Thermophysical Properties of $Ca_{1-x}Eu_xMnO_3$ (x = 0, 0.05, 0.10, 0.15) Simulated by Classical Molecular Dynamics Method

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ABSTRACT

The thermophysical properties of $CaMnO_3$ hold important keys affecting its thermoelectric properties and performance. This work simulated the lattice parameters, compressibility, linear thermal expansion coefficient, heat capacity and thermal conductivity of $Ca_{1-x}Eu_xMnO_3$ (x = 0, 0.05, 0.10, 0.15) compounds at a temperature range from 300K to 700 K by the classical molecular dynamics (MD) method calculated by using the MXDORTO code. In the simulation, the Morse-type potential functions were added to the Busing-Ida type potential for interatomic interaction. The interatomic potential parameters were determined by fitting the potential functions to the experimental data of the lattice parameters at various temperatures obtained from the available literature. It was found that, with increasing temperature, the simulated lattice parameters, compressibility, linear thermal expansion coefficient and heat capacity increased, whereas thermal conductivity decreased. The simulated results are in good agreement with reported experimental data.

Keywords: Classical molecular dynamics, $Ca_{1-x}Eu_xMnO_3$, Lattice parameter, Heat capacity, Thermal conductivity

INTRODUCTION

Thermophysical properties are important factors of thermoelectric performance. The efficiency of thermoelectric materials are determined from the dimensionless figure of merit $ZT = S^2\sigma T/\kappa$, where S, σ, T and κ are the Seebeck coefficient, electrical conductivity, absolute temperature and thermal conductivity, respectively. Furthermore, thermal conductivity is a function of temperature, which has a strong effect on thermoelectric efficiency. Therefore, the thermophysical properties have a large effect on thermoelectric properties.

Calcium manganese oxide ($CaMnO_3$) compound is an N-type thermoelectric material that can convert heat to electrical energy (Park et al., 2009; Fergus and Eur, 2012). In theory, $CaMnO_3$ has two lattice structures. One lattice is the perovskite structure (space group number: 221, space group symbol: $Pm\bar{3}m$) with

lattice parameters $a = b = c = 7.46$ Å. The other lattice is the orthorhombic structure (space group number : 62, space group symbol: *Pnma*) with lattice parameters $a = 5.2812$ Å, $b = 5.2753$ Å and $c = 7.48$ Å (Trang et al., 2011). $CaMnO_3$ is a good oxide thermoelectric material, because it has relatively low thermal conductivity at room temperature (Sneve, 2006). The classical molecular dynamics method (MD) has been a popular tool for calculating the thermophysical properties of thermoelectric materials (Seetawan et al., 2010).

In this work, we are interested in the improved thermophysical properties of $CaMnO_3$ by doping Eu for $Ca_{1-x}Eu_xMnO_3$, when x = 0, 0.05, 0.10, 0.15. By using the MD simulation method, we investigated how the lattice parameters, compressibility, linear thermal expansion coefficient, heat capacity and thermal condctivity evolved in the Eu-doped $CaMnO_3$ ($Ca_{1-x}Eu_xMnO_3$)

Simulation details

The MD calculation for thermophysical properties of $Ca_{1-x}Eu_xMnO_3$ (x = 0, 0.05, 0.10, 0.15) was performed for a system of 320 ions (160 anions and 160 cations). The unit cell was initially arranged in a 2×2×2 cubic structure. A molecular dynamics program based on MXDORTO (Kawamura and Hirao, 1994) was used. The run time was set to 10^5 steps for total energy and 10^5 steps for heat flux energy. The performed thermodynamics equilibrium MD calculations include the constant pressure-temperature (NPT) and the constant volume-temperature (NVT). An additional quantum effect (Wigner, 1932) is used in this calculation.

The simulations were calculated at temperatures between 300 K and 700 K and pressures between 0.1 MPa and 1.500 GPa. The pressure and temperature of the system were controlled independently, through a combination of the Andersen method (Andersen, 1980) and Nose method (Nose, 1984). We employed the semi-empirical, two-body, potential function proposed by Ida (Ida, 1976) for cation-anion interactions. The potential is a partially ionic model, including a covalent contribution (Morse, 1929).

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

$$+D_{ij}\left\{\exp\left[2\beta_{ij}\left(r_{ij} - r_{ij}^*\right)\right] - 2\exp\left[-\beta_{ij}\left(r_{ij} - r_{ij}^*\right)\right]\right\} \qquad (1)$$

where f_0 is set to 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 interatomic 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. In this potential function, D_{ij} and β_{ij} describe the depth and shape of this potential, respectively.

The thermophysical properties composed of the compressibility β, the linear thermal expansion coefficient α_{lin}, the heat capacity at constant volume C_v, the heat capacity of lattice dilational term C_d, the heat capacity at constant pressure C_p and the thermal conductivity κ. The β is evaluated by:

$$\beta = \frac{3}{a(P_0)}\left(\frac{\partial a(P)}{\partial P}\right)_T \tag{2}$$

where $a(P)$ is the lattice parameter at pressure $P(Pa)$ and P_0 is atmospheric pressure. The α_{lin} is evaluated by:

$$\alpha_{lin} = \frac{1}{a(T_0)}\left(\frac{a(T)-a(T_0)}{T-T_0}\right)_P \tag{3}$$

where $a(T)$ is the lattice parameter at $T(K)$ and T_0 is room temperature. The C_v, C_d and C_p are evaluated by:

$$C_V = \left(\frac{\partial E(T)}{\partial T}\right)_V \tag{4}$$

$$C_d = \frac{(3\alpha_{lin})^2 V_m(T)}{\beta}T \tag{5}$$

$$C_p = C_V + C_d \tag{6}$$

where $E(T)$ is the internal energy at $T(K)$ and V is the molar volume.
The κ is calculated by the Green–Kubo relation (Zwanzig, 1965):

$$\kappa = \frac{V}{3k_B T^2}\int_0^\infty \langle S(t)S(0)\rangle dt \tag{7}$$

where k_B is the Boltzmann constant, T is the absolute temperature and $S(t)$ is the heat flux autocorrelation function (ACF). The heat flux $S(t)$ is described as:

$$S(t) = \frac{1}{V}\left[\sum_j E_j v_j + \frac{1}{2}\sum_j \sum_{i\neq j} r_{ij}\left(f_{ij}v_j\right)\right] \tag{8}$$

The instantaneous excess energy of atom j is Ej, described as:

$$E_j = \left\{\frac{1}{2}m_i v_j^2 + \frac{1}{2}\sum_{i\neq j} U_{ij}\left(r_{ij}\right)\right\} - E_{av} \tag{9}$$

where m_j and v_j are the mass and velocity of atom j, r_{ij} and f_{ij} are the interatomic distance and force between atom i and j, U_{ij} is the potential between atom i and j, and E_{av} is the average energy of the system.

For the simulations, the values of the interatomic potential parameters used in the present study were initially set as summarized in Table 1.

Table 1. Values of the interatomic potential function parameter for $Ca_{1-x}Eu_xMnO_3$ (x = 0, 0.05, 0.10, 0.15).

| Ions	Z	a	b	c
O	−1.2	1.894	0.16	20
Mn	+2.4	1.057	0.18	25
Ca	+1.2	1.198	0.16	10
Eu	+1.2	1.165	0.14	0

Pair	D_{ij}	β_{ij}	r_{ij}^*
Mn–O	4.224	2.815	2.1921
Ca–O	2.411	1.180	2.7614
Eu–O	2.211	1.180	2.7614

RESULTS AND DISCUSSION

The temperature dependence of the lattice parameters (a) for $Ca_{1-x}Eu_xMnO_3$ simulation by MD method is shown in Figure 1. Lattice parameters increase upon doping Eu into $CaMnO_3$ and the parameters also increase upon increasing temperature. These lattice parameters of $CaMnO_3$ agree well with experimental data measured at 300 K by Thuy et al. (2011).
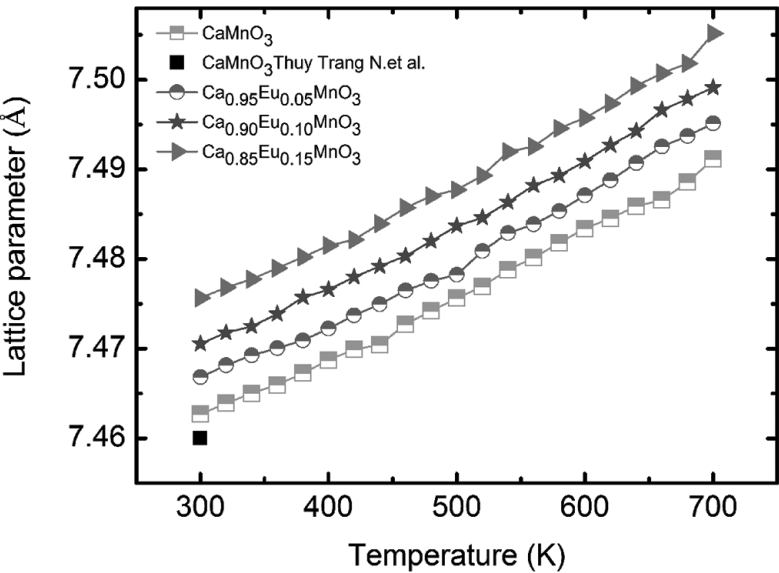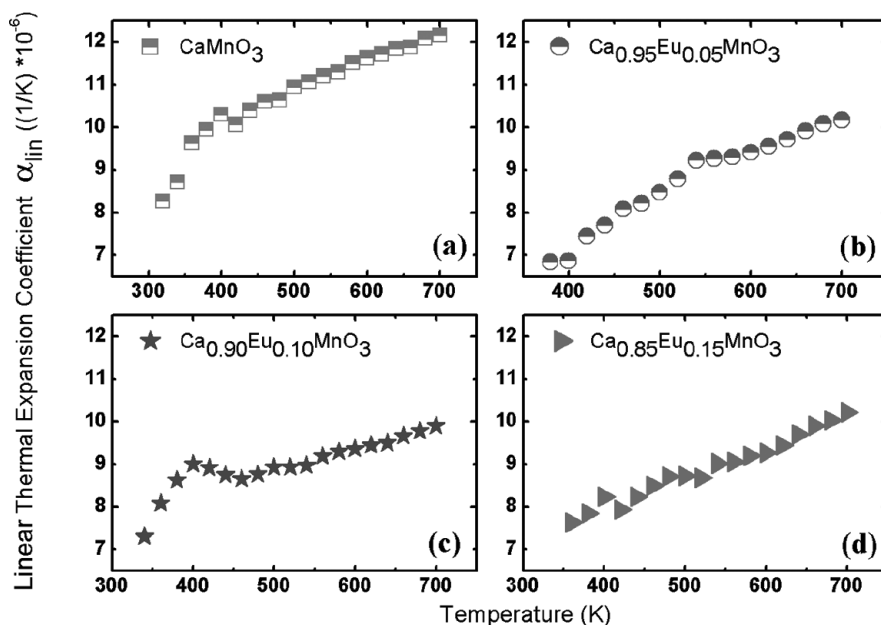

Figure 1. Temperature dependence of lattice parameter for $Ca_{1-x}Eu_xMnO_3$ (x = 0, 0.05, 0.10, 0.15), together with Thuy et al. (2011).

With the calculated lattice parameters, the temperature dependence of compressibility (β) for $Ca_{1-x}Eu_xMnO_3$ was then simulated as shown in Figure 2. Compressibility was calculated from the lattice parameter change in the pressure range between 0.1 MPa to 1.5 GPa. From the graph, compressibility of $CaMnO_3$ tends to increase with increasing temperature. For the doped compounds, compressibility appears fluctuate more with temperature.
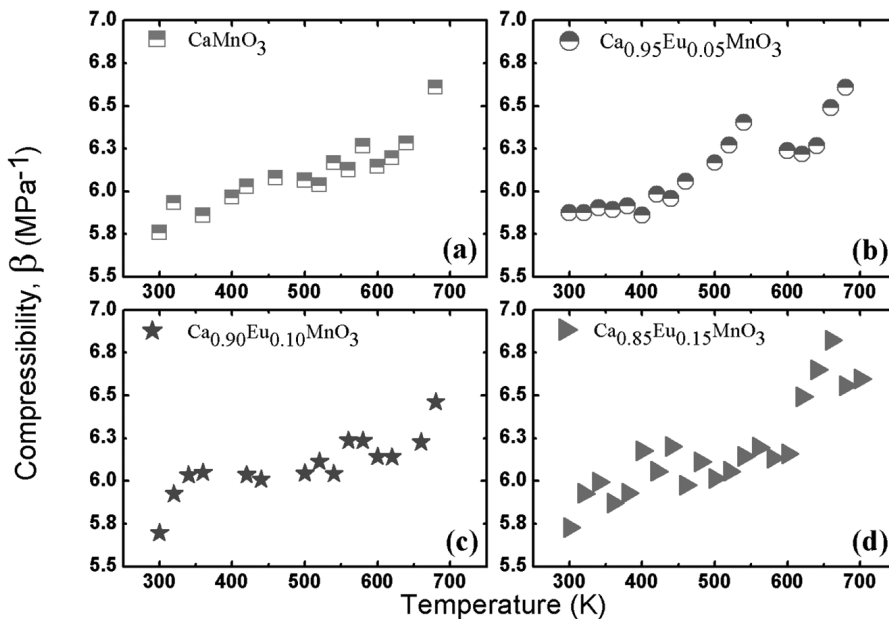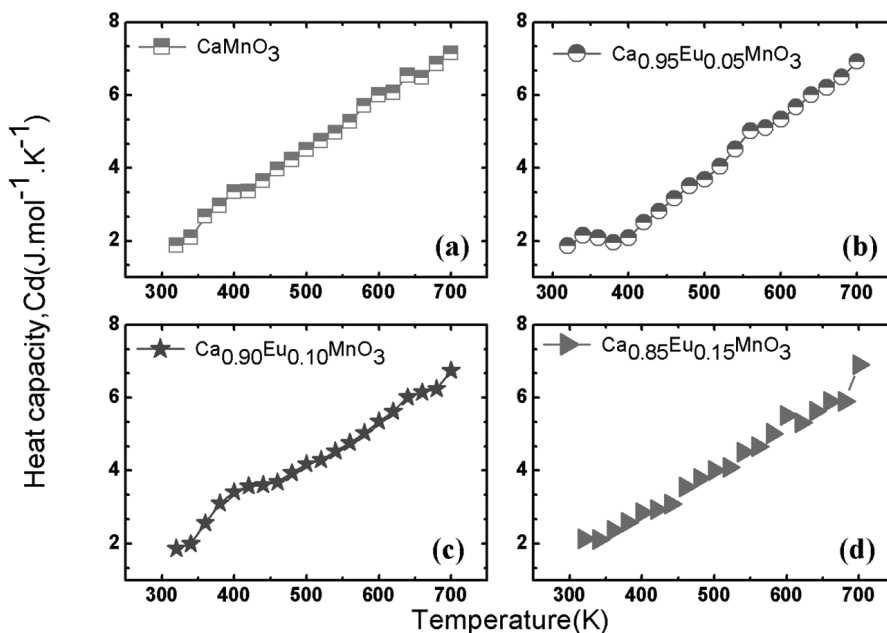

Figure 2. Temperature dependence of compressibility for $Ca_{1-x}Eu_xMnO_3$ (x = 0, 0.05, 0.10, 0.15).

Figure 3 shows the calculation of linear thermal expansion coefficient (α_{lin}) for $Ca_{1-x}Eu_xMnO_3$. Interestingly, α_{lin} of the doped compounds appears to become significantly lower than the linear thermal expansion coefficient of undoped $CaMnO_3$.
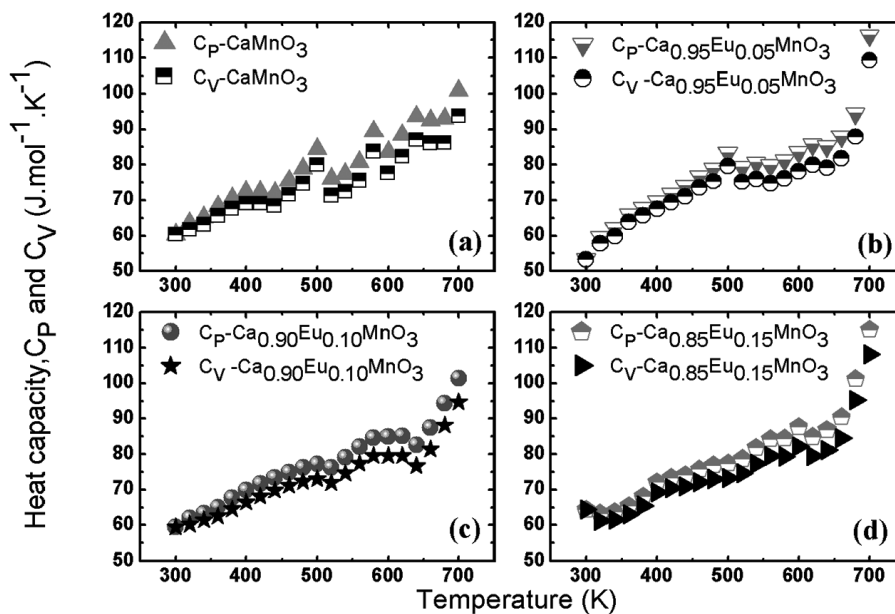
Figure 3. Temperature dependence of linear thermal expansion coefficient for $Ca_{1-x}Eu_xMnO_3$ (x = 0, 0.05, 0.10, 0.15).

Then, the temperature dependence of heat capacity of the lattice dilational term (D_d) for $Ca_{1-x}Eu_xMnO_3$ was calculated as shown in Figure 4. Heat capacity of the lattice dilational term was calculated using values of compressibility and linear thermal expansion coefficient obtained from the constant pressure-temperature (NPT). The temperature dependence of heat capacity at constant volume (C_v) and temperature dependence of heat capacity at constant pressure (C_P) for $Ca_{1-x}Eu_xMnO_3$ are shown in Figure 5. Heat capacity at constant volume was calculated from a differential of the internal energy by temperature obtained from the constant volume-temperature (NVT). As the heat capacity increases at higher temperature, it is likely that the Seebeck coefficient will increase with temperature.
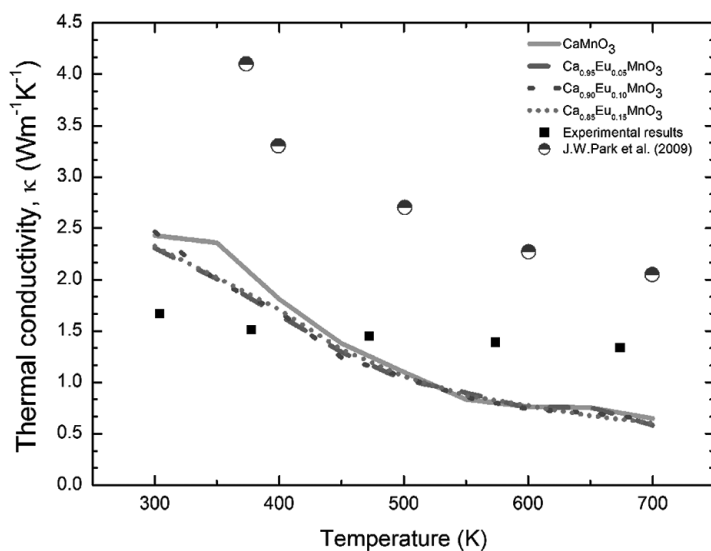
Figure 4. Temperature dependence of heat capacity of lattice dilational term for $Ca_{1-X}Eu_XMnO_3$ (x = 0,0.05,0.10,0.15).

Figure 5. Temperature dependence of heat capacity at constant volume and Temperature dependence for heat capacity at constant pressure of $Ca_{1-x}Eu_xMnO_3$ (x = 0, 0.05, 0.10, 0.15).

Heat capacity at constant pressure was calculated by summing the values of heat capacity at constant volume and heat capacity of the lattice dilational term. Heat capacity at constant pressure begins to be roughly constant at temperatures between 500 K and 650 K, similar to the Dulong-Petit law.

The temperature dependence of thermal conductivity (κ) for $Ca_{1-x}Eu_xMnO_3$ together with the laser face method results (Park et al., 2009) is shown in Figure 6. The Green-Kubo relationship is suitable for calculating the thermal conductivity for the MD method. In this study, thermal conductivity at temperatures between 300 and 700 K was calculated. Thermal conductivity by MD method has 2.5 W/m.K at 300 K - 0.5 W/m.K at 700 K. Thermal conductivity from the result of $CaMnO_3$ mean by laser face method is 1.66 W/m.K at 304 K – 1.33 W/m.K at 673 K. As shown in Figure 6, the thermal conductivity becomes largely reduced at higher temperature. This behavior will enhance the thermoelectric performance greatly (i.e., improving the thermoelectric figure of merit, $ZT = \sigma S^2 T/\kappa$). Together with the potential enhancement of the Seebeck coefficient, S, as discussed above, the simulation suggests a significant enhancement of the ZT value, upon increasing the temperature.

Figure 6. Temperature dependence of thermal conductivity for $Ca_{1-x}Eu_xMnO_3$ (x = 0, 0.05, 0.10, 0.15) together with experimental results and Park et al.

CONCLUSION

The thermophysical properties of $Ca_{1-X}Eu_XMnO_3$ (x = 0, 0.05, 0.10, 0.15) were simulated by the MD method. The simulations show that the lattice parameter, compressibility and linear thermal expansion coefficient are increased upon increasing temperature. Heat capacity is slightly increased at high temperature,

while thermal conductivity decreases with increasing temperature. In addition, it was found that doping Eu into $CaMnO_3$ should decrease thermal conductivity, which will improve thermoelectric performance. This research suggests that the MD method may have good potential for further investigating the thermophysical properties of CEMO, and possibly other compounds.

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