

CHAPTER 3

METHODOLOGY

The applied molecule method based on DV-X α and MXDORTO is comprised of the molecular orbital method and the molecular dynamics method. Firstly, the cluster atom models were designed for calculating the possible outcomes of CNTs-added CaMnO₃, which consists of added, substitute and doping. Secondly, the electronic structure was calculated by the DV-X α method. Thirdly, calculation of the thermal properties were calculated by the molecular dynamics method. Fourthly, the electronic structure and thermal properties were analyzed. The thermoelectric properties are composed of the Seebeck coefficient, electrical conductivity, electron thermal conductivity and lattice thermal conductivity; calculated by using equations (80), (113), (105) and (119), respectively. Finally, the Dimensionless Figure of Merit was estimated using the following equation (142);

$$ZT = \frac{S^2 \sigma}{\kappa} T = \frac{S^2 \sigma}{\kappa_e + \kappa_{lat}} T \quad (142)$$

where S is the Seebeck coefficient, σ is electrical conductivity, and κ is total thermal conductivity [which composed of electron thermal conductivity (κ_e) and lattice thermal conductivity (κ_{lat})]. T is absolute temperature.

The applied molecule methodology is shown in Figure 29.

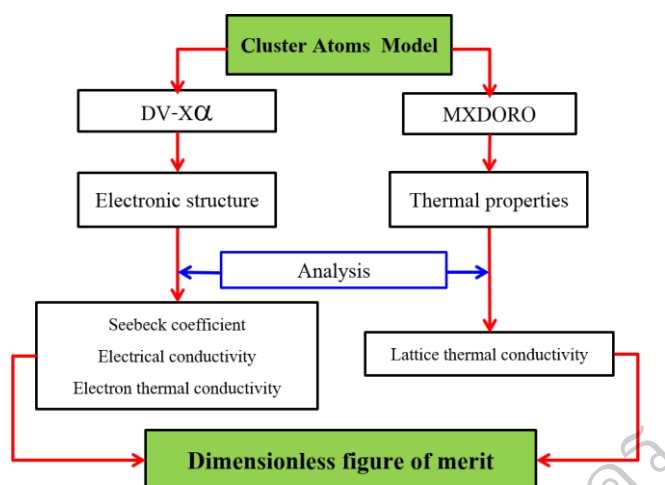


Figure 29 Methodology of applied molecule method

Cluster atom models

The cluster atom models were designed by displat code on a DOS system, which was composed of CMO, CNTs-added CMO and C-substitute CMO case studies. The crystallography data of each cluster atoms model is shown in Tables 1 – 3.

Table 1 Crystallography data of CMO

data	CaMnO ₃	CaMnO ₃
Space group	221 (<i>Pm-3m</i>)	62 (<i>Pnma</i>)
Lattice parameters	a=b=c=3.73 Å	a=5.2812 Å, b=7.4571 Å, c=5.2753 Å
Atomic position		
Ca (x, y, z)	1/2, 1/2, 1/2	0.0288, 0.250, -0.008
Mn (x, y, z)	0, 0, 0	0, 0, 0.5
O (x, y, z)	1/2, 0, 0	0.489, 0.250, 0.067 (for O1) 0.285, 0.033, 0.711 (for O2)

Table 2 Crystallography data of CMO and CNTs-added CMO

data	CNTs-added CaMnO
Space group	221 ($Pm\bar{3}m$)
Lattice parameters	$a=b=c=3.73 \text{ \AA}$
Atomic position	
Ca (x, y, z)	1/2, 1/2, 1/2
Mn (x, y, z)	0, 0, 0
O (x, y, z)	1/2, 0, 0
CNTs $\tilde{C}(n,m)$	$\tilde{C}(3,3)$

Table 3 Crystallography data of C-substitute CMO

data	C-substitute CaMnO ₃
Space group	62 ($Pnma$)
Lattice parameters	$a=5.2812 \text{ \AA}$, $b=7.4571 \text{ \AA}$, $c=5.2753 \text{ \AA}$
Atomic position	
Ca (x, y, z)	0.0288, 0.250, -0.008
C (x, y, z)	0.0288, 0.250, -0.008
Mn (x, y, z)	0, 0, 0.5
O (x, y, z)	0.489, 0.250, 0.067 (for O1) 0.285, 0.033, 0.711 (for O2)

DV-X α calculation

In the DV-X α method, calculation was achieved using the Hartree-Fock-Slater approximation, together with the linear combination of atomic orbital method, and self-consistent field (Adachi et al., 1978, pp.875-883; Tanabe et al., 1978, pp.49-58; Adachi et al., 1979, pp.1528-1537). The calculations were carried out on 100,000 sample points per atom in the self-consistent field. The positions of the sample points with Gaussian distribution around each atom were selected randomly. The calculation was continued until the difference of the orbital population of all the atoms between the initial and final state came to less than 0.005. Though each atom

had some representative point, the results written below were obtained by the inner atom for each cluster, in order to avoid the effect of surface.

The three-dimension problem can be solved by using Schrödinger's equation, followed by equation (142);

$$\left\{ -\frac{\hbar^2}{2m} \nabla^2 + V_{eff}(r) \right\} \Psi_i(r) = E_i \Psi_i(r) \quad (142)$$

where Ψ is molecular wave function, E is energy, m is electron mass, $\hbar = 1.05 \times 10^{-34}$ J s, $V_{eff}(r)$ is effective potential of the position r followed by;

$$V_{eff}(r) = V_{ion}(r) + V_H(r) + V_{xc}(r) = \sum \frac{-Z_N}{|r - R_N|} + \int \frac{\beta(r')}{|r - r'|} dr' - 3\alpha \left[\frac{3}{8\pi} \rho(r) \right]^{\frac{1}{3}} \quad (143)$$

where $V_{ion}(r)$ is ion Coulomb potential, $V_H(r)$ is the Hartree potential, $V_{xc}(r)$ is the exchange-correlation potential term as given by the statistical local expression, α is the HFS parameter constant and fixed = 0.7 (Adachi et al., 1978, pp.875-883) and $\rho(r)$ is the molecular electron density at the position r .

The Seebeck coefficient and electrical conductivity which were derived in chapter 2, can be evaluated using the following equations;

$$S(T) = -\frac{1}{eT} \left(E_F(T) - k_B T \left(r + \frac{5}{2} \right) \right) \quad (144)$$

$$\sigma(T) = \frac{2e^2}{3m} \frac{(2m)^{3/2}}{\pi^2 \hbar^3} k_B T \left(r + \frac{3}{2} \right) \exp \left(\frac{E_F(T)}{k_B T} \right) \quad (145)$$

$$E_F(T) = E_{F0} - \frac{\pi^2}{12} \frac{(k_B T)^2}{E_{F0}} \quad (146)$$

where E_{F0} is Fermi energy at 0 K and r is the number of total orbitals, carried out by DV-X α calculation.

MD calculation

In the MD calculation, the atom positions and velocities from Newton's equation of motion were used by Verlet's algorithm (Verlet, 1967, pp.98–103.), using a run time per step of 2×10^{-15} s and Ewald summation (Wigner, 1932, pp.749–759), to evaluate the total internal energy. The potential function $U(r)$ for interatomic interaction used Morse-type potential functions (Morse, 1929, pp.57-65) adding the Busing-Ida (Ida, 1976, pp.97–104) as show in equation (147).

$$U_{ij}(r_{ij}) = \frac{z_i z_j e^2}{r_{ij}} + f_0 (b_i + b_j) \exp\left(\frac{a_i + a_j - r_{ij}}{b_i + b_j}\right) - \frac{c_i c_j}{r_{ij}^6} + D_{ij} \left\{ \exp\left[-2\beta_{ij}(r_{ij} - r_{ij}^*)\right] - 2\exp\left[-\beta_{ij}(r_{ij} - r_{ij}^*)\right] \right\} \quad (147)$$

where, $f_0 = 4.186$, z_i and z_j are the effective partial electronic charges on the i^{th} and j^{th} ions, r_{ij} is the inter-atomic distance, r_{ij}^* is the bond length of the cation-anion pair in vacuum, and a , b and c are the characteristic parameters depending on the ion species. The potential functions, D_{ij} and β_{ij} describe the depth and shape of this potential, respectively. The first term describes the Coulomb interactions and the second term denotes core repulsions. The third term is a Morse-type potential and applied only to cation-anion pairs.

The heat capacity was composed of a lattice dilatational term, constant volume term and constant pressure term. The heat capacity of the lattice dilatational term (C_d) can be evaluated using lattice parameters, the linear thermal expansion coefficient and compressibility. The heat capacity at constant volume (C_v) can be evaluated by the gradient of the total internal energy. Subsequently, the heat capacity at constant pressure (C_p) is a sum of C_v and C_d , as described following equations;

$$C_p = C_v + C_d = \left(\frac{\partial E(T)}{\partial T}\right)_V + \frac{(3\alpha_{lin})^2 V_m(T)}{\beta} T \quad (148)$$

$$\beta = \frac{3}{a(P_0)} \left(\frac{\partial a(P)}{\partial P}\right)_T \quad (149)$$

$$\alpha_{lin} = \frac{1}{a(T_0)} \left(\frac{a(T) - a(T_0)}{T - T_0} \right)_{P_0} \quad (150)$$

where $E(T)$ is total internal energy, α_{lin} is the linear thermal expansion coefficient, β is compressibility, V_m is molar volume, $a(P)$ is the lattice parameter at pressure $P(\text{Pa})$, P_0 is atmospheric pressure (1 MPa), $a(T)$ is the lattice parameter at temperature $T(\text{K})$ and T_0 is room temperature.

The lattice thermal conductivity (κ_{lat}) can be evaluated from the time integral of the heat flux auto-correlation function (ACF), using the Green-Kubo relation (Zwanzig, 1965, pp.67-102), as show in the following equations;

$$\kappa_{lat} = \frac{V}{3k_B T^2} \int_0^{\infty} \langle S(t)S(0) \rangle dt \quad (151)$$

$$S(t) = \frac{1}{V} \left[\sum_j E_j v_j + \frac{1}{2} \sum_j \sum_{i \neq j} r_{ij} (f_{ij} v_j) \right] \quad (152)$$

$$E_j = \left\{ \frac{1}{2} m_i v_j^2 + \frac{1}{2} \sum_{i \neq j} U_{ij}(r_{ij}) \right\} - E_{av} \quad (153)$$

Where $S(t)$ is the auto-correlation function, m , v , r_{ij} , f_{ij} , $U_{ij}(r_{ij})$ are mass, velocity, interatomic distance between atom i and j , force and Busing-Ida potential between atom i and j , respectively. Lastly E_{av} is the average energy of the system.

The auto-correlation function was obtained from MXDORTO with 1×10^6 run steps. To ensure the accuracy of results, the lattice thermal conductivity was averaged over ten simulations with the different results of the auto-correlation function.

Finally, the Seebeck coefficient, electrical conductivity and thermal conductivity all contributed to the evaluation of the ZT, as shown in equation;

$$ZT = \frac{\left[\frac{1}{eT} \left(E_F(T) - k_B T \left(r + \frac{5}{2} \right) \right) \right]^2 \left[\frac{2e^2}{3m} \frac{(2m)^{3/2}}{\pi^2 \hbar^3} k_B T \left(r + \frac{3}{2} \right) \exp \left(\frac{E_F(T)}{k_B T} \right) \right]}{\frac{2e^2}{3m} \frac{(2m)^{3/2}}{\pi^2 \hbar^3} k_B T^2 \left(r + \frac{3}{2} \right) \exp \left(\frac{E_F(T)}{k_B T} \right) \frac{\pi^2 k_B^2}{3e^2} + \frac{V}{3k_B T^2} \int_0^{\infty} \langle S(t)S(0) \rangle dt} \quad (154)$$