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Thermal properties of perovskite $RCeO_3$ (R = Ba, Sr)

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ABSTRACT

We have investigated the bulk modulus and thermal properties of proton conducting perovskite $RCeO_3$ (R = Ba, Sr) for the first time by incorporating the effect of lattice distortion in modified rigid ion models (MRIM). The computed bulk modulus, specific heat, thermal expansion coefficient and other thermal properties of $BaCeO_3$ and $SrCeO_3$ reproduce well with the available experimental data. In addition the cohesive energy (ϕ), molecular force constant (f), reststrahlen frequency (ν), Debye temperature (θ_D) and Gruneisen parameter (γ) are also reported and discussed. The specific heat results can further be improved by taking into account the spin and the orbital ordering contribution in the specific heat formulae.

1. Introduction

Presently, universal attention is being paid to explore the new ways of energy sources and conversion methods. In this respect, hydrogen energy and solid oxide fuel cell (SOFCS) have been well-known as excellent energy sources. The proton conducting oxides is one of the best choices to expend such energy source membranes, which is competent of producing pure hydrogen stream. This is an innovative class of materials, exhibits high proton conductivities between 300 °C and 800 °C, are generally termed as high temperature proton conductor (HTPCS). Additionally, high temperature proton conductor ceramics have gathered broad interest on behalf of their proton conducting appliance. The HTPCs can be used in electrochemical applications such as hydrogen sensors, steam sensors, electrolyte materials for solid oxide fuel cells, hydrogen purification [1,2].

The proton conduction phenomena in proton conducting oxides ABO_3 began in the early 1980s by Iwahara et al. [3]. They recognized the main features of the mechanism of proton transport in these oxides. The basis of proton conduction is Grotthus mechanism in protons are located in the crystal lattice close to the oxide ions because of the electrostatic attraction and are capable of rotating as well as migrating between the nearby anions [4–8]. Recently, the simple perovskite-structured rare-earth-doped alkaline earth based cerates such as $BaCeO_3$ and $SrCeO_3$ have also attracted great attention because of their highest level of proton conductivity. These cerates easily react with humid atmospheres at high temperatures as a consequence of their thermodynamic instability in such situation [9–11].

The structure of $BaCeO_3$ as a function of temperature was first correctly determined by Knight and reported three types of structural phase transitions in $BaCeO_3$. At comparatively low temperatures up to 563 K, $BaCeO_3$ shows a primitive orthorhombic structure with space group *Pnma*. Above the temperature 563 K $\leq T \leq$ 673 K, the structure can be described as body-centered orthorhombic with space group *Imma*. At 673 K, $BaCeO_3$ transforms into a rhombohedral structure with space group *R*-3*c*. Finally, at temperatures over 1200 K, the structure turns to the ideal cubic perovskite pattern with space group *Pm*-3*m* [12]. Structural differences are interconnected to the positions of the barium atoms with the oriented of the CeO_6 octahedra in $BaCeO_3$. Most neutron diffraction or XRD patterns of $SrCeO_3$ have been interpreted in orthorhombic space group *pnma* and no high temperature structure phase transition is reported up to 1273 K [13].

Introduction of proton conducting type materials and behavior of protonic defects is an essential part to understand the proton conduction within these materials. These defects usually acquiesce a protonic conductivity, the long-range diffusion of protons resulting from alternative hopping connecting two oxygen atoms and reorientation motion [1,9]. In ABO_3 perovskite structures have four types of distortion introduced by Knight, first one is the distortion of the BO_6 octahedra, this mechanism identified as the Jahn–Teller distortion observed in $LaMnO_3$ types of perovskite structure. $RCeO_3$ (R = Ba, Sr) are not Jahn–Teller active because of alkaline or rare earth with a considerably larger ionic radius than Ce^{4+} [12,14]. The second and third mechanism is the displacement

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of the B-site or A-site cation within the octahedron, which is attributes of ferroelectric distortions of the $BaTiO_3$ type of structure. The fourth mechanism is the most common and appropriate in $RCeO_3$ type of perovskite materials. In this mechanism, tilting of the octahedrons when the A-site is too small compared to one another such as Sr and Ba in $SrCeO_3$ and $BaCeO_3$ [12].

Ceramic proton conducting electrolytes are being favored to oxide ion conducting electrolytes in SOFC in the intermediate temperature for their low activation energies than oxide ion conductor. Consequently, to identify with the thermodynamic behavior of these cerates is important to understand to valuable application. The main focus of the present paper is to explore the effect of lattice distortion on cohesive, elastic and thermal properties of $BaCeO_3$ and $SrCeO_3$ between $300\,K \le T \le 1300\,K$ using modified rigid ion model (MRIM) that has been successfully characterized the thermal behavior of perovskite manganite, cobalts and vanadates [15–17]. It has been found that MRIM is successful in describing the thermodynamic properties of pure cerates. The necessary of model formalism and the results obtained from its application are presented in Section 2 and 3 respectively.

2. Formalism of MRIM

The major contribution to pair potential of modified rigid ion model (MRIM) is long-range (LR) Coulomb attractions which are balance by the short-range (SR) Hafemeister–Flygare-type (HF) [18] overlap repulsion effective up to the second nearest neighbor atoms approach. The effective interionic potential corresponding to the MRIM framework is expressed as:

$$\phi = \frac{-e^2}{2}\sum_{kk'} Z_k Z_{k'} r_{kk'}^{-1} + \sum_i \left[\begin{array}{l} n_i b_i \beta_i^{kk'} \exp\left\{\left(\frac{r_k + r_{k'} - r_{kk'}}{\rho_i}\right)\right\} + b_i n' \beta_i^{kk} \exp\left\{\left(\frac{2r_k - r_{kk}}{\rho_i}\right)\right\} \\ + b_i \frac{n_i'}{2} \beta_i^{k'k'} \exp\left\{\left(\frac{2r_{k'} - r_{k'k'}}{\rho_i}\right)\right\} \end{array} \right] \quad (1)$$

here the first term is attractive LR coulomb interaction energy and the second term is overlap repulsive energy represented by the Hafemeister–Flygare-type (HF) interaction extended up to the second neighbors. The $r_{kk'}$ represents the separation between the nearest neighbors while $r_{k'k}$ and $r_{k'k'}$ appearing in the next terms are the second neighbor separation. r_k ($r_{k'}$) is the ionic radii of k (k') ion. n (n') is the number of nearest (next nearest neighbor) ions. In ABO_3 perovskite structure, k represents cation (A, B) and k' denotes the (O_1, O_2) type of ions. The summation is performed over all the kk' ions. b_i and ρ_i are the hardness and range parameters for the ith cation-anion pair ($i = 1, 2$) respectively, and $\beta_{kk'}$ is the Pauling coefficient [19] expressed as:

$$\beta_{kk'} = 1 + \left(\frac{Z_k}{N_k}\right) + \left(\frac{Z_{k'}}{N_{k'}}\right) \quad (2)$$

With Z_k ($Z_{k'}$) and N_k ($N_{k'}$) as the valence and number of electrons in the outermost orbit of k (k') ions respectively. The model parameters, hardness (b) and range (ρ) are determined from the equilibrium condition.

$$\left[\frac{d\phi}{dr}\right]_{r=r_0} = 0 \quad (3)$$

And using the bulk modulus

$$B = \frac{1}{9} K r_0 \left[\frac{d^2\phi}{dr^2}\right]_{r=r_0} \quad (4)$$

here r_o and r are the interionic separations in the equilibrium and pairwise states of the system, respectively. The symbol K is the crystal structure constant. The model parameters obtained from the Eqs. (3) and (4) have been used to compute the thermal properties.

The lattice Specific heat is computed using the well known expression

$$C_{V(\text{lattice})} = 9R\left(\frac{T}{\Theta_D}\right)^3 \int_0^{\Theta_D/T} \frac{e^x x^4}{e^x - 1} dx \quad (5)$$

And at very low temperatures ($T < \theta_D/50$) the specific heat is calculated

$$C_V = \frac{12\pi^4 p}{5}\left[N K_B \left[\frac{T}{\Theta_D}\right]^3\right] \quad (6)$$

Also, heat capacity $C = C_V + \alpha^2 B_T V T$(7)where T is the temperature, B_T is the isothermal bulk modulus, V is the unit cell volume and α is the volume thermal expansion coefficient calculated by

$$\alpha = \frac{\gamma C_V}{B_T V} \quad (8)$$

here B_T,V, C_V is the isothermal bulk modulus, unit formula volume and specific heat at constant volume respectively and γ is the Gruneisen parameter given as

$$\gamma = -\frac{r_0}{6}\left[\frac{\phi'''_{kk'}(r)}{\phi''_{kk'}(r)}\right]_{r=r_0} \quad (9)$$

where r_0 is the equilibrium distance between the k th and k'th ions and the primes in $\phi_{kk'}$ (r) denoted the third- order and second-order derivatives of the $\phi_{kk'}$ (r) with respect to the interionic separations (r).

The Debye temperature (Θ_D) is given by the expression

$$\Theta_D = \frac{h\nu}{k_B} \quad (10)$$

with h as the Planck constant and ν as the reststrahlen frequency

$$\nu = \left(\frac{1}{2\pi}\right)\left[\frac{f}{\mu}\right]^{1/2} \quad (11)$$

where μ is the reduced mass and f *is* the molecular force constant given by:

$$f = \frac{1}{3}\left[\phi''^{SR}_{kk'}(r) + \frac{2}{r}\phi'^{SR}_{kk'}(r)\right]_{r=r_0} \quad (12)$$

with $\phi^{SR}_{kk'}(r)$ the short-range nearest neighbor part of ϕ (r). The primes over them denote the first-order and second-order derivatives of the $\phi^{SR}_{kk'}$(r) with respect to the interonic separations (r).

3. Results and discussion

3.1. Model parameter

The values of input data similar to unit cell parameter (a, b, c) and other interionic distances are directly in use from Ref. [1,13] for the $RCeO_3$ (R = Ba, Sr) and this data is used for the evaluation of