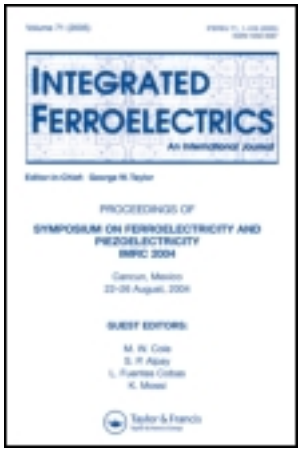

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Theoretical Enhancement of Thermoelectric Properties of $Sr_{1-x}La_xTiO_3$

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The electronic structure and density of state (DOS) of $Sr_{1-x}La_xTiO_3$ ($x = 0$, 0.06, 0.125, and 0.25) have been investigated on the first principle molecular orbital calculation. The La was substituted Sr site in $SrTiO_3$ and caused an increase of electrical conductivity. The electronic structure, DOS and band structure of $Sr_{1-x}La_xTiO_3$ ($x = 0$, 0.06, 0.13, and 0.25) were calculated by discrete variational (DV)-Xα method and Material studio to estimated the thermoelectric properties. The Seebeck coefficient and electrical conductivity of $Sr_{1-x}La_xTiO_3$ were estimated form DOS by Boltzmann theory: Mott and Jones equation. It was found that, the substitution of La made high electrical conductivity, made high power factor and enhancement thermoelectric properties. The $Sr_{0.87}La_{0.13}TiO_3$ cluster shows maximum power factor about 2.55×10^{-3} W/m·K^2 at 1200 K. For maximum enhancement thermoelectric properties of $SrTiO_3$ $x = 0.13$ should be used in the synthesis of $Sr_{1-x}La_xTiO_3$.

Keywords: Thermoelectric; DV-Xα; strontium titanate

I. Introduction

Thermoelectric material can directly convert heat to electricity [1]. Oxide thermoelectric materials have drawn much attention in recent years because of their high thermal stability, lower cost and no toxicity [2]. The efficiency of TE materials increases with the power factor ($S^2\sigma$), where S is the Seebeck coefficient and σ the electrical conductivity [3]. Therefore more Seebeck coefficient and electrical conductivity of thermoelectric materials are needed for higher power factor. The $SrTiO_3$ have been stable with high Seebeck coefficient but low electrical conductivity which made less power factor. The thermoelectric properties common found as is that replacement of strontium (Sr) on lanthanum (La) [1]. The La was substituted Sr in $SrTiO_3$ to increase electrical conductivity. However, it is very difficult to vary x value in synthesize $Sr_{1-x}La_xTiO_3$. In 2012 A. Vora-ud *et al*. calculated the energy gab and Fermi level density of state values for the evaluated electrical conductivity and Seebeck coefficient of Sb_2Te_3. The electrical conductivity and Seebeck coefficient agreed with the literature experimental data at the same temperature range [4]. T. Seetawan *et al*.

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proposed the evaluations of Seebeck coefficient of Na_xCoO_2 systems by Boltzmann theory: Mott expression and Fermi energy from the discrete variational (DV)-Xα method. Seebeck coefficients were positive values and increased with temperature increasing which indicates the p-type thermoelectric materials which is in agreement with the experimental data [5].

Molecular orbital calculation was performed by means of a DV-Xα cluster method in the Hartree-Fock-Slater approximation together with linear combination of atomic orbital (LCAO) method and self-consistent one-electron local density theory [13–14]. The DV-Xα is a non-relativistic first-principles using Slater's Xα potential as the exchange-correlation potential. In order to evaluate the overlap population, the Mulliken population analysis was employed [6].

This paper calculated energy level and density of state of $Sr_{1-x}La_xTiO_3$ (x = 0, 0.06, 0.13, and 0.25) by DV-Xα method to estimate Seebeck coefficient, electrical conductivity and power factor. Moreover, we compared thermoelectric properties of $SrTiO_3$, $Sr_{0.94}La_{0.06}TiO_3$, $Sr_{0.87}La_{0.13}TiO_3$, and $Sr_{0.75}La_{0.25}TiO_3$ for ideas to enhance thermoelectric properties.

II. Computational Detail and Estimate

The steps of computational detail of DV-Xα method is start from Makeunit program for define space group number ($SrTiO_3$: 221), lattice parameter (3.90 Å), atomic symbol (Sr, Ti, O) and position of atom (Sr(0, 0, 0), Ti(0.5, 0.5, 0.5),O(0.5, 0, 0)). Atoms (614 atoms) was automatic generated by Makelat program and operate number of atoms in unit cell is 5. The cluster model of atoms can edit in Displat program and this program is preparing data files for calculate energy level and density of state. The Seebeck coefficient and electrical conductivity of $Sr_{1-x}La_xTiO_3$ were estimated by energy gab and DOS by Boltzmann theory: Mott and Jones equation. The clusters of $SrTiO_3$, $Sr_{0.94}La_{0.06}TiO_3$, $Sr_{0.87}La_{0.13}TiO_3$, and $Sr_{0.75}La_{0.25}TiO_3$ were designed to calculated density of state. The electrical conductivity and Seebeck coefficient are estimate from Eq. (1–3) and Eq. (4), respectively.

The relationship between the electrical conductivity and temperature revised Mott formula of the semimetal is given by Eq. (1) and the semiconductor given by Eq. (2).

$$\sigma(T) = \sigma_0 \exp\left(-\frac{\Delta E}{k_B T}\right) \tag{1}$$

$$\sigma(T) = \sigma_0 \exp\left(-\frac{\Delta E}{2k_B T}\right) \tag{2}$$

Where ΔE is the temperature dependent activation energy of hopping and σ_0 is the minimum metallic conductivity at $T = 0$ K. σ_0 is determined by the scattering of electron by phonons at high temperature using Mott's equations given by Eq. (3)

$$\sigma_0 = \frac{2\pi e^2 \hbar^3}{3m^2} L_0 \{DOS(E_F)\}^2 \tag{3}$$

Where L_0 is estimated from the lattice parameter, e is the absolute charge of carriers, $\hbar$ is Planck constant and $DOS(E_F)$ is determined from the DV-Xα at the Fermi level.

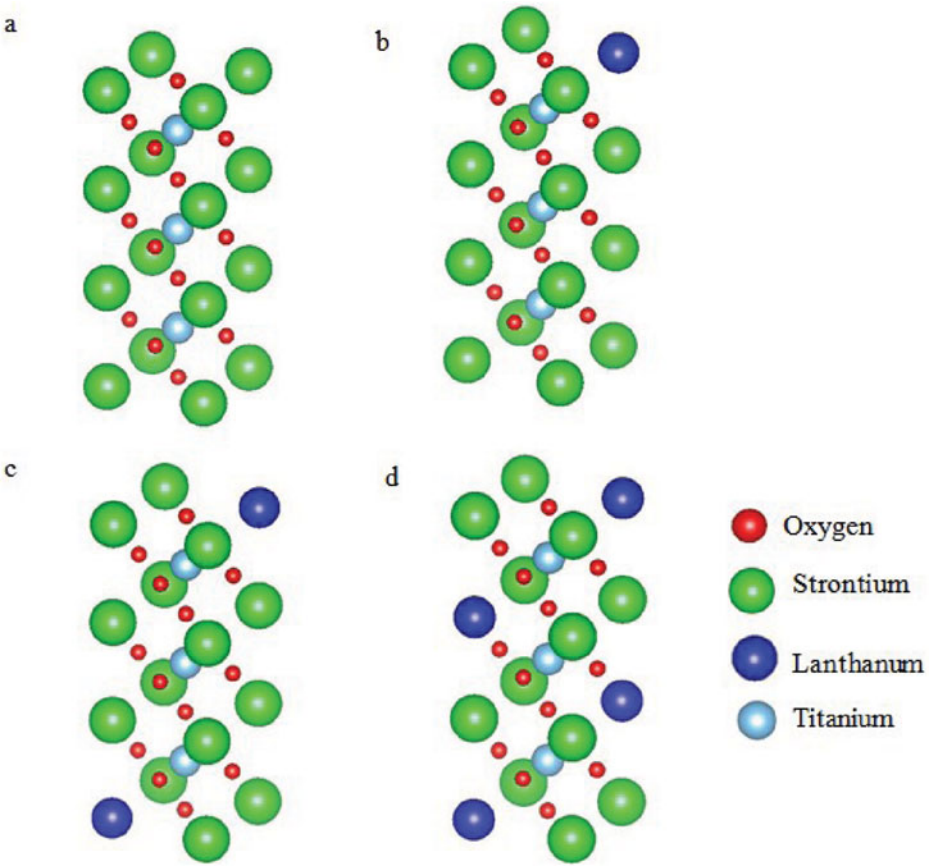

Figure 1. Cluster atom model of (a) $SrTiO_3$, (b) $Sr_{0.94}La_{0.06}TiO_3$, (c) $Sr_{0.87}La_{0.13}TiO_3$, and (d) $Sr_{0.75}La_{0.25}TiO_3$.

The Seebeck coefficient was given by the Boltzmann theory: Mott and Jones equation: Eq. (4). This equation have derived carefully by T. Seetawan *et al*. [5]

$$S(T) \approx -\frac{\pi^2 k_B^2 T}{3eE_F}\left(\frac{3}{2}+r\right) \tag{4}$$

Where π is constant; 3.14, r is number of total orbital from D04 file generated by the DV-Xa method and E_F is Fermi energy, the Fermi energy at a temperature T [5] is defined by

$$E_F(T) \approx E_{F0}\left[1-\frac{\pi^2}{12}\left(\frac{k_B T}{E_{F0}}\right)^2\right] \tag{5}$$

Where E_{F0} is the Fermi energy at a temperature T = 0 K.

III. Results and Discussion

Cluster Atom Models

Cluster atom models of $SrTiO_3$, $Sr_{0.94}La_{0.06}TiO_3$, $Sr_{0.87}La_{0.13}TiO_3$, and $Sr_{0.75}La_{0.25}TiO_3$ are shown in Figs. 1a–d, respectively. The entire clusters calculations used three unit cells and have cubic structure. The substitute of La in Sr 1 atom, 2 atoms, and 3 atoms are shows in Figs. 1b–d, respectively. The selection position of La is regard symmetry of cluster calculation. The cluster a, c and d have symmetry but cluster b has non symmetry because put only one atom of La in corner cluster atom model.

Band Structure

The band structures of $SrTiO_3$, $Sr_{0.94}La_{0.06}TiO_3$, $Sr_{0.87}La_{0.13}TiO_3$, and $Sr_{0.75}La_{0.25}TiO_3$ were calculated by Material studio, and the effects of the doping La atoms on the electronic properties and thermoelectric properties of $SrTiO_3$ were studied. All geometric configurations used in calculations were fully optimized. The band gap of $SrTiO_3$ is calculated to be 1.89 eV, which is lower than the experimental result of around 3.2 eV mainly due to the well-known shortcoming of exchange-correction functional in describing excited states using GGA approximation [11]. However the band gap of $Sr_{0.94}La_{0.06}TiO_3$, $Sr_{0.87}La_{0.13}TiO_3$, and $Sr_{0.75}La_{0.25}TiO_3$ has been over lap band structure.

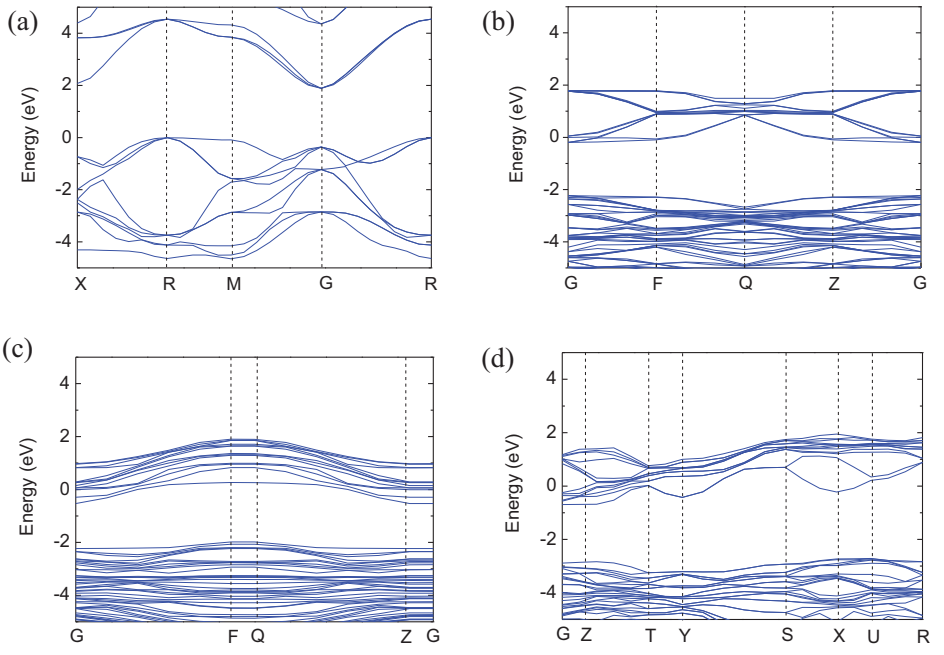

Figure 2. Band structure of (a) $SrTiO_3$, (b) $Sr_{0.94}La_{0.06}TiO_3$, (c) $Sr_{0.87}La_{0.13}TiO_3$, and (d) $Sr_{0.75}La_{0.25}TiO_3$ cluster atom models.

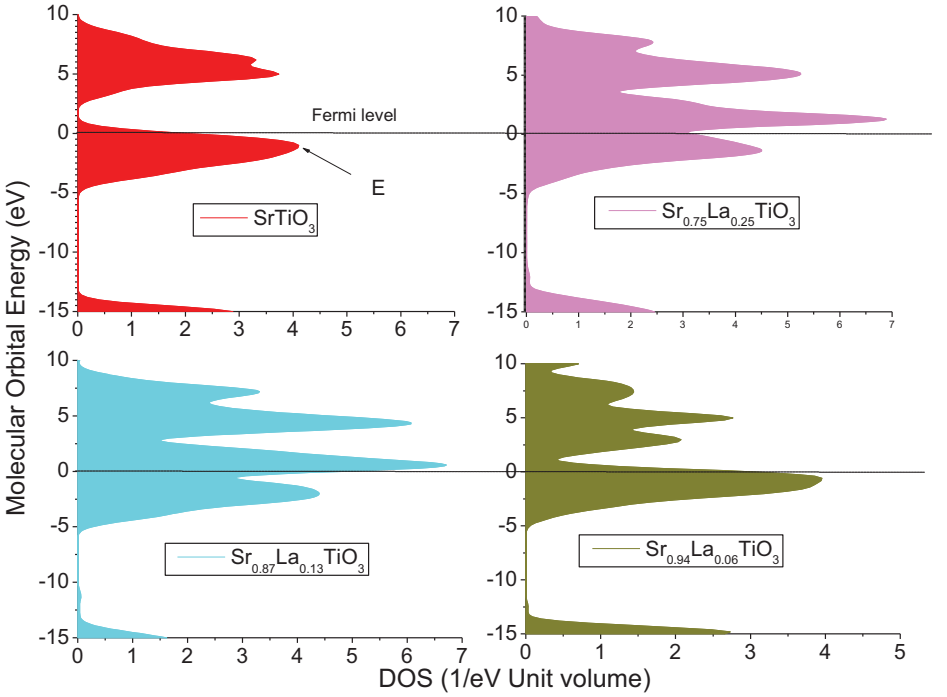

Figure 3. Total density of states of cluster atom model calculation.

Total Density of State

Total density of states of $Sr_{1-x}La_xTiO_3$ (x = 0, 0.06, 0.13, and 0.25) are shown in Fig. 3. The orbitals of $SrTiO_3$ were composed of the Ti3d, Ti4s, Ti4p, O2s, O2p, Sr3d, Sr4s, Sr4p and Sr5s. The orbitals of $Sr_{1-x}La_xTiO_3$ (x = 0.06, 0.13, and 0.25) were composed of the Ti3d, Ti4s, Ti4p, O2s O2p, La4f, La5d, Sr3d, Sr4s, Sr4p and Sr5s. The total density of state was obtained Fermi energy to estimate electrical conductivity and Seebeck coefficient. The DOS $Sr_{1-x}La_xTiO_3$ (x = 0, 0.06, 0.13, and 0.25) were indicated the metallic behavior.

Seebeck Coefficient

Figure 4 shows the Seebeck coefficient of $Sr_{1-x}La_xTiO_3$ (x = 0, 0.06, 0.13, and 0.25) at temperature range of 300–1200 K together with literature experiment data [9 and 10]. The absolute value of Seebeck coefficient was increased with increasing temperature. The La substitutes at Sr site has been increased Seebeck coefficient except $Sr_{0.75}La_{0.25}TiO_3$ because this cluster calculation obtained high Fermi energy. The $Sr_{0.87}La_{0.13}TiO_3$ cluster is show good thermoelectric property because this cluster show high Seebeck coefficient and larger than $SrTiO_3$.

Electrical Conductivity

The electrical conductivity was estimates from the temperature dependent activation energy of hopping and DOS by Mott equation show in Eq. (1). The DOS obtained from DV-xα

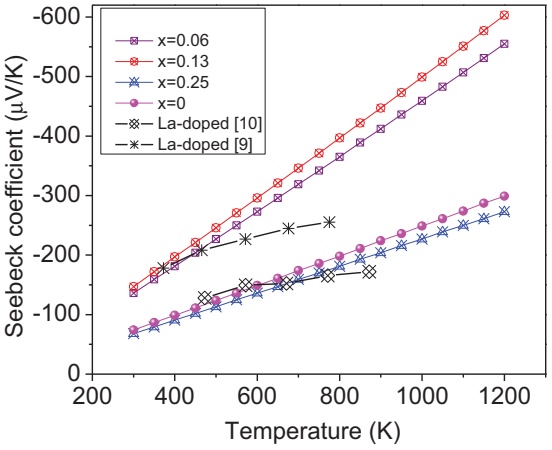

Figure 4. Temperature dependence of Seebeck coefficient for $Sr_{1-x}La_xTiO_3$ (x = 0, 0.06, 0.13, 0.25) cluster calculation with literature experiment data [9 and 10].

method for difference x value. Fig. 5 shown electrical conductivity of $Sr_{1-x}La_xTiO_3$ (x = 0, 0.06, 0.13, and 0.25) in temperature range 300–1200 K compare with literature data [7 and 15]. The entire substitutes Sr by La is increase electrical conductivity. The electrical conductivity was increases with increasing temperature.

Power Factor

Figure 6 shows the power factor of $Sr_{1-x}La_xTiO_3$ (x = 0, 0.06, 0.13, and 0.25) with temperature range 300–1200 K. The cluster of $SrTiO_3$ and $Sr_{0.75}La_{0.25}TiO_3$ were obtained power factor are low because these clusters have low electrical conductivity and Seebeck coefficient. The $Sr_{0.87}La_{0.13}TiO_3$ was obtained highest power factor which adapted chose to device thermoelectric high efficiency.

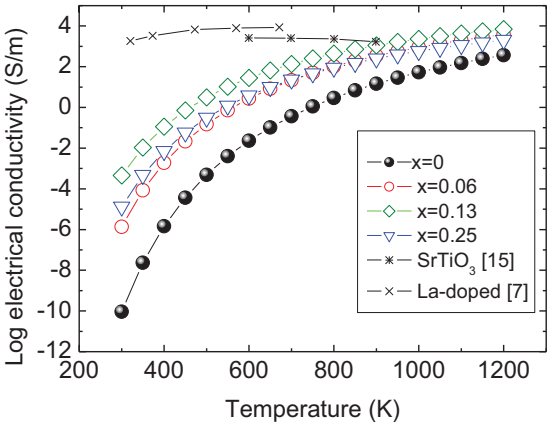

Figure 5. Temperature dependence of electrical conductivity for $Sr_{1-x}La_xTiO_3$ (x = 0, 0.06, 0.13, 0.25) cluster calculation with literature experiment data [7 and 15].

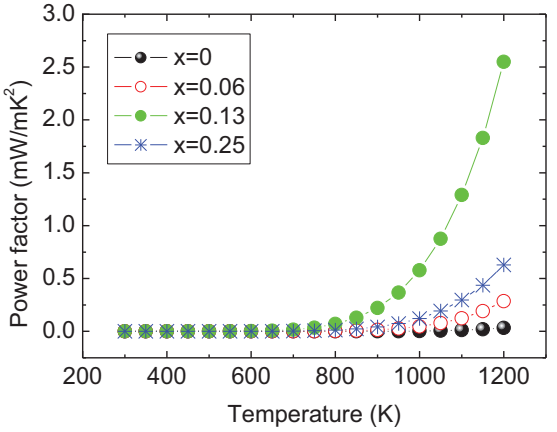

Figure 6. Temperature dependence of power factor for $Sr_{1-x}La_xTiO_3$ (x = 0, 0.06, 0.13 and 0.25) cluster calculation.

IV. Conclusion

Energy level and density of state of the $Sr_{1-x}La_xTiO_3$ (x = 0, 0.06, 0.13, and 0.25) were calculated by DV-Xα method. Boltzmann theory: Mott and Jones equation was used to estimate Seebeck coefficient and electrical conductivity. The entire substitutes Sr by La can reduce energy gap which can increase electrical conductivity. The $Sr_{0.87}La_{0.13}TiO_3$ cluster shows maximum power factor about 2.55 mW/m·K^2 at 1200 K. The synthesis of $Sr_{1-x}La_xTiO_3$ with x = 0.13 was used for enhancement of thermoelectric properties of $SrTiO_3$.

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