Defect Structure of Cerium Oxide Doped with Nd

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Solutions of neodymium nitrate and cerium nitrate were prepared. Ammonium hydroxide was added to produce cerium dioxide doped with 5 ~ 60 cation % Nd. These materials were fired at 900 ~ 1400°C for various length of time. Lattice parameter of them was measured by the powder X-ray diffraction method and theoretical densities based on two different defect models were calculated. Density was also directly measured by the densimeter. Comparing these densities, it was concluded that in Nd-doped cerium dioxide, anion vacancy is predominant defect.

1. INTRODUCCTION

CeO$_2$ forms solid solution with Nd over an extend range of dopant concentration. It was generally said that Ce^{4+} was replaced by Nd^{3+} in the lattice to yield anion vacancy, because solid solution of CeO$_2$ exhibit high oxygen ionic conductivity. CeO$_2$ doped with rare earth element has been expected to be utilized as an electrolyte of solid oxide fuel cells (SOFCs) or oxygen sensors that control exhaust gas. However, only limited studies on non-stoichiometry of CeO$_2$ solid solution were carried out [1-4] and defect structure of CeO$_2$ doped with Nd was not clearly studied. In the present study, CeO$_2$ doped with Nd were prepared to clarify defect structure of thus solid solution.

## 2. EXPERIMENTAL

2.1 Sample preparation

Ce(NO$_3$)$_3$·xH$_2$O (x=5.82, Rare Metallic Co. , Ltd) and Nd(NO$_3$)$_3$·xH$_2$O (x=5.94, Rare Metallic Co. , Ltd) were dissolved in deionized water to prepare neodymium nitrate and cerium nitrate solutions. The concentration of each of these solutions was determined. These solutions were, then, mixed at appropriate ratios and ammonium hydroxide was added to precipitate CeO$_2$ doped with 5~50 cation % Nd. These precipitates were dried and calcined in alumina crucible at 800 °C for 2h. The samples were then ground and pressed into discs by uniaxial pressing. The discs were sintered in alumina crucible at 1400°C. The samples were then crashed and ground again to form powder. The powder sample were used for various measurements.

2.2 Characterization

Undoped CeO$_2$ and CeO$_2$ doped with 5~60 cation % Nd were studied by X-ray powder diffraction in rigion of 2θ =20° ~120° on X-ray Diffractometer (CuKα, RINT2000VHF, Rigaku Corporation), using MgO as an inner standard. Precise lattice parameter of samples was

determined by a computer program. Theoretical densities of CeO_2 doped with Nd were calculated assuming two different defect structures. If anion vacancy predominated the defect structure of this solid solution, a quasi-chemical reaction could be written as

$$Nd_2O_3 \rightarrow 2Nd_{Ce}{}' + 3O_O{}^\times + V_O{}^{..} \qquad (1)$$
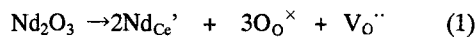
This can be expressed by a chemical formula:

$$Ce_{1-x}Nd_xO_{2-x/2} \qquad (2)$$

If cation interstitial predominated, another quasi-chemical reaction could be written as

$$2Nd_2O_3 \rightarrow 3Nd_{Ce}{}' + 6O_O{}^\times + Nd_i{}^{...} \qquad (3)$$

This can be shown by a chemical formula:

$$Ce_{1-x}Nd_{x+x/3}O_2 \qquad (4)$$

Density of samples was measured by two different methods. In the first experiment, Archimedes method using water as an immersing liquid was used to determine the density of sintered body. In the second experiment, a densimeter (AccuPyc1330, Shimadzu) was used to determine the density of pressed powder.

3 RESULT

X-RD patterns of CeO_2 doped with Nd sample sintered at 1400 °C for 4h are shown in Fig.1. As dopant concentration increased, peak was shifted to lower angle. It is an indication of the fact that solid solution of CeO_2 doped with Nd was made. Lattice parameter of samples is shown in Fig.2. Lattice parameter increases linearly as the dopant concentration increases up to 30 cation % Nd and the slope of the curve becomes less steep above 30 cation % Nd. In the X-RD pattern, weak peaks other han those of CeO_2 were observed when the concentration of Nd exceeded 45 cation %. However, lattice parameter increases even if the concentration of Nd exceeds 30 cation % up to 60 cation %. This phenomenon was also observed in the result of Bevan et al [5] for CeO_2 doped

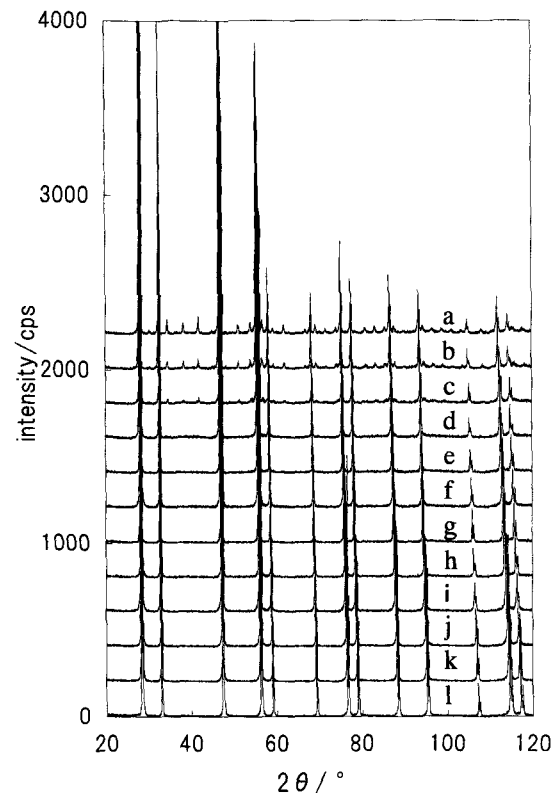with rare earth elements. It was considered to be caused by ordering of impurity or another materials effect.

Fig.1 XRD patterns of undoped CeO_2 and CeO_2 doped with Nd sintered at 1400°C for 4h.

a:60 cation % Nd, b:50% Nd, c:45 % Nd, d:40% Nd, e:35% Nd, f:30% Nd, g:25% Nd, h:20% Nd, i:15% Nd, j:10% Nd, k:5% Nd, l:undoped CeO_2.
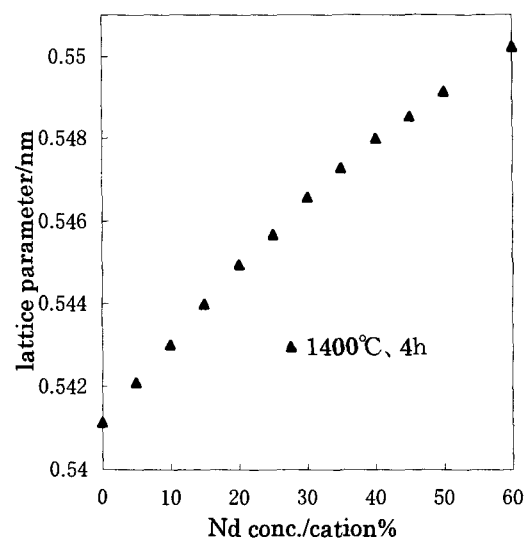

Fig2. Lattice parameter of CeO_2 doped with Nd.

Using equations (2) and (3), and the lattice parameters in Fig.2, theoretical densities of cation interstitial model and anion vacancy model are calculated and are shown in Fig.3. For cation interstitial model, density increased as dopant concentration increased. For anion vacancy model, just opposite effect was observed. The density decreased as dopant concentration increased.
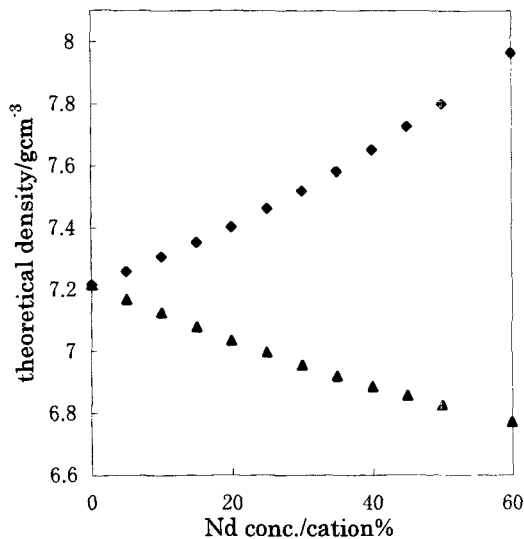
et al. [2] studied the defect structure of CeO_2 doped with SrO and CaO, respectively. They also measured the density of specimens to determine the defect structure. Anion vacancy was also predominant defect in this sample.
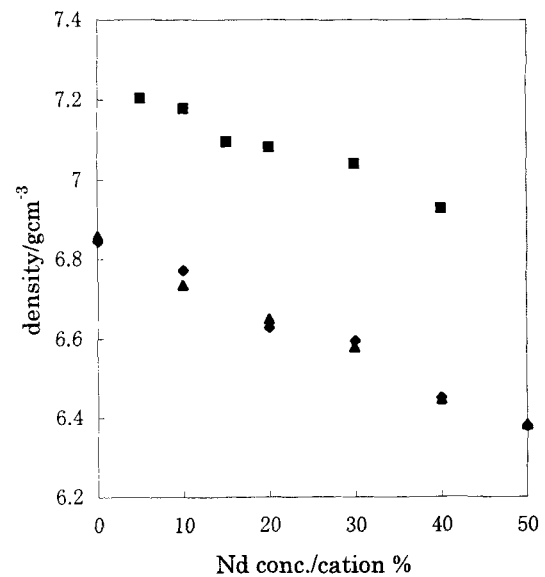

Fig.3 Theoretical density.

◆cation interstitial model, ▲anion vacancy model.

Fig.4 Measured density of CeO_2 doped with Nd.

■densimeter, ◆Archimedes method (1st measurement),

▲Archimedes method (2st measurement).

Densities measured by Archimedes method and densimeter are shown in Fig.4. Density of both Archimedes method and densimeter decreased as dopant concentration increased. Density determined by Archimedes method was always lower than that of densimeter. This is the effect of closed pores in sintered body. Consequenthy the density determined by densimeter is reliable and will be used in the next step.

Theoretical and measured densities are compared in Fig.5. Measured density (densimeter) agreed well with theoretical density of anion vacancy model. Defect structure of sample sintered at 1400 °C for 4h is, therefore, concluded to be anion vacancy model.

In the past, Blumenthal and Garnier [1] and Blumenthal
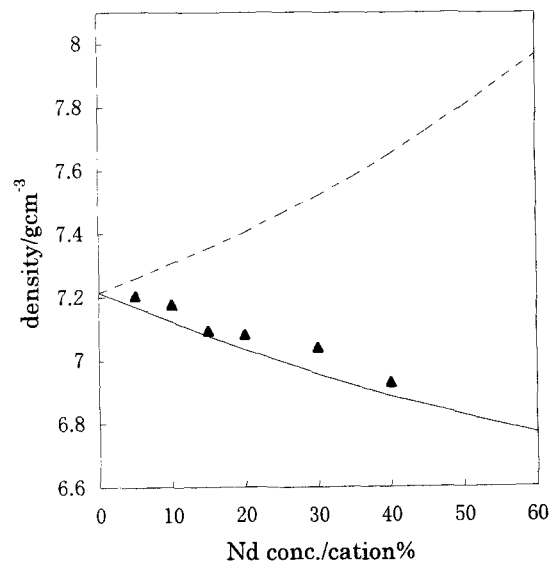

Fig.5 Theoretical and measured densities(1400°C,4h).

----- cation interstitial model, ——— anion vacancy model

▲densimeter.

4. CONCLUSION

Comparing theoretical density which was calculated from lattice parameter with experimental density measured by densimeter, it was found that anion vacancy is predominate defect in cerium oxide doped with Nd.

5. REFERENCES

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