Development of Geothermal Thermoelectric Converters

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Geothermal heat can be directly converted into electricity with thermoelectric (TE) converters. The challenge is to convert "cold" geothermal fluids into electric power using solid state oxide TE devices. Advantages of TE power generation are (i) electric power source without moving part, (ii) energy recovery from geothermal heat e.g. (iii) and long operating lifetime.

The geothermal resources can be classified as low temperature ($T < 363$ K), moderate temperature ($363 \text{ K} < T < 423$ K), and high temperature ($T > 423$ K). Up to now, the highest geothermal temperature resources are only used for the steam conversion to electric power. In established power plants, conventional steam turbines using geothermal energy operate minimum at 450 K. At relatively small temperatures, heat-to-electricity conversion efficiencies are too low for steam conversion. The main geothermal reservoirs are ($T \approx 380$ K) available for thermoelectric conversion while conventional steam turbines require more heat energy.

The performance of thermoelectric materials is evaluated by the so-called Figure of Merit, *ZT*, where $Z = S^2\sigma/\kappa$ (S is the Seebeck coefficient; σ and κ are the electrical and thermal conductivities, respectively). A large Seebeck coefficient is obtained in low carrier concentration semiconductors or insulators. High carrier concentration metals are required for a large electrical conductivity. Thus the power factor ($S^2\sigma$) can be optimized for materials between semimetals and semiconductors. Good thermoelectric properties involve also materials with low thermal conductivity. Heat transport in a solid is mainly governed by the motion of phonons and electrons. The lattice heat conduction is caused by the travel of the phonons while the electronic thermal conductivity is induced by the carrier concentration. The electronic term is directly related to the electrical conductivity through the Wiedemann-Franz law: $\kappa_e = L\,\sigma\,T$, where the Lorenz factor L, depends on the band structure of the material. Thus good electrical conductor materials present a large thermal conductivity. The key problem to improve the efficiency of TE converter is to decrease the thermal conductivity keeping a large power factor.

A thermoelectric generator consists of thermocouples, comprising *p*- and *n*-type thermoelement connected electrically in series and thermally in parallel. Heating one side of a semi-conducting thermoelectric material allows electrons and holes to thermally diffuse along the temperature gradient and to carry their charge with them. These charges create an electrical potential directly proportional to the temperature gradient and the Seebeck coefficient. Thermopower, electrical and thermal conductivities are interrelated by the specific electronic structure of the material. Thus the material development requires theoretical and practical considerations.

Thermal properties of materials

Thermal conductivity measurements

The thermal conductivity can be determined at Empa by the laser flash method using the NETZSCH LFA 457 *Microflash* (see Figure 1). Measurements can be performed for materials with thermal conductivities between 0.1 and 2000 W/mK. The front side of a plan parallel is heated by a short laser pulse. The heat propagates through the sample and causes a temperature increase on the rear surface. This temperature rise is measured versus time using an infrared detector. The thermal diffusivity (D) and the specific heat capacity (Cp) can be ascertained using the measured signal. If the density (ρ) is known, the thermal conductivity (κ) can be determined: $\kappa(T) = D(T)\ .\ \rho(T)\ .\ Cp(T)$. This non-destructive measurement technique can be employed for a large temperature range (25°C < T < 1000°C). The laser flash method is adapted for bulk materials as well as multi-layer systems.

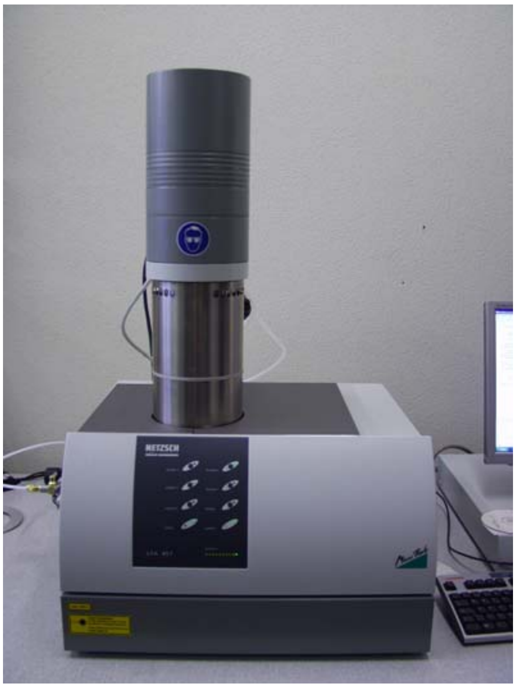

Figure 1: LFA 457 Microflash apparatus

Thermogravimetric and calorimetric analyses

A proper utilisation of these novel functional materials presupposes a thorough understanding of a large number of properties such as phase formation, phase stability, phase relations. Thermal analyses methods are a powerful tool to study the influence of the synthesis parameters and the thermal behaviour of materials. The Thermogravimetric Analyses (TGA) can be performed at Empa using a Netzsch STA 409 CD thermobalance usually coupled to a mass spectrometer (MS) (see Figure 2). Simultaneously recorded thermogravimetric (TG) and differential thermal analysis (DTA) can be monitored in situ from room temperature to 1500°C in inert or reactive atmosphere. The Netzsch QMS 403 C Aëlos mass spectrometer allows to identify gaseous reaction products released during heating. Phase transition, melting point, specific heat determination can be evaluated by Differential Scanning Calorimetry (DSC).

DSC measurements can be also carried out on the Netzsch STA 409 CD apparatus up to 1300°C.

Figure 2: Thermogravimetric set up (TGA) coupled with the mass spectrometer (MS)