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Theoretical oxygen potential change of quaternary solid solution, $A_y^{2+}B_z^{3+}U_{1-y-z}O_{2+x}$, by configurational entropy calculation

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Abstract

The change of oxygen potential, $\Delta\bar{G}_{O_2}$, for the solid solutions of general formula $A_y^{2+}B_z^{3+}U_{1-y-z}O_{2+x}$ was studied by the method of configurational entropy calculation for cations and cation complexes. A part of Mg atoms (fraction m) were assumed to occupy the interstitial 4b sites of the solid solution, and the number of ways of arranging the free ions and intra-cation complexes was calculated followed by differentiation of the logarithm of this number with respect to oxygen non-stoichiometry to obtain partial molar entropy of oxygen. As the complexes, $(A^{2+}U^{5+})$, $(A^{2+}2U^{5+})$ and $(B^{3+}U^{5+})$ were assumed to be formed. For the first two complexes, an average composition $(A^{2+}\alpha U^{5+})$ was defined, and for $(B^{3+}U^{5+})$ a fraction, β, of B^{3+} was considered to form the complex. The O/M ratio ($M = A + B + U$) which gave the steepest change of $\Delta\bar{G}_{O_2}$ was calculated. Below this O/M ratio to $2 - y - (1-\beta)z/2$, the solid solution possibly satisfied the relation $m = X/(2y)$, where $X = -x$. In the region where this relation held, the solid solution was supposed to be oxygen stoichiometric. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Oxygen potential, $\Delta\bar{G}_{O_2}$, is one of the most important thermodynamic properties of the oxide fuels. The high temperature stability of fuel and cladding materials [1,2] as well as the control of formation of fission product mixed oxides [3] could be evaluated by this quantity which changes depending on the irradiation condition and burnup of the fuels through non-stoichiometry and temperature. For solid solutions, $A_yU_{1-y}O_{2+x}$ $\left(x \gtreqless 0\right)$, the thermodynamic properties are more complicated than those for UO_2 because of the increased number of the components in the system. On the other hand, there is a hastening demand to elucidate the thermodynamic properties of certain kinds of UO_2 solid solutions since they are considered to be formed and accumulated in fuel during irradiation. Another reason is that the solid solution fuels such as MOX fuel and burnable-poison UO_2 fuel containing gadolinium (gadolinium solid solution) have been used in light water reactors.

The thermodynamic properties of solid solutions have been studied by means of a variety of methods. There are two main techniques on which most of the methods were developed. The first one is the use of the mass-action law: The reactions of defect formation and extinction are described as equilibrium equations by which the concentrations of ions and/or defects are related in the specified regions [4–7]. In some cases, the mass-action law is assumed to hold for representing a hypothetical solution in solid phase with a chosen set of two binary oxides, where one is the lower oxide and the other the higher oxide [8,9]. Calculations of the activity of the chemical species and excess free energy have been made successfully for MOX [10] and for $Y_yU_{1-y}O_{2+x}$ [11]. The second one is based on the statistical mechanical techniques: To express the interaction of defects

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adequately, the fraction valence model [12], spacing statistics [13–16] and site-blocking model [17] have been introduced. The partition functions were obtained and calculated for various solid solution systems containing complex defects.

If the solid solution is of ideal type, then the partial molar enthalpy of oxygen, $\Delta\bar{H}_{O_2}$, is zero and hence the partition functions need not be calculated. In this case, the configurational partial molar entropy of oxygen, $\Delta\bar{S}_{O_2}$, alone can explain satisfactorily the thermodynamic properties of solid solutions [18–21]. The phenomenon that the O/M ratio causing to yield the steepest change in $\Delta\bar{G}_{O_2}$ shifts to a smaller value than $O/M = 2$ can be explained by calculating $\Delta\bar{S}_{O_2}$. For magnesium solid solution, $Mg_y^{2+}U_{1-y}O_{2+x}$ $\left(x \gtreqless 0\right)$, the experimental data showed that such a change in $\Delta\bar{G}_{O_2}$ took place at the O/M ($M = Mg + U$) ratio which was significantly smaller than 2. This shift is understood as due to the configurational entropy change. If two kinds of clusters, namely ($Mg^{2+}U^{5+}$) and ($Mg^{2+}2U^{5+}$), are present in the solid solution and the equilibrium constant for the second cluster formation reaction, $(Mg^{2+}U^{5+}) + U^{5+} = (Mg^{2+}2U^{5+})$ is not large, an infinite change in $\Delta\bar{S}_{O_2}$ occurs at $O/M < 2$ [22]. The refinement of the lattice statistics of this treatment has been carried out [23]. Also, it was shown by the same technique that a part of magnesium in $Mg_y^{2+}U_{1-y}O_{2+x}$ could occupy the interstitial 4*b* position of the *Fm*$\bar{3}$*m* fluorite lattice. If the solid solution is formed by the reaction of MgO and stoichiometric UO_2, which means that uranium takes on exclusively +4 valence state without any U^{5+} ions in the solid solution, the calculated $\Delta\bar{G}_{O_2}$ should become the lowest either at 50% substitutional Mg–50% interstitial Mg or at 100% substitutional Mg [24]. This result was obtained on the assumption that the $\Delta\bar{H}_{O_2}$ change for magnesium to take the interstitial sites is low enough to realize the partition of magnesium between substitutional and interstitial sites. The result could rationalize the oxygen potential change of magnesium solid solution with O/M ratio under very low oxygen partial pressures.

In this work, the following two subjects were studied. First, the possible change of $\Delta\bar{G}_{O_2}$ as a function of the ratio of interstitial magnesium to total magnesium ions with mean uranium valency was formulated. Although occupation of interstitial sites by magnesium has been observed in the atmosphere of low oxygen partial pressures where almost all uranium ions in the solid solution were in +4 state, the $\Delta\bar{G}_{O_2}$ change in relation with the occupation ratio and the mean valency of uranium in the solid solution has not been closely analyzed. Here, a quantitative relationship will be derived for the ratio of interstitial to total magnesium ions which decreases as the mean uranium valency increases. Next, the extension of the configurational entropy method to apply to quaternary $A_y^{2+}B_z^{3+}U_{1-y-z}O_{2+x}$ solid solutions was made. A part of the A^{2+} ions are assumed to occupy the interstitial 4*b* sites of the fluorite lattice at low oxygen partial pressures. The change of $\Delta\bar{G}_{O_2}$ is expressed as a function of non-stoichiometry. The general formula $A_y^{2+}B_z^{3+}U_{1-y-z}O_{2+x}$ includes the $z = 0$ case, i.e., $A_y^{2+}U_{1-y}O_{2+x}$.

2. Solid solution with partially interstitial A^{2+} ions

The A and B solid solution with metal mole fractions *y* and *z*, respectively, is expressed as $A_yB_zU_{1-y-z}O_{2+x}$ if both the A and B atoms occupy the substitutional 4*a* position of the fluorite crystal. If a part of the A metal atoms are located on the interstitial 4*b* sites, the expression of the solid solution should be changed to

$$A_yB_zU_{1-y-z}O_{2+x} \rightarrow u\left(A_{\frac{y_1}{u}}B_{\frac{z}{u}}U_{\frac{1-y-z}{u}}\right)\{A_{\frac{y_2}{u}}\}O_{\frac{2+x}{u}}, \tag{1}$$

where the parentheses and the braces indicate the 4*a* and 4*b* positions, respectively, and

$$y_1 + y_2 = y \quad \text{and} \quad u = 1 - y + y_1. \tag{2}$$

The above description is necessary because the cation sublattice is considered to be fully occupied. This requirement is filled by dividing all concentrations by *u*. In Eq. (2), y_1 and y_2 show the concentrations of substitutional and interstitial A atoms, respectively. Then, if the ratio of the interstitial A atoms to the total A atoms is denoted by *m*, i.e.

$$m = \frac{y_2}{y_1 + y_2} = \frac{y_2}{y} \tag{3}$$

the right-hand side of Eq. (1) can be rewritten as

$$(1 - my)\left(A_{((1-m)y)/(1-my)}B_{z/(1-my)}U_{(1-y-z)/(1-my)}\right) \times \left\{A_{(my)/(1-my)}\right\}O_{(2+x)/(1-my)}. \tag{4}$$

In terms of ionic representation, the above formula becomes

$$(1 - my)\Big(A^{2+}_{((1-m)y)/(1-my)}B^{3+}_{z/(1-my)}U^{4+}_{(1-2x-3y-2z)/(1-my)} \times U^{5+}_{(2x+2y+z)/(1-my)}\Big)\left\{A^{2+}_{(my)/(1-my)}\right\}O^{2-}_{(2+x)/(1-my)}. \tag{5}$$

3. Concentration of chemical species in the solid solution

Since uranium dioxide is regarded as a basically ionic crystal, in stoichiometric UO_2 all uranium and oxygen atoms take on +4 and −2 valences, respectively. Then, the A^{2+} and B^{3+} cations introduced in UO_2 are regarded as −2 and −1 charged negative defects with respect to the +4 state of uranium, respectively, while the oxidized U^{5+} ions are regarded as +1 charged positive defects [25]. The positive defects and the negative defects interact electrostatically resulting in formation of complexes. The supposed complexes formed are ($\mathrm{B}^{3+}\mathrm{U}^{5+}$), ($\mathrm{A}^{2+}\mathrm{U}^{5+}$) and ($\mathrm{A}^{2+}2\mathrm{U}^{5+}$). The ($\mathrm{A}^{2+}2\mathrm{U}^{5+}$) complexes are formed by way of interaction of ($\mathrm{A}^{2+}\mathrm{U}^{5+}$) and U^{5+}, because the ($\mathrm{A}^{2+}\mathrm{U}^{5+}$) complex is still a -1 charged defect. The ($\mathrm{B}^{3+}\mathrm{U}^{5+}$) complex does not cause any large effect on the thermodynamic properties if it is formed quantitatively in $\mathrm{B}_y^{3+}\mathrm{U}_{1-y}\mathrm{O}_{2+x}$ ternary solid solutions [22,23]. However, for the present quaternary solid solutions this complex plays a certain role and thus it is taken into account by introducing β as the fraction of the B^{3+} ions which combine to give the 1:1 complexes by the reaction

$$\mathrm{B}^{3+} + \mathrm{U}^{5+} = (\mathrm{B}^{3+}\mathrm{U}^{5+}). \tag{6}$$

These ($\mathrm{B}^{3+}\mathrm{U}^{5+}$) complexes are defined as the nearest neighbor pairs of the B^{3+} and U^{5+} ions in the $4a$ sites. The formation of the ($\mathrm{A}^{2+}\mathrm{U}^{5+}$) complexes is assumed to be quantitative, i.e., the equilibrium constant of the reaction

$$\mathrm{A}^{2+} + \mathrm{U}^{5+} = (\mathrm{A}^{2+}\mathrm{U}^{5+}) \tag{7}$$

is nearly infinitely large. However, for the reaction to form the ($\mathrm{A}^{2+}2\mathrm{U}^{5+}$) complex

$$(\mathrm{A}^{2+}\mathrm{U}^{5+}) + \mathrm{U}^{5+} = (\mathrm{A}^{2+}2\mathrm{U}^{5+}), \tag{8}$$

the equilibrium constant is assumed not to be large. The ($\mathrm{A}^{2+}2\mathrm{U}^{5+}$) complex would be a linear $\mathrm{U}^{5+} - \mathrm{A}^{2+} - \mathrm{U}^{5+}$ type to minimize the repulsion of two U^{5+} ions. However, the concentration of the ($\mathrm{A}^{2+}2\mathrm{U}^{5+}$) complex would not become high since more cation sites around a ($\mathrm{A}^{2+}2\mathrm{U}^{5+}$) complex having this linear conformation are enveloped, which possibly leads to give not a very large equilibrium constant for the reaction shown in Eq. (8).

Since all ($\mathrm{A}^{2+}\mathrm{U}^{5+}$) complexes do not change to the ($\mathrm{A}^{2+}2\mathrm{U}^{5+}$) complexes, both types of the complexes are present in the solid solution. Then, we define the mean atom ratio of A^{2+} and U^{5+} in the two complexes as

$$\mathrm{A}^{2+} : \mathrm{U}^{5+} = 1 : \alpha. \tag{9}$$

Calculation of thermodynamic quantities is carried out for the two regions of the x values of the $\mathrm{A}_y\mathrm{B}_z\mathrm{U}_{1-y-z}\mathrm{O}_{2+x}$ solid solution. In the first region, the number of A^{2+} and B^{3+} ions available for complex formation is larger than the number of U^{5+} ions for complex formation, i.e., $\alpha[\mathrm{A}^{2+}]_{\mathrm{sub}+}\beta[\mathrm{B}^{3+}] > [\mathrm{U}^{5+}]$. Therefore, all U^{5+} ions are used for forming the complexes whereas some A^{2+} ions remain uncombined. The above inequality relation yields

$$x < -\left\{1 - \frac{\alpha}{2}(1-m)\right\}y - \frac{1-\beta}{2}z.$$

The second region is

$$x > -\left\{1 - \frac{\alpha}{2}(1-m)\right\}y - \frac{1-\beta}{2}z.$$

In this region, all A^{2+} ions in the substitutional sites are consumed for forming the ($\mathrm{A}^{2+}\mathrm{U}^{5+}$) and ($\mathrm{A}^{2+}2\mathrm{U}^{5+}$) complexes and no available B^{3+} ions remain to form ($\mathrm{B}^{3+}\mathrm{U}^{5+}$). Some free U^{5+} ions are present uncombined, instead. The numbers of ions, defects and defect complexes are listed in Table 1 for each of the above two regions. In the table $X = -x$, $L = N(1 - my)$ and $Q = \{-2X + 2y + (1-\beta)z\}/\alpha$.

4. $\Delta\overline{S}_{\mathrm{O}_2}$ and $\Delta\overline{G}_{\mathrm{O}_2}$ of the solid solution

4.1. Region $x < -\{1 - \frac{\alpha}{2}(1-m)\}y - \frac{1-\beta}{2}z$

The numbers of the A^{2+}(sub), B^{3+}, ($\mathrm{B}^{3+}\mathrm{U}^{5+}$), U^{4+}, ($\mathrm{A}^{2+}\mathrm{U}^{5+}$) and ($\mathrm{A}^{2+}2\mathrm{U}^{5+}$) are $\{(1-m)y - Q\}L$, $(1-\beta)zL$, βzL, $(1 + 2X - 3y - 2z)L$, $(2-\alpha)QL$ and $(\alpha - 1)QL$ from Table 1, respectively. These numbers give the total number of the chemical species in the $4a$ sites as $\{1 + 2X - (2+m)y - z\}L$. Then, the number of ways of arranging the above chemical species over the cation sublattice, W_1, is

$$W_1 = \frac{[\{1 + 2X - (2+m)y - z\}L]!}{D(1)D(2)}, \tag{10}$$

Table 1
Numbers of ions, defects and defect complexes in the solid solution $\mathrm{A}_y^{2+}\mathrm{B}_z^{3+}\mathrm{U}_{1-y-z}\mathrm{O}_{2+x}$; $X = -x$, $L = N/(1 - my)$ and $Q = \{-2X + 2y + (1-\beta)z\}/\alpha$

	$x < -\{1 - \frac{\alpha}{2}(1-m)\}y - \frac{1-\beta}{2}z$	$x > -\{1 - \frac{\alpha}{2}(1-m)\}y - \frac{1-\beta}{2}z$
A^{2+}(sub)	$\{(1-m)y - Q\}L$	0
B^{3+}	$(1-\beta)zL$	$(1-\beta)zL$
($\mathrm{B}^{3+}\mathrm{U}^{5+}$)	βzL	βzL
U^{4+}	$(1 + 2X - 3y - 2z)L$	$(1 + 2X - 3y - 2z)L$
U^{5+}	0	$\alpha\{Q - (1-m)y\}L$
($\mathrm{A}^{2+}\mathrm{U}^{5+}$)	$(2-\alpha)QL$	$(2-\alpha)(1-m)yL$
($\mathrm{A}^{2+}2\mathrm{U}^{5+}$)	$(\alpha-1)QL$	$(\alpha-1)(1-m)yL$
A^{2+}(int)	myL	myL
O^{2-}(int)	$(-X + 2my)L$	$(-X + 2my)L$

where

$$D(1) = [\{(1-m)y - Q\}L]!\{(1-\beta)zL\}!(\beta zL)!, \tag{11}$$

$$D(2) = \{(1+2X-3y-2z)L\}!\{(2-\alpha)QL\}! \times \{(\alpha-1)QL\}!. \tag{12}$$

The numbers of A^{2+}(int), O^{2-}(int) and vacancies in the interstitial sublattice with total number N (= Avogadro's number) are myL, $(-X+2my)L$ and $(1+X-4my)L$, respectively. Hence, the number of ways of arranging them over the interstitial sublattice, W_2, is

$$W_2 = \frac{N!}{(myL)!\{(-X+2my)L\}!\{(1+X-4my)L\}!}. \tag{13}$$

Using the Stirling's approximation, the partial molar entropy of oxygen per mole of O_2 is obtained as

$$\begin{aligned}\Delta\bar{S}_{O_2} &= 2kN\left[\frac{\partial\ln(W_1W_2)}{\partial\{N(x+2my)/(1-my)\}}\right]_{N,m,y}\\ &= -2kN(1-my)\left[\frac{\partial\ln(W_1W_2)}{\partial(XN)}\right]_N\\ &= 4\mathrm{R}\ln\frac{1+2X-(2+m)y-z}{1+2X-3y-2z}\\ &\quad+\frac{4\mathrm{R}}{\alpha}\ln\frac{(1-m)y-Q}{Q}+2\mathrm{R}\ln\frac{1+X-4my}{-X+2my}\\ &\quad-\frac{4\mathrm{R}}{\alpha}\{(2-\alpha)\ln(2-\alpha)+(\alpha-1)\ln(\alpha-1)\}.\end{aligned} \tag{14}$$

To the right-hand side of this equation, a factor which includes the vibrational entropy of the crystal and the standard entropy of oxygen is usually to be added. However, since this value does not significantly vary with composition [18], it was disregarded in this work. The above equation shows that $\Delta\bar{S}_{O_2}$ lowers to $-\infty$ as $(1-m)y-Q \to 0$, i.e., $x \to -\{1-\alpha(1-m)/2\}y - (1-\beta)z/2$. Therefore, $\Delta\bar{G}_{O_2}$ increases sharply towards $+\infty$ on approaching this x value since $\Delta\bar{G}_{O_2} = \Delta\bar{H}_{O_2} - T\Delta\bar{S}_{O_2}$ and $\Delta\bar{H}_{O_2}$ is assumed to be finite. Eq. (14) also shows that $\Delta\bar{S}_{O_2}$ rises to $+\infty$ if $-X+2my \to 0$. The latter result is understood rather as specifying the m value. That is to say, the thermodynamically stable m value is

$$m = \frac{X}{2y}. \tag{15}$$

4.2. Region $x > -\{1-\frac{\alpha}{2}(1-m)\}y - \frac{1-\beta}{2}z$

The numbers of B^{3+}, $(B^{3+}U^{5+})$, U^{4+}, U^{5+}, $(A^{2+}U^{5+})$ and $(A^{2+}2U^{5+})$ are $(1-\beta)zL$, βzL, $(1+2X-3y-2z)L$, $\alpha\{Q-(1-m)y\}L$, $(2-\alpha)(1-m)yL$ and $(\alpha-1)(1-m)yL$ from Table 1, respectively, which yield the total number of the chemical species in the 4a sites as $\{1-(\alpha+m-\alpha m)y-\beta z\}L$. Then, the number of ways of arranging the above chemical species over the cation sublattice, W_1, is written as

$$W_1 = \frac{[\{1-(\alpha+m-\alpha m)y-\beta z\}L]!}{D(1)D(2)}, \tag{16}$$

where

$$D(1) = \{(1-\beta)zL\}!(\beta zL)!\{(1+2X-3y-2z)L\}!, \tag{17}$$

$$D(2) = [\alpha\{Q-(1-m)y\}L]!\{(2-\alpha)(1-m)yL\}! \times \{(\alpha-1)(1-m)yL\}!. \tag{18}$$

The number of ways of arrangement in the interstitial sublattice, W_2, is the same as that in the $x < -\{1-\alpha(1-m)/2\}y - (1-\beta)z/2$ region. Hence, the configurational partial molar entropy of oxygen per mole of O_2 is obtained as

$$\begin{aligned}\Delta\bar{S}_{O_2} &= -2kN(1-my)\frac{\partial\ln(W_1W_2)}{\partial(XN)}\\ &= -4\mathrm{R}\ln\frac{\alpha\{Q-(1-m)y\}}{1+2X-3y-2z}\\ &\quad+2\mathrm{R}\ln\frac{1+X-4my}{-X+2my}.\end{aligned} \tag{19}$$

The above equation shows that $\Delta\bar{S}_{O_2}$ increases to $+\infty$ as $Q-(1-m)y \to 0$, i.e. as x approaches $-\{1-\alpha(1-m)/2\}y - (1-\beta)z/2$ from the larger value side. It causes a sharp decrease of $\Delta\bar{G}_{O_2}$ towards $-\infty$ near this x value.

5. Thermodynamic quantities as related to the m, α and β values

The interstitial A^{2+} ions are not defined for $X < 0$ (i.e., $x > 0$) in Eq. (15). The redefinition of m in this range of x values is unnecessary since the A^{2+} ions enter into the interstitial sites only at low oxygen partial pressures at high temperatures, where the solid solutions exhibit considerably negative x values [26]. Eq. (15) also shows that the m value is not affected by the B^{3+} atoms since m is not a function of the z variable. Then, m is the same for $A_y^{2+}U_{1-y}O_{2+x}$ and $A_y^{2+}B_z^{3+}U_{1-y-z}O_{2+x}$ solid solutions if x and y are the same in these solid solutions. In the preceding paper [24], the m value for $Mg_yU_{1-y}O_{2-y}$ solid solution with all uranium ions in the +4 oxidation state was calculated to be 1/2. The corresponding condition is $z = 0$ and $2x+2y+z = 0$ in formula (5), which yields $X = y$, giving $m = 1/2$ by Eq. (15).

The range of the x values in which $m = X/(2y)$ holds may change depending on individual solid solutions, but generally it can be said that the above relation holds only for solid solutions in equilibrium with low oxygen partial pressures. In the case of $Mg_yU_{1-y}O_{2+x}$ solid solution [24,27], the steepest change of $\Delta\bar{G}_{O_2}$ occurs with a $\Delta\bar{G}_{O_2}$ jump from near −200 to −400 kJ mol^{-1}. The

$\Delta\bar{G}_{O_2}$ value of -200 kJ mol^{-1} corresponds to $p_{O_2} = 6 \times 10^{-4}$ Pa at 1000°C or $p_{O_2} = 8 \times 10^{-3}$ Pa at 1200°C. In the course to lower $\Delta\bar{G}_{O_2}$ to this value, a part of the magnesium atoms of the solid solution precipitate as MgO if the y value is large, viz. 0.1.

It means that there can be a state of two solid phases (if y is large) in which the reaction proceeds as

$$\begin{aligned}&\mathrm{Mg}_y\mathrm{U}_{1-y}\mathrm{O}_{2+x}(s)\\&\quad= \left\{1 - \frac{\Delta y}{1-(y-\Delta y)}\right\}\mathrm{Mg}_{y-\Delta y}\mathrm{U}_{1-(y-\Delta y)}\mathrm{O}_{2+x}(s)\\&\qquad+ \frac{\Delta y}{1-(y-\Delta y)}\mathrm{MgO}(s) + \frac{1}{2}\frac{\Delta y}{1-(y-\Delta y)}(1+x)\mathrm{O}_2(g).\end{aligned} \tag{20}$$

The decrease of oxygen potential of magnesium solid solution is brought about by decreasing either y or x value of $\mathrm{Mg}_y\mathrm{U}_{1-y}\mathrm{O}_{2+x}$. The decrease of the y value is accompanied by the precipitation of MgO, while that of the x value is made only by liberating oxygen to the gas phase. The former route is energetically less favorable because of the formation of another solid phase in the solid solution, so that the non-stoichiometric oxygen, x, is usually decreased. However, there is a lower limit of this x value on account of crystal energy requirements. Then, if the gaseous oxygen pressure is still decreased, then the solid solution begins to attain equilibrium by lowering y value, i.e., precipitating MgO from $\mathrm{Mg}_y\mathrm{U}_{1-y}\mathrm{O}_{2+x}$. The x values of $\mathrm{Mg}_y\mathrm{U}_{1-y}\mathrm{O}_{2+x}$ and $\mathrm{Mg}_{y-\Delta y}\mathrm{U}_{1-(y-\Delta y)}\mathrm{O}_{2+x}$ in Eq. (20) are, therefore, the same if they are the boundary values regardelsss of the magnitude of Δy. The oxygen potential of the magnesium solid solution in this solid two-phase region is expected to drop vertically (without changing the O/M ratio of the solid solution) precipitating MgO. Such oxygen potentials are just near those for the onset of the steepest change. Therefore, the vertical drop might hardly be observed. On further decrease of oxygen pressure, the y value attains the lower limit. After the limit, a part of the magnesium atoms enter into the interstitial sites with increasing m value.

The relation of Eq. (15) would not be realized in the solid solution if $\Delta\bar{H}_{O_2}$ for the migration of magnesium atoms into interstitial sites is high. If the fluorite crystal is destabilized by $\Delta\bar{H}_{O_2}$ increase due to, e.g., electrostatic repulsion or steric hindrance, the occupation of the interstitial sites by magnesium cannot take place. The relation $m = X/(2y)$ is regarded as that which lowers $\Delta\bar{G}_{O_2}$ on the basis that the occupation of interstitial sites is allowed in terms of $\Delta\bar{H}_{O_2}$ change.

It is possible that the above relation for m is valid in the O/M range below the O/M ratio which gives the steepest $\Delta\bar{G}_{O_2}$ change. In this case, the numbers of chemical species should be rewritten as Table 2 using Eq. (15). For the x values below $\{-2(2-\alpha) - 2(1-\beta)z\}/(4-\alpha)$ which is equivalent to $-\{1-\alpha(1-m)/2\}y - (1-\beta)z/2$, $\Delta\bar{S}_{O_2}$ would be expressed as

$$\begin{aligned}\Delta\bar{S}_{O_2} = &-3\mathrm{R}\ln\left(1 + \frac{3}{2}X - 2y - z\right)\\&+ 4\mathrm{R}\ln(1 + 2X - 3y - 2z)\\&+ \left(\frac{4}{\alpha} - 1\right)\mathrm{R}\ln\left(y - \frac{X}{2} - Q\right) - \frac{4}{\alpha}\mathrm{R}\ln Q\\&- \frac{4}{\alpha}\mathrm{R}\{(2-\alpha)\ln(2-\alpha) + (\alpha-1)\ln(\alpha-1)\}.\end{aligned} \tag{21}$$

Table 2
Numbers of ions, defects and defect complexes in a range of x values $x < \{-2(2-\alpha)y - 2(1-\beta)\}/(4-\alpha)$ where the relation $m = X/(2y)$ holds

Chemical species	Number
A^{2+}(sub)	$\{(y - \frac{X}{2}) - Q\}L$
B^{3+}	$(1-\beta)zL$
$(\mathrm{B}^{3+}\mathrm{U}^{5+})$	βzL
U^{4+}	$(1+2X-3y-2z)L$
U^{5+}	0
$(\mathrm{A}^{2+}\mathrm{U}^{5+})$	$(2-\alpha)QL$
$(\mathrm{A}^{2+}2\mathrm{U}^{5+})$	$(\alpha-1)QL$
A^{2+}(int)	$\frac{X}{2}L$
O^{2-}(int)	0

Eq. (21) shows that $\Delta\bar{S}_{O_2}$ steeply decreases towards $-\infty$ (and hence $\Delta\bar{G}_{O_2}$ increases towards ∞) as X decreases to

$$X = \frac{2(2-\alpha)y + 2(1-\beta)z}{4-\alpha} \quad (\text{i.e., } y - x/2 - Q \to 0). \tag{22}$$

Also, it shows that $\Delta\bar{S}_{O_2}$ steeply increases towards ∞ (and hence $\Delta\bar{G}_{O_2}$ decreases towards $-\infty$) as X increases to

$$X = y + \frac{1-\beta}{2}z \quad (\text{i.e., } Q \to 0). \tag{23}$$

For the X values larger than that of Eq. (23), the solid solution is supposed to be decomposed into its component binary oxides.

The change of $\Delta\bar{G}_{O_2}$ with O/M ratio in the two regions of x values is outlined in Fig. 1. The steepest change of $\Delta\bar{G}_{O_2}$ occurs at the X values given by Eqs. (14), (19), (22) and (23).

It should be noted that the concentration of interstitial oxygen is seen to be zero from Table 2 in the x region, where Eq. (15) is valid. The oxygen non-stoichiometry is given by

$$H = \frac{2+x}{1-my} - 2, \tag{24}$$

which becomes zero if $m = X/(2y)$. The solid solution is possibly oxygen stoichiometric in the range of x values $-y-(1-\beta)z/2 < x < -\{1-\alpha(1-m)/2\}y-(1-\beta)\times z/2$. That is to say, the m value linearly increases with increasing X in this region. One explanation for this stoichiometry is that the formation of oxygen vacancies causes to enhance the activity for magnesium migration to the interstitial sites up to the equivalent amount of the m value that gives oxygen stoichiometry according to Eq. (24). On the other hand, the O/M ratio, $2+x$, is not affected by the interstitialcy of the A^{2+} ions, and it can lower to $2-y-(1-\beta)z/2$ as shown in Fig. 1.

In this work, the change of partial molar enthalpy of oxygen, $\Delta\bar{H}_{O_2}$, was disregarded because $\Delta\bar{H}_{O_2}$ was thought to vary more slowly with x, y and z than $\Delta\bar{S}_{O_2}$. However, for finer study of thermodynamic properties of $A_y^{2+}B_z^{3+}U_{1-y-z}O_{2+x}$ solid solutions at high temperature its effect needs to be included. $\Delta\bar{H}_{O_2}$ is related to the enthalpy of formation of the complexes as well as the migration energy to the interstital sites for magnesium. If crystallographic restriction is large, it reflects on enthalpy as a high $\Delta\bar{H}_{O_2}$ value.

For the X value of Eq. (23), the number of U^{5+} ions $(-2X+2y+z)L$ is βzL. This number should approach zero at $Q=0$ since the concentrations of $(A^{2+}U^{5+})$ and $(A^{2+}2U^{5+})$ are zero at $Q=0$ from Table 2. The quantities α and β are seen to decrease with decreasing x value towards 1 and 0, respectively. They are associated with the enthalpy of formation of the $(A^{2+}U^{5+})$ and $(A^{2+}2U^{5+})$ complexes and the $(B^{3+}U^{5+})$ complexes, although all A^{2+}, B^{3+} and U^{5+} ions are on the 4*a* position. That is to say, the distribution of ionic species on the same crystallographic position is given by the numbers of the above complexes. At very high temperatures these ions would distribute randomly after decomposition of the complexes. The temperature effect becomes large as the term $-T\Delta\bar{S}_{O_2}$ controls $\Delta\bar{G}_{O_2}$ at high temperature. The configurational entropy becomes important and these ions distribute randomly. For the decomposition temperature of the complexes, no information is available so far. But there could be a possibility that the specific heat rise for UO_2 at 1500 K, which has been explained as due to the formation of electron–hole pairs [28,29], has some relation with the defect energies.

As for magnesium solid solution and europium solid solution, the α value was reported to be almost unchanged with y. For $Mg_yU_{1-y}O_{2+x}$, α was obtained as 1.50 and 1.56 for $y=0.02$ and 0.05, respectively. For $Eu_yU_{1-y}O_{2+x}$, the same α value of 1.66 was obtained for $y=0.1$ and 0.3 [22]. A positive correlation between the α and β values is assumed to exist, although this point has not been studied yet.

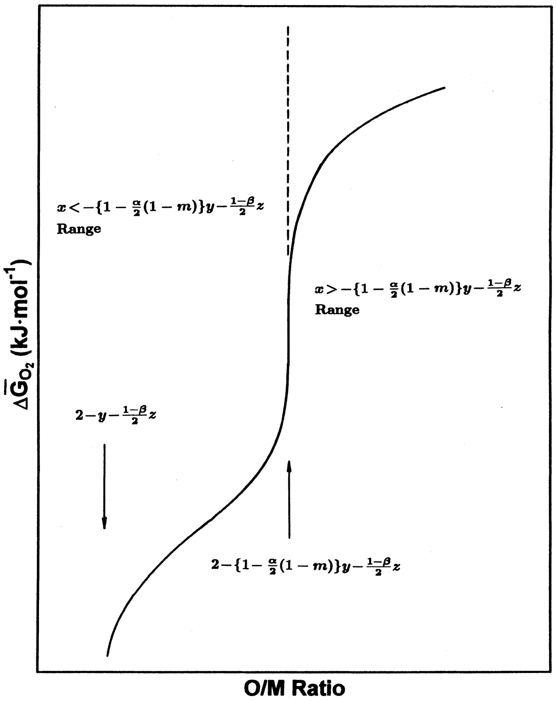

Fig. 1. Change of oxygen potential of $A_y^{2+}B_z^{3+}U_{1-y-z}O_{2+x}$ solid solution as a function of O/M ratio.

6. Conclusions

The change of oxygen potential, $\Delta\bar{G}_{O_2}$, for $A_y^{2+}B_z^{3+}U_{1-y-z}O_{2+x}$ solid solutions was studied by the method of configurational entropy calculation. In this work, a part of magnesium atoms were assumed to occupy the interstitial sites (4*b* position of space group *Fm*$\bar{3}$*m*). Since the metal sublattice (4*a* position) is fully occupied by A^{2+}, B^{3+}, U^{4+} and U^{5+} ions, the formula $A_y^{2+}B_z^{3+}U_{1-y-z}O_{2+x}$ should be rewritten as below defining m as the ratio of the interstitial A^{2+} atoms to the total A^{2+} atoms:

$$(1-my)\Big(A^{2+}_{(1-m)y/(1-my)}B^{3+}_{z/(1-my)}U^{4+}_{(1-2x-3y-2z)/(1-my)}\\ \times U^{5+}_{(2x+2y+z)/(1-my)}\Big)\Big\{A^{2+}_{my/(1-my)}\Big\}O^{2-}_{(2+x)/(1-my)}.$$

The O/M ratio which yields the steepest change in $\Delta\bar{G}_{O_2}$ was calculated as

$$O/M = 2+x = 2-\Big\{(1-\frac{\alpha}{2}(1-m)\Big\}y-\frac{1-\beta}{2}z,$$

where α is the ratio of U^{5+} to A^{2+} in the two complexes of $(A^{2+}U^{5+})$ and $(A^{2+}2U^{5+})$, and β is the fraction of B^{3+} ions to form the complex $(B^{3+}U^{5+})$. Below this x value, the m value is considered to vary with X as

$$m = \frac{X}{2y},$$

where $X = -x > 0$ in the region of $x < 0$. The oxygen potential again decreases steeply on lowering the x value to

$$x = -y - \frac{1-\beta}{2}z.$$

Below this x value the solid solution would be decomposed into the component binary oxides. In the range between the above two x values, the solid solution is possibly oxygen stoichiometric. Oxygen vacancies seem to cause the magnesium migration to the interstitial position up to the equivalent amount of the m value that gives the solid solution with stoichiometric oxygen.

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