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THERMODYNAMIC PROPERTIES OF CERIA THIN FILM: TEMPERATURE AND PRESSURE DEPENDENCES

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Abstract. *The moment method in statistical (SMM) dynamics is used to study the thermodynamic quantities of the* CeO_2 *thin films taking into account the anharmonicity effects of the lattice vibrations and influence of high pressure. The thermodynamic quantities of the* CeO_2 *thin films are calculated as a function of the temperature and pressure. The SMM calculations are performed by using the Buckingham potential for the* CeO_2 *thin films. In the present study, the influence of temperature, pressure and thickness on the thermodynamic quantities of* CeO_2 *thin film have also been studied, using three different interatomic potentials. We discuss the temperature, pressure, and thickness dependences of the thermodynamic quantities of the* CeO_2 *thin films and compare our calculated results with those of the experimental results.*

I. INTRODUCTION

Extensive studies of elastic and thermodynamic properties of oxide materials (like as cerium dioxide, and zicona ZrO_2) appear because of their important applications in high frequency resonators. These materials are systematically fabricated by film deposition techniques in devices and their elastic constants are definitely required. Knowledge of mechanical and thermodynamic properties of thin films is essential for designing MEMS devices.

Cerium dioxide (or ceria) possesses a cubic fluorite structure with a lattice parameter of 5.411 $\overset{0}{A}$, where in the unit cell the cations occupy the fcc lattice sites, while the Ce^{+4} anions are located at the eight tetrahedral sites. Cerium dioxide (CeO_2) is important oxide materials used as high and low index films in multi-layer optical thin film devices. CeO_2 thin films have been deposited and characterized using different techniques [1]. Among oxide materials, CeO_2 has attracted more and more attention because of its desirable properties such as high stability against mechanical abrasion, chemical attack and high temperatures [2,3]. It is known that the size effect of the phonon frequency is attributed to the phonon confinement, the surface pressure, or the interfacial vibrations. Therefore, the understanding the size effect of elasticity on the thermodynamic properties and their theoretical mechanism is important.

Most previous theoretical studies, however, are concerned with the materials properties of CeO_2 bulk and thin film at absolute zero temperature, and temperature dependence of the thermodynamic quantities have not been studied in detail. Temperature and pressure dependences of the thermodynamic and elastic properties of bulk cerium dioxide have been studied using the analytic statistical moment method (SMM) [4,5,6]. The purpose of the present article is to investigate the temperature, pressure and thickness dependences of the thermodynamic properties of CeO_2 thin film using the SMM [7].

II. THEORY

Usually, the theoretical study of the size effect has been carried by introducing the surface energy contribution in the continuum mechanics or by the computational simulations reflecting the surface stress, or surface relaxation influence. In the present research, the influence of the size effect on thermodynamic properties of ceria thin film is studied by introducing the surface energy contribution in the free energy of cerium and oxygen ions of surface layers.

Let us consider a ceria free thin film of n layers with the film thickness d. Suppose two top and bottom layers (surface layers) of ceria thin film are layers of cerium atoms.

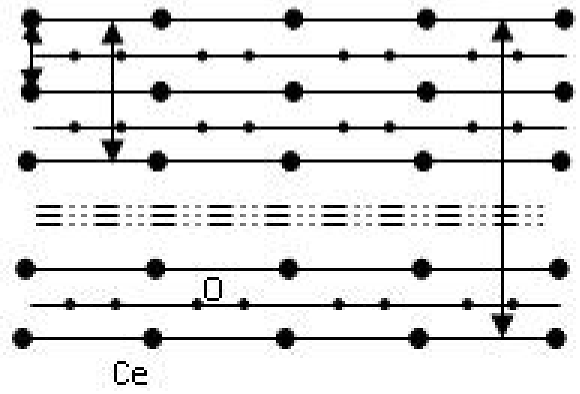

Fig. 1. Ceria free thin film with the surface layers of cerium atoms.

Ceria free thin film consisting 2 cerium surface layers, 2 oxygen next surface layers, and (2n-2) oxygen internal layers and (2n-1) cerium internal layers. The general expression of the Helmholtz free energy ψ of cerium dioxide thin film is given as follows:

$$\Psi = 2N_{Ce}\Psi_{Ce}^{side} + 2N_O\Psi_O^{side} + (2n-2)N_O\Psi_O^{\text{inter}} + (2n-1)N_{Ce}\Psi_{Ce}^{\text{inter}} - TS_C \tag{1}$$

where the numbers of cerium and oxygen ions of a layer are simply denoted by $N_{Ce} = N_0$ and $N_O = 2N_0$, respectively, Ψ_{Ce}^{side} (or Ψ_{Ce}^{inter}) and Ψ_O^{side}(or Ψ_O^{inter}) denote the free energy of Ce and O ions being on the surface (or internal) layers, respectively, and S_C - the configurational entropies. Pressure P is determined by

$$P = -\left(\frac{\partial\psi}{\partial V}\right)_T = -\frac{a}{3V}\left(\frac{\partial\psi}{\partial a}\right)_T \tag{2}$$

From E.q (1), it is easy to derive an equation of states for a surface (or internal) of ceria thin film at zero temperature

$$Pv = \ -a_{side}\{C_{Ce}\left[\frac{1}{6}\frac{\partial u^{side}_{o-Ce}}{\partial a_{side}} + \frac{\hbar\,\omega^{side}_{Ce}(0)}{4k^{side}_{Ce}}\frac{\partial k^{side}_{Ce}}{\partial a_{side}}\right] + \ C_O\left[\frac{1}{6}\frac{\partial u^{side}_{o-O}}{\partial a_{side}} + \frac{\hbar\,\omega^{side}_{O}(0)}{4k^{side}_{O}}\frac{\partial k^{side}_{O}}{\partial a_{side}}\right]\} \tag{3}$$

$$Pv = \ -a_{\text{inter}}\{C_{Ce}\left[\frac{1}{6}\frac{\partial u^{\text{inter}}_{o-Ce}}{\partial a_{\text{inter}}} + \frac{\hbar\,\omega^{Ce}_{\text{inter}}(0)}{4k^{\text{inter}}_{Ce}}\frac{\partial k^{\text{inter}}_{Ce}}{\partial a_{\text{inter}}}\right] + C_O\left[\frac{1}{6}\frac{\partial u^{\text{inter}}_{o-O}}{\partial a_{\text{inter}}} + \frac{\hbar\,\omega^{\text{inter}}_{O}(0)}{4k^{\text{inter}}_{O}}\frac{\partial k^{\text{inter}}_{O}}{\partial a_{\text{inter}}}\right]\} \tag{4}$$

where P denotes the hydrostatic pressure and v is the atomic volume, $\omega(0)$ is the value of ω at zero temperature, u^{inter}_{Ce} (or u^{side}_{Ce}) and u^{inter}_{O} (or u^{side}_{O}) represent the sum of effective pair interaction (or surface) energies for Ce and O ions being on the internal (or surface) layers in ceria thin film

$$u^{\text{inter}}_{Ce} = \sum_i \phi^{Ce-\text{inter}}_{io}(|r_i|) \quad and \quad u^{\text{inter}}_{O} = \sum_i \phi^{O-\text{inter}}_{io}(|r_i|) \tag{5}$$

$$u^{side}_{Ce} = \sum_i \phi^{Ce-side}_{io}(|r_i|) \quad and \quad u^{side}_{O} = \sum_i \phi^{O-side}_{io}(|r_i|) \tag{6}$$

and ω is the atomic vibration frequencies, and it can be approximated in most cases to the Einstein frequency ω_E, given by

$$k = \frac{1}{2}\sum_i \left(\frac{\partial^2 \phi_{io}}{\partial u^2_{ix}}\right)_{eq} \equiv m\omega^2_E \tag{7}$$

and ϕ_{io} is the interatomic potential energy between the central 0th and ith sites, and u_{ix} is the atomic displacement of the ith atom in the x-direction.

Using Eqs.(3) and (4), one can find the nearest neighbor distance at pressure P and zero temperature $T = 0K$, $a(P, 0)$. It is known that the Buckingham potential has been very successful for calculations of thermodynamic properties of CeO_2. The atomic interactions are described by a potential function which divides the forces into long-range interactions (described by Coulombs Law and summated by the Edwald method) and short-range interactions treated by a pairwise function of the Buckingham form

$$\phi_{ij}(r) = \frac{q_i q_j}{r} + A_{ij}\exp(-\frac{r}{B_{ij}}) - \frac{C_{ij}}{r^6} \tag{8}$$

where q_i and q_j are the charges of ions i and j respectively, r is distance between them and A_{ij}, B_{ij} and C_{ij} are the parameters particular to each ion-ion interaction. In the Eq.(8), the exponential term corresponds to electron cloud overlap and the last term corresponds to the attractive dispersion or Van der Waals force. Potential parameters A_{ij}, B_{ij} and C_{ij} have most commonly been derived by the procedure of empirical fitting, i.e., parameters are adjusted, usually by a least-squares fitting routine, so as to achieve the best possible agreement between calculated and experimental crystal properties. The potential parameters are listed in the Table 1.

In principle Eqs.(3), and (4) permit to find the nearest neighbor distance $a_{side}(P,0)$ (or $a_{\mathrm{inter}}(P,0)$ at zero temperature for the surface (or next surface) layer, or internal layer. Using the MAPLE program, Eqs.(3), and (4) can be solved and we find the values of the nearest neighbor distances $a_{side}(P,0)$ and $a_{\mathrm{inter}}(P,0)$. We assume that the average nearest-neighbor distance of the surface layers and internal layers for cerium dioxide thin film at temperature T can be written as

$$a_{side}(P,T) = a_{side}(P,0) + C_{Ce}y_{Ce}^{side}(P,T) + C_O y_O^{side}(P,T) \tag{9}$$

$$a_{\mathrm{inter}}(P,T) = a_{\mathrm{inter}}(P,0) + C_{Ce}y_{Ce}^{\mathrm{inter}}(P,T) + C_O y_O^{\mathrm{inter}}(P,T) \tag{10}$$

in which $y_{Ce}^{side}(P,T)$ (or $y_{Ce}^{\mathrm{inter}}(P,T)$), and $y_O^{side}(P,T)$ (or $y_O^{\mathrm{inter}}(P,T)$) are the atomic displacements of Ce and O atoms from the equilibrium position in the surface (or internal) layers.

The thickness d of thin film can be given by

$$d = 2a_{side}(P,T) + (n-2)a_{\mathrm{inter}}(P,T) \tag{11}$$

Therefore, the average lattice constant $a(P,T)$ of thin film is determined as

$$a(T) = \frac{d}{n} = \frac{2a_{side}(T) + (n-2)a_{\mathrm{inter}}(T)}{n} \tag{12}$$

Using Eqs. (9), and (10), and defination of the thermal expansion coefficient, it is easy to obtain the expression of the thermal expansion coefficient for the surface and internal layers

$$\alpha_{CeO_2}^{\mathrm{inter}} = C_{Ce}\ \alpha_{Ce}^{\mathrm{inter}} + C_O\ \alpha_O^{\mathrm{inter}} \tag{13}$$

$$\alpha_{CeO_2}^{side} = C_{Ce}\ \alpha_{Ce}^{side} + C_O\ \alpha_O^{side} \tag{14}$$

Where

$$\begin{aligned}
\alpha_{Ce}^{\mathrm{inter}}(P,T) &= \frac{k_B}{a_{\mathrm{inter}}(P,0)}\frac{dy_{Ce}^{\mathrm{inter}}(P,T)}{d\theta}\\
\alpha_{O}^{\mathrm{inter}}(P,T) &= \frac{k_B}{a_{\mathrm{inter}}(P,0)}\frac{dy_{O}^{\mathrm{inter}}(P,T)}{d\theta}\\
\alpha_{Ce}^{side}(P,T) &= \frac{k_B}{a_{side}(P,0)}\frac{dy_{Ce}^{side}(P,T)}{d\theta}\\
\alpha_{O}^{side}(P,T) &= \frac{k_B}{a_{side}(P,0)}\frac{dy_{O}^{side}(P,T)}{d\theta}
\end{aligned} \tag{15}$$

Therefore, the average thermal expansion coefficient of CeO_2 thin film can be determined in the approximate form:

$$\alpha_{thin\ film} = \frac{2a_{01}^{side}\alpha_{CeO_2}^{side} + (n-2)a_{01}^{\mathrm{inter}}\alpha_{CeO_2}^{\mathrm{inter}}}{2a_{01}^{side} + (n-2)a_{01}^{\mathrm{inter}}} \tag{16}$$

$$C_V = -T\frac{\partial^2\psi}{\partial T^2} = \frac{6}{6n+1}C_V^{\text{inter}} + \frac{6n-5}{6n+1}C_V^{side} = C_V^{\text{inter}} + \frac{6}{6n+1}\left(C_V^{side} - C_V^{\text{inter}}\right) \qquad (17)$$

III. Results and discussion

In this section we compare lattice constant of internal layer for CeO_2 thin film to some experimental and other theoretical results.

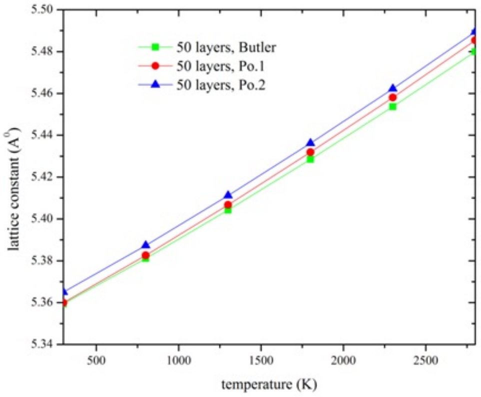

Fig.2: Temperature dependence of lattice constant for CeO_2 thin film at P=5Gpa using three potentials.

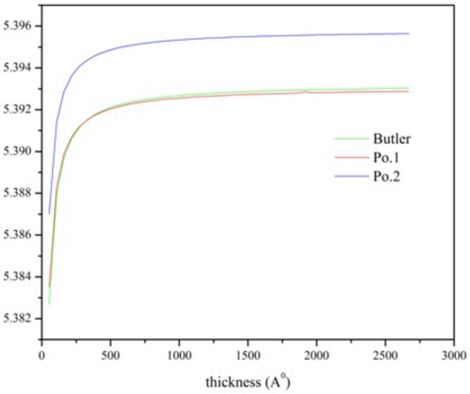

Fig.3: Thickness dependence of lattice constant for CeO_2 thin film at T=300K and pressure P=5Gpa using three Buckingham potentials.

Table 1 . Potential parameters of CeO_2

Interaction potential	A(eV)	B(A^o)	C($eV.A^{o^6}$)	
O^{2-} - O^{2-} Ce^{4+} - O^{2-}	9547.92 1809.68	0.2192 0.3547	32.00 20.40	Potential 1
O^{2-} - O^{2-} Ce^{4+} - O^{2-}	9547.92 2531.5	0.2192 0.335	32.00 20.40	Potential 2
O^{2-} - O^{2-} Ce^{4+} - O^{2-}	22764.3 1986.83	0.149 0.35107	43.83 20.40	Butler

In Figs.3 and 4 we present the temperature and thickness dependence of the lattice constant and thermal expansion coefficient of ceria thin film using the potentials 1, 2 and Butler potential. Figs 3 and 4 show the lattice constant and thermal expansion coefficient of ceria thin film, calculated by using the Buckingham potentials, as a function of the thickness d of thin film. One can see in Figs.3 and 4 that the lattice constant and thermal expansion coefficient increase with the thickness d, when the thickness $d \geq 400A^0$(or the number n of layers of thin film $n \geq 80$ the average lattice constant $a(T)$ and thermal expansion coefficient of thin film $(a(T) \sim 5.41 \overset{0}{A})$ in agreement with the experimental results of bulk CeO_2 . In Figs.2 we depict the temperature dependence of SMM lattice parameter of CeO_2 thin films using the potentials 1, 2 and Butler potential.

Figs 5 show the speciffic heat Cv of ceria thin films, calculated by using the Buckingham potentials, as a function of the pressure.

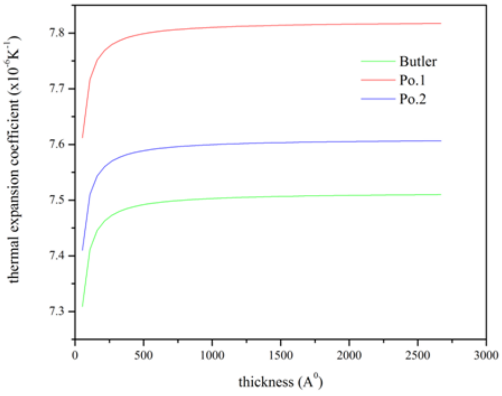

Fig.4: Thickness dependence of thermal expansion coefficient for CeO_2 thin film at P=5GPa, T=300K using three Buckingham potentials.

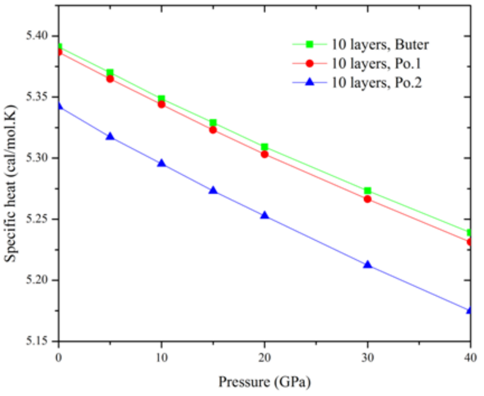

Fig.5: Pressure dependence of speciffic heat C_V for CeO_2 thin film at T=300K using three Buckingham potentials.

IV. Conclusions

In conclusion it should be noted that the statistical moment method really permits us to investigate the temperature, pressure, and thickness dependences of CeO_2 thin films. The results obtain by this method are in good agreement with the experimental data. We have calculated thermodynamic quantities for CeO_2 thin films with different thickness using potentials 1, 2 and Butler potential at various pressures, and these calculated SMM thermodynamic quantities are in good agreement with other calculations and experiment for bulk CeO_2. This research is funded by Vietnam National Foundation for Science and Technology Development (NAFOSTED) under grant number 103.01-2011.16

REFERENCES

[1] L. N. Raffaella, G. T. Roberta, M. Graziella, and L. F. Ignazio, *J. Matter. Chem.,* **15**(2005) 2328-2337.
[2] A. J. Farah et al.,*J. of Nuclear and Related Tech.***Vol. 6, No. 1**(2009) 183.
[3] K. N. Rao, L. Shivlingappa, and S. Mohan, *Mater. Scien. and Engineering*, **B 98**(2003) 38-44.
[4] V.V.Hung, B.D. Tinh, and Jaichan Lee, S. Ohnuma, A. Natori, *Modern Phys. Letter B* **Vol.25 No.12**&**13** (2011)1001-1010.
[5] V. V. Hung, L. T. M. Thanh, and K. Masuda-Jindo, *Comput. Mat. Science* **Vol.49** (2010)355-358.
[6] V. V. Hung and L. T. M. Thanh, *Physica B* **406** (2011) 4014-4018.
[7] V. V. Hung, J. Lee, and K. Masuda-Jindo, *J. Phys. Chem.* **Sol 67** (2006) 682-689.

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