Journal of Alloys and Compounds, 213/214 (1994) 378–380
JALCOM 4086

Electrical conductivity and defect structure of lanthanum-doped $(U,Pu)O_{2\pm x}$

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Abstract

The electrical conductivities σ of $La_z(U_{0.8}Pu_{0.2})_{1-z}O_{2\pm x}$ ($z=0.01$ and 0.1) were measured in the range 10^{-15} Pa $\leqslant P_{O2} \leqslant 10^{-1.5}$ Pa at 1273 K. Three different dependences of σ on P_{O2} for $La_z(U_{0.8}Pu_{0.2})_{1-z}O_{2\pm x}$ ($z=0.01$ and 0.1) were observed, similar to the results for the sample not containing lanthanum ($z=0$). An additional dependence of σ on P_{O2} was observed for the sample with $z=0.1$, similar to that of the hypostoichiometric $La_{0.1}U_{0.9}O_{2-x}$ phase, suggesting the existence of the hypostoichiometric $La_{0.1}(U_{0.8}Pu_{0.2})_{0.9}O_{2-x}$ phase. The effect of doping on the defect structure and the electrical conduction mechanism of $La_z(U_{0.8}Pu_{0.2})_{1-z}O_{2\pm x}$ ($z=0.01$ and 0.1) is discussed.

1. Introduction

Mixed oxide fuel $(U,Pu)O_{2\pm x}$ is of interest in reactor engineering for use as fuel for fast breeder reactors and plutonium enriched thermal reactors. In preceding papers [1–3], we reported the electrical conductivities σ of $U_{1-y}Pu_yO_{2\pm x}$ ($y=0.05$, 0.10, 0.20, 0.30, 0.50 and 0.90) under an oxygen partial pressure P_{O2} ranging from 10^{-15} to $10^{-1.5}$ Pa at 1273 K. Three different dependences of σ on P_{O2} were observed irrespective of y. The defect structure and the electrical conduction mechanism in these three regions were discussed.

In this study, the effect of doping on the electrical conductivities of $La_z(U_{0.8}Pu_{0.2})_{1-z}O_{2\pm x}$ ($z=0.01$ and 0.1) was investigated in the oxygen partial pressure range from 10^{-15} to $10^{-1.5}$ Pa at 1273 K.

2. Experimental details

Purified uranium, plutonium and lanthanum nitrate solution were mixed in appropriate concentrations, and the mixed solution was gently evaporated and dried in a mantle heater. Powder of the mixed oxide was obtained by calcining the solid nitrate at 1073 K in air. After pressing the powder at about 20 kg mm^{-2}, the pellet was sintered in vacuum at 1673 K for 3–4 h. The electric conductivity was measured and the oxygen partial pressure was controlled in the range 10^{-15}–$10^{-1.5}$ Pa as described in our previous papers [1–3].

3. Results and discussion

The dependences on oxygen partial pressure of the electrical conductivity for $La_z(U_{0.8}Pu_{0.2})_{1-z}O_{2\pm x}$ ($z=0.01$ and 0.1) samples obtained at 1273 K are shown in Fig. 1, where the result of log σ *vs.* log P_{O2} for undoped $U_{0.8}Pu_{0.2}O_{2\pm x}$ obtained by the present authors [2] is shown for comparison. In Fig. 1, three different dependences of σ on P_{O2} for lanthanum-doped samples ($z=0.01$ and 0.10) are seen, similar to that for the undoped sample ($z=0$). (1) Above $P_{O2}=10^{-2}$ Pa (region I), the slope of the log σ *vs.* log P_{O2} curve decreases with increasing oxygen partial pressure, presumably owing to the onset of the phase transition from a single-phase MO_{2+x} to a two-phase MO_{2+x}–M_4O_{9-x} region. (2) Between $P_{O2}=10^{-4.5}$ and 10^{-2} Pa (region II), log σ increases linearly with increasing log P_{O2}, and the slope is smaller for the specimens with larger z values. (3) Between $P_{O2}=10^{-5}$ and 10^{-11} Pa (region III), the electrical conductivity is independent of P_{O2}. An additional dependence of σ on P_{O2} is observed for the sample with $z=0.1$ below $10^{-11.5}$ Pa (region IV) as seen in Fig. 1, where the electrical conductivity increases with increasing oxygen partial pressure. This behavior is similar to that of the hypostoichiometric $La_{0.1}U_{0.9}O_{2-x}$

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SSDI 0925-8388(94)04086-J

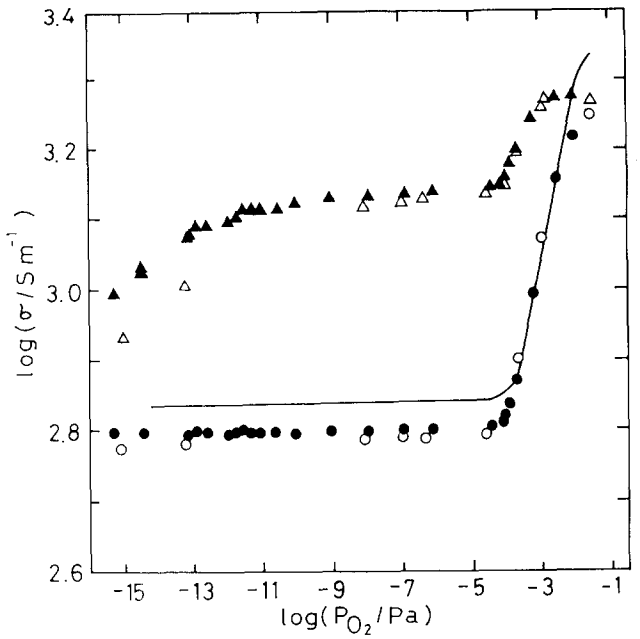

Fig. 1. Dependence on oxygen partial pressure of the electrical conductivity of $La_z(U_{0.8}Pu_{0.2})_{1-z}O_{2\pm x}$ for $z=0.01$ (○, ●) and 0.1 (△, ▲) at 1273 K. The result of log σ *vs.* log P_{O2} for undoped $U_{0.8}Pu_{0.2}O_{2\pm x}$ (—) obtained by us [2] is shown for comparison. The electrical conductivities were reversible for increasing (open symbols) and decreasing (closed symbols) oxygen partial pressures, except for the low oxygen partial pressure region for the sample with $z=0.10$.

phase [4], suggesting the existence of the hyposto-ichiometric $La_{0.1}(U_{0.8}Pu_{0.2})_{0.9}O_{2-x}$ phase.

From the slope in region II shown in Fig. 1, the values of n in the relation $\sigma \propto P_{O2}1/n$ for $z=0$, 0.01 and 0.10 were calculated as 4.1, 5.1 and 9.9 respectively. The formation of the complex defect $\{2(O_i a_{O_i} b_{V_O})\}m'$, similar to the case for undoped $(U,Pu)O_{2+x}$ [1–3], is represented by

$$2V_i^a + 2V_i^b + 2O_O + O_2(g) = \{2(O_i a_{O_i} b_{V_O})\}m' + mh^{\cdot} \quad (1)$$

where $h^{\cdot}$ is a hole and m is the charge of the complex defect. The dependences of $n=4.1$ (for $z=0$) and $n=5.1$ (for $z=0.01$), where $n=m+1$, observed for $La_z(U_{0.8}Pu_{0.2})_{1-z}O_{2+x}$ samples from the log σ–log P_{O2} relation can be found from eqn. (1) by taking the values $m=3$ and $m=4$ respectively. For the defect structure of the sample with $z=0.1$ where the deviation from the stoichiometric composition ($x=0$) is considered to be small, the formation of the complex defect $(2O_i a_{O_i} b_{2V_O})m'$ is assumed:

$$2V_i^a + V_i^b + 2O_O + (1/2)O_2(g) = (2O_i a_{O_i} b_{2V_O})m' + mh^{\cdot} \quad (2)$$

The dependences of σ on P_{O2}, $n=10$, where $n=m+1$, can be found from eqn. (2) taking $m=9$.

In regions III and IV, the dependence of oxygen partial pressure on the compositional deviation x is needed in order to discuss the defect structure.

The electrical conductivities at 1273 K around $P_{O2}=10^{-9}$ Pa which are independent of P_{O2} in Fig. 1 are shown in Fig. 2, where the solid line represents the theoretical change in electrical conductivity with the atomic ratio [M]/[M+U] (M≡Pu) reported by us [2]. The theoretical line is calculated using the dis-proportionation reaction $Pu^{4+} + U^{4+} = Pu^{3+} + U^{5+}$. In the figure, the electrical conductivities of $UO_{2\pm x}$ doped with lanthanum [4], gadolinium [5] and yttrium [6] at 1273 K are also shown for comparison. As seen in Fig. 2, the electrical conductivities of $La_z(U_{0.8}Pu_{0.2})_{1-z}O_{2\pm x}$ ($z=0.1$) and yttrium-doped $UO_{2\pm x}$ deviate from the theoretical curve calculated by the disproportionation reaction.

According to a hopping model in $UO_{2\pm x}$ proposed by Aronson *et al.* [7], when an interstitial oxygen ion is introduced in UO_2, two U^{5+} ions are formed, and each U^{5+} ion is considered as a site for one hole which can jump to a U^{4+} site. If we apply this model to hyperstoichiometric $(U_{1-y}Pu_y)O_{2+x}$ by assuming the plutonium to be tetravalent, the following equation can be derived:

$$\sigma T = \sigma_0(2x)(1-y-2x)\exp(-E_a/kT) \quad (3)$$

where E_a is the activation energy for the hopping of holes. In region III, if $x=0$ is assumed as a crude

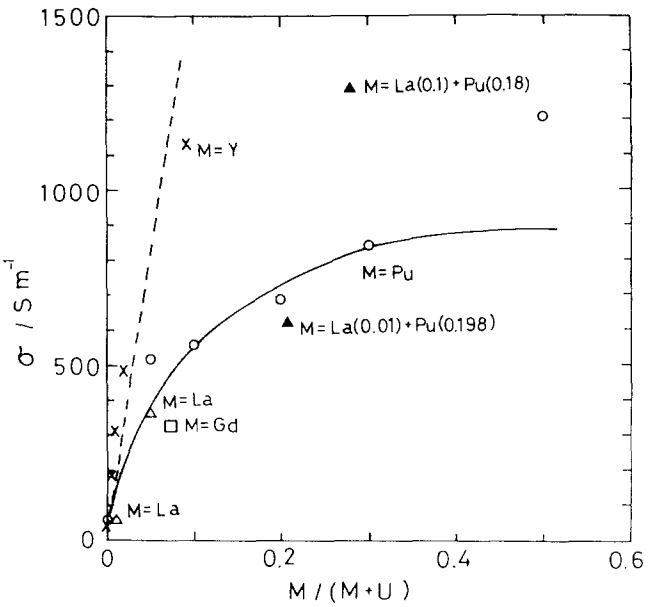

Fig. 2. Electrical conductivities at 1273 K around $P_{O2}=10^{-9}$ Pa in Fig. 1 as a function of the atomic ratio [M]/[M+U]. In the figure the solid and dotted lines represent the theoretical changes in electrical conductivity calculated by the disproportionation reaction [2] and by the hopping model for holes between U^{5+} and U^{4+} ions respectively: ○, M≡Pu, ▲, M≡La+Pu, △, M≡La, □, M≡Gd, ×, M≡Y.

approximation, the ionic species of rare earth doped uranium dioxide $R_zU_{1-z}O_2$ can be expressed as $R_z^{3+}U_{1-2z}^{4+}U_z^{5+}O_2^{2-}$. If we use eqn. (3) with $E_a = 0.3$ eV and $\sigma_0 = 3.8 \times 10^8$ S m^{-1} for UO_{2+x} from Aronson *et al.* [7] and substitute z and $1-2z$ for $2x$ and $1-y-2x$ respectively, then a theoretical line for the electrical conductivity for the hopping of holes between U^{5+} and U^{4+} ions can be calculated as shown by the dotted line in Fig. 2. The theoretical line fits well the results for yttrium-doped UO_2 and is larger than the experimental values for gadolinium- and lanthanum-doped UO_2. A similar calculation for $La_{0.1}^{3+}U_{0.62}^{4+}U_{0.1}^{5+}Pu_{0.18}^{4+}O_2^{2-}$ yields the calculated electrical conductivity 1.20×10^3 S m^{-1}, which is certainly comparable with the observed value of 1.29×10^3 S m^{-1}. Therefore, in yttrium-doped UO_2 and lanthanum-doped $(U,Pu)O_2$, electrical conduction is considered to be caused mainly by the hopping of holes between U^{4+} and U^{5+} ions resulting from the charge neutrality condition, and the contribution from the disproportionation reaction is small.

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