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THERMOPOWER: PRINCIPLES AND MODERN DEVELOPMENT

Did you know that the heat produced by your vehicle by fuel combustion in the engine or during braking is lost for more than 70%? The recovery of this so-called fatal heat to save fossil fuels is therefore the subject of much research. This is where thermoelectric (TE) materials are of interest, as they have the particularity of producing an electrical voltage under the effect of a flow of heat passing through them (effect discovered by Thomas Johann Seebeck). A TE generator (Figure 1) combines two types of materials in the form of two bars thermally mounted in parallel, and these pairs of bars are connected in series to electrodes to generate a voltage which is the sum of the Seebeck voltages of each pair.

However, there are still steps to take to improve the efficiency of such devices and the first one lies in the performance of materials: they should be good enough electrical conductor for electricity to flow through it, but not too good a thermal conductor to maintain a temperature gradient between hot and cold sides. The TE power of a material is defined by the Seebeck coefficient ($S = \Delta V/\Delta T$ in V/K), which reflects the voltage ΔV created between hot and cold ends under the effect of a temperature difference ΔT. This coefficient must be high. The properties sought for these materials are therefore antagonistic: a metal is not suitable because its thermal conductivity is too high and its coefficient S too low, neither is an insulating material

because although its thermal conductivity (κ) is low, its electrical resistivity (ρ) is gigantic and therefore opposes the passage of the current!

(a) (b)

Fig. 1. TE generator: (a) block diagram and (b) commercial device. In (a), when the heat flow passes through the module, a temperature gradient is created between the faces (hot and cold sides). The bars of TE materials mounted thermally in parallel and in series electrically generate a voltage by Seebeck effect between the 2 connectors. Copyrights: (a) after the thesis of Driss Kenfaui, University of Caen (2011), (b) Thermoelectricity Wikipedia

The known materials responding to this compromise are therefore all semiconductors which thus have a high coefficient S of the order of a few tenths of mV/K, the sign and absolute value of which can be adjusted by checking for doping impurities, an electrical resistivity of the order of mΩ.cm and a thermal conductivity that is often still too high (a few W/(Km)). This explains why the most widely used commercial material in current applications is bismuth telluride (Bi_2Te_3 doped with electrons (*n* type) or holes (*p* type)).

As the concentration of charge carrier increases, the electrical resistivity ρ and S decrease. This is why there is an optimum concentration of charge carriers in the

material corresponding to the best power factor, PF = S^2/ρ. The chemist therefore strives to find the best dopants to approach this optimum.

For that, he/she can exploit the different nature of the transport mechanisms of electrons (electricity) and heat (thermal conductivity, κ). In the great majority of TE materials, the heat transport is mainly done by vibrations of the atomic network called "phonons". At high conversion temperatures, it is mainly so-called "acoustic" phonons - because they are typical of the propagation of sound in the material - which transport heat. At an equivalent power factor, the chemist can play on the structure of the material at different scales from the atom, to reduce the contribution of phonons to thermal conductivity. This path to follow consists in decoupling the transport of electric charges (ideally that of a perfect crystal "electronic crystal") from that of phonons (ideally that of a glass "phonon glass liquid"). Thus, among the best known TE performances, those of Bi_2Te_3/Sb_2Te_3 superlattices can be explained by this decoupling: by periodically depositing atomic layers of these two materials with similar electrical properties, the electrons moving according to the stacking direction are not disturbed by the coherent interfaces between these materials, the PF therefore remains unchanged. Conversely, the difference in atomic mass of the bismuth and antimony atoms very strongly disturbs the vibrations of the network, reducing the contribution of phonons to thermal conductivity. The performance of the resulting material is improved by more than a factor of 2 compared to the two constituent materials.

The inter-growth between two TE materials shows in a very educational way how to approach the lower limit of thermal conductivity which corresponds to that of a glass. There are therefore several chemical strategies to control the size of the crystallites within the material in order to create interfaces which are coherent for the electrons but de-coherent for the phonons: thus in ZnO-type oxide ceramics, the introduction of planar defects created by the presence of indium atoms (Figure 2) breaks the propagation of phonons, the thermal conductivity at room temperature is then divided by 5! These results show that the search for new TE materials has only just begun. This will be illustrated by the n- and p-type transport asymmetry found in

transition metal oxides, the strongly correlated physics of the latter having led to study a lot of new oxides in connection with their anomalous TE power. Also, the coupling between magnetism and TE power, recently established in transition metal TE sulfides, pyrites and thiospinels, opens another route to seek for multi-functional materials.

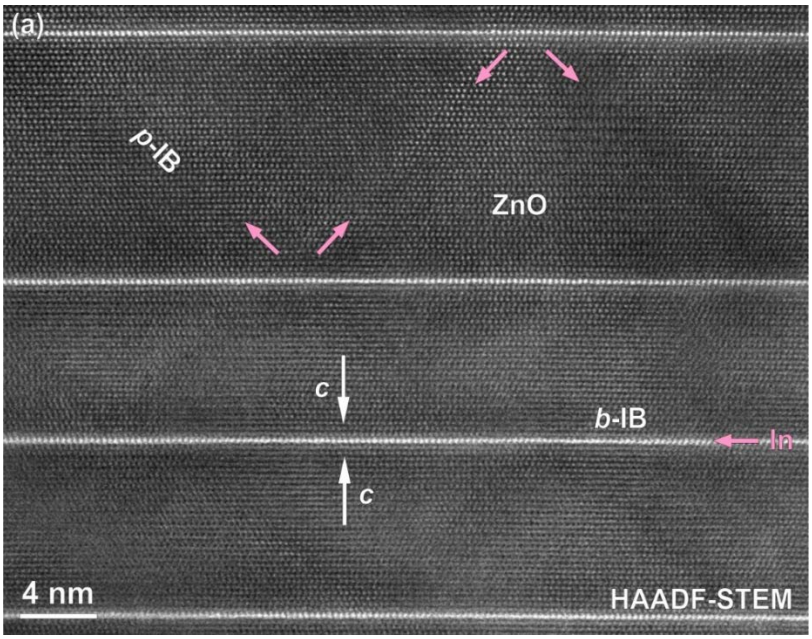

Fig. 2. High resolution electron microscopy image of a ZnO oxide ceramic showing the presence of planar defects (noted p-IB and b-IB) formed by indium ions voluntarily substituted during the synthesis of the material. As these defects hinder the propagation of phonons, thermal conductivity is divided by a factor of 5 at ambient temperature. White dots represent heavy atoms, zinc and indium. From: ACS Appl. Mater. Interfaces 2018, 10, 7, 6415-6423

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