This suggests that there exist much oxide ion vacancies introduced by substitution of tetravalent zirconium ions by trivalent ytterbium ions.

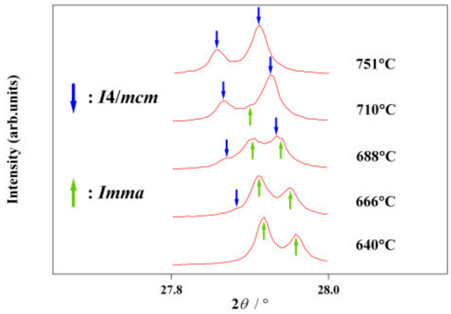

Fig. 1. Synchrotron X-ray diffraction patterns of 10 mol% Yb-doped $SrZrO_3$ in the 2θ range of 27.8° to 28.0°.

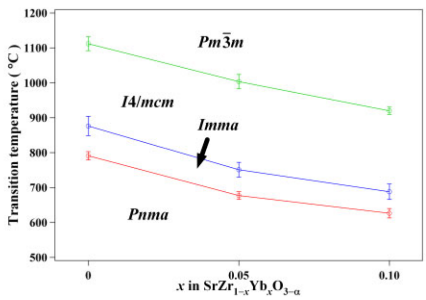

Fig. 2. Transition temperatures for $SrZr_{1-x}Yb_xO_{3-\delta}$ against Yb concentration x.

References

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