

가 (U_{1-y}M_y)O_{2±x}

Review of Defect Models in (U_{1-y}M_y)O_{2±x} system

150

Ln Nb⁵⁺ 가 (U_{1-y}M_y)O_{2±x}

(U,Er)O₂, (U,Gd)O₂, (U,Nb)O₂

Abstract

Previously reported data about the dependencies of oxygen nonstoichiometry and electrical conductivity on oxygen partial pressure in Lanthanide and Nb⁵⁺ doped UO₂ systems have been reviewed. It was found that consistency between oxygen nonstoichiometry and electrical conductivity was somewhat poor and consequently, the suggested defect models were incongruent with each other. A new stoichiometric oxygen composition was proposed to solve this inconsistency and the oxygen partial pressure dependency of nonstoichiometry and electrical conductivity was reanalyzed in (U,Er)O₂, (U,Gd)O₂ and (U,Nb)O₂ system.

1.

oxide) UO₂ (oxygen-excess nonstoichiometric UO_{2+x} Willis [1]

$(2O_i^a \cdot 2V_o \cdot 2O_i^b)$ cluster

[2-6].

U 가가 , 가 ,
 MOX Pu, Nb 가
 UO₂ UO₂ [7].
 UO₂ hypostoichiometric

$(U_{1-y}M_y)O_{2\pm x}$

$(U_{1-y}M_y)O_{2\pm x}$

[8-15].

(x)

(σ)

$$x \propto P_{O_2}^{1/n}, \quad s \propto P_{O_2}^{1/n'}$$

가 .

mass action law

가

가 . O/M 가 2

UO₂ $(2O_i^a \cdot 2V_o \cdot 2O_i^b)$ cluster

$(O_i^a \cdot 2V_o \cdot 2O_i^b)$ cluster model

. O/M 가 2

hypostoichiometric

carrier

+3가

가 가

+5가

가 가 Nb⁵⁺

가 UO₂

가

가

2.

가 $(U_{1-y}M_y)O_{2\pm x}$

3+

가 가

UO₂

가

. , UO₂

가 (U_{1-y}M_y)O_{2+x} O/M 가 2 hypostoichiometric ,
O/M 가 가 가 .
. O/M 가 2
hypostoichiometric 가 O/M 가
stoichiometric 가 O/M 가 2 hyperstoichiometric
가 .

2.1. Hyperstoichiometric

Hyperstoichiometric UO_{2+x}
(2O_i^a · 2V_o · 2O_i^b) (O_i^a · 2V_o · 2O_i^b) defect cluster model . Kroger-Vink

$$2V_i^a + 2V_i^b + 2O_o + O_2 \leftrightarrow [2O_i^a \cdot 2V_o \cdot 2O_i^b]^{n'} + nh^{\bullet} \quad (1)$$

$$V_i^a + 2V_i^b + 2O_o + 1/2O_2 \leftrightarrow [O_i^a \cdot 2V_o \cdot 2O_i^b]^{n'} + nh^{\bullet} \quad (2)$$

$$n[(2O_i^a \cdot 2V_o \cdot 2O_i^b)^{n'}] = h^{\bullet} \quad (3)$$

$$n[(O_i^a \cdot 2V_o \cdot 2O_i^b)^{n'}] = h^{\bullet} \quad (4)$$

가 .

$$[(2O_i^a \cdot 2V_o \cdot 2O_i^b)^{n'}] = x \quad (5)$$

$$[(O_i^a \cdot 2V_o \cdot 2O_i^b)^{n'}] = \frac{1}{2}x \quad (6)$$

mass action law

$$x, S \propto P_{O_2}^{1/(n+1)} \text{ for } (2O_i^a \cdot 2V_o \cdot 2O_i^b) \text{ cluster model} \quad (7)$$

$$x, S \propto P_{O_2}^{1/2(n+1)} \text{ for } (O_i^a \cdot 2V_o \cdot 2O_i^b) \text{ cluster model} \quad (8)$$

n 1~2 가 Ln
10mol% 가 n 2~4 가 .
n
hyperstoichiometric

$$(2O_i^a \cdot 2V_o \cdot 2O_i^b) \quad (2O_i^a \cdot 2V_o \cdot 2O_i^b) \quad (O_i^a \cdot 2V_o \cdot 2O_i^b)$$

2.2. Hypostoichiometric

Hypostoichiometric

hyperstoichiometric

가

hypostoichiometric

hyperstoichiometric

p-type

hypostoichiometric

n-type

가 가

가

Dudney[3]

3+가

Ln

charge compensation

hole 가

가

Ohmichi [17]

hypostoichiometric

O/M 가

가

Matsui [14]

$(U_{1-y}La_y)O_{2\pm x}$

가

가

가

hole

carrier

가

Ln

가

hypostoichiometric

가

2.3.

UO_{2+x}

Ln

가

가

가

가

UO_{2+x}

U^{5+}

U^{4+}

Ln

U

3+

가

가

$(U_{1-y}M_y)O_{2\pm x}$

U^{5+}, U^{4+}, Ln^{3+}

O/M가 2.0

Ln³⁺ U⁴⁺ U⁵⁺ U⁵⁺ 가
 . O/M 가 2.0 가
 U⁵⁺ 가
 U⁵⁺ U⁴⁺ U⁴⁺ U³⁺
 U⁴⁺ Ln³⁺
 가 가

$$(U_{1-y}Ln_y^{3+})O_{2-\frac{y}{2}} \quad (9)$$

가

$$(U_{1-y-2x}^{4+}U_{2x}^{5+}Ln_y^{3+})O_{2-\frac{y}{2}+x} \quad (10)$$

가 UO₂ 2.0 (9)

가 가 가

system

$$2.4. (U_{1-y}Er_y)O_{2-\frac{y}{2}+x}$$

가

$$(U_{1-y}Ln_y)O_{2\pm x}$$

(U_{1-y}Er_y)O_{2±x}

. (U_{1-y}Er_y)O_{2±x}

Kim[13]

Kang[15]

Kim

2.0

hyperstoichiometric

가

hyperstoichiometric

$$x \propto P_{O_2}^{1/2}$$

$$\text{가 } (O_i^a \cdot 2V_o \cdot 2O_i^b)$$

$$s \propto P_{O_2}^{1/4}$$

$$\text{가 } (O_i^a \cdot 2V_o \cdot 2O_i^b) \quad (2O_i^a \cdot 2V_o \cdot 2O_i^b) \quad \text{가}$$

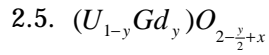
(9)

1 (9)

, Er 0.06mol

(U_{0.94}Er_{0.06})O_{1.97+x}

가



hyperstoichiometric

. Hypostoichiometric

Gd가

UO₂

가

가

(9)

(10)

UO₂

가

Gd가

UO₂

가

hypostoichiometric

가

carrier

hole

, Dudney[3]가

hole

가

2

Gd가

0.087mole

(U_{0.913}Gd_{0.087})O_{1.9565+x}

. Er

가

Fujino[18-24]

2+가

3+가

가

$(U_{1-y}M_y)O_{2\pm x}$

2.0

가

configurational entropy

cluster

hypostoichiometric

가

U⁵⁺

configurational entropy가

∞

가

가

, 가

Nakajima [25]

Y₂O₃가

UO₂

mass spectroscopy

$(1-x)UO_2-xYO_{1.5}$ 가 $UO_{2-0.5x}$ 가 (9)

가

3. $(U_{1-y}Nb_y)O_{2\pm x}$

Nb $(U_{1-y}Nb_y)O_{2\pm x}$ 가 가 Ln^{3+} 가
 . Matsui [16] Nb가 UO_2 가
 . Nb가 UO_2 O/M 가 O/M Nb
 hyperstoichiometric 가 . 가 O/M 가
 가 가 . O/M 가
 UO_2 . 가
 가 가 가 . Matsui

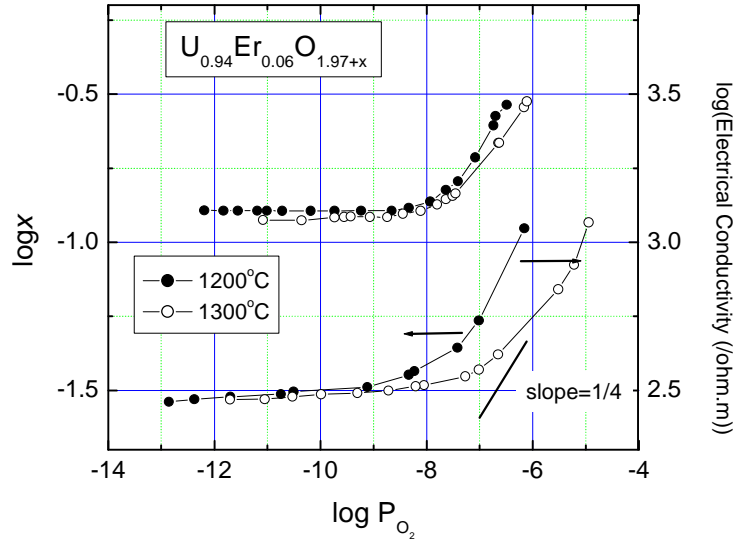
가

Nb Ln^{3+} 4+ 5+ 가 가 . O/M 가 2.0
 Nb Nb^{4+} . 가 U^{4+} Nb^{4+} 가 5+ 가
 가 . O/M 가 UO_2 Nb^{4+} 가
 U^{4+} Nb^{5+} U^{4+} 가 U^{5+} 가 .
 가 U^{4+} Nb^{5+} .
 $(U_{1-y}Nb_y)O_{2+0.5y\pm x}$ (11)

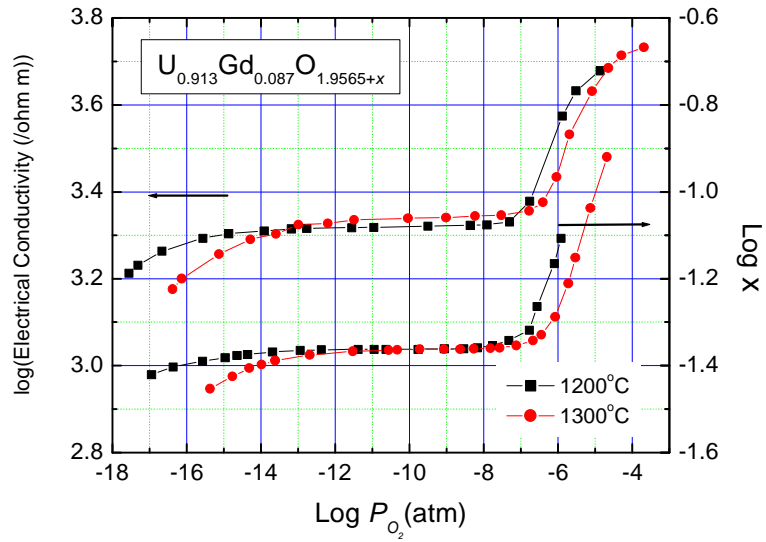
Nb^{5+} 가 Nb^{4+}

가 가 U^{4+} 가 U^{5+} 가
 hole 가 가 .
 3 Nb가 0.05mol UO_2

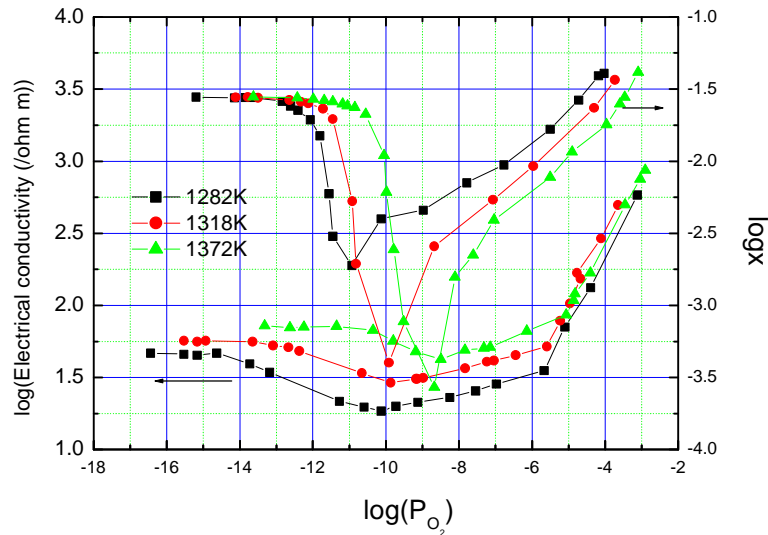
O/M =2.0



1. $(U_{0.94}Er_{0.06})O_{1.97+x}$



2. $(U_{0.913}Gd_{0.087})O_{1.9565+x}$



3. $(U_{0.95}Nb_{0.05})O_{2.028 \pm x}$

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