Study of thermodynamic properties of cerium dioxide under high pressures

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ABSTRACT

The statistical moment method (SMM) is used to study the thermodynamic quantities of the cubic fluorite cerium dioxide taking into account the anharmonicity effects of the lattice vibrations and hydrostatic pressures. The thermodynamic quantities of CeO₂ are calculated as a function of the pressure. The SMM calculations are performed by using the Buckingham potential for the cerium dioxide. The effects of the three different potential parameter sets of the Buckingham potential on some thermodynamic properties for CeO₂ are also investigated.

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1. Introduction

Cerium dioxide (CeO₂) has been the subject of the recent studies because of its technological applications and theoretical implications [1–5]. A large number of experimental and theoretical studies have been carried out on lattice vibrational [6], and structural [7] properties of cerium dioxide, and stability, morphology of stoichiometric ceria crystallites [8]. Electronic, structural, bonding, optical and magnetic properties of CeO₂ were calculated by means of the full-potential linear muffin-tin orbital (FP-LMTO) method in the framework of the density functional theory (DFT) [9]. The elastic constants of CeO₂ have been measured [10] and first-principles calculations of elastic properties have been reported for CeO₂ [11,12].

Studies of CeO₂ under pressure are interesting because they can be related to the systematics of the high-pressure behavior of the lanthanide and actinide dioxides [11]. Advancements in the field of high-pressure studies were made for CeO₂, revealing a pressure-induced structural phase transformation from the cubic fluorite structure to an orthorhombic structure of a PbCl₂-type [13,14]. The high-pressure X-ray diffraction results at room temperature show that the phase transformation of CeO₂ from fluorite to an orthorhombic PbCl₂-type structure began at about 31 GPa and was completed at about 38 GPa [15]. Raman spectrum and angle-dispersive X-ray diffraction measurements have been carried out on the effects of high temperature on the high-pressure behavior of bulk CeO₂ [16]. Recently, studies of structure phase transformation of nanosized CeO₂ at room temperature also show that the cubic structure changes to a PbCl₂-type structure at pressures of 22.3–26.5 GPa, which are much lower than that for bulk material [17,18].

Most the previous theoretical studies, however, are concerned with the materials properties of CeO₂ at absolute zero temperature, and temperature and pressure dependences of the thermodynamic quantities have not been studied in detail. Temperature dependence of the thermodynamic properties of cerium dioxide at zero pressure has been studied using the analytic statistical moment method (SMM) [19]. The purpose of the present article is to investigate the pressure dependence of the thermodynamic properties of cerium dioxide using the SMM [19–23]. The equation of states is derived from the Helmholtz free energy, and the pressure dependence of the thermodynamic properties like the thermal lattice expansion coefficient, specific heats at constant volume and those at the constant pressure \( C_V \) and \( C_P \), and elastic modulus is presented taking into account the anharmonicity effects of the thermal lattice vibrations. In the present study, the influences of the temperature and pressure on the thermodynamic quantities of CeO₂ have been studied, using three different interatomic potentials. Each set of potentials is based on a fully ionic description of the fluorite (CaF₂) lattice. We will compare the results of the present calculations with those of the previous theoretical calculations as well as with the available experimental results.

2. Theory

We will present the SMM formulation for the oxide material with fluorite (CaF₂) structure like CeO₂, as schematically shown...
in Fig. 1a. The concentration of cerium and oxygen ions are simply denoted by \( C_{Ce} = (N_{Ce}/N) \), and \( C_{O} = (N_{O}/N) \), respectively. The free energy of cerium dioxide are then written by taking into account the configurational entropies \( S_{C} \), via the Boltzmann relation as [19]

\[
\psi = \psi_{Ce} - C_{Ce} + S_{C} = -RT S_{C}
\]

where \( \psi_{Ce} \) and \( \psi_{O} \) denote the free energy of Ce and O ions, respectively. Since pressure \( P \) is determined by

\[
P = -\left( \frac{\partial \psi}{\partial V} \right)_T = -\frac{a}{3V} \left( \frac{\partial \psi}{\partial a} \right)_T
\]

from (1), it is easy to take out an equation of states for the cerium dioxide at zero temperature:

\[
P V = -r_{i} \left[ \frac{1}{6} \sum_{a} \frac{\partial \psi_{a}^{Ce}}{\partial r_{a}} + \frac{\hbar \omega_{Ce}}{4k^{2}^{Ce}} \right] + C_{0} \left[ \frac{1}{6} \sum_{a} \frac{\partial \psi_{a}^{O}}{\partial r_{a}} + \frac{\hbar \omega_{O}}{4k^{2}^{O}} \right]
\]

where

\[
k^{Ce} = \frac{1}{2} \sum_{a} \left( \frac{\partial^{2} \psi_{a}^{Ce}}{\partial r_{a}^{2}} \right)_{eq} = m^{*} \omega_{Ce}^{2}
\]

and \( k^{O} = \frac{1}{2} \sum_{a} \left( \frac{\partial^{2} \psi_{a}^{O}}{\partial r_{a}^{2}} \right)_{eq} = m^{*} \omega_{O}^{2} \)

and \( \nu \) is the atomic volume \( V/N \) of the crystal, \( \psi_{a}^{Ce} \) and \( \psi_{a}^{O} \) represent the sum of effective pair interaction energies for Ce ion and oxygen ion, respectively.

\[
U_{a}^{Ce} = \frac{N_{1}}{2} \sum_{i} \phi_{a}^{Ce}(r_{i}), \quad U_{a}^{O} = \frac{N_{2}}{2} \sum_{i} \phi_{a}^{O}(r_{i})
\]

where \( r_{i} \) is the equilibrium position of the ith atom, \( u_{a} \) denotes \( \alpha \)-Cartesian component of the atomic displacement of ith atom and \( \phi_{a}^{Ce} \) (or \( \phi_{a}^{O} \)) the effective interaction energy between the zeroth Ce (or zeroth O) and ith atoms, respectively. Using Eq. (3), one can find the nearest-neighbor distance at pressure \( P \) and zero temperature \( T = 0 \): \( r_{i}(P,0) \). With the use of the moment method in statistical dynamics, we calculated the equation of states of cerium dioxide with the cubic fluorite structure. In discussing the equation of states of cerium dioxide, the Buckingham potential has been very successful:

\[
\phi_{a}(r_{i}) = \frac{q_{a} q_{i}}{r_{i}} + A_{a} \exp \left( -r_{i} / B_{a} - C_{a} / r_{i}^{6} \right)
\]

where \( q_{a} \) and \( q_{i} \) are the charge of ions \( i \) and \( j \) respectively, \( r_{i} \) is the distance between them and \( A_{a} \), \( B_{a} \) and \( C_{a} \) are the parameters particular to each ion–ion interaction (listed in Table 1). The ionic Coulomb term in Eq. (6) can be summed explicitly using the Ewald method. In Eq. (6), the exponential term corresponds to electron cloud overlap and the \( 1/r^{6} \) term originates from attractive Van der Waal’s force. Potential parameters \( A_{a} \), \( B_{a} \) and \( C_{a} \) 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 used in the present study were taken from Ref. [8]. Using the effective pair potentials of Eqs. (6) and (5), and the MAPLE program, Eq. (3) can be solved, we find the values of the nearest-neighbor distance \( r_{i}(P,0) \) or lattice parameter \( a(P,0) = 4/\sqrt{3} \ r_{i}(P,0) \) (Table 2). We assume that the average nearest-neighbor distance of the cubic cerium dioxide at temperature \( T \) and pressure \( P \) can be written as

\[
r_{i}(P,T) = r_{i}(P,0) + C_{Ce}^{O} y_{i}^{Ce} + C_{O} y_{i}^{O}
\]

In which \( y_{i}^{Ce} \) and \( y_{i}^{O} \) are the atomic displacements of Ce and O atoms from the equilibrium position in the fluorite lattice. In Eq. (7) \( y_{i}^{Ce} \) and \( y_{i}^{O} \) are determined as Ref. [23]. From the definition of the linear thermal expansion coefficient, it is easy to derive the formula

### Table 1

<table>
<thead>
<tr>
<th>Interaction</th>
<th>( A ) (eV)</th>
<th>( B ) (Å)</th>
<th>( C ) (eV Å(^{6}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>( O^{2-} - O^{2-} )</td>
<td>9547.92</td>
<td>0.2192</td>
<td>32.00</td>
</tr>
<tr>
<td>( Ce^{4+} - O^{2-} )</td>
<td>1809.68</td>
<td>0.3547</td>
<td>20.40</td>
</tr>
<tr>
<td>( O^{2-} - O^{2-} )</td>
<td>9547.92</td>
<td>0.2192</td>
<td>32.00</td>
</tr>
<tr>
<td>( Ce^{4+} - O^{2-} )</td>
<td>2531.5</td>
<td>0.335</td>
<td>20.40</td>
</tr>
<tr>
<td>( O^{2-} - O^{2-} )</td>
<td>22764.3</td>
<td>0.149</td>
<td>43.83</td>
</tr>
</tbody>
</table>

| \( Ce^{4+} - O^{2-} \) | 1986.83 | 0.35107 | 20.40 |

### Table 2

Calculated results for the lattice parameter \( a(P,0) = 4/\sqrt{3} \ r_{i}(P,0) \) of cerium dioxide at zero temperature and pressure \( P \).

<table>
<thead>
<tr>
<th>( P ) (GPa)</th>
<th>( a(P,0) ) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Potential 1</td>
</tr>
<tr>
<td>0</td>
<td>5.3513</td>
</tr>
<tr>
<td>5</td>
<td>5.3210</td>
</tr>
<tr>
<td>15</td>
<td>5.2659</td>
</tr>
<tr>
<td>25</td>
<td>5.2167</td>
</tr>
<tr>
<td>40</td>
<td>5.1516</td>
</tr>
</tbody>
</table>
moduli capacity at a constant pressure, energy of Eq. (1) as

\[ C_V = \frac{1}{T} \left( \frac{\partial^2 \psi}{\partial P^2} \right) T \]

where

\[ C_V = \frac{k_B}{T} \left( \frac{\partial^2 \psi}{\partial P^2} \right) T \]

The bulk modulus of cerium dioxide is derived from the free energy of Eq. (1) as

\[ B_T = -V_0 \left( \frac{\partial^2 \psi}{\partial P^2} \right)_T = -V_0 \left( \frac{\partial^2 \psi}{\partial T^2} \right)_T = C_{Ce} B_T^0 + C_{O} B_T^{O} \]

where \( V_0 \) is the lattice volume at zero temperature, and the bulk moduli \( B_T^c \) and \( B_T^0 \) are given by

\[ B_T^c = -\frac{k_B}{2V_0(P,T)} \left( \frac{\partial^2 \psi_{Ce}}{\partial T^2} \right)_T \]

\[ B_T^{O} = -\frac{k_B}{2V_0(P,T)} \left( \frac{\partial^2 \psi_{O}}{\partial T^2} \right)_T \]

Due to the anharmonicity of thermal lattice vibrations, the heat capacity at a constant pressure, \( C_p \), is different from the heat capacity at a constant volume, \( C_V \). The relation between \( C_V \) and \( C_p \) is

\[ C_V(P,T) = C_V(P,T) - T \left[ \frac{\partial^2 \psi}{\partial T^2} \right] \]

\[ = C_V(P,T) + 3V_0 \left( \frac{\partial P}{\partial T} \right)_T - B_T \cdot V(P,T) \cdot T \]

where the heat capacity at constant volume of the cerium dioxide is given by

\[ C_V = C_{Ce} C_{V}^{Ce}(P,T) + C_{O} C_{V}^{O}(P,T) \]

The partial specific heats at constant volume \( C_V^{Ce} \) and \( C_V^{O} \) of cerium dioxide are directly derived from the partial free energies \( \psi_{Ce} \) and \( \psi_{O} \) [19].

3. Results and discussion

To calculate the thermodynamic quantities of CeO\(_2\) with fluorite structure, we will use three different potentials [8], which include the electrostatic Coulomb interactions and two-body terms to describe the short-range interactions. In Table 3, we compare the calculated results of lattice parameters and moduli of CeO\(_2\) obtained by using the SMM analytic formula with the simulation results (absolute zero temperature) of Ref. [8] using the same Buckingham potentials.

### Table 3
Calculated lattice constants and bulk moduli of CeO\(_2\) at zero pressure.

<table>
<thead>
<tr>
<th>Method</th>
<th>( a ) (Å)</th>
<th>( B_T ) (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Potential 1</td>
<td>Potential 2</td>
</tr>
<tr>
<td>Simulation</td>
<td>5.411</td>
<td>5.411</td>
</tr>
<tr>
<td>SMM</td>
<td>5.3513</td>
<td>5.4325</td>
</tr>
<tr>
<td>Expt</td>
<td>5.411</td>
<td>5.4088</td>
</tr>
<tr>
<td>TBLMOM</td>
<td>5.410</td>
<td>5.2208</td>
</tr>
<tr>
<td>Butler</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Expt [28]</td>
<td>5.4165</td>
<td>5.2716</td>
</tr>
</tbody>
</table>

All three sets of potentials give reasonable lattice constants of CeO\(_2\), near the experimental 5.411 Å even when we take into account the contributions of thermal lattice vibrations. In Table 3, we also compare the present SMM calculations of the bulk moduli \( B_T \) with those by the simulation method [8] and tight-binding linear muffin-tin orbital method (TBLMOM) within local density approximation [26] and first-principles calculations [27]. The SMM results of bulk modulus are in good agreement with experimental results [24,25] and the agreement is better for the SMM calculations with potentials 1 and 2, rather than the calculations by Butler potential.

In Table 4, we compare the SMM results of lattice constants of CeO\(_2\) at temperature \( T = 300 \) K and various pressures using the three different potentials with the experimental results [28]. The calculated lattice parameters by potential 2 and Butler potential are almost identical, while the potential 1 gives somewhat smaller values, shifted upwards about 0.05 for pressure range of 0 GPa \( \leq P \leq 40 \) GPa. Therefore, pressure dependence of the lattice parameters by three potentials are similar for wider pressure range. As shown in Table 4 the calculated SMM results for the lattice constants of CeO\(_2\) are in good agreement with experiment.

The calculated thermal expansion coefficients of CeO\(_2\) at various pressures using the three potentials are presented in Fig. 1b. As shown in Fig. 1b, the thermal expansion coefficient depends strongly on the pressure and the parameters of the potentials. The thermal expansion coefficients calculated by using the Butler potential are larger (~20% at various pressures) than those values by using the potential 1. The different results obtained by potential 1 from those by the Butler potential arise from the parameterization of oxygen–oxygen potentials. One also can see in Fig. 1b that the calculated thermal expansion coefficients by potential 2 are

### Table 4
Calculated lattice constants of CeO\(_2\) at various pressures and \( T = 300 \) K.

<table>
<thead>
<tr>
<th>Method</th>
<th>( a ) (Å)</th>
<th>( B_T ) (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
<td>5</td>
</tr>
<tr>
<td>SMM</td>
<td>5.3576</td>
<td>5.3576</td>
</tr>
<tr>
<td>Expt [28]</td>
<td>5.4354</td>
<td>5.4354</td>
</tr>
<tr>
<td>Butler</td>
<td>5.4165</td>
<td>5.3940</td>
</tr>
<tr>
<td>Expt [28]</td>
<td>5.4165</td>
<td>5.3940</td>
</tr>
</tbody>
</table>

Fig. 2. Compressibility obtained from SMM calculations using three potentials as a function of pressure for bulk-CeO\(_2\) together with experimental results [27].
larger (~10% at various pressures) than those values by potential 1. The small difference between the two calculations simply comes from the difference in cerium–oxygen interaction potentials, since the ionic Coulomb contribution and the oxygen–oxygen potential are the same for potentials 1 and 2. We also calculated compressive behaviors for bulk-CeO₂. As shown in Fig. 2, the SMM calculated results for cerium dioxide are in good agreement with experiment [27]. In addition to the high-pressure angle-dispersive X-ray diffraction measurements for study the bulk matter and nanocrystalline CeO₂, first-principles electronic structure calculations were performed to study the compressive behavior and bulk modulus [27]. Our SMM theory predicts compressibility (V/V₀) to decrease rapidly with pressure in agreement with those calculated by using the ab initio method and experiment [27].

In Fig. 3, we show the calculated bulk moduli Bₚ of CeO₂ at temperature T = 300 K, as a function of the pressure P. We have found that the bulk modulus Bₚ depends sensitively on the potential parameters and it is increasing function of the pressure P. The lattice constants decrease due to the effect of increasing pressure, therefore the bulk modulus becomes larger. The potentials 1 and 2 give the larger values of the bulk modulus, while the Butler potential gives the lowest. The low bulk modulus predicted by the Butler potential is due to the choice of the oxygen–oxygen interaction potentials.

The calculated specific heat at constant pressure Cₚ of CeO₂ compound is presented in Fig. 4. As shown in Fig. 4, the specific heat Cₚ depends strongly on the pressure. The Butler potential gives much larger Cₚ than those by potentials 1 and 2 for the pressure range of 0 GPa ≤ P ≤ 40 GPa. We see that the large difference in oxygen–oxygen interatomic potential of potentials 1, 2 and Butler potential (the exponential term corresponds to electron cloud overlap term, ∆exp(−r/B), and attractive term, (C/r³), determined the role of the various contributions to the thermodynamic properties of cerium dioxide.

4. Conclusions

The SMM calculations are performed using the Buckingham potential for the cerium dioxide with fluorite structure. The thermodynamic quantities of the cerium dioxide are calculated as a function of the pressure. The calculated lattice constants, bulk moduli and compressibility of the cerium dioxide are compared with the available experimental results. The calculated bulk moduli are in good agreement with experimental results and the agreement is better for the SMM calculations with potentials 1 and 2, rather than the calculations by Butler potential. The potentials 1 and 2 give the larger values of the bulk modulus while the Butler potential gives the lowest. This is originating from the different parameter values used for the oxygen–oxygen interactions in the potentials 1, 2 and Butler potential.

Acknowledgement

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References