GREEN ENERGY HARVESTING - STATE OF THE ART

July 2022

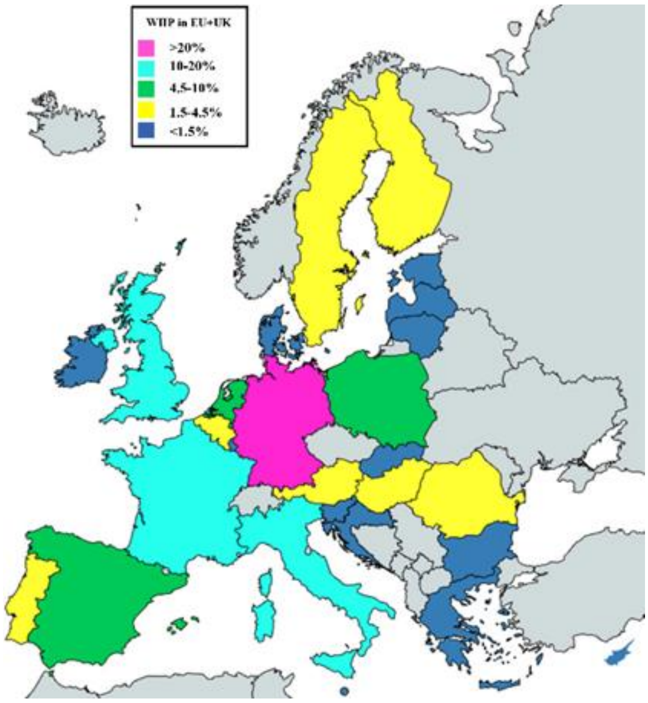

Figure 1 Shares of WHR potential in the EU Industry by member state.

Green energy harvesting aims to supply electricity to electric or electronic systems from an energy source present in the environment (e.g., thermal energy (thermoelectricity)) without grid connection or utilisation of batteries. Almost all manufacturing processes ranging from steel to food production generate heat (the so called "waste heat"), as do all machines from jet engines to microprocessors[2]. The possibility of using a thermoelectric (TE) device to capture and to directly convert this waste heat into electric power is a very attractive and valuable approach to improve the overall energy efficiency and, thus, promotes a sustainable future.

In fact, it is estimated that around two-thirds of the primary energy produced worldwide is lost as waste heat[3]. This means that the search for effective TE harvesting systems has great potential for reducing the consumption of fossil fuels by increasing the overall efficiency of energy producing and consuming systems. Recently, the waste heat recover (WHR) potential in EU has been estimated to be 300 – 350 TWh/year based on the energy consumption breakdown (Figure 1)[4]. This is an important amount of energy saving compared to the 3217.85 TWh energy consumption of 2016. This amount of recoverable heat has the potentiality to avoid tens of millions of tons of CO_2 emissions. For example, considering the 72 TWh/yr of WHR potential for the iron and steel industry, it is estimated that 42.5 million tonnes of CO_2 can be saved by using the recovered energy[3].

TE energy harvesting has a unique edge as a sustainable power supply in all scales and, by turning the waste heat energy released to the environment in emissions-free electricity, it has become an increasingly important contributor to sustainable renewable energy ecosystems. The global TE technology market share was anticipated to double from 1.2 EUR billion in 2014 to 2.63 EUR billion in 2020[5], and is expected to grow at a compound annual growth rate slightly higher than 9% from 2021 to 2026[6].

The TE energy harvesting technology mainly depends on the operation of the TE generator device, which exploits the Seebeck effect (heat becomes electricity). A TE device is made from a number of TE junctions electrically connected in series that consist of n- and p-type TE semiconductor materials (thermoelements) (Figure 2(A)[7]). Thermally, these junctions are connected in parallel so that heat can flow through the TE materials. Electrical insulation on the hot and cold sides stabilises the junctions arranged in this manner, completing the device.

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[1] G. Bianchi, et al., Energ. Ecol. Environ. (2019) 4(5):211–221, 10.1007/s40974-019-00132-7.

[2] J. Mater. Chem. C, 2020, 8, 441, 10.1039/c9tc05710b.

[3] Fitriani et al./Renewable and Sustainable Energy Reviews 64 (2016) 635–659.

[4] R. Agathokleous, et al., Energy Procedia 161 (2019) 489–496, 10.1016/j.egypro.2019.02.064.

[5] Report prepared for the European Commission, Energy harvesting to power the rise of the Internet of Things, 2017.

[6] Thermoelectric Generators Market by Application (accessed in July 2022).

The TE device is a robust and highly reliable solid-state energy converter with unique features: no moving parts, no maintenance, quiet operation, and absence of production of environmental deleterious waste. Due to this green behaviour, TE devices are expected to play a key role in clean and sustainable energy technologies. The conversion efficiency of a TE device is limited by the Carnot efficiency (that is, the maximum thermodynamically possible efficiency of a heat engine) and by the efficiency of the TE material itself, characterized by the 'figure of merit' (*zT*, Figure 2(B)). The goal is to maximize *zT*, which means that high performance requires large S and low κ, characteristic of non-metallic systems, in combination with high σ, more usually found in metals[2]. Consequently, S, σ and k cannot be optimized independently, presenting a challenge in the design of high-performance materials.

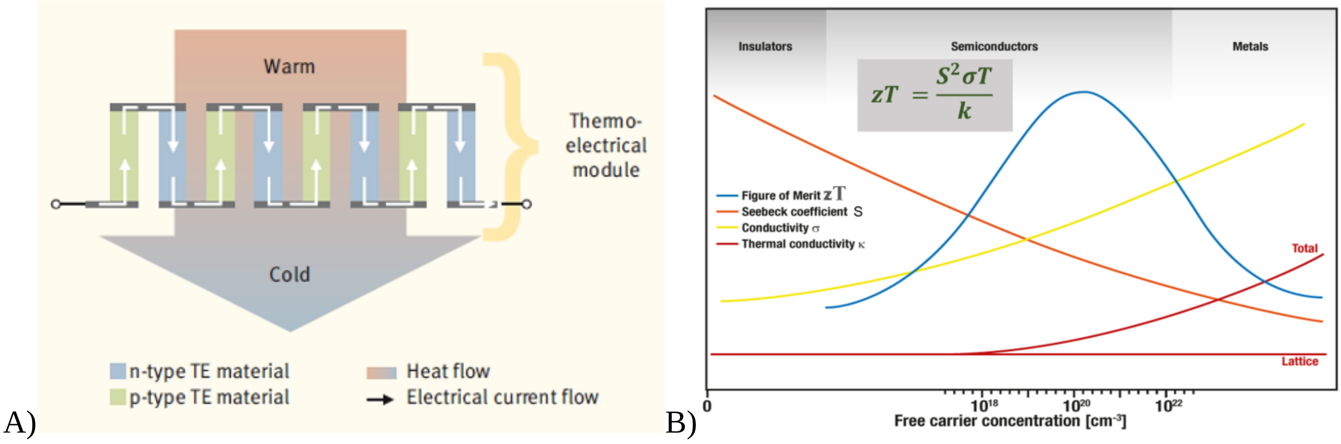

Figure 2 (A) Design and operation of a TE device. The heat flow creates an electric current[7]; (B) The efficiency of a thermoelectric material is governed by its 'figure of merit', termed zT. This depends on the Seebeck coefficient (S), electrical conductivity (σ), thermal conductivity (κ), and the temperature of operation, T. The graph shows the behaviour of the Seebeck coefficient, electrical conductivity, and thermal conductivity vs carrier concentration[8].

Currently, good TE materials have zT values slightly above unity in a specific temperature range. State of the art TE materials of commercial devices, for low to mid temperature applications (up to 500 ºC), consist of telluride-based bulk materials (Bi_2Te_3 and PbTe compounds, appropriately doped to produce the required n- and p-type variants), while $Si_{1-x}Ge_x$ materials are used for higher temperatures[2]. However, besides technological aspects, political and economic considerations are relevant to define the best-suited TE material. In this regard, the telluride-based TE technology possesses two major drawback that hinder its large-scale adoption in Europe[2,9].

(1) Abundance and geographic concentration of production; tellurium is a relatively scarce element, with a terrestrial abundance of ca. 1 ppb, and, simultaneously, Europe is heavily dependent on imports, as China accounts for more than 60% of its production.
(2) Processability and scalable production; the manufacturing processes are generally costly and complex (use of specialized synthesis methods and long duration heat treatments), potentially leading to compositional inhomogeneities and unsuited to provide large quantities of material.

In consequence, replacing telluride-based TE materials by tetrahedrite ($Cu_{12}Sb_4S_{13}$), one of the most abundant sulfosalt minerals in the earth's crust[10], will reduce the demand for such scarce commodity and will result in less demanding processing conditions. These factors provide a strong driver regarding the relevance of sustainable TE materials based on tetrahedrite.

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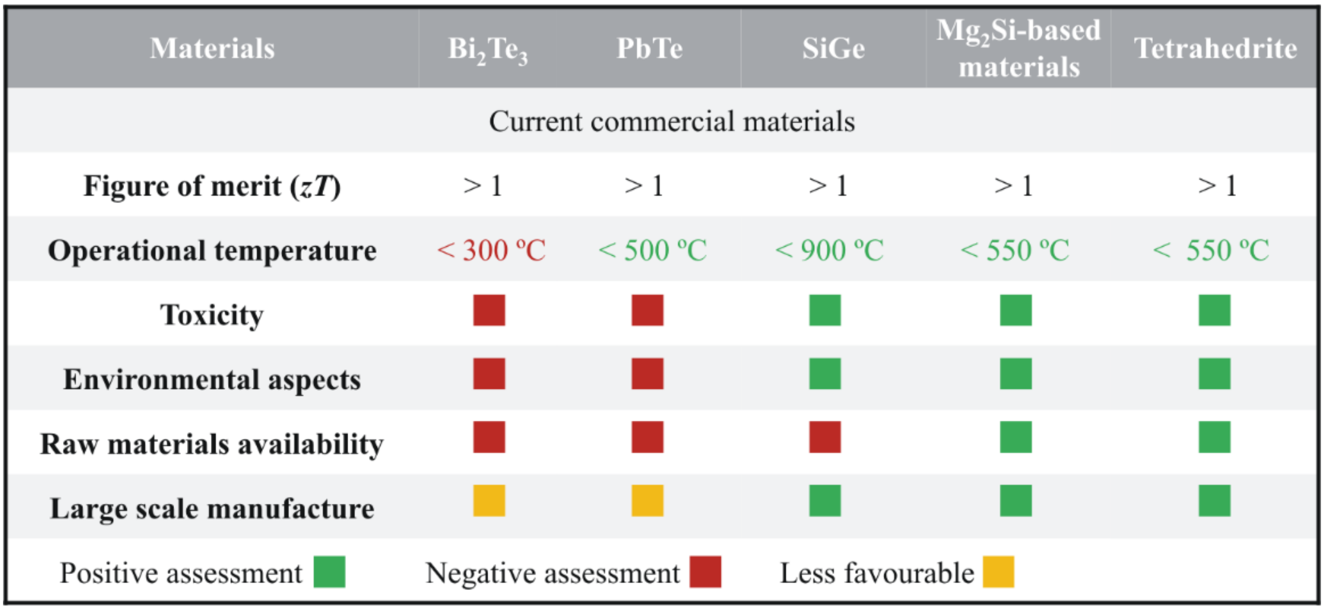
[7] BINE Themeninfo: Thermoelectrics: power from waste heat (I/2016).
[8] Adapted from W. G. Zeier, et al., Nature Reviews Materials 1, 16032 (2016).
[9] Emsbo, P., et al., (2021), Eos, 102, 10.1029/2021EO154252.
[10] R. Parker, Outcrop, vol. 66, no 7, July 2017, 22-29.

Tetrahedrites are p-type semiconductors with high Seebeck coefficient, and extremely low κ due to its complex cubic crystal structure[11]. By adjusting the content of the doping element, competitive zT values, higher than 1, have been obtained between 300 ºC and 450 ºC making tetrahedrites one of the bulk materials with the highest TE performance in this temperature range[12]. Figure 3 compares some characteristics of the tetrahedrites with other TE materials.



Materials	Bi_2Te_3	PbTe	SiGe	Mg_2Si-based materials	Tetrahedrite
Current commercial materials					
Figure of merit (zT)	> 1	> 1	> 1	> 1	> 1
Operational temperature	< 300 ºC	< 500 ºC	< 900 ºC	< 550 ºC	< 550 ºC
Toxicity	🟥	🟥	🟩	🟩	🟩
Environmental aspects	🟥	🟥	🟩	🟩	🟩
Raw materials availability	🟥	🟥	🟥	🟩	🟩
Large scale manufacture	🟨	🟨	🟩	🟩	🟩

Positive assessment 🟩 Negative assessment 🟥 Less favourable 🟨

Figure 3 Characteristics of commercially relevant thermoelectric materials and comparison with tetrahedrites[7,12,13].

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[11] F. Neves, et al., Minerals Engineering, 164 (2021) 106833, 10.1016/j.mineng.2021.

[12] A.V. Powell, J. Appl. Phys. 126, 100901 (2019), doi: 10.1063/1.5119345.

[13] H. Huang, et al., J. Alloys and Compounds 881 (2021) 160546