

THEORETICAL INVESTIGATION OF THERMODYNAMIC PROPERTIES OF SAMARIA-DOPED CERIA

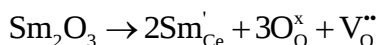
Lo Ngoc Dung* and Nguyen Thi Thuy An
Tay Bac University

Abstract: The thermodynamic properties of Samaria-doped Ceria (SDC) are investigated using statistical moment method. The explicit expressions of thermal expansion coefficient and heat capacities at constant pressure and volume are derived including the anharmonicity effects of lattice vibrations. This study finds the dependences of the thermal expansion coefficient and heat capacities on temperature and dopant concentration. Our results are compared with experimental data.

Key words: Thermodynamic properties, Samaria-doped Ceria, Statistical moment method.

1. INTRODUCTION

Ceria (CeO_2) is the interesting subject due to its application in catalysis, electrolyte materials, gas sensor, and resistive random access memory [1-4]. Samaria-doped Ceria (SDC) crystal in the cubic fluorite structure (space group $Fm\bar{3}m$), is created by aliovalent doping with Sm^{3+} ions, which substitute Ce^{4+} ions on the face-centered cubic (fcc) cation lattice. Insertion of the lower valent cations Sm^{3+} creates high concentration oxygen vacancies according to Eq. (1) with the Kröger -Vink notation [5]



Many experimental and theoretical studies have been carried out on the thermodynamic properties of SDC crystal [6,7]. G. Neilsen *et al.* [6] measured the heat capacity of CeO_2 doped Nd or Sm samples with dopant concentrations $x = 0.047 - 0.154$. They reported the thermodynamic functions based on theoretical fits $C_{p,m}^0$, ΔS_m^0 , ΔH_m^0 , and Φ_m^0 of measured data. Here, $C_{p,m}^0$ is the heat capacity at constant pressure, ΔS_m^0 is molar entropy, ΔH_m^0 is molar enthalpy, and Φ_m^0 is Gibbs-energy based Massieu potential. T. Hisashige *et al.* [7] found the thermal expansion and Debye temperature of pure CeO_2 and rare earth-doped CeO_2 using an ultrasonic pulse method. They showed that the thermal expansion coefficient of rare earth-doped

CeO_2 increase with the increasing of dopant concentration and is larger than that of pure CeO_2 .

Previously, statistical moment method (SMM) has been used to investigate diffusion and electrical properties of SDC crystal [8,9]. In this paper, we use SMM to calculate the thermodynamic quantities of SDC crystal. Compared with other theoretical methods, the SMM gives mathematically simple with comprehensive descriptions of the characteristic properties of crystal lattice. The calculated results reveal the dependences of the thermal expansion coefficient and heat capacities on temperature and dopant concentration.

2. THEORY

The general formula of SDC crystals taking into account the presence of oxygen vacancies is $\text{Ce}_{1-x}\text{Sm}_x\text{O}_{2-x/2}$, where x is the concentration of Sm^{3+} ions.

In the SMM, $\text{Ce}_{1-x}\text{Sm}_x\text{O}_{2-x/2}$ crystals are characterized by the anharmonic vibrations of Ce^{4+} , Sm^{3+} , and O^{2-} ions with the force constants $k_{\text{Ce}}, k_{\text{Sm}}, k_{\text{O}}$ the vibration frequencies $\omega_{\text{Ce}}, \omega_{\text{Sm}}, \omega_{\text{O}}$, and the anharmonic parameters $\rho, \gamma_1^{\text{Ce}}, \gamma_1^{\text{Sm}}, \gamma_1^{\text{O}}, \gamma_2^{\text{Ce}}, \gamma_2^{\text{Sm}}, \gamma_2^{\text{O}}, \gamma_{\text{Sm}}, \gamma_{\text{O}}$ [8].

$$k_{\text{Ce,Sm,O}} = \frac{1}{2} \sum_j \left(\frac{\partial^2 \phi_{j0}^{\text{Ce,Sm,O}}}{\partial u_{ja}^2} \right)_{eq} = m^* \omega_{\text{Ce,Sm,O}}^2, \quad (1)$$

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

$$\gamma_1^{\text{Ce,Sm,O}} = \frac{1}{48} \sum_j \left(\frac{\partial^4 \phi_{j0}^{\text{Ce,Sm,O}}}{\partial u_{j\alpha}^4} \right)_{\text{eq}} \quad (3)$$

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

$$\gamma_{\text{Ce,Sm,O}} = 4(\gamma_1^{\text{Ce,Sm,O}} + \gamma_2^{\text{Ce,Sm,O}}) \quad (5)$$

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

The Helmholtz free energy of $\text{Ce}_{1-x}\text{Sm}_x\text{O}_{2-x/2}$ crystal is given by [8, 9]

$$\Psi \approx \Psi_{\text{CeO}_{2-x/2}} + \Psi_{\text{Sm}} - N_{\text{Sm}} u_0^{\text{Ce}} - TS_c^* \quad (6)$$

where Ψ_{Sm} and N_{Ln} are total Helmholtz energy and the number of Sm^{3+} ions, respectively, in $\text{Ce}_{1-x}\text{Sm}_x\text{O}_{2-x/2}$ crystals, S_c^* is the configurational entropy of this crystal, and u_0^{Ce} is the average interaction potential of a Ce^{4+} ion in $\text{Ce}_{1-x}\text{O}_{2-x/2}$ crystal that determined through the Helmholtz free energies of Ce^{4+} and O^{2-} ions [10].

In the SMM, the Helmholtz free energies of Ce^{4+} , Sm^{3+} and O^{2-} ions can be written as [8, 9]

$$\begin{aligned} \Psi_{\text{Ce}} = & E_0^{\text{Ce}} + 3N_{\text{Ce}} \theta \left[S_{\text{Ce}} + \ln(1 - e^{-2S_{\text{Ce}}}) \right] + \\ & + 3N_{\text{Ce}} \left\{ \frac{\theta^2}{k_{\text{Ce}}^2} \left[\gamma_2^{\text{Ce}} S_{\text{Ce}}^2 - \frac{2\gamma_1^{\text{Ce}}}{3} a_1^{\text{Ce}} \right] + \right. \\ & + \frac{2\theta^3 a_1^{\text{Ce}}}{k_{\text{Ce}}^4} \left[\frac{4}{3} (\gamma_2^{\text{Ce}})^2 S_{\text{Ce}} - \right. \\ & \left. \left. - 2 \left((\gamma_1^{\text{Ce}})^2 + 2\gamma_1^{\text{Ce}} \gamma_2^{\text{Ce}} \right) (1 + S_{\text{Ce}}) \right] \right\}, \end{aligned} \quad (7)$$

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

$$\begin{aligned} & + 3N_{\text{Sm}} \left\{ \frac{\theta^2}{k_{\text{Sm}}^2} \left[\gamma_2^{\text{Sm}} S_{\text{Sm}}^2 - \frac{2\gamma_1^{\text{Sm}}}{3} a_1^{\text{Sm}} \right] + \right. \\ & + \frac{2\theta^3 a_1^{\text{Sm}}}{k_{\text{Sm}}^4} \left[\frac{4}{3} (\gamma_2^{\text{Sm}})^2 X_{\text{Sm}} - \right. \\ & \left. \left. - 2 \left((\gamma_1^{\text{Sm}})^2 + 2\gamma_1^{\text{Sm}} \gamma_2^{\text{Sm}} \right) (1 + X_{\text{Sm}}) \right] \right\}, \end{aligned} \quad (8)$$

$$\begin{aligned} \Psi_{\text{O}} = & E_0^{\text{O}} + 3N_{\text{O}} \theta \left[S_{\text{O}} + \ln(1 - e^{-2S_{\text{O}}}) \right] + \\ & + 3N_{\text{O}} \left\{ \frac{\theta^2}{k_{\text{O}}^2} \left[\gamma_2^{\text{O}} S_{\text{O}}^2 - \frac{2\gamma_1^{\text{O}}}{3} a_1^{\text{O}} \right] + \right. \\ & + \frac{2\theta^3 a_1^{\text{O}}}{k_{\text{O}}^4} \left[\frac{4}{3} (\gamma_2^{\text{O}})^2 S_{\text{O}} - \right. \\ & \left. - 2 \left((\gamma_1^{\text{O}})^2 + 2\gamma_1^{\text{O}} \gamma_2^{\text{O}} \right) (1 + S_{\text{O}}) \right] \right\} + \\ & + 3N_{\text{O}} \left\{ \frac{\theta \rho}{6\xi \gamma_{\text{O}}} \left(\frac{k_{\text{O}}}{\xi} - 1 \right) + \right. \\ & + \frac{\theta^2 \rho}{\xi} \left[\left(\frac{2\gamma_{\text{O}} a_1^{\text{O}}}{3\xi^3} \right)^{\frac{1}{2}} - \frac{\rho a_1^{\text{O}}}{9\xi^2} + \frac{\rho k_{\text{O}} a_1^{\text{O}}}{9\xi^3} + \right. \\ & \left. \left. + \frac{\rho k_{\text{O}} a_1^{\text{O}}}{9\xi^3} + \frac{\rho}{6\xi k_{\text{O}}} (S_{\text{O}} - 1) \right] \right\}, \end{aligned} \quad (9)$$

$$S_{\text{Ce,Sm,O}} = \frac{\hbar \omega_{\text{Ce,Sm,O}}}{2}, \quad a_1^{\text{Ce,Sm,O}} = 1 + \frac{S_{\text{Ce,Sm,O}}}{2},$$

$$S_{\text{Ce,Sm,O}} = s_{\text{Ce,Sm,O}} \coth s_{\text{Ce,Sm,O}},$$

where $\theta = k_B T$, k_B is the Boltzmann constant, $\omega_{\text{Ce,Sm,O}}$ is the vibrational frequencies of ions, $\hbar$ is the Planck constant and E_0^{Ce} , E_0^{Sm} , E_0^{O} are the total interaction potentials of Ce^{4+} , Sm^{3+} , and O^{2-} ions at the equilibrium position, respectively.

The average ion displacements of Ce^{4+} , Sm^{3+} , and O^{2-} ions from the equilibrium position at temperature T are given by [8,9]

$$y_{\text{Ce,Sm}}(T) \approx \sqrt{\frac{2\gamma_{\text{Ce,Sm}} \theta^2}{3k_{\text{Ce,Sm}}^3}} A_{\text{Ce,Sm}} \quad (10)$$

$$y_o \approx \sqrt{\frac{2\gamma_o\theta^2}{3k_o^3}} A_o - \frac{\rho}{3\gamma_o} + \frac{1}{\xi} \left(1 + \frac{6\gamma_o^2\theta^2}{\xi^4} \right) x$$

$$x \left(\frac{1}{3} + \frac{\gamma_o\theta}{3k_o^2} (X_o - 1) - \frac{2\rho^2}{27\gamma_o k_o} \right), \quad (11)$$

where $A_{\text{Ce,Sm}}$ and A_o are determined as in Refs. [10] and [11].

The average nearest-neighbor distance at temperature T can be written as

$$r_1(T) = r_1(0) + c_{\text{Ce}} y_{\text{Ce}}(T) + c_{\text{Sm}} y_{\text{Sm}}(T) + c_o y_o(T). \quad (12)$$

The definition of the thermal expansion coefficient enables us to derive the fomula [10,11]

$$\alpha(T) = \frac{c_{\text{Ce}} \alpha_{\text{Ce}}(T) + c_{\text{Sm}} \alpha_{\text{Sm}}(T) + c_o \alpha_o(T)}{r_1(0)} \quad (13)$$

with c_{Ce} , c_{Sm} , c_o denote the concentration of Ce^{4+} , Sm^{3+} and O^{2-} ions, respectively, and

$$\alpha_{\text{Ce,Sm,O}}(T) = \frac{k_B}{r_1(0)} \frac{\partial y_{\text{Ce,Sm,O}}(T)}{\partial \theta} \quad (14)$$

The heat capacities of Ce^{4+} , Sm^{3+} and O^{2-} ions at constant volume C_V^{Ce} , C_V^{Sm} , C_V^{O} can be defined from the partial free energies of ions Eq. (7) – Eq. (9). Then, the heat capacity at constant volume can be written as [10,11]

$$C_V = c_{\text{Ce}} C_V^{\text{Ce}} + c_{\text{Sm}} C_V^{\text{Sm}} + c_o C_V^{\text{O}} \quad (15)$$

with

$$C_V^{\text{Ce}} = -T \left(\frac{\partial^2 \Psi_{\text{Ce}}}{\partial T^2} \right), \quad C_V^{\text{Sm}} = -T \left(\frac{\partial^2 \Psi_{\text{Sm}}}{\partial T^2} \right),$$

$$C_V^{\text{O}} = -T \left(\frac{\partial^2 \Psi_o}{\partial T^2} \right)$$

The heat capacity at constant pressure is calculated based on the relation as [10,11]

$$C_p = C_V + 9\alpha^2 B_T V T \quad (16)$$

here, B_T denotes the bulk modulus of SDC crystal.

3. NUMERICAL 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 [12]

$$\phi_{mn}(r) = \frac{q_m q_n}{r} + A_{mn} e^{-\frac{r}{B_{mn}}} - \frac{C_{mn}}{r^6}, \quad (18)$$

where q_m , q_n are the effective charges of the m th and n th 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 SDC crystal [12].

Interaction	A_{mn} (eV)	B_{mn} (Å)	C_{mn} (eV.Å ⁶)
$\text{O}^{2-} - \text{O}^{2-}$	9547,96	0,2192	32,00
$\text{Ce}^{4+} - \text{O}^{2-}$	1809,68	0,3547	20,40
$\text{Sm}^{3+} - \text{O}^{2-}$	1944,44	0,3414	21,49

Fig. 1 shows the lattice constant of SDC crystal at the room temperature as a function of dopant concentration.

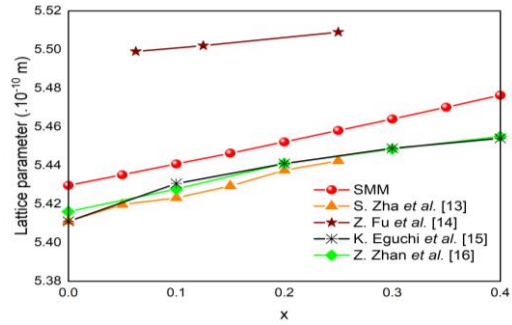


Figure 1. The dopant concentration dependence of lattice constant at $T = 300$ K. The experimental results [13-16] is shown for comparison.

One can see that the lattice constant is little larger than that of CeO_2 crystal ($x = 0$). As the dopant concentration increases, an increase in the lattice constant is found. The lattice expansion due to doping arises from the larger radius of Sm^{3+} ions compared with that of Ce^{4+} ions. Our theoretical calculations are in good accordance with experiments [13-16]. The experimental results [15,16] increase rapidly with an increase in dopant concentration at $x \leq 0.2$ but vary more slowly as the dopant concentration comes close to the solubility limit, $x = 0.4$.

The calculated results of thermal expansion coefficient of SDC crystal at 600 K are presented in Fig. 2. One can see that the thermal expansion coefficient increases linearly with the increasing of dopant concentration. This dependence reveals

the larger value of thermal expansion coefficient of SDC crystal in comparison with that of CeO_2 crystal. The substitution Ce^{4+} ions by Sm^{3+} ions promotes the thermal vibration of ions and therefore, the ions vibrate stronger due to temperature. The measured results using Rigaku Thermo Plus TMA [17] is also shown in Fig. 2. Our obtained SMM thermal expansion coefficients are in relatively good with the experimental data [13]. The errors are only about 3 – 5 %.

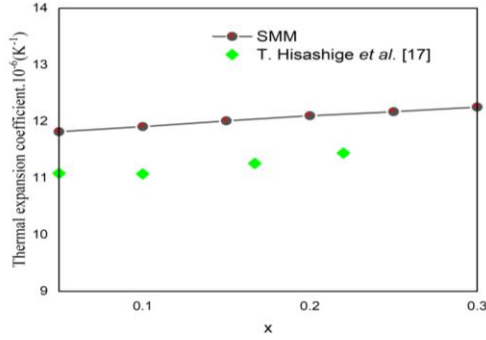


Figure 2. The dopant concentration dependence of thermal expansion coefficient at $T = 600$ K. The experimental results [17] is shown for comparison.

Fig. 3 presents the SMM results of thermal expansion coefficient of SDC crystal at the dopant concentration $x = 0.2$. The thermal expansion coefficient is shown as a function of the dopant concentration. The thermal expansion coefficient increases as the temperature increases. Notably, the thermal expansion coefficient rises quickly in the high temperature range, $T > 2000$ K. This property arises from the anharmonicity effects of thermal lattice vibrations. T. Hisashige *et al.* [18] measured the thermal expansion coefficient of SDC crystal at $x = 0.2$ using X-ray powder diffractometer. The obtained data is very close with the SMM results.

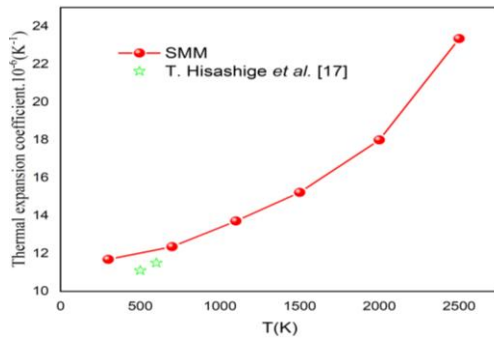


Figure 3. The temperature dependence of thermal expansion at $x = 0.2$. The experimental results [17] is shown for comparison.

In Fig. 4, the calculated results of heat capacities at constant volume C_V and pressure C_P are presented. One can see that the heat capacity at constant volume C_V depends weakly on temperature, but the heat capacity at constant pressure C_P changes quickly with temperature and becomes a nonlinear function of temperature.

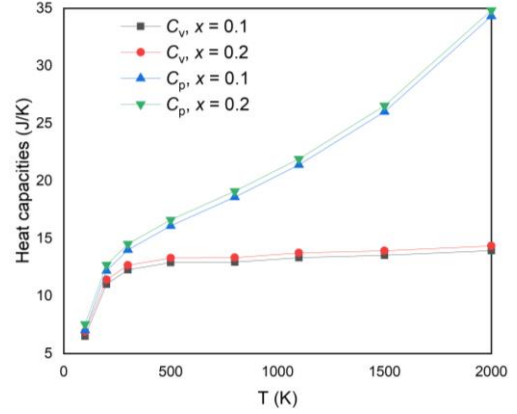


Figure 4. The temperature dependence of heat capacities in the temperature range $T = 100 - 2000$ K at $x = 0.2$.

The strongly anharmonic lattice vibration under high temperature is the principal reason for the anomalous increase of the heat capacity at constant volume C_V near melting temperature. This property is also found in metallic materials, such as Cu, Pd, Ag, ... [18]. The heat capacities at the different dopant concentrations ($x = 0.1$; $x = 0.2$) show the dopant concentration dependence of the heat capacities. The heat capacities become larger as the dopant concentration increases.

4. CONCLUSION

In this paper, the SMM model is used to investigate the thermodynamic properties of SDC crystal. The thermal expansion coefficient and heat capacities are calculated as a function of dopant concentration and temperature. The anomalous increase of thermal expansion coefficient and heat capacity at constant volume near melting temperature arises from the strongly anharmonic lattice vibration. Our results are compared with the experimental data.

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NGHIÊN CỨU CÁC TÍNH CHẤT NHIỆT ĐỘNG CỦA CERIA PHA TẠP SAMARIA

Lò Ngọc Dũng và Nguyễn Thị Thúy An
Trường Đại học Tây Bắc - UTB

Tóm tắt: Các tính chất nhiệt động của Ceria pha tạp Samaria (SDC) được nghiên cứu bằng phương pháp thống kê momen. Các biểu thức giải tích của hệ số giãn nở nhiệt và nhiệt dung đẳng áp, nhiệt dung đẳng tích được suy ra bao gồm các hiệu ứng phi điều hòa trong dao động mạng tinh thể. Chúng tôi đã tìm thấy sự phụ thuộc của hệ số giãn nở nhiệt và các nhiệt dung riêng vào nhiệt độ và nồng độ tạp chất. Các kết quả tính toán được so sánh với các số liệu thực nghiệm.

Từ khóa: Tính chất nhiệt động, Ceria pha tạp Samaria, Phương pháp thống kê momen.

Liên lạc: Lò Ngọc Dũng; Email: longocdung@utb.edu.vn

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Ngày đăng bài: 9/11/2023

Liên lạc: longocdung@utb.edu.vn