

THEORETICAL CALCULATIONS AND ANALYSIS MODELING FOR THE THERMAL CONDUCTIVITY OF NiO

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ABSTRACT

The electronic structure of NiO was calculated by the discrete variational- $X\alpha$ (DV- $X\alpha$) molecular orbital method for prediction electrical thermal conductivity. The lattice thermal conductivity and heat capacity of NiO were calculated by molecular dynamic (MD) simulation. The $Ni_{13}O_{14}$ clusters was designed rock salt structure of NiO, symmetry of $27(O_h)$ for calculation the electronic structure and designed $Ni_{256}O_{256}$ super clusters for calculation the lattice thermal conductivity and thermal properties. The results, electronic structure of $Ni_{13}O_{14}$ cluster composed of total energy level and density of state. The energy gap NiO can be evaluated form energy level and density of state was indicated small mixing orbital of O 2p and Ni 3d in valence band near Fermi level. The electrical thermal conductivity was calculated by using energy gap values. The heat capacity of can be calculated by sum heat capacity in other terms to investigate the thermal conductivity of NiO.

KEYWORDS: thermal conductivity, NiO, electronic structure, DV- $X\alpha$ method, molecular dynamics

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INTRODUCTION

NiO (nickel (II) oxide) is a chemical compound, the only well characterized oxide of nickel although NiO, Ni_2O_3 and NiO_2 have been claimed [1] and classified as a basic metal oxide as an intermediate in the production of nickel alloys [2]. NiO can be prepared by multiple methods. Upon heating above 400 °C, nickel powder reacts with oxygen to give NiO. In some commercial processes, green nickel oxide is made by heating a mixture of nickel powder and water at 1,000 °C; the rate for this reaction can be increased by the addition of NiO [3]. The simplest and most successful method of preparation is through paralysis of nickel (II) compounds such as the hydroxide, nitrate, and carbonate, which yield a light green powder [1]. Synthesis from the elements by heating the metal in oxygen can yield grey to black powders, which indicates nonstoichiometry [1]. The application of NiO was also a component in the nickel-iron battery, also known as the Edison Battery, and is a component in fuel cells. It is the precursor to many nickel salts, for use as specialty chemicals and catalysts. More recently, NiO was used to make the NiCd recharge-

able batteries found in many electronic devices until the development of the environmentally superior Lithium Ion battery [3]. Therefore, the NiO is anti ferromagnetic has in 3-d transition metal oxides, if the electron from material were dope could be replace hole which has been p-type semiconductor. Therefore, how the free electron of NiO moves affects thermal conductivity or electrical conductivity. The prototypical crystal structure of NiO is NaCl (rock salt) and the geometry of Ni is octahedral. In addition, we were interested to develop NiO into thermoelectric material. Thus, we aimed to study electronic structure and thermal property of NiO because the electronic structure of solid material is fundamental to understanding virtually all the properties of materials, including the arrangement of atoms and molecules, thermodynamic properties, mechanical properties, and electronic properties [4]. The efficient thermoelectric materials depend on the ZT values, i.e., the larger ZT value indicates the more efficiency of heat-to-electric conversion at temperature T . The ZT is defined as

$$ZT = \frac{S^2 \sigma T}{\kappa} \quad (1)$$

where σ is electrical conductivity, S is Seebeck coefficient, κ is the thermal conductivity and T is absolute temperature. We focused on the thermal conductivity terms as defined in the following in eq. 2;

$$\kappa = \kappa_l + \kappa_e \quad (2)$$

where κ_l is the lattices thermal conductivity and κ_e is the electrical thermal conductivity; which the κ_l value can be calculated by MD method (molecular dynamics method) and the κ_e value can be estimated from calculation of electronic structure by DV-X α method (Discrete Variational-X α method). The DV-X α method is followed by Hartree-Fock-Slater (HFS) approximation [5] and self-consistent charge (SCC) approximation [6]. It can be used to calculate the electronic state such as energy level, density of state etc. The thermal properties could be predicted by MD method calculation technique particularly mix oxides fuels had been reported the thermal properties of actinide dioxides (NpO₂ and AmO₂) by MD method [7] which the NiO potential parameter were applied from dioxides data could be obtain to the lattice parameter, heat capacity at constant pressure and lattice contribution of thermal conductivity.

In this study, we calculated the electronic structure such as energy level and density of state by DV-X α method for predication electrical thermal conductivity. On the other hand, we calculated heat capacity (C_p) and lattice thermal conductivity by MD simulation and investigation to thermal conductivity of NiO.

MATERIALS AND METHODS

The DV-X α method is a MO calculation method assuming the Hartree-Fock-Slater approximation [5, 6, 8]. The exchange-correlation between electrons, V_{xc} , is expressed using Slater's X α potential [9],

$$V_{xc} = -3\alpha \left[\frac{3}{8\pi} \rho(r) \right]^{1/3} \quad (3)$$

Where $\rho(r)$ is the electron density at position r , the parameter α is fixed at 0.7, and the self-consistent charge approximation is used in the calculation. The matrix elements of the Hamiltonian and the overlap integrals are constructed by a linear combination of numerically generated

atomic orbitals (LCAO). The Ni₁₃O₁₄ cluster of unit cell cluster were designed by DV-X α method using ordinary data of space group; 225 (F4-3m) and position atom x, y, z; Ni = 0, 0, 0 and O = 0.5, 0.5 0.5, the Ni₁₃O₁₄ cluster as shown in figure 1(a). Interatomic interaction of NiO atoms in cubic structure were defined from initial position velocity and kinetic energy which could be obtained from potential function of many atom according to eq. (4). In this study we investigated from pair potential function of atom i and j

$$U(r) = \sum_{ij} U_{ij}(r) + \sum_{ijk} U_{ijk}(r) + \sum_{ijkl} U_{ijkl}(r) + \dots \quad (4)$$

The MD processes of NiO were calculated from ions system totalling 512 ions consisting of O 256 anions and Ni 256 cations as shown in figure 1(b), which is applied from PuO₂ cubic type structure [10]. In the present MD, the MXDORTO program [11] could be performed for calculation by molecular dynamics in materials. In this investigating, it was performed on temperature range from 300-2000 K and in the pressure range from 0.001, 0.75, 1.5 GPa. The motion equation given by Verlet's algorithm and integration time step of 2×10^{-15} s and the atom had initial velocity assume as the random velocities about 0.01 \AA fs^{-1} and the equilibrium run were used controlled 10000 step add on vary temperature and pressure. Therefore, the thermal conductivity calculation was introduced by Andersen and Nose method [12, 13] for controlling the temperature and pressure. The total potential function of two body atoms interaction included the covalent contribution as in the following Eq. (5);

$$U_{ij}(r_{ij}) = \frac{z_i z_j e^2}{r_{ij}} + f_0 (b_i + b_j) \exp \left(\frac{a_i + a_j - r_{ij}}{b_i + b_j} \right) - \frac{c_i c_j}{r_{ij}^6} + D_{ij} \left\{ \exp \left[-2\beta_{ij} (r_{ij} - r_{ij}^*) \right] - 2 \exp \left[-\beta_{ij} (r_{ij} - r_{ij}^*) \right] \right\} \quad (5)$$

where z_i, z_j are effective particle electronic charge on the i th and j th, r_{ij} is interatomic distance, r_{ij}^* is bond length of the cation-anion pair in vacuum, f_0 equals $4.186 D_{ij}$, β_{ij} replace depth and shape of this potential, a, b and c are characteristic parameters. The parameters (a, b, c and D_{ij}, β_{ij}) were constructed from lattice parameter experiment reference that calculation produced the heat capacity at constant pressure and lattice contribution of thermal conductivity.

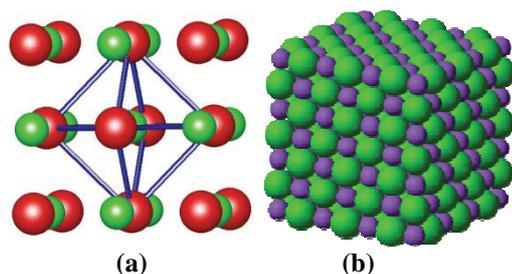


Fig. 1. (a) $\text{Ni}_{13}\text{O}_{14}$ cluster for DV-X α method and $\text{Ni}_{256}\text{O}_{256}$ super cluster for MD method which the small circles and large circles denote Ni and O, respectively

RESULTS AND DISCUSSION

The electronic structure of $\text{Ni}_{13}\text{O}_{14}$ cluster composed of total energy level and density of state were calculated by DV-X α method as shown in Fig. 2. The comparison of total energy level and density of state of O 2p and Ni 3d orbitals is shown. The total energy level of the cluster model was defined by the top most filled level setting to zero and indicated characteristic band gap energy. The *dot line* shows conduction bands and *solid line* shows valence bands yield the band gap energies. We determined the energy gap from energy difference of valence bands and conduction bands and the value of energy gap is 4.15 eV which agrees well with literature data as shown in Table 1. The density of state calculated by DV-X α method giving the possibility of these cluster models for further calculations. It has been shown the small mixing orbital of O 2p and Ni 3d in valence band near Fermi level.

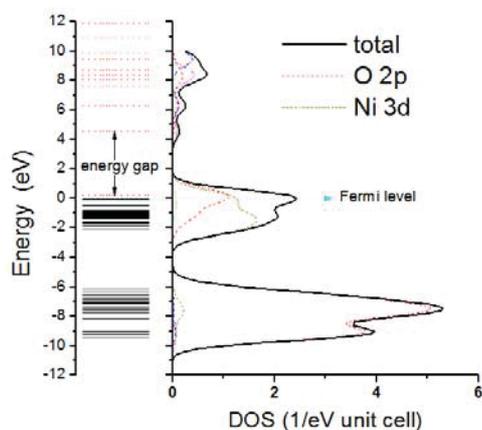


Fig. 2. The total energy level and density of state of $\text{Ni}_{13}\text{O}_{14}$ cluster

Table 1. Energy gaps calculation within the DV-X α method comparison to the HSE03, HSE03 + G_0W_0 and Experimental data

Method	Energy gap (eV)
DV-X α (this work)	4.15
HSE03	4.5 ^[15]
HSE03 + G_0W_0	5.2 ^[15]
Exp (photoem.)	4.3 ^[16]
Exp (cond)	3.7 ^[17]
Exp (opt. abs.)	3.7 ^[18] , 3.87 ^[19]

The potential parameters of NiO were used in this study as shown in Table 2. The calculation was obtained from the lattice parameter at room temperature about 4.179 Å according to M.R. Notis et al. [20] and M. Königstein et al. [21]. The lattice parameter could be produced the linear thermal expansion coefficient (α_{lin}), compressibility (β).

Table 2. The interatomic potential function parameters of NiO which determined from trial and error using values of the lattice parameters with temperature and pressure

Ions	z	A	B	c	D_{ij}	β_{ij}	r_{ij}^*
O	-1.2	1.39	0.08	20	pair-ions O-Ni	40	1.59
Ni	-1.4	1.29	0.08	0.00			

Interatomic interaction was studied from lattice parameters which vary with temperature by using parameters. The evaluation of heat capacity (C_p) of NiO could be calculated approximately from a sum of the heat capacity at constant volume (C_V), heat capacity of lattice dilation (C_d), heat capacity of electron conduction (C_{el}), heat capacity of Schottky term (C_{sch}), and heat capacity of small polarons term (C_{sp}) from the Eq. (6).

$$C_p = C_V + C_d + C_{el} + C_{sch} + C_{sp} \quad (6)$$

For MD calculation, heat capacity at constant pressure value can be obtained from $C_V + C_d$ only when C_V was evaluated from the ratio of internal energy system (E) and temperature

(T) variation as in Eq. (6), and the C_d was calculated from Eq. (7)

$$C_V = \left(\frac{\partial E(T)}{\partial T} \right)_V \quad (6)$$

$$C_d = \frac{(3\alpha_{lin})^2 VT}{\beta} \quad (7)$$

where α_{lin} is the linear thermal expansion coefficient, β is compressibility, V is the molar volume and T is the absolute temperature. Figure 3 shows calculation result of C_p obtained from this study, and from experiment literature [22, 23]. The C_p value from this MD calculation was lower than literature data at temperature range 300-900 K due to the effect from the heat capacity of electron conduction, Schottky and small polarons term. However at high temperature the free electron has nonconvenient transfer. The atom of NiO had deflected therefore the C_p of literature data had decreased simultaneously and the C_p of MD calculation had increased with increasing temperature gradually with tendency, in agreement with literature data at about 900 K and have been in boundary condition of Dulong-Petit law.

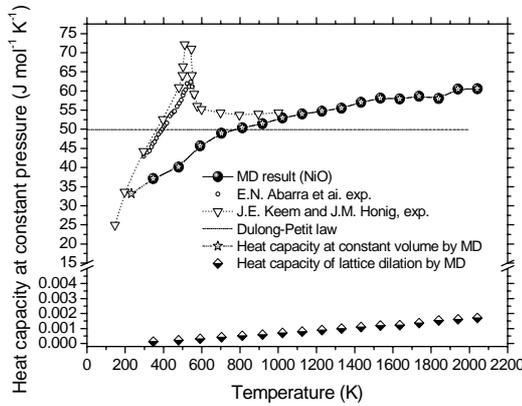


Fig. 3. The heat capacity at constant volume, heat capacity of lattice dilation and heat capacity at constant pressure by MD calculation with temperature range 300-2000 K together with C_p experiment by E.N. Abarra et al. [8] and J.E. Keem and J.M. Honig [9]

The large energy gap and high density of state not near Fermi level of NiO was indicated

insulator, which it maybe low electrical conductivity but it interested of thermal property for thermoelectric materials. Thermoelectric properties as Mott equations for electrical conductivity description can be as follows [14];

$$\sigma_0 = \frac{2\pi e^2 \hbar^3}{3m^2} L_0 \{N_0(E_F)\}^2, \quad (8)$$

$$\sigma = \sigma_0 \exp \left[\frac{-E_g}{2k_B T} \right]$$

where L_0 is the electron free path, and $N_0(E_F)$ is the Fermi level density of states.

The thermal conductivity as general of Wiedemann–Franz law for description can be as in the following;

$$\kappa_e = L\sigma T \quad (9)$$

where L is Lorenz number as $L = \frac{\pi^2}{3} \left(\frac{k_B}{e} \right)^2$

so that the eq. (9) obtaining

$$\kappa_e = \frac{2\pi^3 k_B^2 \hbar^3}{9m^2} T \exp \left[\frac{-E_g}{2k_B T} \right] \quad (10)$$

The free electron carry and phonon-phonon interaction were indicated thermal and electrical conductivity of NiO, which the total of thermal conductivity was sum as the thermal conductivity of lattice contribution, the thermal conductivity of electron contribution. In this study, we were interested in the thermal conductivity by lattice contribution producing by Green Kubo function [24] have been the normalize heat current of time $\langle S(t) \cdot S(0) \rangle$ of the system following by Eq. (11).

$$\kappa_l = \frac{V}{3k_B T^2} \int_0^\infty \langle S(t) \cdot S(0) \rangle dt \quad (11)$$

where k_B is Boltzmann constant, V is volume, T is absolute temperature, the energy current calculated from this follow from Eq. (12)

$$S(t) = \frac{1}{V} \left[\sum_j E_j v_j + \frac{1}{2} \sum_j \sum_{i \neq j} r_{ij} (f_{ij} \cdot v_j) \right] \quad (12)$$

$$E_j = \left\{ \frac{1}{2} m_j v_j^2 + \frac{1}{2} \sum_{i \neq j} U_{ij} (r_{ij}) \right\} - E_{av} \quad (13)$$

and E_j is instantaneous excess energy of j th ion, m_j , v_j are mass and velocity of j th and

$f_{ij}, r_{ij}, U_{ij}(r_{ij})$ are force, interatomic distance, potential energy between i th, j th ions and E_{av} is the energy average of system. The autocorrelation function were calculated from 10^5 step and taken time every 10 step from origin.

The thermal conductivity of NiO was shown in Figure 4, which the lattice thermal conductivity had decreased with increasing temperature. Therefore they had a little lower than experiment literature data [25, 26] at low temperature range and had tendency agreement literature above 900 K due to electron-phonon interaction that the free electron had obstructed transfer consequence the thermal conductivity had decreased with increasing temperature.

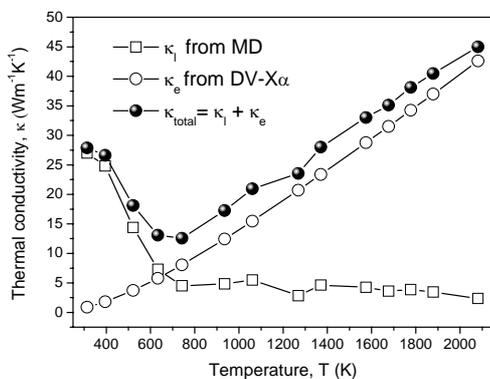


Fig. 4. The thermal conductivity of NiO

CONCLUSION

The electronic structure of $Ni_{13}O_{14}$ cluster was composed of total energy level and density of state calculated by DV-X α method. The energy gap of $Ni_{13}O_{14}$ cluster is 4.15 eV which agrees well with literature data. The density of state has been shown the small mixing orbital of O 2p and Ni 3d in valence band near Fermi level. The heat capacity was calculated by MD in which the initial behavior has transformed in case electron-phonon scattering evaluated from the potential parameter obtaining the heat capacity and lattice contribution of thermal conductivity, in agreement with literature data at high temperature.

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