Protonic conduction in Zr-doped $Ba_2In_2O_5$ at intermediate temperatures

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Introduction

Perovskite type protonic conductors such as $SrCeO_3$ and $BaCeO_3$ have a large potential to use as an electrolyte in high efficiency power generators. These materials indicate the protonic conduction at high temperatures (~1273K) but this high operating temperature leads to a lack of reliability of their system. Thus, the material which indicates higher protonic conduction at lower temperatures (873~1073K) has been expected.

$Ba_2In_2O_5$, which has brownmillerite structure, is known to have relatively high proton conductivity and solubility[1,2], but this material is not in practical use because of its poor chemical stability. On the other hand, $BaZrO_3$ is rather stable, but has low proton conductivity [3]. Thus, solid solutions between $Ba_2In_2O_5$ and $BaZrO_3$ are expected to have both merits. In this paper, Zr-doped $Ba_2In_2O_5$ was studied by impedance measurement in dry argon and water saturated argon atmospheres.

Experimental

$Ba_2(In_{1-x}Zr_x)_2O_{5+x}$ specimens where x = 0.05, 0.10 and 0.12 (BIZO5, 10, 12) were prepared by solid state reaction. Starting powder materials of $BaCO_3$, In_2O_3 and ZrO_2 were mixed and grounded in alumina mortar with methanol, and calcined in air at 1473K for 3h. The powder was then die-pressed into disks and isostatic-pressed at 200MPa. These disks were sintered at 1673K for 5h, and the size of disks was 8mm in diameter and 1mm in thickness. The crystal structure was characterized by powder X-ray diffraction.

Impedance measurements were carried out in dry argon or water saturated argon (wet) atmosphere at the temperatures from 673K to 1273K and frequencies from 5Hz to 13MHz.

Results and Discussion

The powder X-ray diffraction patterns showed that all specimens had orthorhombic brownmillerite structure, and they approached to cubic symmetry with increasing Zr content.

Total conductivities of specimens in dry and wet argon atmospheres are shown in Fig.1. Higher Zr-doped $Ba_2In_2O_5$ indicated higher conductivity, and order-disorder transition temperatures of BIZO5, BIZO10 and BIZO12 were about 1043, 893, 843K, respectively. In wet argon condition, the conductivities of all specimens rose from values of dry state, especially in a lower temperature region. In BIZO12 at 673K (1000/T~1.5), deviation from Arrhenius equation was observed. This variation may stem from phase transition of this material caused by a large amount dissolution of H_2O[2].

Assuming that protonic conduction is independent of other carriers' contribution to the conductivity, the pure protonic conductivity, σ_H, represents as followed equation,

$$\sigma_H = \sigma_{wet} - \sigma_{dry}.$$

Protonic conductivities calculated from this equation are shown in Fig.2. These values of conductivities are relatively high compared to other perovskite type oxides in a temperature range which is lower than the order-disorder temperatures of these oxides.

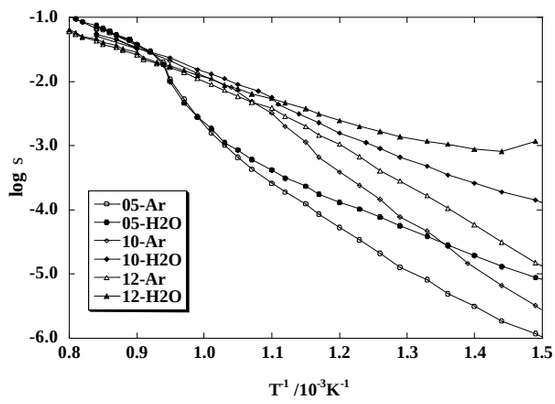

Fig.1. Total conductivities in various atmosphere.

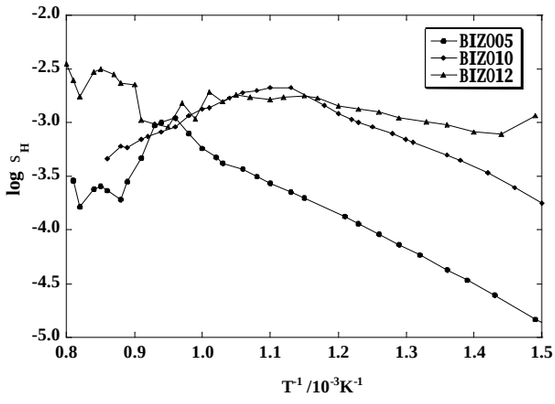

Fig.2. Protonic conductivities, $\sigma_H = \sigma_{wet} - \sigma_{dry}$.

References

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