SIMULATING ELECTRONIC STRUCTURE OF Ag-DOPED $Ca_3Co_4O_9$ BY FIRST PRINCIPLES

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ABSTRACT

We simulated the electronic structure of Ag-doped $Ca_3Co_4O_9$ by using the Cambridge Serial Total Energy Package (CASTEP) based on density functional theory. The P-type thermoelectric Ag-doped $Ca_3Co_4O_9$ was found to be more stable via total energy minimization calculations; the calculated energy band structure reveals its band overlap. The valence band in the Ag-doped $Ca_3Co_4O_9$ is composed only of Co 3d and O 2p orbitals; the bands that have the Co 3d component must be enhanced at the Co 2p-3d resonance and heavy carriers in valence bands that should favour high thermoelectric properties. The Co-3d and O-2p orbitals are responsible for energy bands near Fermi level and they contribute to electronic property.

KEYWORDS: thermal conductivity, NiO, electronic structure, DV-Xα method, molecular dynamics

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INTRODUCTION

Today, thermoelectric materials are renewed interest as clean energy conversion into electric energy [1]. The thermoelectric material performance is considered by 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. Good thermoelectric materials should simultaneously exhibit lowest κ and highest S and σ [2]. The largest figures of merit have been achieved with tellurium-, antimony- and germanium- based compounds [3-9]. However, the stability and toxicity of these compounds is an issue for some applications [10]. We focused on oxide thermoelectric materials because of their low toxicity and environment-friendliness such as $NaCo_2O_4$ compound [11-13] and Ca-Co-O system compounds [14-15]. Moreover, Y. Miyazaki et al. [15] reported neutron scattering indicated that $[Ca_2CoO_3]_{0.62}CoO_2$ compounds consisted of two structures which were $[Ca_2CoO_3]$ and $[CoO_2]$, respectively. Lattice parameters a, c and angle ß of the two structures are the same, i.e. a = 4.8339 Å, c = 10.8436 Å and ß = 98.14º. However, b_1 is 2.82 Å for $[CoO_2]$ and b_2 is 4.56 Å for $[Ca_2CoO_3]$. The highest thermoelectric material performance of Ca-Co-O system compounds is calcium cobalt oxide ($Ca_3Co_4O_9$) P-type [16] because large Seebeck coefficients around 150 μVK^{-1} by the low spin of Co^{+3} [17], the electrical conductivity around 10^{-4} Sm^{-1} and the thermal conductivity around 2 $WK^{-1}m^{-1}$ [16]. The crystal structure of $Ca_3Co_4O_9$ was presented by H. Fukutomi et al [18], which very interested for dopant other atomic for enhancement material properties. For example, the bismuth dopant shows increase both the electrical conductivity and Seebeck coefficient as well as decrease the thermal conductivity [10].

In this work, we designed the geometric crystal structures and calculated the band structures and density of states of Ag-doped $Ca_3Co_4O_9$ by first principle calculation method to investigated the thermoelectric properties.

MATERIALS AND METHODS

The first principle calculation used data of $Ca_3Co_4O_9$ compounds such as space group 8 (*Cm*), lattice parameters and ß angle [15-18]. The ultra-soft pseudo-potential plane wave method and generalized gradient approximations (GGA) based on density functional theory (DFT) performed using the CASTEP method [19]. The Pseudo atomic calculation for O ($2s^2$, $2p^4$), Ca ($3s^2$ $3p^6$ $4s^2$) and Co ($3d^5$ $4s^2$) was performed. The electron-ion interaction was described by a Vanderbilt's ultra-soft pseudo-potentials. The exchange correlation interaction energy was described using Perdew Burke Ernzerh (BPE) functional within GGA framework. In the total energy calculations, integrations over the Brillouin zone were performed for the unit cell. The valence electronic wave functions were expanded in a plane-wave basis set up to an energy cutoff of 300 eV. In the electronic structure calculation, the Monkhorst-pack grid 4×7×2 was used for k-point sampling. Then the electronic structure was analyzed in terms of the band structure and density of states (DOS).

RESULTS AND DISCUSSION

The default crystal structures of $Ca_3Co_4O_9$ compounds and doped Ag atoms in unit cell shown in Fig. 1.

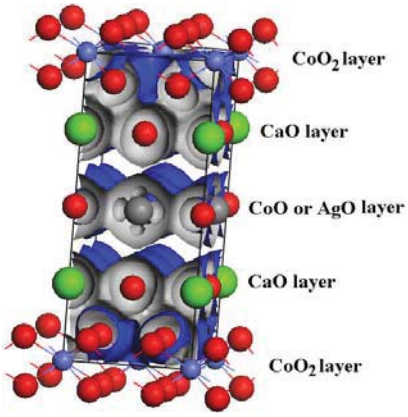

Fig. 1. The Ag doped $Ca_3Co_4O_9$ crystal structures

Figure 1, the considering crystal structures of $Ca_3Co_4O_9$ compounds were composed of CoO_2 layers on top and bottom of unit cell side which outer CdI_2 structure type together with triangular lattices consist of edge-sharing CoO_6 octahedrons [2, 6] and Ca_2CoO_3 layer on halve of unit cell at a distorted rock-salt structure type with lattice parameter constant of 4.56 Å [2, 6-7]. However, the Ca_2CoO_3 layer is rock-salt structure which not showed and considered which in this calculation used unit cell of CoO_2 is essentially. The Ag doped on $Ca_3Co_4O_9$ crystal structures in (0.5, 0.5, 0.5) positions.

The calculated band structures of $Ca_3Co_4O_9$ and Ag dope $Ca_3Co_4O_9$ comparing with the total density of states of are shown in Fig. 2 and 3, respectively.

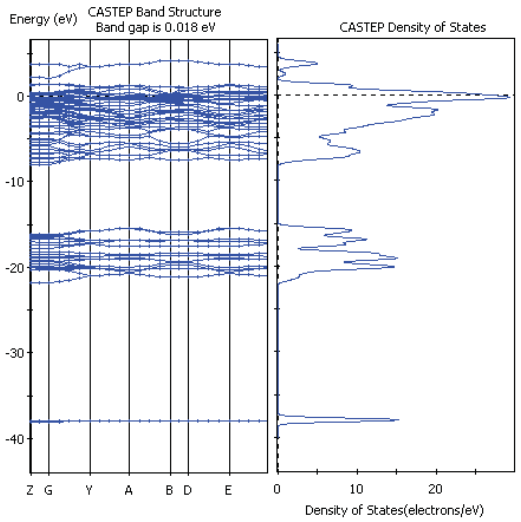

Fig. 2. The calculated band structures of $Ca_3Co_4O_9$

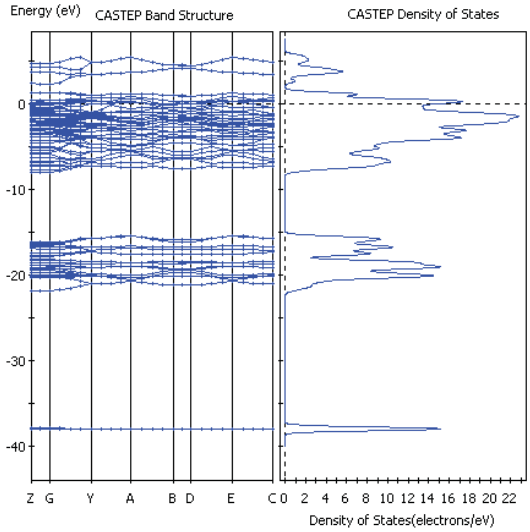

Fig. 3. The calculated band structures of Ag dope $Ca_3Co_4O_9$

In Fig. 2, the band structures of $Ca_3Co_4O_9$ Compounds are obtained the energy gap of 0.018 eV, show semi-metal behaviors. Figure 3, the effected of Ag doped on $Ca_3Co_4O_9$, its band overlapped and show metallic behaviors. The calculated partial density of state of $Ca_3Co_4O_9$ and Ag doped $Ca_3Co_4O_9$ are shown in Fig. 4 and 5, respectively.

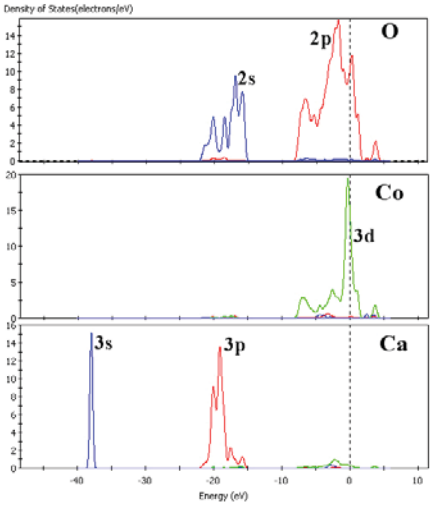

Fig. 4. The calculated partial density of state of $Ca_3Co_4O_9$

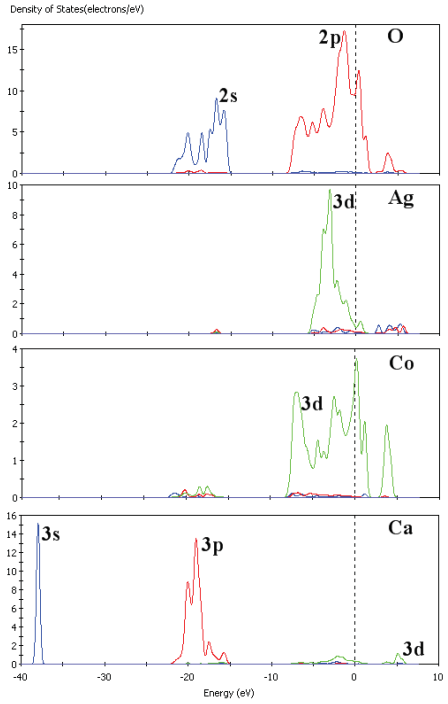

Fig. 5. The calculated partial density of state of Ag doped $Ca_3Co_4O_9$

CONCLUSION

The crystal structure and state electronic structure of $Ca_3Co_4O_9$ and Ag doped $Ca_3Co_4O_9$ compounds can be simulated by first principle calculation of CASTEP. The band structures show band over-lapping between O 2p and Co 3d orbitals in agreement with highest density of state at just under Fermi level. The investigation on thermoelectric properties show the $Ca_3Co_4O_9$ compounds to have metallic behaviors and exhibit P-type thermoelectric materials with highest density of state under Fermi level.

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