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Efficiency assessment of novel materials based flexible thermoelectric devices by a multiscale modeling approach

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ABSTRACT

The presented work demonstrates a multiscale approach for evaluating novel materials for room temperature thermoelectric applications and provides some insights into the development of flexible devices composed of those materials. Tetrahedrite is studied as it is a promising *p*-type thermoelectric material that exhibits good thermoelectric properties at room temperature. Considering our target application, analysis of the theoretical results reveals that tetrahedrite is an interesting surrogate material to bismuth telluride for room temperature applications with a power factor ranging from 4.16 μW/cm K^2, for the pristine tetrahedrite compound, to around 9 μW/cm K^2, for a doped tetrahedrite. A single thermocouple made of *p*-type pristine tetrahedrite and *n*-type natural chalcopyrite has an optimum output power of 5.53 nW/K. This output power can reach 7.47 nW/K when optimally doping tetrahedrite.

1. Introduction

The complete understanding of thermoelectric phenomena has concentrated years of intensive work from materials study to device integration in self-powered systems [1,2]. Thermoelectricity, capitalizing on waste heat recuperation, offers good prospects for the development of autonomous systems in the case of wearable electronics. The most critical obstacle for technology development is to obtain thermoelectric materials that exhibit high efficiencies under low thermal gradient. These target materials should be made of abundant, non-toxic chemical elements. The main issue regarding materials currently used for room temperature wearable thermoelectric applications, bismuth telluride alloys, is their scarcity and reported health hazardousness [3]. The aim of this study is thus to propose a solution for flexible thermoelectric generators based on novel abundant, cheap and non-health hazardous materials.

In this perspective, tetrahedrite material is studied as it is promising *p*-type thermoelectric material for room temperature applications which transport properties can be significantly improved by chemical substitutions [4]. Targeting the development of flexible printed thermoelectric devices, we propose an innovative approach for device optimization based on the multiscale modeling of a complete thermoelectric system. In this scope, two levels of modeling are addressed, from nano to macroscale. At the nanoscopic level, quantum density-functional theory is used in conjunction with semi-classical approach using Boltzmann transport theory to calculate electronic properties such as Seebeck coefficient and electrical conductivity [5] of tetrahedrite. Simulation results are then compared with experimental data. The impact of doping on thermoelectric properties is also investigated. An interesting way of fabricating low cost flexible devices is by using printing techniques as it enables the processing of flexible substrates under standard temperature and pressure conditions. Beside the technological challenges (ink preparation, printing parameters control, post treatment), it is necessary to evaluate the efficiency of an "ideal" printed device. In this context, a virtual prototype of a flexible thermoelectric device with an innovative design is proposed and evaluated with finite-elements simulation.

2. Computational methods and models

2.1. Atomistic simulation of the $Cu_{12}Sb_4S_{13}$ compound

Tetrahedrite with classical formula $Cu_{12}Sb_4S_{13}$ is used as the starting material. The general nature of the tetrahedrite structure

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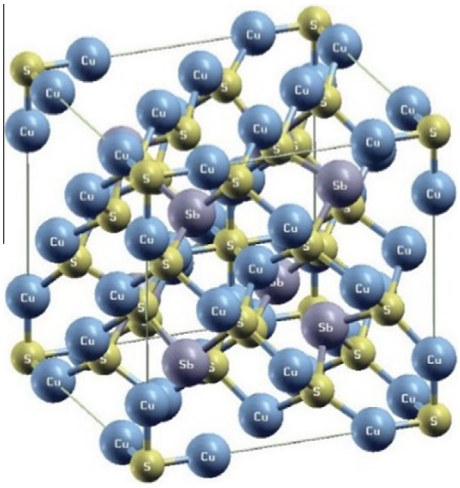

Fig. 1. Crystal structure of $Cu_{12}Sb_4S_{13}$.

was first described by Machatschki (1928). The ideal structure was determined to be Cu_3SbS_3. The correct formula $Cu_{12}Sb_4S_{13}$ has been first found and described by Pauling and Neuman (1934) from experimental analysis of the composition. However the crystallographic structure proposed was found to be slightly inaccurate. A correction, for atomic positions in particular, has been provided by Wuensch (1963) [6].

Tetrahedrite crystallizes in the cubic system with $a = 10.33$ Å (space group $I\bar{4}3m$) at room temperature. Atoms form SbS_3 pyramids, CuS_4 tetrahedra, and unique CuS_3 triangles. The tetrahedrite has 58 atoms in the unit cell (Fig. 1).

The electronic band structure is calculated using *ab initio* Density Functional Theory (DFT) [7,8] and GGA-PW91 exchange correlation functionals [9]. Calculations are performed using the Quantum Espresso software (v4.3.2) [10]. The kinetic energy cutoff is 460 eV. The structure is optimized (atomic positions and cell parameters) at hydrostatic pressures equal to 0 GPa. The *k*-point selection is based on the Monkhorst–Pack scheme. The *k*-point mesh used to sample the Brillouin zone is set to $30 \times 30 \times 30$.

2.2. Electronic transport simulation

Electronic transport properties were calculated by solving the Boltzmann transport equation within the constant relaxation time approximation (CRTA) as implemented in the BoltzTraP code [11]. From the solution of the Boltzmann equation, in the relaxation time approximation, the transport coefficients, namely the electrical conductivity σ and the Seebeck coefficient S, can be written as [12]:

$$\sigma = e^2 \int d\varepsilon \left(-\frac{\partial f_0}{\partial \varepsilon}\right) \Xi(\varepsilon), \tag{1}$$

$$S = \frac{ek_B}{\sigma} \int d\varepsilon \left(-\frac{\partial f_0}{\partial \varepsilon}\right) \Xi(\varepsilon) \frac{\varepsilon - \mu}{k_B T}; \tag{2}$$

where τ is the relaxation time, f_0 is the Fermi distribution, μ the chemical potential, ε and k_B the Boltzmann's constant. Ξ is the transport distribution and is expressed as follows:

$$\Xi = \sum_{\vec{k}} \vec{v}_{\vec{k}} \vec{v}_{\vec{k}} \tau_{\vec{k}} \tag{3}$$

$\vec{v}$ is the group velocity and τ is the relaxation time.

A dense *k*-mesh of over 3000 *k*-points in the IBZ was used for transport calculations to minimize possible band-crossing effects [11].

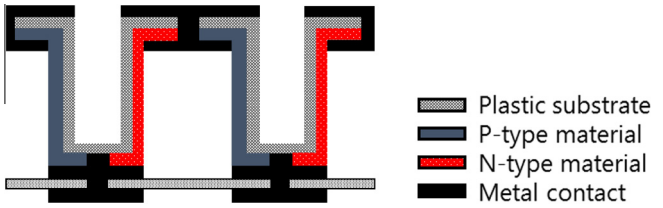

Fig. 2. Schematic representation of the device.

2.3. Finite-element analysis of an innovative flexible TEG architecture

The main issue preventing the widespread use of TE modules as human body heat energy scavengers is their low efficiency under low thermal gradient consequence of their poor ability to evacuate heat. A solution for keeping the thermal gradient naturally present between skin and air across the device can be achieved by increasing the device surface at the cold side in contact with air. We thus propose the following device architecture:

The device architecture is represented in Fig. 2. The plastic substrate is used as a thermal insulator for the hot part (bottom side Fig. 2) and the metal contacts as heat sinks for better heat removal (top side Fig. 2).

A thermoelectric generator is made of multiple thermocouples, and each thermocouple is composed of an *n*-type and a *p*-type material. In our model, tetrahedrite is used for the *p*-type part. Chalcopyrite $CuFeS_2$ can be considered as an interesting *n*-type counterpart to $Cu_{12}Sb_4S_{13}$ as it is also a natural occurring and abundant mineral. Compared with tetrahedrite, chalcopyrite shows a higher power factor that can be increased by adjusting the Cu/Fe ratio. The thermoelectric properties of the $CuFeS_2$ compound considered in our model for the device simulation are taken from natural samples characterization [13]. Chalcopyrite can be either *n*-type or *p*-type depending on the exact stoichiometry.

The numerical analysis of the device is carried out using COMSOL Multiphysics, a finite-element method based code. The equations governing the temperature and electrical potential distributions and implemented in the software are [14]:

$$\vec{q} = -k\nabla T + P\vec{J} \tag{4}$$

$$\vec{J} = -\sigma\nabla V - \sigma S\nabla T \tag{5}$$

where k is the thermal conductivity, $\vec{q}$ represents the heat flux and $\vec{J}$ the electric current "flux" and:

$$\vec{E} = -\nabla V \tag{6}$$

$$Q = \vec{J} \cdot \vec{E} \tag{7}$$

$\vec{E}$ is the electric field and Q joule heating.

Before applying this model to our specific configuration, it has been tested on a commercially available module model and validated by comparison between simulated and experimental characterization data.

Cooling of the device by natural convection in air is modeled by adding an air channel around the device and defining the following boundary conditions: air at 297 K flows through the channel and the bottom of the device is kept at 307 K.