European Commission

EMMC case study:
IMRA and Ruhr Universität Bochum

Discovery of new thermoelectric materials

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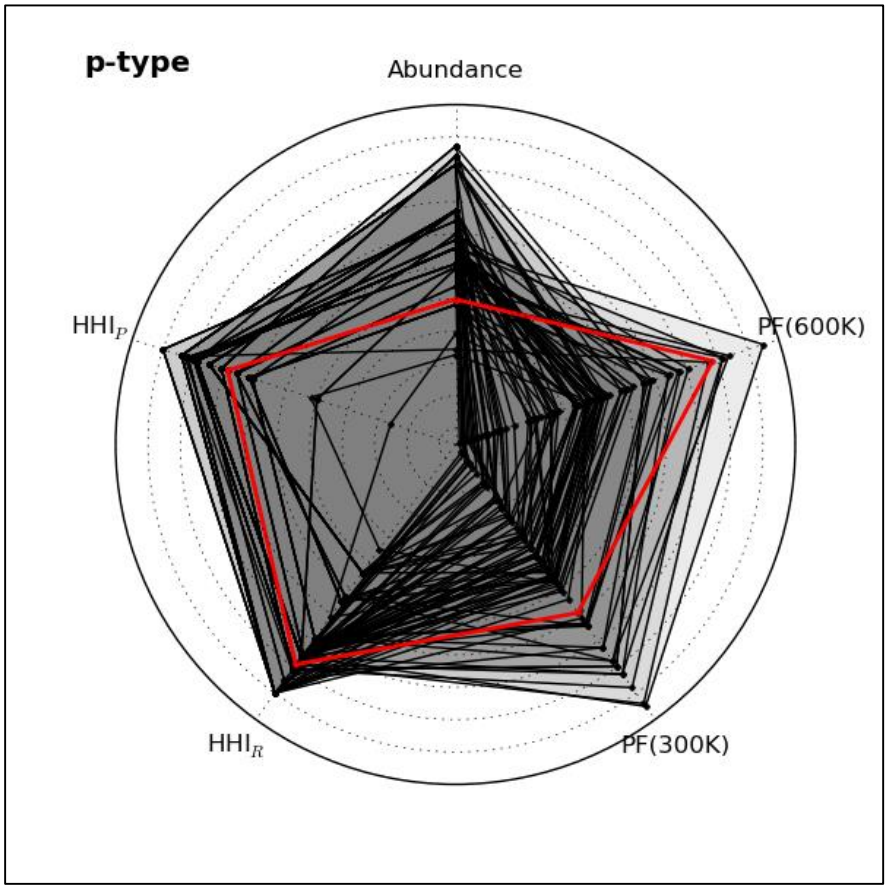

Radar plot of the abundance, supply risk (HHIproduction and HHIreserve) and calculated thermoelectric power factor PF for a range of binary sulfides. Each ring corresponds to one calculated semi-conducting phase. The red path corresponds to tin sulphide. (adapted from Reference [1])

Which are your objectives as an industrial consumer of modelling?

a. *Description of the industrial problem:*
Thermoelectric (TE) materials enable the interconversion of a temperature gradient and electricity. They can thus be utilized for solid state cooling and harvesting of waste heat and potentially play an important part in more energy efficient technologies. The main factors holding back widespread use of thermoelectric materials are cost, scarcity and toxicity of their components. Presently widespread materials are Bi_2Te_3 and PbTe. The aim of the project was to identify potentially new non-toxic, low-cost TE materials.

b. Classification of the project:

i. *Material:* The focus was put on sulfide based materials, which are a major expertise of IMRA.
ii. *Scale of the material phenomena to be described:*
The required fundamental properties of TE materials require a material description at the nanometre scale. Typical crystal structure models used had a size of approximately 1-2 nm^3 (number of atoms = 100)
One TE device will typically contain a few tens of legs (roughly 2x2x8 mm^3) weighing each about 0.5 grams.
iii. *Industrial application:* The development focused on a solid state material development for components, subsystems and systems.
iv. *Industrial sector:* Renewable energy, waste heat recovery, automobile, housing.
v. *Weakness of approach used up until now:* The usual development of new TE materials in industrial environment is mainly carried by intuition driven trial and error test. Considering that:
   - Inorganic TE materials are crystalline.
   - About 250,000 inorganic crystalline materials are currently known and there are many more as yet unknown structures.
   - It takes on average about 1 person-year to synthesize, characterize and assess the TE potential of a given materials without any modelling help.
     In the specific case of sulfide materials there are thousands of known materials. Without the help of materials modelling, screening these materials for new TE "blockbusters" would take thousands of person years. Experimental brute force screening of the thermoelectric properties of sulfides would be unfeasible, especially for a company of IMRA's size.

c. *Requirements and expected results to understand the material behaviour.*
Due to the large number of potential materials a computational screening approach was required to determine key performance indicators (see below for further details) which could be used to limit the number of candidates to a feasible amount.

2. How did materials modelling play a key role in problem solving?

The thermoelectric efficiency is quantified by the thermoelectric figure of merit, $zT=S^2\sigma T/\kappa$, where S is the Seebeck coefficient, σ the electronic conductivity and κ the thermal conductivity. The modelling approach we consider focuses on the

electronic behaviour of the materials, that is the power-factor $PF=S^2\sigma$. This allows us to assess the TE potential of a given material, within a first approximation.

Once a candidate TE material was identified, modelling was also used to verify that this materials can be p- or n-doped, and if yes, how (by adding which element).

Both doping limits and transport properties together screened out approximately 90% of the potential candidates in a very efficient manner.

3. What tools and methodologies have been applied?

The starting crystal structures of the sulfide materials to be investigated were taken from the "Pearsons crystallographic database". Then a series of electronic models were applied:

Electronic DFT models were used to calculate the ground state energies, structures and band structures. These calculations were carried out with the WIEN2k and VASP codes.

The resulting structures, energies and band structures serve as input to a tool to determine the Seebeck and electron transport coefficients. The method is based on the linearized Boltzmann Transport Equation for electrons, using the so-called "constant relaxation time approximation" (CRTA).

A smoothed Fourier interpolation of the bands yields an analytical representation from which the derivatives necessary for the transport distributions are calculated. The calculations were carried out using BoltzTraP, an in house developed and publicly available code.

Finally, computational defect thermodynamics (in-house developed continuum codes) was used to screen the doping limits. The method is based on the super cell calculation of point defect formation energies. The corresponding chemical potential limits are mapped out based on data available in databases such as Materials Project and Aflowlib.

We used experimental validation, in order to increase the accuracy of the theoretical models. Thereby it was demonstrated that it is essential to include oxide formation in the chemical potential limits. Furthermore the validity of the CRTA was demonstrated

4. What are the expected improvements of the material behaviour simulation?

Future improvements could include the thermal conductivity, mechanical properties (manufacturability) and electronic mobility.

5. What investments were made during the project?

IMRA Europe has subcontracted the Ruhr-Universität Bochum to conduct the high throughput calculations. Two and a half man years were allocated for the entire length of the project. Furthermore, approximately 100.000 core hours were consumed per month.

6. What technical and technological benefits and business impacts resulted from the project?

Three patents have been taken out on discoveries which would not have been made if the modelling had not been performed.

Two further benefits for IMRA can be mentioned. First of all, there is an increased visibility within the community, due to four co-authored papers. Secondly, the ability to understand and critically evaluate the substantial theoretical literature on thermoelectric and photo-voltaic materials has grown adding to the intellectual capital of IMRA.

It is difficult to quantify the total benefit for IMRA at this stage (no new materials on the market yet). However, our research offer has become more efficient as similar R&D activities can now be carried out with only about 1/5th of the effort that would have been required if we only applied experimental trial and error approaches.

References

[1] C. Bera, S. Jacob, I. Opahle, N.S. Gunda, R. Chmielowski, G. Dennler, G.K. Madsen, Integrated computational materials discovery of silver doped tin sulfide as a thermoelectric material, Phys. Chem. Chem. Phys. 16, 19894 (2014)