

REACTION OF CERIUM DIOXIDE WITH ALKALI METAL ALKOXIDES.

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ABSTRACT

The gas-solid reaction process using volatile alkali metal alkoxides has many advantages in producing the uranates(plutonates) which are expected to improve the dissolution behavior of the fuel into nitric acid. In this work, the reactions of CeO_2 , which was used as a non-radioactive stand-in of PuO_2 , with $MOBu^I$ ($M=Li, K$) under several conditions were examined. In the case of the $M_xCe_{1-y}O_{2-x}$ synthesized by an aqueous method, the lattice parameter was slightly increased with increasing M concentration, y, up to 0.20. When the $LiOBu^I$ vapor reacted with CeO_2 , a new fluorite phase having $a=5.4935 \text{ \AA}$, $y=0.044$, $x=0.30$ was formed over 973 K. A similar compound ($a=5.4797 \text{ \AA}$, $y=0.035$, $x=0.22$) was observed by the reaction of CeO_2 with $KOBu^I$.

Keywords : solid solution, alkoxide, cerium oxide, gas-solid reaction, MOX fuel, volatile process.

1. INTRODUCTION

Mixed oxide formation with alkali metal from plutonium-uranium dioxide fuel is expected to result in great enhancement of the dissolution rate of spent fuel into nitric acid. For producing such uranates(plutonates), the gas-solid reaction process using volatile compounds of alkali metals, is advantageous comparing with the solid-solid reaction in reaction efficiency and homogeneity of the formed mixed uranium oxides. One of such volatile compounds is metal alkoxides($M(OR)_x$).

Generally speaking, alkoxides have increasing volatility with increasing side chain of alcohol, while they are increasingly hygroscopic and thermally unstable¹⁾. Butoxides($MOBu^I$) are known to have the highest volatility among alkali metal alkoxides(MOR)²⁾.

CeO_2 is used as a non-radioactive stand-in of PuO_2 . Since UO_2 and alkali metals form many types of compounds such as Li_2UO_4 ³⁾, $M_xU_{1-y}O_{2+x}$ ³⁾, similar reaction can be expected to take place between CeO_2 and $LiOR$. On the other hand, the nonstoichiometry of CeO_2 has long been studied in connection with thermodynamics⁴⁻⁶⁾, structure^{7,8)} and electrical conduction⁹⁾. The subphase diagram was given by Bevan et al¹⁰⁾, showing many oxygen deficient oxides, CeO_{2-x} ($0.01 < x < 0.1$). The reac-

tion of CeO_2 and metal calcium forms CaO and CeO at 1273 K¹¹⁾.

In this paper, we study the reaction between CeO_2 and $MOBu^I$ ($M=Li, K$) for the formation of complex oxide under several conditions, comparing with those obtained by an aqueous method.

2. EXPERIMENTALS

2.1 Sample preparation

Lithium and potassium t-butoxide were synthesized by the reaction of each metal with t-BuOH. The t-BuOH was dehydrated using dried molecular sieves before use because of the hygroscopic properties of the metal alkoxides. Special commercial grade of CeO_2 and t-BuOH from Wako Pure Chemicals Co. Ltd. were used.

The CeO_2 solid solution containing the known amount of lithium or potassium was obtained by drying homogenized solution of $Ce(NH_4)_2(NO_3)_6$ and $LiOH \cdot H_2O$ or $K_2C_2O_4$ from Wako Pure Chemicals Co. Ltd., followed by calcination in air at 1173 K for 10 hours.

2.2 Reaction procedure

CeO_2 and $MOBu^I$ were placed in a quartz double cell separately after weighing in an argon atmospheric glove box. The double cell was set in a two stage heater as shown in Figure 1 after sealing under vacuum. The $MOBu^I$ was heated for vaporizing to react with CeO_2 at high temperature part. After the reaction, the identification of the product by X-ray diffraction and chemical analysis were conducted.

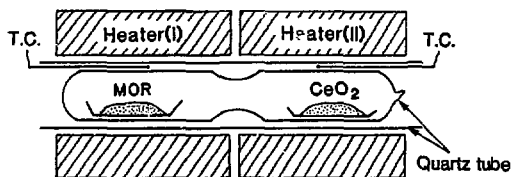


Figure 1 Experimental apparatus.

2.3 X-ray Measurement

X-ray diffraction experiments were carried out with a Rigaku RAD-1B diffractometer system using CuK α radiation. The slit system used was 1.0-0.3mm-1.0. The diffraction angle was corrected using a silicon standard sample. The lattice parameter, *a*, was determined by the Nelson-Riley extrapolation method for the high angle peaks ($60^\circ < 2\theta < 135^\circ$).

2.4 Chemical analysis of oxygen and alkali metal

The oxygen content in the products was determined by inert gas fusion analysis. The alkali metal concentration in the product was determined by atomic absorption analysis after dissolving the product in H₂SO₄-HF(10:1) solution.

3. RESULTS AND DISCUSSIONS

3.1 Relation of lattice parameter with *x* and *y* of

M₂Ce_{1-y}O_{2-x} (M=Li,K) obtained by aqueous method
Fluorite type solid solutions of M₂Ce_{1-y}O_{2-x} were formed from the aqueous solution of Li⁺ and Ce⁴⁺ as well as that of K⁺ and Ce⁴⁺. Results of lattice parameters, *x*- and *y*-values of M₂Ce_{1-y}O_{2-x} are given in Tables 1 and 2.

Table 1 *y*-, *x*-values and lattice parameter of Li₂Ce_{1-y}O_{2-x} prepared by aqueous method.

	①	②	③	④
<i>y</i>	0.023	0.055	0.105	0.188
<i>x</i>	0.020	0.067	0.170	0.348
<i>a</i> (Å)	5.4115	5.4117	5.4122	5.4138

Table 2 *y*-, *x*-values and lattice parameter of K₂Ce_{1-y}O_{2-x} prepared by aqueous method.

	①	②	③	④
<i>y</i>	0.020	0.050	0.102	0.200
<i>x</i>	0.028	0.066	0.128	0.267
<i>a</i> (Å)	5.4112	5.4115	5.4118	5.4124

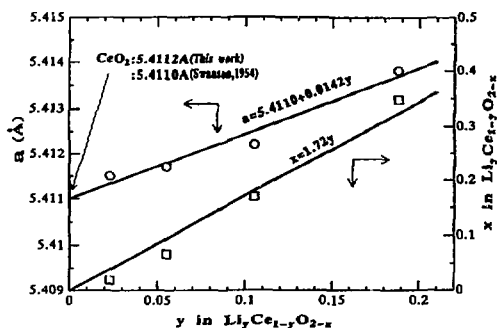


Figure 2 Relation between lattice parameter, *x* and *y* values of Li₂Ce_{1-y}O_{2-x} prepared by aqueous method.

In the case of Li₂Ce_{1-y}O_{2-x}, the lattice parameter was slightly increased with increasing lithium concentration, *y* up to 0.19 as shown in Figure 2. The relation between the values of *x* and *y* also is shown as a straight line acrossing zero point as seen in Figure 2.

The lattice parameter and *x*-value of K₂Ce_{1-y}O_{2-x} were increased linearly with increasing potassium concentration up to 0.20 as shown in Figure 3.

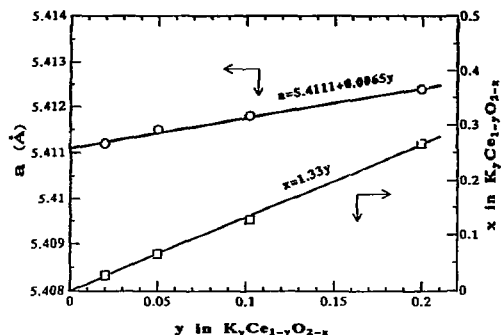


Figure 3 Relation between lattice parameter, *x* and *y*-values of K₂Ce_{1-y}O_{2-x} prepared by aqueous method.

3.2 Reaction of CeO₂ with MOBu' (M=Li,K)

When the gaseous LiOBu' was reacted with CeO₂ in a sealed tube, a black compound was produced. Results of X-ray diffraction analysis for this compound at elevated temperatures are shown in Figure 4. The reaction time

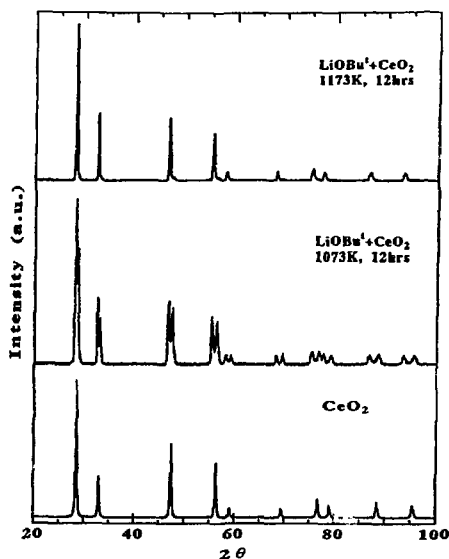


Figure 4 X-ray diffraction patterns for Li₂Ce_{1-y}O_{2-x} at elevated temperature prepared by the reaction of CeO₂ with LiOBu'.

was fixed for 12 hours. The X-ray diffraction patterns of the new phase was observed for the sample heated at about 973K. It was seen that the intensity of the peaks for the new phase increased with increasing temperature. Finally, the CeO₂ phase disappeared and the new fluorite phase was in a single phase above 1173 K. The new phase was formed within an hour and the CeO₂ phase disappeared completely after 5 hours.

The lattice parameters of the solid solutions, M_yCe_{1-y}O_{2-x}, are given in Table 3. The lattice parameter of lithium containing new phase is 5.4937 Å which is 1.5% larger than that of CeO₂ (5.4110 Å)¹². The expansion of the lattice parameter seems to be caused by the formation of solid solution, Li_yCe_{1-y}O_{2-x}. No diffraction lines for the compounds, Li₈CeO₆¹³ and LiCeO₂¹⁴ were formed. The composition of the solid solution determined is given in Table 3. The experimental value of oxygen content of CeO₂ (18.58 wt%) is in good agreement with the calculated value (18.59 wt%). The chemical formula of the solid solution is given as Li_{0.044}Ce_{0.956}O_{1.62} from the results of chemical analyses.

Table 3 Chemical composition and lattice parameter of M_yCe_{1-y}O_{2-x} prepared by the reaction of CeO₂ with MOBu^t (M=Li,K).

	O (wt%)	M (wt%)	Chemical formula	Lattice parameter (Å)
Li _y Ce _{1-y} O _{2-x}	16.14	0.19	Li _{0.044} Ce _{0.956} O _{1.62}	5.4937
K _y Ce _{1-y} O _{2-x}	16.72	0.84	K _{0.035} Ce _{0.965} O _{1.71}	5.4797

The reaction of CeO₂ with KOBu^t was similar to that of CeO₂ with LiOBu^t. The new X-ray diffraction patterns of single phase which had a fluorite structure were obtained

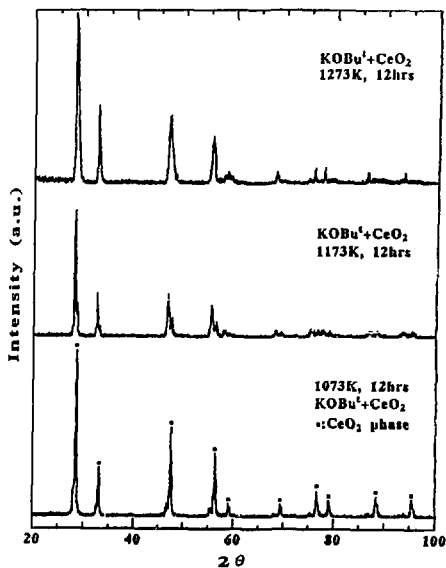


Figure 5 X-ray diffraction patterns for K_yCe_{1-y}O_{2-x} at elevated temperature prepared by the reaction of CeO₂ with KOBu^t.

over 1273 K as seen in Figure 5. The composition of the products was K_{0.035}Ce_{0.965}O_{1.71} as given in Table 3 from the results of chemical analyses.

3.3 Evaluation of oxygen analysis

When a part of the oxygen of CeO₂ is removed forming CeO_{2-x}, the weight decrease of CeO₂ during the process is 0.76wt% for x=0.1 and 0.07wt% for x=0.01. Then the analytical error in determination of oxygen content seems to be critical for the analysis of M_yCe_{1-y}O_{2-x}, the evaluation of oxygen analysis was conducted. The oxygen contents in K_yCe_{1-y}O_{2-x} were estimated by using the difference between the calculated value and observed one of the mixture of potassium peroxide, KO₂, and CeO₂. The results of Tables 1 and 2 were corrected in Tables 4 and 5 for Li_yCe_{1-y}O_{2-x} and K_yCe_{1-y}O_{2-x}, respectively.

Table 4 y-value, corrected x-value and lattice parameter change with y of Li_yCe_{1-y}O_{2-x} prepared by aqueous method.

	①	②	③	④
y	0.023	0.055	0.105	0.188
x	0.019	0.096	0.175	0.372
δ a / δ y	-0.350	-0.759	-0.808	-0.857

Table 5 y-value, corrected x-value and lattice parameter change with y of K_yCe_{1-y}O_{2-x} prepared by aqueous method.

	①	②	③	④
y	0.020	0.050	0.102	0.200
x	0.052	0.090	0.155	0.294
δ a / δ y	-1.144	-0.786	-0.663	-0.641

On the other hand, the solid solutions were synthesized in air. The valence state of cerium in M_yCe_{1-y}O_{2-x} should be +4. Then the x-value can be calculated by the charge neutrality condition. The results are given in Tables 6 and 7 for Li_yCe_{1-y}O_{2-x} and K_yCe_{1-y}O_{2-x}, respectively. From these results, the oxygen contents in the above solid solutions were calculated. The differences between the estimated and calculated values were in the range of 0.03wt% - 0.8wt%. The inert gas fusion analysis seems to give the determined values of which the precision is somewhat insufficient as the oxygen content of M_yCe_{1-y}O_{2-x}.

Table 6 y-value, calculated x-value and lattice parameter change with y of Li_yCe_{1-y}O_{2-x} prepared by aqueous method.

	①	②	③	④
y	0.023	0.055	0.105	0.188
x	0.019	0.096	0.195	0.372
δ a / δ y	-0.657	-0.651	-0.653	-0.646

Table 7 y -value, calculated x -value and lattice parameter change with y of $K_yCe_{1-y}O_{2-x}$ prepared by aqueous method.

	①	②	③	④
y	0.020	0.050	0.102	0.200
x	0.030	0.075	0.153	0.300
$\delta a / \delta y$	-0.660	-0.654	-0.654	-0.654

As for the $M_yCe_{1-y}O_{2-x}$ prepared by the reaction of CeO_2 and $MOBu^t$, the corrected chemical formulas are $Li_{0.044}Ce_{0.956}O_{1.70}$ and $K_{0.035}Ce_{0.965}O_{1.78}$. The values of x obtained are larger than those obtained by the aqueous method. It is considered that dissolution of alkali metal in CeO_2 by the reaction with $MOBu^t$ was restricted because of the reductive condition caused by the carbarization reaction of derivatives of alkoxides compared with that obtained by the aqueous method.

3.4 Lattice parameter change of $M_yCe_{1-y}O_{2-x}$

When the expansion of lattice parameter, a , depends on the value x - and y -values, a is expressed by the following relation:

$$a = a_0 + \frac{\delta a}{\delta x} x + \frac{\delta a}{\delta y} y \quad (1)$$

where a_0 is the lattice parameter of CeO_2 , $\delta a/\delta x$ and $\delta a/\delta y$ are lattice parameter changes with x and y , respectively.

In the case of $Li_yCe_{1-y}O_{2-x}$, the values of a , x and y in Table 5 and $a = 5.4112 \text{ \AA}$ for CeO_2 are substituted into the equation (1). The value of -0.44 as $\delta a/\delta x$ for CeO_2 obtained from the linear relation of lattice constant between cubic Ce_2O_3 (11.26 \AA)¹⁵ and CeO_2 is also substituted into this equation. The obtained values of $\delta a/\delta y$ were varied from -0.35 for $y=0.023$ to -0.86 for $y=0.188$. On the other hand, lattice parameter change with y were also calculated as given in Table 6 by using the data in Table 6. The difference between the two sets of values are increasing at the low y -values. This might be caused by the limitation of oxygen analysis.

In the case of $K_yCe_{1-y}O_{2-x}$, the lattice parameter changes with y obtained by using experimental and calculated x values are given in Tables 5 and 7, respectively. These two values are in good agreement at higher concentration of y over 0.1.

The lattice parameter of $M_yCe_{1-y}O_{2-x}$ is obtained by the following equation (2) when the value of -0.65 is used as $\delta a/\delta y$.

$$a(\text{\AA}) = 5.4112 + 0.44x - 0.65y \quad (2)$$

If the values of a and y of $K_yCe_{1-y}O_{2-x}$ obtained from the reaction of $KOBu^t$ and CeO_2 in Table 3 are substituted into equation (2), the obtained x -value (0.21) is well in accord with the experimental x -value (0.22).

3.2 Stability of $M_yCe_{1-y}O_{2-x}$ in air.

The stability of $M_yCe_{1-y}O_{2-x}$ was investigated under several conditions by X-ray diffraction. When the sample was stored in argon, no change of diffraction patterns for solid solution was observed. However, when the sample

was exposed to air, over one day, the intensity of diffraction peaks of the new phase decreased, while the peaks for CeO_2 phase appeared. The peaks of the solid solution disappeared over 40 hours exposure to air. The same phenomenon was observed in dried oxygen atmosphere. These facts show that the this solid solution is susceptible to oxidation forming stable CeO_2 phase and inter-lattice lithium by the reaction with oxygen.

4. CONCLUSIONS

The reaction of CeO_2 with $MOBu^t$ ($M=Li, K$) was studied with the aim to form new compound. The obtained results showed that no compound with different crystal structure was formed but the solid solution which contains alkali metal, $M_yCe_{1-y}O_{2-x}$ was formed. The conclusions of the present study are summarized as follows:

- 1) The reaction of CeO_2 with $MOBu^t$ occurs over 1173 K for $LiOBu^t$ and 1273 K for $KOBu^t$ forming fluorite type solid solution, $M_yCe_{1-y}O_{2-x}$, which have larger lattice parameters than that of CeO_2 .
- 2) The relations between the y -value and lattice parameter or x -value of $M_yCe_{1-y}O_{2-x}$ are linear.
- 3) The chemical formulas of the solid solutions are $Li_{0.044}Ce_{0.956}O_{1.70}$ and $K_{0.035}Ce_{0.965}O_{1.78}$.
- 4) The lattice parameters of $M_yCe_{1-y}O_{2-x}$ are expressed as a linear combination of lattice parameter of CeO_2 and lattice parameter changes with x and y .
- 5) The solid solution is oxidized to CeO_2 by prolonged air oxidation.

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