

## DEFECT STRUCTURE AND OXYGEN DIFFUSIVITY OF NIOBIA DOPED CERIA

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### INTRODUCTION

Recently donor-doped ceria has been reported as an attractive material for anode of solid oxide fuel cells [1]. Compared to acceptor-doped ceria, however, only a few reports are available about their properties [2, 3]. In our previous study [4], electrical conductivity of niobia-doped ceria was measured as a function of oxygen partial pressure and temperature. Consequently, we deduced the defect model including defect association and oxygen interstitial. This paper aims to confirm the validity of the proposed defect model by thermogravimetric measurement and oxygen isotope diffusion experiment.

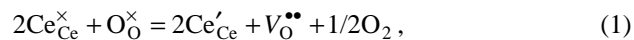
### EXPERIMENTAL

Powder of 0.8 mol% niobia doped ceria (NbDC) was made by a coprecipitation method. X-ray diffraction measurement confirmed that the powder was a fluorite single phase. Specimens for thermogravimetry and oxygen isotope diffusion were sintered at 1673 K for 12 h and 1873 K for 5 h, respectively. Isothermal thermogravimetric measurement was employed for the determination of oxygen nonstoichiometry,  $\delta$ , with variation in oxygen partial pressure and temperature. Oxygen tracer diffusion coefficient was determined by isotope exchange depth profiling with secondary ion mass spectrometry (SIMS).

### RESULTS AND DISCUSSION

Figure 1 shows the dependence of oxygen nonstoichiometry,  $\delta$ , on oxygen partial pressure. Solid and dotted curves are estimated values from conductivity data by the following defect model [4]:

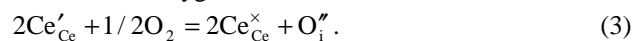
Equilibrium between gaseous phase and NbDC:



Formation of defect association:



Formation of oxygen interstitial:



Here, defect equation 2 and 3 can be almost neglected in oxidizing and reducing atmospheres, respectively. Thermogravimetry data are essentially consistent with the estimated values. There is, however, difference under slightly reducing condition at 973 K. This suggests that defect equation 2 don't necessarily hold at 973 K. In high oxygen partial pressure region, oxygen content became higher than stoichiometric composition ( $2-\delta > 2$ ). This result supports the existence of oxygen interstitial in NbDC.

Oxygen isotope exchange depth profiling with SIMS was done in order to reveal the existence of oxygen interstitial. Oxygen tracer diffusion coefficients,  $D^*$ , are plotted against oxygen partial pressure in Fig. 2. It was found that  $D^*$  is proportional to a half power of oxygen partial pressure. Here, when the concentration of oxygen interstitial is very low ( $[\text{O}_i^{\bullet}] \ll [\text{Ce}'_{\text{Ce}}]$ ), the relationship,

$[\text{O}_i^{\bullet}] \propto P_{\text{O}_2}^{1/2}$ , is derived from equation 3 and electro-neutrality condition. In addition, the following relationship holds between  $D^*$  and  $[\text{O}_i^{\bullet}]$ ,

$$D^* \propto D_{\text{O}} = D_i [\text{O}_i^{\bullet}] / [\text{O}_{\text{O}}^{\times}] \propto [\text{O}_i^{\bullet}] (\propto P_{\text{O}_2}^{1/2}) \quad (4)$$

where  $D_{\text{O}}$  and  $D_i$  are self-diffusion coefficients of oxygen and oxygen interstitial, respectively. This is the same tendency as the results of tracer diffusion experiment. As a result, existence of oxygen interstitial is confirmed.

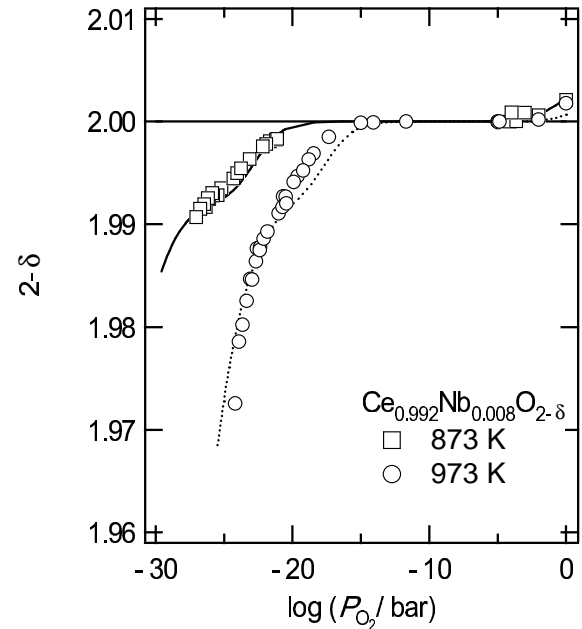


Fig. 1 Oxygen nonstoichiometry of  $\text{Ce}_{0.992}\text{Nb}_{0.008}\text{O}_{2-\delta}$ : Solid and dotted curves are calculated values from conductivity data [4] at 873 and 973 K, respectively.

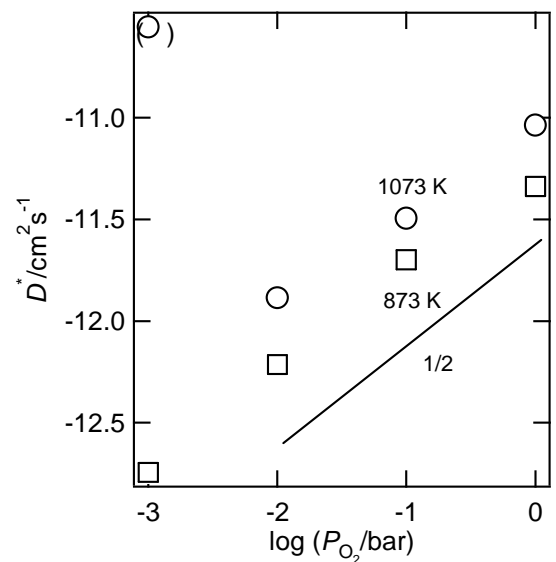


Fig. 2 Oxygen tracer diffusion coefficient of  $\text{Ce}_{0.992}\text{Nb}_{0.008}\text{O}_{2-\delta}$

### REFERENCES

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