EXAFS STUDY OF REDUCED $Ce_{1-x}Ln_xO_{2.00-y}$ (Ln = Y, Sm, Gd and Yb) (II)

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Introduction

Anomalous increases in the heat capacity curves of some reduced ceria doped with Gd were observed at temperatures about 860-960 K, depending both on the Gd concentration and on the oxygen deficiency[1,2]. This anomaly 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 cations in $Ce_{1-x}Ln_xO_{2.00-y}$ (Ln = Y, Sm, Gd and Yb)[3].

In this study, we made X-ray absorption measurements on the Sm- and Yb-doped samples with different concentration.

Experimental

The X-ray absorption measurement near the Ce-L3 edge at room temperature was made with synchrotron radiation by use of the EXAFS facilities on the beam line 9A. The reduced samples were prepared by heating the single fluorite $Ce_{1-x}Ln_xO_{2-x/2}$ (Ln = Sm and Yb; x = 0.20 and 0.30) at 1273K for 24h in H_2 and cooled slowly to room temperature. The oxygen deficiencies of the reduced samples were determined from the difference in weight. Some of the reduced samples were quenched in a sealed silica tube from 1273 K to investigate the local structures at high temperature.

Results and Discussion

The Ce-O interatomic distances of $Ce_{1-x}Ln_xO_{2.00-y}$ calculated from the least-square fitting are shown in fig.1 with our previous data[3]. The result of the reduced 20% Sm doped sample was replaced from previous one since the previous reduced sample was re-oxidized after heating in H_2 gas. The Ce-O interatomic distances were decreased with increasing the oxygen deficiency and by quenching. The decreasing of Ce-O interatomic distances in $Ce_{1-x}Ln_xO_{2-x/2}$ (Ln = Y and Gd) was explained by the increase of the association of oxygen vacancies and dopant cations[4,5]. The decreasing the order of these associations is thought to cause the decrease of the Ce-O interatomic distance since the vacancies could be distributed near Ce and oxygen ions relaxed toward their adjacent vacancies. The decrease of Ce-O interatomic distances by quenching

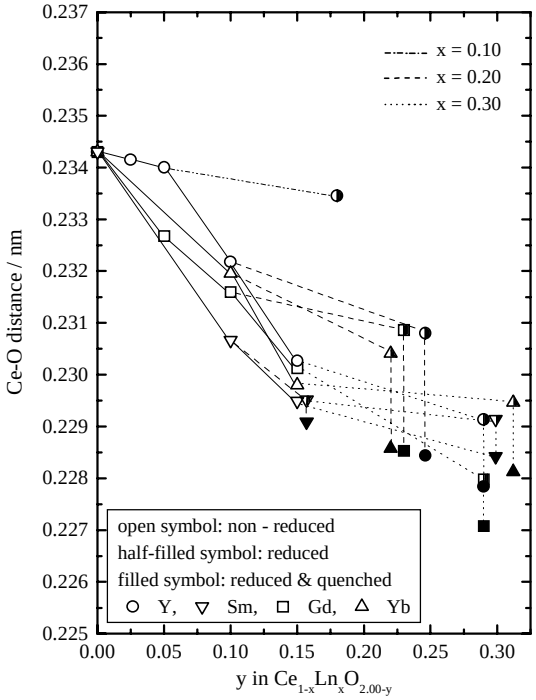

fig. 1 The Ce-O interatomic distances in $Ce_{1-x}Ln_xO_{2.00-y}$ as a function of the oxygen deficiency (y).

suggested that the association of oxygen vacancies and the dopants and ordering of oxygen vacancies were dissociated and vacancies were distributed more randomly in the high temperature region. This is consistent with the results that the phase transition due to disordering was observed in some reduced doped-ceria though this transittion was observed in only doped with Gd at present in the temperature range up to 1300 K[2].

References

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