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The molecular dynamics method is used to simulate the thermophysical properties of $SrTiO_3$ thermoelectric material in the temperature range 300–2200 K. The Morse-type potential functions added to the Busing–Ida type potential for interatomic interaction are used in the simulation. The interatomic potential parameters are determined by fitting to the experimental data of lattice parameters with temperature and the data reported in literature. The linear thermal expansion coefficient, heat capacity and lattice contributions to the thermal conductivity are analyzed. The results agree with the data reported in the literature.

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Strontium titanate ($SrTiO_3$) is a perovskite-type oxide, ceramic material. It has shown photonic conductivity at high temperature,[1] a large potential for use in fuel cells, steam electrolysis and hydrogen gas sensors,[2–4] oxygen-gas sensors,[5] usage as a grain-boundary barrier layer capacitor,[6,7] epitaxial growth substrate of high temperature superconductor thin films,[8] catalytic material and dielectric material,[9,10] n-type thermoelectric material;[11] the thermal conductivity is 10 $Wm^{-1}K^{-1}$ at 300 K.[11] In experiment, $SrTiO_3$ has been employed to elucidate the transport mechanism at protons,[12] infrared absorption spectra[13] and conductivity charges with temperature following thermal activation-type behavior.[14] In theory, $SrTiO_3$ shows crystallographic cubic structure, its space group number is 221, $Pm\bar{3}m$, the lattice parameters are $a = b = c = 0.39050$ nm, the number of atoms in the unit cell is 5. Recently, we reported thermophysical properties of PuO_2 and AmO_2 simulated by molecular dynamics and the electronic structures of $SrTiO_3$ calculated by the DV-Xα molecular orbital method, in agreement with the experimental data.[15,16]

The molecular dynamics program is based on MXDORTO,[17] $SrTiO_3$ is performed for a system of 320 ions (O = 192, Ti = 64, Sr = 64), as shown in Table 1. The thermophysical properties are simulated in the temperature range from 300 to 2200 K in the pressure range 0.1–1.5 GPa, composed of 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 lattice contributions to the thermal conductivity $\kappa_{\rm lat}$. Here $\alpha_{\rm lin}$ is evaluated by

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

where $a(T)$ is the lattice parameter at T (K) evaluated from the interatomic potential parameters, and T_0 is room temperature. C_V, C_d, and C_P are evaluated by

$$C_V = \left(\frac{\partial E(T)}{\partial T}\right)_V, \tag{2}$$

$$C_d = \frac{(3\alpha_{\rm lin})^2 VT}{\beta}, \tag{3}$$

$$C_P = C_V + C_d, \tag{4}$$

where $E(T)$ is the internal energy at T (K), and V is the molar volume, $\kappa_{\rm lat}$ is calculated by the Green–Kubo relation,[17]

$$\kappa = \frac{V}{3k_B T^2}\int_0^\infty \langle S(t)\cdot S(0)\rangle dt, \tag{5}$$

where k_B is the Boltzmann constant (1.38066×10^{-23} J·K^{-1}), and $S(t)$ is the heat flux autocorrelation function (ACF)

$$S(t) = \frac{1}{V}\left[\sum_j e_j v_j - \frac{1}{2}\sum_j\sum_{i=j} r_{ij}(f_{ij}\cdot v_j)\right], \tag{6}$$

and the instantaneous excess energy of atom j, i.e. e_j, is described as

$$e_j = \left\{\frac{1}{2}m_j v_j^2 + \frac{1}{2}\sum_{i=j} u(r_{ij})\right\} - e_{av}, \tag{7}$$

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where m_j and v_j are the mass and velocity of atom j; r_{ij}, f_{ij}, and u are the interatomic distance, force, and potential between atom i and j; e_{av} is the average energy of $SrTiO_3$. We employ the semi-empirical two-body potential function proposed by Ida for cation-anion interaction.[18] The potential is a partially ionic model including a covalent contribution:

$$U_{ij}(r_{ij}) = \frac{z_i z_j e^2}{r_{ij}} + f_0(b_i + b_j)\exp\left(\frac{a_i + a_j - r_{ij}}{b_i + b_j}\right) - \frac{c_i c_j}{r_{ij}^6} + D_{ij}\{\exp[-2\beta_{ij}(r_{ij} - r_{ij}^*)] - 2\exp[-\beta_{ij}(r_{ij} - r_{ij}^*)]\}, \quad (8)$$

where z_i and z_j are the effective partial electronic charges on the ith and jth ions, r_{ij} is the interatomic distance, r_{ij}^* is the bond length of the cation-anion pair in vacuum, a, b, and c are characteristic parameters depending on the ion species, $f_0 = 4.19$; D_{ij} and β_{ij} are the depth and shape of this potential, respectively. The potential parameters and characteristic parameters are summarized in Table 1.

Table 1. Values of the interatomic potential function for $SrTiO_3$.

Ions	z	a	b	c	Pairs	D_{ij}	β_{ij}	r_{ij}
O^{2-} (192)	−1.2	1.926	0.160	20				
Ti^{4+} (64)	2.4	1.055	0.180	25	Ti-O	4.23	3.82	2.1923
Sr^{2+} (64)	1.2	1.198	0.160	10	Sr-O	2.41	1.18	2.7615

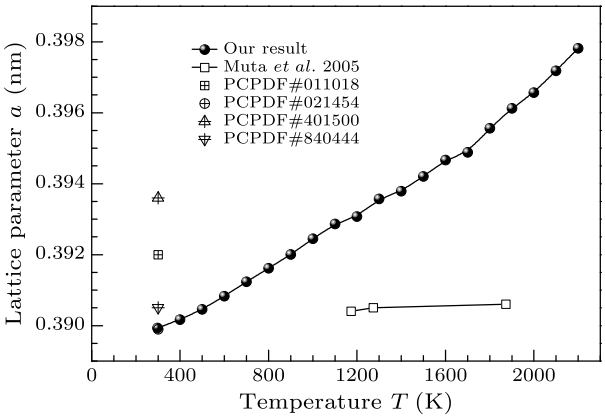

Fig. 1. Temperature dependence of the lattice parameter for $SrTiO_3$, together with PCPDF # 011018, 021454, 401500, 840444, and Muta *et al.*[11]

Figure 1 shows the temperature dependence of the lattice parameter of $SrTiO_3$ evaluated by the MD method, together with the PCPDFWIN Card Nos 011018, 021454, 401500, 840444, and Muta *et al.*[11] The lattice parameter of about 0.389 nm at 300 K increases to 0.397 nm at 2200 K. The evaluated values of lattice parameter at room temperature keep up a correspondence with the PCPDF#021454. However, the evaluated results with other PCPDF Cards and Muta *et al.*[11] are slightly lower and higher in the order of pico-meters. The lattice parameter of $SrTiO_3$ changed with pressure in the range from 0.1 GPa to 1.5 GPa at room temperature. These results indicate that the potential function in the present simulations describes the changes in the lattice parameters with both temperature and pressure.

Figure 2 shows the temperature dependence of $\alpha_{\rm lin}$ of $SrTiO_3$. Here $\alpha_{\rm lin}$ value is $0.57\times10^{-5}\,K^{-1}$ at 300 K, and it increases to $1.23\times10^{-5}\,K^{-1}$ at 2200 K. However, the evaluated values of $\alpha_{\rm lin}$ swing at the temperature range 1050–1500 K because the $SrTiO_3$ structure has changed to a tetragonal structure and attains the cubic structure of $SrTiO_3$ again at high temperature.

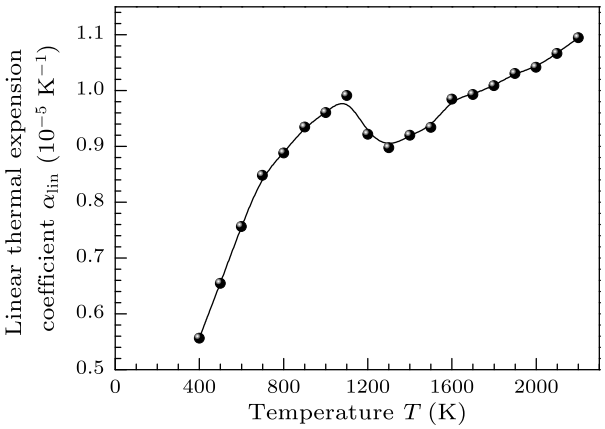

Fig. 2. Temperature dependence of the linear thermal expansion coefficient for $SrTiO_3$, together with de Ligny *et al.*[19]

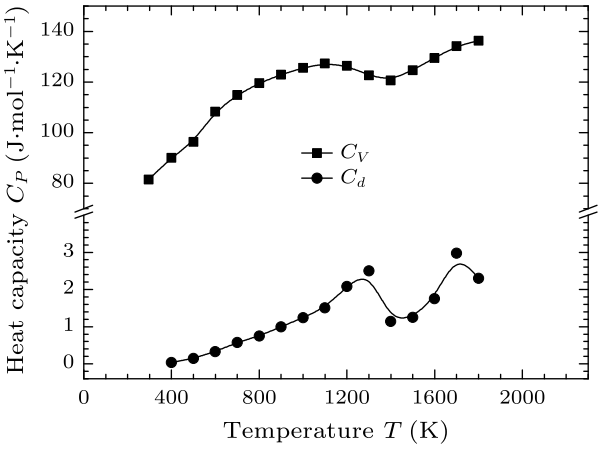

Fig. 3. Temperature dependence of the heat capacity at constant volume and the heat capacity of lattice dilatational.

Figure 3 shows the temperature dependence of C_V, and C_d of $SrTiO_3$. C_V is 81.50 $Jmol^{-1}K^{-1}$ at 300 K, and it increases to 136.37 $Jmol^{-1}K^{-1}$ at 1800 K. C_d is 0.0396 $Jmol^{-1}K^{-1}$ at 400 K, and it increases to 2.2995 $Jmol^{-1}K^{-1}$ at 1800 K. However, the C_d and C_V values show systematic differences at high temperature, which indicates the cubic structure ($Pm\bar{3}m$).[19] Temperature dependence of C_P of $SrTiO_3$ is shown in Fig. 4, together with de Ligny *et al.*[19] and Coughlin *et*

al.[20] C_P is 90.08 $\mathrm{Jmol^{-1}K^{-1}}$at 400 K, and it increases to 138.66 $\mathrm{Jmol^{-1}K^{-1}}$ at 1800 K, this agrees with the data in the literature, which indicates that the potential function used in the present study describes well the change in the internal energy of $SrTiO_3$ with temperature.

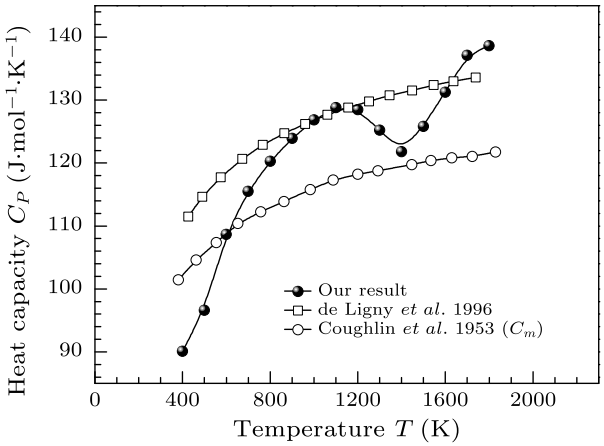

Fig. 4. Temperature dependence of the heat capacity at constant pressure for $SrTiO_3$, together with de Ligny *et al.*[19] and Coughlin *et al.*[20]

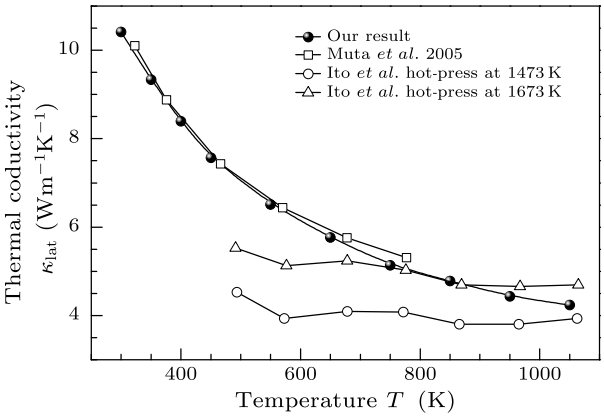

Fig. 5. Temperature dependence of lattice contributions to the thermal conductivity for $SrTiO_3$, together with Muta *et al.*[11] and Ito *et al.*[21]

Figure 5 shows the temperature dependence of κ_{lat} of $SrTiO_3$, together with Muta *et al.*[11] and Ito *et al.*[21] Here the κ_{lat} value is 12.64 $\mathrm{Wm^{-1}K^{-1}}$ at 300 K, and it decreases to 2.25 $\mathrm{Wm^{-1}K^{-1}}$ at 1100 K, it almost agrees with the data of Muta *et al.*[11] in the temperature range from 300 to 800 K. It indicates that our model can describe the thermal conductivity of $SrTiO_3$. Of course, the total thermal conductivity κ_{total} is evaluated from the relationship:

$$\kappa_{\mathrm{total}} = \kappa_{\mathrm{lat}} + \kappa_{\mathrm{el}} + \kappa_{\mathrm{other}}, \qquad (9)$$

where κ_{el} is the electrical contribution to the thermal conductivity, and κ_{other} is the other contribution to the thermal conductivity. The evaluated results of the molecular dynamics simulation represent κ_{lat} only.

In summary, the molecular dynamics method has been used in simulation of the thermophysical properties of $SrTiO_3$.We obtain the results that the lattice parameter, linear thermal expansion coefficient, and heat capacity increase with increasing temperature, and the decreases of lattice contributions on the thermal conductivity with increasing temperature agree with data in the literature. It shows that the molecular dynamics simulation is very useful for evaluating the thermophysical properties of thermoelectric materials such as $SrTiO_3$. Supported by the Commission on Higher Education, CHE-RES-PD project, Ministry of Education, Thailand.

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