ELECTRICAL CONDUCTIVITY AND CRYSTAL STRUCTURE OF $Ba_2In_2O_5$ AT HIGH TEMPERATURES UNDER VARIOUS OXYGEN PARTIAL PRESSURES

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It has been reported that the crystal structure of $Ba_2In_2O_5$ changes from brownmillerite structure with ordered oxide-ion vacancies to perovskite structure with randomly distributed oxide-ion vacancies at 910 °C and that electrical conductivity increases by about two order at this phase transition.[1] Since the electrical conductivity of $Ba_2In_2O_5$ more than 910 °C is higher than that of yttria stabilized zirconia, it is expected as a new electrolyte material for solid oxide fuel cells, oxygen sensor and so on. However, electrical conduction mechanism of $Ba_2In_2O_5$ at high temperature has not been experimentally established. The measurement of electrical conductivity at various oxygen partial pressures, Po_2, is one of the methods to analyze electrical conduction mechanism. Moreover, the data of electrical conductivity and crystal structure under various Po_2 at high temperatures are essential to estimate potential of $Ba_2In_2O_5$ as an electrolyte material. So far, Kakinuma et al., [2] reported electrical conductivity of $Ba_2In_2O_5$ under various Po_2 at high temperatures. However, their measurements were limited under log Po_2 of 0.0 ~ -3.5 and at temperatures of 550 ~ 1000 °C.

Recently, we have found another structural phase transition at 1070 °C in $Ba_2In_2O_5$. It has been clarified that crystal structure of $Ba_2In_2O_5$ at 910 ~ 1070 °C is distorted perovskite and that phase more than 1070 °C is perovskite with smaller distortion.[3] Electrical conductivity measurement in air revealed that the phase of $Ba_2In_2O_5$ more than 1070 °C has the highest electrical conductivity and the lowest activation energy for electrical conduction, suggesting that this phase should be the most promising as a new electrolyte material.[4] However, no report has appeared on conduction mechanism of this high temperature phase. In this study, we have measured electrical conductivity of $Ba_2In_2O_5$ under various Po_2 at 850 ~ 1200 °C for analysis of conduction mechanism and estimation of potential as a new electrolyte material of $Ba_2In_2O_5$ including newly discovered phase.

The polycrystalline $Ba_2In_2O_5$ ceramics were prepared with conventional solid-state reaction method. The prepared specimens were confirmed to be brownmillerite single phase at room temperature. High temperature electrical conductivity measurements under various Po_2 were carried out by four-probe method using Pt electrode. Various Po_2 was prepared by mixing N_2 and O_2 or H_2 and H_2O vapor and it was monitored by zirconia O_2 sensor set at downstream of the apparatus. High temperature X-ray diffraction under various Po_2 was also carried out in order to analyze crystal structure and stability of $Ba_2In_2O_5$. Dilatometry and differential scanning calorimetry (DSC) were performed under various Po_2 for measurement of the phase transition behavior.

Figure 1 shows electrical conductivity under various oxygen partial pressures. Temperatures are shown as parameters. Constant logσ against $logP_{O2}$ were observed at 850 ~ 1200 °C under $logP_{O2}$ of –0.7~ –3, suggesting oxide-ion conduction in this temperature and $logPo_2$ range. These results showed agreement with those of Kakinuma and coworkers.[2] Below 900 °C, linear relationship with proportional constant of –1/4 was observed between logσ vs. $logP_{O2}$ under $logP_{O2}$ < –3. This suggested that oxide-ion vacancies were generated in $Ba_2In_2O_5$ under this Po_2 region and concentration of electron increased under these reduction atmospheres. Generation of oxide-ion vacancy was also deduced from reduction expansion under $logP_{O2}$ of –12 observed by high temperature X-ray diffraction.

The electrical conductivity increased in the order from 900 °C to 1000 °C under $logP_{O2}$ of -1 ~ -4, which could be ascribed to the phase transition also observed by both dilatometry and DSC. At 1000 ~ 1100 °C under log Po_2 range below -3, the electrical conductivity decreased with decrease of $logP_{O2}$. Since the X-ray diffraction measurements revealed that the crystal structure of $Ba_2In_2O_5$ at 1000 ~ 1200 °C was independent on $logP_{O2}$ in the range -1 ~ -4, the decrease of electrical conductivity could be attributed to generation of oxide-ion vacancy. It was suspected that decrease of oxide-ion mobility by vacancy appeared under $logP_{O2}$ < –3 at 1000 ~ 1100 °C. Also suspected was that the oxide-ion mobility at 1200 °C is so high that the decrease of oxide-ion mobility by oxide-ion vacancy was not apparent.

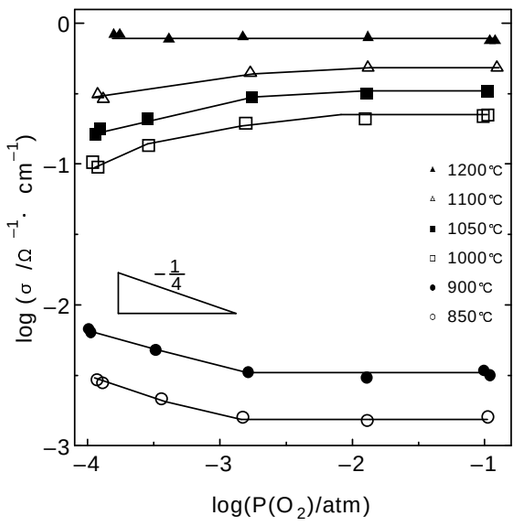

Fig. 1 Dependence of electrical conductivity of $Ba_2In_2O_5$ on $logP_{O2}$

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