OXYGEN VACANCY DISTRIBUTION IN Ln_2O_3-DOPED CeO_2 ELECTROLYTES
(Ln = Sm, Gd, Y, Dy)

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Abstract: *Oxygen vacancy distribution around dopant Ln^{3+} in Ln_2O_3-doped CeO_2 electrolytes (Ln = Sm, Gd, Y, Dy) was investigated using statistical moment method. The explicit expressions of vacancy-dopant association energies at the first nearest neighbor (1NN) or the second nearest neighbor (2NN) sites relative to Ln^{3+} ions were derived including the anharmonicity effects of lattice vibrations. The findings showed that local deformation was generated from preferential distribution of oxygen vacancies in the vicinity of Ln^{3+} cations. The findings of this study were compared to earlier research.*

Keywords: *Oxygen vacancy distribution, Ln_2O_3-doped CeO_2 crystals (Ln = Sm, Gd, Y, Dy), statistical moment method.*

INTRODUCTION

With the increasing demand of renewable energy sources, solid oxide fuel cells (SOFCs) are one the most competitive candidates for future energy application [1,2]. SOFCs have the potential to be the high energy efficiency and ability to reduce environmental emissions [3,4]. Nowadays, rare earth oxide doped ceria (CeO_2) with the high ionic conductivity become the most promising electrolytes for SOFCs [5,6]. The popular rare earth oxide used in these electrolytes are Sm_2O_3, Gd_2O_3, Y_2O_3, and Dy_2O_3 [7].

The oxygen vacancy distribution in Ln_2O_3-doped CeO_2 is determined by the theoretical [8,9] and experimental [10] methods. Using density-functional theory (DFT), M. Nakayama and M. Martin [8] showed that the oxygen vacancies form associations with dopant cations and vacancy-dopant association energy is influenced by dopant radii. The vacancy distribution is controlled by the vacancy-dopant association energy. The vacancy-dopant association energy decrease with the increasing ionic radius as already found by S. Grieshammer *et al.* [9]. H. Natani *et al.* [10] using X-ray diffraction (XRD) indicated that the oxygen vacancies are located homogeneously over the crystal lattice nor distributed near dopant cations. The preferential location of oxygen vacancies depends on the dopant concentration.

In this study, the oxygen vacancy distribution in Ln_2O_3-doped CeO_2 crystals (Ln = Sm, Gd, Y, Dy) is investigated by statistical moment method (SMM). Compared with other theoretical methods, the SMM gives mathematically simple with comprehensive descriptions of the characteristic properties of crystal lattice. The calculated results for vacancy-dopant association energies reveal the favourite location of oxygen vacancies around dopants.

THEORY

Because doping CeO_2 with Ln_2O_3 creates many oxygen vacancies to maintain the charge

neutrality of the crystal lattice, the general formula of Ln$_2$O$_3$-doped CeO$_2$ crystals is Ce$_{1-x}$Ln$_x$O$_{2-x/2}$, x is the concentration of Ln^{3+} ions.

In the SMM, Ce$_{1-x}$Ln$_x$O$_{2-x/2}$ crystals are charactered by the anharmonic vibrations of Ce^{4+}, Ln^{3+}, and O^{2-} ions with the Hook constants k_{Ce}, k_{Ln}, k_O, the vibration frequencies ω_{Ce}, ω_{Ln}, ω_O, and the anharmonic parameters ρ, γ_1^{Ce}, γ_1^{Ln}, γ_1^{O}, γ_2^{Ce}, γ_2^{Ln}, γ_2^{O}, γ_{Ce}, γ_{Ln}, γ_O, [11]

$$k_{Ce,Ln,O} = \frac{1}{2}\sum_j \left(\frac{\partial^2 \phi_{j0}^{Ce,Ln,O}}{\partial u_{j\alpha}^2}\right)_{eq} = m^* \omega_{Ce,Ln,O}^2, (1)$$

$$\rho = \frac{1}{2}\sum_j \left(\frac{\partial^3 \phi_{j0}^{O}}{\partial u_{j\alpha}\partial u_{j\beta}\partial u_{j\gamma}}\right)_{eq}, \quad \xi = k_O - \frac{\rho^2}{3\gamma_O},$$

$$(2)$$

$$\gamma_1^{Ce,Ln,O} = \frac{1}{48}\sum_j \left(\frac{\partial^4 \phi_{i0}^{Ce,Ln,O}}{\partial u_{j\alpha}^4}\right)_{eq}, \quad (3)$$

$$\gamma_2^{Ce,Ln,O} = \frac{1}{8}\sum_j \left(\frac{\partial^4 \phi_{j0}^{Ce,Ln,O}}{\partial u_{j\alpha}^2 \partial u_{j\beta}^2}\right)_{eq}, \quad (4)$$

$$\gamma_{Ce,Ln,O} = 4\left(\gamma_1^{Ce,Ln,O} + \gamma_2^{Ce,Ln,O}\right), \quad (5)$$

where $\alpha = x$, y or z, $u_{j\alpha}, u_{j\beta}$ are Cartesian components of the ionic displacement of jth ion, ϕ_{jo}^{Ce} (or ϕ_{jo}^{Ln} or ϕ_{jo}^{O}) is the interaction potential between 0th and jth Ce^{4+} (or Ln^{3+}, or O^{2-}) ions, and m is the average ionic mass.

The Helmholtz free energy of Ce$_{1-x}$Ln$_x$O$_{2-x/2}$ crystal is given by [12]

$$\Psi \approx \Psi_{CeO_{2-x/2}} + \Psi_{Ln} - \mathbb{N}_{Ln} u_0^{Ce} - TS_c^*, \quad (6)$$

with Ψ_{Ln} and $\mathbb{N}_{Ln}$ are total Helmholtz energy and the number of Ln^{3+} ions, respectively, in Ce$_{1-x}$Ln$_x$O$_{2-x/2}$ crystals, S_c^* is the configuration

entropies of this crystal, and u_0^{Ce} is the average interaction potential of a Ce^{4+} ion in Ce$_{1-x}$O$_{2-x/2}$ crystal that determined through the Helmholtz free energies of Ce^{4+} and O^{2-} ions [13].

In the SMM, the Helmholtz free energies of Ce^{4+}, Ln^{3+} and O^{2-} ions can be written as [11]

$$\Psi_{Ce} = E_0^{Ce} + 3N_{Ce}\theta\left[s_{Ce} + \ln\left(1 - e^{-2s_{Ce}}\right)\right] +$$

$$+ 3\mathbb{N}_{Ce}\left\{\frac{\theta^2}{k_{Ce}^2}\left[\gamma_2^{Ce}S_{Ce}^2 - \frac{2\gamma_1^{Ce}}{3}a_1^{Ce}\right] +\right.$$

$$+ \frac{2\theta^3 a_1^{Ce}}{k_{Ce}^4}\left[\frac{4}{3}\left(\gamma_2^{Ce}\right)^2 S_{Ce} - \right.$$

$$\left.\left. -2\left(\left(\gamma_1^{Ce}\right)^2 + 2\gamma_1^{Ce}\gamma_2^{Ce}\right)\left(1 + S_{Ce}\right)\right]\right\}, (7)$$

$$\Psi_{Ln} = E_0^{Ln} + 3\mathbb{N}_{Ln}\theta\left[s_{Ln} + \ln\left(1 - e^{-2s_{Ln}}\right)\right] +$$

$$+ 3\mathbb{N}_{Ln}\left\{\frac{\theta^2}{k_{Ln}^2}\left[\gamma_2^{Ln}S_{Ln}^2 - \frac{2\gamma_1^{Ln}}{3}a_1^{Ln}\right] +\right.$$

$$+ \frac{2\theta^3 a_1^{Ln}}{k_{Ln}^4}\left[\frac{4}{3}\left(\gamma_2^{Ln}\right)^2 X_{Ln} - \right.$$

$$\left.\left. -2\left(\left(\gamma_1^{Ln}\right)^2 + 2\gamma_1^{Ln}\gamma_2^{Ln}\right)\left(1 + X_{Ln}\right)\right]\right\}, (8)$$

$$\Psi_O = E_0^O + 3\mathbb{N}_O\theta\left[s_o + \ln\left(1 - e^{-2s_o}\right)\right] +$$

$$+ 3\mathbb{N}_O\left\{\frac{\theta^2}{k_O^2}\left[\gamma_2^O S_O^2 - \frac{2\gamma_1^O}{3}a_1^O\right] +\right.$$

$$+ \frac{2\theta^3 a_1^O}{k_O^4}\left[\frac{4}{3}\left(\gamma_2^O\right)^2 S_o - \right.$$

$$\left.\left. -2\left(\left(\gamma_1^O\right)^2 + 2\gamma_1^O\gamma_2^O\right)\left(1 + S_o\right)\right]\right\} +$$

$$+ 3\mathbb{N}_O\left\{\frac{\theta\rho}{6\xi\gamma_O}\left(\frac{k_o}{\xi} - 1\right) +\right.$$

$$+ \frac{\theta^2\rho}{\xi}\left[\left(\frac{2\gamma_o a_1^o}{3\xi^3}\right)^{\frac{1}{2}} - \frac{\rho a_1^o}{9\xi^2} + \frac{\rho k_o a_1^o}{9\xi^3} + \right.$$

$$+\frac{\rho k_o a_1^o}{9\xi^3}+\frac{\rho}{6\xi k_o}\left(S_o-1\right)\Bigg]\Bigg\},\quad (9)$$

$$s_{Ce,Ln,O}=\frac{\hbar\omega_{Ce,Ln,O}}{2},\; a_1^{Ce,Ln,O}=1+\frac{S_{Ce,Ln,O}}{2},$$

$$S_{Ce,Ln,O}=s_{Ce,Ln,O}\coth s_{Ce,Ln,O},$$

here, k_B is Boltzmann constant, E_0^{Ce}, E_0^{Ln}, E_0^O are the total interaction potentials of Ce^{4+}, Ln^{3+}, and O^{2-} ions at the equilibrium position, respectively.

The vacancy-dopant association energy is assumed as the energy difference of crystal lattice comprising the oxygen vacancy and Ln^{3+} cations at the associated and separated states [14]. In this study, the vacancy-dopant association energy is calculated according to the formula [12]

$$E_{ass}=\left(\Psi_{Ce_{\mathbb{N}_{Ce}}Ln_{\mathbb{N}_{Ln}}O_{\mathbb{N}_O}}+\Psi_{Ce_{\mathbb{N}_{Ce}-2}Sm_{\mathbb{N}_{Ln}+2}O_{\mathbb{N}_O-1}}\right)-$$

$$-\left(\Psi_{Ce_{\mathbb{N}_{Ce}-1}Ln_{\mathbb{N}_{Ln}+1}O_{\mathbb{N}_O}}+\Psi_{Ce_{\mathbb{N}_{Ce}-1}Ln_{\mathbb{N}_{Ln}+1}O_{\mathbb{N}_O-1}}\right),\quad (10)$$

where the Helmholtz free energies are calculated from Eqs. (7) - (9).

Due to oxygen vacancy-Ln^{3+} cations associations, the oxygen vacancies could be posited at the first nearest neighbor (1NN) or the second nearest neighbor (2NN) sites around Ln^{3+} ions. At the 1NN and 2NN sites, the average interaction potentials of an ion in $Ce_{\mathbb{N}_{Ce}}Ln_{\mathbb{N}_{Ln}}O_{\mathbb{N}_O}$, $Ce_{\mathbb{N}_{Ce}-1}Ln_{\mathbb{N}_{Ln}+1}O_{\mathbb{N}_O}$, $Ce_{\mathbb{N}_{Ce}-2}Ln_{\mathbb{N}_{Ln}+2}O_{\mathbb{N}_O-1}$ and $Ce_{\mathbb{N}_{Ce}-1}Ln_{\mathbb{N}_{Ln}+1}O_{\mathbb{N}_O-1}$ crystals are completely different.

a) At the 1NN site:

For $Ce_{\mathbb{N}_{Ce}}Ln_{\mathbb{N}_{Ln}}O_{\mathbb{N}_O}$ crystal:

$$u_{Ce}=\sum_{i\geq1}c_i^{Ce-Ce}\phi_{i0}^{*Ce-Ce}+\frac{\mathbb{N}_O}{2\mathbb{N}}\sum_{i\geq1}c_i^{Ce-O}\phi_{i0}^{*Ce-O},$$

(11)

$$u_{Ln}=\frac{\mathbb{N}_{Ln}}{\mathbb{N}-1}\sum_{i\geq1}b_i^{Ln-Ce}\phi_{i0}^{*Ln-Ce}+\frac{\mathbb{N}_{Ln}-1}{\mathbb{N}-1}\sum_{i\geq1}c_i^{Ln-Ln}\phi_{i0}^{*Ln-Ln}$$

$$+\sum_{i\geq1}c_i^{Ln-O}\phi_{i0}^{*Ln-O}-\frac{\mathbb{N}_{va}}{\mathbb{N}_{Ln}}\phi_{10}^{*Ln-O}-$$

$$-\sum_{i\geq2}\frac{\mathbb{N}_{va}\left(\mathbb{N}_{Ln}-1\right)}{2\mathbb{N}_{Ln}\left(\mathbb{N}-4\right)}c_i^{Ln-O}\phi_{i0}^{*Ln-O},\quad (12)$$

$$u_o=\sum_{i\geq1}c_i^{O-Ce}\phi_{i0}^{*O-Ce}+\frac{\mathbb{N}_O-1}{2\mathbb{N}-1}\sum_{i\geq1}c_i^{O-O}\phi_{i0}^{*O-O}.\quad (13)$$

For $Ce_{\mathbb{N}_{Ce}-1}Ln_{\mathbb{N}_{Ln}+1}O_{\mathbb{N}_O}$ crystal:

$$u_{Ce}=\sum_{i\geq1}c_i^{Ce-Ce}\phi_{i0}^{*Ce-Ce}+\frac{\mathbb{N}_O}{2\mathbb{N}}\sum_{i\geq1}c_i^{Ce-O}\phi_{i0}^{*Ce-O},$$

(14)

$$u_{Ln}=\frac{\mathbb{N}_{Ln}-1}{\mathbb{N}-1}\sum_{i\geq1}c_i^{Ln-Ce}\phi_{i0}^{*Ln-Ce}+\frac{\mathbb{N}_{Ln}}{\mathbb{N}-1}\sum_{i\geq1}c_i^{Ln-Ln}\phi_{i0}^{*Ln-Ln}$$

$$+\sum_{i\geq1}c_i^{Ln-O}\phi_{i0}^{*Ln-O}-\frac{\mathbb{N}_{va}}{\mathbb{N}_{Ln}+1}\phi_{10}^{*Ln-O}-$$

$$-\sum_{i\geq2}\frac{\mathbb{N}_{va}\mathbb{N}_{Ln}}{2\left(\mathbb{N}_{Ln}+1\right)\left(\mathbb{N}-4\right)}c_i^{Ln-O}\phi_{i0}^{*Ln-O},(15)$$

$$u_o=\sum_{i\geq1}c_i^{O-Ce}\phi_{i0}^{*O-Ce}+\frac{\mathbb{N}_O-1}{2\mathbb{N}-1}\sum_{i\geq1}c_i^{O-O}\phi_{i0}^{*O-O}.$$

(16)

For $Ce_{N_{Ce}-2}Ln_{N_{Ln}+2}O_{N_O-1}$ crystal:

$$u_{Ce}=\sum_{i\geq1}c_i^{Ce-Ce}\phi_{i0}^{*Ce-Ce}+\frac{\mathbb{N}_O-1}{2\mathbb{N}}\sum_{i\geq1}c_i^{Ce-O}\phi_{i0}^{*Ce-O},\quad (17)$$

$$u_{Ln}=\frac{\mathbb{N}_{Ln}-2}{\mathbb{N}-1}\sum_{i\geq1}c_i^{Ln-Ce}\phi_{i0}^{*Ln-Ce}+\frac{\mathbb{N}_{Ln}+1}{\mathbb{N}-1}\sum_{i\geq1}c_i^{Ln-Ln}\phi_{i0}^{*Ln-Ln}$$

$$+\sum_{i\geq1}c_i^{Ln-O}\phi_{i0}^{*Ln-O}-\frac{\mathbb{N}_{va}+1}{\mathbb{N}_{Ln}+2}\phi_{10}^{*Ln-O}-$$

$$-\sum_{i\geq2}\frac{\left(\mathbb{N}_{va}+1\right)\left(\mathbb{N}_{Ln}+1\right)}{2\left(\mathbb{N}_{Ln}+1\right)\left(\mathbb{N}-4\right)}c_i^{Ln-O}\phi_{i0}^{*Ln-O},(18)$$

$$u_o=\sum_{i\geq1}c_i^{O-Ce}\phi_{i0}^{*O-Ce}+\frac{\mathbb{N}_O-1}{2\mathbb{N}-1}\sum_{i\geq1}c_i^{O-O}\phi_{i0}^{*O-O}.$$

(19)

For $Ce_{\mathbb{N}_{Ce}-1}Ln_{\mathbb{N}_{Ln}+1}O_{\mathbb{N}_o-1}$ crystal:

$$u_{Ce} = \sum_{i\geq 1} c_i^{Ce-Ce}\phi_{i0}^{*Ce-Ce} + \frac{\mathbb{N}_o-1}{2\mathbb{N}}\sum_{i\geq 1} c_i^{Ce-O}\phi_{i0}^{*Ce-O},$$

(20)

$$u_{Ln} = \frac{\mathbb{N}_{Ln}-1}{\mathbb{N}-1}\sum_{i\geq 1} c_i^{Ln-Ce}\phi_{i0}^{*Ln-Ce} + \frac{\mathbb{N}_{Ln}}{\mathbb{N}-1}\sum_{i\geq 1} c_i^{Ln-Ln}\phi_{i0}^{*Ln-Ln}$$

$$+\left(1-\frac{\mathbb{N}_{Ln}+1}{2\mathbb{N}\mathbb{N}_{Ln}}\right)\sum_{i\geq 1} c_i^{Ln-O}\phi_{i0}^{*Ln-O} - \frac{\mathbb{N}_{va}}{\mathbb{N}_{Ln}+1}\phi_{10}^{*Ln-O} -$$

$$-\sum_{i\geq 2}\frac{(\mathbb{N}_{va}+1)(\mathbb{N}_{Ln}+1)}{2(\mathbb{N}_{Ln}+1)(\mathbb{N}-4)}c_i^{Ln-O}\phi_{i0}^{*Ln-O}, \quad (21)$$

$$u_o = \sum_{i\geq 1} c_i^{O-Ce}\phi_{i0}^{*O-Ce} + \frac{\mathbb{N}_o-2}{2\mathbb{N}-1}\sum_{i\geq 1} c_i^{O-O}\phi_{i0}^{*O-O}.$$

(22)

b) At the 2NN site:

For $Ce_{\mathbb{N}_{Ce}}Ln_{\mathbb{N}_{Ln}}O_{\mathbb{N}_o}$ crystal:

$$u_{Ce} = \sum_{i\geq 1} c_i^{Ce-Ce}\phi_{i0}^{*Ce-Ce} + \frac{\mathbb{N}_o}{2\mathbb{N}}\sum_{i\geq 1} c_i^{Ce-O}\phi_{i0}^{*Ce-O}, \quad (23)$$

$$u_{Ln} = \frac{\mathbb{N}_{Ln}}{\mathbb{N}-1}\sum_{i\geq 1} c_i^{Ln-Ce}\phi_{i0}^{*Ln-Ce} + \frac{\mathbb{N}_{Ln}-1}{\mathbb{N}-1}\sum_{i\geq 1} c_i^{Ln-Ln}\phi_{i0}^{*Ln-Ln}$$

$$+\sum_{i\geq 1} c_i^{Ln-O}\phi_{i0}^{*Ln-O} - \frac{\mathbb{N}_{va}}{\mathbb{N}_{Ln}}\phi_{20}^{*Ln-O} -$$

$$-\sum_{i\geq 2}\frac{\mathbb{N}_{va}(\mathbb{N}_{Ln}-1)}{2\mathbb{N}_{Ln}(\mathbb{N}-16)}c_i^{Ln-O}\phi_{i0}^{*Ln-O}, \quad (24)$$

$$u_o = \sum_{i\geq 1} c_i^{O-Ce}\phi_{i0}^{*O-Ce} + \frac{\mathbb{N}_o-1}{2\mathbb{N}-1}\sum_{i\geq 1} c_i^{O-O}\phi_{i0}^{*O-O}. \quad (25)$$

For $Ce_{\mathbb{N}_{Ce}-1}Ln_{\mathbb{N}_{Ln}+1}O_{\mathbb{N}_o}$ crystal:

$$u_{Ce} = \sum_{i\geq 1} c_i^{Ce-Ce}\phi_{i0}^{*Ce-Ce} + \frac{\mathbb{N}_o}{2\mathbb{N}}\sum_{i\geq 1} c_i^{Ce-O}\phi_{i0}^{*Ce-O},$$

(26)

$$u_{Ln} = \frac{\mathbb{N}_{Ln}-1}{\mathbb{N}-1}\sum_{i\geq 1} c_i^{Ln-Ce}\phi_{i0}^{*Ln-Ce} + \frac{\mathbb{N}_{Ln}}{\mathbb{N}-1}\sum_{i\geq 1} c_i^{Ln-Ln}\phi_{i0}^{*Ln-Ln}$$

$$+\sum_{i\geq 1} c_i^{Ln-O}\phi_{i0}^{*Ln-O} - \frac{\mathbb{N}_{va}}{\mathbb{N}_{Ln}+1}\phi_{20}^{*Ln-O} -$$

$$-\sum_{i\geq 3}\frac{\mathbb{N}_{va}\mathbb{N}_{Ln}}{2(\mathbb{N}_{Ln}+1)(\mathbb{N}-16)}c_i^{Ln-O}\phi_{i0}^{*Ln-O}, \quad (27)$$

$$u_o = \sum_{i\geq 1} c_i^{O-Ce}\phi_{i0}^{*O-Ce} + \frac{\mathbb{N}_o-1}{2\mathbb{N}-1}\sum_{i\geq 1} c_i^{O-O}\phi_{i0}^{*O-O}.$$

(28)

For $Ce_{\mathbb{N}_{Ce}-2}Ln_{\mathbb{N}_{Ln}+2}O_{\mathbb{N}_o-1}$ crystal:

$$u_{Ce} = \sum_{i\geq 1} c_i^{Ce-Ce}\phi_{i0}^{*Ce-Ce} + \frac{\mathbb{N}_o-1}{2\mathbb{N}}\sum_{i\geq 1} c_i^{Ce-O}\phi_{i0}^{*Ce-O},$$

(29)

$$u_{Ln} = \frac{\mathbb{N}_{Ln}-1}{\mathbb{N}-1}\sum_{i\geq 1} c_i^{Ln-Ce}\phi_{i0}^{*Ln-Ce} + \frac{\mathbb{N}_{Ln}}{\mathbb{N}-1}\sum_{i\geq 1} c_i^{Ln-Ln}\phi_{i0}^{*Ln-Ln}$$

$$+\sum_{i\geq 1} c_i^{Ln-O}\phi_{i0}^{*Ln-O} - \frac{\mathbb{N}_{va}+1}{\mathbb{N}_{Ln}+2}\phi_{20}^{*Ln-O} -$$

$$-\sum_{i\geq 3}\frac{(\mathbb{N}_{va}+1)(\mathbb{N}_{Ln}+1)}{2(\mathbb{N}_{Ln}+2)(\mathbb{N}-16)}c_i^{Ln-O}\phi_{i0}^{*Ln-O}, \quad (30)$$

$$u_o = \sum_{i\geq 1} c_i^{O-Ce}\phi_{i0}^{*O-Ce} + \frac{\mathbb{N}_o-1}{2\mathbb{N}-1}\sum_{i\geq 1} c_i^{O-O}\phi_{i0}^{*O-O}.$$

(31)

For $Ce_{\mathbb{N}_{Ce}-1}Ln_{\mathbb{N}_{Ln}+1}O_{\mathbb{N}_o-1}$ crystal:

$$u_{Ce} = \sum_{i\geq 1} c_i^{Ce-Ce}\phi_{i0}^{*Ce-Ce} + \frac{\mathbb{N}_o-1}{2\mathbb{N}}\sum_{i\geq 1} c_i^{Ce-O}\phi_{i0}^{*Ce-O},$$

(32)

$$u_{Ln} = \frac{\mathbb{N}_{Ln}-1}{\mathbb{N}-1}\sum_{i\geq 1} c_i^{Ln-Ce}\phi_{i0}^{*Ln-Ce} + \frac{\mathbb{N}_{Ln}}{\mathbb{N}-1}\sum_{i\geq 1} c_i^{Ln-Ln}\phi_{i0}^{*Ln-Ln}$$

$$+\left(1-\frac{\mathbb{N}_{Ln}+1}{2\mathbb{N}\mathbb{N}_{Ln}}\right)\sum_{i\geq 1} c_i^{Ln-O}\phi_{i0}^{*Ln-O} - \frac{\mathbb{N}_{va}}{\mathbb{N}_{Ln}+1}\phi_{20}^{*Ln-O} -$$

$$-\sum_{i\geq 3}\frac{\mathbb{N}_{va}\mathbb{N}_{Ln}}{2(\mathbb{N}_{Ln}+1)(\mathbb{N}-16)}c_i^{Ln-O}\phi_{i0}^{*Ln-O}, \quad (33)$$

$$u_o = \sum_{i\geq 1} c_i^{O-Ce}\phi_{i0}^{*O-Ce} + \frac{\mathbb{N}_o-2}{2\mathbb{N}-1}\sum_{i\geq 1} c_i^{O-O}\phi_{i0}^{*O-O},$$

(34)

here, c_i^{R-Ce} (or c_i^{R-Ln}, or c_i^{R-O}) in Eqs. (14) - (34) is the number of the ith nearest-neighbor sites around R ion (R = Ce^{4+}, Ln^{3+}, O^{2-}) that Ce^{4+} (or Ln^{3+}, or O^{2-})

ions could occupy, respectively, ϕ_{i0}^{*R-Ce} (or ϕ_{i0}^{*R-Ln}, or ϕ_{i0}^{*R-O}) is the interaction energy between the 0th R ion and a Ce^{4+} (or Ln^{3+}, or O^{2-}) ion at the ith nearest-neighbor sites around this R ion, respectively.

RESULTS AND DISCUSSION

To describe the interionic interaction in doped ceria oxides, one often employs the pure Coulomb potential and Buckingham potential including the short-range interactions as [15]

$$\phi_{mn}(r) = \frac{q_m q_n}{r} + A_{mn}e^{-\frac{r}{B_{mn}}} - \frac{C_{mn}}{r^6}, \quad (35)$$

where q_m, q_n are the effective charges of the mth and nth ions, r is the separation between ions, and the potential parameters A_{mn}, B_{mn}, C_{mn} are presented in Table 1.

Table 1. *The parameters of the Buckingham potential in $Ce_{1-x}Ln_xO_{2-x/2}$ crystal [15].*

Interaction	A_{mn}(eV)	$B_{mn}(\overset{\circ}{A})$	$C_{mn}(eV.\overset{\circ}{A}{}^6)$
O^{2-} - O^{2-}	9547,96	0,2192	32,00
Ce^{4+} - O^{2-}	1809,68	0,3547	20,40
Sm^{3+} - O^{2-}	1944,44	0,3414	21,49
Gd^{3+} - O^{2-}	1885,75	0,3399	20,34
Y^{3+} - O^{2-}	1766,4	0,3385	19,43
Dy^{3+} - O^{2-}	1807,84	0,3393	18,77

The oxygen vacancies generated due to dopant cations tend to occupy the 1NN or 2NN sites around Ln^{3+} ions. Due to the electrostatic attraction and the elastic interaction arising from the size mismatch of dopants compared to the host lattice, the associations between oxygen vacancies and Ln^{3+} cations control the relative position of oxygen vacancies to Ln^{3+} cations. Thus, to determine the vacancy distribution, one needs to

calculate the vacancy-dopant association energy at these sites.

The vacancy-dopant association energies at the 1NN and 2NN sites are determined based on Eq. (10) with the average interaction potentials of an ion in Eqs. (11) – (34). The calculated results are presented in Table 2. The negative values of the association energies reveal that the oxygen vacancies can be confined at the 1NN and 2NN sites. On the contrary, the positive values of the association energies exhibit that the oxygen vacancies can be released at these sites. Further, the magnitude of the association energy indicates the favorite distribution of oxygen vacancies.

Table 2. *The vacancy-dopant association energies at 1NN and 2NN sites relative to Ln^{3+} cations in $Ce_{1-x}Ln_xO_{2-x/2}$ crystals.*

Material	Method	E_{ass}^{1NN} (eV)	E_{ass}^{2NN} (eV)
Sm_2O_3 doped-CeO_2	SMM	-0,1981	-0,1280
	DFT + MC [16]	-0,2250	-0,1350
Gd_2O_3 doped-CeO_2	SMM	-0,2017	-0,1629
	DFT + MC [16]	-0,2984	-0,1178
Y_2O_3 doped-CeO_2	SMM	-0,2971	0,4835
	DFT [17]	-0,0860	0,1055
Dy_2O_3 doped-CeO_2	SMM	-0,2197	0,3295
	DFT + MC [16]	-0,0647	0,11403

The results in Table 2 show that for Sm_2O_3 doped-CeO_2 and Gd_2O_3 doped-CeO_2 crystals, E_{ass}^{1NN} and E_{ass}^{2NN} have the negative values. This suggests that the oxygen vacancies can be located at the 1NN and 2NN sites. Due to $E_{ass}^{1NN} < E_{ass}^{2NN}$,

the oxygen vacancies prefer to be positioned at the 2NN site around Sm^{3+} and Gd^{3+} cations. For Y_2O_3 doped-CeO_2 and Dy_2O_3 doped-CeO_2 crystals, $E_{ass}^{1NN} < 0$ and $E_{ass}^{2NN} > 0$ show that the Y^{3+} and Dy^{3+} cations trap the oxygen vacancies at the 1NN site, but repel them from the 2NN site. The sensitive equilibrium between electrostatic and elastic interactions in the crystal causes the favor distribution of oxygen vacancies. The theoretical results obtained by DFT and Monte Carlo (MC) simulations [16,17] are indicated to confirm the oxygen vacancy distribution in the vicinity of Ln^{3+} cations. The preferential distribution of oxygen vacancies creates the local deformation of the crystal lattice.

CONCLUSION

In this paper, the SMM model is extended to investigate the oxygen vacancy distribution around dopant cations in Ln_2O_3-doped CeO_2 crystals. The expressions of the vacancy-dopant association energies at the 1NN and 2NN sites are derived in closed analytic forms. The oxygen vacancies are trapped at the 1NN site in Y_2O_3 doped-CeO_2 and Dy_2O_3 doped-CeO_2 crystals while they prefer to be positioned at the 2NN site in Sm_2O_3 doped-CeO_2 and Gd_2O_3 doped-CeO_2 crystals. Consequently, the Ln_2O_3-doped CeO_2 crystal lattice occurs the local distortion. The other theoretical results are compared with the calculated results.

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SỰ PHÂN BỐ VACANCY OXY TRONG CÁC CHẤT ĐIỆN PHÂN CeO₂ PHA TẠP Ln₂O₃ (Ln = Sm, Gd, Y, Dy)

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Tóm tắt: *Sự phân bố vacancy oxy xung quanh tạp chất Ln³⁺ trong các chất điện phân CeO₂ pha tạp Ln₂O₃ đã được nghiên cứu sử dụng phương pháp thống kê momen. Các biểu thức giải tích rõ ràng của các năng lượng liên kết vacancy-tạp chất ở các vị trí lân cận gần nhất thứ nhất (1NN) và vị trí lân cận gần nhất thứ hai (2NN) đối với các ion Ln³⁺ được suy ra có tính đến các hiệu ứng phi điều hòa của các dao động mạng. Nghiên cứu này đã tìm thấy sự biến dạng địa phương được sinh ra từ sự phân bố ưu tiên của các vacancy oxy ở vùng lân cận của các cation Ln³⁺. Các kết quả của chúng tôi được so sánh với các tài liệu khác.*

Từ khóa: *Sự phân bố vacancy oxy, các tinh thể CeO₂ pha tạp Ln₂O₃ (Ln = Sm, Gd, Y, Dy), phương pháp thống kê momen.*