CHAPTER 1

INTRODUCTION

Motivation

The thermoelectric effect has been an interesting area of study for researchers. Because thermoelectricity involves the conversion of thermal energy directly into electrical energy, the development of thermoelectric (TE) materials has become very important and much needed. The performance of TE materials can be evaluated by a dimensionless figure of merit in the equation $ZT = S^2\sigma T / \kappa$. Ideally, good TE materials exhibit a large Seebeck coefficient (S), high electrical conductivity (σ), and low thermal conductivity (κ) when both such conductivites are measured at absolute temperature (T) (Rowe, 2006, p.1–1).

Conventional TE materials, such as, Si–Ge (Tritt, 1999, pp.804–805), Bi_2Te_3, PbTe (Poudel et al., 2008, pp.634–638; Li, Wang, Wang, Yin & Zhou, 2009, pp.869–874), and skutterudites (Yan et al., 2014, pp.221–229) show high ZT at low – middle temperatures, but they are toxic and non–suitable at high temperatures. Oxide thermoelectric materials such as, $NaCo_2O_4$ (Terasaki, Sasago & Uchinokura, 1997, p.R12685), Ca–Co–O (Masset et al., 2000, pp.166–175; Xu, Funahashi, Shikano, Matsubara & Zhou, 2002, p. 3760–62), and $Bi_2Sr_2Co_2O_y$ (Funahashi, Matsubara, & Sodeoka, 2000, pp.2385–2387; Funahashi & Matsubara, 2001, p. 362–4; Xu, Funahashi, Shikano, Matsubara & Zhou, 2002, p. 4344) exhibit high ZT, *p*–type TE material, and are strong candidates for selection. However, TE devices need *p*–type TE material combined with *n*–type TE material for generator or refrigerator applications. $CaMnO_3$ is an *n*–type oxide TE material and highly favoured due to its large S, low κ and easily enhanced TE properties (Ohtaki, Koga, Tokunaga, Eguchi

& Arai, 1995 pp.105–111). In addition, $CaMnO_3$ has a non–toxic composition and low cost. It is also easily synthesized with *p*–type TE material for applications requiring this combination. (Seetawan, Singsoog & Srichai, 2013, pp.220–223). So far, more and more researchers are focused on enhancing the thermoelectric property of $CaMnO_3$ by metal doping and adding Ca site doping, such as, $Ca_{0.9}M_{0.1}MnO_3$ (M = Y, La, Ce, Sm, In, Sn, Sb, Pb, Bi) (Ohtaki et al., 1995, pp.105–111), $Ca_{1-X}Na_XMnO_3$ (X = 0.01, 0.02, 0.025) (Yamashita, 2007, pp.461–464), $Ca_{1-X}RE_XMnO_3$ (RE = Nd, Tb, Ho, Yb, Lu; X = 0.1, 0.2) (Funahashi et al., 2008, p. 124), $Ca_{1-X}Ho_XMnO_3$ ($0.1 \leq X \leq 0.4$) (Sousa, et al., 2008, pp.311–319), $Ca_{1-X}La_XMnO_3$ (X = 0, 0.02, 0.04, 0.06, 0.08) (Lan et al., 2009, pp.535–538), $Ca_{3.95}RE_{0.05}Mn_3O_{10}$ (RE = Ce, Nd, Sm, Eu, Gd, Dy) (Lemonnier, Guilmeau, Goupil, Funahashi & Noudem, 2010, pp.887–891), $Ca_{0.9}R_{0.1}MnO_3$ (R = La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb) (Wang et al., 2010, pp.6306–6316), $Ca_{1-X}Pr_XMnO_3$ (X = 0, 0.06, 0.08, 0.1, 0.12, 0.14) (Feipeng et al., 2013, pp.885–890), $Ca_{1-X}R_XMnO_3$ (R = Yb, Dy, Sm, Bi; X = 0, 0.1) (Mouyane, Itaalit, Bernard, Houivet & Noudem, 2014, pp.71–77), $Ca_{1-X}Bi_XMnO_3$ (X = 0, 0.02, 0.03, 0.04, 0.06, 0.10) (Kabir et al., 2015, pp.347–351). Mn site doping, such as, $CaMn_{1-X}M_XO_3$ (M = Nb and Ta; $0 \leq X \leq 0.3$) (Xu et al., 2004, pp.147–151); and double doping, such as$Ca_{0.96}Dy_{0.02}$ $RE_{0.02}MnO_3$ (RE = Ho, Er, Tm) (Zhu et al., 2014, pp.15531–15536), $Ca_{0.95}La_{0.05}$ $Mn_{1-X}Nb_XO_3$ ($0 \leq x \leq 0.1$) (Villa & Rodríguez, 2014, pp.22–25), $Ca_{1-2X}Dy_XYb_XMnO_3$ ($0 \leq x \leq 0.1$) (Zhu et al., 2015, pp.1535–1539), and $Ca_{0.96}Dy_{0.02}R_{0.02}MnO_3$ (R = La, Pr, Sm, Er, Ho, Yb) (Zhu et al., 2015, pp.105–109), can also enhance ZT. This is because the Mn atom has a +4 valence in $CaMnO_3$. Metal–doping gives an electron to Mn^{4+} which causes the number of valence electrons to change from +4 to +3 thus modifying the TE property. In theoretical studies, density functional theory (DFT) with Dmol3 calculates the electric structure of $CaMnO_3$ (Trang et al., 2011, pp. 3613–3621) $R_{0.25}Ca_{0.75}MnO_3$ (R = rare earth) (Linh, Trang, Cuong, Thao & Cong, 2010, pp.2–5). A DFT study of $CaMnO_3$ and electron–doped $CaMnO_3$ (Zhang, Lu, Zhang & Zhang, 2011, pp.542–545; Zhang, Zhang, Lu, Zhang & Liu, 2011, pp.4171–4175; Zhang et al., 2011, pp.1258–1262) shows good potential calculation for enhanced TE properties.

Recently, TE properties have been calculated in such ways as, $CaMnO_3$ (Zhang, Lu, Zhang & Zhang, 2013, pp.1859–1864) and $Ca_{0.75}R_{0.25}MnO_3$ (R = rare earth) calculated by DFT and Boltzmann theory (Zhang et al., 2015, pp.1–5);

$Ca_{0.8}M_{0.2}MnO_3$ (M = Cu, Ag, Bi) calculated by discrete variational–Xα (DV–Xα) (Seetawan, 2014, pp.9–14); and $Ca_{1-X}Eu_XMnO_3$ (X=0, 0.05, 0.10, 0.15) calculated by molecular dynamics (Rittiruam, Wattanasarn, & Seetawan, 2014, pp.585–593). Hence, thermoelectric theory is an important part of the study of TE materials. Because of their ability to enhance TE properties by adding them within TE materials, carbon nanotubes (CNTs) have created a lot of interest lately. CNTs exhibit good electrical conductivity (more than 10^3 that of copper)They also have good thermal conductivity along their length and good thermal resistance through the cross–section of the tubes. These qualitites make them particularly useful. Recently, Thongsri & Seetawan (2013, pp.327–330) successfully decreased the thermal conductivity of $CaMnO_3$ by adding CNTs. But, they didn't study the electrical conductivity and Seebeck coefficient which is important for TE materials. In the case of oxide materials, CNTs can reduce the energy gap and enhance the ZT of rutile TiO_2 (Lai et al., 2014, p. 8120–4) CNTs can also enhance the thermal conductivity and Seebeck coefficient of $Ca_3Co_4O_9$ (*p*–type) while electrical resistivity was increased (Tang et al., 2015, pp.961–965). CNTs therefore do not improve the ZT of $Ca_3Co_4O_9$.

Using computer simulation, this work has focused on the study of TE properties resulting from the addition of carbon nanotubes to $CaMnO_3$.

Research Objectives

1. To calculate the electronic structure and thermal properties of CNTs–added $CaMnO_3$.
2. To predict the thermoelectric properties of CNTs–added $CaMnO_3$.

Scope and Limitation of the Thesis

1. A Cluster atoms model was used for two separate case studies; i.e., CNTs–added $CaMnO_3$ and C–substitute $CaMnO_3$.
2. Electronic structure viz., density of state, energy level and Fermi energy.

3. Thermal properties viz., lattice parameters, heat capacity, heat flux and thermal conductivity.

4. Thermoelectric properties viz., Seebeck coefficient, electrical conductivity, power factor and dimensionless figure of merit.

Anticipated Outcomes of the Thesis

The expected outcomes for the thesis are to obtain the electronic structure, thermal properties and thermoelectric properties of CNTs–added $CaMnO_3$.

Thesis structure

This thesis consists of 5 chapters; Chapter 1 introduces motivation, objectives, scope, limitation, place of work and benefits of this thesis. Chapter 2 reviews the fundamental thermoelectric theory, history and thermoelectric properties of $CaMnO_3$ as well as carbon nanotubes. The research methodology is presented in Chapter 3. The results and discussion of this thesis are illustrated in Chapter 4. Finally, the conclusion and suggestion for further work are reported in Chapter 5.

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