EXAFS study of reduced $Ce_{1-x}Ln_xO_{2.00-y}$ (Ln = Y, Sm, Gd and Yb) (III)

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Introduction

Anomalous increases in the heat capacity curves of some reduced ceria doped with Gd were observed at temperatures around 860-960 K, depending on both the Gd concentration and the oxygen deficiency[1,2]. This increase was interpreted as due to disordering of the ordered phase related to the association of oxygen vacancies and the dopants, and/or ordering of oxygen vacancies. Therefore, we have used EXAFS spectrometry to determine the local structure around cerium ion in $Ce_{1-x}Ln_xO_{2.00-y}$ (Ln = Y, Sm, Gd and Yb)[3].

In this study, we made EXAFS measurements around doped cations and discussed the defect models.

Experimental

The X-ray absorption measurement near the Y-K and RE-L3 edge (RE = Sm, Gd and Yb) at room temperature was made with synchrotron radiation by use of the EXAFS facilities on the beam line 9A.

Results and Discussion

The Ln-O interatomic distances of $Ce_{1-x}Ln_xO_{2.00-y}$ calculated from the least-square fitting are shown in Fig.1. The Ln-O interatomic distances were decreased with increasing the oxygen deficiency and by quenching except Gd-O distances in the quenched samples. The decrease in Ln-O interatomic distances in $Ce_{1-x}Ln_xO_{2-x/2}$ was explained by the increase of the association of oxygen vacancies and dopant cations[4-6]. Four association models for stabilized zirconia proposed by Yashima et al. [7], showing the local structures around vacancies shown in Fig.2, were adopted. The increase in Gd-O inter-atomic distances in quenched samples, though the increase was very slight, suggested that the vacancies were distributed more randomly in the high temperature region. On the other hand, Y-O and Yb-O interatomic distances in quenched samples decreased, suggesting that the degree of association of dopant cation and oxygen vacancy increased. In the quenched samples, oxygen vacancies may gather around smaller Y^{3+} or Yb^{3+} ions since the samples were annealed above the reduction temperature before quenching, and as a result the Y-O and Yb-O distances in quenched samples may decrease from reduced samples. This suggested that the associations of smaller dopant cations and oxygen vacancies were more stable, being consistent with the result that the stability of reduced phase for doped ceria increased with decreasing the ionic radius of dopant.

References

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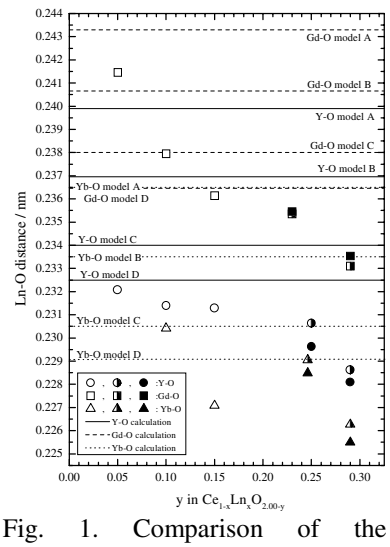

Fig. 1. Comparison of the calculated lines of the average Ln-O inter-ionic distances and the experimental Ln-O distances in $Ce_{1-x}Ln_xO_{2.00-y}$. Each of open, half-filled and filled symbols stands for the data of non-reduced, reduced and quenched samples, respectively.

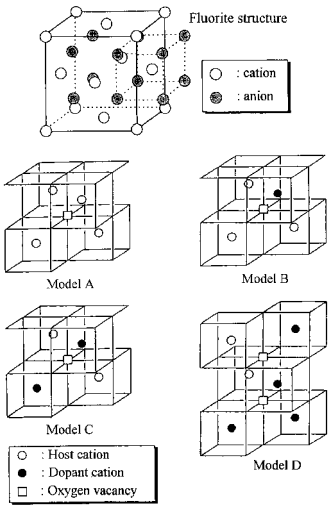

Fig. 2. Four models showing the local structures around vacancies.