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Investigated CoSb3 as a Skutterudite and Some of its Applications in Thermoelectric

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Abstract The aim of this paper is investigation $CoSb_3$ as a skutterudite and showing some of its applications. The meaning of Seebeck effect: In connected two different materials with different temperatures T_1 and T_2 in the connected point is a thermal voltage obtained. The inverse of the Seebeck effect " Peltier effect": the generation of a temperature gradient by a current flow.
Keywords- skutterudite, thermoelectric, Seebeck effect, Peltier effect, four probe method.

I. Introduction

Due to the flexible application possibilities of thermoelectric components, industrial interest in the use of thermoelectricity has increased more and more in the last two decades. Thermoelectric has been known since 1821, when *Thomas Johann Seebeck* discovered the so-called Seebeck effect, which described the generation of an electrical voltage through a temperature gradient. In 1834 *Jean Peltier* researched the reverse principle (Peltier effect). Since this discovery, there have been a variety of approaches to increase the efficiency of thermoelectric generators (TEG) and Peltier coolers.

With the TEG it is possible to convert thermal energy into electrical energy. The problem is that the used thermoelectric materials achieve to date only an efficiency of less than 4.5% [1]. Therefore, further applications are not economical, for which the efficiency of these materials would have to be increased fivefold.

II. Materials and Methods

1) Thermoelectric

Thermoelectric materials with high efficiency have a large Seebeck coefficient S, a high electrical conductivity σ and a small thermal conductivity. To compare different materials, the quality factor $ZT = \frac{S^2\sigma}{\kappa}T$ is introduced [2]. It must be noted that all three coefficients S, σ and depend on each other. Changing one coefficient results in changing the other coefficients, causing problems in increasing ZT.

By using nanostructures, it is possible to achieve a decoupling of the parameters. The increase in the charge carrier concentrations when the dimensions are restricted leads, for example, to an increase in the Seebeck coefficient or the electrical conductivity [3, 4, 5]. The second way to increase ZT is minimization the thermal conductivity by increasing phonon scattering through creation of defects or interfaces without changing the electrical properties [6]. For this purpose, novel groups of materials such as skutterudite are being investigated.

2) Seebeck effect and Peltier effect

The Seebeck effect was the first of the thermoelectric effects to be described in 1821 by its discoverer *Thomas Johann Seebeck* [7]. If two different materials (A) and (B) are connected to form an open circuit and if the contact points have different temperatures T_1 and T_2, a thermal voltage is obtained (see Fig. 1, a).

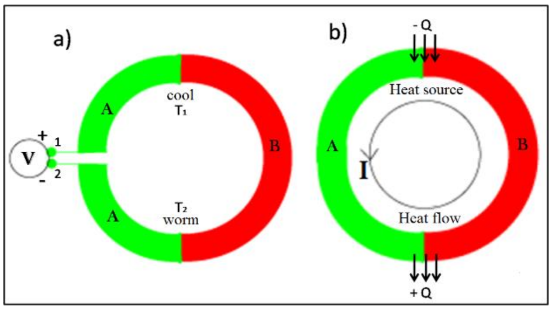

Fig. 1 a) Seebeck effect: two materials A and B form an open conductor ring. If the contact points have different temperatures, a thermal voltage arises. b) Peltier effect: two materials A and B form a closed conductor ring. When a current I flows through the ring, Heat is transported from one contact point to another [8].

Equation applies to the thermal voltage U_{Thermo} [10]

$$U_{Thermo} = \int_{T_1}^{T_2} (S_A - S_B)dT$$

S_A and S_B are the temperature dependent Seebeck coefficients of material A and material B. The inverse of the Seebeck effect, the generation of a temperature gradient by a current flow, was discovered by *J. Peltier* in 1835. If a current is sent through a closed ring of two metals, heat transfer takes place from one contact point of the metals to another (see Fig. 1, b). This effect is used to create a heat source.

3) Skutterudite

In 1995, the realization of a solid-state system " Phonon-Glass / Electron- Crystal " (PGEC) was by G.A. Slack described. In this model solid, the electrical conductivity should not be reduced by scattering of the charge carriers at point defects or other disturbances in the lattice periodicity (ideal crystalline behavior), but the thermal conductivity should be reduced by scattering of the phonons at these lattice disturbances. The skutterudites are considered a good candidate for a PGEC. They got their name from the Skutterud site in Norway, where in 1928 the mineral $CoAs_3$ was found as a natural mineral. Skutterudites have the general formula TX_3. T is the transition metal from the 9th group of the periodic table (cobalt, rhenium, iridium) and X from the 5th main group (phosphorus, arsenic, antimony). In this work, T = cobalt and X = antimony. $CoSb_3$ has a body-centered cubic structure. The structure is often illustrated with the cubic unit cell from figure 2.

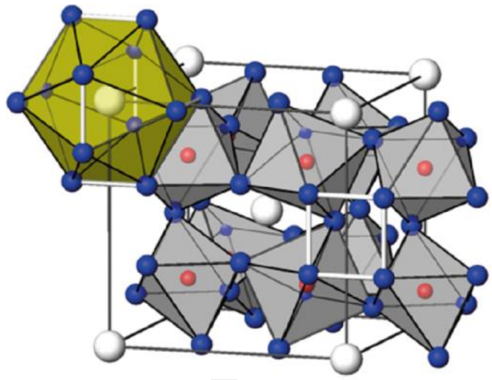

Fig. 2 structure of $YbCo_4Sb_{12}$, red: Co, bleu: Sb, white: Yb [9, 10].

III. Results and Discussion

In order to convert a heat flow into an electrical voltage, a TE-generator based on the Seebeck effect must be placed between two heat reservoirs with temperatures TK and TH. The efficiency η of a generator is defined by the ratio of the generated electrical power P_{el} to the heat Q_{th} used: $\eta = \frac{P_{el}}{Q_{th}}$ [11]. Since the generator forms a bridge between the heat reservoirs and the quality increases with the temperature difference, it is necessary to have a low thermal conductivity. In order to generate high thermal voltage, a high Seebeck coefficient S is required. In order to ensure maximum performance, the generator must have a low internal resistance and therefore high electrical conductivity σ. These properties are described with the thermoelectric figure of merit ZT (" figure of merit "):

$$ZT = \frac{S^2}{\,} T$$

where T is the working temperature. ZT depends on the efficiency η of the material using the following formula [12, 13].

$$\eta = \frac{T_H - T_K}{T_H} \frac{\sqrt{1+ZT}-1}{\sqrt{1+ZT}+\frac{T_K}{T_H}}$$

TH is the high and TK is the low temperature at the ends of the TE-generator.

An increase in ZT is made more difficult by the dependence between the material coefficients, *S*,. An increase in electrical conductivity leads, for example, to an increase in thermal conductivity (Wiedemann-Franz law) [14] and the figure of merit remains approximately constant. For a long time, substances with ZT ≤ 1 were the best available thermoelectric materials and a value greater than 2 was not achievable. An overview of different material groups and the associated material coefficients is shown in Figure (2.2).

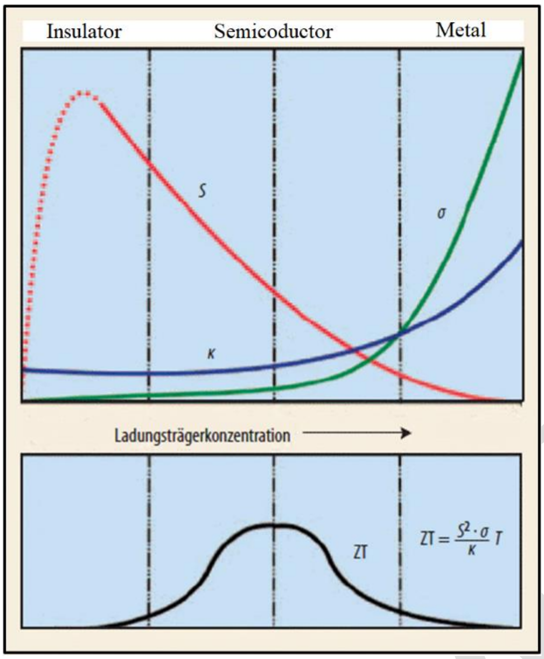

Fig. 3 material coefficients and figure of merit ZT depending on the type of material.

Metals have high electrical conductivity but a small Seebeck coefficient. In contrast, insulators have a large Seebeck coefficient but their electrical conductivity is small. Semiconductors have two different types of charge carriers that contribute to the Seebeck coefficient with different signs and thus compensate each other. Semiconductors offer the best conditions and are the group of materials with the highest quality factor. This is why they have established themselves in thermoelectrics [15]. Figure 4 shows the dependence between temperature and ZT of some current n-/p-type thermoelectric materials.

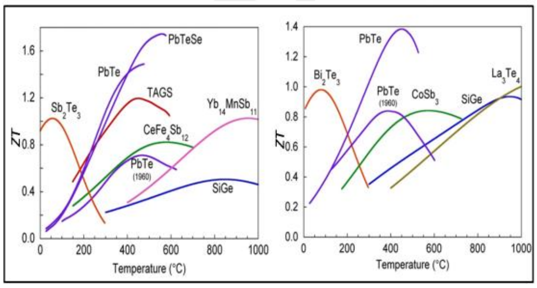

Fig. 4 ZT as a function of temperature for different materials. Left: p-conducting, right: n-conducting materials [16, 17].

La-Te and Si-Ge compounds are suitable for applications in the high-temperature range, while Bi-Te compounds and Sb-Te compounds are suitable for applications in the room temperature range [18, 19]. CoSb3 is a promising material for the medium temperature range around 500 K.

- **Measuring the specific electrical resistance by four probe method**

The four probe method is available for determining the specific electrical resistance of a layer ρ at room temperature RT. Figure (5, a) shows the schematic representation of the four probe method. We consider four tips arranged in a row. A current I0 flows through the two outer ones (1 and 4) and the voltage U1 can be measured through the inner ones. In the case of equal distances between the tips s, the result is [10, 20]

$$\rho_0 = \frac{U_1}{I_0} 2\pi s$$

A correction must be made for a thin layer with thickness d. It is given by [10]

$$\rho^* = \frac{\rho_0}{2s} \frac{d}{ln ln\ 2} = \frac{U_1}{I_0} \frac{\pi\, d}{ln ln\ 2}$$

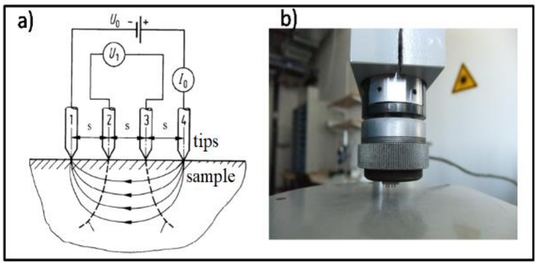

Fig. 5 a) four probe measurement method: four probes are arranged in a row on the sample. If a current flows across 1 and 4, the voltage U_1 is measured across 2 and 3 [21], b) photograph of the arrangement of the tips.

IV. CONCLUSIONS

Semiconductors have established themselves in thermoelectrics. They offer the best conditions and are the group of materials with the highest quality factor. CoSb3 as a skutterudite is a promising material for the medium temperature range around 500 K.

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