

FABRICATION AND CHARACTERIZATION OF CERIUM OXIDE DOPED WITH GADOLINIUM

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Cerium oxide doped with 0~50 mol% $GdO_{1.5}$ was prepared by co-precipitation method, which was found to be much better than solid state reaction method. The formation of solid solution at CeO_2 doped with 10 mol% $GdO_{1.5}$ was recognized even without firing the precipitate. X-ray diffraction (50 kV, 200 mA) study of sample fired at 1300°C revealed that fluorite structure existed in samples with 0~35 mol% $GdO_{1.5}$. At composition with higher concentration of $GdO_{1.5}$, superlattice peaks were identified. This indicated the existence of a fluorite phase with superlattice or the formation of rare earth C-type structure.

Key words : solid solution, lattice constant, fluorite structure, superlattice

1. INTRODUCTION

Cerium oxide can form solid solution with the rare earth elements in wide range of concentration. The oxide can also absorb oxygen in oxidizing atmosphere and release it in reducing atmosphere, so that it is used as one of the catalysts for exhaust gas of automobiles. The oxide shows high electric conductivity at lower temperatures compared with ZrO_2 . Consequently it is one of the candidate materials for solid electrolyte of the solid oxide fuel cell. Gadolinium doped cerium oxide is one of the solid solutions which attracted attentions¹⁾ with this respect.

Lattice parameter of $GdO_{1.5}$ - CeO_2 system was studied by several researchers. Brauer and Gradinger²⁾ reported that samples treated at 1400°C formed a solid solution of fluorite structure in the range of 0~30 mol% $GdO_{1.5}$ and another solid solution of rare earth C-type structure in the range of 40~95 mol% $GdO_{1.5}$. They also reported that the lattice parameter changed continuously in 0~100 mol% $GdO_{1.5}$. Bevan et al.³⁾ also reported continuous lattice parameter change between 0~55 mol% $GdO_{1.5}$ for the samples fired at 1400~

1600°C and reported a discontinuous change of lattice parameter between 55~70 mol% $GdO_{1.5}$. Kudo and Obayashi⁴⁾ prepared the solid solution at 1800°C and observed almost linear increase of lattice parameter in the range of 0~35 mol% $GdO_{1.5}$ and did not observe any change in lattice parameter between 40~50 mol% $GdO_{1.5}$. In spite of the change in slope of lattice parameter vs. composition plot, they claimed that the solid solution was in fluorite structure in the range of 0~50 mol% $GdO_{1.5}$. The literature indicates that there is discrepancy in the change of lattice parameter of $GdO_{1.5}$ - CeO_2 solid solution and in the range of fluorite solid solution. In this paper, we prepared the solid solution by a method which can produce the intimate mixture within short time and samples were examined by stronger X-ray diffraction beams.

2. EXPERIMENTAL

CeO_2 doped with Gd was prepared using both solid state reaction and co-precipitation methods for comparison, although most of the samples were prepared by co-precipitation method. For solid

state reaction method, CeO_2 and Gd_2O_3 powders were mixed by ball-milling, and were sintered at 1300°C for 206 h.

For co-precipitation method, $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ were used as starting materials because they were easy to get. $\text{Ce}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ (Rare Metallic Co., Ltd., 99.99%) of about 500 g was dissolved into deionized water of about 1 L. The concentration of the solution was determined by the following method. A part of the solution was taken and excess amount of ammonia water was added to the solution to form precipitate. The precipitate was filtered and heated to about 1300°C to form CeO_2 which was verified by X-ray diffraction. The weight of CeO_2 was measured and the concentration of the aqueous solution of $\text{Ce}(\text{NO}_3)_3$ was calculated. Aqueous solution of $\text{Gd}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ (Rare Metallic Co. Ltd., 99.99%) was also prepared and the concentration of the solution was determined in the similar manner.

To make CeO_2 doped with 10~50 mol% $\text{GdO}_{1.5}$, aqueous solutions of $\text{Ce}(\text{NO}_3)_3$ and $\text{Gd}(\text{NO}_3)_3$ were mixed at various ratios, and excess amount of ammonia water was added while the solution was slowly stirred. Precipitate was filtered and was calcined at 800°C for 2 h. The powder was well ground with agate mortar and uniaxially pressed into pellets at 147 MPa for 10 min. The pellet was placed in a platinum crucible and was hung from top of an electric furnace. Temperature of pellets was increased at a rate of $10^\circ\text{C}/\text{min}$ and was sintered at 1300°C for 4 h. The sample was quenched by taking the crucible out of the furnace and dropping it into deionized water. The sample was well ground with agate mortar, and characterized by X-RD (Rigaku, rint-2000) (50 kV, 200 mA).

3. RESULTS AND DISCUSSION

In order to find the effect of preparation method, results of X-RD of samples prepared by solid state reaction and co-precipitation method are shown in Fig. 1. Sample of solid state reaction method was sintered at 1300°C for 206 h, and sample of co-precipitation method was sintered at

1300°C for only 4 h. The figure indicates that sample prepared by solid state reaction is still a mixture of undoped CeO_2 and Gd doped CeO_2 . On the other hand, sample prepared by co-precipitation method is in single phase composed of Gd-doped CeO_2 . Although sample of solid state reaction was sintered more than 50 times as long as sample of co-precipitation, sample of solid state reaction is not in single phase yet. Consequently, samples presented in the rest of this paper were prepared by co-precipitation method. Results of X-RD of precipitates before calcination are shown in Fig. 2. These samples are 10 and 30 mol% Gd-doped CeO_2 . The result of undoped CeO_2 which was sintered at 1300°C for 4 h was also shown in the figure for comparison. In the figure, the peaks with circle are the peaks of cerium oxide. The figure shows that the peaks of only cerium oxide appear in the sample of 10 mol% Gd doped CeO_2 . Therefore, in those specimens prepared by co-precipitation, CeO_2 already formed a solid solution with Gd.

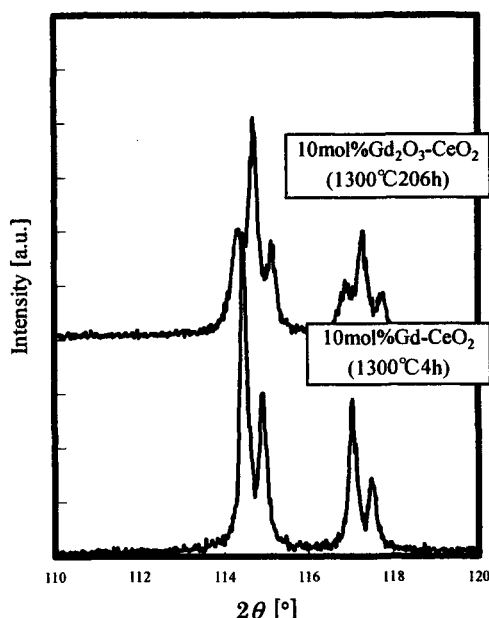


Fig. 1 X-ray diffraction patterns of samples prepared by co-precipitation method (sintered at 1300°C for 4h) and solid state reaction method (sintered at 1300°C for 206h).

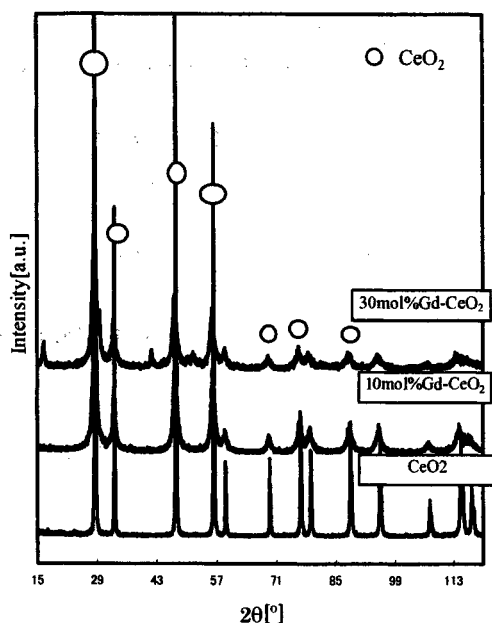


Fig. 2 X-ray diffraction patterns of CeO_2 doped with 10 mol% and 30 mol% Gd before sintering and undoped CeO_2 sintered at 1300°C for 4h.

Results of X-RD of 0~50 mol% Gd-doped CeO_2 and undoped Gd_2O_3 prepared by sintering at 1300°C for 4 h are shown in Fig. 3. The figure shows that peaks of fluorite structure appears only for CeO_2 doped with 0~30 mol% Gd, but peaks of other than fluorite structure also appear for CeO_2 doped with more than 40 mol% Gd. The existence of peaks other than fluorite structure may indicate^{3,4)} that the diffraction patterns are obtained from a fluorite-type phase with superlattice (or superstructure) or from rare earth C-type structure. Bevan et al.³⁾ reported the existence of peaks other than fluorite structure. However, they were not specific about the concentration where these peaks appeared. Kudo and Obayashi⁴⁾ did not observe these peaks up to 50 mol% Gd. However, in this study we observed these peaks at 40~50 mol % Gd. The difference could be due to the firing temperature: Kudo and Obayashi fired their sample at 1800°C and we fired our sample at 1300°C . Alternatively we may have increased the detection limit of these peaks by using strong X-ray beams in this study. Lattice parameters of

these oxides obtained by X-ray diffraction are shown in Figure 4. Vegard's law was followed in the composition range of 0~35 mol% and at higher concentration of Gd the lattice parameter seems to be constant. This range of concentration where Vegard's law is followed coincides with range where X-ray diffraction patterns correspond to fluorite structure. At concentration higher than this range, lattice parameter is constant and we also observed fluorite structure with superlattice or rare earth C-type structure. Since the X-ray diffraction patterns of fluorite structure with superlattice is very similar to rare earth C-type structure, we must perform further research before the nature of these peaks other than fluorite structure and consequently the solubility limit of Gd in CeO_2 could be discussed.

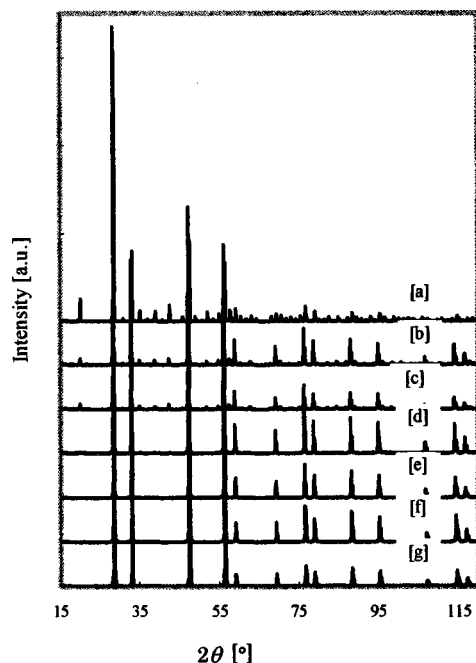


Fig. 3 X-ray diffraction of CeO_2 doped with 0 ~ 50 mol% Gd and undoped Gd_2O_3 . These samples were sintered at 1300°C for 4h. [a] Gd_2O_3 , [b] 50 mol% Gd- CeO_2 , [c] 40 mol% Gd- CeO_2 , [d] 30mol% Gd- CeO_2 , [e] 20 mol% Gd- CeO_2 , [f] 10 mol% Gd- CeO_2 , [g] CeO_2 .

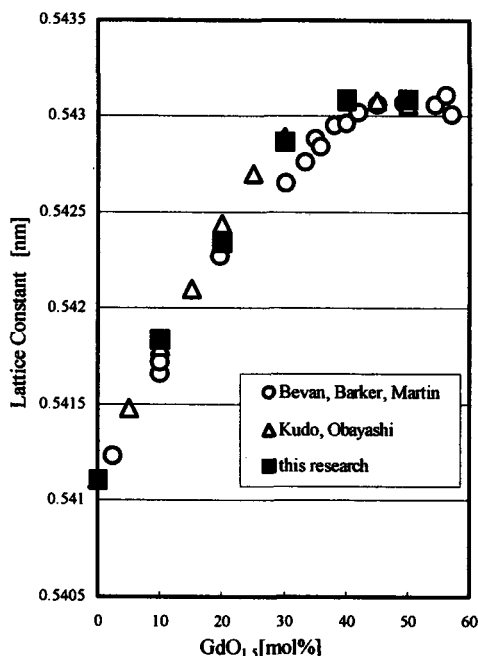


Fig. 4 Relationship between lattice parameter and Gd concentration. The results reported in the literature are also included.

4. CONCLUSIONS

Cerium oxide doped with Gd was fabricated by co-precipitation method and solid state reaction method. Sample prepared by solid state reaction method never reached complete solid solution after firing at 1300°C for 206 h. However, samples prepared by co-precipitation method formed solid solution after firing for 4 h. In some composition, a solid solution was formed even after the formation of precipitate. CeO₂ doped with Gd formed at 1300°C was in fluorite structure in the range of 0~35 mol% Gd. At composition of 40~50 mol% it developed superlattice peaks. These peaks were due to either a fluorite-type phase with superlattice or the formation of rare earth C-type structure.

5. ACKNOWLEDGEMENT

This work was funded in part by a grant from the Japanese Ministry of Education (NO. 12650675).

6. REFERENCES

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(Received December 20, 2001; Accepted January 31, 2002)