Thermoelectric Properties of Zn-doped CdO

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Authors' contributions

This work was carried out in collaboration between all authors. All authors read and approved the final manuscript.

Original Research Article

ABSTRACT

Thermoelectricity is a technology that achieves thermal-to-electric conversion and vice versa. It requires high performance thermoelectric compounds for effective conversion efficiency. The thermoelectric properties of CdO in the rocksalt structure, obtained by first principle calculations are presented. Many thermoelectric materials have low figures of merit hence low conversion efficiency. This research sought to carry out an *ab initio* study of thermoelectric properties of pristine and Zn-doped cadmium oxide. The properties were obtained by calculating the electronic structure dependent properties. Post processing of the DFT calculation was done using the BoltzTraP and Phono3py codes. From the seebeck coefficient CdO was found to be an n-type semiconductor with a figure of merit (ZT) of 0.30. All the results obtained on pure CdO systems were comparable to the existing literature. Doping was done using the supercell technique. We found 4% doping sufficient to yield a high PF of 10×10^{-4} W/mK^2 at 1000K. Hence, Zn doping enhances thermoelectric properties of CdO.

Keywords: Thermoelectricity; CdO; power factor.

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1. INTRODUCTION

Thermoelectric (TE) materials is a very important class of materials that enable us to have direct conversion from waste heat to electricity and vice-versa.

The choice of materials for thermoelectricity, involves the search for materials that possess good thermoelectric properties, besides having mechanical and thermal characteristics that allow their use over a wide temperature range in practical thermoelectric generators. The inherent advantages of Oxide TE materials such as abundantly available, high thermal and chemical stability in air [1] has made them superior for the use in high temperature TE applications.

Statistical results show that more than 60 percent of energy is lost in vain worldwide, most in the form of waste heat [2]. High performance thermoelectric (TE) materials that can directly and reversibly convert heat to electrical energy have thus drawn growing attention of governments and research institutes [3]. This is due to the increasing global energy concerns, for instance, a large percentage of global energy, is being generated from depleting fossil fuels such as natural gas, coal and petroleum [4]. Approximately 30-40% of energy obtained from burnt fossil fuels is utilised as useful energy; the rest is wasted in the form of heat [5]. Capturing some of this heat and converting it to useful electric energy can help reduce the dependence on the depleting fossil fuels.

Thermoelectric technology has been in existence for as long as since 1821. Due to the wide availability of fossil fuels throughout this century [6], very little attention was geared towards exploration of better TE materials.Thermoelectric devices are reliable source of energy despite the major challenges faced by the existing thermoelectric materials. Some of the key problems related to TE materials are cost, availability, toxicity and stability at high temperatures.

CdO is an n-type semiconductor and a transition metal oxide (TMO) that is cost effective and stable in air at high temperatures [7]. It has a band gap of approximately 2.5 eV with low resistivity [8]. The low resistivity is due to the native defects of oxygen vacancies and Cd interstitials. The oxygen vacancies act as doubly ionised donors, implying that they are generally too high in energy to contribute heavily towards any intrinsic conductivity [9]. Its resistivity can greatly be reduced by adding a suitable dopant having ionic radius smaller or equal to that of host lattice atoms [10]. Zinc (Zn) was chosen as the dopant since its ionic radius (0.074nm) is slightly less than that of Cd^{2+} (0.095nm) [11] hence the zinc ions would easily fit into the CdO matrix.

CdO is a potential thermoelectric material (TE). TE materials are widely regarded as materials that can provide potential solutions for power generation and refrigeration technologies as well as their future advancements [12]. Additionally, they offer opportunities for the development of technologies in areas such as smart sensors, energy harvesting, and the new concept of thermo-power wave source [13]. Cadmium Oxide is an n-type semi-conductor in the rocksalt structure with high carrier mobility. The dimensionless figure of merit (ZT), is an important parameter that is key in determining the performance of TE. ZT is linearly dependent on the temperature as illustrated in equation 1.1

$$ZT = \frac{S^2 \sigma T}{K}. \qquad (1.1)$$

Where σ is the electrical conductivity, S is the Seebeck coefficient, K is the total thermal conductivity and T is the temperature. The power factor is given by ($S^2\sigma$) hence, it is linearly dependent to ZT. Total thermal conductivity is the sum of carrier thermal conductivity (k_e) and the phonon thermal conductivity known as the lattice contribution (k_p). For a high ZT, materials are expected to have a large σ and low K. Unfortunately, according to Wiedmann-Franz law, electrical conductivity is directly proportional to electronic thermal conductivity as in equation 1.2. Hence, this law conspires against having high σ and low K at the same time, making good TE materials to possess very conflicting properties

$$k_e = LT\sigma. \qquad (1.2)$$

This research entails the *ab initio* study of thermoelectric properties of pristine and Zn-doped CdO in order to better probe its power factor at elevated temperatures that is the key determinant of its potential for future thermoelectric application.

2. MATERIALS AND METHODS

All the calculations were done within the Density Functional theory implemented in Quantum ESPRESSO (Q.E) computer code [14]. Post processing of the data was done by the Boltztrap [15] and Phono3py [16] computer codes. The Equation of State (EOS) used was Murnaghan. It is based on the assumption that the bulk modulus varies linearly with pressure. The electron-ion interaction was described by the Norm Conserving formalism. For the exchange – correlation interaction, we used the GGA-PBE [17]. A cut off energy of about 60Ry was used in these calculations. For sampling the Brillouin Zone (BZ), Monkhorst-Pack k-point meshes [18] with grids of 17x17x17 were used. These parameters were found to be sufficient for energy convergence to within 0.1 meV. In the CdO rocksalt structure (NaCl), the Cadmium and Oxygen atoms are positioned at (0,0,0) and (0.5,0.5,0.5) .

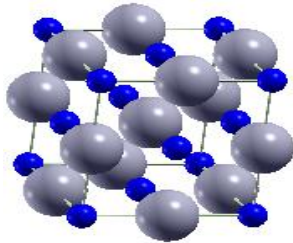The structure of the CdO considered is shown in Fig. 1.

Fig. 1. (Colour online) The crystal structure of CdO. Where the large grey and small blue balls signify Cd and O respectively.

3. RESULTS AND DISCUSSION

3.1 Electronic and Thermoelectric Properties

The band gap problem has remained a major challenge as far as GGA and LDA are concerned since they underestimate the band gap. The band gap, in relation to Kohn-Sham (E_g-KS) is the difference between the eigen values of lowest unoccupied and highest occupied Eigen states [19]. The reason for underestimation of the bandgap in GGAs and LDA may probably be due to the delocalisation error or lack of derivative discontinuity in the exchange correlation potentials [17]. Nevertheless, the band structure calculations are prerequisite for calculations and interpretation of thermoelectric properties.

BoltzTraP code is more of a post-processing code that takes outputs of Q.E as inputs for calculating the electrical conductivity (σ) Seebeck coefficient(S), and the electronic thermal conductivity along the x, y and z axes. A dense k mesh of 50,000 k points in the first Brillouin zone was used in the calculation at constant relaxation time approximation, σ was expressed in units of τ . We did our calculation under a constant relaxation time of 10fms. Thermal conductivity (K) was studied with an emphasis on both electronic and phonon contributions. Using the Phono3py code, the lattice thermal conductivity was calculated by taking in account the force sets derived from the supercell approach. The figure of merit was then obtained using equation 1.1 at various values of T. The thermoelectric properties were calculated using the Boltztrap code in the constant relaxation time approximation.The position of chemical potential (μ) plays an important role with regard to the thermoelectric properties. Position of μ in the band structure determines which electrons in the valence or conduction band take part in the electronic transport and thus influences both the conductivity and the seebeck coefficient. Doping can be used to manipulate the μ by varying the number of valence electrons in compounds. The electrical conductivity, total thermal conductivity and the seebeck coefficient have accumulated effect on the figure of merit.

3.1.1 Electrical conductivity

Conductivity is the measure of the ease at which an electric charge or heat can pass through a material.To be specific, electrical conductivity tells us how well a material will allow electric charge to travel through it. In the pristine CdO, the electrical conductivity decreases with increase in temperature as seen in Fig. 2. This is due to the high carrier concentration of CdO. Since electrical conductivity is given by

$$\sigma = ne\mu . \qquad (1.3)$$

Where n is carrier concentration and μ is the carrier mobility, then carrier concentration increases with temperature resulting to a decrease in mobility hence decreasing conductivity. The electrical conductivity in CdO was similar in the entire three axes. This

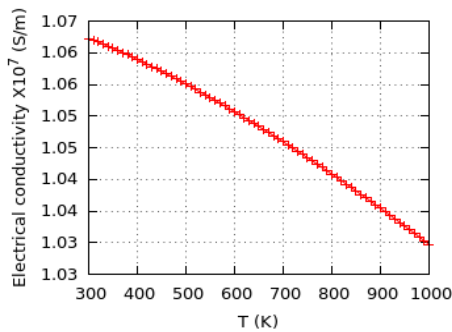confirmed the electrical isotropy in the axes of CdO.

Fig. 2. Variation of electrical conductivity with temperature

3.1.2 Thermal conductivity

Thermal conductivity tells us the ease upon which heat energy can move through a material. Total thermal conductivity is the sum of electronic (k_{el}) and lattice contribution (k_{ph}) of the crystal. Fig. 3 shows the variation of electronic and lattice contribution of thermal conductivity with respect to temperature. The electronic contribution increases with increasing temperature. This is due to increase in carrier concentrations. The lattice part decreases with increasing temperature. With increasing temperature, phonon concentration increases and causes increased scattering. Thus lattice scattering lowers the carrier mobility more and more at higher temperatures. Increased phonon scattering increases the resistance of electrons to conductivity.
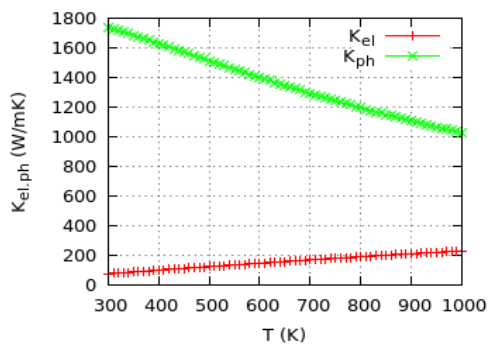

Fig. 3. Variation of electronic and lattice contribution of thermal conductivity with respect to temperature.

3.1.3 Seebeck coefficient (S)

Seebeck Coefficient is a measure of the magnitude of an induced thermoelectric voltage in response to a temperature difference across that material as induced by the seebeck effect. The variation of seebeck coefficient with temperature shows a downward trend as seen in Fig. 4. The seebeck coefficient values are negative implying that the conduction is due to electrons hence CdO is an n-type semiconductor.
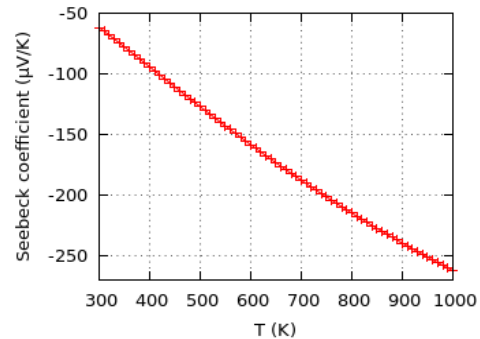

Fig. 4. Variation of Seebeck coefficients with temperature

3.1.4 Figure of Merit (ZT)

The figure of merit is a dimensionless quantity used to characterise the performance of a material relative to its alternatives. It is actually used to measure the thermoelectric efficiency of a material. The higher the value of ZT the better the thermoelectric efficiency. It is a temperature dependent material property derived from temperature dependent properties (S, σ and K). It is clear from Fig. 5 that the ZT increases with temperature. A ZT value of 0.30 at 1000K is obtained. This is in good agreement with experiments that obtained a maximum ZT of 0.34 at 1023K for pure CdO [3].

3.2 Thermoelectric Properties of Zn Doped CdO

A 3x3x3 supercell was made comprising of 54 atoms. Substitution doping was then done at 2%, 4% and 6%. The doping percentage was arrived by taking the effective mass of zinc divided by the total mass of the other elements multiplied by 100%.

Since the figure of merit is directly proportional to the power factor (PF) at a given temperature, the power factor at various concentrations was calculated and it was noted that on doping, there was a significant shift in the powerfactor. This implies that, there is a significant positive change on the figure of merit once doping is done on

CdO. At 4%, the greatest power factor of 10×10^{-14} W/mk^2 was obtained at 1000K as shown in Fig. 8.
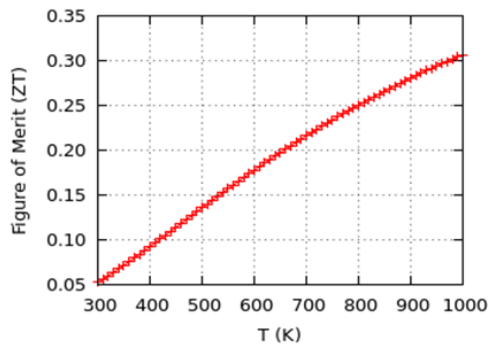

Fig. 5. Variation of figure of merit with temperature

The conductivity depends on the mobile charge concentration and the mobility. As the doping increases, the carrier concentration increases and the mobility decreases. In relatively low doping the carrier concentration increases linearly with doping concentration while the mobility decreases in a lesser extent with doping resulting to an increase in power factor as seen in the trends of 2% and 4% doping in Fig. 8. At heavy doping, an increased fraction of the doping atoms was not ionised and remained inactive. If the impurity was increased beyond the solid solubility limit, the dopants would be clustered in the material and the electron concentration no longer increases while these doping atoms cause larger scattering of the electrons and a larger decrease in the mobility. Hence, the Power factor began to fall at certain specific doping concentration which is 6% doping as observed in Fig. 8, where below 550K, the PF shows a positive trend before saturation sets in and it drops drastically. This implies that ,4% is the best percentage for doping that yields Zn-CdO that is effective for waste heat conversion.
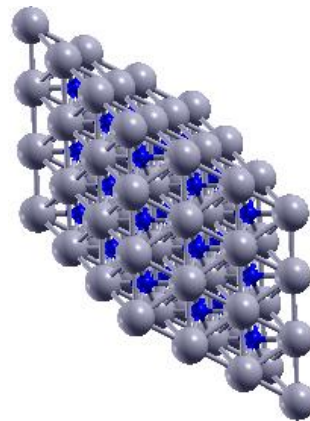

Fig. 6. (Colour online) A 3x3x3 supercell of CdO. The large grey and small blue balls represent Cd and O respectively.
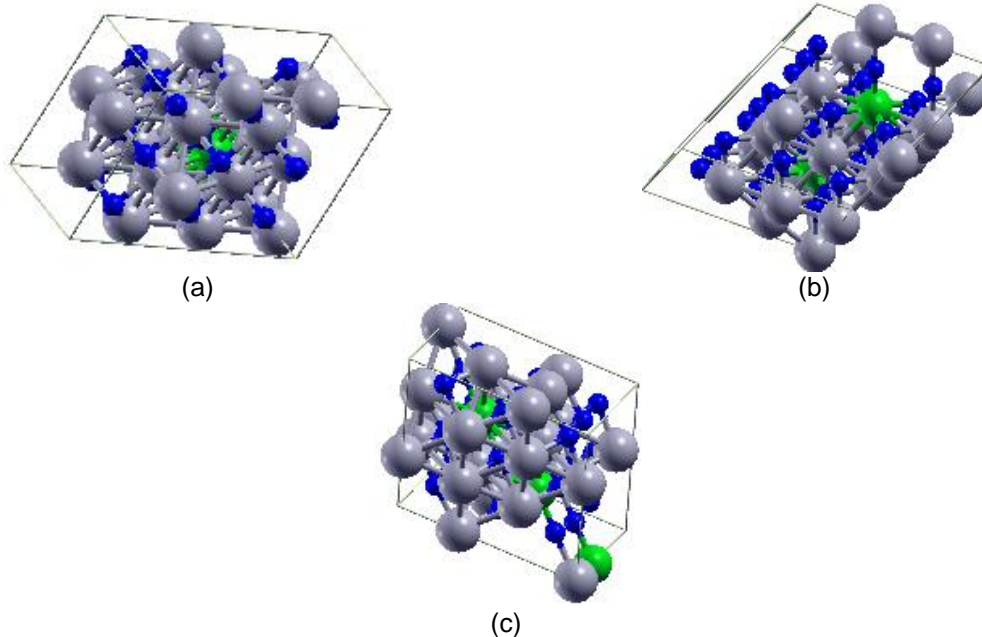

(a)

(b)

(c)

Fig. 7. (Colour online) Doped supercells of the CdO at (a) 2%, (b) 4% and (C) 6%, the large grey, Small blue and Medium green balls represents Cd, O and Zn respectively
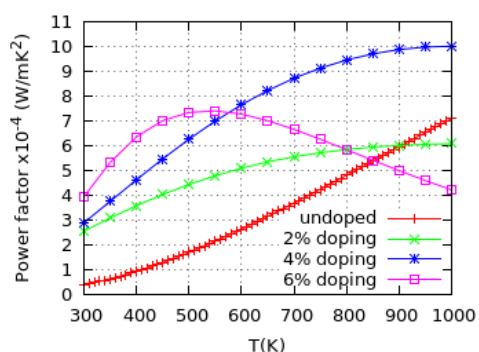
Fig. 8. An illustration of the power factor at different concentrations of doping

4. CONCLUSION

Thermoelectric properties of pristine CdO were determined by calculating the electronic structure dependent properties. The boltztrap code and the phono3py code were essential in the post processing in order to obtain thermoelectric properties. For thermoelectric properties, the pristine CdO was found to have a ZT of 0.3 at 1000K. Doping enhanced the power factor of CdO. We found 4% doping sufficient to yield an improved PF of $10 \times 10^{-4} W/mK^2$. CdO at 4% doping showed a positive rise of power factor implying greater capability to convert waste heat into useful electrical energy.

ACKNOWLEDGEMENTS

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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