Thermoradiative Cells Based on a p -type Cu_3SbSe_4 Semiconductor: Application of a Detailed Balance Model

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Thermoradiative cells (TRCs) are power generators that efficiently convert low temperature waste heat into electricity. Although there is a growing interest in this potential technology, most of the works dealing with the study of efficient TRCs are focused on the theoretical analysis of their performance. In this work, a Cu_3SbSe_4 semiconductor is proposed to be applied in TRCs. Firstly, the electronic structure of Cu_3SbSe_4 has been obtained by using density functional theory (DFT) calculations. Then, DFT calculated bandgap values are employed to assess the efficiency of TRCs based on Cu_3SbSe_4 . For this purpose, the power conversion efficiency has been calculated by using the Shockley–Queisser framework through a detailed balance model adapted to TRCs that includes the doping level through its effect on the energy barrier appearing at the pn-junction.

Key words: Energy conversion systems, thermoradiative cells, detailed balance model, density functional theory, semiconductors

INTRODUCTION

Thermoradiative cells (TRCs) are emerging as a new technology to efficiently convert heat into electricity. A thermoradiative cell converts part of the heat (Q_i) supplied to keep the cell at a constant temperature (T_c) to electricity (see Fig. 1a).^{1–4} The working principle of an ideal TRC was firstly proposed by Strandberg,¹ while the potential of TRCs has been experimentally demonstrated by Santhaman et al.² For an unbiased semiconductor diode in thermal equilibrium with its surroundings, the number of photons absorbed and emitted by the semiconductor are equal. When the temperature of the surroundings decreases, the number of emitted photons will be higher than absorbed ones. If photon

emission and absorption processes are restricted to transitions across the bandgap (E_g), the number of electrons and holes is reduced. This leads to a shift in the quasi-Fermi levels (QFL) of both hole and electron carriers. Since the starting point was thermal equilibrium, the QFL for the holes is higher than that of the electrons. In this way, the QFL difference will increase until the balance between emitted and absorbed photons is re-established.

The simplest form of a TRC consists of a pn-junction (see Fig. 1b). In this structure, an electron–hole pair recombines radiatively over the bandgap (1); the electron increases its energy by thermal excitations (2) up to the right energy to be extracted to an external circuit via an adequate contact (3). Finally, the electron is reinserted to the CB of the cell through a external circuit (4).^{1,3} This ideal TRC must meet the following requirements: (1) the main part of cell is formed by an active material (semiconductor) whose electrons can only be excited

Fig. 1. (a) Scheme explaining the working mechanism of a TRC: the heat Q_{in} and energy from its surroundings E_{abs} are absorbed, while radiative energy E_{rad} is emitted and a work W is delivered as electrical power to an external circuit; (b) Electronic band diagram of a TRC, which consists of a pn-junction, showing a possible route for an electron going through the cell: the thermally excited electrons and holes originating from non-radiative process flow oppositely so that a positive current will flow to load and generate electricity. Black dotted lines stand for the quasi-Fermi levels of holes (left) and electrons (right), while $\Delta\mu$ represents the difference in the chemical potential (quasi-Fermi levels split) between them.

across the energy bandgap by photons, while de-excitations over the energy gap are only allowed if the excess energy is emitted as a photon; (2) the cell only absorbs and emits photons with energy larger than the bandgap, since the absorptivity of photons with energy lower than the E_g is zero; (3) electrons are inserted (or removed) to CB (from VB) states by an ideal contact, which ensures lossless transport of electrons between the contact and an external electric circuit; (4) the electrons have an infinite mobility in the TRC so their movements do not imply any energy loss; (5) the back side of the device is a perfect reflector, which serves as a layer optical insulator, prevents emission of photons from the heat source to the cell, and avoids emission of sub-energy gap photons.¹ Note that this structure is similar to that defined for an ideal photovoltaic cell.⁵

Most works dealing with the design of new and efficient TRCs are focused on the theoretical analysis of their working principle and the fundamental limit of the power conversion efficiency,^{1-4,6,7} while research works dealing with the study of semiconductors to be used in TRCs are still scarce. Tetrahedrally coordinated copper-based chalcogenides are widely studied for energy conversion applications, including photovoltaics, photocatalysis and thermoelectricity.⁸⁻¹³ Among them, Cu_3SbSe_4 is one of the most studied semiconductor materials because it possesses a small bandgap¹⁴⁻¹⁶ (0.1–0.4 eV) as well as abundant, inexpensive and non-toxic constituent elements.^{17,18} Concerning the optimal bandgap of a TRC semiconductor, Strandberg found that for small non-radiative rates both the TRC maximum output power (MOP) and the efficiency at which it is delivered (η_{MOP}) exponentially decrease with E_g . Moreover, if the non-radiative recombination rate increases in the TRC both the MOP and η_{MOP} present a maximum for a value for E_g that is not zero. Specifically, Strandberg shown

that for medium non-radiative recombination rates of about the 15–25% total optimal MOPs and efficiencies are found for bandgap values between 0.20 eV and 0.30 eV if the TRCs work with a temperature difference to the environment of about 200 K.¹ Cu_3SbSe_4 has been extensively studied as active material to be used in thermoelectric devices.^{14,17,19-26} As matter of fact, we have recently published a systematic theoretical work on the electronic structure and thermoelectric properties of doped- Cu_3SbSe_4 semiconductors by using density functional theory (DFT) calculations and semiclassical Boltzmann theory.²⁷ In this paper, we propose a detailed analysis of TRCs based on *p*-type Cu_3SbSe_4 semiconductor (Cu_3SbSe_4 TRC). Concretely, an accurate description of the electronic structure of Cu_3SbSe_4 is obtained through DFT calculations. Then, the calculated electronic bandgap is employed to assess the power conversion efficiency using the Shockley–Queisser framework through a Detailed Balance Model (DBM) adapted to TRCs.^{1,5}

THEORETICAL DETAILS

Density Functional Theory Calculations

Electronic structure calculations were carried out using VASP code^{28,29} in combination with the projected augmented wave (PAW) method.^{30,31} The PBE exchange correlation functional,³² along to the formalism proposed by Dudarev et al. (GGA + U) have been applied.³³ We use $U_{\text{eff}} = 15$ eV for the Cu-3d states in concordance with previous works.^{14-16,24} The model system Cu_3SbSe_4 was defined through a tetragonal unit cell with 144 atoms ($\text{Cu}_{54}\text{Sb}_{18}\text{Se}_{72}$). A plane-wave energy cutoff of 450 eV, an energy convergence criterion of 10^{-4} eV, and a Methfessel-Paxton first-order scheme were used to carry out the calculations. For the Brillouin

zone integration, a $12 \times 12 \times 12$ Monkhorst–Pack scheme k-point mesh was used.³⁴

Detailed Balance Model for Thermoradiative Cells

In a detailed balance model (DBM) of a TRC,⁵ the most relevant parameters defining the working properties of the cell are the energy difference (ΔE_F) between the QFL of the electrons and the QFL of the holes and the cell working temperature (T_c). According to this formalism, we can assume that in the material performing the thermoradiative conversion each absorbed photon forms an electron–hole pair and that every electron–hole recombination happening in the TRC results in the emission of a photon. Moreover, we also assume that the absorption coefficient of the TRC is zero for photons with energy under some threshold and one for photons with energy above this threshold. Strandberg assumed that both the threshold energy for absorptions and emissions and the energy difference at which the electrons are exchanged to the external circuit are equal to the bandgap of the semiconductor.

In the works published up to now about TRCs and using the DBM, ΔE_F is taken to be constant and equal to the bandgap of the TRC ($E_g = \Delta E_F$). This value is used to calculate the number of transitions happening over the TRC bandgap and to establish the cell output power (P).^{1,3,7,35–37} In TRCs, the electronic current (I), the output power (P) and the efficiency (η) are defined by the excess of recombinations over excitations. In the DBM approximation that excess is calculated assuming that each excitation comes from the absorption of a photon from the ambient ($N(T_a, 0)$), and that every recombination results in the emission of a photon from the TRC (and $N(T_c, V)$). Hence, it is assumed that absorbed/emitted photons have the temperature and the chemical potential of the environment/TRC and only photons with an energy larger than the bandgap are absorbed/emitted. In addition, another very important condition is assumed: every electron–hole pair formed in the junction results in the transport of an electron through the cell and in the production of an electron to the external circuit. This last condition is reasonable in photovoltaic cells where it only refers to assume that no electrons are losses in the transport (i.e., that no defect exists in the cell). However, in TRCs, where the electrons must overcome the energy potential barrier appearing in the junction, this last condition has a deeper significance: we are assuming that all the electrons that de-excite to the VB are able to overcome the energy barrier. However, it is known that some of them could be unable to do it. A simple way to include the possibility of an electron not able to reach the output contact is to assume that the electronic current depends on the value of the contact potential (V_0) that appear in the junction.

It is well known that a pn-junction is formed by doping p-side of an intrinsic semiconductor with an acceptor concentration of N_A impurities per cm^3 and its n-side with a concentration of N_D impurities, also per cm^3 . In this situation, an energy barrier defining the junction is formed. The energy-height for this barrier is:

$$V = \frac{K_B T_c}{q} \text{Ln} \left(\frac{N_A N_D}{n_i^2} \right) \quad (1)$$

where K_B , q and n_i are the Boltzmann constant, the electron charge and the intrinsic carrier concentration, respectively. This expression shows that the number of electrons that could overcome the energy barrier in the TRC while working is related to the charge carrier concentration of the two sides of the junction (N_A and N_D). Thus, Eq. (1) can be used to develop a simple model in which the changes of the number of dopants in both the n- and the p-side of TRCs modify their output power and efficiency. To build the model, we have defined a reference situation corresponding to have an electron carrier concentration that makes the Fermi level to be placed at the energy $E_V + E_G/2$. In this reference situation, the doping levels are N_A^* and N_D^* and the potential barrier V_0 at the junction is zero.

$$V_0 = \frac{K_B T_c}{q} \text{Ln} \left(\frac{N_A^* N_D^*}{n_i^2} \right) = 0 \quad (2)$$

This reference situation corresponds to the situation analyzed in Strandberg's work.¹ Then, we can calculate the variation produced on the potential barrier height (ΔV) due to considering other electronic concentrations:

$$\begin{aligned} \Delta V &= \frac{K_B T_c}{q} \text{Ln} \left(\frac{N_A N_D}{n_i^2} \right) - \frac{K_B T_c}{q} \text{Ln} \left(\frac{N_A^* N_D^*}{n_i^2} \right) \\ &= \frac{K_B T_c}{q} \text{Ln} \left(\frac{N_A N_D}{N_A^* N_D^*} \right) \end{aligned} \quad (3)$$

That is, the electronic current of the TRC depends now on the number of impurities introduced in the two sides of the junction, which is due to a change in the height of the barrier formed in the junction. We also assume that the energy barrier change is given by Eq. 3, and that it is introduced in the calculations assuming that the edge of the conduction band shifts its energy in relation to its position in a reference case. The reference case is $N_A = N_A^*$ in the p-side and $N_D = N_D^*$ in the n-side of the cell. Thus, our analysis will only account for the changes that happen in the TRC working properties (output power and efficiency) measured with respect to the standard situation presented above.

Finally, we present a summary of the main equations used to calculate the working properties of TRCs. According to the DBM, the electronic current I of the TRC can be calculated as the

difference between the number of absorbed and that of emitted photons^{5,35}:

$$I = q [\dot{N}(T_a, 0) - \dot{N}(T_c, V + \Delta V)] \quad (4)$$

where the terms $\dot{N}(T_a, 0)$ and $\dot{N}(T_c, V + \Delta V)$ are calculated using the energy integral over the distribution of bosons in energy:

$$\dot{N}(T_c, V + \Delta V) = \frac{2\pi}{h^3 c^2} \int_{E_g}^{\infty} \frac{\varepsilon^2}{\exp[(\varepsilon - q(V + \Delta V))/kT_c] - 1} d\varepsilon \quad (5)$$

In this equation, h and c are the Planck constant and the speed of light, respectively. The lower integration limit is defined as E_g^* , which points out that instead of the energy corresponding to the bandgap, we will use the corrected value that includes the dependence on the charge carrier concentration (see above). As in previous works, we also acknowledge that the radiation coming from the surroundings of the TRC has a chemical potential equal to zero ($\Delta\mu = 0$) and that it is in thermal equilibrium with the environment, i.e., its temperature is that of the environment T_a . For the radiation leaving the TRC, we assume that its chemical potential corresponds to the voltage applied to the TRC and that it is emitted in thermal equilibrium with the material forming the TRC, i.e., its temperature is T_c . The TRC output power ($P(V)$) is defined as:

$$P(V) = (V + \Delta V) [\dot{N}(T_a, 0) - \dot{N}(T_c, V + \Delta V)] \quad (6)$$

with ΔV defined in Eq. 3.

The efficiency of the TRC is defined as the ratio between the output power and the heat power $\dot{Q}_i$ that is provided to the TRC to keep its temperature constant while working. Assuming that in the TRC the energy is conserved, we know that the heat power provided to the TRC is:

$$\dot{Q}_i = \dot{E}_{\text{rad}} + P(V) - \dot{E}_{\text{abs}} \quad (7)$$

$\dot{E}_{\text{rad}}$ and $\dot{E}_{\text{abs}}$ are the energy radiated from the TRC to the environment and the energy absorbed from the environment, respectively:

$$\dot{E}_{\text{rad}} = \dot{E}(T_c, V + \Delta V) = \frac{2\pi}{h^3 c^2} \int_{E_g}^{\infty} \frac{\varepsilon^3}{\exp[(\varepsilon - q(V + \Delta V))/kT_c] - 1} d\varepsilon \quad (8)$$

$$\dot{E}_{\text{abs}} = \dot{E}(T_a, 0) = \frac{2\pi}{h^3 c^2} \int_0^{\infty} \frac{\varepsilon^3}{\exp[(\varepsilon)/kT_a] - 1} d\varepsilon \quad (9)$$

Once we know the TRC output power and the energy that must be supplied to get that output power, the efficiency (η) is obtained as:

$$\eta = \frac{P}{\dot{Q}_i} = \frac{P}{P + \dot{E}_{\text{rad}} - \dot{E}_{\text{abs}}} \quad (10)$$

RESULTS

Electronic Structure of the Cu_3SbSe_4 Semiconductor

As said, we have recently reported a systematic study the effects of substitutional doping on the electronic structure of Cu_3SbSe_4 .²⁷ Therefore, only the main features are here discussed. As seen in Fig. 2, the calculated E_g of Cu_3SbSe_4 is about 0.27 eV, in agreement with experimental data (0.1–0.4 eV).^{14–16} The electronic structure near the valence band maximum (VBM) is mainly due to Cu-3d and Se-4p states, while the conduction band minimum (CBM) is mainly attributed to Sb-5s and Se-4p states.

Working Properties of TRCs Based on a Cu_3SbSe_4 Semiconductor

In this section we study the properties of TRCs made up of the host material Cu_3SbSe_4 working at different temperatures in different environments. The calculation of results has been carried out using the formulas presented in the work of Strandberg³⁶ and assuming that the TRCs work in terrestrial conditions. That is, we assume that the TRC has a large emissivity in the energy range (0.0959–

Fig. 2. Electronic band structure of Cu_3SbSe_4 . Main energy differences measured at Γ are also displayed. Red, green, and blue stand for the main contribution of Cu, Sb and Se atoms. The zero of energy has been set at the valence band energy, while the black dotted line corresponds to the Fermi level (E_{Fermi}) (Color figure online).

1.551 eV) corresponding to the atmospheric transparent region and very small emissivity at other wavelengths where the atmosphere is opaque.³⁸ To carry out the simulations on the working properties of Cu_3SbSe_4 TRCs, we use an energy bandgap $E_g = 0.27$ eV, according to DFT calculations. Moreover, we also assume that the charge carrier concentration of the material forming the TRC corresponds to the situation in which the Fermi energy level is at the energy $E_V + E_g/2$ (as well as $N_A = N_A^*$ and $N_D = N_D^*$), being E_V the energy corresponding to the top of the valence band. These conditions to carry out the calculation are the same as previously used by Strandberg.³⁵ Hence, the TRC efficiencies and output powers calculated are directly comparable to the results found before.

Figures 3 and 4 display the output power and the efficiency of a Cu_3SbSe_4 TRC for different voltages between 0 and $V_{OC} = E_g(1 - \frac{T_c}{T_a})$. In all these calculations the environment is at $T_a = 300$ K, while three different working temperatures have been studied: $T_c = 400, 500$ and 600 K. Those three working temperatures are reasonable since they are more than 100 K below the Cu_3SbSe_4 melting temperature (730 K).³⁹ The temperatures also are realistic considering, for example, that the temperature near to the steam going out of a commercial turbine or besides a blast furnace are much larger than 600 K.⁴⁰

For $T_c = 400$ K the Cu_3SbSe_4 TRC only produces a very small output power ($\text{MOP} = 1.4 \text{ W/m}^2$). On the other hand, when the TRC works at the higher $T_c = 600$ K it is able to produce a much higher output power for every voltage. At $T_c = 600$ K, $\text{MOP} = 56 \text{ W/m}^2$, which is at the same order of magnitude of silicon photovoltaic cells.⁴¹ As seen in Figs. 3 and 4, at $T_c = 400$ K a smaller output power

Fig. 3. Output power of Cu_3SbSe_4 TRC working at $T_c = 400, 500$ and 600 K in an environment at $T_c = 300$ K. The MOP is calculated for every value of V between the short-circuit $V_{SC} = 0$ V and the open-circuit $V_{OC} = E_g(1 - \frac{T_c}{T_a})$ voltages. In the calculation we use DFT calculated $E_g = 0.27$ eV and assume terrestrial working conditions.

($\text{MOP} = 1.4 \text{ W/m}^2$) is delivered to the external circuit and the efficiency is $\eta_{\text{MOP}} = 8\%$. At $T_c = 600$ K, the MOP (56.0 W/m^2) is delivered at a much larger efficiency of 13%. Figures 5 and 6 present the values of the MOP and η_{MOP} of Cu_3SbSe_4 TRCs that work with temperatures T_c between 300 and 500 K in environments with temperatures T_a between 50 and 300 K. These two figures show that if we consider normal terrestrial environments ($T_a = 300$ K), and we want to obtain reasonable output powers above the 50 W/m^2 then the TRCs must work with $T_c > 450$ K. If the working temperature of the TRCs is lower than 450 K, the TRC output power will

Fig. 4. Efficiency (η) of a Cu_3SbSe_4 TRC working at $T_c = 400, 500$ and 600 K in an environment at $T_c = 300$ K. η is calculated for every value of V between the short-circuit $V_{SC} = 0$ V and the open-circuit $V_{OC} = E_g(1 - \frac{T_c}{T_a})$ voltages. In the calculation we use DFT calculated $E_g = 0.27$ eV and assume terrestrial working conditions.

Fig. 5. MOP (in W/m^2) of ideal Cu_3SbSe_4 TRCs emitting and absorbing energy through the atmospheric energy window.

Fig. 6. η_{MOP} of ideal Cu_3SbSe_4 TRCs emitting and absorbing energy in the full-spectrum.

Fig. 7. Variation of the MOP of ideal Cu_3SbSe_4 TRCs emitting and absorbing energy in the full-spectrum in terms of the non-radiative recombinations. The environment temperature is $T_a = 300$ K and the cell working is $T_c = 500$ K. We show values of the MOP for non-radiative recombination rates between 5% and 50%.

decrease dramatically leading to a situation in which the TRC almost does not produce output power. Moreover, we also notice that the requirement $T_c > 450$ K is also basic to obtain conversion efficiencies above 10%.

In Fig. 7 we present the variation of the MOP of Cu_3SbSe_4 TRCs in terms of the percentage of non-radiative recombinations. For every working temperature, the MOP is a linearly decreasing function of the non-radiative recombination rate. The decrease of MOP is larger for the TRC working at low $T_c = 400$ K. For this temperature, an increase in the non-radiative recombination rate from 5% to 50% leads to a decrease in the MOP of 4 W/m^2 that supposes around 12% of the MOP calculated with a

Fig. 8. Variation of η_{MOP} of ideal Cu_3SbSe_4 TRCs emitting and absorbing energy in the full-spectrum in terms of the non-radiative recombinations. The environment temperature is $T_a = 300$ K and the cell working is $T_c = 500$ K. We show values of η_{MOP} for non-radiative recombination rates between 5% and 50%.

recombination rate of 5%. For $T_c = 600$ K the influence of the non-radiative recombination rate is much lower. Now the MOP decreases less than 1 W/m^2 , in a total MOP of about 150 W/m^2 , when the non-radiative recombination rate increases from 5% to 50%. Figure 8 shows the variation of η_{MOP} in terms of the non-radiative recombination for Cu_3SbSe_4 TRCs. As it happened with the MOP, η_{MOP} is a decreasing function of the non-radiative recombination rate. The decrease is more important for TRCs working with the lowest temperatures ($T_c = 400, 500$ K). Thus, when $T_c = 400$ K η_{MOP} decreases about 3%, from 10% to 7%. That is, for larger recombination rates the TRC η_{MOP} decreases 20% of its total value. For $T_c = 500$ K, the decrease of η_{MOP} is much lower as it only decreases less than 0.8% when the non-radiative recombination rate changes from 5% to 50%. Finally, for $T_c = 600$ we find that the recombination rate plays a negligible role and the variations noted in η_{MOP} are despicable.

As pointed out for photovoltaic cells, the non-radiative losses (mostly due to the Auger recombination or similar mechanisms) can be represented as contributions to the electronic current that are positive (i.e. they flow opposite to the electronic current that is generated in the TRC). Hence, these non-radiative losses could reduce the total output power of the TRC.^{42–44} This reduction leads to situations where the TRC is unable to produce output power. As seen in Figs. 7 and 8, this situation is most likely to occur for TRCs working at low temperatures. That is, the TRC working temperature T_c must be balanced. Some authors have fixed the upper limiting value of T_c at about 800 K.⁴⁴ However, practical implementations of Cu_3SbSe_4 TRCs should restrict the value of T_c to temperatures slightly lower of about 500–600 K,

Fig. 9. Variation of the MOP of ideal Cu_3SbSe_4 TRCs as function of the electronic carrier concentration. The environment temperature is $T_a = 300$ K and the cell working is $T_c = 500$ K. We show values of the MOP for changes in the electronic carrier concentration that range from $10^{-3}N_D$ to 10^3N_D .

which are more than a hundred Kelvin below the Cu_3SbSe_4 melting temperature (730 K).

Up to now, we have considered that Cu_3SbSe_4 TRCs have an electron carrier concentration that makes their QFLs to be placed at the energy $E_V + E_G/2$. However, as previously discussed in “Detailed Balance Model for Thermoradiative Cells” section, the barrier height that is formed in the pn-junction depends on the carrier concentration levels in each one of the two sides of the junction. That is, the consideration of different carrier concentrations would change the energy height of the barrier at the junction and would also modify the electronic current that overpasses the barrier for every voltage applied to the TRC. Since the TRC output power and efficiency depend ultimately on the magnitude of that electronic current, they must also depend on the concentration of electronic carriers in the material forming it. Figures 9 and 10 display the changes on the TRC MOP and η_{MOP} when the electronic carrier concentration changes from $10^{-3}N_D^*$ to $10^3N_D^*$. The values of the graph corresponding to $N_D/N_D^* > 1$ stand for TRCs with an electronic carrier concentration larger than that of the undoped material. For these TRCs and according to Eq. 3, the energy barrier formed in the pn-junction is lower than that of the undoped material. In these circumstances, the thermal excitation of the electrons (process marked as 2 in Fig. 1b) is easier and the electronic current flowing in the TRC is larger. Since this effect happens for every external voltage applied to the TRC its MOP grows very fast. This behavior is somehow the expected one since a decrease in the height of the energy barrier formed in the p-n junction enables the enhancement of several mechanisms (tunneling, thermal escape) that assist the thermal excitations happening in the TRC. In the region $N_D/N_D^* < 1$ we find the opposite situation. Now the energy barrier formed in the

Fig. 10. Variation of η_{MOP} of ideal Cu_3SbSe_4 TRCs as function of the electronic carrier concentration. The environment temperature is $T_a = 300$ K and the cell working is $T_c = 500$ K. We show values of η_{MOP} for changes in the electronic carrier concentration that range from $10^{-3}N_D$ to 10^3N_D .

junction is larger in energy. That causes a decrease on the number of the electrons that overcome the barrier upon thermal excitation leading to a decrease of the electronic current resulting in a decrease of the TRC output current and output power. The physical effects caused upon the change in the number of carriers described in this paragraph also explain the behavior of η_{MOP} upon changes in the concentration of dopants in the TRC. The increase (or decrease) is now linear (and not exponential as was the increase of the MOP) since in the calculation of the efficiency we have to take into account the changes that happen in the energy that is exchanged between the TRC and the environment. Since our calculations assume that there is a one-to-one correspondence between the number of photons exchanged and the energy exchanged, it is normal to expect a cancellation on the calculation of the efficiency leading to the linear behavior shown in Fig. 10. The graph shows that for every studied case the η_{MOP} changes less than 5%.

Finally, once we have discussed the working properties of Cu_3SbSe_4 -based TRCs, our results are compared to other thermal cell to assess their advantages. In the scarce literature on materials suitable to build TRCs we find two main materials: HgCdTe , that has been the material selected by Ono et al.⁴⁵ to build the first operating TRC and InAs .³⁵ This second material has not been used to build a real TRC, but it was considered in Strandberg’s work to show the capabilities of TRCs since its electronic properties at high temperatures are found in the literature and the material presents all the required characteristics (bandgap, suppression of Klemen’s decay, etc.) that make a material suitable to build TRCs. Here, Cu_3SbSe_4 as active materials for TRCs was proposed for several reasons: (1) there exists ample literature on the electronic properties of these materials since this

material is widely used in thermoelectricity; (2) this compound is constituted of abundant, inexpensive and non-toxic elements^{17,18}; (3) The figure of merit ($ZT \sim 1.4$) has a large value compared to other materials for TRCs. This ZT value implies that the material has large conductivity while its thermal resistance is low. In TRCs that implies a reasonable facility of keeping the cell hotter than its surroundings (what is necessary) using very reasonable amounts of energy. As an example of this advantage, let us mention that the first operating prototype of TRC has been proved very recently in the lab by Ono et al.⁴⁵ In the proven setup the TRC was done using an infrared HgCdTe photodiode (Vigo's PV-4TE-10.6) with $ZT = 0.10$ ⁴⁶ that has a very low conductivity. Note that the Cu_3SbSe_4 figure of merit is quite much large what could lead to obtain much larger current from TRCs using setups similar to that used by Ono et al.; (4) The electronic structure and thermoelectric properties of the material can be tuned through the chemical doping.²⁷ Thus, larger ZT values could lead to an improvement of properties involved in thermoradiative conversion, such as rate of recombination, diffusion lengths and change of resistivity with temperature. Under this scope, the consideration of Cu_3SbSe_4 , a material that can change its electronic properties (not only the bandgap) somehow in an easy way upon chemical doping, is of paramount importance to start the path of finding alternative candidates to build high-efficiency TRCs.

CONCLUSION

In summary, we have carried out simulations on TRCs formed by Cu_3SbSe_4 to characterize the working properties of this material as an energy emissive harvester. For this, the electronic structure of Cu_3SbSe_4 as well as the bandgap have been obtained through accurate DFT calculations. Then, the calculated bandgap has been used to calculate the power conversion efficiency through a detailed balance model adapted to TRCs. Our results show that TRCs made up of this material working under terrestrial conditions only provide output powers larger than 50 W/m^2 if their working temperatures are above 450 K. We have also shown that if TRC working temperature drops below 450 K, the MOP of the TRCs falls too low making the TRCs useless. Concerning the efficiency of Cu_3SbSe_4 TRCs as a function of the non-radiative recombination, both the MOP and η_{MOP} decrease with the non-radiative recombination rate. This decreasing trend is larger for the lowest working temperatures ($T_c = 400, 500 \text{ K}$). The influence of the carrier concentration in the working properties of the Cu_3SbSe_4 TRCs has been also studied. Our calculations have shown that if the electronic carrier changes lead to a reduction in the number of electrons, both the MOP and η_{MOP} decrease. Meanwhile, when the number of electrons

in the TRC is increased, the MOP and η_{MOP} also increase.

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